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Tetsuya Tokano Editor

Water on Mars and Life



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Water on Mars and Life

Advances in Astrobiology and Biogeophysics

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This series aims to report new developments in research and teaching in the interdisciplinary fields of astrobiology and biogeophysics. This encompasses all aspects of research into the origins of life – from the creation of matter to the emergence of complex life forms – and the study of both structure and evolution of planetary ecosystems under a given set of astro- and geophysical parameters. The methods considered can be of theoretical, computational, experimental and observational nature. Preference will be given to proposals where the manuscript puts particular emphasis on the overall readability in view of the broad spectrum of scientific backgrounds involved in astrobiology and biogeophysics.

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- Lectures on a new field, or presenting a new angle on a classical field
- Suitably edited research reports
- Compilations of selected papers from meetings that are devoted to specific topics

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Water on Mars and Life

With 88 Figures and 9 Tables



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Preface

This book surveys recent advances made in the research of water on Mars and its astrobiological implication. Meanwhile, the presence of abundant frozen H_2O on present Mars is beyond question and recent spacecraft are unveiling the manifold appearances of Martian water largely hidden from visual inspection. Ground ice in the polar region and water ice in the southern polar cap recently detected by Mars Odyssey and Mars Express, respectively, may be the tip of the Martian iceberg, also in a figurative sense, and encourages the planetary and astrobiological community to strengthen their efforts to follow the water on Mars. Liquid water is generally considered to have played a major role in the evolution of terrestrial-type life. Under this premise, water on Mars inevitably becomes one major subject of astrobiology, which is currently being established as a new interdisciplinary research field.

However, the majority of Martian water is not liquid and has probably not been liquid throughout much of history. Bodies of liquid water at one time are likely to have existed at other times in some another form in different planetary reservoirs, unless they have been lost to space. Therefore, a comprehensive study of all possible forms of water on Mars since the planetary formation and the processes related to them becomes necessary.

This book covers all major aspects related to water on Mars and their possible biological implication that have been discussed in the literature, and consists of 13 chapters written by scientists from various disciplines. New aspects and results are discussed more exhaustively, sometimes in separate chapters, than more "classical" subjects such as outflow channels or valley networks. The assemblage of these separate chapters ultimately merges into a comprehensive story of water on Mars.

Part I (Chapters 1–4) reviews the water on early Mars and its history, and discusses how it may have been involved in the planetary evolution. The story begins with water extracted from Martian meteorites, which can tell us something about the possible origin of Martian water. The following chapter considers how the global inventory of water may have evolved in the course of billions of years as a result of atmospheric and geological processes. In the third chapter we undertake a fascinating palaeontological excursion to early Earth, which may have had some similarities with early Mars. The fourth chapter looks at water-bearing minerals on the surface, which contain clues to the environmental, particularly aqueous, conditions of early Mars.

Part II (Chapters 5–8) deals in detail with various water reservoirs on present Mars as actually evidenced by observations from orbiters, landers and telescopes. The survey begins with the recent detection of subsurface hydrogen by Mars Odyssey, the first firm observational evidence of H_2O in the subsurface. The next chapter discusses the polar caps, which not only represent the largest water reservoir on the surface, but also bear a climatic record of the past. The following chapter reviews ground ice as the largest putative water reservoir on Mars from a geological point of view. Part II concludes with an inspection of the global water

cycle in the atmosphere, which acts as an important medium for the water exchange between the planetary water reservoirs.

Part III (Chapters 9–13) focuses on some particular putative aqueous environments on past or present Mars and their possible terrestrial analogues of possible astrobiological importance. The book first guides the reader to those parts of Artctic and Antarctica which are the most Mars-like environment on Earth and where life still flourishes. The next chapter discusses geological evidences of lakes on early and recent Mars and the environmental conditions relevant for life. Microbial life in impact craters filled with water and salty environments in the subsurface together with their implication for Mars are illustrated in the following two chapters. Finally, we dive into the hydrothermal vents in the deep sea, where early life on Earth may have diversified, and learn about prospects for the future search for life on Mars.

Our knowledge about water on Mars is certainly incomplete and we may gain further new insight in the future through Mars missions as well as by observational, experimental and theoretical studies. Mars Express Orbiter as well as the Mars Exploration Rovers Spirit in Gusev Crater and Opportunity in Meridiani Planum in operation since early 2004 seem to become quite promising. The results of these missions could not be discussed in this book, so the reader is referred to press releases and publications in journals for the most recent findings. However, in this book the reader finds background information as well as a discussion on what potential new results can tell us about the history of water on Mars. I hope that this book can serve as a convenient and representative guide for all those interested in Mars research and astrobiology.

I would like to express my big thanks to all the authors for their tremendous efforts writing a chapter within the framework of this interdisciplinary book. Gerda Horneck of the Editorial Board of this book series "Advances in Astrobiology and Biogeophysics" and Christian Caron of the Springer-Verlag, who both encouraged and assisted me during the entire production process are greatly acknowledged.

Köln, April 2004

Tetsuya Tokano

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List of Abbreviations

APXS	Alpha Proton X-Ray Spectrometer
ASCA	Advanced Satellite for Cosmology and Astrophysics
ASPERA	Automatic Space Plasma Experiment with a Rotating Analyser
AWRS	"Arabian water-rich spot"
ATP	adenosine triphosphate
AU	astronomical unit
BIF	banded iron formation
CNRS	Centre national de la recherche scientifique
CRISM	Compact Reconnaissance Spectrometer for Mars
DNA	deoxyribonucleic acid
DSC	differential scanning calorimetry
DTA	differential thermal analysis
EGA	evolved gas analysis
EPS	extracellular polymeric substance
EUVE	Extreme Ultraviolet Spectroscopic Explorer
FUSE	Far Ultraviolet Spectroscopic Explorer
FYSP	faint young Sun problem
Ga	billion years
GCM	general circulation model
GC-MS	gas chromatograph mass spectrometer
GRS	Gamma-Ray Spectrometer
GSH	Gamma Sensor Head
HEND	High Energy Neutron Detector
HRSC	High Resolution Stereo Camera
HST	Hubble Space Telescope
IMP	Imager for Mars Pathfinder
IR	infrared
IRS	Infrared Spectrometer
IRTM	Infrared Thermal Mapper
ISM	interstellar medium; Imaging Spectrometer for Mars
IUE	International Ultraviolet Explorer
ka	thousand years
KHz	Kelvin-Helmholtz
LD	Large Detector
$L_{\rm s}$	areocentric longitude of the Sun
LTE	local thermal equilibrium
Ma	million years
MAG/ER	Magnetometer/Electron Reflectometer
MARSIS	Mars Advanced Radar for Subsurface and Ionospheric Sounding
MAWD	Mars Atmospheric Water Detector
MCNPX	Monte Carlo N-Particle code
MD	Medium Detector
MDIM	Mars digital image mosaic
MER	Mars Exploration Rover

MHD	magnetohydrodynamic
MO	Mars Odyssey
MOC	Mars Orbiter Camera
MOLA	Mars Orbiter Laser Altimeter
MPN	most probable number method
MSL	Mars Science Lab
NCAR	National Center for Atmospheric Research
NPR	Northern permafrost region
NS	Neutron Spectrometer
OMEGA	Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité (Visible and Infrared Mineralogical Mapping Spectrometer)
PCR	polymerase chain reaction
PIXE	particle induced X-ray emission
PVO	Pioneer Venus Orbiter
RH	relative humidity
RNA	ribonucleic acid
ROSAT	Röntgen Satellite
SD	Small Detector
SEM	scanning electron microscope
SMOW	standard mean ocean water
SNC	Shergotty, Nakhla and Chassigny
SPR	Southern permafrost region
TEGA	Thermal Evolved Gas Analyzer
TEM	transmission electron miscroscope
TES	Thermal Emission Spectrometer
TF	terrestrial fractionation
TGA	thermogravimetric analysis
THEMIS	Thermal Emission Imaging System
TSW	terrestrial seawater
UV	ultraviolet
VL	Viking lander
VNIR	visible/near-infrared
wt %	weight %
XRD	X-ray diffraction
XRF	X-ray fluorescence
XUV	extreme ultraviolet
ZAMS	zero age mean sequence

1 The Origins of Martian Water: What We Can Learn from Meteorites

Lee Baker, Ian A. Franchi and Ian P. Wright

In 1877 telescopic observations of apparent lines on the Martian surface were interpreted by Giovanni Schiaparelli as resembling channels. Others, notably Percival Lowell, soon interpreted these as having been made by intelligent life. Today, the notion of canals and advanced forms of life have long since been dispelled by technological improvements in optical equipment and the advent of space missions. Yet the most recent images provided by Mars Global Surveyor (MGS) continue to show channels apparently cut by water. The question is no longer whether or not water is or was present, but how much there is, where did it originate and what does this mean for the possible evolution of life forms on the planet.

Since the 1980s the general acceptance that a group of meteorites, already at that time sitting in collections around the world, originated on Mars has provided an additional means of assessing the volume and provenance of water on Mars. Wide ranging geochemical investigations of these meteorites have provided a wealth of information about their age, composition and formation. More recently, isotopic analyses of water extracted from hydrated minerals in a few of these Martian meteorites, which now number about 30, have been completed. The results of these studies is the focus of this first chapter and will be used to help elucidate both the Martian water inventory and its origins.

1.1 Water in the Solar System

The history of water in the Solar System is still subject to debate and continual revision of ideas. It is, however, useful to have a basic idea of the active history of Solar System water. The ideas presented below are a brief overview of some of the more recent hypotheses that have gained some popularity with workers in the field.

 H_2O and OH^- seem likely to have been present in the universe since the first stars completed their life-cycles and released oxygen into the interstellar medium. Indeed H_2O is thought to be one of the most abundant interstellar molecules [1]. Despite this, the vast majority (>99 %) of material making up the early solar nebula would have been hydrogen and helium. As the early nebula collapsed, water mainly in the form of ice, would have been subject to the same inward movement and increase in pressure and temperature as all other nebula components. As star formation proceeded and the central portion of the solar nebula heated further, water and ice would have been forced into the vapour phase and driven outwards, perpendicular to the axis of rotation of the sun to greater

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heliocentric distances. Eventually a point would have been reached where it could once again condense, probably at about the same distance as Jupiter is now, ~5.2 AU [2]. The "snow line", as it has been called may, therefore, have been populated by a large number of icy bodies that in turn may have been responsible for the early, rapid formation of Jupiter [3]. Those bodies escaping Jupiter's growing attraction, essentially comets, may then have been available to play a major role in the distribution of water within the developing Solar System, the inner portions of which were by now essentially dry. Some may have been scattered to outer regions of the Solar System by interaction with Jupiter's gravity while others may have migrated inwards again. A drag force acting on larger icy bodies, forcing them to slow and fall inwards towards the sun [4], together with a migration of the snow line inwards to at least 3 AU as the sun settled to become a mainstream star [2], meant that water may then have been redistributed to inner parts of the Solar System where the terrestrial planets were forming. Much of the water that subsequently became part of the present inventory of inner Solar System bodies from asteroids to planets may have been subject to this very active history. The record of water movement has important implications for the distribution of deuterium within the Solar System. Water originating in the interstellar medium (ISM) is enriched in deuterium resulting from ion-molecular chemistry taking place in the cold of interstellar space [5]. In contrast deuterium is destroyed within stars leading to a reservoir around the sun of deuterium depleted hydrogen that can exchange with water vapour. Water migrating from central parts of the developing Solar System to beyond the snow line may therefore be depleted in deuterium compared to that around it, leading to a population of comet like bodies with distinct isotopic compositions [6]. The range of deuterium enrichment found in different Solar System bodies makes the use of D/H measurements for assessing the provenance of water on either the Earth or Mars potentially very complicated. In contrast the oxygen isotopic composition of water has the potential to be a much more powerful geological indicator on account of the fact that it is a 3 - rather than a 2 - isotope system. The presence of three isotopes distinction between normal isotopic fractionation/homogenisation allows processes and isotopic heterogeneity retained from precursor material.

1.2 Early Ideas of the Martian Hydrosphere

There are several possible sources of the water inventory presently found on Mars. These are: 1. remnants of an original steam atmosphere condensed after a period of global melting had ended and the planet had cooled; 2. out-gassing of juvenile water from the planetary interior during volcanic activity; 3. water originating from the impact of asteroids with a composition similar to carbonaceous chondrites; 4. water originating as part of a veneer of cometary material toward the end of the period of heavy bombardment. Arguments for all these possible sources have been proposed, based upon either observational evidence or geochemical evidence provided by studies of meteorites.

Early ideas regarding the quantity of water present on Mars stemmed from evidence provided by images returned from spacecraft. Numerous studies of morphological features such as outflow channels, presumed to be cut by water, and relict basins, assumed to have been oceans, resulted in estimates (expressed as the depth of a hypothetical layer across the entire planet) ranging from a few tens of metres up to 440 metres [7, 8]. The first clues as to the isotopic composition of the Martian hydrosphere came from Earth based telescopic measurements looking at spectra derived from the Martian atmosphere [9]. These measurements showed that atmospheric water was enriched in deuterium, compared to that in the Earth's atmosphere, by a factor of about six. Assuming that the atmosphere was closely coupled with the hydrosphere, it seemed that either water on Mars never had the same composition as the Earth, or that through some means had evolved to become isotopically distinct from that on Earth. The most readily understandable method of producing a different D/H ratio was to invoke a net loss of hydrogen from the atmosphere by either thermal or non-thermal escape (see Chap. 2 by Lammer et al.). Hydrogen, as the lighter isotope, has a higher scale height and as such is preferentially concentrated at outer parts of the atmosphere. Thermal losses (Jeans escape) result in a preferential loss to space of hydrogen over deuterium from the top of the atmosphere as a result of random, temperature-controlled motion. Non-thermal escape results from interaction of molecules with energetic particles in the upper atmosphere and again results in the preferential removal of hydrogen (see [10] for a complete description of these processes). Loss of all light gases would have been particularly efficient on Mars because of its relatively low gravity.

The initial measurements of the D/H ratio of Martian water were used by many groups to try to calculate the volume of the Martian water inventory. But without knowing the isotopic composition of the initial water reservoir, or indeed, if a later influx of volatiles may have reset the original isotopic composition, it proved difficult to estimate the amount that might have been lost. Discussions [9, 11] were, in common with most works at the time, based upon the assumption that Martian water, having been derived from a similar source to that on Earth, would have possessed the same starting D/H composition. It was suggested [9] that the present D/H of Martian water meant that atmospheric loss only amounted to the equivalent of around 3 m of water, assuming that the hydrogen escape flux represents an upper limit for an equivalent water loss to space. However, as this contrasted so sharply with geologic estimates, the authors interpreted this as meaning that the initial loss rates, and therefore the initial water inventory, must have been much greater. A more recent study based on the hydrogen escape flux [63] suggests that a water equivalent depth of around 5 m may be more realistic, while those models that use the total oxygen escape rate as an upper limit for water loss [e.g. 64, 65, 66, 67, Chap. 2 by Lammer et al.] imply even greater equivalent depths of 12–30 m. While the remote sensing data fuelled much speculation, further information was required to allow meaningful modelling of the evolution of water on Mars. This information was provided by the analysis of the Martian meteorites.

1.3 Martian Meteorites

Meteorites that are now generally accepted as being samples of Mars were for many years known as SNC meteorites after three individuals were originally identified as being similar to one another yet distinct from other groups [12]. These were Shergotty, Nakhla and Chassigny, each conventionally named after the place nearest to where they were recovered. These and other, similar meteorites are a petrologically diverse group of basalts and ultramafic igneous rocks [13]. Since they lack the chondrules present in many other groups of silicate-rich meteorites they are known as achondrites. There are, however, many different types of achondritic meteorites and it was not until the oxygen isotopic composition of SNC meteorites was measured that their common ancestry was confirmed [14]. A list of presently known Martian meteorites is given in Table 1.1.



Plate 1.1 One of the specimens comprising the Martian meteorite Los Angeles 001, a basaltic Shergottite. The meteorite comprised of two stones, each displaying a well defined fusion crust. They were originally found in the Mojave Desert but only identified in 1999 in Los Angeles. The stone shown has a mass of 245 g and is shown next to a 1 cm square cube for scale. Photograph reproduced courtesy of Ron Baalke 2000.

Measurement of the oxygen isotopic composition of silicate minerals in meteorites has played a crucial role in identifying and characterising those belonging to discrete groups. So, for instance, it is possible to tell that one group of meteorites originated on a different parent body to any other (in most cases the parent bodies are different asteroids, but there are also lunar meteorites and, of course, the SNCs).

Meteorite	Paired	Wt.(g)	Ту	Where	Date
			ре		
ALHA77005		482	LS	Antarctica	1977 (Find)
ALH 84001		1,931	0	Antarctica	1977 (Find) 1984 (Find)
Chassigny		4,000	C	France	1904 (Fill)
Dar al Gani 476		2,015	BS	Sahara	1913 (Find)
Dar al Gani 489	DaG 476	2,015	BS	Sahara	1990 (Find)
Dar al Gani 670	DaG 476	1,619	BS	Sahara	1999 (Find)
Dar al Gani 735	DaG 476	588	BS	Sahara	1996 (Find)
Dar al Gani 876	DaG 476	6	BS	Sahara	1998 (Find)
Dhofar 019	Duo Iro	1,056	BS	Oman	2000 (Find)
Dhofar 378		15	BS	Oman	2000 (Find)
EETA 79001		7,982	BS	Antarctica	1979 (Find)
Governador Valadares		158	N	Brazil	1958 (Find)
GRV9927		9.97	LS	Antarctica	1999 (Find)
Lafayette		800	N	USA (Indiana)	1931 (Find)
LEW 88516		13	LS	Antarctica	1988 (Find)
Los Angeles (LA 001)		698	BS	USA (Mojave Desert)	1999 (Find)
Nakhla		10,000	N	Egypt	1911 (Fall)
NWA 480	NWA 1110	28	BS	NW Africa	2000 (Find)
NWA 817		104	N	NW Africa	2000 (Find)
NWA 856	NWA 1110	320	BS	NW Africa	2001 (Find)
NWA 1068		654	BS	NW Africa	2001 (Find)
NWA 1110		118	PS	NW Africa	2001 (Find)
QUE 94201		12	BS	Antarctica	1994 (Find)
Sayh al Uhaymir 005		1,344	BS	Oman	1999 (Find)
Sayh al Uhaymir 008	S. al U. 005	8,579	BS	Oman	1999 (Find)
Sayh al Uhaymir 051	S. al U. 005	436	BS	Oman	2000 (Find)
Sayh al Uhaymir 060	S. al U. 005	42	BS	Oman	2001 (Find)
Sayh al Uhaymir 090	S. al U. 005	95	BS	Oman	2002 (Find)
Sayh al Uhaymir 094	S. al U. 005	223	BS	Oman	2000 (Find)
Shergotty		5,000	BS	India	1865 (Fall)
Y-793605		16	LS	Antarctica	1979 (Find)
Y-000593		13,700	Ν	Antarctica	2000 (Find)
Y-000749	Y-000593	1,300	Ν	Antarctica	2000 (Find)
Y-A1075		55	LS	Antarctica	2000 (Find)
Zagami		18,100	BS	Nigeria	1962 (Fall)

Table 1.1. Martian meteorites as at 1^{st} June 2003. Samples include 35 specimens of 23 separate meteorites.

BS: Shergottite, LS: Lherzolitic Shergottite, PS: Picritic Shergottite

C: Chassignite, N: Nakhlite, O: Orthopyroxenite.

Three stable isotopes of oxygen exist with atomic masses of 16, 17 and 18. Originally only the two most abundant isotopes were measured, i.e. molecules having masses of 32 and 34 ($^{16}O + {}^{16}O$ and ${}^{16}O + {}^{18}O$ respectively). The relative abundance of the two isotopes in terrestrial samples, typically ${}^{16}O = 99.763 \%$, ${}^{18}O$ = 0.1995 % [15], varies slightly according to the mineral in question and the temperature at which it formed, a property that has been widely used as a means of assessing alteration temperatures in metamorphic mineral assemblages. As analytical methods and mass spectrometers improved during the 1960s it became possible to measure accurately the third and least abundant isotope of oxygen, ¹⁷O (typical abundance 0.0375 %), as mass 33 (¹⁶O+¹⁷O). It was this advance that became of crucial importance in studies of extraterrestrial materials [16]. The abundance of the isotopes is usually expressed as a ratio of the minor to major isotopes relative to a standard (Standard Mean Ocean Water, SMOW is used for oxygen) and is quoted as a δ (delta) value ($\delta^{17}O$, $\delta^{18}O$ for 17/16 and 18/16 ratios, δD for D/H ratios). The details of the notation need not concern us here, suffice it to say that the resulting values are expressed in parts per thousand or per mil (‰). (For a full explanation see, for instance [17].) Efficient mixing of all terrestrial material during the period of global melting, which accompanied formation of the Earth, means that with the exception of a few sulphate rocks that derive an isotopic anomaly ultimately from stratospheric processes [18], there remains a constant relationship between ¹⁷O/¹⁶O and ¹⁸O/¹⁶O ratios of all oxygen-bearing materials (i.e. mantle rocks, sedimentary rocks, the oceans, the atmosphere, etc.). In other words the planet-forming event served to homogenise any isotopic variability present in the constituent planetesimals, dust and gas. Subsequent geological activity has caused changes in the initial oxygen isotopic ratios but in a way that is understood from normal chemical and physical principles. During most chemical and physical reaction processes, the behaviour of the two less abundant isotopes means that they fractionate between reactant and product in proportions that are approximately equal to the difference in mass between the isotopes. A rule of thumb is that the effects registered in ¹⁸O are twice as large as those in ¹⁷O, relative in both cases to 16 O (i.e. 18 - 16 = 2 and 17 - 16 = 1). In fact the details of this phenomenon are quite complicated and there are all kinds of subtle variations inherent to different systems [19]. For our purposes it is sufficient to note that on a plot of δ^{17} O against δ^{18} O (known as a three isotope plot, [20]) all terrestrial samples fall on a straight line referred to as the terrestrial fractionation line (TF line; see Fig. 1.1). It transpires that the slope of this line is about 0.52. In contrast, extraterrestrial materials possess a wide range of abundances of the minor isotopes that reflect the relative contributions by material accreting to form their respective parent bodies and any processes of exchange between materials that may have taken place [16]. As such meteorites plot in different regions of a three isotope plot.

The abundance of the minor isotopes, ¹⁷O and ¹⁸O, in Martian meteorites is internally consistent yet distinctly different to that measured in terrestrial samples [21, 22]. In every case they possess a small excess of ¹⁷O, which means that on a three isotope plot they lie on a line parallel to, but displaced from the TF line

(Fig. 1.1). The magnitude of deviation from the TF line is defined as the Δ^{17} O value. The consistent magnitude of the Δ^{17} O offset found in these samples is powerful evidence that they originated on a single parent body elsewhere in the Solar System. The spread of points along the line reflects the operation of geological processes that post-date planetary formation. As only relatively large bodies undergo global scale melting the possible source of these meteorites must be restricted to larger planetary bodies. Furthermore the relatively young age at which the rocks were still molten, ~1.3 Ga (billion years) ago for Nakhla and Chassigny, as deduced from analysis of radiogenic isotopes [23, 24] and as low as a few tens or hundreds of Ma (million years) for some of the other members of the group [13], meant that the source has remained volcanically active until the relatively recent past.

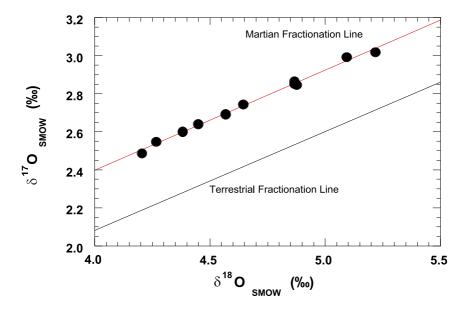


Fig. 1.1 Three isotope plot showing the relationship of δ^{17} O and δ^{18} O for oxygen extracted from terrestrial reservoirs (TF Line) and Martian meteorites (MF Line). In each case oxygen from Martian silicates is displaced by around 0.32 ‰ in δ^{17} O, i.e. has Δ^{17} O values of + 0.32 ‰ [22].

While it was clear from their oxygen isotopic compositions that the SNC meteorites had a common source, a Martian provenance was not firmly established until pockets of gas found to be trapped in shock-produced minerals within one of the meteorites (EETA 79001) were analysed. Noble gases, Ar, Ne, Kr and Xe were measured first by Bogard and Johnson [25] and found to have isotopic ratios different from any other meteorite group but, crucially, similar to the values measured by the Viking space missions in 1976 on the Martian surface. Subsequently other workers [26] analysing different gases, notably N_2 trapped in

EETA 79001 and other Martian meteorites, confirmed the similarity to the Viking values and dispelled any real doubt about an origin on Mars.

1.4 Water in Martian Meteorites

The notion of extracting sufficient water from any of the Martian meteorites for isotopic analysis appears on first appraisal rather unlikely. Yet all members contain some hydrated minerals, either primary or secondary and by carefully gauging the water content and the sample size available, useful measurements can be achieved. Two distinct types of hydrated minerals are present in Martian meteorites: 1. those formed as primary magmatic phases such as biotite, amphibole and apatite that crystallised at high temperatures in the presence of water vapour and 2. those that were formed at low temperature at, or close to, the Martian surface in the presence of liquid water, e.g. aluminosilicate clays. Magmatic minerals are uncommon but have been positively identified in a number of Martian meteorites, including Chassigny, Shergotty and Zagami. Their relative paucity is believed to reflect the low water content of Martian magmas [27]. Processes of secondary alteration are reflected by minerals such as illite, calcium sulphate and magnesium sulphate along with phases such as iddingsite and various phyllosilicates. These entities require the presence of liquid water over an extended period of time and at temperatures sufficiently high (>0°C) to promote alteration of the silicates. Small quantities of various of these alteration products have been observed in many of the Martian meteorites [28].

The timing of the formation of hydrated phases could be an important factor in identifying the source of water but is generally poorly defined. Radiometric isotopes can provide some clues in that crystallisation ages indicate the age of original magmatic phases. The only other constraint we have is from shock ages, usually provided by Ar/Ar dating techniques. However, Martian meteorites possess complex shock histories including large shock events early in their history, as well as that resulting from the final ejection impact. The isotopic evidence of such a sequence of shock events can be difficult to unravel, and as each shock has the potential to mobilise components within the rock, particularly important when studying D/H ratios [29], this makes understanding the age and origin of any water-related components very difficult. Consequently while we have a good idea of the age of any original magmatic water, the timing of any subsequent alteration that this may have undergone or the timing of the formation of any new hydrous phases is less clear. The exception to this rule is ALH 84001 for which the carbonates have been dated at about 4 billion years old, close to the crystallisation age [30].

The overall water abundance in different Martian meteorites varies not only with the prevalence of indigenous hydrated minerals, but crucially also on the amount of terrestrial alteration and contamination that has taken place. In those meteorites that are observed entering the Earth's atmosphere and collected soon after (known as "falls") the amount of alteration is usually small. While in those

that are not observed to fall and merely collected ("finds"), a protracted period of terrestrial residence may mean that the majority of water released during analysis originates from terrestrial alteration products. The contribution of terrestrial contamination will also depend upon the surface conditions at the site of collection and has been found to be particularly severe for those meteorites recovered from desert locations. For example DaG 476, a meteorite collected from the Libyan desert, was found to have a water content of an order of magnitude greater than most other Martian samples so far analysed [31]. This probably results from aggressive physical weathering, which allows access to water vapour and liquid water from sporadic rainfall. The quantities of indigenous water (after a precombustion stage to remove terrestrial contamination) were found to range between 130 and 350 ppm [32]. Those meteorites possessing the greatest indigenous water contents were those observed during mineralogical studies to possess aqueous alteration products assumed to have been formed during hydrothermal processes [33]. The Nakhlites in particular are recognised to have interacted with fluids to create iddingsite, a composite of a range of smectite clays, sulphates and carbonates [34], while others, notably ALH 84001, EETA 79001 and Chassigny have all been found to contain carbonates, again suggesting interaction with Martian crustal fluids [35, 36, 37].

1.5 Isotopic Studies of Water from Martian Meteorites

Wide ranging, light element isotopic studies of Martian meteorites have been carried out for many years with the majority of early analyses concentrating on carbon, nitrogen and oxygen extracted from silicates and other anhydrous phases. Analysis of these elements from apparent Martian weathering products gave the first clues to the presence of products derived from hydrous alteration [e.g. 38]. However, the first analyses of water [39, 40], in studies that focussed on D/H ratios, found only terrestrial signatures. These studies were probably hampered by the relatively small indigenous water contents of the meteorites and restricted sample availability as subsequent studies found water with non-terrestrial signatures. The relatively anhydrous character of Martian meteorites, coupled with their precious nature, has limited the number of viable techniques available and therefore also the number of completed studies. Despite this, several other groups have made D/H measurements of water in these meteorites [e.g. 41, 42], each identifying hydrogen indigenous to the meteorites that would initially have been in the form of water. Studies reporting the measurement of oxygen isotopes from water include those by [33] and [31]. Both of these studies identified indigenous water in addition to terrestrial contamination.

More recently, measurements of D/H in Martian meteorites have been made using ion microprobes [27, 42, 29], which allow an appraisal of spatial variations in solid samples. This technique is not applicable to oxygen analysis due to the high oxygen content of host silicates. However, while the ion microprobe offers an unrivalled ability to analyse well characterised phases in polished thin sections, it is of little use when minerals are part of complex mixtures, as is often the case with hydrous, aqueous alteration phases. For such phases, ratios of D/H together with ¹⁷O/¹⁶O and ¹⁸O/¹⁶O are more accurately characterised using a technique of stepped heating, where crushed samples are subjected to progressively higher temperatures (typically increments of $100 - 200^{\circ}$ C are used) either in a vacuum or in a flow of helium. It is important to note at this point that while a relatively small number of hydrated minerals has been identified in many of the meteorites (Section 1.3), the water extracted upon stepped heating may originate from several different sites within these phases. In all such relatively anhydrous samples, a large proportion of the water lost will be that adsorbed to sample surfaces. This is usually lost at low temperatures during stepped heating and will inevitably be of terrestrial origin. The next water to be lost from samples is that existing as water molecules held between layers in clay minerals. Only smectite-type or expanding clays hold such water, but this can represent a considerable proportion of the total yield. This inter-layer water can move relatively freely and thus is always liable to reflect the latest environment in which the samples were kept and thus will also produce a terrestrial signature. Finally all hydrated minerals contain structural O-H groups that are bound more tightly within the minerals and thus generally liberate water at temperatures in excess of 250°C. It is these that can potentially retain an indigenous isotopic signature.

1.5.1 D/H Ratios

The variable results of the earliest investigations of the D/H ratios present in Martian meteorites [39, 40] probably reflected degrees of contamination by terrestrial reservoirs during analysis. The first study that recognised a significant deuterium enrichment [41] was completed using large samples of 2.0 and 2.8 g from Shergotty and Lafayette. Values for δD of up to +800 ‰ were measured in water released at temperatures between 450 and 1050°C (water extracted up to 450°C was assumed to be largely terrestrial in origin and so was discarded). A more extensive study of D/H ratios [27] was completed using an ion microprobe to allow targeting of individual magmatic phases in three Martian meteorites. Water contents of the phases were also measured. The minerals targeted were kaersutite (an amphibole), biotite and apatite and in each case analyses showed large enrichments in deuterium ranging from +500 to +4400 ‰, much greater than had been measured previously. The water contents of these phases did not conform with terrestrial counterparts either, with each of the phases measured yielding only around 10 % of the expected water.

A later study [34] used a more conventional method of analysis. Large wholerock samples (0.42 - 2.56 g) of eight Martian meteorites were subjected to a regime of step heating to extract volatiles with D/H measurements on the resulting water. A range of δ D values from + 250 to + 2100 ‰ were found in seven of the meteorites, with the highest values measured from the higher temperature steps. All measured compositions were assumed to be minimum values with a variable contribution from terrestrial contamination. One meteorite, Chassigny, was found to have water possessing a terrestrial value from all but the highest temperature step, possibly reflecting nearly complete replacement of indigenous water with that derived from terrestrial reservoirs.

In a return to microprobe analysis, meteorite QUE 94201 was analysed in an attempt to better characterise the D/H ratio of primary water extracted from magmatic minerals [42]. Apatite grains were again targeted and produced a range of δD values of between +1700 and +3600 ‰. The observed range in δD seemed to show an anti-correlation with the amount of water present in the apatite samples, with a minimum in δD coinciding with a maximum initial water content.

The analyses of water in SNC meteorites [27, 41] revealed a wide range of hydrogen isotopic compositions that were nearly always enriched in deuterium relative to Earth-derived reservoirs, but did not result in any specific predictions of the water inventory on Mars. However, they did go a long way to confirming the large positive δD values of atmospheric measurements made in remote sensing studies and suggested that a link existed between the atmosphere and the hydrosphere. Interpretation of the deuterium excess found in these studies can be explained using a water inventory derived from one or a number of the above mentioned sources (Section 1.2).

The composition of Mars' initial inventory was assumed [41, 27] to be similar to that of the Earth and the increased D/H ratio was the result of atmospheric loss processes of the types discussed previously. A further assumption [27] was that pristine magmatic minerals should reflect this. However, to explain the large deuterium excesses found during subsequent analysis of the minerals, it was suggested that isotopic enrichment was by alteration on the Martian surface with deuterium-enriched fluids. This would require conditions similar to terrestrial hydrothermal circulation and alteration, and would also require close linkage between the atmosphere and hydrosphere. In this case analysis of magmatic phases would provide more information about water involved in a hydrological cycle than about the composition of primordial Martian water. In a subsequent study [42] the composition of hydrated, magmatic minerals was found to vary according to their presumed original water content. Those minerals with the greatest initial contents of water suffered less isotopic alteration during hydrothermal activity. The conclusion of this study was that the initial magmatic water composition on Mars actually had a D/H ratio approximately twice that of terrestrial water (i.e. δD of ~ + 900 ‰) and that this initial enrichment was the result of an earlier period of hydrodynamic escape resulting from an enhanced flux of UV from the developing sun (see [43] for a full explanation). If this were the case, then all estimates of the Martian water inventory based upon the assumption of a terrestrial-like starting composition would be in error. However, a recent, more detailed ion microprobe study of D/H ratios in a suite of Martian meteorites [29] revealed δD compositions with values ranging to as low as 0 %. The magmatic minerals targeted were found in melt inclusions in ALHA 77005 and Chassigny, and with no evidence of shock alteration the authors' conclusion was that the initial composition of Martian water was indeed similar to that measured on Earth.

A study using measured hydrogen isotopic compositions of hydrated minerals in Martian meteorites [44] and an estimate of the loss rate of hydrogen from the atmosphere both now and in the past, showed that a conservative estimate of the amount of water present 4.5 Ga ago was equivalent to a layer of 42 - 280 m. The range suggested depends upon the age at which the minerals in the Martian meteorite Zagami were at equilibrium with water in the Martian hydrosphere, assuming a steady loss rate. However, if as many believe, loss rates were higher early in Mars history, either as a result of higher atmospheric temperatures or pressures, a possibility that is not prohibited by the isotopic data, then the original water inventory may have been equivalent to a 2200 m layer. This, in turn, would suggest that the amount remaining today in the Martian crust may be as much as 190 m equivalent depth [44].

The idea that it was largely Mars' initial inventory of water that was retained and modified by loss processes to produce what we see today is not universally accepted. Thus while conclusions of most of the major studies of D/H in Martian meteorites include the effect of atmospheric loss processes, the measured excesses can also be accounted for by a variety of other explanations. A study of Martian magmatism [33] concluded that juvenile water alone may have produced a global equivalent depth of around 200 m. These calculations were based upon the assumption that pre-eruptive magmas on Mars contained around 1.4 wt % water, together with an estimate of the volume of magma erupted in the last 3.9 billion years. As this water would have been in addition to any retained and did not include that erupted prior to 3.9 Ga ago, it was considered a lower limit. However, the actual water content of the hydrated phases [27] was only around 10 % of that expected and consequently the estimate based upon juvenile water had to be reduced from 200 to 20 m. This is a similar quantity to a 10 - 20 m estimate which was also based upon the water content of Martian meteorites [45]. This study suggested that the remainder of any initial water inventory was consumed by total oxidation of available iron during accretion with loss of hydrogen to space.

The D/H excesses measured in different Martian meteorite studies prompted other theories to be developed as to the possible source of water. Impacting bodies with a range of compositions are thought by many to have played an important role in contributing to the atmospheres of the terrestrial planets [e.g. 46, 47]. After several studies of D/H in carbonaceous chondrites [48] a D/H excess in these meteorites is well established and carbonaceous chondrites, which can contain up to around 20 wt % water, have been proposed as a possible source of the deuterium-rich water on Mars.

An alternative theory [49] recently revised [46], suggests that the majority of volatiles, including water, originated from impacts of cometary bodies towards the end of the late, heavy bombardment. This theory also suggests that the original atmosphere resulting from accretion had been lost. The authors do not attempt to estimate a depth for the Martian water layer, indeed they favour a model where repeated cycles of development and loss of atmosphere occurred through Mars' evolution. In each cycle, the water composition may have been different depending on the exact nature of the comets, which were envisioned as being

variable in volatile composition depending upon the location and temperature at which they formed.

Water derived from impact delivery either of carbonaceous or cometary material is inherently deuterium-rich. This is the result of incorporation of deuterium enriched molecules from the cold outer parts of the solar nebula. The deuterium enrichments themselves were imparted by ion-molecule reactions in cold parts of the inter-stellar medium prior to formation of the Solar System [5, 50]. However, as explained in Section 1.2, water in some comets may have undergone isotopic exchange with a deuterium depleted reservoir close to the sun, and consequently may differ markedly from other comets formed at greater heliocentric distances. Thus the measured deuterium enrichment may have resulted from comets derived from a combination of sources, each having a unique deuterium signature which may then have been subject to further evolution resulting from preferential loss of hydrogen to space.

A major problem for estimates of Mars' inventory based upon isotopic compositions as measured in Martian meteorites is the assumption that all available water is active within any Martian hydrological cycle. Recent Mars Odyssey data suggest that a considerable amount of water exists just below the Martian surface (Chap. 5 by Mitrofanov) and this may well be actively participating in the atmosphere/hydrosphere system within geological timescales (Chap. 8 by Tokano). However, it is entirely possible that a great deal more may lie deeper within the crust, isolated from the active contingent. Suggestions as to how such a situation may have developed [51] seem quite plausible and it may, therefore, be that isotopic ratios of O₂ and H₂ are only providing a measure of the surface, exchangeable reservoir. Assessing the extent of interaction of the total water inventory during Mars history is crucial. If, in the past, a larger proportion of the Martian crustal inventory was actively exchanging with the atmosphere, then the implication is that the total water inventory will be small. If, however, the majority of crustal water has been isolated, then D/H ratios do not preclude the possibility that much greater quantities of water exist in subsurface regions. The recent report [52] that Mars lacks any concentrated deposits of carbonates, at face value seems to preclude the presence, in the past, of any large-scale water-bearing bodies at the surface (oceans etc.). This is yet a further constraint on models of water evolution to take into account.

1.5.2 Oxygen Isotopic Studies

Studies of the oxygen composition of Martian meteorites have been dominated by those looking at isotopic abundance in silicates. As described in Section 1.3, these measurements were vital in establishing the provenance of the meteorites.

The importance of making oxygen isotopic measurements of water is that the data provide a way of distinguishing unequivocally between water of terrestrial origin and that which is indigenous to the meteorite. The first study to make such measurements from Martian meteorites, that included the important ¹⁷O measurement, were completed by Karlsson et al. [33]. This work looked at six

individual meteorites with water being extracted from large samples of between 2.0 and 3.4 g, over a range of temperatures from 0 to around 1000°C. Despite the large size of the samples, their anhydrous nature meant that the heating profile was restricted to 4 individual steps. Total water contents ranged from only 0.04 wt % in Zagami to 0.4 wt % in Lafayette. The results of the study produced δ^{18} O values that, while far from identical, did display some inter-sample consistency. The Δ^{17} O values (reproduced in Fig. 1.2) show a more consistent pattern, with most samples typically releasing water close to the terrestrial fractionation line in the first one or sometimes two steps (150 and 350°C) before rising to positive values at higher temperatures (650 and 1000°C). Three of the meteorites produced Δ^{17} O values of particular note, Shergotty and EETA 79001 because they were exceptions to the general trend and Chassigny because it *did* follow the trend and as such contradicted the results of D/H measurements on bulk rock [34]. In fact the oxygen isotope data from Chassigny seem to indicate the presence of water indigenous to Mars whereas the results of D/H measurements on bulk rock were only able to detect water of terrestrial origin. The other two meteorites (both Shergottites) do not appear to show any convincing evidence of Martian water, a direct contradiction of the D/H bulk rock measurements that clearly indicated the presence of water derived from indigenous sources. A further observation resulting from the study was the lack of isotopic equilibrium between the water and the silicates, a point discussed below. A more sophisticated study of water in Martian meteorites used a continuous flow technique that required considerably less gas for analysis and consequently has greatly reduced sample requirements. This study [31], analysed samples from four Martian meteorites; EETA 79001, Nakhla, ALH 84001 and DaG 476. Samples analysed were all around 50 mg but were usually able to produce sufficient water to allow at least six separate temperature steps and so allow clearer distinction between terrestrial and indigenous water.

Two of these meteorites were also included in the previous study, however, ALH 84001 which is notable for its great age, around 4 billion years [53, 54] and DaG 476 a desert meteorite, had not previously been analysed and provided interesting new data. The results from this study, shown in Fig. 1.3, are consistent with those previously gained [33] with low temperature water displaying a terrestrial composition and higher temperature water indicating indigenous reservoirs. The greater number of temperature steps afforded by the improved sensitivity [31], produced an improvement in resolution and in all cases allowed clearer distinction between terrestrial water and indigenous water and also suggested a mixture at intermediate temperatures. In the case of DaG 476 the large water content of the meteorite allowed many individual steps but suggested that the results of weathering in harsh desert conditions had overprinted most of the indigenous signature with terrestrial water. The analysis of ALH 84001 provided the most interesting data with a large anomaly in the Δ^{17} O value being recorded in water driven off at 300°C.

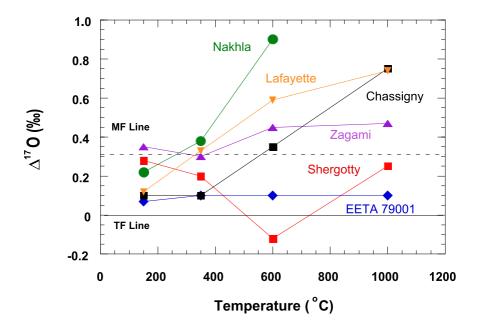


Fig. 1.2 Plot shows the Δ^{17} O values measured at increasing pyrolysis temperature for all six samples analysed [33]. The first two steps for each meteorite plot close to the terrestrial fractionation line (solid line at 0 ‰) while data for the high temperature steps plot distinctly above the higher, broken line at ~ +0.3 ‰ representing the composition of silicates on Mars [22].

The peak of up to 4 ‰ was recorded in three separate aliquots of the ALH 84001 sample with the remaining temperature steps following a similar pattern to other Martian samples. Of the two samples common to both studies Nakhla gave consistent results but EETA 79001, which had previously displayed only terrestrial water was found to have an extraterrestrial signature.

The oxygen isotopic data have a number of interesting implications for the provenance and history of water on Mars. Although some variation between individual studies exist, the general trend is one of water extracted at low temperature (< 250° C) reflecting contamination following the arrival of the meteorites on Earth with higher temperature water reflecting indigenous sources. The mineralogic source of the indigenous water in these samples is of importance to our understanding of the processes that the samples underwent prior to leaving the Martian surface and also has implications regarding the ultimate source of Martian water. Whilst the ion microprobe offers the potential to analyse individual minerals, the technique suffers from other limitations. As such our best indication of the mineralogic water source is the temperature of release.

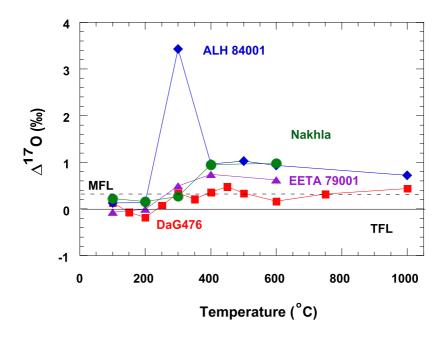


Fig. 1.3 A similar style of plot to that of Fig. 1.2 again showing the Δ^{17} O values for samples relative to the TF line and the MF line. (Note different scale to that of Fig. 1.2.) Data from [55].

It is assumed that minerals breaking down at the lowest temperatures are also those formed at relatively low temperatures, either on Mars or on Earth and as such should display isotopic compositions reflecting either terrestrial water or that taking part in the Martian hydrological cycle. However, in such anhydrous mineral dominated samples any indigenous signature present in water released below ~150°C is likely to be overwhelmed by adsorbed terrestrial water. From these studies it is impossible to determine whether or not the water extracted at low temperatures originates from minerals formed in the terrestrial environment, or whether in fact the minerals are originally Martian, their water having been completely replaced on Earth. In the case of DaG 476 the former option is probably the case as the sample appeared weathered and rusty prior to analysis, yet even this sample seemed to retain an indigenous component in higher temperature water. The sample extracted at intermediate temperatures can be understood in terms of a mixture - some Martian and some terrestrial - but with the majority of that adsorbed to the sample already removed, most should originate from within minerals. As such the dominant source will be either interlayer water from expanding clays or from the water of hydration from minerals such as sulphates. Water released at higher temperatures will largely originate from the structural OH⁻ groups present in phyllosilicates and also primary hydrated phases such as amphiboles and micas. If, as suggested by D/H measurements, the water in primary minerals has been altered to reflect

hydrothermal fluids, then all indigenous water will isotopically reflect surface reservoirs in contact with the atmosphere. However, if primary water retains its original signature, assumed to be the same as silicates (i.e. + 0.32 ‰, Δ^{17} O), then this will only serve to dilute that originating from hydrothermal fluids possessing a greater ¹⁷O enrichment. The lack of equilibrium between oxygen in hydrated phases and that held in the structure of silicates is one of the most important pieces of information to emerge from studies of water in Martian meteorites. The now well established Δ^{17} O value of the oxygen isotopic composition of silicates (+ 0.32 %) appears distinct from that found in indigenous water which extends up to +0.8% or even higher. The easiest explanation of this discrepancy is that while water has interacted with the silicates to produce hydrated minerals, the reactions have not been of sufficient duration or at a sufficiently high temperature to allow isotopic equilibrium to be achieved and the water signature erased. However, this still leaves us with the question of where the distinct isotopic composition of water originated. Fractionation during atmospheric loss of oxygen, as a result of Jeans escape, can produce a small ¹⁷O anomaly that might be capable of generating the general enrichment observed in most meteorites [56]. A possible alternative solution to the problem [18] was suggested after identification of a non-mass dependent isotopic fractionation processes in upper parts of the Earth's atmosphere. One reaction suggested was the photolysis of ozone that ultimately created a ¹⁷O enrichment in CO, that could subsequently be transferred to water. In a later study [57] it was suggested that there may be many such reactions involving UV radiation capable of fractionating oxygen to produce gaseous reservoirs enriched in ¹⁷O. On Mars the thin atmosphere allows energetic particles much nearer the surface, therefore any resulting reservoir of isotopically enriched gas would be in more intimate contact with the hydrosphere. Mixing and exchange between water in the hydrological cycle and oxygen in the atmosphere then enabled transfer of the anomaly to water and subsequently to hydrated minerals in the crust. An alternative source for isotopically distinct water is that of a veneer of cometary water as discussed below.

ALH 84001

While the general excess of ¹⁷O observed over a range of temperatures in Martian meteorites can be explained by internal and atmospheric processes, the anomolous peak observed at about 300°C in ALH 84001 may be best explained by a more fundamental process. In numerous studies of primitive meteorites it has been established that the oxygen isotopic composition of the initial water inventory present on their parent bodies possessed a significant excess of ¹⁷O [e.g. 58, 59]. It seems highly likely that this water reflected the majority of that present in the early Solar System, which in turn possessed a composition that may have been inherited from material in the original solar nebula. With a formation age of 4 - 4.5 Ga, ALH 84001 is recognised as being much older than other Martian meteorites. It may, therefore, record isotopic evidence of fluids present at or shortly after this time, e.g. carbonates from ALH 84001 have been dated at about

3.9 Ga old [30]. Assuming that the hydrated minerals were formed on Mars prior to the homogenising effect of the proposed warm/wet phase, hydrated minerals may retain the composition of water arriving as a late veneer. Two possible sources of late veneer volatiles have been suggested based upon D/H evidence, either asteroidal or cometary. Had the source of this water been from asteroidal bodies such as those with a primitive carbonaceous chondrite composition, then water would have reflected the composition found after parent body processes (i.e. after reaction between water and solids whilst part of the asteroid), and as such would have had Δ^{17} O values of close to or below 0 % [60]. However, if the source of water had been from impacting cometary bodies containing large amounts of primitive, relatively unaltered water, then hydrated minerals formed may reflect a water composition possessing a Δ^{17} O of + 4 ‰ or greater. As discussed previously, this does not constrain the composition of the D/H ratio which can alter independently of the oxygen in different Solar System water bodies. The warm wet phase that was believed to follow the heavy bombardment would, very likely, have resulted in mixing and loss of the majority of any extreme isotopic signature. But had the cometary contribution been sufficiently large, it, rather than atmospheric effects, could have been the source of the moderate Δ^{17} O excesses seen in most other indigenous phases. Unfortunately our lack of knowledge as to the depth to which any water-crust interaction took place prohibits calculation of the amount of water that may have been involved and consequently oxygen isotopes have little to say about the ultimate quantities of the present Martian water inventory.

1.6 Conclusions

Isotopic data of hydrogen (D/H) and oxygen (18O/16O, 17O/16O) extracted from hydrated minerals in Martian meteorites have provided new but sometimes conflicting estimates of the global inventory of Martian water and of the probable origins of that water. Estimates of the global water inventory based upon the geochemistry of Martian meteorites rarely approach those suggested by images of the Martian surface. Results from different studies generally correlate well and indigenous water is nearly always enriched in both deuterium and the heavy isotopes of oxygen, relative to Earth-derived reservoirs. It is clear that atmospheric loss processes have played an important part in the composition of hydrogen found in Martian water, and while some of the studies discussed conclude that rather small inventories of water may now be present at least one suggests an amount consistent with estimates based upon geological features. The key stumbling blocks to an accurate estimate are the poorly constrained rate at which atmospheric loss processes have occurred over Mars' history and the extent of interaction between the atmosphere and the hydrosphere on one hand and the lithosphere on the other. Measured D/H ratios do not rule out a veneer of cometary material as a source of at least some of the water. Like hydrogen, oxygen isotopes in hydrated minerals that are indigenous to the meteorites have been identified but they are clearly out of equilibrium with the silicate portions of samples. They suggest an environment where hydrothermal activities are limited in duration/intensity allowing fluids to retain some measure of their original identity. Yet the presence of the ¹⁷O excess in the majority of samples is consistent with alteration being widespread. If the source of the anomalous oxygen is atmospheric, then this suggests Mars must at some stage have had a well developed atmosphere-hydrosphere system and widespread interaction between this water and the underlying crust. The extreme Δ^{17} O values measured in ALH 84001 suggests that it is possible for some minerals to retain ancient water with a composition originally inherited from a cometary source.

Whilst a veritable armada of spacecraft are either on their way to Mars or already there, it is clear that as far as the isotope stories are concerned we may need to wait for specific, selected samples to be returned to Earth for analysis before we can fully understand the details. In the meantime Beagle 2 with its on-board gas processing system and stable isotope ratio mass spectrometer may whet our appetite by attempting in-situ measurements of the isotopic compositions of hydrogen and oxygen early in 2004 [61]. Furthermore by using a combination of the facilities on Beagle 2 it may be possible to gain an insight into the water profile of the immediate surface environment down to a depth of 1.5 m [62].

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1.7 References

- Irvine WM, Schloerb FP, Hjalmarson A, Herbst E (1985) The chemical state of dense interstellar clouds: an overview. In: Black DC, Mathews MS (eds) Protostars and Protoplanets II. University of Arizona Press, Tucson, pp 579-620
- 2 Cyr KE, Sears WD, Lunine JI (1998) Distribution and evolution of water ice in the solar nebula: implications for Solar System body formation. Icarus 135: 537-548
- 3 Stevenson DJ, Lunine JI (1988) Rapid formation of Jupiter by diffusive redistribution of water vapor in the Solar System. Icarus 75: 146-155
- 4 Sears WD (1993) Diffusive redistribution of water vapor in the Solar System revisited. 26th Lunar Planet. Sci. Conf. 1271
- 5 Delsemme AH (1999) The deuterium enrichment observed in recent comets is consistent with the cometary origin of seawater. Planet. Space Sci. 47: 125-131
- 6 Deloule E, Robert F, Doukhan JC (1998) Interstellar hydroxyl in meteoritic chondrules: implications for the origin of water in the inner Solar System. Geochim. Cosmochim. Acta 62: 3367-3378
- 7 Carr MH (1986) Mars: a water-rich planet? Icarus 68: 187-216

- 8 Baker VR, Strom RG, Gulick VC, Kargel JS, Komatsu G, Kale VS (1991) Ancient oceans, ice sheets and the hydrological cycle on Mars. Nature 352: 589-594
- 9 Owen T, Maillard JP, De Bergh C, Lutz BL (1988) Deuterium on Mars: the abundance of HDO and the value of D/H. Science 240: 1767-1770
- 10 Jakosky BM (1991) Mars volatile evolution: evidence from stable isotopes. Icarus 94: 14-31
- 11 Yung YL, Wen J-S, Pinto JP, Pierce KK, Allen M (1988) HDO in the Martian atmosphere - implications for the abundance of crustal water. Icarus 68: 146-159
- 12 Stolper EM, McSween Jr HY, (1979) Petrology and origin of the Shertgottite meteorites. Geochim. Cosmochim. Acta 43: 1475-1498
- 13 McSween Jr HY (1994) What we have learned about Mars from SNC meteorites. Meteoritics 29: 757-779
- 14 Clayton RN, Mayeda TK (1983) Oxygen isotopes in Eucrites, Shergottites, Nakhlites and Chassignites. Earth Planet. Sci. Lett. 62: 1-6
- 15 Garlick GD (1969) The stable isotopes of oxygen. In: Wedepohl KH (ed) Handbook of Geochemistry. Springer-Verlag, Berlin
- 16 Clayton RN, Grossman L, Mayeda TK (1973) A component of primitive nuclear composition in carbonaceous meteorites. Science 182: 485-488
- 17 Hoefs J (1997) Stable Isotope Geochemistry. 4th edition. Springer-Verlag, Berlin
- 18 Thiemens MH, Jackson TL, Brenninkmeijer CAM (1995) Observation of a mass independent oxygen isotopic composition in terrestrial stratospheric CO₂, the link to ozone chemistry, and the possible occurrence in the Martian atmosphere. Geophys. Res. Lett. 22: 255-257
- 19 Miller MF (2002) Isotopic fractionation and the quantification of ¹⁷O anomalies in the oxygen three-isotope system: an appraisal and geochemical significance. Geochim. Cosmochim. Acta 66: 1881-1889
- 20 Clayton RN (1993) Oxygen isotopes in meteorites. Ann. Rev. Earth Planet. Sci. 21: 115-149
- 21 Clayton RN, Mayeda TK (1996) Oxygen isotope studies of achondrites. Geochim. Cosmochim. Acta 60: 1999-2017
- 22 Franchi IA, Wright IP, Sexton AS, Pillinger CT (1999) The oxygen isotopic composition of Earth and Mars. Meteorit. Planet. Sci. 34: 657-661
- 23 Nakamura N, Unruh DM, Tatsumoto M, Hutchison R (1982) Origin and evolution of the Nakhla meteorite inferred from the Sm-Nd and U-Pb systematics and REE, Ba, Sr, Rb abundances. Geochim. Cosmochim. Acta 46: 1555-1573
- 24 Bogard DD, Nyquist LE (1979) 40Ar/39Ar chronology of related achondrites. Meteoritics 14: 356
- 25 Bogard DD, Johnson P (1983). Martian gases in an Antarctic meteorite. Science 221: 651-654
- 26 Becker RH, Pepin RO (1984) The case for a Martian origin of the Shergottites: nitrogen and noble gases in EETA 79001. Earth Planet. Sci. Lett. 69: 225-242
- 27 Watson LL, Hutcheon ID, Epstein S, Stolper EM (1994) Water on Mars: clues from deuterium/hydrogen and water contents of hydrous phases in SNC meteorites. Science 265: 86-90
- 28 Gooding JL (1992) Soil mineralogy and chemistry on Mars: possible clues from salts and clays in SNC meteorites. Icarus 99: 28-41
- 29 Boctor NZ, Alexander CMO'D, Wang J, Hauri E (2003) The sources of water in Martian meteorites: clues from hydrogen isotopes. Geochim. Cosmochim. Acta. 67: 3971-3989
- 30 Borg LE, Connelly JN, Nyquist LE, Shih CY, Wiesmann H, Reese Y (1999) The age of the carbonates in Martian meteorite ALH 84001 Science 286: 90-94

- 31 Baker L, Franchi IA, Wright IP, Pillinger CT (1998) Oxygen isotopes in water from Martian meteorites. Meteorit. Planet. Sci. 33: A11
- 32 McSween Jr HY, Harvey RP (1993) Outgassed water on Mars: constraints from melt inclusions in SNC meteorites. Science 259: 1890-1892
- 33 Karlsson HR, Clayton RN, Gibson EK, Mayeda TK (1992) Water in SNC meteorites: evidence for a Martian hydrosphere. Science 255: 1409-1411
- 34 Leshin LA, Epstein S, Stolper EM (1996) Hydrogen isotope geochemistry of SNC meteorites. Geochim. Cosmochim. Acta 60: 2635-2560
- 35 Wentworth SJ, Gooding JL (1995) Carbonates in the Martian meteorite: waterborne but not like the SNCs. 26th Lunar Planet. Sci. Conf. 1489
- 36 Gooding JL, Wentworth SJ, Zolensky ME (1988) Calcium carbonate and sulphate of extraterrestrial origin in the EETA 79001 meteorite. Geochim. Cosmochim. Acta 52: 909-915
- 37 Mittlefehldt DW (1994) ALH 84001, a cumulate orthopyroxenite member of the Martian meteorite clan. Meteoritics 29: 214-221
- 38 Wright IP, Grady MM, Pillinger CT (1988) Carbon, oxygen and nitrogen isotopic compositions of possible Martian weathering products in EETA 79001. Geochim. Cosmochim. Acta 52: 917-924
- 39 Fallick AE, Hinton RW, McNaughton NJ, Pillinger CT (1983) D/H ratios in meteorites: some results and implications. Annal. Geophys. 1: 129-134
- 40 Yang J, Epstein S (1985) A study of stable isotopes in the Shergotty meteorite. 16th Lunar Planet. Sci. Conf. Suppl. A25-26
- 41 Kerridge JF (1988) Deuterium in Shergotty and Lafayette (and on Mars?). 19th Lunar Planet. Sci. Conf. 599
- 42 Leshin LA (2000). Insights into Martian water reservoirs from analysis of Martian meteorite QUE94201. Geophys. Res. Lett. 27: 2017-2020
- 43 Zahnle K, Kasting JF, Pollack JB (1990) Mass fractionation of noble gases in diffusion limited hydrodynamic hydrogen escape. Icarus 84: 503-527
- 44 Donahue TM (1995) Evolution of water reservoirs on Mars from D/H ratios in the atmosphere and crust. Nature 374: 432-434
- 45 Wänke H, Dreibus G (1988) Chemical composition and accretion history of the terrestrial planets. Phil. Trans. R. Soc. London A235: 545-557
- 46 Owen T, Bar-Nun A (1995) Comets, impacts and atmospheres. Icarus 116: 215-226
- 47 Bogard DD, Clayton RN, Marti K, Owen T, Turner G (2001) Martian volatiles: isotopic composition, origin and evolution. Space Sci. Rev. 96: 425-458
- 48 Kerridge JF (1985) Carbon, hydrogen and nitrogen in carbonaceous chondrites: abundances and isotopic compositions in bulk samples. Geochim. Cosmochim. Acta 49: 1707-1714
- 49 Weatherill GW (1975) Late heavy bombardment of the moon and terrestrial planets. 6th Lunar Sci. Conf. 1539-1561
- 50 Meier R, Owen T (1999) Cometary deuterium. Space Sci. Rev. 90: 33-43
- 51 Carr MH, Wänke H (1992) Earth and Mars: water inventories as clues to accretional histories. Icarus 98: 61-71
- 52 Bandfield JL, Glotch TD, Christensen PR (2003) Spectroscopic identification of carbonate minerals in the Martian dust. Science 301: 1084-1087
- 53 Ash RD, Knott SF, Turner G (1996) A 4 Gyr shock age for a Martian meteorite and implications for the cratering history of Mars. Nature 380: 57-59
- 54 Turner G, Knott SF, Ash RD, Gilmour JD (1997) Ar-Ar chronology of the Martian meteorite: evidence from stable isotopes and mineralogy. Geochim. Cosmochim. Acta 61: 3835-3850
- 55 Baker L, Franchi IA, Wright IP, Pillinger CT (1998) Unpublished data.

- 56 Jakosky BM (1993) Mars volatile evolution: implications of the recent measurement of ¹⁷O in water from the SNC meteorites. Geophys. Res. Lett. 20: 1591-1594
- 57 Thiemens MH (1999) Mass-independent isotope effects in planetary atmospheres and the early Solar System. Science 283: 341-345
- 58 Clayton RN, Mayeda TK (1984) The oxygen isotope record in Murchison and other carbonaceous chondrites. Earth Planet. Sci. Lett. 67: 151-161
- 59 Choi BG, McKeegan KD, Krot AN, Wasson JT (1993) Extreme oxygen isotopic compositions in magnetite from unequilibrated ordinary chondrites. Nature 392: 577-579
- 60 Baker L, Franchi IA, Wright IP, Pillinger CT (2001) The oxygen isotopic composition of water from Tagish Lake: its relationship to low-temperature phases and to other carbonaceous chondrites. Meteorit. Planet. Sci. 37: 977-985
- 61 Wright IP, Sims MR, Pillinger CT (2003) Scientific objectives of the Beagle 2 lander. Acta Astronaut. 52: 219-225
- Tokano T, Richter L, Pillinger CT, Wright IP (2003) Intercomparison of the soil humidity conditions at the Beagle 2 and Viking lander sites. Geophys. Res. Abstr. 5: EAE03-A-00815
- 63 Lammer H, Stumptner W, Bauer SJ (1996) Loss of H and O from Mars: implications for the planetary water inventory. Geophys. Res. Lett. 23: 3353-3356
- 64 Lammer H, Lichtenegger HIM, Kolb C, Ribas I, Guinan EF, Abart R, Bauer SJ (2003) Loss of water from Mars: implications for the oxidation of the soil. Icarus 165: 9-25
- 65 Luhmann JG, Johnson RE, Zhang MGH (1992) Evolutionary impact of sputtering of the Martian atmosphere by O^{*} pick up ions. Geophys. Res. Lett 19: 2151-2154
- 66 Kass DM, Yung YL (1999) Water on Mars: isotopic constraints on exchange between the atmosphere and surface. Geophys. Res. Lett. 26: 3653-3656
- 67 Krasnopolsky VA, Feldman PD (2001) Detection of molecular hydrogen in the atmosphere of Mars. Science 294: 1914-1917

2 Atmospheric Evolution and the History of Water on Mars

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The discovery of high concentrations of water-ice just below the Martian surface in polar areas by the Mars Odyssey spacecraft has strengthened the debate about the possibility of life on Mars. Generally, it is believed that life on Earth emerged in liquid water through the processing of organic molecules. The possible origin of life on early Mars would have been related to the evolution of the planetary water inventory, so it is important to estimate the present amount of water-ice below the planetary surface.

There are also indications that large standing bodies of water ranging from lakes to an ocean may have existed in the past history of Mars. The high resolution altimetric data from the Mars Orbiter Laser Altimeter (MOLA) support this hypothesis since the flatness and smoothness of some surface areas suggest that they may have been part of the largest watershed on early Mars. Because present pressure conditions on the Martian surface prevent the formation of large amounts of stable liquid water, the atmosphere had to be much denser in the past.

In this second chapter we give an overview of all atmospheric loss processes related to the Martian water inventory during the planetary history. First, we show that XUV-driven hydrodynamic escape of hydrogen related to a more active young Sun may have affected the water inventory during the first few hundred Ma. Further, by using the observed atmospheric D/H ratio of the atmospheric water vapour on Mars, measured D/H ratios in SNC meteorites and D/H ratios related to the initial water source together with our atmospheric loss simulations, we estimate the present and early water-ice reservoirs which could exchange with the atmosphere, and discuss also the exobiologically relevant implications related to the incorporation of atmospheric oxygen to the Martian surface.

2.1 The First Billion Years

The Martian atmospheric history can be divided into early and late evolutionary periods [e.g., 1, 2, 3]. Early in the pre-3.5 Ga period, heavy noble gases like non-radiogenic Xe isotopes may have been hydrodynamically fractionated to their present composition, with corresponding depletions and fractionations of lighter primordial atmospheric species like deuterium (D) or H atoms [1]. Subsequently the CO_2 pressure history and the isotopic evolution of atmospheric species during this early period were dictated by the interplay of estimated losses with impact erosion, carbonate precipitation, additions by outgassing and carbonate recycling, and perhaps also by the feedback stabilisation under greenhouse conditions [1, 3]. The

second period is characterised by a uniform atmospheric loss to the present pressure of about 7 mbar, enhanced due to Mars' vanished intrinsic magnetic field and various non-thermal atmospheric escape processes.

2.1.1 The Source of Martian Water

There is much evidence from chemical and dynamical reasons that the source for the terrestrial crustal and surface water originated from planetary embryos, which have their origin in the asteroid belt [4]. This source is consistent with the isotopic record of the water content of the asteroid belt, by the chondrite record [5] and in the role of gas giants in clearing the asteroid belt [6]. The observed D/H ratio is consistent with the isotopic record of D/H in carbonaceous chondrites and terrestrial seawater (TSW) whose principal source is the asteroid belt.

The ratio of D/H isotopes of the water vapour in the current Martian atmosphere is about 5.2 times the terrestrial seawater value [7], where the cause for this difference is commonly assumed to be the isotopic fractionation during atmospheric escape of water, which can exchange with sources of water in the Martian crust and surface [7, 8]. Although the original D/H ratio in Martian water obtained from planetesimals is not well known, there are three known possibilities for the delivery of water to growing terrestrial planets, i.e. planetary embryos from beyond 2.5 AU, small asteroids from beyond 2.5 AU and comets from the Jovian orbital distance and beyond.

A recent study determined how much water on Mars could have been acquired from asteroid and comet populations [9]. By estimating the cumulative collision probability between asteroids and comets with Mars and by assuming that comets consist by about 50 % of water ice with a D/H ratio about twice the terrestrial value and that asteroids have about 10 wt. % water with D/H values comparable to the terrestrial ocean water value based on carbonaceous chondrites, it was found that Mars can acquire an amount of water equivalent to 6-27 % of the terrestrial oceans, with a D/H ratio of about 1.6 and 1.2 times the TSW ratio [9].

This study indicates that Mars actually received more water from small comets and asteroids with semi-major axes greater than 2.5 AU than the Earth, while the Earth may have received the bulk of its water from large embryos. By using this result one finds that the estimations of 6-27 % of the terrestrial oceans on Mars correspond to an equivalent global ocean depth of about 600 to 2700 m in the Martian crustal regolith and on the surface. (The water amount on Mars is often expressed in terms of the depth of a hypothetical ocean covering the entire Mars. Hereafter, we refer this simply to as the "equivalent depth".) This is in agreement with previous studies [10, 11], where an outgassed amount with an equivalent depth of about 500 m on the Martian surface corresponds to a total accreted amount corresponding to 1000 m [9]. The D/H ratio of about 1.2 to 1.6 times the TSW ratio is below the average value of about 2.3 measured in Martian Shergottite meteorites [12], while an enrichment of about 1.6 times the TSW value is in agreement with the D/H ratio measured in the 3.9 Ga old Martian meteorite ALH 84001.

The difference between the D/H ratio in the Shergottites and the asteroidcomet collision study can be interpreted as follows: either the D/H ratio in Martian meteorites was derived from magmatic water, which represents a primordial Martian value obtained from accretion of a mixture of asteroidal and cometary water or it was enhanced from the primordial value due to XUV-driven hydrodynamic escape caused by a more active young Sun [9, 12]. See also Chap. 1 by Baker et al. for the discussion of D/H ratios gathered from various Martian meteorites.

2.1.2 The Early Martian Atmosphere and the Radiation and Particle Environment of the Young Sun

Standard stellar evolutionary models constructed for the Sun show that the Zero-Age-Main-Sequence (ZAMS) Sun some 4.5 Ga ago was cooler by about 200 K and smaller by about 10 % than today, resulting in a luminosity of about 70 % of that of the present Sun. The lower luminosity of the young Sun should therefore have led to a much cooler surface temperature on early Earth and Mars, preventing a long-time stability of liquid water on the surface. In early studies of the variation of planetary climate due to the evolution of solar luminosity this problem became known as the "faint young Sun paradox" (FYSP) [14].

Later, a climate regulation model controlled by the CO₂ cycle was proposed [15], where CO₂ is released in the atmosphere by volcanic activity and removed by forming carbonates. As the formation of carbonates is most efficient in the presence of liquid water, the surface temperature should not drop below 0°C for a long geological period. At high surface temperatures, the atmosphere is wet and thus water erosion and carbonate formation are enhanced. This scenario implies that CO₂ was the predominant greenhouse gas in the early atmospheres. Radiative-convective models [e.g. 16] suggest that only about 300 mbar CO₂ was required on early Earth to sustain the surface temperature above 0°C 4 Ga ago.

An implied warm climate on early Mars is more difficult to understand than on early Earth. On Mars, pressure levels of about 2 bars would be required for this, but at high CO₂ pressures, CO₂ condenses because of the low temperature in the middle atmosphere, forming high altitude ice clouds that strongly increase the albedo and thus decrease the surface temperature [17]. On the other hand, CO₂ ice clouds can be responsible for greenhouse warming due to the scattering of emitted infrared radiation from the surface, which may be stronger than the cooling effect due to the visible reflectivity of the clouds [18]. An efficient process known to limit CO₂ warming is Rayleigh back-scattering by air molecules in a dense atmosphere with pressure levels \geq 5 bars, where the incoming visible radiation cannot reach the surface due to the scattering.

A recent study showed [19] that at high pressure a photochemically produced ozone layer may evolve on Mars, which can warm the middle atmosphere and prevent the formation of CO_2 ice clouds. Taking into account the uncertainties in the collision-induced absorption (efficient at high pressures) of CO_2 , even a 1 bar CO_2 atmosphere may have been enough to sustain 0°C at the Martian surface. High levels of CO_2 would have produced carbonates that have not been observed until now, neither on the oldest terrestrial rocks nor on Mars. On Earth, the missing carbonates would imply a CO_2 pressure lower than 10 mbar [20] 3 Ga ago, so an increase of the greenhouse effect by CH_4 was proposed, where the CH_4 production could have been related to biological activity. For the earliest stage of the Earth, before the emergence of life, it is not known if the temperature was maintained above 0°C by a high level of CO_2 , abiotic CH_4 [21] or NH_3 [22] or if the Earth was globally frozen [23] at the exception of post-impact periods or local volcanic warming.

Another approach to a solution of these problems is the use of mass-losing solar models which are consistent with helio-seismology. Surface temperatures resulting in stable liquid water on Mars yield an initial mass between 1.03 to 1.07 times the present solar mass (M_{sun}) [24]. Such considerations were recently supported by Hubble Space Telescope (HST) observations of HI Ly- α absorption lines from the region where stellar winds of young solar-like stars collide with the interstellar medium [25]. It was found that the mass loss rates of solar-like stars with the age of our Sun are of the same order and the loss rates of stars which arrived at ZAMS are 1000 times or more higher than at present. The cumulative mass loss rate obtained from these observations would yield a mass of the young Sun of about $1.03 \times M_{sun}$ [25]. Such a slightly more massive young Sun together with a lower amount of greenhouse gases could have also been responsible for an early warm and wet Mars.

Problems in long-time stability of liquid water on the Martian surface are that such a massive young Sun would have lost most of its mass during the first hundred million years of its lifetime [22, 25]. The mass loss of the young Sun is directly related to a much denser early solar wind, which has important implications for the interaction with the Martian upper atmosphere after the planet's intrinsic magnetic field vanished.

Further, the time-dependence of the solar X-ray and extreme ultraviolet (EUV) flux I_{xUV} is critical for the evolution of thermal escape, ionisation, and photodissociation during the history of a planetary system. Estimates of the solar highenergy flux evolution are indirectly possible by the study of stellar proxies for the Sun at different ages. Multi-wavelength (from X-rays to the UV) observations have been collected for a sample of solar proxies within the *Sun in Time* program containing stars that represent most of the Sun's main sequence lifetime from 130 Ma to 7 Ga [26].

Observations obtained with the ASCA, ROSAT, EUVE, FUSE and IUE satellites cover a range between 1 and 3300 Å, except for a gap between 360 and 920 Å, which is a region of very strong interstellar medium absorption [26].

The resulting relative XUV fluxes yield an excellent correlation between the emitted flux and stellar age. In the relevant wavelength region of 1 to 1000 Å, the fluxes follow a power-law relationship $I_{XUV}(t)/I_{XUV} = 6.13 \times [t \text{ (Ga)}]^{-1.19}$.

Table 2.1 XUV flux normalised to the present value as a function of time after the Sun arrived at ZAMS.

Age [Ga]	0.1	0.3	0.5	1	1.5	2	2.5	3	3.5	4	4.5
$I_{\rm XUV}(t)/I_{\rm XUV}$	95	25.7	14	6.13	3.78	2.68	2.07	1.66	1.38	1.17	1

The relationship shown in Table 2.1 indicates XUV fluxes of about $6 \times I_{XUV}$ about 3.5 Ga ago, and about $100 \times I_{XUV}$ about 100 Ma after the Sun's arrival at ZAMS. Thus, these high XUV fluxes of the young Sun heated the early upper Martian atmosphere and were responsible for large thermal escape rates of water-based photo-dissociated hydrogen as well as for efficient photo-ionisation and photo-dissociation reactions of atmospheric constituents like CH₄ or NH₃, which are important for greenhouse effects.

2.1.3 XUV-Driven Hydrodynamic Escape

Recent modelling of atmospheric evolution on terrestrial planets has focused on fractionation from primordial source compositions during XUV-driven hydrodynamic escape [e.g. 27]. The upper atmospheres of terrestrial planets are mainly controlled by absorption of XUV radiation [28] and additionally by energy deposited in the upper atmospheres by large impacts [29]. By knowing the evolution of the solar XUV radiation with time, one can apply a scaling relation for the estimation of the exosphere temperature (T_{∞}) responsible for thermal escape over the Martian history. This relation is based on the assumption of equilibrium between XUV heat input and downward heat transport by conduction.

Below the exosphere (in the thermosphere), the effective heat production is balanced by the divergence of a conductive heat flux of the XUV radiation leading (after some approximations) to $T_{\infty}^{\epsilon} \approx [(\varepsilon I_{XUV} k\sigma_c)/(k_0 mg\sigma_a)] + T_0^{\epsilon}$, where ε is the heating efficiency, σ_c and σ_a are the collision and absorption cross sections, respectively, *k* is the Boltzmann constant, *s* depends on the thermospheric composition in the thermal conductivity coefficient $K(T) = K_0 T^{\epsilon}$, *m* is the mass of the main thermospheric constituent, *g* is the acceleration of gravity and T_0 is the mesopause temperature. By knowing the planetary parameters at present time t_1 one can estimate T_{∞} in the Martian past t_0 from the scaling relation $(T_{\infty}^{\epsilon} - T_0^{\epsilon})_1/(T_{\infty}^{\epsilon} - T_0^{\epsilon})_0 \approx I_{XUV1}g_0/I_{XUV0}g_1$ [30].

When T_{∞} is large and the thermal escape parameter $X = GMm/kT_{\infty}r$ (where G is the gravitational constant, M is the planetary mass and r is the planetary distance) reaches values ≤ 1.5 , the exosphere becomes unstable and hydrostatic equilibrium no longer applies [31].

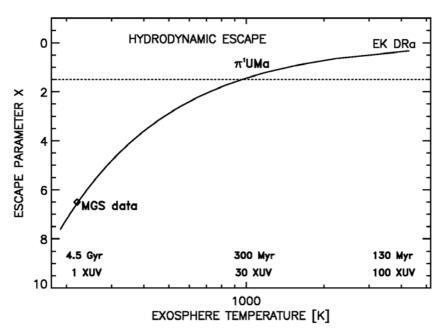


Fig. 2.1. Escape parameter *X* for H atoms on Mars as a function of exosphere temperature T_{∞} and XUV flux at an orbital distance of 1.5 AU and time. The dotted line marks the area where hydrodynamic escape becomes important since $X \leq 1.5$. MGS corresponds to the present exosphere temperature observed by Mars Global Surveyor. One can see that an early Martian CO₂ atmosphere was probably affected by hydrodynamic escape for hydrogen during the first 300 Ma (age of solar proxy π^1 UMa) after the origin of the planet. The efficient loss of hydrogen during this period may have removed the majority of the initial Martian water by diffusion-limited escape and could have been responsible for the enrichment of D isotopes close to the cometary D/H ratio as found in Martian Shergottite meteorites.

By considering the hydrodynamic treatment it is found that for Mars $T_{\infty} \ge 1000$ K, the thermal energy becomes comparable to the gravitational potential energy $(3kT_{\infty} > 2MmG/r)$ and the light atmospheric constituents like hydrogen flow away, limited only by the incoming XUV flux and by the diffusion through the heavy major atmospheric constituent CO₂ [e.g. 27]. One can see from Fig. 2.1 that Mars experienced diffusion-limited hydrodynamic escape of hydrogen from its primordial water inventory at least during the first 300 Ma after the planetary formation. Studies on diffusion-limited hydrodynamic loss due to the young Sun predict escape rates of hydrogen in the order of about 10^{28} to 10^{29} s⁻¹ from Mars [8, 27, 32]. These escape rates are large enough to remove the amount of hydrogen from an equivalent terrestrial ocean in about 300 Ma.

Under such extreme conditions, the hydrogen escape fluxes are large enough to exert upward drag forces on heavier atmospheric constituents sufficient to lift them out of the atmosphere. Lighter species are entrained with the out-flowing hydrogen and lost more readily than heavier ones, leading to mass fractionation of the residual atmosphere.

2.1.4 Impact Erosion

Over the last few decades, it has become clear that impacts of asteroids, comets and other Solar System bodies played a fundamental role in the evolution of terrestrial planets and their atmospheres. As discussed in Section 2.1.1, impacts are a primary mechanism of planetary accretion and are responsible for the delivery of water and organic matter to young planetary bodies. Large impactors may have also inhibited the formation of life in the early history of planetary formation.

Thus, the impact of a planetesimal can erode part of an existing atmosphere or it can add volatiles to it. The balance on delivery and loss from an atmosphere depends on the composition of the impactor and on the mass of the growing planet [27, 33]. When Venus and Earth attained their present masses and escape velocities, impact erosion became very inefficient, but Mars with its smaller mass was rather vulnerable and still would it be if the impact population had not essentially died out. Impact studies on Mars show that the planet could have lost a CO_2 atmosphere between 5 and 10 bars due to impact erosion over the first Ga [33]. Once an atmosphere had been eroded, it could have been resublimed by comets [34].

There is also evidence that the Martian water after the end of the heavy bombardment may have been enriched with cometary sources, after the majority of the initial water was lost by diffusion-limited hydrodynamic escape, because the average value of about 2.3 times the TSW ratio measured in the Shergottites [12, 35, Chap. 1 by Baker et al.] fits well the observed D/H ratio in comets Halley [36], Hyakutake [37] and Hale-Bopp [38]. These rates are all about twice the value for terrestrial seawater, but are consistent with rates in "hot cores" of molecular clouds. It is believed that ion-molecule reactions in dense molecular clouds at temperatures close to 35 K can produce these D/H enrichments.

2.1.5 The Early Martian Magnetic Field

Intrinsic planetary magnetic fields are responsible for the protection of atmospheres against the solar wind. The available data of an early Martian magnetic field are restricted to measurements by Mars Global Surveyor (MGS) and the study of Martian meteorites [e.g. 39]. In 1997, MGS started with the global mapping of the Martian magnetic environment and found that the planet does not have a significant global intrinsic magnetic field [40]. However, these measurements also established the presence of significant, local, small-scale, crustal, remnant magnetisation.

This local magnetisation appears mainly in the ancient southern highlands, and is absent in the regions were large impacts occurred (like Hellas and Argyre). Since these impact basins were formed about 4 Ga ago, it is generally argued that the Martian dynamo ceased before this time [41]. Another study used the same data and suggested that the Martian dynamo turned on less than 4 Ga ago, and turned off at an unknown time since then, with the only limitation that the present magnetic field strength must be achieved [42].

Magnetic studies of the Martian meteorite ALH 84001 revealed that about 4 Ga old carbonates contained magnetite and pyrrhotite, which carried a stable natural remnant magnetisation [43]. This result implies that Mars had established a geodynamo within 450 to 650 Ma after its formation with an intensity within an order of magnitude of that of the present Earth. Moreover, these results support the theory that an ancient strong dynamo ceased about 4 Ga ago. The remnant magnetism of Martian SNC meteorites, which formed 1.3 Ga to 180 Ma ago, is consistent with both theories since such field strengths could appear at the surface of Mars even at present [44].

The assumed/indicated intrinsic magnetic field, which is comparable to the terrestrial one, should have protected the atmosphere from the dense solar wind of the young Sun. On the other hand, these studies indicate that the Martian atmosphere may have been unprotected and affected by various non-thermal escape processes by the solar wind plasma during the past 3.5 Ga.

2.2 Thermal Atmospheric Escape (Jeans Escape)

Light molecules in the exosphere can be thermally driven to escape (Jeans escape) when the velocity exceeds the escape velocity.

The order of the thermal escape flux of hydrogen atoms from present Mars can be estimated, by assuming an exosphere temperature which fits H Ly- α day glow observations, to be about 1.8×10^8 cm⁻² s⁻¹ (1.5×10^{26} s⁻¹) [45]. Recent observations of four H₂ lines in a spectrum of Mars with the FUSE satellite revealed a column abundance of molecular hydrogen of 1.17×10^{13} cm⁻², 140 km above the Martian surface, resulting in an H₂ mixing ratio of 15 ± 5 parts per million in the lower Martian atmosphere [46]. By using this value, one gets a thermal H₂ escape flux of about 4×10^6 cm⁻²s⁻¹ (3.3×10^{24} s⁻¹). One can see that the thermal H₂ loss rate is thus negligibly small when compared to the atomic H loss rate. Therefore, one derives a total thermal escape flux of present hydrogen atoms of about 1.8×10^8 cm⁻²s⁻¹ (1.5×10^{26} s⁻¹). However, significant progress in the determination of uncertainties of the Martian exosphere temperature and related hydrogen loss rates is expected from Mars Express in 2004 and 2005.

2.3 Non-Thermal Atmospheric Escape

2.3.1 Ion Pick Up

Neutral gas particles can get ionised above the Martian ionopause and picked up by the solar wind. Measurements by the ASPERA (Automatic Space Plasma Experiment with a Rotating Analyser) instrument aboard the Phobos 2 spacecraft have shown that the plasma tail of Mars consists mainly of ions coming from the Martian atmosphere [e.g. 47]. For studying the O⁺ ion pick up escape rates from Mars we used a test particle model that involves the motion in the environmental electric and magnetic fields based on the *Spreiter-Stahara* model [e.g. 48, 49] and obtained for average solar activity conditions a total pick up escape flux for hydrogen ions of about 3×10^6 cm⁻²s⁻¹ (3.0×10^{24} s⁻¹).

For the calculation of past pick up ion escape rates and pick up ion sputtering, one must be able to estimate the hot oxygen corona density in the Martian past. One can use the National Center for Atmospheric Research (NCAR) non-LTE (local thermal equilibrium) one-dimensional code as a modelling tool for the estimation of the average properties of the ancient Martian thermosphere and ionosphere for the calculation of the hot particle coronae [50]. By deducing the corona profiles from the results of the code mentioned above, one can study the role of molecular species in pick up ion sputtering of the ancient Martian atmosphere [51, 52].

By using similar density profiles for the average pick up O⁺ ion loss estimations of about 4.5×10^7 cm⁻²s⁻¹ (3.8×10^{25} s⁻¹) and about 9.6×10^8 cm⁻²s⁻¹ (8×10^{26} s⁻¹) for the 2 Ga and 3.5 Ga periods, we note that O⁺ ion pick up loss rates in a previous study [50] are about 10 times and 2 times larger, respectively, than those found in our calculations. The main reason for these discrepancies is their use of different solar wind density values for the 2 Ga and 3.5 Ga epochs, for which we used the observation-based stellar wind data [22] as discussed above.

2.3.2 Detached Ionospheric Clouds Triggered by Magnetohydrodynamic Instabilities

Another atmospheric loss process on Mars is the occurrence of magnetohydrodynamic (MHD) instabilities at the boundary layer between the solar wind and the atmospheric plasma [53, 54]. Since there is a shear velocity between the plasma flow in the solar wind (magnetosheath) and the plasma in the ionosphere, the so called Kelvin-Helmholtz (KHz) instability can develop and evolve into a nonlinear stage, where ionised atmospheric constituents can detach from the ionosphere in the form of plasma clouds [55].

It was found by the Pioneer Venus Orbiter (PVO) that plasma clouds are a common feature caused by the solar wind-ionosphere interaction on Venus [56]. Analysis of data by the MAG/ER (Magnetometer/Electron Reflectometer) instru-

ment of MGS revealed cold electrons above the Martian ionopause, which indicate the presence of plasma clouds also on Mars [40].

It is found that near the Martian subsolar point the velocity shear is very small, indicating that this region is stable against the KHz-instability [57]. But near the terminator, the KHz-instability can occur since the velocity shear is much larger there. The highest velocity in the magnetosheath appears at the flanks near the terminator plane due to the Lorentz force accelerating the plasma. Therefore, we assume that the KHz-instability appears also in this region.

A statistical analysis of the situation on Venus [56] scaled to Martian conditions for the estimation of O⁺ ion escape shows that this process can contribute to present escape fluxes between 1.2×10^5 cm⁻² s⁻¹ and 6×10^6 cm⁻² s⁻¹ (10^{23} s⁻¹ and 5×10^{24} s⁻¹). Due to the higher solar wind mass flux and ionospheric densities in the past [51] we estimate O⁺ ion escape fluxes of about 9.5×10^6 cm⁻² s⁻¹ (8×10^{24} s⁻¹) 2 Ga ago and about 2.3×10^8 cm⁻² s⁻¹ (2×10^{26} s⁻¹) 3.5 Ga ago.

2.3.3 Ion Loss due to Momentum Transport Effects

The outflow of cold ionospheric ions from the Martian terminator regions was also observed by the ASPERA instrument on board of the Phobos 2 spacecraft, which indicates a strong interaction between the solar wind plasma and the cold ionospheric plasma in the Martian topside ionosphere in a way that the solar wind plasma transfers momentum directly to the ionosphere in a dayside transition region to the deep plasma tail [47]. PVO measured on Venus the median velocity field of O⁺ ions on the outbound portion of orbits from periapsis to the ionopause and found that the bulk velocity of the ions near the terminator is about 5 km s⁻¹ [58], which is the escape velocity of O atoms on Mars.

The results of several studies [58, 59, 60] suggest that the solar wind momentum transport seems to be capable of accelerating ionospheric O⁺ ions to velocities $\geq 5 \text{ km s}^{-1}$ ($\geq 2 \text{ eV}$) resulting in energies larger than the Martian escape energy. In a previous study [58], it was shown that cool ion escape due to momentum transport effects may have removed water from Mars equivalent to a global ocean with a thickness of about 10 to 30 m, depending on the uncertainties of solar wind parameters and the Martian plasma environment in the past.

We studied this loss process by using the observed average stellar wind data of young solar-like stars [22, 52] and the ionospheric density profiles corresponding to the Martian history [50] and found an additional escape rate of oxygen of about 1×10^{25} s⁻¹ at present, about 2×10^{26} s⁻¹ 2 Ga ago and about 2×10^{27} s⁻¹ 3.5 Ga ago. One can see that this loss process may have played an important role in the Martian history because it is strongly related to the solar wind and ionospheric density, which was much larger due to the more active young Sun.

2.3.4 Atmospheric Sputtering

Particles which hit the Martian atmosphere are responsible for sputtering loss of neutral constituents. Loss rates for O atoms and CO₂ molecules on Mars were studied in the past [52 and references given therein] and yielded escape flux values of about 3.6×10^5 cm⁻²s⁻¹ (3×10^{23} s⁻¹) both for O atoms and for CO₂ molecules. A 1-D Monte Carlo type atmospheric sputtering model, which considered anisotropic scattering functions and energy-dependent cross sections, resulted in sputtering fluxes for O and CO₂ of about 5.6×10^6 cm⁻²s⁻¹ (4.7×10^{24} s⁻¹) and 2.9 $\times 10^6$ cm⁻²s⁻¹ (2.4×10^{24} s⁻¹), respectively [e.g. 61]. In a recent study, the sputtered population inside the hot corona was modelled and the escaping particles were studied by using a sophisticated 3-D test particle model, whereas the heating effect due to the incident particle flux was described by using a 2-D direct Monte Carlo simulation [51].

The results of such a sophisticated model yield a present Martian average sputtering escape flux of O atoms of about 7×10^5 cm⁻²s⁻¹ (6.5×10^{23} s⁻¹) and indicate that the standard 1-D models overestimate the sputtering yield by about 15 - 25 % when corrected for coronal ejection. Further, by coupling a test particle Monte Carlo approach with a molecular dynamic model to describe the collisions between hot particles and cold molecules in the Martian atmosphere, one finds total present sputtering escape fluxes for O atoms of about 5.2×10^5 cm⁻²s⁻¹ (4.3×10^{23} s⁻¹) [52]. By using this 3-D model, an O escape flux for sputtering of about 1.5×10^8 cm⁻² s⁻¹ (1.3×10^{26} s⁻¹) 2 Ga ago and of about 1.8×10^9 cm⁻² s⁻¹ (1.5×10^{27} s⁻¹) 3.5 Ga ago is found.

2.3.5 Dissociative Recombination

Dissociative recombination of ionospheric O_2^+ ions produces very low energetic neutral O atoms, where a fraction can escape and the other part can form a planetary corona. Based on the first measurements obtained by Mariner 4, an average escape flux into space of hot O atoms produced via this process on the dayside hemisphere is about 6×10^7 cm⁻²s⁻¹ (5.0×10^{25} s⁻¹) and was estimated by the simplified assumption that atoms are emitted with equal probability in the upward and downward directions [62].

Monte Carlo models that followed the hot O atoms by including collisions and energy loss on their way up to the exosphere [52 and references given therein] found a reduction in the average escape flux of hot O atoms by about one order of magnitude, i.e. 6×10^6 cm⁻²s⁻¹ (5×10^{24} s⁻¹). The observational results for the evolution of the solar XUV flux with time obtained by solar proxies agree well with the values used by [50]. Thus, the exospheric O escape fluxes of about 3.6×10^7 cm⁻² s⁻¹ (3×10^{25} s⁻¹) 2 Ga ago and about 9.7×10^7 cm⁻² s⁻¹ (8×10^{25} s⁻¹) 3.5 Ga ago may be accurate and should represent realistic values [50, 63].

2.3.6 Oxygen Loss into the Martian Soil

Our escape studies show that the H:O escape ratio of 2:1 assumed by some equilibrium photo-chemical atmospheric models requiring a steady state [64] cannot be maintained due to the heavier mass of O. Since oxygen can react with the surface, the ratio can be obtained. We estimate that about 10^{42} oxygen particles have been incorporated into the Martian soil since about 2 Ga ago. Ferric oxides and sulphates are the most important candidate phases in regard to oxidation products. In the light that Martian precursor mineralogy, introduced by meteoritic infall [65] and indigenous rocks, comprises such polyvalent elements as iron and sulphur in considerable lower oxidation states than present in ferric oxides and sulphates, this is an important sink of atmospheric oxygen [52 and references given therein].

Based on the meteoritic contribution to the Martian surface [66] typical soils analysed by Mars Pathfinder appear to contain three components: lithic fragments, meteoritic matter and physical fractionation products of parent andesites with typical initial oxidation states. Analyses of ferric absorption edges in reflectance spectra of Alpha Proton X-Ray Spectrometer (APXS) spots give hints to absolute oxidation states of the soil if combined with variation in the chemical space. Assuming correspondingly initial Fe³⁺/Fe^{tot} ratios of 0.4 and final ones of 0.6 this would lead to global soil horizons between 4 to 15 metres. Using models of meteoritic gardening [67, 68, 69], this would yield regolith depths between 7 and 150 metres resulting in corresponding oxidant extinction depths between 2 and 5 metres. These results span a range of extreme values depending on sulphate formation from emanation of sulphitic volcanic gases or from oxidation of magmatic sulphides [52]. However, the modelling of oxidant extinction depths and meteoritic gardening given in [67] are based on oxidant diffusion into the soil column. If oxidation processes occur outside of the soil, e.g. during atmospheric entry of cosmic matter [66] or in the context of heat input above the threshold for thermal oxidation associated with impact processes [70], the oxidant extinction depths would be significantly reduced.

Further, the strong atmosphere-surface interaction between oxygen and the Martian soil may produce adsorbed superoxides (O_2^-) . Such species were observed on Martian analogue materials upon UV-illumination by means of experiments under simulated Martian environmental conditions [71]. Although the formation processes and diffusive capabilities of superoxides and related oxidants are far from being resolved [72], it seems to be evident that *in situ* oxidation on the Martian surface is an active process. Photo-oxidation experiments on magnetite as the precursor material found that such a process should be involved in active and efficient oxidation on the Martian surface [73]. That the Martian surface is oxidizing not only at the top surface due to UV-radiation but also in the subsurface was confirmed by the negative response of Viking biology experiments and the evidence for reversibly bound oxygen bearing agents as an outcome of Viking gas exchange experiments on subsurface soil samples [74, 75].

2.3.7 Total Water Loss Since 3.5 Ga

Age [Ga]	Present [s ⁻¹]	2 Ga ago $[s^{-1}]$	$3.5 \text{ Ga ago } [\text{s}^{-1}]$
$PU: O^+$	3×10^{24}	3.8×10^{25}	8×10^{26}
DR: O	2.8×10^{24}	3×10^{25}	8×10^{25}
SP: O	2.2×10^{23}	7×10^{25}	1.3×10^{27}
SP: CO	3.5×10^{22}	2.3×10^{24}	4×10^{25}
$SP: CO_2$	5×10^{22}	2×10^{24}	2.5×10^{25}
$PC: O^+$	1×10^{24}	8×10^{24}	2×10^{26}
MT: O^+	1×10^{25}	2×10^{26}	2×10^{27}
Total O loss	1.7×10^{25}	$6.5 imes 10^{26}$	5.4×10^{27}

Table 2.2 Summary of oxygen-related atmospheric constituents lost from Mars over the past 3.5
 Ga. Given are the number of molecules or atoms.

The maximum total loss of oxygen-related constituents from Mars (Table 2.2) caused by ion pick up (PU), dissociative recombination (DR), sputtering (SP), plasma clouds (PC) and momentum transport (MT) over the past 3.5 Ga was estimated to be equivalent to a global Martian water ocean with a layer thickness of about 35 m by using oxygen as an upper limit for the water loss [76] as assumed by equilibrium photochemical atmospheric models, which require a steady state between the H:O escape ratio of 2:1 [64]. However, by assuming that the hydrogen escape flux represents an upper limit for an equivalent water loss to space one obtains a lower value of 5 m [79, 80, 81]. If this assumption is true and the stoichiometrically desirable ratio 2:1 of H and O escape was not maintained before 2 Ga ago, the majority of oxygen lost to space would have to have originated from CO₂ instead of H₂O. One can see from Table 2.2 that the 2:1 ratio between the H:O loss to space is not established at present. The present uncertainties in the estimation for the atmospheric escape rates caused by plasma instabilities and momentum transport processes will be minimised after the analysis of Mars Express' ASPERA-3 data.

2.4 Evolution of the Martian Water Inventory

The D isotopes in the Martian atmosphere have been detected by the resolution of several Doppler-shifted lines of HDO vapour near 3.7 micrometre in the planetary spectrum, which revealed an enrichment compared to the D/H ratio of the TSW value by a factor 5 [7, 8]. Given the large size of water reservoirs on Earth, one can assume that the D/H ratio has not changed much in the terrestrial seawater during the past billion years.

As discussed before, the initial D/H ratio in Martian water reservoir originates from impacts of asteroids and comets and may have been in the order of about 1.2

to 1.6 times the TSW ratio [9]. Measurements in Martian SNC meteorites also yield D/H ratios of about 1 to 2.3 times the TSW value [35, 76]. The measured D/H ratio of the 3.9 Ga old ALH 84001 meteorite is about 1.6 times the TSW. The simplest interpretation of the D enrichment in the Martian atmosphere is that an appreciable amount of H associated with the original water or water-ice reservoir escaped to space.

By knowing the fractionation factor *f* between D and H and the initial isotope ratio one can estimate the value $r(t) = [R(t_1)/R(t_0)]^{[1/(1-f)]}$, which indicates how many times the water-ice reservoir, which is in isotopic exchange with the present Martian atmosphere, was larger in the past. Observations with the Goddard High-Resolution Spectrograph at the HST indicate that *f* lies between 0.016 and 0.02 in the lower Martian atmosphere [76]. *R* is the isotope ratio between D and H at two different times t_0 (earlier) and t_1 .

By using *f* of about 0.016, one finds that the Martian water-ice reservoir was about 5.26 times larger if the initial isotope ratio was the TSW value and about 4.36 times larger for 1.2 times the TSW, 3.26 times larger for 1.6 times the TSW, and 2.25 times larger for 2.3 times the TSW, respectively. By knowing the total amount of water $L_{\rm H20}$ (equivalent depth) lost over the Martian history, one obtains a constraint on the thickness $s(t) = L_{\rm H20}/[r(t)-1]$ in terms of an equivalent depth [e.g. 8, 76]. Figure 2.2 shows the present water-ice reservoir, which is in isotopic exchange with the Martian atmosphere, as a function of the equivalent depth $L_{\rm H20}$ lost from the planet over 3.5 Ga. Since the Martian obliquity oscillates on time scales of about 10⁵ to 10⁷ years between 0° and 60°, one can expect dramatic climate changes and effective isotope exchange between the ice deposits and the atmosphere [77].

The solid line in Fig. 2.2 corresponds to the TSW ratio, the dashed-dotted line to a D enrichment of 1.2 times the TSW ratio, the dashed line to a D enrichment of 1.6 times the TSW ratio [9], and the dashed-dotted-dotted line to a D enrichment of about 2.3 times the corresponding TSW ratio as measured in Martian SNC meteorites and comets [35], respectively. One can see from the estimates in Fig. 2.2 that Mars should presently possess a water-ice reservoir which can interact with the atmosphere with an equivalent depth of a few m up to 27 m, depending on initial isotope D/H ratios and water loss rates.

By using the values obtained for r(t) we find a water-ice reservoir exchangeable with the Martian atmosphere 3.5 Ga ago with an equivalent depth of about 15 to 60 m, depending on the initial D/H ratios assumed.

From MOLA data an ice volume can be estimated, which corresponds to an equivalent depth of about 9 m [13]. One can see from Fig. 2.2 that this value agrees with our estimation if the initial D/H ratio was close to the TSW value or 1.2 times the TSW ratio and an equivalent global water layer with a depth of about 34 m was lost to space. On the other hand, if the initial D/H isotope ratio was 1.6 times the TSW ratio, an equivalent depth of about 15 m should have been lost to space over 3.5 Ga. If the initial D/H ratio was about 2.3 times the TSW value, the lower escape value would yield an equivalent depth of about 11 m, while the upper escape rate would yield about 27 m [76].

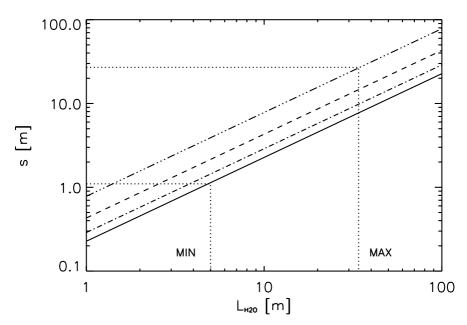


Fig. 2.2 Estimated minimum (MIN) and maximum (MAX) present Martian surface waterice reservoir in terms of the equivalent depth *s* (dotted lines), which is in isotopic exchange with the atmosphere, as a function of total water lost $L_{\rm H20}$ from Mars over the past 3.5 Ga with various initial D/H isotope ratios. The solid line has an initial D/H ratio equal to the TSW value. The dashed-dotted and dashed lines have D/H ratios of 1.2 times and 1.6 times the TSW value [9], respectively, and the dashed-dotted-dotted line correspond to the average D/H value measured in Martian Shergottite meteorites of about 2.3 times the TSW value which is comparable to the D/H ratio in comets [35].

Although there are uncertainties, our estimation shows that the water-ice reservoir which is in isotopic exchange with the atmosphere can be lower but also three times the estimated water-ice available in the Martian northern polar cap. By using the estimated water reservoirs 3.5 Ga ago related to the 2.3 times the TSW value we can estimate the minimum and maximum reservoirs, where the D/H isotope ratio was enriched from 1.2 or 1.6 times the TSW value due to hydrodynamic escape. One gets water reservoirs affected by isotopic fractionation with an equivalent depth of between 35 and 115 m, depending on the initial isotope ratios in Martian water 4.5 Ga ago.

2.5 Conclusions

Our study obtained from atmospheric evolution shows that Mars may presently contain a subsurface water-ice reservoir which can exchange with the atmosphere with an equivalent depth of a few metres to 27 m. Much better estimations of the

present and past Martian water-ice reservoirs in isotopic exchange with the atmosphere over the planetary history will probably be possible after exact ion and neutron particle outflow measurements by the ASPERA-3 instrument on board the Mars Express. These observations will reduce the uncertainties in the current estimations of atmospheric loss caused by solar wind plasma interactions with the ionospheric environment. If the Martian subsurface also hides a bulk water-ice reservoir which is not exchangeable with the atmosphere and is a remainder of the initial water source, it could only be determined by radar sounding such as by the MARSIS instrument on board of Mars Express. Should MARSIS not detect such an additional reservoir, this would mean that such a reservoir may have been lost due to hydrodynamic escape and impact erosion before 3.5 Ga ago.

Further, by assuming that all hydrogen lost to space originates from water, our study suggests that the stoichiometrically desirable H:O escape ratio of 2:1 to space could not be maintained since about 2 Ga ago. This result implies an oxygen surface sink and a strong atmosphere-surface interaction, which may be responsible for an enhanced soil/surface oxidation process. It is possible to incorporate this amount of oxygen into the regolith by oxidation of inorganic soil-precursors. Depending on different models of meteoritic gardening, the expected range for the oxidant extinction depth should be between 2 and 5 m. These constraints on the oxidant extinction depth are important for the search of organic material since *in situ* excavation of samples from the subsurface with penetrating moles or drilling equipment.

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2.6 References

- 1 Pepin RO (1994) Evolution of the Martian Atmosphere. Icarus 111: 289-304
- 2 Hutchins KS, Jakosky BM (1996) Evolution of Martian atmospheric argon: implications for sources of volatiles. J. Geophys. Res. 101 (E6): 14933-14949
- 3 Carr MH (1999) Retention of an atmosphere on early Mars. J. Geophys. Res. 104 (E9): 21897-21909
- 4 Morbidelli A, Chambers J, Lunine JI, Petit JM, Robert F, Valsecchi GB, Cyr KE (2000) Source regions and timescales for the origin of water on Earth. Meteorit. Planet. Sci. 35: 1309-1320
- 5 Robert F (2001) The origin of water on Earth. Science 293: 1056-1058
- 6 Petit J-M, Morbidelli A, Chambers J (2001) The primordial excitation and clearing of the asteroid beld. Icarus 153: 338-347
- 7 Owen TC (1992) The composition and early history of the atmosphere of Mars. In: Kieffer HH, Jakosky BM, Snyder CW, Matthews MS (eds) Mars. University of Arizona Press, Tucson, pp. 818-834
- 8 Donahue TM (1995) Evolution of water reservoirs on Mars from D/H ratios in the atmosphere and crust. Nature 374: 432-434

- 9 Lunine JI, Chambers J, Morbidelli A, Leshin LA (2003) The origin of water on Mars. Icarus 165: 1-8
- 10 Carr MH (1996) Water on Mars. Oxford University, New York
- 11 Baker VR (2001) Water and the Martian landscape. Nature 412: 228-236
- 12 Leshin LA (2000) Insights into Martian water reservoirs from analysis of Martian meteorite QUE94201. Geophys. Res. Lett. 27: 2017-2020
- 13 Zuber MT, Smith DE, Solomon SC, Abshire JB, Afzal RS, Aharonson O, Fishbaugh K, Ford PG, Frey HV, Garvin JB, Head III JW, Ivanov AB, Johnson CL, Muhleman DO, Neumann GA, Pettengill GH, Phillips RJ, Sun X, Zwally HJ, Banerdt WB, Duxbury TC (1998) Observations of the north polar region of Mars from the Mars Orbiter Laser Altimeter. Science 282: 2053-2060
- 14 Sagan C, Mullen G (1972) Earth and Mars: evolution of atmospheres and surface temperatures. Science 177: 52-56
- 15 Walker JCG, Hays PB, Kasting JF (1981) A negative feedback mechanism for the long-term stabilization of Earth's surface temperature. J. Geophys. Res. 86: 9776-9782
- 16 Kasting J (1988) Runaway and moist greenhouse atmospheres and the evolution of Earth and Venus. Icarus 74: 472–494
- 17 Kasting J (1991) CO, condensation and the climate of early Mars. Icarus 94: 1-13
- 18 Forget F, Pierrehumbert RT (1997) Warming early Mars with carbon dioxide clouds that scatter infrared radiation. Science 278: 1273-1276
- 19 Selsis F, Despois D, Parisot J-P (2002) Signature of life on exoplanets: can Darwin produce false positive detections? Astron. Astrophys. 388: 985-1003
- 20 Rye R, Kuo PH, Holland HD (1995) Atmospheric carbon-dioxide concentrations before 2.2-billion years ago. Nature 378: 603-605
- 21 Pavlov AA, Kasting JF, Brown LL, Rages KA, Freedman R (2000) Greenhouse warming by CH, in the atmosphere of early Earth. J. Geophys. Res. 105(E5): 11981-11990
- 22 Sagan C, Chyba C (1997) The early faint Sun paradox: organic shielding of ultravioletlabile greenhouse gases. Science 276: 1217-1221
- 23 Sleep NH, Zahnle, K (2001) Carbon cycling and implications for climate on ancient Earth. J. Geophys. Res. 106(E1): 1373-1400
- 24 Sackmann I-J, Boothroyd AI (2003) Our Sun. V. A bright young Sun consistent with helioseismology and warm temperatures on ancient Earth and Mars. Astrophys. J. 583: 1024-1039
- 25 Wood BE, Müller H-R, Zank G, Linsky JL (2002) Measured mass loss rates of solarlike stars as a function of age and activity. Astrophys. J. 574: 412-425
- 26 Guinan EF, Ribas I (2002) Our changing Sun: the role of solar nuclear evolution and magnetic activity on Earth's atmosphere and climate. In: Montesinos B, Giménz A, Guinan EF (eds) The Evolving Sun and its Influence on Planetary Environments, ASP Conference Proc. 269: 85-107
- 27 Hunten DM, (1993) Atmospheric evolution of the terrestrial planets. Science 259: 915-920
- 28 Bauer SJ (1971) Solar cycle variation of planetary exospheric temperatures. Nature 232: 101-102
- 29 Pepin RO (1997) Evolution of Earth's noble gases: consequences of assuming hydrodynamic loss driven by giant impact. Icarus 126: 148-156
- 30 Bauer SJ, Hantsch MH (1989) Solar cycle variation of the upper atmosphere temperature of Mars. Geophys. Res. Lett. 16: 373-376
- 31 Öpik EJ (1963) Selective escape of gases. Geophys. J. Roy. Astron. Soc. 7: 490-509
- 32 Kasting JF, Pollack JB (1983) Loss of water from Venus I. Hydrodynamic escape of hydrogen. Icarus 53: 479-508
- 33 Melosh HJ, Vickery A (1989) Impact erosion of the primordial atmosphere of Mars. Nature 338: 487-489

- 34 Owen T, Bar-Nun A, Kleinfeld I (1992) Possible cometary origin of noble gases in the atmospheres of Venus, Earth and Mars. Nature 358: 43-46.
- 35 Leshin LA, Epstein S, Stolper EM (1996) Hydrogen isotope geochemistry of SNC meteorites. *Geochim. Cosmochim. Acta* 60: 2635-2650
- 36 Eberhardt P, Reber M, Krankowsky D, Hodges RR (1995) The D/H and ¹⁸O/¹⁶O ratios in water from comet P/Halley. Astron. Astrophys. 302: 301-316
- 37 Bockelée-Morvan D, Gautier D, Lis DC, Young K, Keene J, Phillips T, Owen TC, Crovisier J, Goldsmith PF, Bergin EA, Despois D, Wooten A (1998) Deuterated water in comet C/1996 B2 (Hyakutake) and its implications for the origin of comets. Icarus 133: 147-162
- 38 Meier M. Owen TC, Matthews HE, Jewitt DC, Bockelée-Morvan D, Biver N, Crovisier J, Gautier D (1998) A determination of the HDO/H₂O ratio in comet C/1995 O1 (Hale Bopp). Science 279: 842-844
- 39 Kieffer HH, Jakosky BM, Snyder CW, Matthews MS (eds) (1992) Mars. University of Arizona Press, Tucson
- 40 Acuña MH and 19 colleagues (1998) Magnetic field and plasma observations at Mars: initial results of the Mars Global Surveyor mission. Science 279: 1676-1680
- 41 Acuña MH and 19 colleagues (1999) Global distibution of crustal magnetization discovered by the Mars Global Surveyor MAG/ER experiment. Science 284: 790-793
- 42 Schubert G, Russell CT, Moore WB (2000) Timing of the Martian dynamo. Nature 408: 666-667
- 43 Weiss BP, Vali H, Baudenbacher FJ, Kirschvink JL, Stewart ST, Shuster DL (2002) Records of an ancient Martian magnetic field in ALH84001. Earth Planet. Sci. Lett. 201: 449-463
- 44 Cisowski SM (1986) Magnetic studies on Shergotty and other SNC meteorites. Geochim. Cosmochim. Acta 50: 1043-1048
- 45 Anderson Jr. DE, Hord CW (1971) Mariner 6 and 7 ultraviolet spectrometer experiment: analysis of hydrogen Lyman-Alpha data. J. Geophys. Res. 76: 6666-6673
- 46 Krasnopolsky VA, Feldman PD (2001) Detection of molecular hydrogen in the atmosphere of Mars. Science 294: 1914-1917
- 47 Lundin R, Dubinin EM, Koskinen H, Norberg O, Pissarenko N, Barabash SW (1991) On the momentum transfer of the solar wind to the Martian topside ionosphere. Geophys. Res. Lett. 18: 1059-1062
- 48 Spreiter JR, Stahara SS (1980) Solar wind flow past Venus: theory and comparisons. J. Geophys. Res. 85: 7715-7738
- 49 Lichtenegger HIM, Dubinin EM (1998) Model calculations of the planetary ion distribution in the Martian tail. Earth Planets Space 50: 445-452
- 50 Zhang MHG, Luhmann JG, Bougher SW, Nagy AF (1993) The ancient oxygen atmosphere of Mars: implications for atmosphere evolution. J. Geophys. Res. 98 (E6): 10915-10923
- 51 Leblanc F, Johnson RE (2002) Role of molecular species in pick up ion sputtering of the Martian atmosphere. J. Geophys. Res. 107(E2): 5010, 10.1029/2000JE001473
- 52 Lammer H, Lichtenegger HIM, Kolb C, Ribas I, Bauer SJ (2003) Loss of water from Mars: implications for the oxidation of the soil. Icarus 165: 9-25
- 53 Elphic RC, Ershkovich AI (1984) On the stability of the ionopause of Venus. J. Geophys. Res. 89: 997-1002
- 54 Chandrasekhar S (1961) Hydrodynamic and Hydromagnetic Stability. Oxford University Press, New York
- 55 Wolff RS, Goldstein BE, Yeates CM (1980) The onset and development of Kelvin-Helmholtz instability at the Venusian ionopause. J. Geophys. Res. 85: 7697-7707
- 56 Brace LH, Theis RF, Hoegy WR (1982) Plasma clouds above the ionopause of Venus and their implications. Planet. Space Sci. 30: 29-37

- 57 Penz T, Erkaev NV, Lammer H, Amerstorfer UV, Biernat HK, Gunell H, Kallio E, Barabash S, Orsini S, Milillo A, Baumjohann W (2003) Ion loss on Mars caused by the Kelvin-Helmholtz instability. Submitted to Planet. Space Sci.
- 58 Pérez-de-Tejada H (1992) Solar wind erosion of the Mars early atmosphere. J. Geophys. Res. 97 (A3): 3159-3167
- 59 Pérez-de-Tejada H (1998) Momentum transport in the solar wind erosion of the Mars ionosphere. J. Geophys. Res. 103 (E13): 31499-31508
- 60 Amerstorfer UV (2004) Solar wind flow past Venus and Mars. Master's Thesis. University of Graz
- 61 Jakosky BM, Pepin RO, Johnson RE, Fox JL (1994) Mars atmospheric loss and isotopic fractionation by solar-wind induced sputtering and photochemical escape. Icarus 111: 271-288
- 62 McElroy MB (1972) Mars: an evolving atmosphere. Science 175: 443-445
- 63 Luhmann JG (1997) Correction to "The ancient oxygen exosphere of Mars: implications for atmospheric evolution". J. Geophys. Res. 102 (E1): 1637-1638
- 64 Nair H, Allen M, Anbar AD, Yung YL, Clancy RT (1994) A photochemical model of the Martian atmosphere. Icarus 111: 124-150
- 65 Flynn GJ, McKay DS (1990) An assessment of the meteoritic contribution to the Martian soil. J. Geophys. Res. 95(B9): 14497-14509
- 66 Kolb C, Abart R, Lammer H (2003) The meteoritic component on the surface of Mars: evidence for a global dust unit and implications for oxidation states of the Martian surface. Submitted to Icarus
- 67 Zent AP (1998) On the thickness of the oxidized layer of the Martian regolith. J. Geophys. Res. 103 (E13): 31491-31498
- 68 Carr MH (1981) The Surface of Mars. Yale University Press, New Haven
- 69 Neukum G, Ivanov BA (1994) Crater size distributions and impact probabilities on Earth from lunar, terrestrial-planet, and asteroid cratering data. In: Gehrels T (ed) Hazards due to Comets and Asteroids. University of Arizona Press, Tucson
- 70 Bell III JF, McSween Jr. HY, Crisp JA, Morris RV, Murchie SL, Bridges NT, Johnsen JR, Britt TD, Golombek MP, Moore HJ, Ghosh A, Bishop JL, Anderson RC, Brückner J, Economou T, Greenwood JP, Gunnlaugsson HP, Hargraves RM, Hviid S, Knudsen JM, Madsen MP, Reid R, Rieder R, Soderblom L (2000) Mineralogic and compositional properties of Martian soil and dust: results from Mars Pathfinder. J. Geophys. Res. 105(E1): 1721-1755
- 71 Yen AS, Kim SS, Hecht MH, Frant MS, Murray B (2000) Evidence that the reactivity of the Martian soil is due to superoxide ions. Science 289: 1909-1912
- 72 Patel MR, Bérces A, Kolb C, Lammer H, Rettberg P, Zarnecki JC, Selsis F (2003) Seasonal and diurnal variations in Martian surface UV irradiation: biological and chemical implications for the Martian regolith. Int. J. Astrobiol. 2: 21-34
- 73 Huguenin RL (1973) Photostimulated oxidation of magnetite 1. Kinetics and alteration phase identification. J. Geophys. Res. 78: 8481-8493
- 74 Biemann K, Oró J, Toulmin III P, Orgel LE, Nier AO, Anderson DM, Simmonds PG, Flory D, Diaz AV, Rushneck DR, Billier JE, Lafleur AE (1977) The search for organic substances and inorganic volatile compounds in the surface of Mars. J. Geophys. Res. 82 (B28): 4641-4658
- 75 Oyama VI, Berdahl BJ (1977) The Viking Gas Exchange Experiment results from Chryse and Utopia surface samples. J. Geophys. Res. 82 (B28): 4669-4676
- 76 Lammer H, Kolb C, Penz T, Amerstorfer UV, Biernat HK, Bodiselitsch B (2003) Estimation of the past and present water-ice reservoirs by isotopic constraints on exchange between the atmosphere and the surface. Int. J. Astrobiol. 2: 195-202
- 77 Pollack JB (1979) Climatic change on the terrestrial planets. Icarus 37: 479-553

3 Early Life on Earth and Analogies to Mars

Frances Westall

One of the prime necessities of life is liquid water [87]. The presence of liquid water on a planet therefore naturally leads to the question of whether that planet hosted or still hosts life. Although there is much dispute at the moment as to how much water Mars had in its early history and at what temperature, there is sufficient evidence for its presence in substantial quantities in the form of geomorphological features [1–4], as well as the evidence for aqueous alteration of minerals in the Martian meteorites [Chap. 1 by Baker et al., 5-7] and possibly water-lain hematite [8, 9], to stimulate hypotheses regarding the possibility of life on Mars. This chapter will concentrate on the possibility of life having arisen on Mars early in its (watery) history using, as the closest analogy in time and environmental conditions, the early Earth and early terrestrial life. I will state at the outset that, given the rarity of rock remains from the early Earth's history, there is a heated debate at the moment concerning the early environmental conditions of the Earth during the Hadean (4.56 - 4.0 Ga ago) and early Archaean (4.0 - 3.2 Ga ago), not to speak of whether life already existed on Earth before 3 Ga ago and in what form [10, 11]. In the following, I will review of the situation to date, present the evidence for life by about 3.5 Ga ago, and then examine the relevance of early Earth studies for Mars.

3.1 Early Earth

3.1.1 The Environment of the Early Earth

As noted above, information regarding the environment of the early Earth is extremely rare, primarily because much of the rock record between the formation of the Earth and about 3.5 Ga has been eliminated by plate tectonic activity, and secondly because most of the fragments that remain from the first billion years of history are so altered that they appear to be the source of more confusion than illumination. I will use the following terms to designate the different periods of Earth's history: Hadean (4.56–4.0 Ga); Early Archaean (4.0–3.2 Ga); Middle Archaean (3.2–2.8 Ga); Late Archaean (2.8–2.5 Ga); Paleoproterozoic (2.5–1.6 Ga); Mesoproterozoic (1.6–1.0 Ga); Neoproterozoic (1.0–0.546 Ga); Phanerozoic (0.546 Ga–Recent).

Theoretically, life could have appeared on Earth as soon as water condensed on the surface but there is much debate as to when this occurred. The presence of ancient grains of zircon that were formed between 4.4 and 4.2 Ga ago but occur in rocks of a much younger age, having been eroded from older material, seems to suggest that there were oceans on the Earth at that early time period [12, 13]. This inference is contested by Kamber et al. [14] on the grounds that the presence of zircons is probably the result of localised differentiation, since zircons are also found in lunar material where there has been no large-scale mantle fractionation. The large number of Hadean age zircons recycled in younger crust, however, does seem to indicate significant Hadean continental crust fractionation and recycling [15]. Ancient gneisses and supracrustal remnants dating from between 4.0 and 3.8 Ga ago, indicate that, at least in the Late Hadean/Earliest Archaean, rocks formed on an Earth that was covered with water.

Better-preserved rock formations occur in the 3.5-3.2 Ga greenstone belts of Barberton (South Africa) and the Pilbara (Australia). These rocks provide important information concerning the geological environment of the early Earth. The predominant lithology was not only volcanic but consisted of the types of rocks that formed under very hot mantle conditions [16]. The Earth at that period was very active volcanically. True continents with true granite cores, continental platforms, and arenitic sediments deposited in intracratonic basins only started to evolve towards the end of the Early Archaean period. Other indications of a hotter planet include the widespread evidence of hydrothermal activity [17, 18], as well as oxygen isotope measurements made on chemical sediments precipitated from the hydrothermal fluids and seawater [19, 20]. Knauth and Lowe [20] suggest that the seawater was highly saturated with hydrothermal fluids. The characteristics of the seawater are another subject of great debate. Estimations for pH values range from slightly acidic [21], to neutral [22, 23] and even to alkaline [24]. Although Hardie's [23] models indicate that seawater chemistry in the Late Archaean was essentially the same as it is today, the high rate of tectonic cycling, the higher temperatures and the high reactivity of the volcanic materials at the surface would have probably increased the amount of dissolved species in the seawater on the Hadean to Early Archaean Earth.

The evidence relating to the composition of the atmosphere of the early Earth is based on comparative planetology, modelling and the types of minerals formed at the surface. The atmosphere during much of the Hadean, after the Moon-forming event, all of the Archaean and for at least part of the Early Proterozoic consisted of a slight reduction to neutral atmosphere of mainly outgassed CO₂, H₂O, and H₂S (with minor amounts of other gases such as CH₄, CO, N₂) [25-27]. The early Earth was therefore anoxic. One problem posed by a mainly CO₂ atmosphere is that of the "faint young Sun paradox" of Sagan and Mullen [28]. Modelling of the evolution of Solar Systems has shown that the young Sun was probably 30 % less luminous than it is today. Given the distance of the Earth from the Sun, how could water have stayed liquid at the surface? Certainly, as noted above, global temperatures on the planet were higher. CO₂, itself, is a greenhouse gas. Kasting [26] and Pavlov et al. [29] calculated that very high CO₂ partial pressures (> 10 bars) would have been necessary to keep the water liquid. Pavlov et al. [29] suggest that, in the Late Archaean, there was probably an additional greenhouse gas that was likely to have been CH4. The lack of O2 meant that there was no protective ozone layer in the upper atmosphere and, hence, the flux of UV

radiation would have been much higher than it is today, influencing exposed surfaces and the upper millimetres of the water column. On the other hand, given the strong volcanic activity, the amount of dust particles in the atmosphere would have absorbed the influx of UV radiation to a certain extent.

A final consideration regarding the early Earth environment is the effect of cataclysmic impacts. While everyone agrees that the inner planets (and moons) were subjected to a high flux of meteorite, cometary and asteroid impacts in their early histories, there is some discussion as to exactly when this happened - was there just a gradual decrease in the number of impactors with time after the formation of the planets [30] - or was there a late stage cataclysm concentrated in the period between 4 and 3.85 Ga ago [31, 32]? Moreover, how cataclysmic were the impacts? There is a growing consensus that most of the impact basins seen on the Moon and Mars were probably formed in a short time period before about 3.85 Ga ago. Bolides of the size that formed the Aitken Basin on the Moon would have evaporated the upper 200 m of the Earth's oceans [33, 34]. Sleep et al [34] calculate that there could have been between zero and six such impacts or larger before 3.85 Ga, one or more of which could have completely sterilised the surface of the Earth by evaporating all the surface volatiles. Ryder [31, 35], on the other hand, found that even the worst-case scenario would have only eliminated the upper 400 m of the water column and that the Earth would therefore not have been completely sterilised. The question is, could life have arisen before the end of one of these major impacts, and if it did, could it have survived? As a final comment, it should not be thought that the impacts stopped completely after 3.85 Ga ago. Although no Ir (which is indicative of an extraterrestrial origin because of its paucity in the Earth's crust) anomalies were detected in the 3.8 Ga-old rocks from Isua in Greenland [36], analyses of tungsten isotopes in the Isua rocks suggest meteoritic input [37]. Moreover, studies of Cr isotopes on spherulite layers in younger rock formations (< 3.5 Ga) in the Pilbara, Australia and Barberton, South Africa greenstone belts show that continued bolide activity was significant [38-401.

In conclusion, the early Earth represented a planet with extreme environmental conditions compared to those on the Earth today. It was hotter, highly volcanically and hydrothermally active, had a higher bolide impact rate, a slightly reducing to neutral, anoxygenic atmosphere, and a high flux of UV radiation. Moreover, the ocean chemistry was probably quite different to the oceans of today with higher mineral ion concentrations and probably higher salinity, although estimates of pH range from acidic to alkaline. However, this extreme environment was then normal and conditions on the Earth today would have been completely inimical for the origin of life and the early evolution of life.

3.1.2 Habitats of Early Terrestrial Life

The habitats for life on the early Earth were more restricted than they are today for reasons related to the gradual geological evolution of the Earth, but nevertheless, they were almost as varied. In the first place, the early Earth appears to have been very much water covered with little exposed landmass. This was due to the fact that the Earth itself was evolving in a tectonic sense; true, exposed continents with true, granitic cores and stablising, underplating keels were formed gradually through the repeated recycling of hydrated, fractionated crust. Early continental crust consisted of "proto-continents" composed of thickened ocean crust intruded by granitoid material ("proto-granites"), or exposed ridge segments, such as Iceland, as well as hot spot volcano peaks. Large continental cratons with broad, shallow continental shelves (a habitat that favoured the proliferation of microorganisms that used oxygenic photosynthesis) did not start forming until about 3.2 Ga ago. Furthermore, the temperature ranges at the surface of the Earth did not allow for the development of temperate (mesophilic) to cold (psychrophilic) environment.

The range of habitats available for microbial colonisation [27, 41, 42] ranged from (i) the marine environment with its hydrothermal vents (possibly life could have started in this kind of environment), sediment and exposed volcanic rocks surfaces, as well as the water column itself, (ii) shallow water environments around the edges of the exposed landmasses, i.e. shallow water basins, lagoons, inlets etc., (iii) the littoral environment between tide levels (*N.B.* tides on the early Earth must have been much greater than they are today because the Moon was closer to the Earth), and (iv) the subaerial environment. Keeping in mind that microbial life is basically surface-bound, all these environments offered detrital and chemical sediment, as well as volcanic rock surfaces and dust or particle surfaces in the case of the planktonic realm. Furthermore, the widespread hydrothermal activity meant that there were probably few habitats not influenced in some way by hydrothermalism.

One further environment to take into consideration is the deep subsurface [43, 44]. Perhaps this niche was already colonised in the Early Archaean period (equivocal C isotope data from hydrothermal veins could be interpreted in this sense, e.g. Ueno et al. [45]). It has even been suggested that the deep habitat could have been the locus for the origin of life [43].

3.2 Early Life

Early life on Earth is, at this present moment, a highly disputed topic. For nearly 40 years, carbon isotope data and body fossils of microorganisms in Early Archaean cherts from the greenstone belts of Isua in southwest Greenland, Barberton in eastern South Africa, and the Pilbara in northwestern Australia, were accepted as evidence of life on Earth in the time period 3.8–3.3 billion years ago.

Recent findings have, however, upset the accepted view of early life and all previous evidence needs to be re-examined. I will briefly review the current status of the disputes before presenting my own evidence for abundant life on the early Earth (this evidence is also disputed by some) and finally discussing its relevance for potential life on Mars.

3.2.1 The Isua Greenstone Belt

The oldest rocks, which could contain a record of life, are the > 3.75 Ga old supracrustal rocks in the Isua greenstone belt of SW Greenland [46]. These rocks represent a collection of igneous and (perhaps) sedimentary deposits that have since undergone high-grade metamorphic alteration (amphibolite to granulite facies). Evidence for the presence of life at the time of the formation of these rocks is based on the analyses of the δ^{13} C isotope ratios and on investigation of microfossil remains [47-54]. In all cases, the rocks analysed for evidence of life were believed to have originally been sedimentary material deposited under water and, because of their high iron oxide content and layered texture, they were termed banded iron formations (BIFs). Most of the isotope measurements were made on bulk rock samples, ground to a powder, and some were made on in situ measurements of graphite inclusions [48]. The microfossil investigations were based on study of thin sections and carbonaceous remains released by acid maceration of the rocks. However, a recent study showed that young (< 8000 years old), endolithic cyanobacteria and fungal hyphae occur as contaminants (sometimes fossilised) in these rocks [55; Westall, unpub. data]. This recent contamination was also identified by stepped combustion isotopic analyses [56]. Endoliths are organisms that have adapted to an endolithic habitat in the cracks and fractures of the rocks in order to protect themselves from the extreme conditions, such as the cold desert conditions in Greenland. Obviously the presence of fossilised and non-fossilised endoliths poses a contamination problem with respect to measurements made, not only on bulk samples, but also on in situ measurements, if previous investigations have not been made to eliminate this possibility.

There is one remaining C isotope study on the Isua rocks that has not been shown to be the result of contamination. Rosing [49] found a δ^{13} C value of -18 % o in what were interpreted to be metamorphosed turbidites, i.e. deep sea sediments. This signature appears to be original to the rock and is not related to contamination [56]. Could it be a signature of life or is it, too, related to abiogenic processes, for instance to meteoritic input because the value is close to that of carbonaceous chondritic meteorites [37]? Furthermore, Myers [57] contends that this rock was not originally of sedimentary origin.

It was believed that the *in situ* graphite in the BIFs at Isua represented the metamorphosed remains of organic carbon of biogenic origin. However, it has been shown that the graphite was most likely produced by abiogenic processes

related to mineralogical reactions in the presence of hot, metasomatic fluids that occurred during the metamorphism of these rocks [56, 58, 59].

Finally, even the sedimentary origin of the supracrustal rocks from Greenland has been called into question [57, 60]. The high level of metamorphism makes interpretation of the original nature of the rocks very difficult.

3.2.2 The Barberton and Pilbara Greenstone Belts

Introduction

The oldest, best-preserved sediments are the 3.5–3.2 Ga old volcaniclastic and chemical sediments from the Barberton greenstone belt in South Africa and the Pilbara greenstone belt in NW Australia (Figs. 3.1a,b). In the localities studied, these sediments have undergone little metamorphism (prehnite-pumpellyite to lower greenschist). They were mainly formed in shallow water environments (above wave base), as well as in deeper water (below wave base) and in the littoral to subaerial zone. Most of the lithologies have been impregnated by hydrothermal silica, especially the sedimentary volcaniclastic horizons, to the extent that even many purely volcanic lithologies are referred to as cherts.

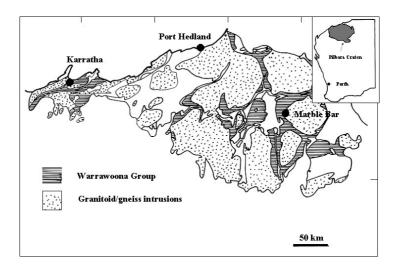
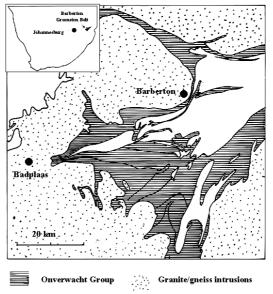


Fig. 3.1a Generalised geological map of the Pilbara craton showing the major plutonic intrusions and the exposure of the Early Archaean Warrawoona Group.

There have been numerous carbon, nitrogen and sulphur isotope studies and microfossil investigations made on these rocks. Most of the isotope measurements were made on bulk sample analyses and most of the microfossil work was done on thin sections of the rocks. Westall [61, 62], however, has recently established



procedures for making reliable observations with the scanning electron microscope.

Fig. 3.1b Generalised geological map of the Barberton greenstone belt showing the major plutonic intrusions and the exposure of the Early Archaean Onverwacht Group.

The isotope investigations were used to provide hints as to the kinds of microorganisms that could have existed in the Early Archaean period, but their interpretations were also heavily based on the microfossil interpretations (e.g. Haves [63]). The strong fractionation of carbon isotopes was attributed to microbial processes, namely to organisms using the RuBisCo enzyme in the Calvin cycle to convert CO₂ to organic matter. This enzyme is common in many prokaryotes, including purple bacteria, cyanobacteria, most chemolithotrophic bacteria and some Archaea (e.g. hyperthermophilic Archaea) [64]. One of the major controversies concerns the interpretation of cyanobacterial microfossils in 3.46 Ga-old rocks from the Pilbara [10, 65] ("Schopf-Brasier controversy"). Carbonaceous filamentous structures, occurring in cherts from the Towers Formation, Marble Bar, were described by Schopf [65] as representing fossil cyanobacteria. Careful re-examination of the sample site indicated that the sample examined was, in actual fact, taken from a hydrothermal chert vein [10]. Moreover, analysis of micrographs taken with the light microscope demonstrated that the structures described [65] do not represent clearly defined filaments, but are part of larger, more complex and irregular carbonaceous forms that did not at all resemble microorganisms [10]. Brasier et al. [10, 11] argue that the carbonaceous material was probably formed hydrothermally (abiogenically) by Fischer-Tropsch synthesis. It, therefore, had no relationship to microorganisms, especially not to cyanobacteria that would not be expected to inhabit a hydrothermal vein. Brasier et al. have taken their hypothesis further, arguing that the isotopic fractionations measured in these samples were also caused by abiogenic processes [11] and now contest all other evidence for life in the Early Archaean. Where do we now stand with respect to the evidence for life in the early Archaean? In the following I will present the evidence for the existence of widespread microbial life forms in shallow water to littoral (intertidal) environments in this epoch.

Methods

The process of identification of signs of life in rocks of this ancient age commences with detailed field study since it is necessary to be able to place the rock samples with the potential evidence for life in a well-defined geological framework, in order to avoid the first error of finding evidence of "life" in an environmental situation which is not conducive to life. Study of the rock sample and subsamples in the hand specimen, in thin section with a light microscope, as well as with the scanning electron microscope and the microprobe and other chemical methods (neutron activation, particle induced X-ray emission PIXE, etc.) can provide further detailed background information concerning sedimentological/ igenous/metamorphic textures and minerals, thus furnishing a more detailed context for structures that are on the micron scale. These investigations also document the history of the rock, such as any mechanical and chemical changes that have taken place over time through diagenesis and metamorphism.

In this way, selected specimens are chosen for further isotope and microfossil study. Considering the silicified nature of the material, delicate etching with HF is necessary to expose the carbonaceous microfossils (the carbonaceous material being more resistant to the HF compared to pure SiO₂) for scanning electron microscope investigations. Contamination in the form of microbial infiltration of cracks and fissures, both on the terrain and in the laboratory, as well as precipitate from the etching process, need to be identified and avoided [61, 78]. The identification of fossil microbial life forms (prokaryotes in this case) is based on three main criteria: (i) the morphology of the structure, including shape, size, cell wall texture (only visible with electron microscope techniques), evidence for cell division, evidence for flexibility (if filamentous), evidence for cell lysis (death); (ii) colonial characteristics including colony formation, association with polymer (extracellular polymeric substances or EPS), biofilm formation, presence of consortia; and (iii) biogeochemical characteristics, such as carbonaceous composition, C, N, S isotope ratios and perhaps the concentration of certain heavy or rare earth elements.

Microfossil and Isotope Evidence for Life

On the basis of the morphological and colonial characteristics, the carbonaceous composition and C and N isotope data, a number of types of microfossils and

biofilm-forming microfossils were identified. The majority of them appear to have been replaced primarily by silica, although in one case, a biofilm was replaced by both calcium carbonate and silica. Remnant carbon can be traced in the micronsized structures by element mapping and is also documented by microprobe analysis (see Westall et al. [61] and Westall [66] for a discussion of the fossilisation process). The microfossils observed in the Early Archaean cherts from Barberton and the Pilbara include (Fig. 3.2): (i) filaments falling into two size ranges: small filaments < 0.25 μ m in width and up to several tens of micrometres in length [67, 68] and larger filaments up to 2.5 μ m wide and about 100 μ m long [69]; (ii) vibroid-shaped structures, 2-3.8 μ m in length and 1 μ m in width [67, 70]; and (iii) spherical to oval structures with size modes centred around 0.4–0.5 μ m, 0.8–1.0 μ m, and about 1.3 μ m [67, 68].

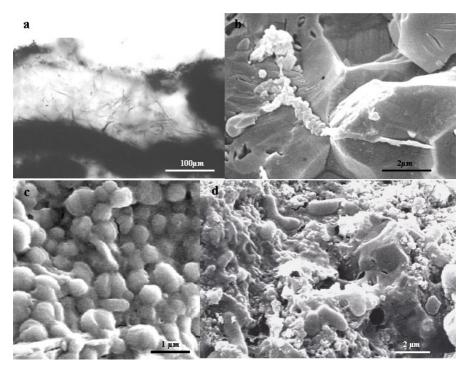


Fig. 3.2 Early Archaean carbonaceous microfossils from Barberton and the Pilbara. (a) Large filamentous microfossils observed in thin section, Kromberg Fm., Barberton; (b) small filament with attached mineral precipitate, Kromberg Fm., Barberton; (c) colony consisting of two types of coccoids (diameter 0.5 μ m and 0.8 μ m), embedded in EPS, Coppin Gap, Pilbara; (d) Small colony of vibroids embedded in EPS, Kromberg Fm., Barberton.

These structures are interpreted as fossil filamentous, vibroid-shaped, and coccoidal bacteria, respectively. They commonly occur as biofilms on the surfaces of specific sedimentological layers, the biofilms consisting often of more than one

type of microorganism, such as filaments and coccoids, or two types of coccoids, as well as EPS, and included authigenically precipitated (and perhaps trapped) mineral grains. The biofilms formed fine, delicate mats in shallow water environments and thicker, more robust mats in more extreme littoral environments [67, 69, 70, 71] (Fig. 3.3). Embedded evaporite minerals and dessication cracks in the more robust mats testify to subaerial exposure. The mats are visible as laterally extensive, fine, crinkly lamina [67, 70, 71] (Fig. 3.3) or as macroscopic domed structures [68]. They are widespread in the shallow water to littoral sediments studied in both the cherts from the Pilbara and from Barberton.

Many isotopic analyses have been made on numerous chert samples from Barberton and the Pilbara. Carbon isotope analyses on samples that contained biofilms and microfossils visible either in thin section (the larger filaments only) or by scanning electron microscopy gave δ^{13} C values of -14 to -36 % [67, 69, 71], which fall well into the realm of biogenic fractionation. A similar interpretation was made for other carbon isotope analyses of cherts from these areas that gave values within the range of -14 to -42 % [10, 45, 72, 73]. The presence of chemosynthetic prokaryotes was inferred from the nitrogen isotope ratios, -9 and -4 %, [74-76]. Shen et al. [77] interpreted the 21.3 to 7.4 ‰ sulphur isotope ratios to indicate sulphur reducing bacterial activity.

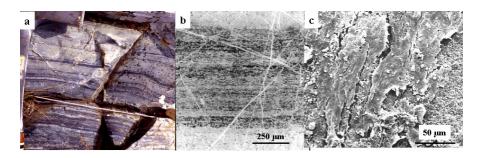


Fig. 3.3 Biofilm formation on the surface of volcaniclastic sediments, Kromberg Fm., Barberton. (a) Field view of finely laminated sediments; (b) laminae are finely wrinkled in thin section view; (c) thick, robust biofilm developed in an exposed littoral environment.

This collection of evidence, including geological context, morphological, colonial and biofilm characteristics, carbonaceous composition and isotope data, points strongly in favour of life having existed in the 3.5–3.3 Ga time frame. The data also indicate, moreover, that it was widespread. It appears most unlikely that all these features could be produced simultaneously by prebiotic organic molecules or mineralogical precipitates (see also experimental work undertaken by Westall et al. [78] on this subject). Obviously, each case needs to be addressed on an individual basis, but if the above guidelines are followed, the risk of obtaining a "false positive" response can thus be minimised.

Early Archaean life

What kinds of microorganisms did the Early Archaean biota represent? From their morphology and biofilm-forming characteristics, they strongly resemble modern prokaryote organisms. It is possible to make inferences regarding the microenvironments in which the microbes lived and their possible mode of life using the combination of the information obtained from the macroscopic to microscopic studies of the geological context, the style of the biofilms and their mineralisation, as well as the various isotope investigations. There are no mineralogical indications that the Early Archaean environment was oxidising [79], although the presence of iron oxide deposits indicates that any oxygen produced by photolysis of H₀O vapour in the upper atmosphere was rapidly consumed by the reduced mineral species. Some of the microbial mats formed in exposed littoral conditions are associated with pyrite crystals (Westall unpub. data), also indicating reducing conditions. It thus appears reasonable to infer that the early Archaean microbes were anaerobes. The high ambient temperatures at this time and the close association with hydrothermal processes further suggest that the organisms were probably thermophilic. [N.B. Although some studies have suggested that life originated as a hyperthermophilic life form, Forterre et al. [80] provide persuasive arguments that it was most likely thermophilic and that the hyperthermophiles are a later evolutionary development.] Some of the microbial mats were formed in exposed, evaporitic conditions [67, 68] indicating that the microorganisms were probably at least halotolerant, if not halophilic. As noted above, the biofilms and mats studied were formed in the photic, shallow water to littoral environment. Could some of them have been formed by photosynthesising organisms? Certainly some of the exposed mats were created by organisms that strongly resembled anaerobic photosynthesisers [67, 68]. Finally, the high UV flux in the ozone-less Early Archaean period would have meant that any exposed microorganisms would have to have been relatively resistant to radiation and had probably already developed rapid gene repair mechanisms. In conclusion, Early Archaean life appears to have been relatively diverse, within the limitations of anaerobiosis.

With this information in mind, we can re-examine the Schopf-Brasier controversy, especially the conundrum posed by the apparently biogenic signal measured in the carbonaceous precipitations in hydrothermal chert samples [10]. The interpretation of Brasier et al. [10, 11] is that the signal is a product of Fischer-Tropsch fractionation. An alternative hypothesis is proposed here, in which the carbon could have been leached from strata bearing carbonaceous fossils by hot hydrothermal fluids to be deposited higher up in the vein. The carbon would no longer have the morphology of a microfossil, but its isotope signature would be biogenic.

A final, important point to address is whether oxygen-photosynthesising organisms, such as cyanobacteria, were present on Earth in this Early Archaean period. The fact that the "cyanobacterial" microfossils described by Schopf [65] are not microfossils does not signify that such microorganisms did not exist. Other

authors have described similar structures from sedimentary chert layers in these Early Archaean formations [45, 69]. Cyanobacteria are photosynthesising microorganisms producing oxygen as a by-product of their metabolic processes by a series of reactions that are relatively advanced in terms of metabolic evolution. They form microbial mats that may be tabular or vertical (domal); in fact, such stromatolites were common in the Late Archaean and the Paleoproterozoic. The latter occurred on broad, shallow, continental platforms. This, however, was an ecological niche that did not exist on a large scale in Early Archaean times, except in the form of small basins around the exposed landmasses. Moreover, cyanobacteria generally (but not always) have quite specific characteristics that are readily recognisable in their fossilised remains, such as a thick, cohesive glycocalyx or outer sheath (trichome) around the chains of cells or around their colonies, specialised cells with different morphologies compared to the other cells, and are generally larger size than other types of bacteria [65]. Such microfossils have not been identified in the Early Archaean formations where they would be expected to occur (sun-bathed shallow water to littoral habitats) and where there is plenty of evidence for biofilm formation by other types of bacteria. I, therefore, conclude that oxygenic photosynthesisers, such as cyanobacteria, had probably not yet evolved.

3.3 Life on Mars?

3.3.1 Water on Mars

Numerous chapters in this book address the occurrence of water on Mars, both in the past and in the present. The presence of bodies of standing water on the planet for considerable periods of time (tens of millions of years) is crucial at least for the origin of life and to enable it to flourish sufficiently for its future survival during the degradation of environmental conditions that occurred on the planet after about 4 Ga ago.

The smaller size of Mars compared to the Earth (about half the size) meant that the planet would have cooled down more quickly and that water could have condensed on the planet earlier than on Earth. However, the greater distance of the planet from the Sun, which was less luminous in the early part of its history, would have meant that the water bodies would have rapidly frozen over, unless there was a greenhouse gas component to the atmosphere, as has been suggested by Kasting [81]. At least in the early part of Mars' history, there is geomorphological evidence for water-carved channels and accessory features [2]. Other factors to take into consideration include the size and longevity of standing bodies of water in volcano and impact crater lakes, whether there was a small northern sea [2], and whether the water bodies were rapidly frozen over. If they existed for biologically-significant periods of time, a frozen surface may not necessarily have inhibited life: they may have been liquid with an icy cap (c.f. Lake Vostok) with heat sources provided by the high heat flow from the mantle and the volcanic and hydrothermal activity. Moreover, the energy provided by the frequent bolide impacts would also have contributed an important, temporary source of heat to the planet surface. Since Mars would also have had a similar inventory of organic carbon molecules as the early Earth, it is, thus, likely that life appeared independently on the planet.

Lazcano and Miller [82] calculated that about 10 Ma was needed for life to appear and evolve to the prokaryote stage on Earth. This is largely sufficient for the appearance of life on Mars, early in its history when the planet was still warm enough to have had liquid water, probably soon after the condensation of water. Once it had taken a foothold, further cooling and coverage of standing bodies of water by ice would not have eliminated life. In fact, Jakosky and Shock [86] consider that there were sufficient mineralogical energy sources to support as much chemolithotrophic life on Mars in its first 10–50 million years, as on early Earth.

Mars also suffered from the late heavy bombardment that affected all the inner planets. Some estimates of the effects of this bombardment suggest significant resurfacing of the planet [83]. If the bombardment were as severe as this and any pre-existing life had been extinguished, would it be possible for life to have reappeared after the end of the heavy bombardment period at about 3.85 Ga ago? By this time the internal heat sources in the planet were running low (but were not extinguished), and the atmosphere was already in the process of being lost by impact erosion, erosion by the solar wind, and by dissolution in water followed by precipitation as mineral salts within the volcanic crust. The surface volatiles were in the process of sublimating and being lost to space, or, in the case of a significant part of the water inventory, they were preserved in the developing cryosphere. This would indeed have been an inhospitable environment for the (re)appearance of life, or even for the continuation of life, if it had appeared previously and survived the late heavy bombardment. However, it is still possible that, given a suitable aqueous environment with a heat source and sufficient time, i.e. about 10 Ma, life could have re-appeared. We know, though, that life is tenacious and it is feasible that it "hung on" in the kind of glacial exposed habitats that are found today on Earth, such as endolithic environments or permafrost, as suggested by Friedmann and Koriem [84] and Gilichinsky [85].

3.3.2 Environments for Life on Early Mars

What kind of environments would have been available for colonisation and what kind of organisms could have evolved, given the special environmental circumstances on Mars? Mars would actually have possessed all the environments that were found on the early Earth. These habitats would have included deepwater environments below wave base in basins of standing water (see Chap. 10 by Cabrol and Grin) and numerous shallow water and littoral environments around

the edges of these basins. In fact, there may have been even more shallow water, littoral and subaerial environments on Mars than there were on Earth simply because of the lack of a global ocean. Volcanic and hydrothermal activity would have been strong on early Mars, although it was about one hundred times less than on the early Earth [86]. Moreover, it is likely that evaporitic conditions would have been common, especially as temperatures started cooling significantly: the production of water ice concentrates salts in the residual water, thus increasing salinity. Finally, the high partial pressure of CO₂ in the atmosphere of early Mars [81] may have resulted in a slightly acidic pH of the water on Mars, as has been postulated for the Earth [21].

3.3.3 Potential Early Life on Mars

In this exercise, we are using information from a terrestrial rock record that formed a billion years and more after the consolidation of the Earth in a period that corresponds to the end of the era when life could have existed at the surface of Mars. How relevant is the information from the Early Archaean in this context? As noted above, the Early Archaean rocks formed in environmental settings that could have been present on early Mars at any time before the degradation of the climate and there are, therefore, many similarities in the types of chemical and physical environments offered by the two planets early in their histories. The fact that, on a global scale, there were major differences, such as the lack of a global ocean, no (proto)continents, nor plate tectonics on Mars, was of little importance for the following reasons. Microbial life occurs on temporal and spatial scales that are many orders of magnitude smaller than geological processes. In fact, from a microbial point of view, a niche of the order of some tens of square microns and a time period of the order of days to weeks are quite sufficient for temporary flourishing growth. Since Mars cooled faster than the Earth and water would have condensed sooner, life could have appeared on that planet earlier than on Earth and could have flourished before climatic degradation made the surface completely inhospitable.

Early life forms on Earth were prokaryote-type organisms. They formed microbial mats in shallow water to littoral environments. All of them were influenced to a greater or lesser degree by hydrothermal activity. The littoral environment mats were influenced by evaporitic conditions and the organisms forming them may possibly have developed anaerobic photosynthesis, but not aerobic photosynthesis. These mats were fossilised by hydrothermal fluids rich in silica and rarely by calcium carbonate.

Given the similar kinds of habitable niches on Mars, analogy with the early terrestrial organisms suggests that, if life did appear on Mars, it is probable that it inhabited the same kind of habitats. Potential Martian life would therefore have been anaerobic and, initially at least, thermophilic. Considering that chemolithotrophy was probably the first metabolic pathway on Earth, the earliest Martian organisms would probably have used a similar process. Given the availability of sunlight-bathed shallow water and littoral environments, Martian life may even have developed anaerobic photosynthesis (*N.B.* Lazcano and Miller [82] calculated that only 10 million years would have been necessary for the appearance of photosynthesis). Moreover, the arid environmental conditions on Mars, as the planet was cooling, would have provided evaporitic and xerophilic (anhydrobiotic) habitats for halotolerant or halophilic types of microorganisms, or organisms with the tolerated low amounts of water, as in desert situations (see also Chap. 12 by Mancinelli). As with the Earth, the potential Martian life forms would necessarily have been relatively tolerant of UV radiation.

The relatively rapid decrease in global planet temperatures on Mars would have provided potential Martian life with a further environmental variable - that of cold and even freezing temperatures. This is a situation that did not exist on the early Earth. Early life on Mars could have therefore been even more diversified than on early Earth, with the development first of all of mesophilic organisms capable of living in moderate temperatures and, finally, psychrophilic organisms that can live in extremely cold conditions. Potential Martian life, if it survived the heavy bombardment, would have had to be tolerant of very dry, exposed conditions.

The hypothetical Martian organisms and biofilms could have been fossilised in exactly the same way as those preserved in the Early Archaean formations, by hydrothermal silica or other hydrothermal fluids (calcium carbonate, iron oxides) or even evaporite minerals.

3.4 Conclusions

Early life on Earth represents an excellent analogue for early life on Mars for many reasons. In the first place, early life on Earth appeared and thrived in circumstances that were similar to the conditions existing on early Mars, before the late heavy bombardment period and the deterioration of climatic conditions. This means that, if life did appear on Mars, it was probably of a simple prokaryote type that may or may not have reached the stage of anoxygenic photosynthesis but certainly would not have reached the oxygenic photosynthesis stage. The organisms would initially have included the same types as occurred on the early Earth, i.e. anaerobic organisms that are UV resistent, thermophilic and that probably also included halophiles and xerophiles. Secondly, the organisms would have formed biofilms or mats in the numerous shallow water to littoral habitats, similar to those on the early Earth, that would have been available on early Mars.

Finally, the difficulties surrounding the acceptance of nearly 3.5 Ga-old life, and what constitutes acceptable evidence for ancient life (not to speak of the debate concerning the evidence for life in Martian meteorite ALH 84001), is a salutary lesson for the even more difficult exercise of searching for evidence of life on Mars. The suite of observations and tests that can be done in the most optimum conditions on Earth, that still allow for discussion of interpretations, means that it will be very difficult to obtain uncontroversial evidence for ancient life on Mars using *in situ* methods, and that sample return will be an absolute

necessity (better still, *in situ* investigations by geologists on Mars – nothing can beat the eye and brain of an experienced geologist).

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3.5 References

- 1 Carr MH (1996) Water on Mars. Oxford University Press, New York
- 2 Carr MH, Malin MC (2000) Meter scale characteristics of Martian channels and valleys. Icarus 146: 366-386
- 3 Clifford SM, Parker TJ (2001) The evolution of the Martian hydrosphere: implications for the fate of a primordial ocean and the current state of the Northern Plains. Icarus 154: 40-79
- 4 Hynek BM, Phillips RJ (2003) New data reveal mature, integrated drainage systems on Mars indicative of past precipitation. Geology 31: 757-760
- 5 Treiman AH, Barrett RA, Gooding JL (1993) Preterrestrial alteration of the Lafayette (SNC) meteorite. Meteoritics 28: 86-97
- 6 Romanek CS, Grady MM, Wright IP, Mittlefehldt DW, Socki RA, Pillinger CT, Gibson EK (1994) Record of fluid-rock interactions on Mars from the meteorite ALH84001. Nature 372: 655-657
- 7 Watson LL, Hutcheon ID, Epstein S, Stolper EM (1994) Water on Mars: clues from deuterium/hydrogen and water contents of hydrous phases in SNC meteorites. Science 265: 86-90
- 8 Christensen PR and 15 colleagues (2000) Detection of crystalline hematite mineralization on Mars by the Thermal Emission Spectrometer: evidence for near-surface water. J. Geophys. Res. 105(E4): 9623-9642
- 9 Christensen PR and 24 colleagues (2001) Mars Global Surveyor Thermal Emission Spectrometer experiment: investigation description and surface science results. J. Geophys. Res. 106(E10): 23823-23871
- 10 Brasier MD, Green OR, Jephcoat AP, Kleppe AK, van Kranendonk M, Lindsay JF, Steele A, Grassineau N (2002) Questioning the evidence for Earth's oldest fossils. Nature 416: 76-81
- 11 Lindsay JF, Brasier MD, McLoughlin N, Green OR, Fogel M, McNamara KM, Steele A, Mertzman SA (2003) Abiotic Earth – establishing a baseline for earliest life, data from the Archaean of western Australia. 34th Lun. Planet. Sci. Conf. 1137
- 12 Wilde SA, Valley JW, Peck WH, Graham CM (2001) Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. Nature 409: 175-178
- 13 Mojzsis SJ, Arrhenius G, Keegan KD, Harrison TH, Nutman AP, Friend CLR (1996) Evidence for life on Earth before 3,800 million years ago. Nature 384: 55-59
- 14 Kamber BS, Moorbath S, Whitehouse MJ (2001) The oldest rocks on earth: time constraints and geological controversies. In: Lewis CLE, Knell SJ (eds) The Age

of the Earth: from 4004 BC to AD 2002. Geol. Soc. Lond. Spec. Pub. 190: 177-203

- 15 Arndt N, Chauvel C (1991) Crust of the Hadean Earth. Bull. Geol. Soc. Denmark 39: 145-151
- 16 Arndt NT (1994) Archean komatiites. In: Condie KC (ed) Archean crustal evolution, Elsevier, Amsterdam, pp 11-44
- 17 Nijman W, de Bruijne, KH, Valkering M (1999) Growth fault control of Early Archaean cherts, barite mounds and chert-barite veins, North Pole Dome, Eastern Pilbara, Western Australia. Precambrian Res. 95: 247-274
- 18 Paris I, Stanistreet IG, Hughes MJ (1985) Cherts of the Barberton greenstone belt interpreted as products of submarine exhalative activity. J. Geol. 93: 111-129.
- 19 De Ronde CEJ, de Wit MJ, Spooner ETC (1994) Early Archaean (> 3.2 Ga) ironoxide-rich, hydrothermal discharge vents in the Barberton greenstone belt, South Africa. Geol. Soc. Am. Bull. 106: 86-104
- 20 Knauth LP, Lowe DR, (2003) High Archean climatic temperature inferred from oxygen isotope geochemistry of cherts in the 3.5 Ga Swaziland Supergroup, South Africa. Geol. Soc. Am. Bull. 115: 566-580
- 21 Grotzinger JP, Kasting JF (1993) New constraints on Precambrian ocean composition. J. Geol. 101: 235-243
- 22 Holland HD (1984) The Chemical Evolution of the Atmosphere and Oceans. Princeton University Press, Princeton
- 23 Hardie LA (2003) Secular variations in Precambrian seawater chemistry and the timing of Precambrian aragonite seas and calcitic seas. Geology 31: 785-788
- 24 Kempe S, Degens ET (1985) An early soda ocean? Chem. Geol. 5: 95-108
- 25 Walker JCG (1985) Carbon dioxide on the early Earth. Orig. Life 16: 117-127
- 26 Kasting JF (1993) Earth's early atmosphere. Science 259: 920-926
- 27 Nisbet EG (1995) Archaean ecology: a review of evidence for the early development of bacterial biomes, and speculation on the development of a global-scale biosphere. In: Coward MP, Ries AC (eds) Early Precambrian Processes. Geol. Soc. London, Oxford, pp 27-52
- 28 Sagan C, Mullen G (1972) Earth and Mars: evolution of atmospheres and surface temperatures. Science 177: 52-56
- 29 Pavlov AA, Kasting JF, Brown LL, Rages KA, Freedman R (2000) Greenhouse warming by CH_4 in the atmosphere of early Earth. J. Geophys. Res. 105(E5): 11981-11990
- 30 Hartmann WK, Ryder G, Dones L, Grinspoon D (2000) The time-dependent intense bombardment of the primordial Earth/Moon system, In: Canup RM, Righter K (eds) Origin of the Earth and Moon. University of Arizona Press, Tucson, pp 493-512
- 31 Ryder G, Koeberl C, Mojzsis SJ (2000) Heavy bombardment on the Earth at ~ 3.85 Ga: the search for petrographic and geochemical evidence. In: Canup RM, Righter K (eds) Origin of the Earth and Moon. University of Arizona Press, Tucson, pp 475-492
- 32 Kring DA, Cohen BA (2002) Cataclysmic bombardment throughout the inner solar system 3.9-4.0 Ga. J. Geophys. Res. 107: 5009, 10.1029/2001JE001529
- 33 Maher KA, Stevenson DJ (1988) Impact frustration of the origin of life. Nature 331: 612-614
- 34 Sleep NH, Zahnle KJ, Kasting JF, Morowitz HJ (1989) Annihilation of ecosystems by large asteroid impacts on the early Earth. Nature 342: 139-142
- 35 Ryder G (2003) Bombardment of the Hadean Earth: wholesome or deleterious. Astrobiology 3: 3-6

- 36 Anbar A, Zahnle KJ, Arnold GL, Mojzsis SJ (2001) Extraterrestrial iridium, sediment accumulation and the habitability of the early Earth's surface. J. Geophys. Res. 106: 3219-3236
- 37 Schoenberg R, Kamber BS, Collerson KD, Moorbath S (2003) Tungsten isotope evidence from ~3.8-Gyr metamorphosed sediments for early meteorite bombardment of the Earth. Nature 418: 403-405
- 38 Lowe DR, Byerly GR (1986) Early Archean silicate spherules of probable impact origin, South Africa and Western Australia. Geology 14: 83-86
- 39 Lowe DR, Byerly GR, Kyte FT, Shukolyukov A, Asaro F, Krull A (2003) Spherule beds 3.47-3.24 billion years old in the Barberton Greenstone Belt, South Africa: a record of large meteorite impacts and their influence on early crustal and biological evolution. Astrobiology 3: 7-48
- 40 Kyte FT, Shukolyukov A, Lugmaor GW, Lowe DR, Byerly GR (2003) Early Archean spherule beds: chromium isotopes confirm origin through multiple impacts of projectiles of carbonaceous chondrite type. Geology 31: 283-286
- 41 Nisbet EG, Sleep NH (2001) The habitat and nature of early life. Nature 409: 1083-1091
- 42 Westall F (2004) The geological context for the origin of life and the mineral signatures of fossil life. In: Martin H, Gardaud, M, Reisse G, Barbier B (eds) The Early Earth and the Origin of Life, Springer-Verlag, Berlin, in press
- 43 Gold T (1999) The Deep Hot Biosphere. Copernicus Books, Springer-Verlag, New York
- 44 Fredrickson JK, Onstott TC (1996) Microbes deep inside the Earth. Sci. Am. 27(4): 42
- 45 Ueno Y, Maruyama S, Isozaki Y, Yurimoto H (2001) Early Archean (ca. 3.5 Ga) microfossils and 13C-depleted carbonaceous matter in the North Pole area, Western Australia: field occurrence and geochemistry. In: Nakashsima S, Maruyama S, Brack A, Windley BF (eds) Geochemistry and the Origin of Life. Universal Acad. Press, Tokyo, pp 203-236
- 46 Appel PWU, Moorbath S (1999) Exploring Earth's oldest geological record in Greenland. Eos 80: 257-264
- 47 Schidlowski M (1988) A 3,800-million-year isotopic record of life from carbon in sedimentary rocks. Nature 333: 313-318
- Mojzsis SJ, Arrhenius G, McKeegan KD, Harrison TM, Nutman AP, Friend CRL (1996) Evidence for life on Earth before 3800 million years ago. Nature 384: 55-59
- 49 Rosing MT (1999) 13C depleted carbon microparticles in > 3700 Ma seafloor sedimentary rocks from West Greenland. Science 283: 674-676
- 50 Pflug HD, Jaeschke-Boyer H (1979) Combined structural and chemical analysis of 3,800-Myr-old microfossils. Nature 280: 483-486
- 51 Pflug HD (2001) Earliest organic evolution. Essay to the memory of Bartholomew Nagy. Precambrian Res. 106: 79-91
- 52 Robbins EI (1987) Appelella ferrifera, a possible new iron-coated microfossil in the Isua Iron Formation, southwestern Greenland. In: Appel PWU, LaBerge GL (eds) Precambrian Iron Formations. Theophrastes, Athens, pp. 141-154
- 53 Robbins EI, LaBerge GL, Schmidt RG (1987) A model for the biological precipitation of Precambrian Iron-Formations – B. Morphological evidence and modern analogs. In: Appel PWU, LaBerge GL (eds) Precambrian Iron Formations. Theophrastes, Athens, pp. 97-139
- 54 Robbins EI, Iberall AS (1991) Mineral remains of early life on Earth? On Mars? Geomicrobiol. J. 9: 51-66

- 55 Westall F, Folk RL (2003) Exogenous carbonaceous microstructures in Early Archaean cherts and BIFs from the Isua greenstone belt: implications for the search for life in ancient rocks. Precambrian Res. 126:313-330
- 56 Van Zuilen M, Lepland A, Arrhenius G (2002) Reassessing the evidence for the earliest traces of life. Nature 418: 627-630
- 57 Myers JS (2003) Isua enigmas: illusive tectonic, sedimentary, volcanic, and organic features of the > 3.8 >3.7 Ga Isua greenstone belt, Southwest Greenland. Geophys. Res. Abstr. 5: EAE-03-A-13823
- 58 Van Zuilen M, Lepland A, Teranes J, Finarelli J, Wählen M, Arrhenius G (2003) Graphite and carbonate in the 3.8 Ga old isua Supracrustal belt, southern West Greenland. Precambrian Res. 126: 331-348
- 59 Lepland A, Arrhenius G, Cornell D (2002) Apatite in early Archean Isua supracrustal rocks, southern West Greenland: its origin, association with graphite and potential as a biomarker. Precambrian Res. 118: 221-241
- 60 Fedo CM, Whitehouse MJ (2002) Metasomatic origin of quartz-pyroxene rock, Akilia, Greenland, and implications for Earth's earliest life. Science 296: 1448-1452
- 61 Westall F (1999) The nature of fossil bacteria: a guide to the search for extraterrestrial life. J. Geophys. Res. 104(E7): 16,437-16,451
- 62 Westall, F. (in prep) On the identification of Early Archaean fossil bacteria and biofilms
- 63 Hayes JM (1994) Global methanotrophy at the Archean-proterozoic transition. In: Bengtson S (ed) Early Life on Earth. Columbia University Press, New York, pp 220-236
- 64 Madigan MT, Martinko JM, Park J (1999) Brock: Microbiology of Microorganisms. Prentice, Upper Saddle River (New Jersey)
- 65 Schopf JW (1993) Microfossils of the Early Archean Apex Chert: new evidence of the antiquity of life. Science 260: 640-646
- 66 Westall F, Boni L, Guerzoni ME (1995) The experimental silicification of microorganisms. Palaeontology 38: 495-528
- 67 Westall F, De Wit MJ, Dann J, Van Der Gaast S, De Ronde C, Gerneke D (2001) Early Archaean fossil bacteria and biofilms in hydrothermally-influenced, shallow water sediments, Barberton greenstone belt, South Africa. Precambrian Res. 106: 93-116
- 68 Westall F, Brack A, Barbier B, Bertrand M, Chabin A (2002). Early earth and early life: an extreme environment and extremophiles - application to the search for life on Mars. Proc. Second European Workshop on Exo/Astrobiology Graz, Austria, 16-19 September 2002. ESA SP-518, European Space Agency, Noordwijk, pp 131-136
- 69 Walsh MM (1992) Microfossils and possible microfossils from the Early Archaean Onverwacht Group, Barberton Mountain Land, South Africa. Precambrian Res. 54: 271-293
- 70 Westall F, Gerneke D (1998) Electron microscope methods in the search for the earliest life forms on Earth (in 3.5–3.3 Ga cherts from the Barberton greenstone belt, South Africa): applications for extraterrestrial life studies. Proc. SPIE 3441: 158-169
- 71 Walsh MM, Lowe DR (1999) Modes of accumulation of carbonaceous matter in the early Archaean: A petrographic and geochemical study of carbonaceous cherts from the Swaziland Supergroup. In: Lowe DR, Byerly GR (eds) Geologic Evolution of the Barberton Greenstone Belt, South Africa, Geol. Soc. Am. Spec. Paper 329: 115-132

- 72 Hayes JM, Kaplan IR, Wedeking KW (1983) Precambrian organic chemistry, preservation of the record. In: Schopf JW (ed) Earth's Earliest Biosphere, Princeton University Press, Princeton, pp 93-134
- 73 Strauss H, Moore TB (1992) Abundances and isotopic compositions of carbon and sulfur species in whole rock and kerogen samples. In: Schopf JW, Klein C (eds) The Proterozoic Biosphere: A Multidisciplinary Study. Camdridge University Press, Cambridge, pp 709-798
- Beaumont V, Robert F (1999) Nitrogen isotope ratios of kerogens in Precambrian cherts: a record of the evolution of atmospheric chemistry? Precambrian Res. 96: 63-82
- 75 Pinti DL, Hashizume K (2001) 15N-depleted nitrogen in Early Archean kerogens: clues on ancient marine chemosynthetic-based ecosystems? Precambrian Res. 105: 85-88
- Pinti DL, Hashizume K, Matsuda J-I (2001) Nitrogen and argon signatures in 3.8 2.8 Ga metasediments: clues on the chemical state of the Archean ocean and the deep biosphere. Geochim. Cosmochim. Acta 65: 2301-2315
- 77 Shen Y, Buick R, Canfield DE (2001) Isotopic evidence for microbial sulphate reduction in the early Archaean era. Nature 410: 77-81
- 78 Westall F, Steele A, Toporski J, Walsh M, Allen C, Guidry S, Gibson E, McKay D, Chafetz H (2000) Polymeric substances and biofilms as biomarkers in terrestrial materials: implications for extraterrestrial materials. J. Geophys. Res. 105(E10): 24,511-24,527
- 79 Rye R, Kuo PH, Holland HD (1995) Atmospheric carbon dioxide concentrations before 2.2 billion years ago. Nature 378: 603-605
- 80 Forterre P, Confalonieri F, Charbonnier F, Duguet M (1995) Speculations on the origins of life and thermophily: review of available information on reverse gyrase suggests that hyperthermophilic procaryotes are not so primitive. Orig. Life Evol. Biosph. 25: 235-249
- 81 Kasting JF (1997) Warming early Earth and Mars. Science 276: 1213-1215
- 82 Lazcano A, Miller SL (1994) How long did it take for life to begin and to evolve to cyanobacteria? J. Molec. Evol. 36: 546-554
- 83 Frey H, Hutchinson L, Sakimoto S, Roark J (2000) A large population of possible buried impact basins on Mars revealed by MOLA topographic data. 21st Lun. Planet. Sci. Conf. 1736
- 84 Friedmann EI, Koriem AM (1989) Life on Mars: how it disappeared (if it was ever there). Adv. Space Res. 9(6): 167-172
- 85 Gilichinsky DA (2002) Permafrost model of extraterrestrial habitat. In: Horneck G, Baumstark-Khan C (eds) Astrobiology, Springer-Verlag, Berlin, pp 125-142
- 86 Jakosky BM, Shock EL (1998) The biological potential of Mars, the early Earth, and Europa. J. Geophys. Res. 103(E8): 19359-19364
- 87 Brack A (2002) Water, the spring of life. In: Horneck G, Baumstark-Khan C (eds) Astrobiology, Springer-Verlag, Berlin, pp 79-88

4 Hydrated Minerals on Mars

Janice L. Bishop

Hydrated minerals on Mars provide information about the aqueous history of the planet, which is an integral aspect of whether or not Mars was suitable for life. These minerals hold clues to the environmental processes involving the abundance and duration of water and the importance of chemical alteration. Mineral identification on Mars is underway through orbital visible-infrared remote sensing in concert with spectroscopic, chemical and magnetic measurements on landed missions. Until the mineralogy of the Martian surface is better constrained it is essential to study the spectral, chemical, magnetic and hydration properties of Martian meteorites and terrestrial analog materials in order to interpret data from telescopic, orbital and landed missions.

Identification of hydrated minerals, such as iron hydroxides/oxyhydroxides, carbonates, sulfates, phyllosilicates, zeolites, and opal, on Mars would imply the presence of water during alteration of the surface material. Some minerals require long-term aqueous processes for formation, while others are formed in short-term hydrothermal events or under conditions of very little moisture. The hydration minerals found or suspected to be present on Mars, as well as the implications of these minerals for water on Mars, are summarized in this chapter.

Visible/near-infrared (VNIR) spectroscopy is particularly powerful for remote identification of hydrated minerals and is one of the techniques employed for characterization of these minerals on Mars. VNIR spectrometers on upcoming missions to Mars will be searching for evidence of hydrated minerals. Mid-IR and Mössbauer spectrometers on current and upcoming Martian missions are also providing information on the surface mineralogy of Mars. Future landed missions are expected to include a wider variety of instruments for *in situ* mineralogy and compositional analyses. The spectral and other properties of a number of hydrated minerals thought to be present on Mars and how these will be used to identify and characterize minerals on Mars are described in this chapter.

4.1 Hydrated Minerals

Minerals are combinations of atoms that form in a specific structure and have common properties such as color, texture, and hardness [e.g. 1]. Minerals are sometimes found in pure outcrops, but more frequently occur in rocks as combinations of minerals, where the grains of many minerals neighbor each other and may be intergrown. Hydrated minerals are usually thought to include water or hydroxyl (OH) in their mineral structures and several examples are listen in Table 4.1. However, they can also include those that readily adsorb water on their grain surfaces because of surface charges. Other anhydrous minerals are discussed in this chapter that use water during formation and can thus be an indicator of aqueous processes on Mars.

The hydrated state of minerals depends on both the character of the mineral and the moisture environment. The atmospheric water inventory on Mars is discussed in detail in Chap. 2 by Lammer et al. The surface water inventory on Mars includes water ice that is discussed in Chap. 5 by Mitrofanov, as well as bound water, adsorbed water and structural OH in minerals that are discussed in this chapter.

Mineral	Formula	Reference
goethite	α-FeOOH	[2]
lepidocrocite	γ-FeOOH	[2]
akaganéite	β-FeOOH	[2]
feroxyhyte	δ-FeOOH	[2]
ferrihydrite	$Fe_{5}HO_{8} \bullet H_{2}O$ or $Fe_{1.55}O_{1.66}(OH)_{1.33}$	[3, 4]
gibbsite	Al(OH) ₃	[5]
brucite	$Mg(OH)_2$	[5]
kaolinite	$Al_2Si_2O_5(OH)_4$	[5]
serpentine	$Mg_3Si_2O_5(OH)_4$	[5]
smectite (Na,Ca)(A	$1,Fe^{3+},Fe^{2+},Mg)_{2-3}(Si_{4-x}Al_x)O_{10}(OH)_2 \bullet nH_2O$	[5]
zeolite	$(Na_2, K_2, Ca, Ba) \{ (Al, Si)O_2 \} x \bullet nH_2O$	[5]
opal	SiO ₂ •2H ₂ O	[5]
imogolite	$SiO_2Al_2O_3•2H_2O$	[6]
allophane	$SiO_2(Al_2O_3)_* nH_2O, n>2, x>1$	[6]
alunite	$(Na,K)Al_3(OH)_6(SO_4)_2$	[7]
jarosite	$(Na,K)Fe_3(OH)_6(SO_4)_2$	[7]
gypsum	$CaSO_4(H_2O)_2$	[7]
kieserite	$CaSO_4H_2O$	[7]
schwertmannite	$\operatorname{Fe}_{16}O_{16}(OH)_{y}(SO_{4})_{z} \bullet nH_{2}O$	[2]
alunogen	${Al(H_2O)_6}_2(SO_4)_3(H_2O)_{44}$	[7]
monohydrocalcite	CaCO ₃ •H ₂ O	[8]
artinite	$Mg_2CO_3(OH)_2 \bullet 3H_2O$	[8]
hydromagnesite	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$	[8]
niter	KNO ₃ •H ₂ O	[1]
nitratine	NaNO ₃ •H ₂ O	[1]
apatite	$Ca_5(PO_4)_3(OH,F,Cl)$	[5]

Table 4.1 The chemical formulas of selected hydrated minerals

Bound water includes H_2O molecules that are part of the actual mineral structure and also H_2O molecules that are chemisorbed onto mineral surfaces. H_2O is a necessary part of the mineral structure for some ferric oxide-bearing minerals, such as ferrihydrite and schwertmannite [2] and for some phyllosilicates, such as smectites [9]. Bound or chemisorbed water means a chemical bond is holding the H_2O molecule in place on the mineral surface and requires a charged surface [e.g. 10]. Bound water typically cannot be removed from a mineral without changing

its structure which can be irreversible. Adsorbed water is merely physisorbed on the surface and can be readily attached and detached as the moisture environment changes. Bound water, adsorbed water, and OH can be detected remotely via specific spectral features. A number of these are listen in Table 4.2.

	wavenumber (cm^{-1})	wavelength (µm)	vibrations
OH bands:	7240-7170	1.38-1.39	2v Mg ₂ OH
	7160-7060	1.40-1.41	2ν Al ₂ OH
	4620-4520	2.16-2.21	$v + \delta Al_{2OH}$
	4380	2.28	$v + \delta Fe_2OH$
	4330-4270	2.31-2.34	$v + \delta Mg_2OH$
	3690-3630	2.71-2.75	V Al ₂ OH
	3585-3570	2.79-2.80	v Fe ₂ OH
	3695-3645	2.70-2.74	v Mg ₂ OH
	955-930	10.5-10.8	δMg_2OH
	940-915	10.6-10.9	δ _{Al₂OH}
	845	11.8	δ _{Fe₂OH}
	820	12.2	δ _{Fe₂OH}
	795	12.6	δ _{Mg₂OH}
	705	14.2	δMg_2OH
water bands:	7000-7100	~1.41	$v + 2\delta H_2Ob$
	6800-6850	1.46	$v + 2\delta H_2Oads$
	5230-5250	1.91	$v + \delta H_{,Ob}$
	~5100	~1.97	$v + \delta H_2Oads$
	3600-3520	2.76-2.84	۷ H,Ob
	3350-3450	2.90-2.99	V H ₂ Oads
	~3230	~3.10	$2\delta_{H_2O}$
	~1650	~6.0	δ_{H_2Oads}
	1617-1630	6.1-6.2	δH_{2Ob}

 Table 4.2 Band assignments for water and structural OH in reflectance/emittance spectra of minerals

OH and H_2O vibrations are labeled with v (stretching) and δ (bending). The subscripts OH, H_2Ob and H_2Oads refer to structural OH, bound (inner sphere) H_2O and adsorbed H_2O , respectively. Selected examples of the octahedral cations are listed, as they greatly influence the OH vibrations.

Hydrated minerals such as smectites and zeolites are common components of terrestrial volcanic alteration products [11, 12] and would be at least partially

hydrated on the surface of Mars [13]. Many nanophase minerals thought to be present on Mars (e.g. poorly crystalline phyllosilicates, opal, some ferric oxidebearing minerals) are hydrated because of their large surface areas and are more difficult to detect in mixtures (and they would be expected to be present in mixtures on the surface of Mars) because the features characteristic of nanophase minerals are typically less distinct in all kinds of measurements. Smectites in ambient lab environments contain ~5-20 wt. % OH/H₂O that is lost on heating to 850°C [14]. The structural OH and chemically bound water together represent ~4 wt. % for smectites, which is what would be expected for smectites on Mars. The variance in water abundance is largely due to adsorbed water which depends on the water vapor pressure at the time of the measurement and the type of interlayer cation; this is discussed in more detail under the properties of smectites. The amount of water present in zeolites is also highly dependent on the moisture environment and the kind of extra-framework cations [15], and zeolites on Mars would be expected to have a few weight percent water [13]. Ferrihydrite contains ~10-20 wt. % OH/H₂O that is lost on heating to 850°C. Typically 2-line ferrihydrite (named for its two broad X-ray diffraction lines) contains more water than 6-line ferrihydrite. Although the structure is not yet well characterized for this mineral, it appears to exist in a variety of hydration states [4, 2]. Ferrihydrite on Mars would probably have at least a couple wt. % OH or H₂O. The water content of precious opal is 6-10 wt. % [5]; however it is unknown how much water could be bound or adsorbed on opal or amorphous silica on Mars. A few carbonate and sulfate minerals contain water in their structures, and many "anhydrous" carbonates, sulfates and nitrates also contain abundant adsorbed water.

4.2 Water Content of the Martian Surface Material

Information about the water content on Mars is available from the Viking experiments, spectral measurements, and H abundance. Combining data from multiple sources and multiple locations provides the most complete estimate of water content on Mars; however, at this time, these are still only estimates. Part of the uncertainty lies in that the water and OH determinations depend on which minerals are present and this is not yet well constrained. Water determined from the Viking experiments and spectral observations are described here, while the H detected by the Gamma-Ray Spectrometer (GRS) on board Mars Odyssey attributed to water ice, plus water and OH in minerals is described in detail in Chap. 5. Briefly, Mitrofanov, Feldman, Boynton and co-workers have identified a layer of OH/H₂O-rich material buried beneath the OH/H₂O-poor surface material on Mars and global measurements show some spatial variations in the density of these surface ice, water and/or OH components [16–18].

A gas chromatograph mass spectrometer (GC-MS) instrument was present on the Viking landers (VL) and measured weight loss as the samples were heated [19]. Although these GC-MS instruments were not designed to measure water on Mars, experiments performed on VL-2 indicate that less than 2 wt. % water was lost from the surface soil when heated to 500°C [19]. This was interpreted as a minimum value because of uncertainties in the procedure that may have lost water before and/or during the experiment. H_2O removed from the Martian soil up to 500°C could include both adsorbed water on mineral or grain surfaces and bound water in minerals, but not structural OH in minerals.

Early spectral analyses identified the presence of water on Mars through a strong absorption near 3 µm [e.g. 20, 21]. Houck et al. [20] analyzed Kuiper Airborne Observatory spectra of Mars in comparison with laboratory spectra of minerals and determined that the 3 µm band observed in the Martian spectra is similar to water features present for most minerals and estimated the water content at 1-2 % on the surface of Mars. Pimentel et al. [21] noted latitudinal variations in the 3 µm band in data from the Infrared Spectrometer (IRS) on Mariner 6 and 7 and suggested that this band may be due to water ice or surface frost as well as water in minerals. Near-infrared spectra measured by the Imaging Spectrometer for Mars (ISM) on Phobos 2 showed confirmation of the strong 3 µm band at higher spatial resolution (~20 km) in several equatorial regions that was attributed to water in surface minerals and not to water ice or frost [22-24]. The water content in the upper Martian surface soil was estimated at 0.5 to 4 wt. % from laboratory experiments and comparison with ISM spectra [25]. This value is comparable to earlier estimates [20] and to the GC-MS data measured by Viking [19]. Regional differences in the depth of the 3 µm band, and hence the water content, on Mars have been observed in telescopic spectra [26] and in Mariner 6 IRS data [27]. More recent analyses of the ISM data suggest differences in the water content that Murchie et al. [28] attribute to variations in ferric minerals or sulfates. They found that about 20 % of the surface measured by ISM exhibited deeper than normal 3 µm bands. Noe Dobrea et al. [29] analyzed Hubble Space Telescope (HST) spectra and found evidence for three distinct (non-icy) surface compositions that contain hydrated minerals, although specific hydration minerals could not be identified.

4.3 Detection of Hydrated Minerals on Mars

Information about hydrated minerals on Mars is available from remote and *in situ* analyses of Mars, as well as studies of the meteorites that came from Mars.

4.3.1 Hydrated Minerals Identified on Mars

The composition of Mars has been inferred from early spectroscopic [30, 31], chemical [32–34] and magnetic [35] data. These and other analyses of early Martian data formed the opinion that the surface material is a basaltic regolith with ferric oxides/oxyhydroxides, silicates including perhaps clay minerals, and sulfates. Spectral data have been used to identify red hematite [36] and grey

hematite [37] on Mars. Summaries of the Martian surface mineralogy include potential hydration minerals that could be present [38–40].

More recent data from the Mars Pathfinder [41–44], Mars Global Surveyor [45–48] and Mars Odyssey [17, 18, 49] missions are consistent with a history of aqueous processes on Mars. The results of this moisture are contained in the mineralogical record, so that when we can better constrain the surface mineralogy on Mars we will better understand the aqueous conditions in past and current environments. Analyses of mixing and alteration of potential surface components provide estimates of potential minerals that might be present [50–54]. Hydration minerals suggested in these studies as components of the Martian surface include ferric hydroxides/oxyhydroxides, smectites and sulfates. Amorphous silica is also a basaltic alteration product that may be present on Mars [55] and this silica could be hydrated. Zeolites have also been suggested recently by Bish et al. [13] and Ruff [56] as a hydration mineral present on the surface of Mars.

Phosphates have been detected at 0.6–1.2 wt. $\% P_2O_5$ in the soils and 0.5–0.7 wt. $\% P_2O_5$ in the rocks, although the mineral form of this P is not known. Apatite is present in several Martian meteorites [57] and could be the form of this P on the Martian surface as well. Nitrogen is an essential element for life and is one of the few biogenic elements that is still uncharacterized in the Martian surface material. The current Martian atmosphere includes a pressure of ~0.2 mbar due to N₂, much less than the 3 to 300 mbar N₂ thought to be present in the early Martian atmosphere [58]. The possibility of N as ammonia in the soil on Mars is discussed by Bishop et al. [59]. Nitrates are a mineral type that form similar to carbonates and could be present on Mars if N was sequestered in the regolith.

Analyses of the Pathfinder Alpha Proton X-Ray Spectrometer (APXS) data [44] indicate that excess oxygen is present in the rocks that is best explained by OH or water bound in minerals and/or glass in the rocks (or coatings on the rocks), rather than water frost. Their arguments are based on the measurement of temperatures and the absence of effects due to frost. One of the interesting results of the Foley et al. [44] study is that excess oxygen, and thus water, is detected in greater abundance in the rocks than in the soils. A reason for this might be that the small particle size of the soil grains facilitates dehydration of these particles in the Martian environment. The H₂O abundance estimates depend on the oxidation state of the iron and the sulfur and maximum water values are derived for 100 % Fe^{2+} (e.g. FeO) and S^{2-} (e.g. FeS). Water estimates for Martian rocks and soils are given in Table 4.3. If water is present in the rocks, then the reduced or intermediate case is probably correct, whereas if water is present in coatings on the rocks, then the oxidized case might be correct. For the Pathfinder soils and the indurated soil, water abundances are only shown for the intermediate and oxidized cases, as it is unlikely to find sulfides in soils on Mars. Of course, it is possible that rocks and soils might contain a mixture of both FeO and Fe₂O₃.

A large deposit of coarse-grained (gray) hematite was discovered in the Sinus Meridiani region through analysis of TES data [37]. A global search identified additional small outcrops of gray hematite in the impact crater Aram Chaos and in parts of Valles Marineris [48]. Although hematite does not contain water or OH in

its structure, it is relevant to this study of hydrated minerals because it may have formed via aqueous processes [37]. Low-grade metamorphism has also been suggested to produce platy hematite grains in the Sinus Meridiani deposit [60]. Catling and Moore [61] argue that a hydrothermal environment is the best possible abiotic scenario to explain the formation of gray hematite in all three locations.

		Wt.% H ₂ O	Wt.% H ₂ O	Wt.% H ₂ O
		FeO, FeS	FeO, $(SO_4)^{2-}$	$Fe_2O_3, (SO_4)^{2-}$
		fully reduced	intermediate	oxidized
Rocks	A-3	2.0±1.3	0.3±1.3	0
	A-7	7.1±1.4	3.4±1.4	1.3±1.4
	A-16	4.2±1.3	1.5±1.5	0
	A-17	5.7±1.3	4.3±1.3	2.2±1.3
	A-18	2.7±1.3	0.1±1.3	0
Indurated soil	A-8	n.d.	2.9±1.6	1.0±1.6
Soils	A-2	n.d.	1.6 ± 1.7	0
	A-4	n.d.	1.2 ± 1.7	0
	A-5	n.d.	0	0
	A-10	n.d.	2.5±1.7	0.3±1.7
	A-15	n.d.	1.0 ± 1.6	0

Table 4.3 Water abundance in Martian rocks from Pathfinder APXS data [44]

The fully reduced case is based on the assumption that ferrous iron and sulfide (e.g. FeO and FeS) are present, the intermediate case assumes that ferrous iron and sulfate are present and the fully oxidized case assumes that ferric iron and sulfate are present. The notation "n.d." refers to not determined.

Analyses of Martian spectral images have been performed in order to search for evidence of hydration minerals, however, this is difficult because the broad 3 µm band discussed earlier is not discriminatory for minerals and other hydration bands are much weaker. Some hydrated minerals exhibit overtones and combinations of the H₂O and cation-OH vibrations in the VNIR. The H₂O overtone near 1.4 µm and the H₂O combination band near 1.9 µm are difficult to detect in remote spectra of Mars because atmospheric CO₂ and H₂O overlap these bands. The cation-OH combination bands occur in the region 2.1 to 2.4 µm depending on the cation and the mineral structure, and should be detectable if present in Martian spectra. Such cation-OH bands are found in minerals such as phyllosilicates, hydroxides, and some sulfates. Identification of bands in this region in Martian spectra is not yet uniquely agreed upon, however, studies by Bell and Crisp [26], Beinroth and Arnold [62], and Murchie et al. [24, 28] have applied different calibration techniques to identify weak bands near 2.2-2.3 µm that are characteristic of these cation-OH bands. Also in this region are carbonate bands near 2.35 and 2.55 µm [63] that have not yet been uniquely identified in Martian spectra [64]. However, weak bands in this spectral region may indicate the presence of carbonate and/or sulfate minerals on Mars [65]. Carbonates also exhibit bands in the mid-IR region near 6.6, 11.3, and 14 μ m [8, 66, 67] that have also been difficult to detect in Martian surface spectra. However, a band near 7 μ m in atmospheric dust is thought to be evidence of a small amount of carbonate in these < 3 μ m sized dust particles [68, 69]. Sulfates exhibit bands near 1.7–1.8, 4.4–5, 8–10, and 15–20 μ m [70–73]. Although sulfates are thought to be present in the Martian surface material from the chemistry, identification of specific sulfate minerals in the spectra has been difficult. VNIR spectra of iron hydroxides and oxyhydroxides contain Fe excitation bands [74], in addition to the H₂O and OH bands described above, and in some cases these minerals can be identified by their Fe excitation bands alone. Analyses of VNIR spectra support the presence of fine-grained hematite in some regions, and ferric hydroxides/oxyhydroxides such as goethite or ferrihydrite in other regions [36, 75, 28].

Past searches for hydrated minerals on Mars have been limited by either spectral or spatial resolution, or both. If a large spatial footprint is included in one pixel then it is more difficult to detect the minor components. If the number of spectral data points is low, it is difficult to resolve individual spectral features. Both the spectral and spatial resolution will be improved in upcoming missions to Mars, as described in Section 4.7, and thus, our chances of detecting hydration minerals on Mars, if they are present, will improve in the near future.

4.3.2 Hydrated Minerals Identified in Martian Meteorites

Water in Martian meteorites is discussed in Chap. 1 by Baker et al. Included here is a brief summary of the hydration minerals identified in Martian meteorites because these rocks are a good source of mineralogical information about Mars [76, 77]. A recent summary of the geologic history of Martian meteorites is given by Nyquist et al. [78]. Hydration minerals such as carbonates, sulfates, phyllosilicates, and iron oxides/oxyhydroxides have been identified in a few Martian meteorites [79–82]. This is complicated by the possibility of terrestrial contamination.

Small quantities of organic material in the vicinity of carbonates and iron oxides were identified in Martian meteorite ALH 84001 by McKay et al. [82] and have sparked vivid discussion and disagreement over what is and what is not a biogenic mineral. Mg- and Fe-rich carbonates and magnetite were found in this meteorite at the time it was recognized as a Martian meteorite [83] and have been under continued study by many researchers in order to determine what link if any might exist between these minerals and living organisms. There is continued debate about the origin of both the carbonate and the magnetite in this rock and, in particular, whether these minerals were formed under low-temperature aqueous conditions and if they might be associated with microorganisms [e.g. 84–87]. Reflectance spectra of both meteorite chip surfaces [88] and a ground sample [89] include readily identifiable carbonate bands for these Martian samples containing small amounts of carbonate, although carbonates have yet to be detected in spectra of the surface of Mars.

4.4 Properties of Hydrated Minerals That May Be Present on Mars

The hydration properties of minerals play an important role in how water cycles between the surface and atmosphere on Mars as described in Chap. 8 by Tokano. This includes the ability of minerals to adsorb (attract and physically attach) water molecules and how fast they can take up this water. Besides adsorbed water, some minerals need bound (chemically attached) H_2O as part of their structure. Other minerals require OH that is usually bound in an octahedral configuration. Most minerals that contain structural OH and H_2O need aqueous conditions to form, but do not necessarily need water in their environment after formation. It is the ability of certain minerals to adsorb and desorb water that is important for understanding the hydrologic cycles on Mars. Thus, hydrated minerals on Mars provide information about the presence of water at the time of formation and about water in the current environment.

XRD (X-ray diffraction) is frequently used in the lab for mineral identification [e.g. 9, 1] and is arguably one of the most accurate techniques for identifying minerals in mixtures. However, XRD presents some challenges for remote investigations and has not yet been sent to Mars on a landed mission. Thermal analysis techniques are most useful for minerals with discrete thermal transitions and a variety of techniques are available in the lab for mineralogy studies [e.g. 90]. These include differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and thermal evolved gas analysis (TEGA) and all measure changes in a physical parameter with temperature. As described in Section 4.7, TEGA is planned for a future mission to Mars. VNIR spectroscopy is best for characterizing metal excitational transitions and water, and is also a good technique for identification of structural OH, CO₄, NO₃, SO₄, PO₄, or CH bonds [e.g. 71]. Mid-IR spectroscopy is most useful in characterizing Si-O and metal-O bonds and also has the advantage that information about sample texture (e.g. particle size) can be determined [e.g. 91]. Mid-IR spectroscopy is also sensitive to structural OH, CO₂, etc. bonds when abundant. Raman spectroscopy is most effective for detecting polarized species such as CO₃, OH and CH, and exhibits sharp bands for most highly crystalline minerals when they are abundant in mixtures [e.g. 92]. Mössbauer spectroscopy provides information about the electronic environment of the iron atom. This includes the oxidation state (e.g. Fe^{2+} , Fe^{3+} , etc.) and the bonding configuration. For geologic samples this is usually Fe-O bonds in either tetrahedral or octahedral coordination and is influenced by other cations bonded to the O. Mössbauer spectroscopy for geologic materials has been summarized recently by Murad and Cashion [93].

The emphasis in this section will be on the VNIR and mid-IR spectral properties of hydrated minerals because these techniques can be performed globally from orbit on Mars. Reflectance spectra are shown for several mineral groups in the following sections. The VNIR spectra span the range of upcoming VNIR instruments to Mars and the mid-IR spectra are shown as inverse reflectance for comparison with emittance spectra measured for Mars. VNIR spectra are commonly measured in wavelength units in remote sensing and emittance spectra in wavenumbers. This convention has been applied here. Selected wavelength units have been added to the upper axes of the mid-IR plots.

4.4.1 Iron Hydroxides/Oxyhydroxides

Iron oxide, hydroxide and oxyhydroxide minerals are common on Earth and are an important component of the surface of Mars. The properties of this mineral group have been described in detail by Cornell and Schwertmann [2]. The VNIR spectral region is dominated by Fe excitational and charge transfer bands from 0.4 to 1 μ m, plus OH vibrations near 1.41, 2.3, and 2.7 μ m, and H₂O vibrations near 1.45, 1.95, and 3 μ m. The mid-IR spectral region contains vibrational bands due to Fe-O, OH and H₂O. Reflectance spectra of selected fine-grained iron oxide-bearing minerals are shown in Fig. 4.1. Hematite (α -Fe₂O₃), maghemite (γ -Fe₂O₃), and magnetite (Fe₃O₄) are included as well because they may be associated with aqueous processes, although they do not contain structural OH or H₂O. The spectral properties of hematite are highly sensitive to grain size and orientation [94, 60]; the coarse-grained hematite identified in the Sinus Meridiani region on Mars is much darker in the VNIR region and exhibits stronger features at longer wavelengths, than the fine-grained hematite spectrum shown here.

Many iron oxide-bearing minerals exhibit characteristic extended visible region spectra that can be used for identification of these minerals [e.g. 95, 96], although this becomes more difficult for mixtures of iron oxide-bearing minerals [97]. Many of the iron oxide-bearing species on Mars are thought to be fine-grained and even nanocrystalline. The spectral properties of nanophase hematite [94], ferrihydrite [98], and schwertmannite [99] have been studied as potential iron oxide phases on Mars. Nanophase iron oxides tend to have broader and weaker spectral features, thus increasing the challenge of uniquely identifying these minerals in mixtures. Temperature also has an effect on at least the Fe excitational bands in spectra of iron oxide-bearing minerals [100].

The presence of Al or Ti is frequently observed in many iron oxide-bearing minerals and can alter the structure and properties, while the presence of Si retards the alteration of hydrated ferric oxides to hematite [2]. Si is frequently present in natural ferrihydrites and appears to be influencing the spectral features [98]. Phosphorous also influences the formation and structure of iron oxide-bearing minerals and slows the alteration of hydrated ferric oxides to hematite [101, 102]. Torrent and Barrón [103] found that lepidocrocite forms preferentially to goethite in the presence of P and they suggest that this P-lepidocrocite would produce maghemite that is more stable under Martian conditions and has magnetic properties consistent with those observed by Pathfinder. Si, Al, Ti and P are all present in the Martian rocks and soils [44] and may be contributing to the properties of the iron oxide-bearing minerals on Mars.

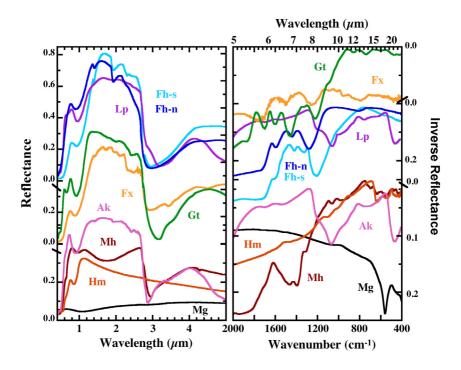


Fig. 4.1 Reflectance spectra of selected fine-grained iron oxides/ hydroxides/oxyhydroxides: magnetite (Mg), hematite (Hm), maghemite (Mh), akaganéite (Ak), goethite (Gt), feroxyhyte (Fx), lepidocrocite (Lp), natural ferrihydrite (Fh-n) and synthetic ferrihydrite (Fh-s).

4.4.2 Carbonates

Carbonates form in a variety of anhydrous and hydrated forms. Even anhydrous carbonates provide information about aqueous processes on Mars because they can form under aqueous conditions [e.g. 5]. The spectral properties of anhydrous carbonates have been studied by Gaffey [104] and Lane and Christensen [67]. The spectral properties of hydrous carbonates have been studied by Calvin et al. [66]. Spectra of calcite (CaCO₃) and siderite (FeCO₃) are shown in Fig. 4.2. In addition to the CO₃ bands observed near 2.30–2.34, 2.50–2.55, 3.5, 4.0, and 4.7 µm in the NIR region and near 1550, 880 and 730 cm⁻¹ in the mid-IR region [8, 104, 66, 67], siderite contains Fe excitational bands. The siderite spectrum shown here also contains bands due to water near 2, 3 and 6 µm that indicate that this sample has become hydrated. Some examples of hydrated carbonate minerals are listed in Table 4.1. Grain size plays an important role in the mid-IR spectral character of

carbonates because of their unique index of refraction. Depending on the grain size, the spectral features will occur either as peaks or as troughs [105].

Much debate has occurred about the carbonates associated with Martian meteorites. Isotopic measurements on Fe-Mg carbonates in ALH 84001 [106, 107] and theories involving precipitation of carbonates [108, 109] suggest a low-temperature origin [106, 107], while grain morphology and fluid reactions suggest high-temperature origins [83, 110, 111]. Despite the evidence for carbonates in Martian meteorites, carbonates on Mars remain elusive.

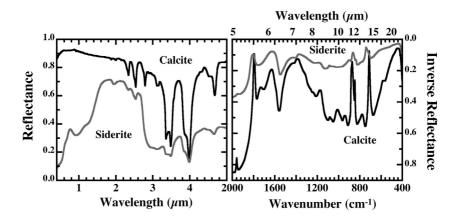


Fig. 4.2 Reflectance spectra of two carbonates. The calcite is $a < 63 \mu m$ separate from [67]. The siderite sample is $a < 125 \mu m$ powder of a sample acquired from Wards.

4.4.3 Sulfates

Sulfate minerals exhibit bands due to SO_4 in the NIR region near 1.7–1.85, 4.4–5, and in the mid-IR region near 1160, 680, 600, and 490 cm⁻¹ [70–73]. Many also contain OH bands near 2.3 µm and water bands near 1.45, 1.95, 3 and 6 µm. As seen in Table 4.1, jarosite and alunite contain OH in their structures, while gypsum and schwertmannite contain H₂O. Reflectance spectra of several sulfates are shown in Fig. 4.3. The VNIR sulfate bands near 1.7–1.85 and 4.5–4.9 µm fall where few other minerals exhibit spectra features, and thus may be useful in upcoming missions for detection of sulfates on Mars.

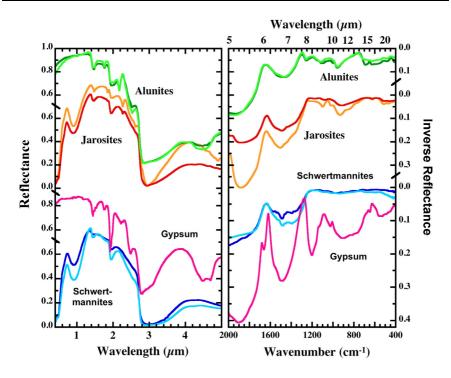


Fig. 4.3 Reflectance spectra of selected sulfates. The alunites and jarosites were prepared for a study by Kodama [112]. The gypsum is a $< 63 \mu m$ separate from [73]. The schwertmannite spectra are from [99].

4.4.4 Phyllosilicates

Phyllosilicates or layer silicates, or more commonly clay minerals, include micas, talc, chlorites, smectites, the kaolin-serpentine group, the chain-structure group (e.g. prehnite, sepiolite, attapulgite), and vermiculites [9, 5]. Smecites, kaolin-serpentines, and chain-structure clays (although they are more rare) are alteration products of volcanic material on Earth and have therefore been thought to be present in the surface dust and soils on Mars [e.g. 12, 5].

Reflectance spectra of selected clay minerals are shown in Fig. 4.4. These spectra include bands due to OH near 1.4, 2.2–2.3, 2.7, and 12 μ m, due to water near 1.45, 1.95, 3, and 6 μ m, due to SiO₄ near 1000–1100 cm⁻¹(9–10 μ m) and 450–550 cm⁻¹ (18–22 μ m). The nontronites and serpentines also exhibit Fe electronic transitions from 0.6 to 1 μ m.

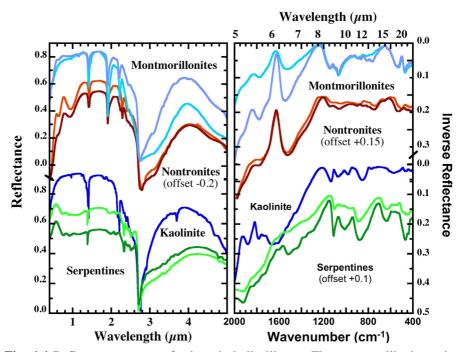


Fig. 4.4 Reflectance spectra of selected phyllosilicates. The montmorillonite and nontronite spectra are from [113] and the kaolinite and serpentine spectra are from [114].

A number of smectites has been collected and characterized by the Clay Minerals Society Source Clays Repository and are available in bulk for study; these include montmorillonites SWy and SAz from Wyoming and Arizona, respectively [14]. Terrestrial smectites are most commonly found with Na and/or Ca interlayer cations [e.g. 14], however, Mg and Fe are also observed and could be present as interlayer cations in smectites on Mars. The polarizing power of these cations increases from Na to Ca to Mg to Fe³⁺ and should be related to how strongly they attract water [10]. A study of the adsorption kinetics for water on Na-smectite indicated that this is too slow to act as a significant diurnal water reservoir on Mars [115]. However, Na-smectite is one of the least hygroscopic forms of this mineral as shown by IR spectra [10], calculations of partial molar enthalpy [116], and calculations of the chemical potential of H₂O in smectite [13]. The effect of the interlayer cation on hydration of smectites is illustrated in Figs. 4.5 and 4.6.

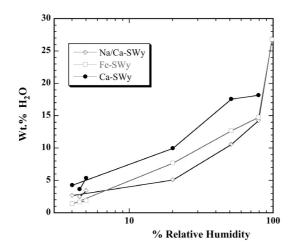


Fig. 4.5 Water content vs relative humidity for montmorillonites with different interlayer cations.

Water abundance in SWy-1 montmorillonite with Na, Ca and Fe³⁺ interlayer cations was determined at several relative humidity (RH) levels by measuring weight loss after heating. Data were averaged for four replicates for the full RH range and six replicates for the low RH range and are shown in Fig. 4.5. The amount of water present, as determined by H₂O lost on heating to 105 and 350°C, increased from Na to Fe³⁺ to Ca. The results of a TGA study with these samples, plus Mg-SWy, are displayed in Fig. 4.6 and show increasing water contents for the trend Na, Fe³⁺, Ca, or Mg interlayer cation [10]. The amount of water present as measured by spectral band strength [10], weight loss on heating (Fig. 4.5) and TGA (Fig. 4.6) all follow the polarizing power trends for Na, Ca, and Mg, but not for Fe³⁺. This implies that Fe³⁺ binds differently than typical interlayer cations in smectites, perhaps because iron is more reactive than the other cations.

Chipera et al. [117] performed XRD measurements on SAz montmorillonite as a function of RH. They found variations in the d-spacing, and hence water content, depending on the interlayer cation. The amount of adsorbed water for a given RH increased from K to Na to Ca. The polarizing power of K is less than that of Na, so this compares well with the trends shown in Figs. 4.5 and 4.6.

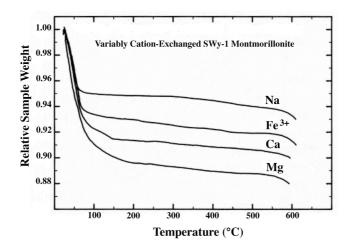


Fig. 4.6 TGA of montmorillonites with different interlayer cations (modified from Bishop et al. [10]).

4.4.5 Other Hydrated Minerals

Other hydrated minerals that could be present on Mars include zeolites, opal, phosphates, and nitrates. Spectra of two apatites, a nitrate and two zeolites are shown in Fig. 4.7. Zeolite spectra contain bands due to bound and adsorbed H_2O that are influenced by the extra-framework cations as well as bands due to SiO_4 and AlO₄ groups near 1000, 800, and 500 cm⁻¹ that vary depending on the zeolite structure and cations present [118]. Opal and amorphous silica are frequently hydrated and exhibit OH and H₂O bands as well. The phosphate mineral apatite contains OH bands when in the hydroxyapatite form, but not F/Cl-apatite. NIR bands are primarily due to OH and H₂O, but the 4.1 µm band is due to phosphate. Bands due to PO₁ include a doublet near 1100 and another band near 600 cm⁻¹, as well as transparency features near 800 cm⁻¹ for fine-grained samples [119, 73]. The nitrate minerals niter (KNO₃) and nitratine (NaNO₃) follow the aragonite and calcite structures, respectively, and hence exhibit related spectral features [119]. The nitrate spectrum shown here is for nitratine and exhibits NO₂ bands near 2.4, 2.6, 3.6, 4.1, and 4.8 μ m in the NIR region as well as NO₃ bands near 1790, 1550, 835, and 724 cm^{-1} in the mid-IR region.

A review of the properties of water in several zeolites including chabazite and clinoptilolite [15], coupled with recent calculations of water on clinoptilolite by Bish et al. [13], indicate that if zeolites are present on the surface of Mars they will be partially hydrated. This has implications for the surface-atmosphere water cycling as discussed in Chap. 8.

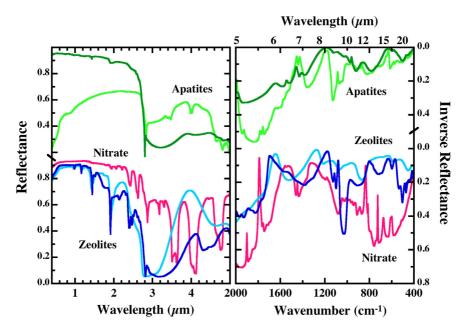


Fig. 4.7 Reflectance spectra of selected apatites, zeolites and a nitrate. The dark green spectrum is of a white hydroxyapatite powder, the light green spectrum is the $< 90 \ \mu\text{m}$ reddish-brown apatite from [73], the sodium nitrate sample is from a museum in Chile (contributed by C.P. McKay), and the zeolites are from Wards.

4.5 Hydrated Minerals Identified in Terrestrial Analogs of Martian Surface Materials

Several terrestrial sites are studied as potential analogs for the surface of Mars in order to learn which minerals are probable there, and how to detect these minerals in the rocks and soil mixtures likely to be found. These include altered volcanic material, especially from dry environments, cold desert environments, and impact craters and are described in this section. Lab experiments have also been performed in order to constrain the composition of rocks and soil on Mars and assist in identifying hydration minerals present there [e.g. 120, 53, 121].

4.5.1 Altered Volcanic Material

The surface of Mars is thought to be largely covered by volcanic material and has likely been altered by a combination of chemical and physical processes. The specific kinds of alteration are unknown; however, a cold and dry environment is likely for much of the planet's history. Altered volcanic ash and tephra have been studied by a number of researchers in order to understand which minerals and phases form during alteration and how these are dependent on the environment. Samples from high elevations in the Hawaiian islands are good analogs for Mars because there is little precipitation or vegetation in these regions. Subglacial volcanic samples in Iceland also represent analogs for alteration in cold environments on Mars, such as in permafrost. Analysis of the minerals formed through volcanic alteration in more temperate and aqueous environments on Earth provide information on the minerals that could be present on Mars if liquid water existed long-term on the surface during earlier times.

Alteration of volcanic material can occur via a variety of mechanisms including palagonitization, pedogenic processes or solfataric processes. Rocks comprised of glassy fragments and alteration minerals were first recognized as palagonitized tuffs in Palagonia, Sicily, by von Waltershausen [122] and have been studied in detail since then [e.g. 11, 123]. Palagonitization is also used to define the altered glassy rinds that form on volcanic ash and tephra [24, 124–126]. Palagonitized tuffs typically form in subglacial or hydrothermal environments [e.g. 127, 128], while palagonitic rinds on ash/tephra typically occur under dehydrated conditions [e.g. 126]. Geochemical and mineralogical studies have been performed on palagonitized volcanic material from the tops of Mauna Kea [124, 129, 130] and Haleakala [125] in the Hawaiian islands, and from subglacial environments in Iceland [131, 132]. Palagonitic tuffs typically contain glass, smectite and hydrated ferric oxides, in contrast to palagonitic rinds that are dominated by glass and poorly crystalline Fe-, Al-, Si-bearing species.

Pedogenic alteration typically occurs under moderate aqueous conditions and is consistent with the formation of minerals such as goethite, ferrihydrite and kaolinite [133, 128, 134].

Solfataric alteration encompasses samples exposed to sulfuric fumes emanating from fumeroles, cinder cones or hydrothermal springs. Samples from these environments are characterized by the presence of sulfates, smectites, and crystalline ferric oxides/oxyhydroxides [135–137, 125, 52].

4.5.2 Cold Desert Environments

Cold, arid environments such as the McMurdo Dry Valleys in Antarctica and the Atacama desert in Chile and Peru provide analogs for alteration in the current environment on Mars. The Atacama desert is extremely arid and is one of the more difficult environments on Earth for life [138]. Many of the rocks here are andesitic, the soils frequently contain quartzite and clays, and nitrate fields are also present. Studies of the geochemistry and mineralogy of volcanic sediments from the Antarctic Dry Valleys found that these are dominated by primary silicate minerals (pyroxene, feldspar, and quartz), and contain small amounts of iron oxides/hydroxides, carbonates, clays, and zeolites [139–143]. Studies of the lake bottom sediments in these environments provide insights into the mineralogy that might be expected in paleolakes on Mars. Polar lakes are described in detail in

Chap. 9 by McKay et al. and potential paleolakes on Mars are described in Chap. 10 by Cabrol and Grin.

4.5.3 Impact Craters

Alteration caused by shock and melting when a meteorite impacts on the surface is another likely process on Mars. The importance of impact craters for water and microbial life is described in Chap. 11 by Cockell and Lim. Geochemical and mineralogical studies of samples from the Manicouagan crater found a combination of glass, hematite, pyroxene and phyllosilicates [144]. The Lonar Lake impact structure in India is another potential analog for impacts on Mars [145]. This study found basaltic impact breccias that were subsequently altered by hydrothermal processes. In addition to glass, these samples contain feldspar, pyroxene, ferric oxide/hydroxide, smectite, and carbonate. The Haughton impact crater on Devon island represents an impact in a colder environment as it is in the Arctic and carbonate rocks are abundant here [146, 147].

4.6 Interactions Between Minerals and Organisms

Minerals can play a role in supporting microbial life as well as preserving evidence of these microorganisms. In a study of minerals formed by organisms Lowenstam [148] ranks carbonates, opal, ferrihydrite and magnetite as the most prevalent biologically formed minerals. Because many organisms can utilize iron as an energy source and because iron oxides/oxyhydroxides frequently form under specific conditions, these minerals can provide important relationships to organisms, serving as a nutrient source, by-product and/or reaction template [e.g. 149, 150]. The study of "iron-bacteria" has a history over one hundred years old and includes numerous bacteria that together are active over a wide range of Eh and pH conditions [151]. One of the most well-known of these types of bacteria is Thiobacillus ferrooxidans, which has been given considerable attention because of its ability to leach metals from sulfide ores and restore acid mine waters. T. *ferrooxidans* is most active in the pH range 2–3.5 and can oxidize iron sulfide minerals either directly, or after aqueous Fe^{2+} is released via mineral dissolution [151]. Another iron-utilizing bacterium is Metallogenium, which is active in the pH range 3.5-4.5, requires Fe²⁺ for growth and contains "encrustations" of ferric iron species in its structure [151]. In neutral pH (~7-8) waters Gallionella ferruginea can oxidize Fe²⁺ to form ferrihydrite [152, 153]. The organism Aquaspirillum magnetotacticum synthesizes nanophase magnetite for directional motility purposes [154, 155]. Matrix-controlled mechanisms can regulate biotic iron oxide formation as well. Intracellular magnetite formed by Aquaspirillum magnetotacticum bacteria 2 billion years ago on the Earth is one example of this controlled mineralization process [155]. Minerals resulting from matrix-controlled processes are arguably distinguishable from abiotically-produced minerals through their crystallographic, morphologic and isotopic characteristics [148, 156].

The idea that clays may have played a role in the origin of life was first suggested by Bernal [157] who envisioned clays as a possible catalyst for life. More recently, Lawless [158] linked clays to the origin of life based on studies showing that nucleotides can be adsorbed from solution onto clay surfaces [159] and, further, that the interlayer cations greatly influence this process [160]. Clays are well-known as catalysts for chemical reactions involving oxidation/reduction, acid-base neutralization and hydrolysis [161-163] and, thus, many of the simple reactions necessary for chemical evolution may have been catalyzed and/or influenced by clays [164, 165]. Hartman et al. [166] proposed that formation of iron-rich clays and polar organics are coupled in carbonaceous chondrites, which can be envisioned as a model for processes that took place on planetary surfaces in the early Solar System. They further suggested that coupled formation of iron-rich clays and polar organics might have been one of the early processes leading to life on Earth. Whether biota on Mars, if present, could have either been catalyzed by constituents in the soil or themselves influenced soil formation are enticing questions that can only be addressed speculatively at this time [167].

As described in Chap. 3 by Westall, modern terrestrial environments exist that are thought to harbor microbial communities similar to those that existed on the early Earth and/or prebiotic organic species that may have been integral in the initial processes leading to the origin of life on Earth. Such environments that allow rapid entombment of microorganisms by relatively stable silicate, phosphate or carbonate minerals may provide a fossil record. Exopaleontology includes the search for fossils in these environments on Mars [168]. Some hydrothermal spring environments foster high rates of mineral precipitation and microbial activity and are thus rife with extant or fossilized microorganisms and would be a promising site on Mars to search for evidence of life on that planet [169, 168]. Evaporites offer an excellent environment for hypersaline bacteria and have been suggested as a potential target on Mars for evidence of life [170]. Evaporite deposits preserved by early replacement with silica or barite would be more likely to persist through time and might be present on Mars at terminal lake basins [168]. Aqueous mineral deposits on Mars containing minerals that are relatively stable and resistant to weathering and alteration processes are likely to contain either information about the prebiotic organic compounds preceding the origin of life or possibly fossils of early life forms [171].

4.7 Upcoming Missions That Will Contribute Towards Identifying Hydrated Minerals on Mars

Several current and upcoming missions have instruments that will provide information on the mineralogy of Mars. VNIR spectroscopy will be utilized by the Mars Express OMEGA instrument and the Mars Reconnaissance Orbiter CRISM instrument for global measurement of hydration minerals on Mars. OMEGA will

provide spectral data from 0.4 to 5.2 µm with a spot size of hundreds of meters [172]. CRISM will collect data from 0.4 to 4 µm for surface spots ranging from 20 to 200 meters [173]. The Thermal Emission Spectrometer (TES) on Mars Global Surveyor continues to measure spectral images that contribute to our understanding of the surface of Mars. TES data are collected from ~5 to 50 µm for regions 3 to 5 km in size on the surface [47]. The Mars Odyssey THEMIS instrument collects a few bands in the extended visible and mid-IR regions that provide some mineralogical information, especially when combined with hyperspectral data from other instruments [49]. The Mars Exploration Rovers (MERs) Spirit and Opportunity contain a number of instruments for characterization of minerals including a miniature Thermal Emission Spectrometer (Mini-TES), a Mössbauer spectrometer, and a multi-channel camera with 11 bands in the extended visible region [174]. The Beagle 2 Lander on Mars Express will study fresh and ground rock surfaces with a microscope and Mössbauer, XRD, and mass spectrometers [175]. A thermal evolved gas analyzer (TEGA) is a component of the recently selected Phoenix mission to Mars in 2007 [176] and will provide information about the mineralogy of soils in the polar region of Mars.

The Mars Science Lab (MSL) is planned for an upcoming mission to Mars and will support a number of mineralogy instruments, probably including some spectrometers such as VNIR, mid-IR, Raman, and Mössbauer, as well as instruments to measure X-ray diffraction (XRD) and thermal properties. Raman and XRD instruments have not yet flown to Mars, but have been proposed recently for landed missions and may be selected for an upcoming opportunity. These include a miniature XRF-XRD spectrometer [177, 178] and a miniature Raman spectrometer [179, 180].

4.8 Summary

The composition of the Martian surface is not yet well constrained and hydration minerals have not yet been uniquely identified, although there is much circumstantial evidence for their presence on Mars. As the instruments sent to Mars become more sophisticated, more information will become available about the variety and abundance of hydration minerals on Mars. These are likely to include iron hydroxides/oxyhydroxides, sulfates, and Si-bearing alteration minerals (e.g. clays, zeolites or opal), and may include carbonates, phosphates or nitrates. Characterizing the hydration minerals on Mars will provide knowledge about the extent and duration of aqueous processes, kinds of chemical alteration, and perhaps biological activity.

4.9 References

- 1 Zoltai T, Stout JH (1984) Mineralogy: Concepts and Principles. Burgess, Minneapolis
- 2 Cornell RM, Schwertmann U (1996) The Iron Oxides. VCH, New York

- 3 Chukhrov FV, Zvyagin BB, Ermilova LP, Gorshkov AI (1973) New data on iron oxides in the weathering zone. Proc. Int. Clay Conf. 333-341
- 4 Stanjek H, Weidler PG (1992) The effect of dry heating on the chemistry, surface area, and oxalate solubility of synthetic 2-line and 6-line ferrihydrites. Clay Miner. 27: 397-412
- 5 Deer WA, Howie RA, Zussman J (1992) An Introduction to the Rock-Forming Minerals. Longman, London
- 6 Newman ACD, Brown G (1987) The chemical constitution of clays. In Newman ACD (eds) Chemistry of Clays and Clay Minerals. John Wiley & Sons, New York, pp 1-128
- 7 Hawthorne FC, Krivovichev SV, Burns PC (2000) The crystal chemistry of sulfate minerals. In Alpers CN, Jambor JL, Nordstrom DK (eds) Sulfate Minerals: Crystallography, Geochemistry, and Environmental Significance. Rev. Mineral. Geochem., Vol 40, pp 1-112
- 8 White WB (1974) The carbonate minerals. In Farmer VC (ed) The Infrared Spectra of Minerals The Mineralogical Society, pp 227-284
- 9 Brindley GW, Brown G (1980) Crystal Structures of Clay Minerals and Their X-ray Identification. Mineral. Soc., London
- 10 Bishop JL, Pieters CM, Edwards JO (1994) Infrared spectroscopic analyses on the nature of water in montmorillonite. Clays Clay Miner. 42: 701-715
- 11 Staudigel H, Hart SR (1983) Alteration of basaltic glass: mechanisms and significance for the oceanic crust-seawater budget. Geochim. Cosmochim. Acta 47: 337-350
- 12 Nesbitt HW, Young GM (1984) Prediction of some weathering trends of plutonic and volcanic rocks based on thermodynamic and kinetic considerations. Geochim. Cosmochim. Acta 48: 1523-1534
- 13 Bish DL, Carey JW, Vaniman DT, Chipera SJ (2003) Stability of hydrous minerals on the Martian surface. Icarus 164: 96-103
- 14 van Olphen H, Fripiat JJ (1979) Data Handbook for Clay Materials and Other Non-Metallic Minerals (eds): Pergamon Press, Oxford
- 15 Bish D, Carey JW (2001) Thermal behavior of natural zeolites. In Bish DL, Ming DW (eds), Natural Zeolites: Occurrence, Properties, and Applications. Mineral. Soc. America Rev. Mineral. Geochem. Vol 45 Mineral. Soc. of America, pp 403-452
- 16 Boynton WV, Feldman WC, Squyres SW, Prettyman TH, Brückner J, Evans LG, Reedy RC, Starr R, Arnold JR, Drake DM, Englert PAJ, Metzger AM, Mitrofanov I, Trombka JI, d'Uston C, Wänke H, Gasnault O, Hamara DK, Janes DM, Marcialis RL, Maurice S, Mikheeva I, Taylor GJ, Tokar RL, Shinohara C (2002) Distribution of hydrogen in the near-surface of Mars: evidence for subsurface ice deposits. Science 297: 81-85
- 17 Feldman PD, Boynton WV, Tokar RL, Prettyman TH, Gasnault O, Squyres SW, Elphic RC, Lawrence DJ, Lawson SL, Maurice S, McKinney GW, Moore KR, Reedy RC (2002) Global distribution of neutrons from Mars: results from Mars Odyssey. Science 297: 75-78
- 18 Mitrofanov I, Anfimov D, Kozyrev A, Litvak M, Sanin A, Tret'yakov V, Krylov A, Shvetsov V, Boynton WV, Shinohara C, Hamara DK, Saunders RS (2002) Maps of subsurface hydrogen from the high-energy neutron detector, Mars Odyssey. Science 297: 78-81
- 19 Biemann K, Oró J, Toulmin III P, Orgel LE, Nier AO, Anderson DM, Simmonds D, Flory PG, Diaz AV, Rushneck DR, Biller JE, LaFleur AL (1977) The search for

organic substances and inorganic volatile compounds in the surface of Mars. J. Geophys. Res. 82(B28): 4641-4658

- 20 Houck JR, Pollack JB, Sagan C, Schaack D, Decker JA (1973) High altitude infrared spectroscopic evidence for bound water on Mars. Icarus 18: 470-480
- 21 Pimentel GC, Forney PB, Herr KC (1974) Evidence about hydrate and solid water in the Martian surface from the 1969 Mariner infrared spectrometer. J. Geophys. Res. 79: 1623-1634
- 22 Bibring J-P, Combes M, Langevin Y, Cara C, Drossart P, Encrenaz T, Erard S, Forni O, Gondet B, Ksanfomality L, Lellouch E, Masson P, Moroz V, Rocard F, Rosenqvist J, Sotin C, Soufflot A (1990) ISM observations of Mars and Phobos: first results. 20th Lunar Planet. Sci. Conf. 461-471
- 23 Erard S, Bibring J-P, Mustard J, Forni O, Head III JW, Hurtrez S, Langevin Y, Pieters CM, Rosenqvist J, Sotin C (1991) Spatial variations in composition of the Valles Marineris and Isidis Planitia regions of Mars derived from ISM data. 21st Lunar Planet. Sci. Conf. 437-455
- 24 Murchie S, Mustard J, Bishop J, Head J, Pieters C, Erard S (1993) Spatial variations in the spectral properties of bright regions on Mars. Icarus 105: 454-468
- 25 Yen AS, Murray BC, Rossman GR (1998) Water content of the Martian soil: laboratory simulations of reflectance spectra. J. Geophys. Res. 103(E5): 11125-11133
- 26 Bell JF III, Crisp D (1993) Groundbased imaging spectroscopy of Mars in the nearinfrared: preliminary results. Icarus 104: 2-19
- 27 Calvin WM (1997) Variation of the 3-μm absorption feature on Mars: observations over eastern Valles Marineris by the Mariner 6 infrared spectrometer. J. Geophys. Res. 102(E4): 9097-9107
- 28 Murchie S, Kirkland L, Erard S, Mustard J, Robinson M (2000) Near-infrared spectral variations of Martian surface materials from ISM imaging spectrometer data. Icarus 147: 444-471
- 29 Noe Dobrea EZ, Bell JF III, Wolff MJ, Gordon KD (2003) H₂O-and OH-bearing minerals in the Martian regolith: analysis of 1997 observations from HST/NICMOS. Icarus 166: 1-20
- 30 Adams JB, McCord TB (1969) Mars: interpretation of spectral reflectivity of light and dark regions. J. Geophys. Res. 74: 4851-4856
- 31 Hanel RA, Conrath BJ, Hovis WA, Kunde VG, Lowman PD, Maguire W, Pearl JC, Pirraglia J, Prabhakara C, Schlachman B (1972) Investigation of the Martian environment by infrared spectroscopy on Mariner 9. Icarus 17: 423-442
- 32 Binder AB, Arvidson RE, Guinness EA, Jones KL, Morris EC, Mutch TA, Pieri DC, Sagan C (1977) The geology of the Viking Lander 1 site. J. Geophys. Res. 82(B28): 4439-4451
- 33 Clark BC, Baird AK, Rose H Jr., Toulmin P III, Christian RP, Kelliher WC, Castro AJ, Rowe CD, Keil K, Huss G (1977) The Viking X ray fluorescence experiment: analytical methods and early results. J. Geophys. Res. 82(B28): 4577-4594
- 34 Clark BC, Van Hart DC (1981) The salts of Mars. Icarus 45: 370-378
- 35 Hargraves RB, Collinson DW, Arvidson RE, Spitzer CR (1977) The Viking magnetic properties experiment: primary mission results. J. Geophys. Res. 82(B28): 4547-4558
- 36 Bell JF III, McCord TB, Owensby PD (1990) Observational evidence of crystalline iron oxides on Mars. J. Geophys. Res. 95(B9): 14447-14461
- 37 Christensen PR, Bandfield JL, Clark RN, Edgett, KS, Hamilton VE, Hoefen T, Kieffer HH, Kuzmin RO, Lane MD, Malin MC, Morris RV, Pearl JC, Pearson R, Roush TL,

Ruff SW, Smith MD (2000) Detection of crystalline hematite mineralization on Mars by the Thermal Emission Spectrometer: evidence for near-surface water. J. Geophys. Res. 105(E4): 9623-9642

- 38 Soderblom LA (1992) The composition and mineralogy of the Martian surface from spectroscopic observations: 0.3-50 μm. In Kieffer HH, Jakosky BM, Snyder CW, Matthews MS (eds.) Mars. University of Arizona Press, pp 557-593
- 39 Roush TL, Blaney DL, Singer RB (1993) The surface composition of Mars as inferred from spectroscopic observations. In Pieters CM, Englert PAJ (eds) Remote Geochemical Analysis: Elemental and Mineralogical Composition. Cambridge University Press, Cambridge, pp 367-393
- 40 Bell JF III (1996) Iron, sulfate, carbonate, and hydrated minerals on Mars. In Dyar MD, McCammon C, Schaefer MW (eds.) Mineral Spectroscopy: A tribute to Roger G. Burns. The Geochemical Society, pp 359-380
- 41 McSween HY Jr., Murchie SL, Crisp JA, Bridges NT, Anderson RC, Bell III JF, Britt DT, Brückner J, Dreibus G, Economou T, Ghosh A, Golombek MP, Greenwood JP, Johnson JR, Moore HJ, Morris RV, Parker TJ, Rieder R, Singer R, Wänke H (1999) Chemical, multispectral, and textural constraints on the composition and origin of rocks at the Mars Pathfinder landing site. J. Geophys. Res. 104(E4): 8679-8715
- 43 Bell JF, III, McSween HY Jr., Murchie SL, Johnson JR, Reid R, Morris RV, Anderson RC, Bishop JL, Bridges NT, Britt DT, Crisp JA, Economou T, Ghosh A, Greenwood JP, Gunnlaugsson HP, Hargraves RM, Hviid S, Knudsen JM, Madsen MB, Moore HJ, Rieder R, Soderblom L (2000) Mineralogic and compositional properties of Martian soil and dust: results from Mars Pathfinder. J. Geophys. Res. 105(E1): 1721-1755
- 43 Brückner J, Dreibus G, Rieder R, Wänke H (2003) Refined data of Alpha Proton X-ray Spectrometer analyses of soils and rocks at the Mars Pathfinder site: implications for surface chemistry. J. Geophys. Res. 108(E12): 8094, 10.1029/2003JE00206.
- 44 Foley CN, Economou T, Clayton RN (2003) Final chemical results from the Mars Pathfinder alpha proton X-ray spectrometer. J. Geophys. Res. 108(E12): 8096, 10.1029/2002JE002019
- 45 Head JW III, Hiesinger H, Ivanov MA, Kreslavsky MA, Pratt S, Thomson BJ (1999) Possible ancient oceans on Mars: evidence from Mars Orbiter Laser Altimeter Data. Science 286: 2134-2137
- 46 Malin MC, Edgett KS (2000) Evidence for recent groundwater seepage and surface runoff on Mars. Science 288: 2330-2335
- 47 Christensen PR, Bandfield JL, Hamilton VE, Ruff SW, Kieffer HH, Titus TN, Malin MC, Morris RV, Lane MD, Clark RL, Jakosky BM, Mellon MT, Pearl JC, Conrath BJ, Smith MD, Clancy RT, Kuzmin RO, Roush T, Mehall GL, Gorelick N, Bender K, Murray K, Dason S, Greene E, Silverman S, Greenfield M (2001) Mars Global Surveyor Thermal Emission Spectrometer experiment: investigation description and surface science results. J. Geophys. Res. 106(E10): 23823–23871
- 48 Christensen PR, Morris RV, Lane MD, Bandfield JL, Malin MC (2001) Global mapping of Martian hematite mineral deposits: remnants of water-driven processes on early Mars. J. Geophys. Res. 106(E10): 23873-23885
- 49 Christensen PR, Bandfield JL, Bell III JF, Gorelick N, Hamilton VE, Ivanov A, Jakosky BM, Kieffer HH, Lane MD, Malin MC, McConnochie T, McEwen AS, McSween HY Jr., Mehall GL, Moersch JE, Nealson KH, Rice JW Jr., Richardson MI, Ruff SW, Smith MD, Titus TN, Wyatt MB (2003) Morphology and composition of the surface of Mars: Mars Odyssey THEMIS results. Science 300: 2056-2061

- 50 McLennan SM (2000) Chemical composition of Martian soil and rocks: complex mixing and sedimentary transport. Geophys. Res. Lett. 27: 1335-1338
- 51 McSween HY Jr., Keil K (2000) Mixing relationships in the Martian regolith and the composition of the globally homogeneous dust. Geochim. Cosmochim. Acta 64: 2155-2166
- 52 Morris RV, Golden DC, Bell III JF, Shelfer TD, Scheinost AC, Hinman NW, Furniss G, Mertzman SA, Bishop JL, Ming DW, Allen CC, Britt DT (2000) Mineralogy, composition, and alteration of Mars Pathfinder rocks and soils: evidence from multispectral, elemental, and magnetic data on terrestrial analogue, SNC meteorite, and Pathfinder samples. J. Geophys. Res. 105(E1): 1757-1817
- 53 Bishop JL, Murchie SL, Pieters CM, Zent AP (2002) A model of dust, soil, and rock coatings on Mars: physical and chemical processes on the Martian surface. J. Geophys. Res. 107(E11): 5097, 10.1029/2001JE001581
- 54 Murchie S, Barnouin-Jha O, Barnouin-Jha K, Bishop JL, Morris RV, Johnson J, McSween HY Jr. (2003) New insights into the geology of the Mars Pathfinder landing site from spectral and morphologic Analysis of the 12-color SuperPan Panorama. Icarus: submitted
- 55 McLennan SM (2003) Sedimentary silica on Mars. Geology 31: 315-318
- 56 Ruff SW (2004) Spectral evidence for zeolite in the dust on Mars. Icarus 168: 131-143
- 57 Meyer C (2003) Mars Meteorite Compendium-2003 (eds): http://wwwcurator.jsc.nasa.gov/curator/antmet/mmc/mmc.htm Astromaterials Research & Exploration Science, NASA-JSC.
- 58 Hunten DM (1993) Atmospheric evolution of terrestrial planets. Science 259: 915-920
- 59 Bishop JL, Banin A, Mancinelli RL, Klovstad ML (2002) Detection of soluble and fixed NH₄⁺ in clay minerals by DTA and IR reflectance spectroscopy: a potential tool for planetary surface exploration. Planet. Space Sci. 50: 11-19
- 60 Lane MD, Morris RV, Mertzman SA, Christensen PR (2002) Evidence for platy hematite grains in Sinus Meridiani, Mars. J. Geophys. Res. 107(E12): 5126, 10.1029/2001JE001832
- 61 Catling DC, Moore JM (2003) The nature of coarse-grained crystalline hematite and its implications for the early environment of Mars. Icarus 165: 277-300
- 62 Beinroth A, Arnold G (1996) Analysis of weak surface absorption bands in the nearinfrared spectra of Mars obtained by Phobos-2. Vibrational Spectroscopy 11: 115-121
- 63 Clark RN, King TVV, Klejwa M, Swayze GA (1990) High spectral resolution reflectance spectroscopy of minerals. J. Geophys. Res. 95: 12653-12680
- 64 Blaney DL, McCord TB (1989) An observational search for carbonates on Mars. J. Geophys. Res. 94(B8): 10159-10166
- 65 Clark RN, Swayze GA, Singer RB, Pollack JB (1990) High-resolution reflectance spectra of Mars in the 2.3 μm region: evidence for the mineral scapolite. J. Geophys. Res. 95(B9): 14463-14480
- 66 Calvin WM, King TVV, Clark RN (1994) Hydrous carbonates on Mars? Evidence from Mariner 6/7 infrared spectrometer and groundbased telescopic spectra. J. Geophys. Res. 99(E7): 14659-14675
- 67 Lane MD, Christensen PR (1997) Thermal infrared emission spectroscopy of anhydrous carbonates. J. Geophys. Res. 102(E11): 25581-25592
- 68 Pollack JB, Roush TL, Witteborn F, Bregman J, Wooden D, Stoker C, Toon OB, Rank D, Dalton B, Freedman R (1990) Thermal emission spectra of Mars (5.4–10.5 μm): evidence for sulfates, carbonates, and hydrates. J. Geophys. Res. 95(B9): 14595-14627

- 69 Bandfield JL, Glotch TD, Christensen PR (2003) Spectroscopic identification of carbonate minerals in the Martian dust. Science 301: 1084-1087
- 70 Ross SD (1974) Sulphates and other oxy-anions of Group VI. In Farmer VC (ed) The Infrared Spectra of Minerals. The Mineralogical Society, pp 423-444
- 71 Gaffey SJ, McFadden LA, Nash D, Pieters CM (1993) Ultraviolet, visible, and nearinfrared reflectance spectroscopy: laboratory spectra of geologic materials. In Pieters CM, Englert PAJ (eds) Remote Geochemical Analysis: Elemental and Mineralogical Composition. Cambridge University Press, Cambridge, pp 43-77
- 72 Blaney DL, McCord TB (1995) Indications of sulfate minerals in the Martian soil from Earth-based spectroscopy. J. Geophys. Res. 100(E7): 14433-14441
- 73 Lane MD, Christensen PR (1998) Thermal infrared emission spectroscopy of salt minerals predicted for Mars. Icarus 135: 528-536
- 74 Burns RG (1993) Mineralogical Applications of Crystal Field Theory. Cambridge University Press, Cambridge
- 75 Mustard JF, Bell JF III (1994) New composite reflectance spectra of Mars from 0.4 to 3.14 μm. Geophys. Res. Lett. 21: 353-356
- 76 McSween HY Jr. (1985) SNC meteorites: clues to Martian petrologic evolution? Rev. Geophys. 23: 391-416
- 77 McSween HY Jr. (1994) What have we learned about Mars from SNC meteorites. Meteoritics 29: 757-779
- 78 Nyquist LE, Bogard DD, Shih C-Y, Greshake A, Stöffler D, Eugster O (2001) Ages and geologic histories of Martian meteorites. Chronology and Evolution of Mars 96: 105-164
- 79 Gooding JL, Wentworth SJ, Zolensky ME (1991) Aqueous alteration of the Nakhla meteorite. Meteoritics 26: 135-143
- 80 Gooding JL (1992) Soil mineralogy and chemistry on Mars: possible clues from salts and clays in SNC meteorites. Icarus 99: 28-41
- 81 Treiman AH, Barrett RA, Gooding JL (1993) Preterrestrial aqueous alteration of the Lafayette (SNC) meteorite. Meteoritics 28: 86-97
- 82 McKay DS, Gibson EK Jr., Thomas-Keprta KL, Vali H, Romanek CS, Clemett SJ, Chillier XDF, Maechling CR, Zare RN (1996) Search for past life on Mars: possible relic biogenic activity in Martian meteorite ALH 84001. Science 273: 924-930
- 83 Mittlefehldt DW (1994) ALH 84001, a cumulate orthopyroxeneite member of the Martian meteorite clan. Meteoritics 29: 214-221
- 84 Golden DC, Ming DW, Schwandt CS, Lauer HV Jr., Socki RA, Morris RV, Lofgren GE, McKay GA (2001) A simple inorganic process for formation of carbonates, magnetite, and sulfides in Martian meteorite ALH 84001. Am. Miner. 86: 370-375
- 85 Thomas-Keprta KL, Clemett SJ, Bazylinski DA, Kirschvink JL, McKay DS, Wentworth SJ, Vali H, Gibson EK Jr., McKay MF, Romanek CS (2001) Truncated hexa-octahedral magnetite crystals in ALH 84001: presumptive biosignatures. Proc. Nat. Acad. Sci. 98: 2164-2169
- 86 Eiler JM, Valley JW, Graham CM, Fournelle J (2002) Two populations of carbonate in ALH 84001: Geochemical evidence for discrimination and genesis. Geochim. Cosmochim. Acta 66: 1285-1303
- 87 Barber DJ, Scott ERD (2003) Transmission electron microscopy of minerals in the Martian meteorite Allan Hills 84001. Meteorit. Planet. Sci. 38: 831-848

- 88 Bishop JL, Mustard JF, Pieters CM, Hiroi T (1998) Recognition of minor constituents in reflectance spectra of ALH 84001 chips and the importance for remote sensing on Mars. Meteorit. Planet. Sci. 33: 693-698
- 89 Bishop JL, Pieters CM, Hiroi T, Mustard JF (1998) Spectroscopic analysis of Martian meteorite ALH 84001 powder and applications for spectral identification of minerals and other soil components on Mars. Meteorit. Planet. Sci. 33: 699-708
- 90 Wendlandt WW (1986) Thermal Methods of Analysis. John Wiley & Sons, New York
- 91 Salisbury JW, Walter LS, Vergo N, D'Aria DM (1991) Infrared (2.1–25 μm) Spectra of Minerals. Johns Hopkins University Press, Baltimore
- 92 Griffith WP (1975) Raman spectroscopy of terrestrial minerals. In Karr CJ (ed) Infrared and Raman Spectroscopy of Lunar and Terrestrial Minerals. Academic Press, Orlando, pp 299-323
- 93 Murad E, Cashion JD (2004) Mössbauer Spectroscopy of Environmental Materials and their Industrial Utilization. Kluwer Academic Publishers, Boston/Dordrecht
- 94 Morris RV, Agresti DG, Lauer HV Jr., Newcomb JA, Shelfer TD, Murali AV (1989) Evidence for pigmentary hematite on Mars based on optical, magnetic and Mössbauer studies of superparamagnetic (nanocrystalline) hematite. J. Geophys. Res. 94(B3): 2760-2778
- 95 Morris RV, Lauer HV Jr., Lawson CA, Gibson EK Jr., Nace GA, Stewart C (1985) Spectral and other physicochemical properties of submicron powders of hematite (α -Fe₂O₃), maghemite (γ -Fe₂O₃), magnetite (Fe₃O₄), goethite (α -FeOOH), and lepidocrocite (γ -FeOOH). J. Geophys. Res. 90(B4): 3126-3144
- 96 Bishop JL, Pieters CM, Burns RG (1993) Reflectance and Mössbauer spectroscopy of ferrihydrite-montmorillonite assemblages as Mars soil analog materials. Geochim. Cosmochim. Acta 57: 4583-4595
- 97 Scheinost AC, Chavernas A, Barrón V, Torrent J (1998) Use and limitations of second-derivative diffuse reflectance spectroscopy in the visible to near-infrared range to identify and quantify Fe oxide minerals in soils. Clays Clay Miner. 46: 528-536
- 98 Bishop JL, Murad E (2002) Spectroscopic and geochemical analyses of ferrihydrite from hydrothermal springs in Iceland and applications to Mars. In Smellie JL, Chapman MG (eds) Volcano-Ice Interactions on Earth and Mars. Geological Society, Special Publication No.202, pp 357-370
- 99 Bishop JL, Murad E (1996) Schwertmannite on Mars? Spectroscopic analyses of schwertmannite, its relationship to other ferric minerals, and its possible presence in the surface material on Mars. In Dyar MD, McCammon C, Schaefer MW (eds) Mineral Spectroscopy: A Tribute to Roger G. Burns. Vol. Special Publication Number 5. The Geochemical Society, pp 337-358
- 100 Morris RV, Golden DC, Bell III JF (1997) Low-temperature reflectivity spectra of red hematite and the color of Mars. J. Geophys. Res. 102(E4): 9125-9133
- 101 Barrón V, Gálves N, Hochella MF, Torrent J (1997) Epitaxial overgrowth of goethite on hematite synthesized in phosphate media: a scanning force and transmission electron microscopy study. Am. Miner. 82: 1091-1100
- 102 Gálves N, Barrón V, Torrent J (1999) Effect of phosphate on the crystallization of hematite, goethite, and lepidocrocite from ferrihydrite. Clays Clay Miner. 47: 304-311
- 103 Torrent J, Barrón V (2000) Key role of phosphorous in the formation of the iron oxides in Mars soils? Icarus 145: 645-647

- 104 Gaffey SJ (1987) Spectral reflectance of carbonate minerals in the visible and near infrared (0.35–2.55 μ m): anhydrous carbonate minerals. J. Geophys. Res. 92: 1429-1440
- 105 Salisbury JW, Wald A (1992) The role of volume scattering in reducing spectral contrast of reststrahlen bands in spectra of powdered minerals. Icarus 96: 121-128
- 106 Romanek CS, Grady MM, Wright IP, Mittlefehldt DW, Soicki RA, Pillinger CT, Gibson EK Jr. (1994) Record of fluid-rock interactions on Mars from the meteorite ALH 84001. Nature 372: 655-657
- 107 Valley JW, Eiler JM, Graham CM, Gibson EK, Romanek CS, Stolper EM (1997) Low-temperature carbonate concretions in the Martian meteorite ALH 84001: evidence from stable isotopes and mineralogy. Science 275: 1633-1638
- 108 Warren PH (1998) Petrologic evidence for low-temperature, possibly flood-evaporitic origin of carbonates in the ALH 84001 meteorite. J. Geophys. Res. 103(E7): 16759-16773
- 109 Greenwood JP, McSween HY Jr. (2001) Petrogenesis of Allan Hills 84001: constraints from impact-melted feldspathic and silica glasses. Meteorit. Planet. Sci. 36: 43-61
- 110 Harvey RP, McSween HY Jr. (1996) A possible high-temperature origin for the carbonates in the Martian meteorite ALH 84001. Nature 382: 49-51
- 111 Treiman AH (1998) The history of Allan Hills 84001 revised: multiple shock events. Meteorit. Planet. Sci. 33: 753-764
- 112 Kodama H (1985) Infrared Spectra of Minerals. Reference Guide to Identification and Characterization of Minerals for the Study of Soils. Agriculture Canada, Ottawa
- 113 Bishop JL, Madejová J, Komadel P, Froeschl H (2002) The influence of structural Fe, Al and Mg on the infrared OH bands in spectra of dioctahedral smectites. Clay Miner. 37: 607-616
- 114 Bishop JL, Murad E, Dyar MD (2002) The influence of octahedral and tetrahedral cation substitution on the structure of smectites and serpentines as observed through infrared spectroscopy. Clay Miner. 37: 617-628
- 115 Zent AP, Howard DJ, Quinn RC (2001) H_2O adsorption on smectites: application to the diurnal variation of H_2O in the Martian atmosphere. J. Geophys. Res. 106(E7): 14667-14674
- 116 Dios Cancela G, Huertas FJ, Romero Taboada E, Sánchez-Rasero F, Hernández Laguna A (1997) Adsorption of water vapor by homoionic montmorillonites: heats of adsorption and desorption. J. Colloid Interface Sci. 185: 343-354
- 117 Chipera SJ, Carey JW, Bish DL (1997) Controlled-humidity XRD analyses: application to the study of smectite expansion/contraction. In Gilfrich JV, Noyan IC, Jenkins R, Huang TC, Snyder RL, Smith DK, Zaitz MA, Predecki PK (eds) Advances in X-ray Analysis. Vol. 39 Plenum, pp 713-722
- 118 Cloutis EA, Asher PM, Mertzman SA (2002) Spectral reflectance properties of zeolites and remote sensing implications. J. Geophys. Res. 107(E9): 5067, 10.1029/ 2000JE001467
- 119 Ross SD (1974) Phosphates and other oxy-anions of group V. In Farmer VC (ed) The Infrared Spectra of Minerals. The Mineralogical Society, pp 383-422
- 120 Banin A, Han FX, Kan I, Cicelsky A (1997) Acidic volatiles and the Mars soil. J. Geophys. Res. 102(E6): 13341-13356
- 121 Minitti ME, Mustard JF, Rutherford MJ (2002) The effects of glass content and oxidation on the spectra of SNC-like basalts: applications to Mars remote sensing. J. Geophys. Res. 107(E5): 5030, 10.2029/2001JE001518

- 122 Von Waltershausen S (1846) Über die submarinen Ausbrüche in der tertiären Formation des Val di Noto im Vergleiche mit verwandten Erscheinungen am Atna. Göttinger Studien 1: 371-431
- 123 Jercinovic M, Keil K, Smith MR, Schmitt RA (1990) Alteration of basaltic glasses from north-central British Columbia, Canada. Geochim. Cosmochim. Acta 54: 2679-2696
- 124 Allen CC, Gooding JL, Jercinovic M, Keil K (1981) Altered basaltic glass: a terrestrial analog to the soil of Mars. Icarus 45: 347-369
- 125 Bishop JL, Fröschl H, Mancinelli RL (1998) Alteration processes in volcanic soils and identification of exobiologically important weathering products on Mars using remote sensing. J. Geophys. Res. 103(E13): 31457-31476
- 126 Morris RV, Golden DC, Ming DW, Shelfer TD, Jørgensen LC, Bell III JF, Graff TG, Mertzman SA (2001) Phyllosilicate-poor palagonitic dust from Mauna Kea volcano (Hawaii): a mineralogical analogue for magnetic Martian dust? J. Geophys. Res. 106(E3): 5057-5083
- 127 Furnes H (1978) Element mobility during palagonitization of a subglacial hyaloclastite in Iceland. Chem. Geology 22: 249-264
- 128 Schiffman P, Spero HJ, Southard RJ, Swanson DA (2000) Controls on palagonitization versus pedogenic weathering of basaltic tephra: evidence from the consolidation and geochemistry of the Keanakako'i ash member, Kilauea volcano. Geochemistry Geophysics Geosystems 1: Paper no. 2000GC000068
- 129 Morris RV, Gooding JL, Lauer HV Jr., Singer RB (1990) Origins of Marslike spectral and magnetic properties of a Hawaiian palagonitic soil. J. Geophys. Res. 95(B9): 14427-14434
- 130 Morris RV, Golden DC, Bell III JF, Lauer HV Jr., Adams JB (1993) Pigmenting agents in Martian soils: inferences from spectral, Mössbauer, and magnetic properties of nanophase and other iron oxides in Hawaiian palagonitic soil PN-9. Geochim. Cosmochim. Acta 57: 4597-4609
- 131 Squyres SW, Wilhelms DE, Moosman AC (1987) Large-scale volcano-ground ice interactions on Mars. Icarus 70: 385-408
- 132 Bishop JL, Schiffman P, Southard RJ (2002) Geochemical and mineralogical analyses of palagonitic tuffs and altered rinds of pillow lavas on Iceland and applications to Mars. In Smellie JL, Chapman MG (eds) Volcano-Ice Interactions on Earth and Mars. The Geological Society, Special Publication No.202, pp 371-392
- 133 Parfitt RL, Childs CW, Eden DN (1988) Ferrihydrite and allophane in four andepts from Hawaii and implications for their classification. Geoderma 41: 223-241
- 134 Schiffman P, Southard RJ, Eberl DD, Bishop JL (2002) Distinguishing palagonitized from pedogenically-altered basaltic Hawaiian tephra: mineralogical and geochemical criteria. In Smellie JL, Chapman MG (eds) Volcano-Ice Interactions on Earth and Mars. The Geological Society, Special Publication No.202, pp 393-405
- 135 Stoiber RE, Rose WI Jr. (1974) Fumarole incrustations at active Central American volcanoes. Geochim. Cosmochim. Acta 38: 495-516
- 136 Bell JF III, Morris RV, Adams JB (1993) Thermally altered palagonitic tephra: a spectral and process analog to the soil and dust of Mars. J. Geophys. Res. 98(E2): 3373-3385
- 137 Morris RV, Ming DW, Golden DC, Bell III JF (1996) An occurrence of jarosite tephra on Mauna Kea, Hawaii: implications for the ferric mineralogy of the Martian surface. In Dyar MD, McCammon C, Schaefer MW (eds) Mineral Spectroscopy: A Tribute to

Roger G. Burns. Vol. Special Publication Number 5. The Geochemical Society, pp 327-336

- 138 McKay CP, Friedmann EI, Gómez-Silva B, Cáceres-Villanueva L, Andersen DT, Landheim R (2003) Temperature and moisture conditions for life in the extreme arid region of the Atacama desert: four years of observations including the El Niño of 1997-1998. Astrobiology 3: 393-406
- 139 Gibson EK, Wentworth SJ, McKay DS (1983) Chemical weathering and diagenesis of a cold desert soil from Wright Valley, Antarctica: an analog of Martian weathering processes. J. Geophys. Res. 88: 13th Lunar Planet. Sci. Conf., Part 2, A912-A928
- 140 Bishop JL, Koeberl C, Kralik C, Froeschl H, Englert PAJ, Andersen DW, Pieters CM, Wharton RA (1996) Reflectance spectroscopy and geochemical analyses of Lake Hoare sediments, Antarctica. Geochim. Cosmochim. Acta 60: 765-785
- 141 Dickinson WW, Grapes RH (1997) Authegenic chabazite and implications for weathering in Sirius group diamictite, Table Mountain, Dry Valleys, Antarctica. J. Sedimentary Res. 67: 815-820
- 142 Doran PT, Wharton Jr RA, Des Marais D, McKay CP (1998) Antarctic paleolake sediments and the search for extinct life on Mars. J. Geophys. Res. 103(E12): 28-48
- 143 Bishop JL, Lougear A, Newton J, Doran PT, Froeschl H, Trautwein AX, Körner W, Koeberl C. (2001) Mineralogical and geochemical analyses of Antarctic sediments: a reflectance and Mössbauer spectroscopy study with applications for remote sensing on Mars. Geochim. Cosmochim. Acta 65: 2875-2897
- 144 Morris RV, Golden DC, Bell III JF, Lauer HV Jr. (1995) Hematite, pyroxene, and phyllosilicates on Mars: implications from oxidized impact melt rocks from Manicouagan Crater, Quebec, Canada. J. Geophys. Res. 100(E3): 5319-5328
- 145 Hagerty JJ, Newsom HE (2003) Hydrothermal alteration at the Lonar Lake impact structure, India: implications for impact cratering on Mars. Meteorit. Planet. Sci. 38: 365-381
- 146 Osinski GR, Spray JG, Lee P (2001) Impact-induced hydrothermal activity within the Haughton impact structure, Arctic Canada: generation of transient, warm, wet oasis. Meteorit. Planet. Sci. 36: 731-745
- 147 Cockell CS, Lee P (2002) The biology of impact craters a review. Biol. Rev. 77: 279-310
- 148 Lowenstam HA (1981) Minerals formed by organisms. Science 211: 1126-1131
- 149 Brock TD (1978) Thermophilic Microorganisms and Life at High Temperatures. Springer-Verlag, New York
- 150 Trudinger PA, Swaine DJ (1979) Biogeochemical Cycling of Mineral-forming Elements (eds). Elsevier, Amsterdam
- 151 Lundgren DG, Dean W (1979) Biogeochemistry of iron. In Trudinger PA, Swaine DJ (eds) Biogeochemical Cycling of Mineral-forming Elements. Elsevier, Amsterdam, pp 211-251
- 152 Chukhrov FV, Zvyagin BB, Gorshkov AI, Ermilova LP, Balashova VV (1973) Ferrihydrite. Izvest. Akad. Nauk, SSSR, Ser. Geol. 4: 23-33
- 153 Murad E (1982) Ferrihydrite deposits on an artesian fountain in lower Bavaria. Neues Jahrbuch für Mineralogie Monatshefte 2: 45-56
- 154 Blakemore RP (1975) Magnetotactic bacteria. Science 190: 337-379
- 155 Blakemore RP (1982) Magnetotactic bacteria. Annu. Rev. Microbiol. 36: 217-238
- 156 Gehring AU, Langer MR, Gerhing CA (1994) Ferriferous bacterial encrustations in lateritic duricrusts from southern Mali (West Africa). Geoderma 61: 213-222

- 157 Bernal JD (1951) The Physical Basis of Life. Routledge and Kegan Paul, London
- 158 Lawless JG (1986) Clay-organic interactions and the origin of life. In Cairns-Smith AG, Hartman H (eds) Clay Minerals and the Origin of Life. Cambridge University Press, Cambridge, pp 135-137
- 159 Odom DG, Rao M, Lawless JG, Oró J (1979) Association of nucleotides with homoionic clays. J. Molec. Evol. 12: 365-36.
- 160 Lawless JG, Banin A, Church FM, Mazzurco J, Huff J, Kao R, Cook A, Lowe T, Orenberg JB, Edelson E (1985) pH profile of the adsorption of nucleotides onto montmorillonite. Orig. Life Evol. Biosph. 15: 77-88
- 161 Mortland MM, Raman KV (1968) Surface acidities of smectites in relation to hydration, exchangeable-cation and structure. Clays Clay Minerals 16: 393-398
- 162 Soloman DH (1968) Clay minerals as electron acceptors and/or electron donors in organic reactions. Clays Clay Minerals 16: 31-39
- 163 Theng BKG (1974) The Chemistry of Clay-Organic Reactions. Halsted Press, New York
- 164 Pinnavaia TJ, Mortland MM (1986) Clay Minerals and the Origin of Life. In Cairns-Smith AG, Hartman H (eds) Cambridge University Press, Cambridge, pp 131-135
- 165 Ding PZ, Kawamura K, Ferris JP (1996) Oligomerization of uridine phosphorimidazolides on montmorillonite: a model for the prebiotic synthesis of RNA on minerals. Orig. Life Evol. Biosph. 26: 151-171
- 166 Hartman H, Sweene MA, Kropp MA, Lewis JS (1993) Carbonaceous chondrites and the origin of life. Orig. Life Evol. Biosph. 23: 221-227
- 167 Bishop JL (1998) Biogenic catalysis of soil formation on Mars? Orig. Life Evol. Biosph. 28: 449-459
- 168 Farmer JD, Des Marais DJ (1994) Biological versus inorganic processes in stromatolite morphogenesis: observations from mineralizing sedimentary systems. In Stal LJ, Caumette P (eds) Microbial Mats: Structure, Development, and Environmental Significance. Vol. NATO ASI Series in Ecological Sciences G35. Springer-Verlag, Berlin, pp 61-68
- 169 Walter MR, Des Marais DJ (1993) Preservation of biological information in thermal spring deposits: developing a strategy for the search for fossil life on Mars. Icarus 101: 129-143
- 170 Rothschild LJ (1990) Earth analogs for Martian life, microbes in evaporites, a new model system for life on Mars. Icarus 88: 246-260
- 171 Farmer JD (1995) Mars exopaleontology. Palaios 10: 197-198
- 172 Omega (http://www.ias.fr/cdp/Omega/welcome.html)
- 173 Murchie S, Arvidson R, Beisser K, Bibring J-P, Bishop J, Boldt J, Bussey B, Choo T, Clancy RT, Darlington EH, Des Marais D, Fasold M, Fort D, Green R, Guinness E, Hayes J, Heyler G, Humm D, Lee R, Lees J, Lohr D, Malaret E, Morris R, Mustard J, Rhodes E, Robinson M, Roush T, Schaefer E, Seagrave G, Silvergate P, Smith M, Strohbehn K, Thompson P, Tossman B (2003) CRISM: compact reconnaissance imaging spectrometer for Mars on the Mars Reconnaissance Orbiter. Sixth Int'l Conf. on Mars, CD-ROM #3062 (abstr.)
- 174 Squyres SW, Arvidson RE, Baumgartner ET, Bell JF III, Christensen PR, Gorevan S, Herkenhoff KE, Klingelhöfer G, Madsen MB, Morris RV, Rieder R, Romero RA (2003) The Athena Mars Rover Science investigation. J. Geophys. Res. 108: 8062, 10.1029/2003JE002121

- 175 Chicarro AF, the-Science-Team (2003) The Mars Express mission and its Beagle 2 lander. Sixth Int'l Conf. on Mars: CD-ROM #3049 (abstr)
- 176 Smith PH (2003) The Phoenix scout mission. Sixth Int'l Conf. on Mars, CD-ROM #3257 (abstr.)
- 177 Vaniman D, Bish D, Blake D, Elliot ST, Sarrazin P, Collins SA, Chipera S (1998) Landed XRD/XRF analysis of prime targets in the search for past or present Martian life. J. Geophys. Res. 103(E13): 31477-31489
- 178 Blake DF, Sarrazin P, Chipera SJ, Bish DL, Vaniman DT, Bar-Cohen Y, Sherrit S, Collins S, Boyer B, Bryson C, King J (2003) Definitive mineralogical analysis of Martian rocks and soil using the CHEMIN XRD/XRF instrument and the USDC sampler. Sixth Int'l Conf. on Mars, CD-ROM #3022 (abstr.)
- 179 Haskin LA, Wang A, Rockow KM, Jolliff BL, Korotev RL, Viskupic KM (1997) Raman spectroscopy for mineral identification and quantification for in situ planetary surface analysis: a pointcount method. J. Geophys. Res. 102(E8): 19293-19306.
- 180 Wang A, Haskin LA, Lane AL, Wdowiak TJ, Squyres SW, Wilson RJ, Hovland LE, Manatt KS, Raouf N, Smith CD (2003) Development of the Mars microbeam Raman spectrometer (MMRS). J. Geophys. Res. 108(E1): 5005, 10.1029/2002JE001902

5 Global Distribution of Subsurface Water Measured by Mars Odyssey

Igor G. Mitrofanov

While the presence of water in minerals of the Martian surface has been known for many years and the storage of ground ice in the past and present was suggested from geomorphologic observations and theoretical calculations, the amount and global distribution of different forms of water were not well constrained until recently. Mars Odyssey for the first time succeeded in mapping gamma rays and neutrons from Mars bearing information on, among others, soil water contents as well as their geographical and vertical distribution in the shallow subsurface.

This chapter presents an overview of this new type of observations and their results. It is already possible to make several robust statements about the water distribution on Mars, which could hardly be changed by future studies. These data can importantly contribute to our understanding of the present state of water on Mars as well as of the evolution of the planetary water inventory.

5.1 Generation of Neutrons and Gamma-Rays in the Martian Subsurface

Because Mars has no planetary magnetic field and a very thin atmosphere with a column density of about 15–25 g cm⁻², galactic cosmic rays propagate to and interact with the surface. Under the cosmic ray bombardment, a large number of secondary neutrons are produced within the subsurface layer of 1-2 meters. Outgoing leakage neutrons interact with nuclei of elements of the subsurface material, producing outgoing leakage flux of neutrons and gamma rays [1-4]. There are two major types of this interaction (Fig. 5.1): inelastic scattering of neutrons on nuclei, which results in emission of nuclear lines of existing nuclei and in moderation of neutrons down to thermal energies; and neutron capture reaction, which absorbs neutrons with creation of new nuclei, usually at the excited states with following emission of gamma-quantum of de-excitation. The first process is more efficient for high energy neutrons, which still have enough energy to excite nuclei, and the second process has a larger cross-section for low energy neutrons. The "forest" of spectral lines of produced gamma-rays unambiguously represents the nuclear composition of the substance in the subsurface layer of 1-2 meters because each particular nucleus corresponds to the set of gamma-ray lines at definite energies (Fig. 5.2).

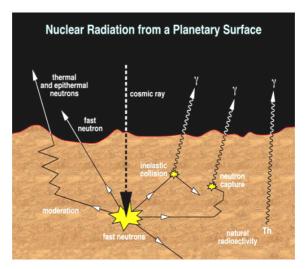


Fig. 5.1 Nucelar interactions in the Martian subsurface according to [1] (reprinted with permission from AGU).

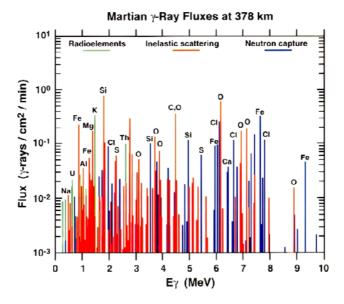


Fig. 5.2 Predicted "forest" of gamma-ray lines from the Martian surface according to [1] (reprinted with permission from AGU).

However, the flux of photons within a nuclear line corresponds to the rate of interaction between particular nuclei and neutrons, and therefore one should know the flux of neutrons for determining the abundance of nuclei. Measurements of gamma-ray lines should be accompanied by measurements of neutrons, which leak from the subsurface after the process of moderation.

The first successful effort in the investigation of the elementary composition of the Martian subsurface by nuclear methods is being accomplished now by the NASA mission Mars Odyssey. This mission includes the Gamma-Ray Spectrometer suite with three separate instruments [2]: Gamma Sensor Head (GSH), Neutron Spectrometer (NS) and High Energy Neutron Detector (HEND). These three instruments presently operate on the orbit around Mars and perform global mapping of the planet. The comprehensive analysis of collected data is now in progress, and has to provide the global map of elementary composition of the Martian soil down to 1-2 meters from the surface. However, one particular element, hydrogen, produces such a "bright" signature of its presence in the subsurface that even at the very beginning of the mapping the hydrogen distribution has become well determined over the entire planet [5–9]. Water is the best (or even only) a candidate for a hydrogen-bearing substance in the Martian subsurface which may contain hydrogen in high abundance. Therefore, detection of hydrogen by nuclear instruments on Odyssey means detection of water in the Martian shallow subsurface. Hereafter we present the very first results of water mapping on Mars by High Energy Neutron Detector.

5.2 Signatures of Hydrogen in the Martian Subsurface in the Leakage Flux of Neutrons and Gamma-Rays

Cosmic rays produce initial neutrons with energies around 20 MeV. The energy spectrum of the leakage flux of neutrons from the surface is produced by a large number of collisions with nuclei, and it depends on the nuclear composition of the subsurface material. A neutron with mass *m* loses a small fraction of its energy ~ m/(M + m) in collision with a heavy nucleus with mass *M*, but the fraction of lost energy is about $\frac{1}{2}$, when a neutron collides with a light nucleus of hydrogen (proton) with the same mass *m*. One collisions with hydrogen makes the same change of neutron energy as -M/2m collisions with heavy nuclei. Even a small content of hydrogen in the substance significantly decreases the leakage flux of epithermal and high energy neutrons and, correspondingly, increases the leakage flux of thermal neutrons. Therefore, a deficit of epithermal and fast neutrons in some regions of Mars is a signature of the presence of water in the subsurface.

Figure 5.3 presents results of numerical calculations of the neutron flux from the Martian subsurface for a soil with different contents of water. These calculations were performed for the so-called Pathfinder composition of the soil: it corresponds to the composition of sand and stones measured at the landing site of Mars Pathfinder, and the fraction of sand and stones is assumed to be 50:50 by mass. A column density of the atmosphere of about 15 g cm⁻² was used. The leakage flux of fast and epithermal neutrons decreases with increasing water content. A decrease factor of about 1.5 could be observed for the flux of epithermal neutrons, provided that as small a quantity of water as 1 wt % would be

added to the soil (Fig. 5.3). A change in the composition of heavy nuclei in the soil could also lead to a change in the flux of leaking neutrons, but this effect is known to be much smaller, i.e. about 15-20 % (e.g. see [11])

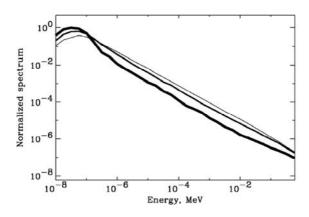


Fig. 5.3 Spectral density of leakage flux of neutrons depending on the water content in the subsurface (according to numerical calculation by MCNPX [21]). The atmospheric column density assumed is 15 g cm⁻². The thin, medium and thick curves are for 0 wt %, 1 wt % and 10 wt % water, respectively.

When neutrons are moderated down to thermal energies, they have a rather high probability of being captured by hydrogen with creation of deuterium nuclei in the excited state, which decay by production of 2.2 MeV photon. Therefore, the emission of photons at 2.2 MeV is another signature of the presence of water in the Martian subsurface. The flux of thermal neutrons, if taken alone, does not "measure" the hydrogen content as robustly as epithermal and high energy neutrons do: while the production of thermal neutrons would increase for an increasing content of hydrogen because of more efficient moderation from the primary particles, the number of leaking thermal neutrons would decrease because of the stronger absorption by capture nuclear reactions. Therefore, measurements of epithermal and high energy neutrons and detection of photons at 2.2 MeV line constitute two complementary methods of remote sensing by nuclear instruments, which together provide the most reliable estimation of the content of water in the shallow Martian subsurface.

5.3 Description of Gamma-Ray Spectrometer Suite on Odyssey

The Gamma-Ray Spectrometer suite [2] puts this approach into practice onboard Mars Odyssey (Fig. 5.4). Germanium Sensor Head (GSH) contains a high-purity

germanium detector about 6.7 cm in diameter and 6.7 cm in length, which is installed at the end of the 6 m deployment boom for decreasing the spacecraft background (Fig. 5.4). GSH is integrated within a passive cryogenic cooler, which provides the operational temperature for the Ge sensor well below 100 K (Fig. 5.5). GSH has perfect energy resolution for the detection of gamma-ray lines: it is about 3.9 keV (full width at half maximum) for the energy of gamma-rays (1461 keV) [2]. GSH was developed in the Lunar and Planetary Laboratory of the University of Arizona (Tucson), with the participation of CNRS (Toulouse, France). The Lunar and Planetary Laboratory is the leading institution for the whole GRS suite as well.



Fig. 5.4 2001 Mars Odyssey on the orbit around Mars (image credit: NASA/JPL).

Neutron Spectrometer (NS) was developed by Los Alamos National Laboratory. This detector measures thermal, epithermal and fast neutrons with energies up to 2 MeV [2]. A detailed description of this instrument is presented in [2] as well as a description of sophisticated methods of neutron measurements using the instrument.

The High-Energy Neutron Detector (HEND) was developed in the Russian Space Research Institute in Moscow [2, 9]. HEND (Fig. 5.6) integrates within one unit a set of four separate sensors for detection of epithermal and high energy neutrons. This set includes three detectors with ³He proportional counters and one scintillation block with two separate scintillators.

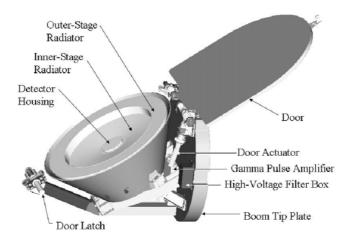


Fig. 5.5 Germanium Sensor Head of Gamma-Ray Spectrometer (according to Boynton et al. [2], courtesy of William Boynton, reprinted with permission from Kluwer).

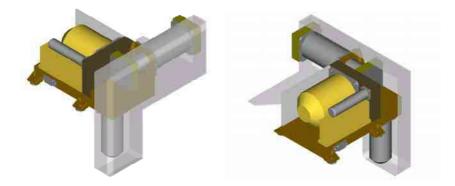


Fig. 5.6 High Energy Neutron Detector with a set of 4 separate sensors for epithermal and high energy neutrons.

The detectors with proportional counters (SD, or Small Detector; MD, or Medium Detector and LD, or Large Detector) are based on three industrial ³He counters LND2517, which are surrounded by thin, medium and thick moderators of polyethylene enclosures inside the cadmium cans, respectively. This counter itself is the most efficient for thermal neutrons below 0.4 eV. Therefore, the detectors measure neutrons with higher energies, which are moderated down to thermal energy inside the surrounding polyethylene enclosures. These detectors

have different efficiencies for neutrons with different energy ranges due to different thicknesses of moderators. Detector SD is the most sensitive for neutrons at the energy range 0.4 eV – 1 keV; MD is the most sensitive at the energy range 0.4 eV – 100 keV; LD is the most sensitive for neutrons at the energy range 10 eV – 1 MeV. These three detectors SD, MD and LD produce three separate signals S_{SD} , S_{MD} and S_{LD} , respectively.

The scintillation block contains the internal scintillator SC/IN with a stilbene crystal and Hamamatsu Photo Multiplier Tube (PMT) R1924. High energy neutrons produce recoil protons in this scintillator, which are detected as neutron-based counts at the energy range 850 keV – 15 MeV. The stilbene is also sensitive to gamma-ray photons, which are detected as electron-based counts at the energy range 60 keV - 2 MeV. Sensor SC/IN has an analog electronic board, which separates neutron-based counts (signal $S_{\text{SC/INNG}}$). The internal scintillator SC/OUT with CsI crystal works for anticoincidence logic, which rejects counts for external protons from the neutron-based counts of the signal $S_{\text{SC/INN}}$.

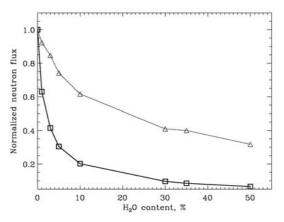


Fig. 5.7 Decrease of fluxes of counts rate in HEND sensor MD (epithermal neutrons, curve with boxes) and SC/IN (high energy neutrons at 0.8 - 2.0 MeV, curve with triangles) depending on the subsurface water content (in wt %) according to numerical simulations by MCNPX [21].

To determine the HEND sensitivity for the detection of subsurface water, a numerical model of neutron flux on the orbit has been calculated and converted with the affected area of HEND neutron sensors [9]. Results of numerical calculations for the change of counts for HEND detectors MD and SD/IN are shown in Fig. 5.7 depending on the different content of water in the homogeneous soil. Comparing a soil without water with a soil containing 3 wt % water, one finds in the second case a decrease of epithermal neutrons and fast neutrons by factors of about 2.5 and 1.2, respectively. This numerical simulation proves that HEND is a rather sensitive instrument for the detection of subsurface water with an accuracy of a few % by weight.

5.4 Mapping of Martian Neutrons by HEND on Odyssey

Gamma-Ray Spectrometer suite provides synchronous measurements by all three detectors of the suite (GSH, NS and HEND). The Central Electronic Block generates a single synchronization pulse for all three, which starts the accumulation of new energy spectra of counts from each sensor and ends the accumulation of previous ones. Presently, the time interval between two successive pulses is about 20 seconds. This means that the mapping data of GRS have a temporal resolution of about 20 sec.

Mars Odyssey has a circular polar orbit with an altitude of about 400 km. With an orbital velocity of about 3 km/sec, it covers 60 km on the surface during a time of 20 sec of data acquisition. This length is the minimal scale of horizontal resolution of orbital mapping by GRS. The physical scale of surface resolution is much larger. All three instruments of Odyssey GRS have no collimators of incoming neutrons or gamma-rays. Formally speaking, any gamma-ray photon or neutron emitted from a point below the visible horizon of the planet could be detected. However, the actual angular diagram of detected neutrons is narrower than the solid angle of the visible planet. The main reason is a finite column density of the Martian atmosphere (15-25 g cm⁻²) along the zenith, which effectively "removes" particles from directions with a large inclination to the zenith. Also, the surface itself does not radiate neutrons isotropically into the upward semi-sphere. Neutrons at different energies have different depths of predominant generation, and they have different free paths in the subsurface. One may suppose that the surface resolutions of orbital measurements are about 300 km, which are better than the distance to the visible horizon from the orbit, but much worse than the length (60 km) of a single exposure.

We believe that surface elements with linear scale of 200–300 km provide the adequate discretization for the mapping of neutron emission of Mars. There are methods of enhanced surface resolution for orbital mapping (e.g. the method of "inverse projection"), but they are model-dependent, and we have not used them at the initial stage of data analysis.

Emission of neutrons from Mars depends on seasons of the Martian year, because during the winter atmospheric carbon dioxide deposits on the poleward surface of the planet. The thickness of the deposition depends on the season, and in the maximum it varies from one place to another from several centimeters up to about 1–2 meters [12, 13], and the production of neutrons significantly varies during the season of CO₂ deposition on the surface [9]. The effect of seasonal variations of neutrons and gamma-rays provides an independent observational method of "weighing" of CO₂ winter deposits in addition to direct measurements of elevation by the laser altimeter (MOLA). It is also quite useful for an independent "in-flight" calibration of the instrument by providing a "reference signal" from the layer on neutron production with well-known nuclear composition.

The study of the seasonal CO_2 cycle by neutrons has been recently developed into a separate area of investigation (see [14–16]), which provides quite an important impact on the main studies of the Martian subsurface. One may determine the summer season for high-latitude regions of Mars, when the surface is CO_2 -free, and its nuclear emission represents the actual composition of 1–2 meters of the subsurface.

Hereafter, we present a synthetic map of the leakage flux of epithermal neutrons from the Martian surface based on the data for the summer season in the northern and southern hemispheres (Fig. 5.8). This global map does not represent any particular season on Mars because the planet usually has seasonal deposition of atmospheric carbon dioxide either in the north or south. The synthetic map of the CO_2 -free surface displays the permanent residual caps at both poles because they are not subject to seasonal variations.

The mapping of Mars from the orbit is influenced by the variable thickness of the atmosphere. Firstly, it has variable thickness above regions with different surface elevations [17]. Even excluding Olympus Mons, the difference of elevations across the Martian surface is about 20 km, which results in a difference in the atmospheric thickness of about 10 g cm⁻² along the nadir direction. One has to take these variations into account when one transforms variations of orbital data of neutron flux into variations of subsurface composition. Also, the atmosphere changes seasonally, and even mapping of the CO₂-free surface of Mars is seasondependent because of that. Orbital data for each region of Mars should be associated with a set of season intervals (as $\Delta L_s=15^\circ$), when the thickness of the atmosphere could be considered as constant. The Ames general circulation model (GCM) [18] is thought to present quite accurate values for describing both regional and seasonal variations of the Martian atmosphere. We use this model for orbital data deconvolution below.

The most important property of the map of epithermal neutron flux of Mars is its very large dynamical range of regional flux variations (Fig. 5.8). The largest flux of epithermal neutrons is associated with the region of Solis Planum with coordinates $246-293^{\circ}E$, $16-53^{\circ}S$. The smallest fluxes are observed at two high-latitude spots in the northern and southern hemisphere with coordinates $(24-28^{\circ}E, 86-90^{\circ}N)$ and $(220-224^{\circ}E, 78-82^{\circ}S)$, respectively. The ratios between the maximal and minimal fluxes of epithermal neutrons in these regions are about 9.4 and 8.8, respectively.

Such a large dynamic range of regional variations (about one order of magnitude) is the main difference between the neutron albedo of Mars and that of the Moon. According to mapping data by the Lunar Prospector [11], regional variations of neutron flux of the Moon are about 15–20 %. They are thought to result from variations in the composition of major soil elements in the lunar subsurface. The surface of Mars may have quite a similar composition of major elements, but the much larger range of regional neutron variations is thought to be associated with the variable content of subsurface hydrogen, i.e. of subsurface water. Hydrogen is a very efficient moderator of high energy neutrons (see Section 5.2), and even small variations of hydrogen (about a few wt %) in the subsurface should produce significant regional variations of the leakage flux of epithermal neutrons across the Martian surface.

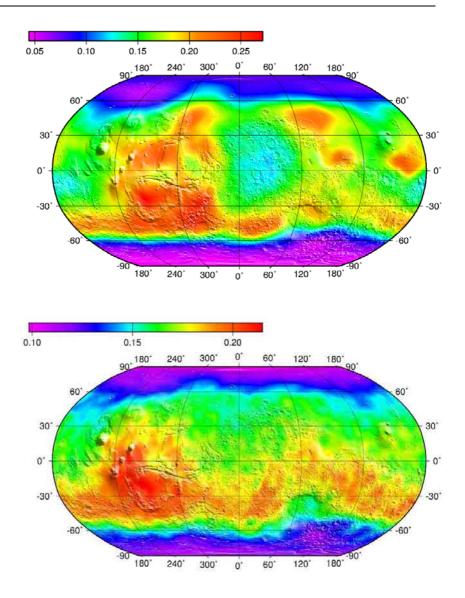


Fig. 5.8 Global map of neutron flux from Mars according to orbital measurements on HEND onboard Mars Odyssey. The upper map presents epithermal neutrons (signal S_{MD} from the sensor MD) and the lower map fast neutrons (signal $S_{\text{SC/IN}}$ from the sensor SC/IN).

The map of epithermal neutrons displays two large poleward regions of strong depressions of the leakage flux (Fig. 5.8). According to preliminary estimations, the subsurface layer of these regions may contain tens of % of water ice by weight

[5–9]. The boundary of the southern region of neutron depression is consistent with the southern boundary of stable water ice in the subsurface [5]. Some parts of the northern depression are far southward of the northern boundary of stable water ice. A possible regional correlation has been found between the boundary of neutron depressions and the presence of polygonal polar terrains (see Fig. 7.15 in Chap. 7). Therefore, one may suggest that the northern and southern regions of neutron depressions on Mars contain very high water ice contents of several tens of wt %. More accurate evaluations of the subsurface composition of the permafrost regions are presented below, addressing several intriguing questions resulting from preliminary studies:

1) Why do northern and southern permafrost regions look so similar (see Fig. 5.8), while the surfaces of these regions are known to have very different geological origin, age, relief properties, elevation, etc.?

2) The estimated volume of water ice of several tens of wt % is much larger than the pore volume of the regolith; how has the subsurface layer with a high content of water ice been formed?

3) What is the main physical condition that determines the observed boundaries of permafrost regions? Is the visible boundary the place where the ice-rich layer extends down to the depth below the thickness of the observable neutron-producing layer, or is it the place of wet-to-dry transition of the subsurface soil?

The answers to these questions are far from complete, but we will try to address them in the following Sects. 5.5 and 5.6 to stimulate further studies and theoretical investigations.

Other surprising features on the neutron maps of Mars are the two large depressions of neutrons at moderate latitudes (Fig. 5.8). There are two opposite equatorial regions with depression of epithermal neutrons: one is the Arabia region with coordinates $(0-45^{\circ}E, 20^{\circ}S-30^{\circ}N)$ and another is the Memnonia region with coordinates $(180-200^{\circ}E, 0-25^{\circ}S)$. The flux of neutrons in these two regions is about 3 times lower in respect to the maximum (Solis Planum). It is not as large as the depression by a factor of 9 in two polar permafrost regions, but it is still sufficiently large for regions at the equator. According to the preliminary numerical estimation (Fig. 5.3), the soil in these regions should contain about 10 wt % water to account for this depression factor, which is very difficult to explain according to the equatorial condition on the planet. This problem will also be addressed in the following section.

5.5 Water Content in Different Regions of Mars According to HEND/Odyssey Data

Estimation of the water content in the subsurface cannot be done using the neutron data alone. The estimation is model-dependent and one has to use the procedure of neutron data deconvolution. In this section we present the first results of HEND data analysis based on the testing of homogeneous and double-layered models of the subsurface (see [19] for details).

5.5.1 Testing Models for Regions with Brightest Emission of Neutrons

For the sake of simplicity, we may start the neutron data analysis by using the depth-homogeneous model of the subsurface layer. According to this model, the subsurface is homogeneous along the depth and each unit of mass contains a part ζ_{hom} of water and a part $(1 - \zeta_{\text{hom}})$ of a soil with 50:50 fraction of sand and stones, which have the abundance of major elements according to the Pathfinder composition [10]. The signals S_{SD} , S_{MD} , S_{LD} and $S_{\text{SC/INN}}$ from 4 sensors of HEND are used for testing this model (see Section 5.3). The Pearson criterion is used to test the model by observational data

$$S(P_j) = \sum_{i} \left(\frac{C_i - M_i(P_j)}{\sigma_i} \right)^2, \qquad (1)$$

where C_i are counts from different sensors i = 1-4, M_i are the model predictions of these counts, $_i$ are the errors of measurements and P_j are the set of model parameters (only one parameter, ζ_{hom} , for the homogeneous model).

According to direct measurements from Viking 1, Viking 2 and Mars Pathfinder, the content of water in the soil is about 1-3 wt % (e.g. [10]). The composition of soil in Solis Planum is thought to be similar to the composition at the landing sites of these missions because there is no considerable difference between them in the brightness of major gamma-ray lines [20]. One may use Solis Planum as the "reference region" for neutron data deconvolution, assuming that it has equal mass fractions (49 wt %) of sand and stones with Pathfinder composition and 2 wt % of water. Variation of neutron flux over this region could only result either from seasonal changes of the atmosphere or from long-term variations of cosmic rays. Changes in the atmosphere were described by the general circulation model (GCM) [18], and the variation of cosmic rays has been evaluated as a free fitting parameter by direct comparison between the observational data at Solis Planum and the model predictions for fixed composition of the soil.

Using the estimated flux of cosmic rays according to data from Solis Planum as one fixed parameter, the thickness of the atmosphere above the selected region as another fixed parameter, and parameters P_j of the structure of the soil as variable fitting parameters for testing the model, the model counts $M_i(P_j)$ were calculated by standard code MCNPX [21]. Using the homogeneous model of the soil, the best fitting value of parameter $\zeta_{hom}(*)$ could be found by minimization of the function $S(P_j)$ in eq (1). This value could be used as the estimation of water content, provided the best fitting model could be accepted according to the statistics of χ^2_3 . However, if the minimum of function $S(P_j)$ is too large for consistency with the statistics of χ^2_3 , the tested model should be rejected, and the best fitting parameter $\zeta_{hom}(*)$ for this model can not be used as an estimation of the water content supported by observations. For verifying the algorithm of the neutron data deconvolution, we used the data for North Hellas and for the Argyre basin, which have the same fluxes of neutrons as Solis Planum (see Fig. 5.8). One may expect that the estimated content of water should be similar to the value of 2 wt % postulated for the "reference region" of Solis Planum. Indeed, the water content was found to be 1.6 wt % for Argyre and 2.2 wt % for North Hellas.

5.5.2 Testing Models for High-Latitude Regions of Permafrost

The homogeneous subsurface model was tested for the northern region of depression of neutron emission at high latitudes (Fig. 5.8). The HEND data for season intervals L_s =(120–150)° was used for the north because it corresponds to the summer surface free of seasonal deposit of CO₂. It was found that the homogeneous model has rather high acceptance probabilities for the latitude belts of the northern region (Table 5.1). We believe that a more complex model of the subsurface is not necessary for the northern permafrost region. The estimated contents of water ice correspond to 44, 25 and 13 wt % for the Northern Polar Region (> 80°N), for the Northern High Latitude Belt (70–80°N) and for the Northern Boundary Belt (60–70°N), respectively. For the spot of northern absolute minimum of neutron emission, the best fitting parameter of water content is about 53 wt % (Table 5.1).

To build the map of water contents, the northern permafrost region was divided into 74 overlapping surface elements (pixels). The pixel sizes approximately correspond to the horizontal resolution of HEND mapping from the orbit. We found the sample of the best fitting parameters of the water ice content $\zeta_{hom}(*)$ for these pixels according to the homogeneous model. The distribution of minimum values $S_{min}(\zeta_{hom}^{(*)})$ of eq (1) for these pixels agrees with the distribution curve for random variable χ^2_3 (Fig. 5.9). The map of water content of the northern region was created by smoothing values $\zeta_{hom}(*)$ for 74 pixels by a filter of 5° degrees (Fig. 5.10). As expected, the largest content of water ice of about 53 wt % is observed in the spot of the absolute minimum of neutron emission, which is at the beginning of the ice canyon Chasma Boreale.

Name of latitude belts and seasons (L_s) of data accumulation	Longitude latitude	Average water content (homogeneo us model)	Acceptance probability (homoge- neous model)	Average water ice content in the bottom layer and thickness of the dry upper layer (double- layered model)	Acceptance probability (double- layered model)
Northern polar region 120–150°	0–360°E > 80°N	44.1 %	0.6		
Northern high latitude belt 120–150°	0–360°E 70–80°N	24.8 %	0.4		
Northern boundary belt 120–150°	0–360°E 60–70°N	12.5 %	0.7		
North. spot of abs. min. of neutron emission 120–150°	24–28°E 86–90°N	53 %	0.8		
Southern polar region 330–360°	0–360°E > 80°S	22.7 %	0.004	55.0 % 16 g cm ⁻²	0.26
Southern high latitude belt 330–360°	0–360°E 70–80°S	19.5 %	0.03	54.0 % 19.2 g cm ⁻²	0.41
Southern boundary belt 330–360°	0–360°E 60–70°S	11.2%	0.07	25.3 % 22.4 g cm ⁻²	0.72
South. spot of abs. min. of neutron emission 330–360°	220– 224°E 78–82°S	25 %	0.02	55.0 % 16.0 g cm ⁻²	0.08

Table 5.1 Estimations of average water ice content in the polar regions of Mars.

One may conclude [19] that the northern region of neutron depression could be identified as the *northern permafrost region* (NPR) with a high content of water ice.

We may suggest the level of 10 wt % of water ice as the boundary of NPR. In the eastern hemisphere (0–180°E) the level of 10 wt % water ice goes along the latitude of about 60°N (Figs. 5.8 and 5.10). In the sector 210–220°E the boundary of NPR is at the latitude of 45°N (Fig. 5.8). In this sector a large area with a very high content of water ice (about 35–40 wt %) was found, which lies outward from the north pole at latitudes 65–75°N.

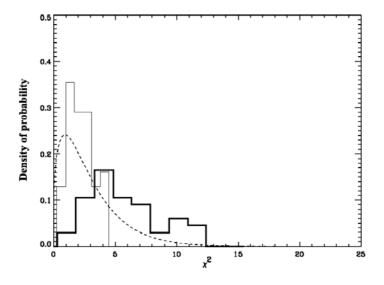


Fig. 5.9 Distribution of minimization values of eq (1) for surface elements of NPR (thin line) and SPR (thick line). The dashed line corresponds to the distribution of random variable χ^2_{3} .

In the second part $(270-360^{\circ}\text{E})$ of the western hemisphere the boundary level of NPR goes up, and it touches the latitude of 75°N in the sector 310-330°E (Figs. 5.8 and 5.10). The estimated content of water ice in the surroundings $(320^{\circ}\text{E}, 70^{\circ}\text{N})$ is less than 10 wt %. The reason for the difference of about 25–20 wt % of water ice content between two areas in the western part of the northern permafrost at longitudes 210–220°E and 310–330°E along the latitude of 70°N is not clear. These two areas have rather different elevations: the first area with a higher content of water ice has a higher elevation. However, there is no clear correspondence between the content of water ice and the elevation for the western segment of NPR of Mars (Fig. 5.11).

We believe that the map (Fig. 5.10) represents the real distribution of subsurface water ice. It is very similar to the map of water content based on independent measurements by the Neutron Spectrometer [22]. This map could be used for a comparison with other sets of data about surface relief, about surface geochemistry and with future data of radio sounding of the shallow subsurface.

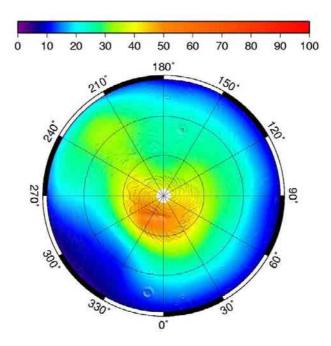


Fig. 5.10 Map of water ice content (in wt %) for the NPR northward of 60°N according to HEND data deconvolution for the homogeneous model [19]. The coordinates shown are east longitudes.

On the contrary, testing of the homogeneous model for latitude belts of the southern permafrost region has not been successful (Table 5.1). We used HEND data for season interval $L_s = (330 - 360)^\circ$ because it corresponds to the summer surface free of seasonal deposit of CO₂. It was found that for all 4 tested cases the minima of eq (1) were too large for acceptance of the model: the probabilities of acceptance are rather small. However, one could guess that the homogeneous model does not work quite well for the latitude belts as a whole because there is a large spread of the water ice contents at different surface elements along the belts. The subsurface could be homogeneous from the depth up to the surface at each surface element, but it could be non-homogeneous over the entire belt. To study this possibility, the homogeneous model was tested for each of the 98 individual surface elements of the SPR (southern permafrost region). The distribution of minimum values $S_{\min}(\zeta_{hom}^{(*)})$ of testing function (1) is shown in Fig. 5.9. It should be observed that this distribution is very different from the reference curve for distribution of χ^2 , provided the differences between observed counts C_i and predicted values M_i arise due to statistical fluctuations. Thus, the model of the homogeneous subsurface should be rejected for the southern permafrost region both for latitude-averaged data and for the sample of 74 surface elements over the entire region.

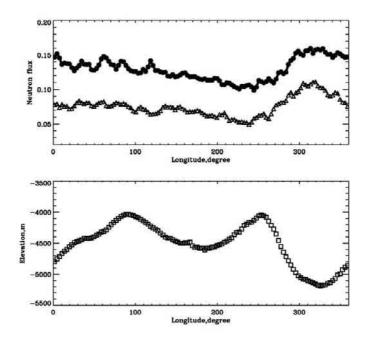


Fig. 5.11 The observation of epithermal neutron flux and surface elevation within the 65–75°N latitude belt. The upper graph contains the dependency of neutron flux from longitude for late northern winter (black dots) and for early northern summer (triangles). The bottom graph presents the dependency of elevation versus east longitude.

The next level of complexity of the model of the subsurface corresponds to the model of the double-layered structure of the subsurface [19]. According to this model, the "dry" layer at the top is assumed to have a variable column density h_{up} but fixed composition of 98 wt % of soil (49 wt % of sand and 49 wt % of stones with the Pathfinder composition [10]) and 2 wt % of water. The bottom "wet" layer has variable fractions of water ice ζ_{down} % and soil $(1 - \zeta_{down})$ % . Again, the soil has 50 % sand and 50 % stones with the Pathfinder composition. Therefore, the double-layered model has two free parameters, h_{up} (g cm⁻²) and ζ_{down} (wt %).

Five observational signals from HEND $S_{\rm SD}$, $S_{\rm MD}$, $S_{\rm LD}$, $S_{\rm SC/IN/N}(0.85-2.5 \text{ MeV})$ and $S_{\rm SC/IN/N}(>2.5 \text{ MeV})$ were used to test the double-layered model: three signals from ³He counters in SD, MD and LD, and two signals from scintillator SC/IN sensor: counts at the energy ranges 0.85-2.5 MeV and above 2.5 MeV. Using five independent signals for testing the model with two free parameters, one may compare statistics of the minimal values $S_{\min}(h_{up}^{(*)}, \zeta_{down}^{(*)})$ of eq (1) with the same distribution of random variable χ^2_3 as for the testing of the homogeneous model (Fig. 5.9).

The average data for southern latitude belts support the double-layered model of the subsurface (Table 5.1). The best fitting values of free parameters correspond to rather high acceptance probability for this model. The column density of the top dry layer is about 16–25 g cm⁻² for all three belts. The average content of water ice is about 55 wt % south of 70°S and decreases down to 25 wt % at the Southern Boundary Belt (60–70°S). There is no noticeable difference between the water ice content at the southern spot of absolute minimum (about 55 wt %) and the average content south of 70°S.

The statistics of the best fitting parameters $h_{up}^{(*)}(g \text{ cm}^{-2})$ and $\zeta_{down}^{(*)}(wt \%)$ was estimated for 98 surface elements of SPR. The double-layered model works rather well, the distribution of minima $S_{min}(h_{up}^{(*)}, \zeta_{down}^{(*)})$ of eq (1) agrees with the statistics for the random variable χ^2_3 (Fig. 5.9). The smoothed surface distributions of the best fitting values $h_{up}^{(*)}(g \text{ cm}^{-2})$ and $\zeta_{down}^{(*)}$ (wt %) represent two maps for the SPR for water ice content and for the surface density of the dry covering layer, respectively (Figs. 5.12 and 5.13).

One may conclude [18] that the southern region of neutron depression could be identified as the *southern permafrost region* (SPR) with a high content of water ice. This region has a double-layered structure of the subsurface: the dry layer at the top covers the layer with a high content of water ice at the bottom. The column density of the top layer is about $16-22 \text{ g cm}^{-2}$. Assuming a soil bulk density of about 1.6 g cm⁻³, one may estimate that the thickness of the dry layer of SPR is about 14 cm. For SPR the boundary level of 10 wt % water ice approximately follows the latitude of 65°S. In the longitude sector (60–150°E) the boundary goes down to moderate latitudes below 60°S and follows the southern edge of the Hellas basin, but surprisingly the permafrost does not come into the basin itself (Figs. 5.8 and 5.12).

In the longitude sector $(300-360^{\circ}E)$ the 50 wt % level of high water ice content goes up to the latitude 82°S. On the contrary, in the symmetrically opposite longitude sector $(120-180^{\circ}E)$ the level of 50 wt % goes down to the latitude of about 68°S. One may note that the 50 wt % contour of water ice and the contour of the southern residual polar cap are shifted in respect to each other along the meridians 150°/330°E (Fig. 5.12). Generally speaking, the double-layered model of the subsurface is not applicable to the area of the residual polar cap because the substance of the cap is a mixture of carbon dioxide and water ice instead of the mixture of soil and water ice assumed in the model. The analysis of the composition of the southern residual polar cap will be presented elsewhere. However, the present model allows us to make some qualitative conclusions about the southern residual cap.

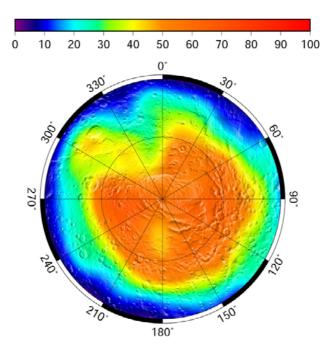


Fig. 5.12 Map of water ice content (in wt %) for the SPR southward of 70°S according to HEND data deconvolution for the double-layered model [19]. The coordinates shown are east longitudes.

According to the map based on the double-layered model (Figs. 5.12 and 5.13), the southern residual cap could be divided into two parts: one part lies north of the latitude 80°S and the other one lies south of it. The poleward part of the permanent cap has about the same content of water ice (> 50 wt %) as the surrounding frost-free area of SPR, and it is covered by a top layer of dry substance (CO₂?) with a thickness of about 17 g cm⁻². This top dry layer of the residual polar cap has about the same thickness as the top layer of dry soil at high latitudes outside the cap (Fig. 5.13). A part of the residual cap south of 80°S also has a high but somewhat smaller content of water ice (about 30–40 wt %) and this layer is also covered by a layer of some dry material (CO₂?) with a smaller thickness of about 10 g cm⁻² (Fig. 5.13).

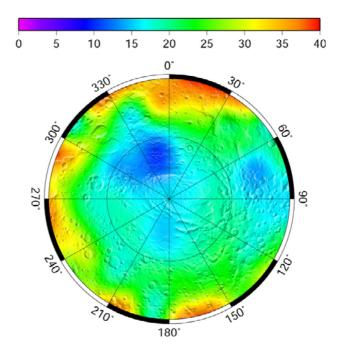


Fig. 5.13 Map of the column density (in g cm⁻²) of the top dry layer above the water-rich layer in the southern permafrost region according to HEND data deconvolution for the double-layered model [19].

The high content of water ice in the southern residual cap is also well-proved by the seasonal variation of neutrons. Indeed, during winter the residual cap is covered by a thick seasonal deposition layer of atmospheric CO_2 . The winter layer contains a small fraction of water, and its accumulation leads to a significant increase of epithermal neutron flux from the surface [15] (Fig. 5.14). Therefore, the southern residual cap as well as the northern residual cap should contain a large fraction of water ice of about 50 wt % according to the present estimations [19]. (See also an independent discussion of polar caps in Chap. 6 by Hvidberg.)

Both permafrost regions NPR and SPR have about the same maximal water ice content of about 50–60 wt %. The ice is lighter than the soil, and this fraction of mass corresponds to a volume fraction of about 60–70 %. In the case of terrestrial permafrost, water ice fills the pore volumes between the grains of the soil, and this volume is about 30 %. The estimations for Martian permafrost indicate that water ice is the dominating material of the subsurface. The regions on Mars with high content of water (> 50 wt %) would be more appropriately named the "frozen oceans of dirty water ice". One has to explain the origin of "frozen oceans" around poles down to latitudes of about 60°. Direct deposition of water ice could be the main process of formation of the subsurface. Sand and stones are the components of the subsurface of these regions, and were delivered either by dust storms or by excavation by asteroids.

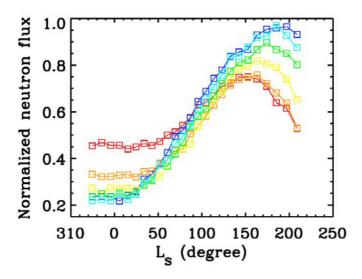


Fig. 5.14 Increase of the flux of epithermal neutrons in the south during the transition from summer ($L_s = 330-360^\circ$) to winter ($L_s = 90-180^\circ$). The flux of neutrons is normalized by the maximal flux for Solis Planum. Fluxes for southern latitude belts 85–90°, 80–85°, 75–80°, 70–75°, 65–70° and 60–65° are shown by dark blue, bright blue, green, yellow, orange and red squares, respectively.

5.5.3 Testing Models for Neutron Depression Regions at Moderate Latitudes

There are two regions at low latitudes on Mars with decreased emission of epithermal neutrons (Fig. 5.8): Arabia and Memnonia. However, one may note that this depression anomaly is not observed on the map for high energy neutrons (Fig. 5.8). The Arabia region is sufficiently large, and it could be divided into the North Arabia and South Arabia regions (Table 5.2). Also, we may select one more particular region, South Hellas, which lies at the boundary of SPR and which could be the best reservoir for accumulation of shallow water at moderate latitudes. All four regions have much smaller emissivity of epithermal neutrons in comparison with Solis Planum. Therefore, the soil in these regions has to contain more water than the 2 wt % assumed for the Solis Planum soil. We used HEND data for a large seasonal interval $L_{\rm s} = (0-150)^{\circ}$ because conditions of the atmosphere remain stable during this interval.

To estimate the content of water in the four regions we may use both models [19]: the homogeneous model of the subsurface with variable content of water ζ_{hom} (wt %) along the depth and the double-layered model with two variable parameters: the thickness of the upper dry layer h_{up} (g cm⁻²) and the content of water in the bottom wet layer ζ_{down} (wt %). For both models we use 5 independent

signals of HEND measurements (S_{SD} , S_{MD} , S_{LD} , $S_{SC/IN/N}$ (0.85–2.5 MeV) and $S_{SC/IN/N}$ (> 2.5 MeV)). (The signal $S_{SC/IN/N}$ from scintillator SC/IN was separated into two signals at energy ranges (0.85–2.5) MeV and above 2.5 MeV.) The best fitting values of parameters for both models are presented in Table 5.2.

The homogeneous model gives similar estimations of water content (5.0–5.2 wt %) for all four regions. For the double-layered model the best fitting values of water content in the bottom layer $\zeta_{down}^{(*)}$ are 9–10 wt %, which is about twice as high as the estimation for the homogeneous model. The thickness of the top dry layer is similar for all four regions studied (26–32 g cm⁻²).

The acceptance probabilites for the homogeneous model are rather small (< 0.15), which means that this model is not well supported by the observations. On the other hand, the observational data clearly support the double-layered model for all four tested regions at moderate latitudes (Table 5.2). The best fitting parameters for the layered model may be used as reliable estimations of parameters of the subsurface $h_{up}^{(*)} = 26-32$ g cm⁻² and $\zeta_{down}^{(*)} = 9-10$ wt % for all four tested regions. For a soil density of 1.6 g cm⁻³ this column density corresponds to a thickness of 16–20 cm. The double-layered structure of the subsurface of Arabia and Mamnonia is illustrated by the maps of epithermal and high energy neutrons. The first map (Fig. 5.8 top) for epithermal neutrons represents a content of water in the layer of about 1–2 m, and this map has well-pronounced depression. The second map (Fig. 5.8 bottom) for high energy neutrons represents the top layer of the subsurface of about 20 cm thickness, and it may not manifest any depression of neutron emission.

Names of regions and seasons (L_s) of data accumulation	Longitude latitude	Estimation of water content (homoge- neous model)	Acceptance probability (homogeneous model)	Estimation of water content and thickness of dry layer (double- layered model)	Acceptance probability (double- layered model)
South Hellas	50–98°E	5.0%	0.1	9.0%	0.2
0–150°	47–53°S			26.0 g cm^{-2}	
North Arabia	0-45°E	5.1%	0.15	9.0%	0.7
0–150°	0-30°S			26.0 g cm^{-2}	
South Arabia	0-45°E	5.2%	0.02	10.0%	0.25
0–150°	0-20°S			32.0 g cm^{-2}	
Memnonia	180-	5.1%	0.1	9.0%	0.7
0–150°	200°E			29.0 g cm^{-2}	
	0-25°S				

Table 5.2 Estimated content of water in regions with depression of epithermal neutrons at moderate latitudes.

The area of Arabia is sufficiently large in comparison with the scale of horizontal resolution for orbital measurements. It was divided into a large number

of surface elements with a size of $2^{\circ} \times 2^{\circ}$ (Fig. 5.15), whose data were individually tested by the double-layered model. For all surface elements the double-layered model is found to agree with the observational data, and this model provides a pair of best fitting parameters $h_{up}^{(\circ)}$ and $\zeta_{down}^{(\circ)}$ of the subsurface composition. One particular surface element with coordinates (30°E, 10°N) has the smallest emission of epithermal neutrons (Fig. 5.15), and the best fitting parameters of the subsurface for this element correspond to a content of water of 16 wt % under the dry layer with a thickness of 29 g cm⁻². The estimation of the dry layer is consistent with the average value found for the entire North Arabia (Table 5.2). Therefore, the high content of water at this surface element is not produced by uncertainties of model-dependent data deconvolution. The value of 16 wt % could correspond to the real minimum of epithermal neutron flux in Arabia. We may name this spot the "Arabian water-rich spot" (AWRS) [19]. It is located around the old eroded crater between the famous craters Cassini and Schiaparelli (Fig. 5.15).

One has take to into account that the water content of 16 wt % in AWRS has been estimated using the simplest numerical model of Martian neutron emission, when the same composition of subsurface is attributed to the entire planet. This approach provides the lowest limit of water content in AWRS because the data accumulated in these surface elements are also contributed by surrounding surface elements with higher fluxes of neutrons. One has to use more sophisticated methods of inverse projection of orbital data to the surface elements to get a more accurate estimation of water contents of AWRS. However, even in the present initial stage of the neutron data analysis one may draw reliable conclusions that the spot at (30°E, 10°N) corresponds to the maximal water content in Arabia, and the corresponding value of 16 wt % is the lowest limit for the real amount in this spot.

This value of 16 wt % could be compared with the theory of water forms in the Martian soil (see Chaps. 4, 7 and 8 for a review). One has to check the first alternative as to whether this content could be associated with the chemically bound water in the minerals. If so, predictions should be drawn about the abundances of elements, which constitute the water-bearing minerals in AWRS. These predictions could be tested by data from the gamma-ray spectrometer. A scenario of water enrichment for these minerals should be developed to explain the condition of the past history of Mars, when 16 wt % of water molecules were implemented into the minerals of shallow subsurface. If this content would be too high to be associated with the chemically bound water in minerals, a second, alternative model of water ice condensation and preservation should be developed. The value of 16 wt % in AWRS just above the equator is challenging for both alternatives, and this conflict between theory and observation is probably the most important contribution of neutron measurements for present Mars science.

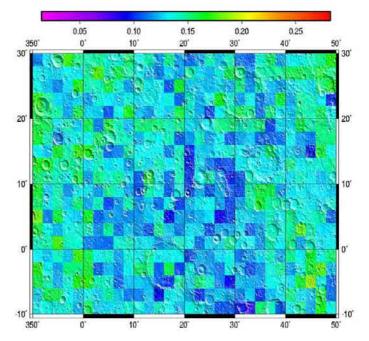


Fig. 5.15 Map of epithermal neutrons (normalized neutron flux) in the Arabia region $(10^{\circ}\text{S}-30^{\circ}\text{N}, 350^{\circ}\text{E}-50^{\circ}\text{E})$ with a surface resolution of $2^{\circ}\times 2^{\circ}$ [19]. The large crater centered at 2.7°S, 16.7°E is the Schiaparelli crater.

5.6 Conclusions from the First Stage of Neutron Mapping and Questions for Further Studies

The analysis of neutron data is presently in the very initial stages: more data should be accumulated, more models could be developed and a better correspondence with other sets of observational data should be established. However, the following initial conclusions could be drawn at present after about one Martian year of neutron mapping. They contain several robust statements about the water distribution on Mars, which could hardly be changed by future studies. However, they also include several model-dependent speculations which reflect the unsolved questions of data analysis and interpretation. It is hoped that they may lead to further studies and the development of new models.

(i) Four types of Martian regions with respect to the content of water in the shallow subsurface

There are four distinguishable types of Martian shallow subsurface, which could be defined according to the estimated water content in the subsurface: (I) **Regions with dry soil**. These regions have a water content of a few wt %. Assuming Pathfinder composition and 50:50 fractions of sand and stones, we assume that the content of water in these regions is about 2 wt %. These regions (Solis Planum, Argyre, etc.) are well seen on the neutron emission map and are shown as red and orange areas (Fig. 5.8).

(II) Northern permafrost region (NPR) with a high content of water ice. There is a very large region around the north pole, which has a very high content of water ice in the subsurface. The subsurface has a homogeneous composition of soil and water ice from the top down to 1-2 m depth and regional variations of water ice vary from about 50 wt % around the pole down to 10 wt % and less at the boundary of NPR. The largest content of water ice (53 wt %) is found at the residual cap. A large water-rich area with a water content of about 40 wt % is located at latitudes around 60°N in the sector 210-240°E (Figs 5.8 and 5.10). Surprisingly, the content of water ice in the residual cap does not differ too much from the content of water in the subsurface around the cap. The contents of water of 44 wt %, 25 wt % and 13 wt % for latitude belts > 80° , 70– 80° and 60° – 70° (Table 5.1) correspond to the volume fractions of water ice of about 56 %, 35 % and 20 %, respectively. Actually, one may speculate that in the northern region of neutron depression we actually see the shallow subsurface of the frozen ocean of dirty water ice, which contains a fraction of ice decreasing from 60 volume % at the pole down to 20 volume % at the boundaries.

One cannot estimate from the neutron data alone how thick the layer of dirty water ice could be. Future radar data on Mars Express and Mars Reconnaissance Orbiter may prove whether this layer is actually the top of a frozen shield with hundreds of meters depth, or this ice shield is only several meters thick. On the other hand, the absence of a dry layer at the top of the frozen ice shield indicates that we may be observing the process of growth of the ice shield in the northern hemisphere, when the sublimation of water to the atmosphere is dominated by condensation of water ice on the surface, either from the seasonal deposition layer or from the atmosphere.

(III) Southern permafrost region (SPR) with a high content of water ice. SPR has a very high content of water like NPR, but it certainly has a double-layered subsurface structure. The layer with water ice is covered by a dry layer at the top with a thickness of about 20 g cm⁻². Neutron data allow us to observe the waterrich layer through the dry layer. There is a very large area of SPR around the south pole where the volume of ice in the ice-rich layer is > 60 wt %. This volume is much larger than the porosity in the regolith (about 30 %).

Therefore, as in SPR water ice is the main substance of the subsurface, but in this case it is covered by a dry layer of soil. The SPR could be also associated with the ice shield of frozen water, but this ice formed a long time ago. Dust storms and water sublimation created the dry layer at the top of the water ice shield, and presently this dry blanket of regolith isolates the water ice from the atmosphere. The relief and craterization of the surface of the southern permafrost region could be explained by the presence of frozen water layer in the shallow subsurface. This surface is very similar to the surface of Mars at moderate latitudes. Also, there is no evident difference in the surface structure southward and northward from the boundary of SPR (Fig. 5.8).

(IV) **Regions with water-rich soil at moderate latitudes.** There are several regions on Mars at equatorial latitudes (Arabia, Memnonia) which have a water-rich layer with about 10 wt % water covered by a dry layer of soil of about 30 g $\rm cm^{-2}$ thickness. The existence of such regions on Mars is probably the largest surprise of the neutron mapping (Figs. 5.8 and 5.14). Indeed, at the present time the water-rich layer of sublimation (desiccation), therefore they could only have been formed in the past history of Mars.

As the first option, one may suppose that Arabia and Memnonia were two opposite Martian poles at the past [23], and their surfaces were covered by caps of water ice and moreover the present poles are covered by the residual caps. However, another critical question arises in this case about the preservation of free water ice at equatorial latitudes below 30 g cm⁻² of dry soil. The contour of the water-rich region of Arabia is known to be quite close to the contour of the area with very low thermal conductivity. The possibility of preservation of water ice in the shallow subsurface for equatorial regions under the present climatic conditions due to low thermal conductivity of the soil has been suggested [24].

Secondly, one may suppose that at the present moment the states of Arabia and Memnonia are not stable [31]. Mars' climate change from cold to hot could take place, the water could sublime from the subsurface, and the thickness of the dry layer at the top could be increasing at these two regions right now. The main problem of this scenario is to explain the creation of the original stage of Arabia and Memnonia before the climate change started, when the layer with a high content of water was formed in the shallow subsurface. The last ice age of Mars probably was 10^5-10^6 years ago [25], and one has to explain the creation of icerich regions at equatorial belts at that time. Also, the rate of sublimation after the ice age must be sufficiently high to remove the water form the top layer of about 30 g cm⁻² thickness.

Thirdly, one may suspect that the high content of water in the subsurfaces of Arabia and Memnonia resulted from stationary global atmospheric waves, which presently produce preferential deposition of dust and water in these two regions [26]. However, the very top surface of these regions is dry, so present atmospheric precipitation seems to be totally disconnected from the water-rich layer below 30 g cm⁻² of dry soil.

As a whole, the origin of water in Arabia and Memnonia is not clear, and further studies based on experimental multi-instrumental data analysis and on theoretical investigations are necessary.

(ii) Three types of ground substance with respect to water content

There are three forms of water which could be associated with the water-rich layers of these regions: physically adsorbed water on the surface of regolith grains, chemically bound water in minerals and free water ice.

Physically adsorbed water consists of unfrozen layers of water molecules on the surface of soil grains. This water could propagate down to the subsurface by condensation from the atmosphere, and it could leak back, when the temperature and vapor pressure are appropriate for dehydration. There are different estimations

of the possible content of adsorbed water in the soil, from < 1 wt % up to 20 wt % in some extreme cases (see Chaps. 4 and 8).

Chemically bound water is associated with the hydration of minerals, whereas water molecules are implemented into the chemical structure of the minerals. The content of bound water scales from a few wt % up to about 10 wt % (see Chap. 4). The major difference between adsorped and bound water is the temperature of dehydration (about 200°C and > 300°C, respectively).

The third form of water is ice. Again, one could distinguish between two cases of water ice presence in the regolith: if the content of water ice is below 20 wt %, the volume fraction of ice is below 30 %, and it could be associated with the porosity volume between grains of the soil. This ice could be accumulated in the regolith from the atmosphere, provided that the temperature is low and water vapor pressure is high enough for condensation. If the content of water ice were to be higher than 20 wt %, the fraction of ice-filled volume would exceed the porosity volume of the dry regolith. The layer of the subsurface with such a high content of water ice cannot be created by condensation of water into the already existing regolith. One may assume in this case that the subsurface was formed by some continuous process of deposition of water ice and sand grains, whereas the ratio between ice and soil resulted from the difference in the deposition rate on the surface.

According to the presented estimations of water content in different regions of Mars (Section 5.5), there are three well-distinguishable types of subsurface depending on the water presence therein. The first case corresponds to "dry substance" with about 2 wt % water. This case is observed in regions with maximal emission of high energy neutrons (regions type (I): Solis Planum, Argyre, etc.). This case also corresponds to the composition of the top dry layer of regions with a double-layered structure (regions (III) and (IV): SPR, Arabia, Memnonia, etc.). One may guess that the "dry substance" interacts with the present atmosphere of Mars, and the content of water corresponds to the present equilibrium of condensation/sublimation processes over the year. Probably water of "dry substance" has the form of adsorbed water, but one cannot exclude the contribution of chemically bound water as well.

The second case corresponds to "wet substance" with a water content of about 10–20 wt %. This case corresponds to the bottom layer of the double-layered model of the shallow subsurface at moderate latitudes (regions (IV): Arabia, Memnonia, etc.). Presently we cannot decide whether the water of "wet substance" is associated with adsorbed water or with bound water. The content itself is not sufficient to enable us to choose between these forms. One has to use either climate or geology evolution scenarios to determine the form of water present in the "wet subsurface" at moderate latitudes.

Finally, the third case corresponds to the "ice-rich subsurface". This case corresponds to the NPR and to the bottom layer of SPR (regions (I) and (II)). Water in this case is in the form of ice. The origin of this type of subsurface could be different, depending on whether the ice content is higher or lower than 20 wt % (see above). The choice of condensation or deposition formation processes of the "ice-rich subsurface" could be based on a comprehensive scenario of Mars' climate evolution. Moreover, it could be that different parts of NPR and SPR were

formed by different processes and surface measurements of neutrons with kmscale resolution would be necessary to resolve the difference between them.

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5.7 References

- 1 Masarik J, Reedy RC (1996) Gamma ray production and transport in Mars. J. Geophys. Res. 101(E8): 18891-18912
- 2 Boynton WV, Feldman WC, Mitrofanov IG; Evans LG, Reedy RC, Squyres SW, Starr R, Trombka JI, d'Uston C, Arnold JR, Englert PAJ, Metzger AE, Wänke H, Brückner J, Drake DM, Shinohara C, Fellows C, Hamara DK, Harshman K, Kerry K, Turner C, Ward M, Barthé H, Fuller KR, Storms SA, Thornton GW, Longmire JL, Litvak ML, Ton'chev AK (2004) The Mars Odyssey Gamma-Ray Spectrometer instrument suite. Space Sci. Rev. 110: 37-83
- 3 Drake DM, Feldman WC, Jakosky BM (1988) Martian neutron leakage spectra. J. Geophys. Res. 93(B6): 6353-6368
- 4 Feldman WC, Boynton WV, Drake DM (1993) Planetary neutron spectroscopy from orbit. In Pieters CM, Englert PAJ (eds) Remote Geochemical Analysis: Elemental and Mineralogical Composition. Cambridge Univ. Press, New York, pp 213-234
- 5 Boynton WV, Feldman WC, Squyres SW, Prettyman T, Brückner J, Evans LG, Reedy RC. Starr R, Arnold JR, Drake DM, Englert PAJ, Metzger AE, Mitrofanov I, Trombka JI, d'Uston C, Wänke H, Gasnault O, Hamara DK, Janes DM, Marcialis RL, Maurice S, Mikheeva I, Taylor GJ, Tokar R, Shinohara C (2002) Distribution of hydrogen in the near-surface of Mars: evidence for subsurface ice deposits. Science 297: 81-85
- 6 Feldman WC, Boynton WV, Tokar RL, Prettyman TH, Gasnault O, Squyres SW, Elphic RC, Lawrence DJ, Lawson SL, Maurice S, McKinney GW, Moore KR, Reedy RC (2002) Global distribution of neutrons from Mars: results from Mars Odyssey. Science 297: 75-78
- 7 Mitrofanov I, Anfimov D, Kozyrev A, Litvak M, Sanin A, Tret'yakov V, Krylov A, Shvetsov V, Boynton W, Shinohara C, Hamara D, Saunders RS (2002) Maps of

subsurface hydrogen from the High-Energy Neutron Detector, Mars Odyssey. Science 297: 78-81

- 8 Mitrofanov IG, Zuber MT, Litvak ML, Boynton WV, Smith DE, Drake D, Hamara D, Kozyrev AS, Sanin AB, Shinohara C, Saunders RS, Tret'yakov V (2003) CO₂ snow depth and subsurface water-ice abundance in the northern hemisphere of Mars. Science 300: 2081-2084
- 9 Mitrofanov IG, Litvak ML, Kozyrev AS, Sanin AB, Tret'yakov VI, Boynton WV, Shinohara C, Hamara D, Saunders S, Drake DM (2003) Search for water in Martian soil using global neutron mapping by the Russian HEND instrument onboard the US 2001 Mars Odyssey spacecraft. Sol. Syst. Res. 37: 366-377 (Astron. Vestnik 37: 400-412)
- 10 Wänke H, Brückner J, Dreibus G, Rieder R, Ryabchikov I (2001) Chemical composition of rocks and soils at the Pathfinder site. Space Sci. Rev. 96: 317-330
- 11 Feldman WC, Lawrence DJ, Elphic RC, Vaniman DT, Thomsen DR, Barraclough BL, Maurice S, Binder AB (2000) Chemical information content of lunar thermal and epithermal neutrons. J. Geophys. Res. 105: 20347-20363
- 12 Smith DE, Zuber MT, Neumann GA (2001) Seasonal variations of snow depth on Mars. Science 294: 2141-2146
- 13 Smith DE, Zuber MT and colleagues (2003) The masses of Mars's seasonal polar icecaps. 3rd Int. Conf. Mars Polar Science. 8063
- 14 Litvak ML, Mitrofanov IG, Kozyrev AS, Sanin AB, Tret'yakov VI, Boynton WV, Shinohara C, Hamara D, Saunders S, Drake D, Zuber MT, Smith DE (2003) Seasonal neutron-flux variations in the polar caps of Mars as revealed by the Russian HEND instrument onboard the NASA 2001 Mars Odyssey spacecraft. Sol. Syst. Res. 37: 378-386 (Astron. Vestnik 37: 413-422)
- 15 Litvak ML and colleagues (2004) Seasonal deposition of carbon dioxide on the surface of Mars according to neutron data by HEND instrument onboard Mars Odyssey. Sol. Syst. Res. (Astron. Vestnik): in press
- 16 Litvak ML and colleagues (2004) Comparison between polar regions of Mars from HEND/Odyssey data. Icarus: in press
- 17 Smith DE and colleagues (1999) The global topography of Mars and implications for surface evolution. Science 284: 1495
- 18 Haberle RM, Pollack JB, Barnes JR, Zurek RW, Leovy CB, Murphy JR, Lee H, Schaeffer J (1993) Mars atmospheric dynamics as simulated by the NASA Ames general circulation model. I - The zonal-mean circulation. J. Geophys. Res. 98(E2): 3093-3123
- 19 Mitrofanov IG and colleagues (2004) Estimation on water content in the subsurface of Mars from neutron measurements by HEND instrument onboard "Mars Odyssey". Sol. Syst. Res. (Astron. Vestnik): in press
- 20 Boynton WV, Taylor GJ, Hamara D, Kerry K, Janes D, Keller J, Feldman W, Prettyman T, Reedy R, Brückner J, Wänke H, Evans L, Starr R, Squyres S, arunatillake S, Gasnault O (2003) Compositional diversity of the Martian crust: preliminary data from the Mars Odyssey Gamma-Ray Spectrometer. 34th Lunar Planet. Sci. Conf. 2108
- 21 Waters LS (1999) MCNPX User's Guide (document LA-UR-99-6058). Los Alamos National Laboratory
- 22 Feldman WC; Prettyman TH, Boynton WV, Squyres SW, Bish DL, Elphic RC, Funsten HO, Lawrence DJ, Maurice S, Moore KR, Tokar RL, Vaniman DT (2003)

The global distribution of near-surface hydrogen on mars. Sixth Int'l Conf. Mars: abstr. 3218

- 23 Schultz PH, Lutz AB (1988) Polar wandering on Mars. Icarus 73: 91-141
- 24 Paige DA (1992) The thermal stability of near-surface ground ice on Mars. Nature 356: 43-45
- 25 Head JW, Mustard JF, Kreslavksy MA, Milliken RE, Marchant DR (2003) Recent ice ages on Mars. Nature 426: 797-802
- 26 Basilevsky AT, Rodin AV, Kozyrev AS, Mitrofanov IG, Neukum G, Werner SC, Head JW III, Boynton W, Saunders RS (2004) Mars: the Terra Arabia low epithermal neutron flux anomaly. 35th Lunar Planet. Sci. Conf. 1091

6 Polar Caps

Christine S. Hvidberg

The permanent polar caps of Mars constitute the largest known reservoirs of H_2O on the planet. The permanent caps are distinguished from the seasonal snow covers that have been known for centuries. The seasonal snow consists of CO_2 that condenses out of the atmosphere in the winter hemisphere [8]. During summer, the seasonal snow cover gradually evaporates, and the permanent cap is exposed. The permanent polar caps are recognisable as topographic domes rising about 3 km above the surrounding terrain. They have an extent of around 1000 km in the north and 400-800 km in the south. They consist of layers of H_2O , dust and CO_2 that have been deposited through millions of years. Bright white areas indicate a currently active interaction with the Martian climate system. Dark areas reveal an extensive layering thought to preserve a record of climate changes on Mars. The caps may contain preserved samples of biological origin, and geological indications of meltwater may be a clue to subsurface environments where life might exist. The polar regions are thus particularly interesting in relation to the search for life on Mars.

This chapter gives an overview of the current understanding of the permanent Martian polar caps from a geophysical/glaciological perspective. Analogies to terrestrial ice sheets are emphasised.

6.1 Appearance and Geological Setting

The white, residual polar ice is immediately visible on summer images of the Martian polar regions (Figs. 6.1 and 6.2). The white part of the north polar cap is centred near the pole with a diameter of around 800 km. The white part of the south polar cap is substantially smaller; it is centred 200 km from the pole with a diameter of around 300 km. The polar caps, however, are larger than indicated by the white residual ice. High-resolution topography data from Mars Orbiter Laser Altimeter (MOLA) [50, 43] show that both polar caps rise to about 3 km above the surrounding terrain (Figs. 6.1 and 6.2). The polar caps are distinguished from the surroundings not only by the topographic relief, but also by the surface, which is smoother than anywhere else on the planet. High-resolution images of scarps in the polar regions reveal an extensive layering, the so-called polar layered deposits. Here, the term polar cap is used to denote the domes of perennial polar ice and polar layered deposits. In the north, the polar residual ice and layered terrain are co-extensive, and the north polar cap occupies a region of around 1000 km around the pole. In the south, the polar layered deposits occupy an area with a diameter of around 1500 km, which is substantially larger than the area covered by the white residual polar ice. The south polar cap occupies an area with a diameter of 400-800 km.

C.S. Hvidberg, Polar Caps. In: *Water on Mars and Life*, Tetsuya Tokano (ed.), Adv. Astrobiol. Biogeophys., pp. 129–152 (2005) springerlink.com © Springer-Verlag Berlin Heidelberg 2005 A distinctive feature of the north polar cap is a pattern of troughs and scarps spiralling outward in a counterclockwise direction from the pole. The troughs are up to 1 km deep, 5–15 km wide, hundreds of kilometres long, and with a spacing of around 50 km between neighbouring troughs. The surface appears white along horizontal and north-facing surfaces, while the steep $(10^{\circ}-15^{\circ})$ south-facing scarps are dark and expose numerous horizontal layers with thickness down to the limit of the resolution. Sometimes, individual layers can be traced within a single trough over hundreds of km (Fig. 6.3). There are several large reentrants (deep valleys opening up at the margin of the cap) on the north polar cap. The largest is Chasma Boreale, which is around 500 km long and up to 100 km wide, and characterised by its steep sides. It almost bisects the cap and separates a large ridge from the central part of the cap.

The north polar cap is centred at the pole in the northern hemisphere plains. They are smooth with a low topographic relief thought to be related to extensive resurfacing by volcanism, followed by a possible ancient ocean floor [21, 46]. The cap is located near the lowest point of the plains with an altitude at the margin of around -5000 m. The terrain slopes downward toward the cap, and indicate an isostatic adjustment of the base due to the weight of the cap. The maximum depression of the base has been estimated to be 0.4-1.2 km [50, 29], leading to an estimated volume of the cap of $1.2 \pm 0.2 \times 10^6$ km³ [50]. This is about half the volume of the Greenland Ice Sheet.

Similar to the north polar cap, a notable feature of the south polar cap is the pattern of scarps and troughs that spiral outward from the centre, here in a clockwise direction. As in the north, an extensive layering is exposed in the dark scarps. Also several reentrants are found within the south polar cap. The largest is Chasma Australe, which has similar dimensions and steep walls to Chasma Boreale in the north. Some of the characteristics differ from those of Chasma Boreale. The base of the reentrant shows, for example, exceptionally little sign of erosion [19].

The south polar cap is located in the southern highlands, which have a much more complex topography than the smooth northern plains. The heavily cratered terrain has been eroded by various processes [46]. The altitude of the surroundings near the margin of the cap is around 1500 m, i.e. 6.5 km higher than the north polar cap. The south polar cap is partly located in the Prometheus Basin, a large, eroded impact basin. The dome of the cap is centred at a location along the rim of Prometheus Basin, displaced around 200 km from the pole.

Both polar caps have only a few large impact craters. In the north, no impact crater larger than 300 m has been identified. This points to a geologically very young surface age of less than about 10^5 years [22]. The absence of large craters may indicate a dynamic interaction between the cap and the atmosphere involving deposition and sublimation processes, and possibly ice flow. If so, the cap could have formed originally millions of years ago, despite the very young age predicted by the crater counts. In the south, approximately 15 craters with diameters larger than 800 m indicate a geological surface age of 7–17 million years, depending on the recent cratering flux [22]. The south polar cap is thus up to two orders of magnitude older than the northern cap. The apparent age difference between north

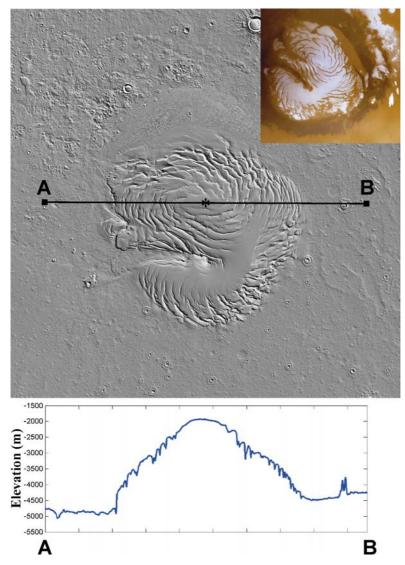


Fig. 6.1 Shaded relief map of the polar region north of 72°N (the pole is marked by an asterisk). The map is constructed from Mars Orbiter Laser Altimeter (MOLA) data (image credit: MOLA science team/NASA GSFC). Inset: Mars Orbiter Camera (MOC) summer image of the north polar cap (image ref.: PIA02800, NASA/Planetary Photojournal). Bottom: MOLA topographic profile from A to B (approximate distance 1800 km).

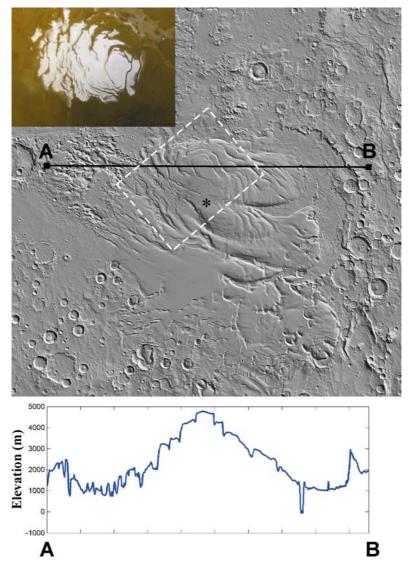


Fig. 6.2 Shaded relief map of the polar region south of 72°S (the pole is marked by an asterisk). The map is constructed from Mars Orbiter Laser Altimeter (MOLA) data (image credit: MOLA science team/NASA GSFC). Inset: Mars Orbiter Camera (MOC) summer image of the south polar cap (image ref.: PIA02393, NASA/Planetary Photojournal). The dashed white line indicates the location of the MOC image. Bottom: MOLA topographic profile from A to B (approximate distance 1800 km).

and south could also indicate a less active interaction between the south polar cap and the atmosphere compared to the north, or a stiff and slowly flowing cap. In fact, colder surface temperatures in the southern highlands dictate that the possible flow in the south would be slower than that in the north. It is therefore premature to discuss age differences between north and south based on the crater chronology solely, without understanding the dynamical processes that are continuously forming the polar caps.

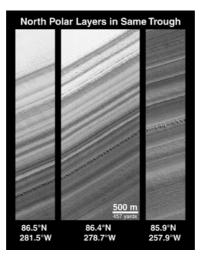


Fig. 6.3 Layered deposits of the north polar cap. Three Mars Orbiter Camera images from the same scarp show the fine-scaled layering, visible down to the limit of the resolution (image ref.: PIA02070, NASA/Planetary Photojournal). The distance between the left and right images is around 100 km.

6.2 Composition

While it has been known for decades that the seasonal caps are composed of CO_2 frost, the composition of the permanent polar caps remained uncertain for much longer. It is now widely accepted that their major constituent is water ice. In addition, the caps contain unknown amounts of dust and possibly layers of solid CO_2 . The evidence came from thermal and spectral observations, and was further consolidated by mapping of subsurface hydrogen by measurements of nuclear emissions from the surface (see Chap. 5 by Mitrofanov).

Thermal mapping of the north polar cap with the Viking Orbiter Infrared Thermal Mapper (IRTM) showed that the summer temperature rises to 205 K, well above the 148 K sublimation temperature of CO_2 [31]. Thus, the seasonal CO₂ cover is presently being completely removed during the northern summer. In

previous climate epochs, however, some CO₂ may have survived the summer, and layers of CO₂ may still remain within the cap. The Viking Orbiter was also equipped with the Mars Atmospheric Water Detector spectrometer (MAWD). MAWD observations, and later Mars Global Surveyor Thermal Emission Spectrometer (TES) data, confirmed that the north polar summer atmosphere is saturated with H₂O (see Chap. 8 by Tokano). These observations demonstrated conclusively that the north polar cap consists of H₂O and that it interacts with the water vapour in the atmosphere. The albedo of the white areas of the north polar cap is relatively low compared to terrestrial snow. The low albedo combined with observations of dark layers on scarps has been attributed to a substantial content of dust [31, 30], although the amount is still uncertain.

The composition of the south polar cap turned out to be more complex than that of the north polar cap. Thermal mapping of the south polar cap with the Viking IRTM showed that the surface temperature of the south polar cap did not increase above the sublimation temperature of CO₂ during summer [30], indicating that some CO, snow survived the southern summer. MAWD data also showed a lower abundance of atmospheric water than that observed in the north. On the basis of the MOLA topographic data, it was later argued that the south polar cap could not be composed of CO₂ ice [39]. The argument was based on a simple glaciological model that considered the rheology of the cap. A south polar cap of pure solid CO₂ would be too soft to allow a cap with a thickness of 3000 m and an estimated age of more than 10 million years [39]. Recently, new results indicate that the residual south polar CO₂ ice may consist of a thin surface layer above H₂O ice. The Mars Odyssey Thermal Emission Imaging System (THEMIS) discovered H₂O ice near the edge of the permanent south polar cap [47], and a comparison with TES and Viking observations indicated that the H₂O ice may be widespread. Repeated highresolution images of characteristic quasi-circular depressions with steep sides and flat floors (so-called Swiss-Cheese terrain) observed on the south polar cap, showed that these depressions were growing between two consecutive years [36]. Modelling of the growth of these features by sublimation in response to solar and infrared radiation constrained the albedo of the floor relative to the walls of these features [5]. Comparison with THEMIS data indicated that the features were formed by an 8 m thick surface layer of CO₂ with H₂O ice beneath. With the present retreat rates, the surface CO₂ layer would be removed in a few centuries. These results suggest concurrently that the main volatile component of the south polar cap is H₂O ice as in the north, and that a perennial, presumably temporary, surface layer of CO₂ ice is partly covering the water ice. As in the north, the south polar cap is thought to contain substantial amounts of dust. Dark layers are exposed at scarps, and the white polar ice covers only part of the south polar cap.

Recently, mapping of subsurface hydrogen has indicated permafrost in the polar regions (see Chap. 5 by Mitrofanov). These observations show that water is abundant in the polar regions, not only within the polar cap themselves.

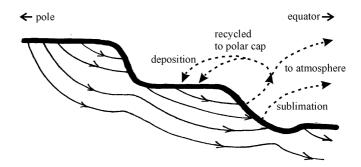


Fig. 6.4 Scarps and troughs are thought to be formed by a combination of sublimation, deposition, wind transport and ice flow (the figure is reproduced after Fisher [12]). Water vapour sublimates from the dark, equator facing scarps. Some vapour is thought to be recycled back to the polar cap and deposited at the white, pole facing surfaces. Dashed lines indicate the transport of water vapour, full lines indicate proposed particle paths due to ice flow of the cap [12], and the bold line indicates the ice cap surface. The suggested flow pattern implies age discontinuities in the cap and along the surface (see Section 6.3.1).

6.3 Flow of the Polar Caps

Terrestrial ice sheets flow under their weight due to gravity. The flow rate depends on the ice temperature, the rheology and possible basal sliding. Terrestrial ice sheets are generally characterised with accumulation of ice in the central areas, and ablation along the margins, mainly as surface melt or break off from icebergs. A layer of snow deposited in the central areas will sink down into the ice sheet and gradually transform to ice as it is buried by subsequent layers of snow. The layer will thin and stretch by compression and shear flow. Eventually, a snow particle deposited in the central areas will reach the margin and be removed by the ablation. The surface ice is oldest at the margin, and it becomes continuously younger with increasing distance to the margin until the accumulation zone, where newly deposited snow is at the surface.

On Mars, the caps are colder than any ice sheet on Earth, gravity is around one third of that on Earth, and the rheology is uncertain due to unknown contents of dust and CO_2 . Any ice mass subject to gravity, however, will flow under its weight, and the Martian polar caps are expected to flow like terrestrial ice sheets. The key issue is how significant the flow is compared to sublimation and deposition rates.

The Martian polar caps are thought to accumulate ice along the white, horizontal or pole-facing surfaces, and to lose mass (ablate) along the dark, steep equator-facing scarps by sublimation due to insolation. They have alternating zones with accumulation and ablation without a terrestrial analogue, which has been referred to as "accublation" [12]. The sublimation at the equator-facing scarps has been proposed to cause slow migration of the scarps towards the poles [24, 12]. Fig. 6.4 shows a cross-section of a scarp/trough system, and how it is thought to be formed by a combination of deposition and erosional processes [12]. The mass exchange processes are further discussed in Section 6.4.

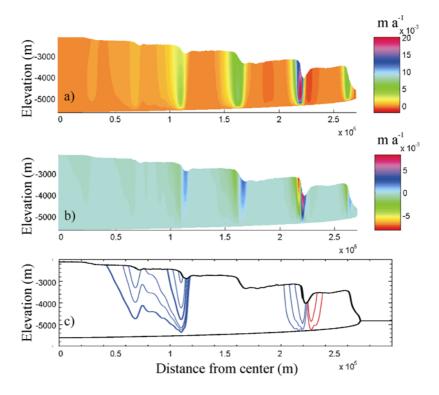


Fig. 6.5 Modelled flow pattern in a cross-section of the north polar cap (from Hvidberg [26]): a) horizontal velocities, b) vertical velocities, and c) corresponding steady state streamlines. In c), blue lines show streamlines with outward motion, and red lines show streamlines with pole-ward motion. The two bold, blue streamlines originate more than 50 km apart, but emerge within less than 5 km. Travel times along the two lines are 150 and 60 million years, respectively (see text for discussion). The cross-section extends from the pole to the margin of the cap in the 160°E-direction along MGS pass 404 [50].

6.3.1 Effects on Topography and Stratigraphy

Although both the northern and southern caps have deep troughs and steep scarps at their surfaces, their overall topographic profiles have a similar dome-shape. The overall dome-shapes of both polar caps are characteristic of an ice sheet flowing under its weight due to gravity [17, 39]. The scarps and troughs, however, suggest that the caps are currently undergoing complex mass balance processes involving erosion and deposition (see Section 6.4). It has been argued that the shape of the north polar cap is controlled by sublimation alone [28], but the model failed to explain the steep surface slopes at the scarps where sublimation is thought to be at maximum.

In terrestrial ice sheets, thickness gradients are generally small, and to a first approximation, ice flow occurs by horizontal shear flow within the ice expressed by the basal shear stress, $_{b} = gh$ in , where is cap density, g is gravity, h is cap thickness, and is surface slope. Generally, ice flows in the direction of the steepest surface slope, and a flowing ice sheet deforming under its weight will always retain the same parabolic scaled shape [39, 40]. Estimated basal shear stress in the Martian polar caps is characteristic of an ice cap consisting of flowing water ice [39]. In the Martian polar caps, modelling the flow is complicated by the troughs and scarps which imply relatively large thickness gradients. Extensive and compressive stresses as in terrestrial ice sheets, but need to be considered.

Assuming that the cap consists of flowing water ice, the overall, current flow rates of the north polar cap are estimated to be in the order of $10^3 \text{ m} \cdot a^1$ [17, 26], about four orders of magnitude smaller than typical flow rates in terrestrial ice sheets. The flow velocities are proposed to be greatly enhanced at the scarps and troughs to the order of 10^{-2} m a^{-1} [13, 26]. Fig. 6.5 shows results from a flow model of a section of the north polar cap of Hvidberg [26]. In this model, ice is assumed to deform according to a power flow law with a temperature dependent rate factor [40, 16]. Ice temperature is calculated from the heat flow equation. The model includes longitudinal stress gradients associated with the troughs, and solves the governing equations with a finite element technique [25, 26]. The model calculates how the cap with its current topography would flow due to gravity. The resulting flow pattern is seen to agree with the accublation hypothesis. Enhanced downward flow beneath the scarps and upward flow beneath the troughs show that flow seeks to smooth the surface. Scarps and troughs are seen to affect the flow not only near the surface, but right down to the base of the cap. The corresponding steady state streamlines are shown to illustrate the current flow pattern associated with the present topography (Fig. 6.5c). It must be emphasised that the streamlines are not proposed trajectories for ice deposited at the surface. The travel time along individual steady state streamlines is in the order of 10^7 - 10^8 years, longer than the estimated age of the caps, and too long for a steady state assumption to be meaningful. As discussed below (Section 6.4.3), the caps are probably never in steady state, but evolving in response to obliquity changes. The scarps are thought to migrate inward on the caps due to sublimation with current migration rates estimated to be in the order of $10^{-1} \text{ m} \cdot a^{-1}$ (Section 6.4.1). As a consequence of accublation combined with ice flow, the system of scarps and troughs has been proposed to imply waviness and discontinuities in the isochrones (internal layers of same age), and age discontinuities in the layers exposed on the dark scarps [13, 26]. The effect depends on the scarp migration rate compared to the ice flow velocity [13]. If the difference is two orders of magnitude as proposed here, the effect is negligible, implying that scarps contain local ice and the internal layers are horizontal [13].

6.3.2 Evidence for Flow

The geologic evidence for flow remains ambiguous. The overall dimensions and dome-shapes of the polar caps suggest that their overall topographies are controlled by ice sheet flow. In terrestrial ice sheets, internal layers are mapped by radar soundings. Possible discontinuities and waviness of the internal layers in the Martian polar caps could provide insight to whether the caps flow and how significant the flow would be. If variations in impurity content would imply changes in electrical conductivity, internal layers would be observable by radar sounding of the caps, but such data are not yet available for Mars.

Layers exposed in scarps may provide some insights. If flow velocities are not generally negligible compared to scarp migration rates (see the discussion above in Section 6.3.1), the surface age of layers exposed in scarps would be discontinuous. The layers above the discontinuity would originate locally upstream from the scarp, while the layers beneath the discontinuity would originate further upstream (Figs. 6.4 and 6.5). The local, younger layers should be more disorganised and non-homogeneous than the older layers that have been thinned and stretched deep in the ice sheet [13], but in the older layers, flow instabilities may have occurred. It has been suggested that local waviness in the exposed layers at MOC images from the south polar cap is due to flow instabilities (boudinage), but the interpretation remains controversial [8, 33]. In a recent study of the possible orbital forcing of layers exposed in a scarp on the north polar cap [35], the stratigraphic record may contain such a discontinuity with the older, more thinned layers beneath, as predicted by Fisher [13] (see Section 6.6).

An independent support for a flowing cap is provided in the following section (Section 6.4). Flow rates from ice sheet models are used to estimate the current sublimation rates from the north polar cap. Agreement with observations of water vapour supports the basic assumption of the model that the cap is flowing.

6.4 Interactions with the Atmosphere: Mass Balance Processes

The alternating white polar ice and exposed layers together with the observed seasonal distribution of water vapour in the atmosphere indicate that the caps continue to have an active interaction with the atmosphere. Through deposition and sublimation processes, they play an active role in the current water cycle (see also Chap. 8 by Tokano). The spiralling pattern of dark scarps and white ice is thus a key to understanding the mass balance processes. As indicated by Fig. 6.4, the system of scarps and troughs is thought to be formed by a combination of sublimation, deposition, wind effects (erosion, redistribution by so-called katabatic winds, cold gravity-driven wind over an ice sheet) and ice flow [12, 13,

23, 28]. The relative importance of these processes is uncertain, but several aspects will be discussed in this section.

Deposition of H_2O and dust is thought to occur together with the seasonal deposition of CO_2 . Atmospheric dust raised from the surface by dust storms is thought to act as condensation nuclei. In autumn, H_2O and CO_2 condense on the dust particles so they precipitate out of the atmosphere [8]. In spring, the seasonal deposition of CO_2 snow is recycled back to the atmosphere, but the dust and part of the H_2O remain at the cap surface. The dark layers exposed in the scarps are thought to reflect changes in dust and ice deposition rates through time.

Ablation is thought to occur by sublimation of H_2O vapour due to insolation and wind erosion. The sublimation occurs during summer and is controlled by surface temperature and wind speed. The Martian atmosphere is thin and the atmosphere is readily saturated. Therefore, wind transport of vapour from the cap constitutes an important control of the sublimation from the cap.

6.4.1 Sublimation from the Caps

Observations of water vapour in the atmosphere have been used to estimate the summer sublimation from the north polar cap [18]. In this section we shall discuss an alternative approach to determine the sublimation of the north polar cap by analysis of its surface topography.

The topography of the cap is a result of geologic and climatic processes working over time. If ice flow was the only active process, it would gradually close the troughs and smooth the surface. It is possible to estimate how much sublimation is needed to prevent the troughs from being closed by ice flow. The current flow velocities may be insignificant compared to current sublimation and deposition rates, but they do provide a constraint on sublimation rates from the caps.

The model introduced above for a cross-section of the north polar cap (Section 6.3.1) [26] is now used to study the evolution of the cross-section with time. Three model runs are shown in Fig. 6.6. The first model run assumes no ablation or accumulation, i.e. the only process involved is ice flow (Fig. 6.6a). The polar cap flows slowly while it is smoothed. Deep troughs will close in the order of 10^5 - 10^6 years, most rapidly within the first tens of thousands of years, where the surface slopes are greatest.

The cap is then evolved in time by assuming patterns of mass balance (i.e. accumulation and ablation). If ablation occurs as sublimation, the mass balance depends on surface slope as well as geographical position. For simplicity, it is assumed that it is a function of surface slope only. North facing or horizontal surfaces are assumed to accumulate with a constant rate *b*, while south facing surfaces are assumed to ablate. The ablation rate is assumed to be proportional to the surface slope with a constant proportionality factor *C*. The second model run assumes a deposition rate of 0.5×10^{-3} m·a⁻¹ and *C* determined in order to have an initial net mass balance along the cross-section (Fig. 6.6b). The time evolution shows that troughs migrate inward while they smooth. The initial migration speed

is in the order of 10^{-2} m·a⁻¹. Sublimation rates are up to 5×10^{-3} m·a⁻¹ at the steepest scarps. Troughs are closing in the order of 10^5 to 10^6 years.

The third model run assumes sublimation rates enhanced by a factor of 10 compared to the net mass balance run, while deposition *b* is unchanged (Fig. 6.6c). Troughs now remain open in time. They migrate inward, while the steep slopes at the scarps are preserved. The migration speed is in order of 10^{-1} m·a⁻¹. Sublimation rates are 5×10^{-2} m·a⁻¹ at the steepest scarps. Comparison with the surface velocity (Fig. 6.6d) shows that troughs remain open, only in the model runs where sublimation rates exceed ice flow velocities. Flow velocities thus provide a constraint on the sublimation rates required to form the troughs.

The results presented in Fig. 6.6 suggest that the troughs are being formed by currently active processes. If not, ice flow would smooth out the troughs on short time scales. The results show further that the sublimation required to keep the troughs open could be parameterised by the surface slope. We have used results from several cross-sections to establish a general relation between required sublimation and surface slope. The MOLA topographic data [50] provide an accurate and high-resolution map of the surface slope. Assuming that the relation holds over the entire polar region, the total sublimation north of 80°N is estimated to be in order of 10^{11} – 10^{12} kg per Martian year. This result agrees with a previous, completely independent estimate of the summer sublimation from the north polar cap based on observations of water vapour in the atmosphere [18].

The estimated sublimation is subject to some uncertainties. It is a minimum estimate, because higher sublimation rates would also keep the troughs open. It is sensitive to the cap temperature (see section below) and the assumed composition of the cap, because the flow depends on cap temperature and dust content. A high dust content, for example, could make the ice stiffer than pure water ice and require smaller sublimation rates to keep troughs open. The agreement between our estimate and the observed atmospheric water vapour levels is, however, a significant result. It suggests that the basic assumptions are valid, i.e. the cap consists of flowing water ice and sublimation may be reasonably expressed in terms of the equator-facing surface slopes.

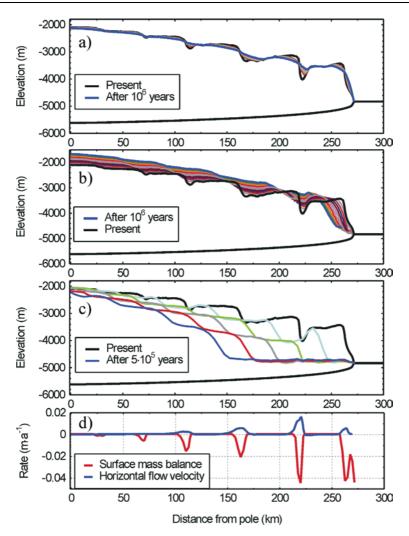


Fig. 6.6 Time-evolution of a cross-section of the north polar cap from an ice sheet flow model (from Hvidberg [26]) with three assumptions regarding the exchange of vapour with the atmosphere. In a), there is no assumed exchange of vapour with the atmosphere. In b) and c), sublimation and deposition rates are assumed to depend on surface slope, in b) with initial balance between sublimation and deposition, and in c) with sublimation rates enhanced 10 times compared to (b). In d), initial horizontal surface flow velocities are shown, together with the initial surface exchange rates assumed in (c). Negative rates correspond to ablation, positive rates to deposition. The cross-section extends from the pole to the margin of the cap in the 160°E-direction along MGS pass 404 [50].

As discussed above (Section 6.2.1), the south polar cap is now known to contain water ice. Atmospheric water vapour has been observed above the south

polar cap in southern summer [45], and although the amount is lower than in the north, it suggests that the south polar cap contributes to the water cycle in a similar manner to the north polar cap. The exposed surfaces with water ice are smaller and more dispersed than in the north. In the north, sublimation does not occur before the seasonal layer of CO₂ frost has evaporated. In the south, the cap is partly covered by a perennial layer of CO₂ that would prevent sublimation of an underlying layer of water ice. Furthermore, a substantial fraction of the south polar cap is covered by dust and the south polar layered deposits extend over an area more than twice as large as the cap itself. The influence of a dust cover on glacier ablation has been studied on Earth. A thin layer of dark dust may enhance ablation, while a thicker layer may prevent ablation and totally isolate the cap from the atmosphere [32]. Although ablation in the terrestrial study occurred primarily as melting, not sublimation, the result may be applicable to Mars. Sublimation from the dust covered parts of the south polar cap and layered deposits may be greatly reduced compared to surfaces with exposed ice, despite the high content of water (see Chap. 5 by Mitrofanov).

6.4.2 The Spiralling Pattern

The spiralling nature of the troughs and scarps – anti-clockwise in the north and clockwise in the south – is not fully understood at present. Understanding the mechanisms behind it is a key to understanding what processes control the mass balance of the polar caps on shorter and longer time scales. In this section, we shall discuss a few characteristics of the features of these mechanisms and some ideas that have been proposed to understand the spiralling nature.

The above section showed that the sublimation process might be well understood in terms of a simple parameterisation by surface slope. It is also clear, however, that the model does not fully capture the mass balance processes involved. In the model runs (Fig. 6.6b+c), a staircase-shaped surface profile develops, but the observed surface profiles are more complex with north facing slopes at the equator-facing side of the troughs and, particularly at the south polar cap, almost no horizontal surfaces. Water vapour may be recycled back to the cap, and wind may contribute to redistribution of material (Fig. 6.4). The surface slopes in the north polar cap form an obvious spiralling pattern, while the south polar cap does not appear to be as well organised. A closer inspection shows, however, that at both polar caps, the steep slopes are oriented systematically $20-30^{\circ}$ west of the equator-ward direction, i.e. SSW in the north, and NNW in the south (Fig. 6.7).

It has been suggested that wind effects have a prominent role in forming the spiralling scarps and troughs [23]. The surface undulations were proposed to be formed by interaction between surface mass exchanges (accublation) and standing waves in the shallow katabatic wind-flow. It is known from terrestrial studies in Antarctica and Greenland that katabatic winds have a remarkably consistent direction and strength [23]. The katabatic winds are directed by topography. They are particularly interesting in the Martian polar regions, because they are deflected by the Coriolis force. The deflection, clock-wise direction in the north, and

counterclock-wise in the south, agrees with the idea that standing waves in the katabatic wind-flow are a contributing mechanism to forming the observed scarps and troughs perpendicular to the wind-direction. On Earth, formations of ripples are known to occur by a similar mechanism, although on a much smaller scale, e.g. sand ripples in deserts or on the ocean floor. In an Antarctic blue-ice field (a dry area with net ablation due to sublimation that implies old ice exposed at the surface), formation of surface ripples perpendicular to the preferred wind direction have been observed [3], although on a much smaller scale than the Martian spiralling troughs. The ripples are a few cm high with a distance between them of about 25 cm.

Alternatively, it was proposed that the spiralling troughs were created by a combination of accublation and ice flow [12]. The idea was developed to explain the characteristic features of the north polar cap. In an ideally circular ice cap with a smooth surface, ice would flow radially outward from the centre. The inward migration of scarps (due to sublimation) occurs on an ice mass that is flowing outward. If the dome of the cap is displaced from the pole, around which the insolation would be symmetrical, a combination of the inward migration of scarps and the outward flowing ice could create a spiralling pattern. Several aspects of the polar troughs may be understood in terms of this hypothesis, for example the orientation of scarps near the mouth of Chasma Boreale [12], and lineations observed on white surfaces of the north polar cap [14]. With the high-resolution MOLA data, some of the basic assumptions behind the accublation and ice flow hypothesis have appeared not to hold. The summit of the north polar cap is obviously not displaced from the pole. Ice flow direction is closely related to the overall cap topography, and the significant differences between the topography of the north and south polar caps cannot explain the systematic orientation of the steep scarps on both caps (Fig. 6.7). A basic assumption behind the hypothesis is that ice flows radially outwards, but most troughs are so deep that ice will flow pole-ward on the equator-facing side of the trough in order to seek to close the trough [26]. We may therefore conclude that if the scarps and troughs are being formed in the current climate on Mars, the ice flow and accublation hypothesis is unlikely to be the main mechanism behind the spiralling nature. Ice flow may still play an important role in providing a control on the depth of the troughs and the spacing between them.

6.4.3 Mass Balance

Although the important processes controlling the interaction with the atmosphere are identified, the current mass balance and its variation on shorter and longer time scales remain an outstanding question.

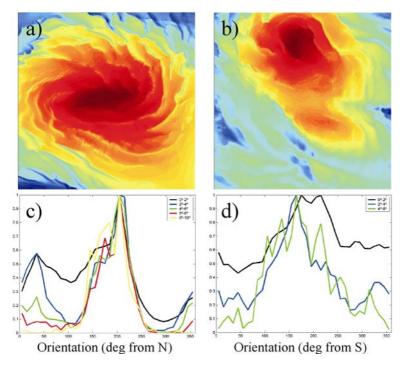


Fig. 6.7 a) and b): MOLA surface topography of a 200-km by 200-km area region around the north and south poles, respectively. Elevations are shown on linear colour-scales, resolution is 2 km. c) and d): normalised surface orientation histograms for different slope intervals for the north and south polar regions, respectively. The surface orientation is measured in degrees from the pole. I.e. the orientation of an east-facing surface is 90° in the north and 270° in the south, the orientation of an equator-facing surface is 180° in both north and south, etc. The histograms show that the steep surfaces (the scarps) are preferentially orientated 25° west of the equator-ward direction in both polar regions, i.e. towards SSW and NNW in the north and south, respectively. In the north, the pole-facing side of the troughs gives rise to a peak at 25° in the almost horizontal slopes (c). In the south, the surface is more irregular than in the north. The histograms for slopes steeper than 6° are not shown, because they are influenced by steep slopes associated with Chasma Australe.

It is not yet known how the system of scarps and troughs originally developed and how it evolves in time. The modelling studies of the north polar cap discussed above suggest that sublimation rates at the scarps are in the order of 10^{-2} m·a⁻¹. These sublimation rates imply that scarps would migrate inward with a speed of the order of 10^{-1} m·a⁻¹. Steep scarps mark the margins of the caps, and the surface slope is at maximum. The 500 m scarps at Mars are without any terrestrial analogue. Assuming that there is currently only minor deposition at the darkerlooking terrain outward of the margin scarps, the suggested migration of scarps could indicate that the cap is currently shrinking, as indicated by Fig. 6.6. This result is supported by geologic evidence of formerly larger ice sheets, both in the north and in the south [9, 10, 20], although the direct connection between our result and the geologic features has not been established.

Current average deposition rates above the polar caps are thought to be of the order of $0.1-1 \times 10^{-3}$ m a⁻¹ [35]. The deposition could locally be higher than the average rate for the polar regions, for example if water vapour is recycled back to the cap and deposited at the top of the scarps as indicated in Fig. 6.4. The net deposition of water vapour could then be significantly higher than assumed in the modelling, thereby changing the suggestion that the north polar cap is currently shrinking.

6.4.4 Orbital Forcing and Evolution of the Caps

Variations in insolation due to changes in the orbital parameters of Mars are thought to lead to significant variations in climate on Mars (see also Chap. 7 by Kuzmin). The obliquity has the strongest influence [35, 8]. The obliquity oscillates with a period of 1.2×10^5 years, and its amplitude varies with a period of 1.3×10^6 years. This leads to variations in obliquity between 15° and 35°, with the present obliquity of 25.2° being close to the mean value over the last two million years. On time scales longer than a few million years the obliquity variation is chaotic [35]. At high obliquity, the poles will experience the longest polar night and the longest midsummer period with continuous sunshine, leading to extreme seasonal temperature fluctuations and a maximum polar mean annual temperature [34]. This situation will imply maximum temperature gradients between the equator and the poles, and thereby a strengthened atmospheric wind circulation. A strengthened wind circulation means an increased capability to transport water vapour from the polar caps. Thus, high obliquity periods are proposed to be associated with extreme interaction between the polar caps and the water vapour in the atmosphere. The net accumulation and ablation would be at a maximum, but the balance between them is uncertain. At low obliquity, the conditions are reversed.

On Earth, variations in the orbital parameters are likewise thought to exert a great influence on the terrestrial climate and to be the main trigger of ice ages with the growth of large continental ice sheets. Internal feedback mechanisms in the terrestrial climate system are thought to enhance the effects [27]. The astronomical forcing of climate on Earth is referred to as the Milankovitch theory. During the terrestrial ice ages, the polar climate is cooled relative to the equatorial climate. Continental ice sheets grow in the northern hemisphere because lower summer temperatures reduce summer melt and allow snow to survive. The cold climate reduces evaporation from the ocean and leads to lower accumulation rates in the central regions of the ice sheets than those observed today.

On Earth, it is natural to estimate glacier mass balance over periods of tens to hundreds of years, to avoid influence from short-term climate fluctuations. On Mars, the dramatic changes in obliquity are thought to lead to periods with almost no exchanges with the atmosphere (low obliquity) followed by periods with active interactions (high obliquity). The polar caps have been proposed to grow and retreat in response to the periodic climatic conditions [17, 34]. Formation of the spiralling system of scarps and troughs may be associated with this proposed alternating "stop and go" behaviour and processes acting on this long time scale [17]. The natural time scale for estimating mass balance of the polar caps may be as long as the period of obliquity variation, while the current (annual) mass balance may be unimportant.

6.5 Cap Temperatures and Potential for Basal Melting

Liquid water is not stable at the surface of Mars today because of the low surface pressure. The freezing point of water is reached several km beneath the surface, where the overlying material implies a higher pressure and provides sufficient insulation. The polar regions are known to be water-rich, and may have provided the necessary conditions for a sub-surface water reservoir to form in the past or even to exist today. The polar cap temperatures are of interest not only because of their potential for basal melting, but also because ice flow depends on temperature.

6.5.1 Temperatures of the Polar Caps

The temperature distributions of the polar caps depend on surface temperature, heat flow from beneath, thermal properties and thickness of the cap. The caps are coldest at their surface, temperatures increase with depth and reach a maximum at the base of the caps. A thicker ice cap provides better insulation against the cold atmosphere than a thin ice cover, and generally, the thicker the overlying cap is, the higher the basal temperatures.

The surface temperature is controlled by radiation balance. Beneath a thin surface layer of 10–20 m, the seasonal variation is smoothed away and the temperature equals the mean annual average [34]. The average Martian heat flux has been estimated to be 30 mW/m² [42], although there may be significant local variation. Additional significant uncertainties are related to the cap composition and thickness.

The polar caps are thought to consist of H_2O ice with some dust and layers of CO_2 . The cap conductivity depends on the relative amounts of the constituents and their distribution within the cap, which is not yet known. Pure H_2O ice has a thermal conductivity of 2–3 W m⁻¹K⁻¹. The effect of a possibly large dust content is not clarified. A study of the thermal conductivity of terrestrial ice-dust mixtures gave values of 0.5–3.5 W m⁻¹K⁻¹ for > 35 % volumetric dust content [7]. Layers of CO_2 would influence the temperature distribution significantly. CO_2 (either dry ice or clathrate) has a thermal conductivity of 0.4–0.6 W m⁻¹K⁻¹ [37].

The thickness of the polar caps is not well constrained. The surface topography is mapped by the high-resolution MOLA laser altimetry data, but no direct observations have been made of the basal topography. The domes rise around 3 km above the surrounding terrain. Estimates of the maximum deflection of the

base beneath the north polar cap are approximately 0.4–1.2 km [50, 29]. In the south, it is uncertain whether the base is depressed [44]. The present ice thickness may thus be around 4 km in the north taking the deflection of the bed into account and 3 km in south assuming that the base is horizontal. These estimates neglect local basal topographic highs or lows.

The Martian polar caps flow so slowly that vertical advection of heat can be neglected, and heat flow through the cap is described by conduction alone [34]. The temperature gradient is approximately constant and determined by the basal boundary condition $\partial T/\partial z = -Q/K$, where *T* is temperature, *z* is a vertical coordinate, *Q* is the basal heat flux, and *K* is the cap conductivity. The temperature thus increases linearly with depth, and basal temperature T_B is determined from $T_B - T_s = Q/K \cdot H$, where T_s is an average surface temperature, and *H* is the cap thickness. Assuming a pure H₂O cap with a conductivity of 2.5 Wm⁻¹K⁻¹ and the average Martian heat flux of 30·mW/m², the cap temperature of 155 K, basal melting at the pressure melting point of pure H₂O ice would require a polar cap thickness of 9.6 km (see also the discussion in [7]).

Therefore, basal melting beneath the polar caps would require a thicker cap than the current average estimates, a lower thermal conductivity than pure water, higher basal heat flow than the estimated average, or a combination of these. The surface temperature is not crucial. It would need to be increased continuously over a long period in order for the heat to be conducted to the base without being attenuated. A surface temperature of 155 K is close to the average over the last 2.5 Myr. During this time, periods of high obliquity with their associated higher mean annual surface temperatures are too short to raise the basal temperature more than a few Kelvin [34].

Given the uncertainties regarding the composition discussed above, local variations of thickness or heat flow could be sufficient to cause basal melting. Assume, for example, that there is a local basal depression of 1 km depth beneath one of the polar caps. The depression could be an ancient impact crater that existed before the cap formed and is now buried beneath the cap. Basal melting in the reservoir at the pressure melting point of pure water would require a cap conductivity of 1.3 $Wm^{-1}K^{-1}$, corresponding to a CO, content of up to 60 % (depending on the effect of dust). If the depth of the reservoir is 2 km and basal heat flux is 35 mW/m², basal melting would require a cap conductivity of 1.8 $Wm^{-1}K^{-1}$, corresponding to a CO₂ content of up to 35 % (depending on the effect of dust). According to observed relations between Martian crater depths and diameters [15], an impact crater with a depth of 2 km would have a diameter of 50-70 km. This is a relatively large crater but it is still possible that it exists beneath the caps, particularly in the south, where the cap is based on old heavily impacted terrain. Alternatively, a basal hot spot could create basal melting. For example, basal melting would occur beneath a 4 km thick ice with a thermal conductivity of 2.5 W $m^{-1}K^{-1}$ as pure water ice, if the basal heat flux locally increased to 73 mW/m², which is close to the average geothermal heat flux on Earth. This is about twice the highest estimate of the average Martian heat flux [7], but the average heat flux earlier in the planet's history is thought to be higher than it is today [42]. Smaller changes would be sufficient in all the above examples, if the dust content (or a hypothetical content of salt) in the cap reduces the pressure melting point below that of pure H_2O ice.

6.5.2 Evidence for Basal Melting

Several studies have discussed possible evidence of former basal melting of the polar caps. Many observations near the polar caps are associated with glaciers that have undergone melting, and appear to be related to meltwater [8, 20, 38, 11].

It has been suggested that outflow of basal melting contributed to formation of the large, characteristic reentrants on the polar caps, including the two major reentrants, Chasma Boreale in the north and Chasma Australe in the south [7, 3, 11, 1]. The outflow may have occurred as a sudden release of meltwater from a basal water reservoir. Alternatively, it was suggested that the polar reentrants were eroded by katabatic wind draining from the polar cap [23] or formed in a combination of accublation and ice flow [12]. The similar characteristics of the two major reentrants in the north and south call for a common formation mechanism. Recently, the formation hypotheses of Chasma Boreale were evaluated against geological evidence. It was concluded that Chasma Boreale and a few smaller reentrants on the north polar cap were originally formed by outflow of sub-cap water with later modification by wind and sublimation. Although the formation hypothesis may then be resolved, several key issues remain unresolved. For example, the source of basal meltwater and the existence of basal reservoirs beneath the cap are not yet identified. The exceptionally steep walls (up to 60°) of the reentrants [6] suggest that they formed relatively recently, or that they are continuously being eroded. If they formed recently, a remnant of the original basal water reservoir may still exist beneath the caps.

Terrestrial examples of outflow events beneath glaciers exist from the past and present. The Icelandic Jökulhaups at Vatnajökull are well-known examples of outflows occurring intermittently [4]. Increased heat flow produces basal meltwater in a sub-glacial lake, Grímsvötn, and outburst floods drain the lake and initiate surges of a nearby glacier.

6.6 Polar Layered Deposits – An Archive of Climate History

One of the most important goals of Martian polar research is to determine whether there is an interpretable record of climatic and geologic history preserved in the polar caps [8]. The polar caps consist of layers deposited through millions of years. Dust particles are deposited together with H_2O and CO_2 , which is partly recycled back to the atmosphere, as described in the sections above. Other impurities may be deposited from the atmosphere as well, e.g. ions and salts. The deposition rates of dust, H_2O , CO_2 and other impurities are thought to vary in time according to climate and geologic changes.

The large-scale layered deposits exposed in scarps on the polar caps are thought to reflect changes in the dust deposition and mass balance over the polar caps. Dust deposition rates depend on the atmospheric circulation and transport (storminess, etc.) and conditions at the dust sources. Mass balance depends on surface temperature, wind circulation and insolation. The layering is thought to be controlled by the periodic variations in the orbital parameters. The first study to demonstrate an orbital forcing of the dark polar layers was done on a sequence of layers observed in a scarp on the north polar cap [35]. A combination of highresolution images, high-resolution topography and new calculations of the orbital and rotational parameters of Mars were used to show a correlation between northern summer insolation and the radiance of the layers. Three similar stratigraphic cycles were observed above some higher-frequency variations: The best fit assumed an average deposition rate of 0.5×10^{-3} m·a⁻¹ in the top 250 m.

Interpretation of the layers is complicated by several factors. Most important is the question whether the stratigraphy is preserved, continuous and undisturbed. The flow pattern proposed in Section 6.3 may imply stratigraphic discontinuities at the surface in the scarps, but it is uncertain how common the proposed discontinuities would be and at which depths they would occur. The transition in the stratigraphic record studied by Laskar et al. [35] could mark such a discontinuity. The higher frequency variation beneath the transition would be due to the more pronounced thinning of the older layers compared to the younger above the transition, because they have flowed longer and deeper in the cap. Another complication is that the deposition rate may vary on shorter and longer timescales concurrently with climate. The problems are well-known from terrestrial studies of the orbital forcing of climate that uses ice cores or deep sea cores to document the correlation [27, 41]. It is critical that all significant orbital and rotational periods are identified precisely in the climate record. On Earth, the climate records are compared to the summer insolation at high northern latitudes, but this measure may not be the primary driver of climate changes on Mars.

The first work by Laskar et al. [35] considered only one sequence of layers in a single trough on the north polar cap. In the future, more studies are needed. A correlation between independent troughs needs to be documented, and the relation between northern and southern layered deposits must be investigated in order to understand fully how orbital variation forces climate on Mars.

6.7 Concluding Remarks

The polar caps on Mars are formed by atmospheric deposition of H_2O , dust and CO_2 . The caps are continuously evolving through various processes, including exchange processes with the atmosphere, ice flow and possibly basal melting. The Martian climate is thought to be controlled by the planet's orbital parameters, and the caps may grow and decay in response to the implied periodic variations in insolation.

There is evidence that basal melting may have occurred beneath the polar caps. Several uncertainties are associated with estimating the thermal conditions at the base of the polar caps, most importantly the cap conductivity, the thickness and the heat flux from beneath. It is possible that reservoirs of basal meltwater may exist in favourable locations at the base of the cap and provide a habitat for life.

Dark layers exposed in scarps on the polar caps reveal an extensive layering. The layers reflect variations in the dust content, and represent a record of the "atmospheric sediment". Together with the deposition of dust and volatiles, various impurities and perhaps traces of ancient biological activity may have deposited on the cap surfaces and are stored in the cap. In order to interpret the exposed layers it is fundamental to understand how the cap has evolved in time in response to flow and mass balance processes, and to date the observed layers. It is one of the key questions of future research to determine whether the layers contain an interpretable record of climatic, geologic and biological history on Mars. Ice cores from terrestrial ice sheets have provided unique records of climate change on Earth. The constantly frozen and pure conditions within an ice sheet provide an optimal storage of biological material, and it has been shown that ancient DNA is preserved in the terrestrial ice sheets and permafrost [48, 49]. If biological activity ever existed on Mars, traces may still be preserved in the polar caps.

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6.8 References

- 1 Anguita F, Babín R, Benito G, Gómez D, Collado A, Rice JW (2000) Chasma Australe, Mars: structural framework for a catastrophic outflow origin. Icarus 144: 302-312
- 2 Benito G, Mediavilla F, Fernández M, Márquez A, Martínez J, Anguita F (1997) Chasma Boreale, Mars: a sapping and outflow channel with a tectono-thermal origin. Icarus 129: 528-538
- 3 Bintanja R, Reijmer CH, Hulscher SJMH (2001) Detailed observations of the rippled surface of Antarctic blue-ice areas. J. Glaciol. 47: 387-396
- 4 Björnsson H (1998) Hydrological characteristics of the drainage system beneath a surging glacier. Nature 395: 771-774
- 5 Byrne S, Ingersoll AP (2003) A sublimation model for Martian south polar ice features. Science 299: 1051-1053
- 6 Byrne S, Murray BC (2002) North polar stratigraphy and the paleo-erg of Mars. J. Geophys. Res. 107(E6): 10.1029/2001JE001615

- 7 Clifford SM (1987) Polar basal melting on Mars. J. Geophys. Res. 92: 9135-9152
- 8 Clifford SM and 52 colleagues (2000) The state and future of Mars polar science and exploration. Icarus 144: 210-242
- 9 Fishbaugh KE, Head JW (2000) North polar region of Mars: topography of circumpolar deposits from Mars Orbiter Laser Altimeter (MOLA) data and evidence for asymmetric retreat of the polar cap. J. Geophys. Res. 105(E9): 22455-22486
- 10 Fishbaugh KE, Head JW (2001) Comparison of the north and south polar caps of Mars: new observations from MOLA data and discussion of some outstanding questions. Icarus 154: 145-161
- 11 Fishbaugh KE, Head JW (2002) Chasma Boreale, Mars: topographic characterization from Mars Orbiter Laser Altimeter data and implications for mechanisms of formation. J. Geophys. Res. 107(E3): 10.1029/2000JE001351
- 12 Fisher DA (1993) If Martian ice caps flow: ablation mechanisms and appearance. Icarus 105: 501-511
- 13 Fisher DA (2000) Internal layers in an "accublation" ice cap: a test for flow. Icarus 144: 289-294
- 14 Fisher DA, Winebrenner DP, Stern H (2002) Lineations on the "white" accumulation areas of the residual northern ice cap of Mars: their relation to the "accublation" and ice flow hypothesis. Icarus 159: 39-52
- 15 Garvin JB, Sakimoto SEH, Frawley JJ, Schnetzler C (2000) North polar region craterforms on Mars: geometric characteristics from the Mars Orbiter Laser Altimeter. Icarus 144: 329-352
- Goldsby DL, Kohlstedt DL (1997) Grain boundary sliding in fine-grained ice I.
 Scripta Materialia 37: 1399-1406
- 17 Greve R (2000) Waxing and waning of the perennial north polar H₂O ice cap of Mars over obliquity cycles. Icarus 144: 419-431
- 18 Haberle RM, Jakosky BM (1990) Sublimation and transport of water from the north residual polar cap on Mars. J. Geophys. Res. 95 (B2): 1423-1437
- 19 Head JW (2001) Mars: evidence for geologically recent advance of the south polar cap. J. Geophys. Res. 106(E5): 10075-10085
- 20 Head JW, Pratt S (2001) Extensive Hesperian-aged south polar ice sheet on Mars: evidence for massive melting and retreat, and lateral flow and ponding of meltwater. J. Geophys. Res. 106(E6): 12275-12299
- 21 Head JW, Hiesinger H, Ivanov MA, Kreslavsky MA, Pratt S, Thomson BJ (1999) Possible ancient oceans on Mars: evidence from Mars Orbiter Laser Altimeter data. Science 286: 2134-2137
- 22 Herkenhoff KE, Plaut JJ (2000) Surface ages and resurfacing rates of the polar layered deposits on Mars. Icarus 144: 243-253
- 23 Howard AD (2000) The role of eolian processes in forming surface features of the Martian polar layered deposits. Icarus 144: 267-288
- 24 Howard AD, Cutts JA, Blasius KR (1982) Stratigraphic relationships within Martian polar cap deposits. Icarus 50: 161-215
- 25 Hvidberg CS (1996) Steady-state thermomechanical modelling of ice flow near the centre of large ice sheets with the finite element technique. Ann. Glaciol. 23: 116-123
- 26 Hvidberg CS (2003) Relationship between topography and flow in the north polar cap on Mars. Ann. Glaciol. 37: in press

- 27 Imbrie J, Imbrie KP (1979) Ice Ages Solving the Mystery. Harvard University Press, Cambridge
- 28 Ivanov AB, Muhleman DO (2000) The role of sublimation for the formation of the northern ice cap: results from the Mars Orbiter Laser Altimeter. Icarus 144: 436-448
- 29 Johnson CL, Solomon SC, Head JW, Phillips RJ, Smith DE, Zuber, MT (2000) Lithospheric loading by the northern polar cap on Mars. Icarus, 144: 313-328
- 30 Kieffer HH (1979) Mars south polar spring and summer temperatures: a residual CO₂ frost. J. Geophys. Res. 84: 8263-8288
- 31 Kieffer HH, Chase SC Jr., Martin TZ, Miner ED, Palluconi FD (1976) Martian north polar summer temperatures: dirty water ice. Science 194: 1341-1344
- 32 Kirkbride MP, Dugmore AJ (2003) Glaciological response to distal tephra fallout from the 1947 eruption of Hekla, south Iceland. J. Glaciol. in press
- 33 Kolb EJ, Tanaka KL (2001) Geologic history of the polar regions of Mars based on Mars Global Surveyor data. II. Amazonian period. Icarus 154: 22-39
- 34 Larsen J, Dahl-Jensen D (2000) Interior temperatures of the north polar cap on Mars. Icarus 144: 456-462
- 35 Laskar J, Levrard B, Mustard JF (2002) Orbital forcing of the Martian polar layered deposits. Nature 419: 375-377
- 36 Malin MC, Caplinger MA, Davis SD (2001) Observational evidence for an active surface reservoir of solid carbon dioxide on Mars. Science 294: 2146-2148
- Mellon MT (1996) Limits of the CO₂ content of the Martian polar deposits. Icarus 124: 268-279
- 38 Milkovich SM, Head JW, Pratt S (2002) Meltback of Hesperian-aged ice-rich deposits near the south pole of Mars: evidence for drainage channels and lakes. J. Geophys. Res. 107(E6): 10.1029/2001JE001802
- 39 Nye JF, Durham WB, Schenk PM, Moore JM (2000) The instability of a south polar cap on Mars composed of carbon dioxide. Icarus 144: 449-455
- 40 Paterson WSB (1994) The Physics of Glaciers. 3rd ed. Pergamon, New York
- 41 Petit JR and 18 colleagues (1999) Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. Nature 399: 429-436
- 42 Schubert G, Solomon SC, Turcotte DL, Drake MJ, Sleep NH (1992) Origin and thermal evolution of Mars. In Kieffer HH, Jakosky BM, Snyder CW, Matthews MS (eds) Mars. Univ. Arizona Press, Tucson, pp 147-183
- 43 Smith DE and 18 colleagues (1999a) The global topography of Mars and implications for surface evolution. Science 284: 1495-1503
- 44 Smith DE, Sjogren WL, Tyler GL, Balmino G, Lemoine FG, Konopliv AS (1999b) The gravity field of Mars: results from Mars Global Surveyor. Science 286: 94-97
- 45 Smith MD (2002) The annual cycle of water vapor on Mars as observed by the Thermal Emission Spectrometer. J. Geophys. Res. 107(E11): 5115, 10.1029/JE001522
- 46 Tanaka KL, Kolb EJ (2001) Geologic history of the polar regions of Mars based on Mars Global Surveyor data. I. Noachian and Hesperian periods. Icarus 154: 3-21
- 47 Titus TN, Kieffer HH, Christensen PR (2003) Exposed water ice discovered near the south pole of Mars. Science 299: 1048-1051

- Willerslev E, Hansen AJ, Christensen B, Steffensen JP, Arctander P (1999)
 Diversity of Holocene life forms in fossil glacier ice. Proc. Nat. Acad. Sci. 96(14): 8017-8021
- Willerslev E, Hansen AJ, Binladen J, Brand TB, Gilbert MTP, Shapiro B, Bunce M, Wiuf C, Gilichinsky DA, Cooper A (2003) Diverse plant and animal genetic records from Holocene and Pleistocene sediments. Science 300: 791-795
- 50 Zuber MT and 20 colleagues (1998) Observations of the north polar region of Mars from the Mars Orbiter Laser Altimeter. Science 282: 2053-2060

7 Ground Ice in the Martian Regolith

Ruslan O. Kuzmin

The long-term existence of extremely cold climate on Mars has led to strong global freezing through upper layers of the planet's crust that has resulted in formation of the global permafrost shell – cryolithosphere. In accordance with the modern thermal regime of the Martian surface and the reasonable values of the planet's heat flow, the thickness of the cryolithosphere may approach 1-2 km in the equatorial zone and 5-6 km in the polar regions. In the presence of such a huge scale of cryolithosphere, most of the Martian water abundance could be captured primarily within the permafrost shell in the form of ground ice and possibly salt solutions. It is not excluded that some amount of the liquid and solid phases of CO₂ (plus clathrate) may also be contained in the cryolithosphere.

The long-term and high-amplitude oscillation of the planetary obliquity values have caused a periodic redistribution of the ground ice within the surface layer of the cryolithosphere due to active processes of its condensation and sublimation. At present and lower (< 25°) values of Mars obliquity the ground ice is stable in the surficial regolith layer of both hemispheres only at latitudes poleward of 45° and it is entirely unstable in the equatorial zone, where it is sublimed from the regolith down to depths of hundreds of meters. At larger obliquity values (> 30°) ice becomes stable within the surface layer of the equator down to a depth of a couple of tens of meters.

On Mars there are different types of features whose morphologic patterns (rampart craters, debris flow, lobate debris aprons, terrain softening and polygonal terrains) certainly indicate the presence of ground ice in the Martian regolith. Detailed studies of the rampart impact craters on Mars (as indicators of the ground ice excavation) have shown that the structure of the cryolithosphere as well as the relative ice content distribution within the frozen regolith are characterized by distinct latitudinal zonality and by the presence of a desiccated regolith layer within the equatorial region and at mid latitudes.

This chapter presents an overview of the main characteristics of the Martian cryolithosphere, the particularities of its structure and the potential water amount within the cryogenic shell of the planet. The ground ice stability on Mars under present and past climatic conditions as well as the observed geomorphic manifestations of the ground ice presence in the surface regolith are also the focus of the chapter. Further, the results of the studies of the polygonal terrain distribution on Mars and the correlation of the results with the global map of the highest hydrogen content within a 1-2 m thick surface regolith layer based on Mars Odyssey HEND (High Energy Neutron Detector) data have also been considered here.

7.1 Global Reservoir of Ground Ice

The great remoteness of Mars from Sun (1.5 times farther away than Earth) and the extreme low density of its atmosphere have predetermined the presence of an extensive cold area around the planet – cryosphere, where temperatures are much below 273 K. The Martian cryosphere begins in the atmosphere at heights of 130–140 km above the surface and extends to below the surface at all latitudes from the equator to the poles [25, 50, 52]. The planet-wide penetration of the cryosphere into the crust of Mars has defined the formation of the cryogenic shell, the cryolithoshere. The cryolithosphere of Mars besides the frozen regolith layer also includes the deposits complex of the polar caps (see Chap. 6 by Hvidberg).

Existing estimates of possible long-period changes in the surface temperature of Mars [33] show that the average temperature of the Martian surface is independent of the planet's degassing character (early, constant, or late) and always remains much below the freezing temperature of water. For this reason a frozen surface layer of the Martian regolith apparently could have been formed in the early stages of the geological history of the planet [25, 26]. In contrast to Earth, where the presence of the frozen layer of rocks and sediments (permafrost) is spatially limited by so-called cryolithozones in both hemispheres of the planet, on Mars the area of the perennially frozen regolith layer attends globally from the equator to the poles. So, the main part of the volatiles (in forms of H₂O and CO₂ phases), which have been released by the degassing of the planet throughout geological history, could be captured in the frozen upper part of the planet's crust, which determined the formation of permafrost (in its usual sense of frozen rocks and sediments containing water in its solid phase) as a global cryogenic shell – cryolithosphere.

7.1.1 Scale of the Cryolithosphere and Potential Amount of Water within the Cryogenic Shell

Like the Earth, Mars constantly loses heat by heat conduction through the outer layer of its crust at a heat flux Q, whose value is a function of the thermal conductivity (k) and the thermal gradient in the frozen layer of the planet (G). To estimate the approximate thickness of the Martian cryolithosphere (as a solute-free medium) is a task which is well known in the geothermy of the Earth [32, 99]. The task of estimating the thickness of a homogeneous layer extending from the surface of the planet (Z_0), where the long-term average surface temperatures at any latitude of Mars are much below 273 K, down to the base of the cryolithosphere, where the temperature is equal to the melting-point temperature of ice (Z_m). At the cryolithosphere base (ice-liquid water phase interface) the values of the heat fluxes in the frozen and thawed rocks are taken to be equal. Hence, the distribution of the temperature in the frozen layer is described by a straight line whose coefficient is determined by the factor Q/k, where k is the thermal conductivity of the regolith materials. Thus, the thermal gradient within the frozen layer will be the same, and the temperature at any depth of the layer will be given by the expression

$$T = Q / k \times Z - T_{\rm as},\tag{1}$$

where $Z_0 < Z < Z_m$, and T_{as} is the average annual surface temperature. Thus, the expression for the thickness of the cryolithosphere will have the form

$$Z_{\rm m} = k \left(T_{\rm m} - T_{\rm as} \right) / Q \tag{2}$$

where $T_{\rm m}$ is the melting-point temperature of ice (or the temperature at the cryo-lithosphere base).

Global geological mapping of Mars even in the scale 1:15,000,000 [31, 98] has shown that the Martian surface is characterized by a wide variety of geological units, that is indicative of the presence of notable compositional and lithological variations of the Martian regolith. Thus, interbedding of the impact crater's ejecta material with volcanic and sedimentary deposits plus variations of the ice content most likely determined the existing variety of the thermal conductivity values of the Martian regolith. Clifford and Fanale [16] assumed that, with such inhomogeneity of the Martian regolith, the range of the thermal conductivity values (1-3 W $m^{-1} K^{-1}$) appears to be reasonable values for the regolith layer down to depths of a few km. Following existing theoretical estimations [23, 25, 111], the possible values of the current heat flux may be in the range of 1.5×10^{-2} to 4.5×10^{-2} W m⁻². Using Eq. (2) for referred values of the thermal conductivity and heat flux, one can estimate the potential range of the cryolithosphere thickness. On the base of the estimations presented by various authors [15, 24-26, 50] the thickness of the present cryolithosphere (depending on the thermal parameter values used) may vary between 1 and 3 km in the equatorial regions and between 3 and 8 km at the poles. In this way the scale of the freezing layer of the Martian crust is tremendous and the cryolithosphere certainly represents a huge receptacle of volatiles on Mars.

The potential storage of ground ice within the cryolithosphere depends on its thickness and the porosities of the composing deposits within it. Taking into account the average porosity of the Martian regolith (~20 %) and the presence of the upper layer of desiccated regolith at middle and low latitudes, the potential amount of water within the cryolithosphere may be ~ 5.4×10^{19} kg [52]. This is equivalent to a ~ 380 m water layer spread evenly over the whole planet. Assuming the range of the reasonable surface material porosity values (20–50 %) and the porosity decay constant for the Martian regolith, Clifford [17] calculated that the total water storage capacity of the cryolithosphere may be equivalent to a 374 and 940 m planetary water layer, respectively, which is notably higher than the suggested water storage capacity of the regolith below the cryolithosphere (177 and 460 m, respectively). Thus, it is not excluded that ~ 2/3 of the all free water amount existing within the Martian crust may be stored within the cryolithosphere.

7.1.2. Possible Existence of CO₂ Solid/Liquid Phases and Salt Solutions within the Cryolithosphere

Given that as the Martian cryolithosphere has planet-wide distribution and reaches a great thickness, the thermodynamic conditions within the cryogenic shell vary considerably with depth and latitude. Therefore it is not possible to exclude that, besides water ice as the main component of the volatiles, both CO₂-ice and CO₂liquid as well as gaseous hydrate (CO₂•6H₂O) as an interaction product may also exist in the cryolithosphere in some amount. The idea about a possible existence of CO, phases and gaseous hydrate within the Martian polar caps and frozen regolith was very popular in the 1970s and has been considered in a series of papers [50, 81, 83]. The research proposed that any excess amount of CO₂ could exist in the global permafrost in the form of clathrate stabilized at some depth by the overburden pressure. On the basis of the analysis of the joint phase diagram of the system H₂O-CO₂ and the Martian geotherms at different latitudes of the planet, Kuzmin [50, 52] compiled a global model of the possible structure and variety of volatile distribution (H₂O and CO₂ phases) within the cryolithosphere. He assumed that the H₂O-ice dominates the phase within the cryolithosphere and it is stable everywhere in the surface regolith, isolating the CO, phases from contact with the atmosphere. According to the approximate model, the cryolithosphere may have patterns of zonal and layered structure resulting from the presence of different CO₂ phases (CO₂-ice, CO₂-liquid and gaseous hydrate CO₂•6H₂O) in addition to the predominant phase of water-ice (see Fig. 7.1).

In the last years there has been again increased debate about whether the Martian subsurface volatile reservoirs within the cryolithosphere are composed only of water ice or solid and liquid phases of CO, and its gaseous hydrates (even methane clathrates) [34, 35, 43, 48, 64, 74, 87]. The debate was stimulated by the "White Mars" hypothesis of Hoffman [34, 35] where liquid and solid phases of CO₂ have been suggested as an alternative to liquid water formation of erosional and collapsed features on both small and large scales. The hypothesis has met a lot of contradictions with the observed morphology of the erosional and collapsed features on Mars [18], but nevertheless, it strongly increased the interest of researchers in the problem of volatile phases other than water phases within the cryolithosphere. The main suggestion of the researchers is that the formation of the young gullies as well as many larger-scale erosional valleys on Mars could have been initiated by decomposition of the liquid or solid phases of CO, and gaseous hydrates due to thermal or pressure breaches within the Martian cryolithosphere provoked by magmatic and tectonic activities. Some other researchers [74] proposed that methane hydrate may be present in substantial quantities within and beneath the cryolithosphere and its dissociation could result in the formation of large-scale collapse features such as the chaotic terrain found at the source of the Martian outflow channels.

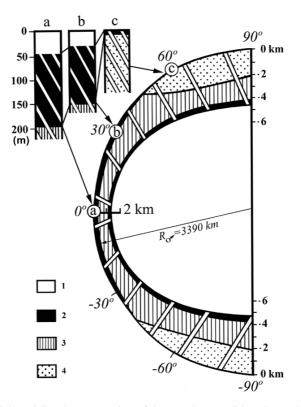


Fig. 7.1 A model meridional cross-section of the Martian cryolithosphere, showing the potential zones of H_2O -ice (1), gas hydrate $CO_2 \cdot 6H_2O$ (2), CO_2 -liquid (3) and CO_2 -ice (4). a, b and c – the cross-section of the upper layer of the cryolithosphere. (Adapted from Kuzmin [53])

Recently, the hypothetical mechanisms involving the liquid and solid phases of CO_2 in the Martian cryolithosphere have been strongly criticized on a theoretical basis by Stewart and Nimmo [108]. Their analysis has shown that under present climate conditions in the Martian near-surface regolith neither condensed CO_2 nor its clathrate hydrate are able to accumulate or are stable in sufficient amounts. They also show that the liquid and solid phases of CO_2 (as well as clathrate hydrates) cannot be stable in the Martian crust over a long geological time and the presence of a thick water-ice rich cryolithosphere would not prevent the CO_2 from diffusion and disruptions (like faulting and impact cratering) at rates faster than it can be replenished. Nevertheless, the question about the possible existence of the liquid and solid phases of the CO_2 and other volatiles within the Martian cryolithosphere continues to be puzzling and intriguing. It is undoubted that the question can be clarified only by a global sounding of the cryolithosphere by means of seismic and radar methods in near-future missions to Mars.

The substantial enrichment of the Martian soil with chlorine and sulfur discovered at the Viking 1 and 2 and Mars Pathfinder landing sites [14, 91, 113] makes it more probable that water-soluble salts (such as chlorides and sulfates) may exist on the Martian surface [14]. Such salts (NaCl, MgCl₂, MgSO₄ and CaCl₂) are considered the most probable candidates for the salts contained in the Martian regolith [13]. The joint presence of ice and salts within the Martian regolith will certainly increase the probability of the appearance of salt solutions (brines) under certain thermal conditions. The solutions of the salts indicated have eutectic points (temperature of total solution freezing) of 252, 238, and 218 K, respectively [6, 120]. If the Martian regolith contains multi-component salt solutions, their eutectic point is lower and will attain 210 K [6]. Hence, if the salt solutions occur within the cryolithosphere (besides water ice), the depth of the ice-bearing regolith base will not be determined by the 273 K isotherm (the melting-point temperature of pure water), but by the eutectic point of the salt solutions. In such a case the thickness of the ice-bearing regolith will be somewhat reduced [106]. On the base of an analysis of the temperature field of the Martian cryolithosphere and of the thermodynamic conditions of the stable existence of possible salt solutions, Kuzmin and Zabalueva [56] proposed a model of the cryolithosphere taking into account regions where zones of potential salt solutions may occur (Fig. 7.2).

According to this model, the occurrence of salt solution zones within the cryolithosphere may be fairly extensive. For example, a zone with eutectic points higher than 221 K can be more than 1 km thick at the equatorial belt and about 2 km thick at latitudes greater than 30° [56]. It is notable that closest to the surface, the position of the eutectic point isotherm of 218 K is in the latitude range $35-40^{\circ}$ at depths of 200–300 m, where it crosses the interface between the dry and icebearing regoliths. Poleward the position of the isotherm becomes deeper (down to ~1 km at 50° latitude). It is interesting that the distribution of the young erosion gullies, which have been recently found on MOC (Mars Orbiter Camera) images [68, 92], begins exactly in the latitude range where the near-surface position of the eutectic point isotherm of 218 K is predicted. The depths of the proposed eutectic point isotherm position and the depths of the gully alcoves are very similar.

The zone of the temporal existence of solutions in the surface regolith may be directly associated with the layer of seasonal temperature variation within the icecontaining regolith. When the temperatures in the layer are higher (seasonally) than the freezing point of the eutectic mixtures (ice + salt), a liquid phase in the soil becomes possible. The ultimate amount of the liquid phase will depend on the proportion of ice and salts amounts in the regolith. The quasi-periodic axialobliquity changes (from minimal to maximal over a period of 125 ka [75, 115]) are one of the main factors responsible for time-dependent changes of the ground ice stability at the Martian surface as a function of latitude.

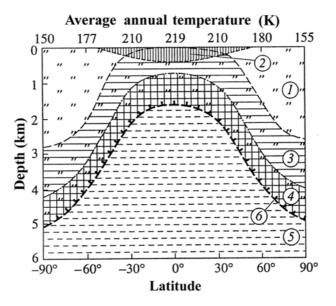


Fig. 7.2 A model cross-section of the Martian cryolithosphere with the zones of stable existence of several water phases and possible salt solutions. 1- zone of stable water-ice existence; 2- zone of desiccated regolith; 3- zone of salt solution stability with eutectic points 218K (CaCl₂•6H₂O + MgCl₂•12H₂O; MgCl₂•12H₂O + MgSO₄•7H₂O); 4- zone of salt solution stability with eutectic point 252K (Na₂SO₄•10H₂O + NaCl•2H₂O; K₂SO₄•10H₂O + KCl); 5- zone of liquid water; 6- lower boundary of the cryolithosphere. (From Kuzmin and Zabalueva [56]).

To estimate the depth range of the surface regolith where the appearance of salt solution in the regolith may be possible, Kuzmin and Zabalueva [57] have performed an analysis of the annual thermal field dynamics within the Martian surface layer for the present climatic conditions (corresponding to 25.2° axial obliquity) and for paleoclimatic conditions (corresponding to maximal obliquity of 45°).

The results of their study (Fig. 7.3) show that the appearance of potential zones with seasonal salt solution within the surface layer at present may occur in a limited range of middle latitudes, but at paleoclimatic conditions (e.g. at an obliquity of 45°) salt solutions with a wider range of eutectic points might appear in the surface layer down to the equatorial zone of Mars because in this period the ice in the surface regolith may be stable even in the low latitude zone [75]. In this case the appearance of salt solutions in the equatorial surface regolith in the past could be responsible for the formation of the (indurated) duricrust layers, which are seen at the landing sites of the Viking and Pathfinder Landers [91, 113]. It has also been proposed [56] that, if salt solutions arose within the surface regolith seasonally (even on the scale of a water film), they may be considered as an analog to the freeze-thaw process, which occurs seasonally in the permafrost regions of the Earth.

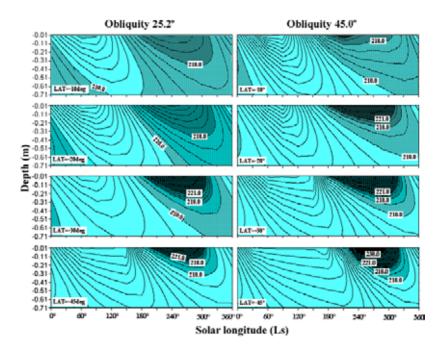


Fig. 7.3 Dynamics of the temperature field in the surface regolith layer with seasonal temperature fluctuations (during period of one year) at different values of the Mars obliquity for the southern hemisphere of the planet. The shaded area represents the zones of potential seasonal salt solution appearance with eutectic points 210–238K. (From Kuzmin and Zabalueva [57]).

7.2 Stability of Ground Ice

The equilibrium of ground ice with the Martian atmosphere or the conditions for its stable existence in the surface layers is determined by the correlation between two fundamental processes: sublimation of ground ice and condensation of atmospheric moisture into the surface regolith [25, 28, 63]. The first process dominates on Mars when ground temperatures are above the frost-point temperature (the temperature at which the atmospheric water vapor will begin to condense) corresponding to the average amount of water in the atmosphere, while the second process becomes effective in an inverse situation. The processes act on the Martian surface on time scales of days, seasons, and up to a year. In order to keep the ground ice stable the temperature must be below the frost-point temperature of atmospheric water vapor. As it requires a long time to reach equilibrium at which the effects of seasonal oscillations in both the atmospheric water amount and in thermal waves in the surface regolith are smoothed, it is appropriate to use average annual values of the atmospheric water vapor density and surface temperature.

Under the present climatic conditions of Mars the average annual surface temperature is much below the water freezing temperature (216 K) everywhere from the equator to the poles, but the frost-point temperature corresponding to an average annual water vapor amount in the atmosphere (~ 10 pr μ m) is roughly 200 K. For this reason, the existence of ground ice in equilibrium with the present content of H₂O vapor in the atmosphere is currently achieved only in the colder regions poleward of about ±40° [25, 28, 63], where the average annual surface temperatures are equal to or lower than the frost-point temperature. Within the latitude band ±40° the ground ice undergoes sublimation and it may exist at some depth, which depends on latitude.

In addition, the ice stability within the regolith layer is determined by the rate of H₂O molecule diffusion through the recovering dry regolith layer and into the atmosphere. The water lost from low-latitude regions would have been trapped within high-latitude areas, being possibly incorporated into both the surface regolith layer and the layered deposits of the polar caps. The main factors which strongly constrain the process of H₂O molecule diffusion through the regolith are both the mean free path of H₂O molecules () in the CO₂ gas (~ 8 µm) and the pore radius (r) of the regolith materials (significantly variable). The values of the ratio (r /) determine the dominant modes of the diffusion transport: bulk molecular diffusion (at r / > 10), when repeated collisions with other molecules in the pores dominate, and Knudsen diffusion (at r / < 0.1), when collisions between the diffusion molecules. In the first mode the diffusion rate of H₂O molecules through the regolith is much higher than in the second one that significantly reduces the efficiency of the diffusion transport process.

Comprehension of the ground ice retention at the Martian surface in diffusive contact with a dry atmosphere is one of the fundamental problems of the water exchange regime between the regolith, atmosphere and the polar caps, and has been the focus of attention of many authors. One of the first, Smoluchowski [107], calculated that in a wide range of the soil particle sizes and porosities $(0.5-1000 \ \mu m)$ and 0.01 to 0.8 respectively) a 10 m layer of ice-bearing soil beneath a dry soil layer of moderate thickness (from several cm to a few hundreds of meters) could have been preserved for around 1 billion years even in the equatorial zone of Mars. A detailed analysis of the duration of ground ice under modern climatic conditions [15, 22, 27] showed that the desiccation of the ice-bearing regolith in the equatorial zone of Mars is a very slow process, which becomes less effective with increasing latitude and is replaced at latitudes > 50° by the process of ice deposition in the surface regolith. Clifford and Hillel [15] studied the lifetime of ice in an initially isothermal 200-m-thick ice-bearing soil layer (with different pore size distributions) buried beneath a 100 m layer of dry soil. They found that for the modern thermal regime of the surface at low latitudes about half of the icebearing soil layer would have lost all their ice over 3.8 billions years. Using more detailed model calculations (taking into account the quasi-periodic changes in planet's obliquity and orbital parameters), Fanale et al. [27] studied the ground ice table retreat due to ice sublimation as a function of time and latitude for a regolith

material with a uniform pore size. They determined that for a regolith material with 10 μ m pore size, the ground ice must have sublimed completely down to few hundred meters depth at low latitudes and down to few tens of meters at moderate latitudes over 3.8 billions years. One of the vital results of their model is that the depth of the ground ice table (as a function of time) is very sensitive to the pore size. Similarly, at a pore size of 1 μ m the depth of the ground ice table is essentially shallower than at a pore size of 10 μ m by a factor of three.

As is well known [42, 112, 115], Mars undergoes significant long-term oscillations on its orbit, which are responsible for the climatic variations and the behavior of the subsurface volatiles. More recent models of the behavior of the ground ice on Mars during the past 2.5 Ma [75, 76, 78, 79] have examined the effect of orbitally induced changes in climate on the thermal and diffusive stability of nearsurface ground ice, using a diffusion and condensation model. Based on the models, the behavior of the ground ice in the past could have been significantly different from that at the present time, resulting from high-amplitude oscillations in obliquity. The oscillations essentially change the distribution of insolation in the high-latitude regions. As a result, the sublimation rate of ice in the residual polar caps will also dramatically change during the obliquity cycle.

Following the existing theoretical estimations [40, 115], the net summertime sublimation at 35° obliquity might be several hundred times higher than at present, while at 15° obliquity the sublimation might be more than 10 times lower than at present. Moreover, the increasing atmospheric water abundance at high obliquity is accompanied by an increase of the frost-point temperature. Thus, in the period of higher obliquity (> 30°), when the average annual surface temperatures are essentially lower than the frost-point temperature, the ground ice becomes stable within the superficial regolith at the equator and mid latitudes, filling the top few meters of the regolith with significant amounts of ice due to the condensation of atmospheric water [76]. Conversely, in the periods of low obliquity the ground ice sublimes, resulting in desiccation of the regolith in most parts of the planet's surface (within the latitude band $\pm 60^{\circ}$).

In the current period the ground ice within the superficial regolith is stable only in 1/3 of the planetary surface in the regions poleward of $\sim 40^{\circ}$ latitude. On the basis of the geographic mapping of the ground ice stability, Mellon and Jakosky [76] estimated the percentage of time during the past 1 Ma in which ice has been stable with respect to sublimation at any depth within the regolith. This percentage is a combination of the length of time at high obliquity where ice is stable and the frequency at which the obliquity reaches values sufficiently high for each geographic location. Thus, in the regions equatorward of 30° latitude, the ground ice is stable about 20 % of the 1 Ma period. Poleward of 30° latitude the percentage of the ice stability time increases rapidly and near 60° latitude the ground ice is stable more than 80 % of the period. It was shown [76] that the water exchange between the regolith and polar caps during an obliquity cycle (about 125 ka) is very essential and the total exchangeable amount of ground ice may be equal to 5.8×10^{16} kg [76]. The ice amount would account for a deposit about 29 m thick on both poles that is consistent with the scale of the individual layers of the polar layered terrain (between 14 and 46 m) measured from the Viking images [3]. It is necessary to note that, as follows from the model, during the last 300 ka the variation of the

ground ice in the top meter of the regolith was considerably subdued because this behavior correlates with a period of a relative quiescence in the obliquity variations.

In contradiction to previous models, Mellon and Jakosky [78] also examined the specific steady-state behavior of ice distribution in the regolith, when the depth of the ground ice table under ice-free (dry) regolith is found by balancing the loss of water to the atmosphere with the resupply rate from the interior of the icecemented regolith. In this case the ground ice table recession incorporated the recondensation of water vapor as it diffuses through the regolith toward the surface, approaching lower temperatures. According to the models the porous ground ice will persist at relatively shallow depths for geologically long periods of time due to recondensation of water vapor. Using models for three different types of regolith (particulate, porous rock and dense rock regolith materials), the authors showed that the maximum ice table depths in equatorial regions may be about 5.8, 87 and 290 m, respectively. Below the ground ice table depth the ice content may gradually increase from 0 to ~100 % of the porosity volume at depths of several hundred meters.

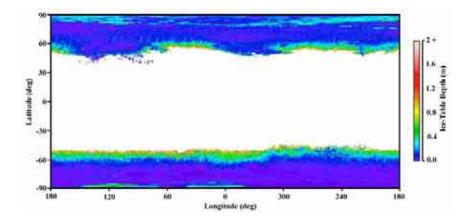


Fig. 7.4 Model prediction of the ice table depth (in the top 1 m) assuming an annual-mean atmospheric water vapor column abundance of 10 pr μ m with a scale height of 10.8 km. (From Mellon et al. [79], courtesy of M.T. Mellon.)

Recently Mellon et al. [79] revised the model of the ground ice stability on Mars, taking into account the thermal conductivity of ice-cemented soil, the effect of the surface elevation on the atmospheric humidity and new observations of thermal inertia of the Martian surface created from TES data. The new model also allows for condensation of water vapor at any depth where the equilibrium conditions are met and includes the geographic distribution of thermal properties, enabling mapping of the distribution of ground ice for periods with different obliquities. Figure 7.4 presents the map of the ground ice distribution and table depth [79]

for modern climatic conditions. As can be seen from Fig. 7.4, the ice-table depth is less than 10 cm at latitudes > 60° , while at some places it may be equal to 20–40 cm. Within the latitudes 40–60° (in the northern hemisphere) and 50–60° (in the southern hemisphere) the position of the ground ice-table is deeper and varies in the polarward direction from ~1 m to 30 cm.

7.3. Morphological Indicators of Ground Ice Existence in the Surface Layers of the Cryolithosphere

Besides theoretical predictions, information about the ground ice distribution on Mars may also be inferred directly from observations of some morphological features on the planet's surface associated with the presence of ground ice. Usually such features have been attributed to rampart craters (craters with fluidized ejecta), lobate debris aprons, terrain softening, polygonal terrains, thermokarst features, askers and moraines, outflow channel and features of volcano-ice interaction [9, 10, 42, 52, 65, 67, 73, 94, 106]. In this section we will consider only those geomorphic features whose morphology is most strongly indicative of past or present existence of ground ice in the Martian regolith. As such features we will discuss the impact craters with fluidized ejecta, debris flows and terrain softening and polygonal terrains. In the description of polygonal terrains very large polygonal structures (with sizes > 1 km) were excluded from our consideration since their origin is generally associated with tectonic processes [67, 88] rather than with frost cracking.

7.3.1 Morphology of the Impact Craters with Fluidized Ejecta as Tools for the Study of the Global Ground Ice Distribution in the Martian Regolith

Most of the fresh Martian impact craters in the size range 1–80 km have unique fluidized ejecta patterns distinctively different from those around impact craters on the Moon and Mercury, which have radial ray-like ejecta patterns that are ballistically deposited. The Martian craters display some type of the layered ejecta morphology, which in the literature was very often called "fluidized" or "lobate" in as far as they have flow-like morphology resembling muddy slurry [8]. As a rule, the ejecta type appears with a certain crater size, which varies from region to region. The smallest fresh craters with fluidized ejecta have diameters of about 1 km, while diameters of the largest crater with this type of ejecta are as large as 80 km. This unique mobility of the Martian crater's ejecta is considered by most researchers as the result of incorporation of ground ice or groundwater during the crater formation [1, 4, 8, 20, 30, 51, 53, 85]. Due to this morphology of the ejecta, the craters have been referred to as rampart craters [8]. As follows from the morphology of rampart craters, their ejecta were emplaced primarily as radially, rather than balistically, directed surface flows (Fig. 7.5). In contrast to ballistically de-

posited crater's ejecta on the Moon and Mercury, the flow-like crater ejecta on Mars very often skirt and streamline the relief of the pre-impact terrain, rather than being superposed as a mantle, serving as a strong argument for the ejecta material being emplaced primarily as surface flow [8] due to a fluid presence within the ejecta.

Experimental work conducted to reproduce the observed ejecta patterns has shown contradictory results. One of the high-velocity experimental impacts into mud [30,118] reproduced the basic morphologic characteristics of the fluidized ejecta, while other similar impact experiments on dry fragmented targets under different atmospheric pressures [96, 97] have shown that the atmosphere could play an important role in forming the fluidized ejecta patterns. Schultz and Gault [96, 97] suggested that the rampart patterns were formed due to the fine ejecta material that was decelerated by the atmosphere and incorporated into groundhugging debris flow with entrained air. Nevertheless, most researchers who have studied the dependence of the rampart crater distribution and morphology on size and latitude are convinced of the ejecta fluidization mechanism due to subsurface volatiles [1, 2, 4, 19, 20, 51, 85, 86, 118]. The recent rampart crater ejecta rheology model [39] and cratering simulation model [108] also verify the idea that shock-melting of the ground ice at the moment of the crater formation will produce large quantities of liquid water in the ejecta material resulting in their fluidization.

Additional confirmation of the ejecta fluidization mechanism due to subsurface volatiles has also been found on the basis of terrestrial impact crater studies. For example the ejecta blanket of the Pechezh-Katunk crater (40-km diameter crater, located on the Russian Plate) very closely resembles the fluidized ejecta pattern of the Martian rampart craters [71]. The structural-lithological characteristics of the crater are strong evidence that the ejecta have been formed through the radial movement of fluidized material like mudflow as a result of impact in the water-saturated sedimentary target materials [72]. Based on the paleographic reconstruction at the time of the Pechezh-Katunk crater formation (Middle Jurassic) the target area has represented seaside plains with numerous lagoons and lakes [89]. In this way, it is highly probable that the morphological indicators of ground ice presence on Mars.

As found by many researchers [1, 4, 9, 19, 36, 51, 52, 55, 85], the craters with fluidized ejecta are spread over Mars in all geological units and at all latitudes from the equator to the periphery of the polar caps and meet at different elevations from -3 km to over 8 km above the planetary datum. Notable regional and global trends in the morphology and morphometry of such craters have also been found [1, 85] and may serve as an indirect indicator of the variability of the ground ice distribution.

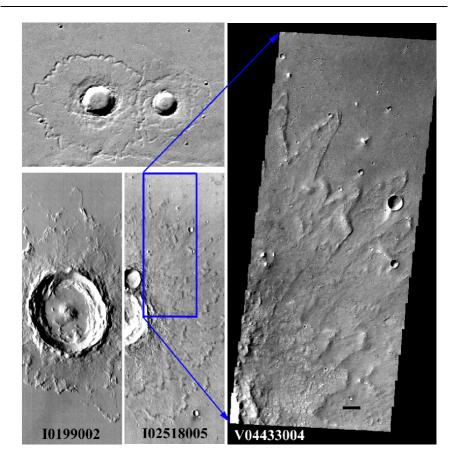


Fig. 7.5 Single-layer (a) and multi-layer (b, c) types of fluidized ejecta of the Martian fresh impact craters. a- fragment of the Viking MDIM; b, c – IR day-time THEMIS images (19.53°N, 152.87°W and 25.76°N, 44.5°W); d- visible THEMIS image (25.76°N, 44.5°W), showing details of the ejecta patterns from (c). Scale bar is 2 km.

According to the physics of the impact process [12, 21, 22, 45, 79], vaporization and melting of the ground ice at the moment of impact may occur in the zone of the subsurface that is shocked to approximately 10 to 100 GPa. It is known [37, 79] that the volume of such a zone is a function of the crater size, becoming larger with increasing crater diameter. In this way, if the desiccated regolith thickness is equal to the crater's excavation depth, no evaporation or melting of the ground ice will be revealed and the crater ejecta patterns will have a radial-like structure. If instead the crater's excavation depth exceeds the ground ice table level, a part of the interstitial ice becomes involved in the crater ejecta. Then the appearence of the ejecta fluidization patterns or their absence can depend on the amount of excavated ice. Thus, the morphology patterns of the fluidized ejecta of the Martian craters and their morphometry provide an effective tool for the study of the ground ice distribution on Mars and for the estimation of the relative ice content within the regolith as a function of latitude and depth.

Early regional studies of fresh impact craters on Mars [4, 50] convincingly have shown that, in a concrete area, a certain threshold crater size (called the onset diameter) exists and, as a rule, craters smaller than this have no fluidized ejecta, while larger craters do. This discovery provided an effective method for subsequent global mapping of the ground ice table depth variations and relative ice content in the surface layer of the Martian regolith.

The global mapping of the onset crater diameter as well as the most complete statistical studies of the geographic distribution of the rampart craters were performed in the 1980s [19, 53]. The global mapping of the ground ice table variations [19] was achieved (using the Viking photomosaics of Mars on the scale 1:2,000,000) based on the analysis of the morphometric parameters and morphological types of all fresh impact craters with fluidized ejecta (9089 craters in the diameter range 1–60 km) and without such ejecta (14,630 craters in the diameter range 1–10 km). The studies found that on Mars there is a very noticeable dependence of the onset diameter of the rampart craters on latitude. In the equatorial zone of Mars the onset diameters are largest and vary from 4 to 7 km, whereas at latitudes of $50-60^{\circ}$ they remarkably decrease to just 1–2 km.

This means that the ground ice table in the equatorial zone is located considerably deeper than at high latitudes. One of the convincing illustrations of this tendency comes from the distribution of the one-size craters (2-km diameter) with and without fluidized ejecta (Fig. 7.6). As can be seen from Fig. 7.6, the spreading of the craters with dry ejecta is dominant mainly in the low-latitude regions of Mars (approximately $\pm 30^{\circ}$), whereas at higher latitudes the craters with fluidized ejecta are mostly prevalent. Such a tendency serves as obvious evidence that the depth of the ground ice table (or the thickness of the desiccated upper layer of the regolith) regularly decreases from the equator to higher latitudes. As one can see, such a tendency is in remarkable agreement with the prediction of thermodynamic models of ground ice stability on Mars (see Section 7.2)

Using a relationship between the observed onset crater diameter and the crater's excavation depth in accordance with the physics of the impact process [21, 22, 38, 109], Kuzmin et al. [50, 53] estimated the depth of the boundary between the upper desiccated regolith layer and the underlying ice-bearing regolith layer, and mapped the parameters regionally and globally. The global map of the parameter variation is shown in Fig. 7.7. As one can see from the map, the depth of the boundary between desiccated and ice-bearing regolith layers is notably variable, depending on latitude, and is typically 300-400 m near the equator and decreases to 200 m at 30° latitude and to 80-100 m at $50-60^{\circ}$ latitude. Moreover, it has been found that at certain latitudes the maximum depths of the boundary correspond to the most elevated regions and to the oldest cratered uplands of the southern hemisphere of Mars [53].

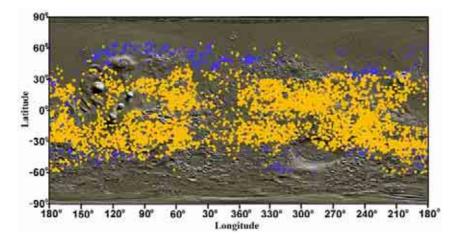


Fig. 7.6 Spatial spreading of the fresh (with 2-km diameter) impact craters on Mars with fluidized (blue) and dry (yellow) ejecta. (From Kuzmin et al. [60].)

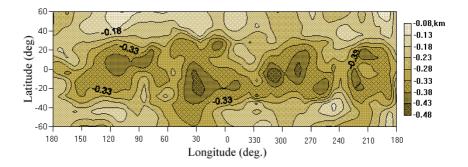


Fig. 7.7 Map of the boundary depths between the upper mostly desiccated regolith layer and the underlying ice-bearing regolith. (Compiled based on the Martian impact crater database from Kuzmin et al. [55].)

It is notable that the axis of the zone with the maximum depths to the top of the ice-bearing regolith is displaced with respect to the equator into the southern hemisphere by $10-15^{\circ}$, which may result from higher surface elevations in this hemisphere. Because some top part of the ice-bearing regolith layer has been excavated during the formation of the onset rampart craters (resulting in the appearance of the ejecta fluidization signs), the estimated depth to the top of the ice-bearing regolith should be regarded as somewhat overestimated. As is known on the base of terrestrial debris flow measurements [89] and rampart crater ejecta rheology models [39], the volume of water necessary for beginning material fluidization is approximately equal to 20 % by volume. In this case, the mapped

depths of the boundary between desiccated and ice-bearing regolith layers may be considered as the thickness of the regolith layer, where an average amount of ground ice is not less than 20 % by volume.

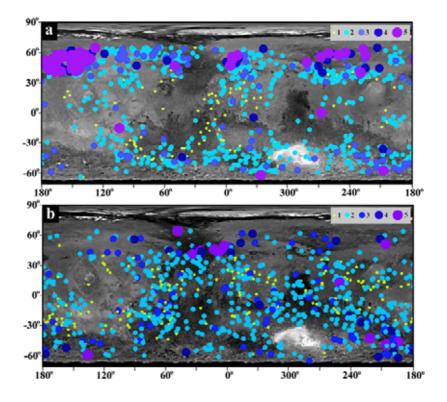


Fig. 7.8 Map of the relative ice content variation within the upper regolith layer equal to the impact crater excavation depth 300 m (a) and 500 m (b). The size of the circles represents the value of the ratio $D_{\rm ef}/D_{\rm cr}$. Legend: 1 - ratio 1-2; 2 - ratio 2.1-3; 3 - ratio 3.1-4; 4 - ratio 4.1-5; 5- ratio 5.1-8. (Compiled based on the Martian impact crater data-base from Kuzmin et al. [55].)

While it is currently impossible to determine the absolute content variations of ground ice in the Martian regolith, it is possible to make an estimation of the relative ground ice content by means of qualitative parameters such as the ratio of the fluidized ejecta diameter to the diameter of the crater itself (ratio D_{ef}/D_{cr}). It was assumed that a more extensive fluidized ejecta diameter for a certain crater diameter is indicative of a higher concentration of ground ice within certain excavated regolith layers. On the basis of many studies [1, 19, 20, 52, 53, 84, 85] a strong

dependence of the parameter on the crater diameter (or the excavation depth) and latitude can be found. The regional and global mapping of the parameter of relative ground ice content [19, 20, 52, 53] has shown that for a narrow range of rampart crater diameters (or the depths of excavation) the parameter is slightly variable within the latitude zone $\pm 30^{\circ}$ and it remarkably increases toward higher latitudes, being notably higher in the northern hemisphere than in the southern one (Fig. 7.8a and b). Thus, the anomalies of the highest values of the relative ground ice content are spread over Utopia, Acidalia and Arcadia Planitias. Statistical analysis of the averaged values of the ratio $D_{\rm e}/D_{\rm cr}$ as a function of the crater diameter and latitude [53] shows a notable tendency of the relative ground ice content to increase with an increase in crater diameter and latitude (Fig. 7.9).

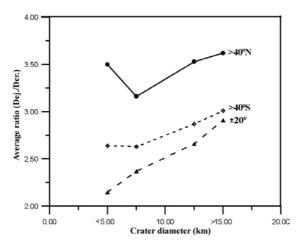


Fig. 7.9 Average relative ice content (D_{ef}/D_{er}) in the different latitude zones as a function of the crater diameter. (Plot based on the Martian impact crater data-base from Kuzmin et al. [55].)

Furthermore, one can see that the high latitudes in the northern hemisphere are characterized by essentially higher averaged values of the relative ice content than in the southern hemisphere and in the equatorial zone. The anomalous rise of the relative ice content, which has been found at northern high latitudes within the excavation layer of the rampart craters less than 5 km in diameter, represents obvious evidence of an enhanced ice concentration in the upper regolith layer in comparison with the underlying layer.

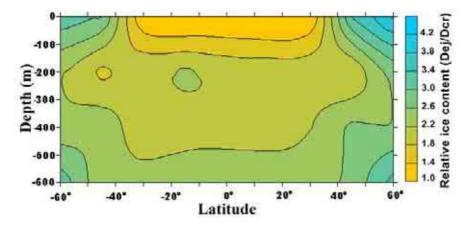


Fig. 7.10 Averaged relative ground ice content on Mars up to 600 m depth as a function of the latitude. (Compiled based on the Martian impact craters data-base from Kuzmin et al. [55].)

A notable tendency of the ratio to increase with increasing rampart crater excavation depth has also been found [53]. This tendency is well seen in Fig. 7.10, representing the global cross-section (down to 600 m depth) of the average relative ground ice content on Mars as a function of latitude. The data also show a notably higher concentration of ground ice at different depths in the northern plains in comparison with the southern hemisphere. One of the possible reasons for the observed asymmetry of the relative ground ice content may be that the northern plains represent mainly a long-term sedimentary basin where a large part of the sediments is associated with flooding of the great Martian outflow channel [10].

7.3.2 Debris Flows and Terrain Softening

Debris flows and terrain softening represent other geomorphic features that are highly suggestive morphological indicators of the distribution of ground ice within the Martian regolith in local areas of the planet [9, 10, 11, 65, 102, 103]. Morphologically both features represent viscous creep formations, which occur mainly in the $30-60^{\circ}$ latitude belts in both hemispheres of the planet. Furthermore, the debris flow features are mostly disposed within regions with fretted terrain separating the northern lowlands from the southern highlands in the longitude interval $280-360^{\circ}$ W. The terrain consists of a great number of plateau-like residual forms surrounded by the lower flat plain surface or separated by the flat-floor valleys. The main regions where the features are mostly spread in the northern hemisphere of Mars are represented by the Mareotis Fossae region ($50-90^{\circ}$ W), the Acheron Fossae region ($130-140^{\circ}$ W) in the Phlegra Montes ($180-200^{\circ}$ W) and the Deu-

teronilus-Protonilus regions (280–360°W). The occurrence of these features in the southern hemisphere of Mars is restricted mainly by massifs on the rim of the Hellas and Argyre basins.

It is remarkable that the debris flows and terrain softening features are found approximately in the latitude belts where ground ice is expected from its stability relations and where viscous flow of ice-bearing material should be most evident due to the dependence of rheology on temperature [10]. Since the most typical characteristic of the features is their distinctive convex-upward topographic profile, it was suggested that they could be formed due to the frost creep mechanism [9], the flow of mixture of the debris and ice incorporated into the debris material as a result of precipitation from the atmosphere [103] and mass-wasted debris due to abundant ground ice within the regolith of the uplands [65]. Although using the suggested mechanisms, other researchers [56] have shown that the processes of the seasonal appearance of salt solutions within the surficial layer of the regolith may also be an important factor in the formation of such subdued features of the relief. They suggested that even the temporal appearance of a small amount of the liquid water phase in the form of salt solution in the ice-containing surface material could have substantially enhanced the shear stress and decreased the resistance of the material to downward movement.

The fact that the considered types of relief are absent at low and high latitudes, where similarly scarps and cliffs occur in the cratered highlands or along the wall of outflow channels, may be explained by the following reasons: the thick surface layer of the desiccated regolith (down to first hundred meters) exists at low latitudes [26, 28, 50, 51], while at latitudes > 60° the ice flow is essentially limited by much lower temperatures at which the strain rate of ice subjected to shear stress decreases significantly [102]. In accordance with morphological studies [103, 104], there are three main types of debris flows represented by the lobate debris aprons at the base of the cliffs, the lineated valley fill, and the concentric crater fill (Fig. 7.11a, b, c, d). It is typical that the lobate debris aprons have very distinct flow fronts, a noticeable convex-upward topographic profile and lineation showing the main trends of the debris flow movements. The extent of lobate debris aprons varies from 10 to 30 km and their surface shows elements of the transverse ridges and grooves as well as longitudinal lineation, which represent typical characteristics of the terrestrial glaciers and rock glaciers [10, 106].

In areas where the residual elevations are divided by relatively narrow valleylike depressions, one may observe a complete filling of their floors by the masswasting material that flows away from the opposing scarp walls. The collision of the flow fronts from opposing scarp walls on the valley floor result in formation of lineal ridges and grooves resembling the median moraines of terrestrial glaciers (Fig. 7.11b, c). The morphology of some viscous flow features associated with the debris flows is very similar to that of the terrestrial rock glaciers [95, 105] formed due to the downward movement of the angular rock debris with internal ice or icecemented slope sediments [116, 117]. In contrast to the lobate debris aprons, which are spread regionally, the concentric crater fill (Fig. 7.11d) and terrain softening (Fig. 7.11a) are much more widely spread in the latitude belts 30–60°.

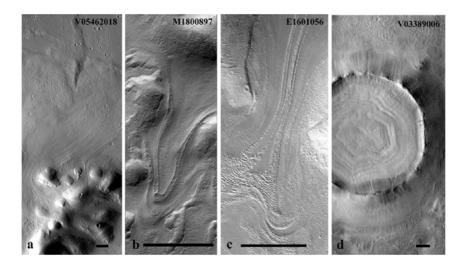


Fig. 7.11 Main morphological types of the lobate debris flow and concentric crater fill commonly prevalent in the latitude belts 30° - 60° . a – lobate debris aprons (THEMIS visible image V05462018); b – rock-glacial like debris flow (MOC image M1800897); c – lineated valley fill resembling the median moraines of terrestrial glaciers (MOC image E1601056); d – concentric crater fill (THEMIS visible image V03389006). Scale bar is 2 km.

As usual the concentric crater fills have a gently rounded and smoothed rim and their interior is strongly filled by deposits whose surface is characterized by distinct concentric ridges and grooves which at places outline the lobe-like features pointing down into the crater. The notable descending fabric of the slope material is often seen on the external and the internal slopes of the crater's rims that are indicative of a viscous flow of the surface material. Moreover, the slope profile of the internal crater walls is principally convex upward which also corresponds to viscous movement of the slope material enriched by ice. The main characteristic of the terrain softening is the gently smoothed, rounded and subdued shape of different surface features such as the rims of the craters in all sizes, the crest of the ridges and the edges of the escarpments, which at low latitudes have very sharp shape outlines. More detailed morphological analysis of the lobate debris aprons and terrain softening based on the new high-resolution images received by MOC of Mars Global Surveyor [11, 69, 70] has shown that the surface of the features has complex pit-an-butte textures at ten-meter scale, which are often oriented along the lineation observed on the Viking images. The origin of such textures was interpreted as a result of the ice sublimation from the upper 10-meters layer that is significantly guided by a network of subsurface fractures associated with the internal deformation process.

The observed morphologic particularities of all the viscous flow features, as well as the fact that they are spread in areas where the expected stability of ground ice is consistent with the suggestion that their formation is provoked by promoting slow creep or viscous flow of the ice-bearing regolith disposed mostly on the sloped relief [104, 106]. Following the calculations in [103], the formation of such debris flows requires at last a few tens of % of ice content. As stated on the basis of the model [41], viscous deformation down to 1 km depth is required to form the lobate debris aprons and the terrain softening.

Recently conducted analysis of the topography of the lobate debris aprons using MOLA data [69] has confirmed the convex-upward shape of the lobes typical of the ground ice creeping mechanism. Finite-element analysis applied to investigate the possible formation of the debris aprons on the $34-45^{\circ}$ scarp [114] has shown that under the present Martian climate viscous creep of the 0.5–1 km thick regolith layer (with 30 % ice content by volume) can occur quite rapidly (in 10^3-10^4 years) with formation of the typical convex-upward shape of the slope topographic profile.

An alternative mechanism for the feature formation has been suggested recently by Milliken et al. [82]. They suppose that large-scale viscous flow features and terrain softening may be a result of many cycles of deposition of an ice-dust mantle. Their study has shown that it is possible for an ice-rich mantle material to flow under current or past Martian surface conditions. Using MOLA topographic data for the slope angle measurements, Milliken et al. [82] estimated that an ice-rich material with a thickness of 10 m may have a basal shear stress of the order of 10^{-2} Mpa, which implies shear strain rates of the order of 10^{-11} – 10^{-16} s⁻¹ at temperatures between 180 and 220 K and ice grain sizes between 10 and 1000 μ m. They stated that for a low strain rate of 10^{-15} s⁻¹, a shear strain of 1.0 would only require an upper age limit of 30 Ma for the viscous flow features formation if one assumes that this strain rate is equivalent to the average one over the lifetime of the features. The study of the impact crater distribution over lobate debris flow [70] shows that the sublimation process, responsible for the formation of the complex pit-an-butte textures on the lobate surface, could have occurred in the last tens of Ma up to the recent past. It is reasonable that the formation of all the viscous flow features occurred during the late Amazonian period of the Martian geologic history, but nevertheless it is still unknown how close to recent time the formation of the viscous flow features was stopped and whether it continued to be active in current time. One possibility of obtaining an answer to this question would be to conduct a photogrammetric analysis of the viscous flow features on the basis of both the MOC high-resolution stereo images and images to be received soon by the High Resolution Stereo Camera (HRSC) of Mars Express.

7.3.3 Polygonal Terrains

As is well known from numerous studies of the terrestrial permafrost zones, the polygonal terrains represented by ice-wedge polygon patterns (Fig. 7.12) are the most widespread features that serve as basic morphological indicators of the presence of ground ice deposits [93, 116]. The main mechanism for the formation of polygonal is the frost cracking process provoked by thermal contraction in the ice-bearing deposits. The frost cracking process is widespread in the permafrost area on Earth and is responsible for the formation of the ice-wedge polygons as the

contraction cracks are repeated along the same fracture plane annually in wintertime. Frost cracks appear when the soil's thermal tensions exceed the threshold durability of the soil [49, 62]. The typical ice wedge polygon sizes on Earth are in the range from 10 to 30 meters, while at some places their maximum size achieves 100–150 m. On Earth the scale of the ice-wedge polygons depends on the amplitude of the winter temperature fluctuations and also on the durability and physicalchemical characteristics of the frozen sediments.

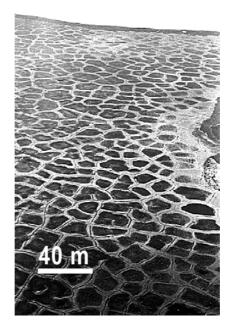


Fig. 7.12 Example of the ice-wedge polygons that are widespread in the Arctic on Earth (the surface of the Kolyma river alluvial plain in Eastern Siberia). Photographed by the author.

The polygonal-like features on Mars with scales approximately similar to terrestrial ice-wedge polygons were first described using Viking Lander 2 panoramic images and Viking Orbiter images [66, 67, 88]. The size of the polygon patterns observed around the Viking Lander 2 is in the range 5–10 m and their troughs have a width of 1 m and a depth about 20 cm, being outlined by small shoulders lifted up to 10–15 cm [88]. The fact that such features are completely absent at the Viking 1 Lander site (22.5°N latitude) agrees with the suggestion that the icebearing material in the area of the Viking Lander-2 site (47°N) may lie very close to the surface. Larger polygonal terrains on Mars (with a size of 50–300 m across) have also been found on the high resolution Viking Orbiter images showing the presence of the polygons at some places at 47°N latitude. Based on the morphology of the polygonal features, many researchers believed that the most probable origin of the Martian polygonal features (in observed size range) is the thermal contraction of ice-rich sediments [7, 53, 65, 66, 88].

High-resolution imaging of Mars received recently by MOC during the MGS mission [68] has shown much more detailed and more numerous views of the Martian polygonal terrains, which are spread mainly at high latitudes. An initial attempt to determine the nature and global distribution of polygonal terrains on Mars has been conducted only on the basis of 68 MOC images [100] and has shown that the Martian polygonal terrains are located mainly at latitudes > 40° in both hemispheres. Recent analyses of MOC images in many regions of the planet have shown that the morphology of the Martian polygonal features is very similar to the morphology of the terrestrial ice-wedge polygons, while their size range (~7-300 m) is somewhat wider [59, 100, 119]. Comparative morphological analyses of the ice-wedge polygons on Earth with polygonal terrains on Mars show that on both planets the features have a very similar morphology [58, 100, 119], their size distribution is analogous, and in both cases the features are characterized by 3-ray and 4-ray intersections of the polygons' sides [58]. Like in Arctic permafrost areas on Earth, the shape of the polygonal patterns on Mars are mostly represented by hexagonal and orthogonal geometry, while at some places their shape has random orthogonal, rectangular and radial orthogonal geometry. The notable morphological similarity between the polygonal features on both planets allows us to suggest that the features on Mars were most likely formed due to the process of thermal-contraction cracking in ice-rich sediments.

Following the morphological study [61], the observed polygonal terrains on Mars may be subdivided into several main types (1, 2, 3, 4 in Fig 7.13a, b, c, d): 1) small-scale (with very regular size), high-center polygonal nets; 2) large-scale, polygonal nets with orthogonal and hexagonal structural elements, located on the different types of high latitude plains; 3) large-scale polygonal nets with a mostly radial orthogonal and rectangular structure, located mainly on the floors of impact craters; 4) large-scale polygonal nets of mostly orthogonal shape and with distinct parallel shoulders (ridges) along the edges of the wedge troughs.

The first type of terrain is characterized by the smallest block sizes (7-30 m across) with wedge's widths at the limit of image resolution (< 2 m). This type is characterized by a very similar size of polygonal patterns with small dispersion of their size varieties and represents the most widespread type found on Mars. When the polygonal patterns of this type are located on sloped surfaces (such as hill slopes, or the interior slopes of craters), the polygon nets acquire a linear orientation along the slope. In this case, the longitudinal axis of the polygons is usually 4–6 times longer than their transverse axis. The other three types of polygonal terrain have a notably wider size range (30–200 m), with wedge widths from a few m to 15 m, and have a more limited random distribution compared to the first type.

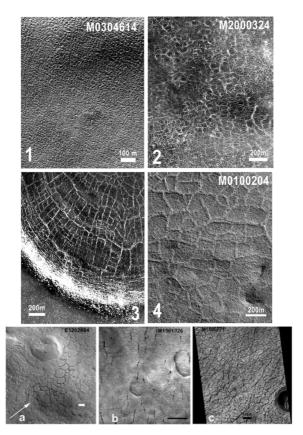


Fig. 7.13 Varieties of morphological types of polygonal terrains (1–4) and shapes of their transformation (a–c) by aeolian and sublimation processes. 1- regular nets of the small, high-centre polygons, which are most widespread on Mars; 2- large-scale polygonal nets with orthogonal and hexagonal structural elements; 3- large-scale polygonal nets of the radial orthogonal and rectangular patterns, located mainly on the floors of impact craters; 4-large-scale orthogonal and hexagonal polygonal nets with distinct parallel shoulders (ridges) along each site of the wedge's troughs; a- eroded subtype of polygonal nets with ridges instead of original wedge troughs (MOC image E1202664), bar scale is 100 m, arrow- direction from Sun; b- sublimated subtype of polygons with distinct fissures and chain pits along the wedge lines, resulting from sublimation of ice (MOC image M1500771); c-degraded subtype representing obliterated polygons by sublimation and deflation processes with unfilled troughs on the place of former wedges (MOC image M1901376), scale bar is 100 m.

The second type of polygon is also widely spread, covers different kinds of plain surfaces as well as flattened hill tops and crater ejecta surfaces and is characterized by notable varieties of the morphological shapes. The third type is morphologically similar to the second type, but it has been only found on crater floors. The fourth type is much less common than the others, and is characterized mainly by an orthogonal structure and shoulders (ridges) present on the edges of the wedge troughs. Sometimes the first type of feature forms joint nets with other types.

Among the polygonal terrains analyzed, three other morphological subtypes (ac in Fig. 7.13e, f, g) have been found [61]: a) polygons with distinct ridges instead of the original wedge troughs (eroded or striped out subtype); b) polygons with distinct fissures and chains of the pits along the wedge patterns (collapsed, sublimated subtype); and c) completely or partly obliterated polygons with unfilled troughs (degraded, paleo-polygons subtype).

That is, the subtypes apparently have been formed at different stages and with different styles of exogenous resurfacing of the main polygonal types. The polygon subtypes are found mainly in equatorward edges of the latitude belts where the polygonal terrains are mostly spread. The existence of such subtypes of polygonal terrains may be considered as evidence in favor of the strong modification of the original polygonal patterns by sublimation of the ground ice from the surface layer and by wind erosion resulting from the climate change on Mars. There are cases when the Martian polygonal terrains have different age correlation with dunes forms, being instead younger or older than the aeolian deposits (Fig. 7.14 a, b).

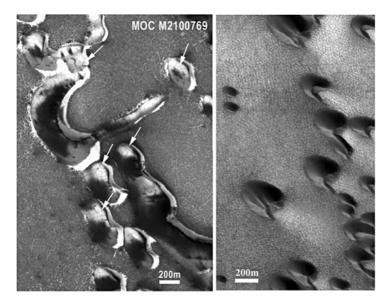


Fig. 7.14 Polygonal patterns observed on the surface of some subpolar paleo-dunes (a) and underneath the active subpolar barhan-dunes (b).

The observed presence of the polygonal patterns directly on the surface of some barchanoid dunes in near-polar areas is convincing evidence that the dunes are non-active in the present time (paleodunes) and are characterized by a frozen state of their surface due to ice cementation. Whereas the rampart craters on Mars serve as morphological indicators of the global distribution of ground ice at some depth (see Section 7.2.1), which depends on latitude, the discovered polygonal terrains are rather indicative of ground ice presence literally in the superficial layer of the Martian regolith. For this reason, the character of the global spreading of the Martian polygonal terrains may serve as a reliable criterion to test the existing theoretical models of the ground ice stability on Mars.

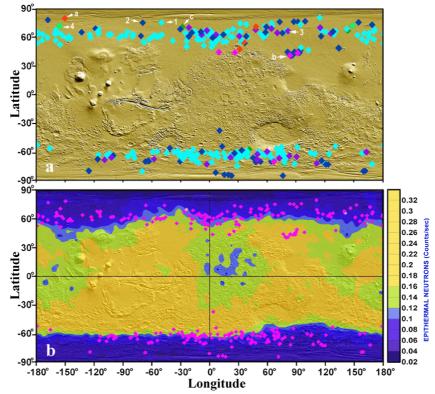


Fig. 7.15 (a) Global map of the polygonal terrain distribution on Mars. Numbers and letters on the map indicate the main morphological types and subtypes of the polygonal patterns, respectively. Background represents MOLA shaded relief with a resolution of 64 pixel/degree. (From Kuzmin and Zabalueva [61].) (b) Global map showing the correlation between distribution of the HEND neutron signature of the free water (ground ice) presence in the surface regolith during summer period (dark blue) and the Martian polygonal terrain (rhombus), mapped based on the analysis of the high-resolution MOC images. (From Kuzmin et al. [59].)

To get a more complete picture of the distribution of the polygonal terrains on Mars, Kuzmin and Zabalueva [61] conducted a global mapping of the terrains on the basis of morphological analysis of the MOC high-resolution images, released in the period between September 1997 and January 2002. For reliable identifica-

tion of polygonal patterns within the latitude range of 40 to 90° (in both hemispheres), they used only the images received under good atmospheric conditions. The results of the global mapping is shown in Fig 7.15a. As one can see from Fig. 7.15a the polygonal terrain on Mars is broadly spread mainly at the latitudes > 45° N and > 55° S. That is, the distribution of the polygonal terrains on Mars is mainly limited by the high latitude belts, where theoretical models [27, 28] suggest that ground ice there must be stable in the near-surface regolith and cracking fractures should readily form in the ice-rich regolith due to high tensile stress in the winter season [77].

It is notable that, within the Martian high latitudes, where polygonal terrain is mainly found, a strong deficit of surface neutron flux has been mapped by the neutron and gamma-ray spectrometers aboard of Mars Odyssey spacecraft [5, 28, 84, Chap. 5 by Mitrofanov]. The neutron flux deficit serves as a direct indicator of hydrogen within the surface layer of the regolith, and has been interpreted to represent high ground ice content $(35 \pm 15 \text{ wt }\%)$ in the uppermost 1–2 m of the surface layer [5, 29, 84]. Analysis of HEND data has shown distinct correlation between the spread area of free water (H₂O ice) in the neutron signature and the distribution area of the polygonal terrains [59–61]. It was found that the predominant part of the mapped polygonal terrains (90 %) directly matched areas of free water (located in both hemispheres) and only 10 % of the polygonal terrains are located a little bit outside the edge of the free water area (Fig. 7.15b). This discrepancy may be explained by the location of ice-rich materials here below a 1-2m thick surface layer associated with the leakage of the epithermal neutron flux measured by HEND. The observed correlation is a strong argument favoring the theory that the polygonal terrains on Mars have been formed mainly due to the frost cracking mechanism within ice-rich sediments, i.e. the polygonal terrains on Mars may serve as an indicator for ground ice in the surface layer of the Martian regolith.

It is not clear yet how old the Martian polygonal terrains are and whether they are relicts of past climatic conditions or continue to form under the current climate. Nevertheless, some polygonal nets on Mars show distinct shoulders along the edges of the wedges (see Fig. 7.13) that may be indicative of their continuous formation in the current time. It is most likely that a mixture of H_2O and CO_2 ice with aeolian sediments may represent the main material filling up the wedge interior of the Martian polygons. As is visible in the MOC images [48, 68], many polygonal terrains have spots of CO_2 ice within their wedge troughs during the spring/summer transit. The existence of CO_2 ice in the wedge grooves could increase the effect of atmospheric water vapor condensation within the cracking fractures. As far as it is probable that salt solutions may exist seasonally within the surface layer of the Martian permafrost under the modern climatic conditions [46, 56, 57], they also may, to some extent, play a similar role to liquid water filling the polygons' cracking fissures on Earth in springtime as a result of snow melting and deluge of the river flood plains.

An interesting result has been obtained recently by Kossacki and Markiewicz [48], who conducted a model analysis of the seasonal evolution of the thermal state and volatile content of the Martian polygonal troughs. They have shown that the presence of water ice in the regolith at depths smaller than the trough's depth

remarkably reduces the autumn-winter condensation rate of CO_2 ice due to higher flux conducted from ground ice toward the facets of the troughs. Hence, it is quite probable that remote observations of CO_2 ice accumulation and sublimation within the polygonal troughs may be a useful tool to determine the presence or absence of the near-surface ground ice.

7.4 Conclusions

The distribution of ground ice on Mars is one of the principle scientific subjects, the knowledge of which is directly related to the problem of the water evolution, its global abundance and its hydrological cycle on the planet during a long-term geological time. Moreover, an understanding of the particularities of the present ground ice distribution within the surface layer of the Martian regolith is important from the point of view that the cryolithosphere may represent a potential habitat for life as well as a main water resource for future human exploration on the planet.

Further, recently conducted studies of life activity in extremely cold environments on Earth strongly increased interest in the problem of the search for life within the Martian cryolithosphere, where a liquid phase of water may exist at temperatures below 0°C in the state of salt solutions (see also Chap. 12 by Mancinelli).

From the viewpoint of comparative planetology, the existence of such a largescaled cryolithosphere on Mars represents an additional indication that during the evolution of the planet's external shells water strived to be excreted in a separate planetary medium, which, depending of the thermodynamic environments on the planet's surface, has acquired a certain dominant state – the hydrosphere on Earth, the cryolithosphere on Mars and icy crusts (and even mantle) on the ice-silicate satellites of Jupiter and Saturn.

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7.5 References

- 1 Barlow NG, Bradley TL (1990) Martian impact craters: correlations of ejecta and interior morphologies with diameter, latitude, and terrain. Icarus 87: 156-179
- 2 Battistini R (1984) L'utilisation des cratères météoritiques a éjectas fluidisés comme moyen d'étude spatiale et chronologique de l'eau profonde (hydrolithosphère) de Mars. Rev. Geom. Dyn. 33: 25-41
- 3 Blasius KR, Cutts JA, Howard AD (1982) Topography and stratigraphy of Martian polar layered deposits. Icarus 50: 140-160

- 4 Boyce JM (1980) Distribution of thermal gradient values in the equatorial region of Mars based on impact morphology. In Reports of Planetary Geology Program-1980, NASA TM 82385: 140-143
- 5 Boynton WV, Feldman WC, Squyres SW, Prettyman T, Brückner J, Evans LG, Reedy RC, Starr R, Arnold JR, Drake DM, Englert PAJ, Metzger AE, Mitrofanov IG, Trombka JI, d'Uston C, Wänke H, Gasnault O, Hamara DK, Janes DM, Marcialis RL, Maurice S, Mikheeva I, Taylor GJ, Tokar R, Shinohara C (2002) Distribution of hydrogen in the near surface of Mars: evidence for subsurface ice deposits. Science 297: 81-85
- 6 Brass GW (1980) Stability of brines on Mars. Icarus 42: 20-28
- 7 Brook GA (1982) Ice-wedge polygons, baydjarakhs and alases in Lunar Planum and Chryse Planitia, Mars. In Reports of Planetary Geology Program-1982, NASA-TM 85127, Washington, DC: 265-267
- 8 Carr MH, Crumpler LS, Cutts JA, Greeley R, Guest JE, Masursky H (1977) Martian impact craters and emplacement of ejecta by surface flow. J. Geophys. Res. 82: 4055-4065
- 9 Carr MH, Schaber GG (1977) Martian permafrost. J. Geophys. Res. 82: 4039-4054
- 10 Carr MH (1996) Water on Mars. Oxford Univ. Press, New York
- Carr MH (2001) Mars Global Surveyor observations of Martian fretted terrains, J. Geophys. Res. 106 (E10): 23571-23593
- 12 Chapman CR, McKinnon WB (1986) Cratering of planetary satellites. In Burns JA, Matthews MS (eds) Satellites. Univ. of Arizona Press, Tucson, pp 492-580
- 13 Clark BC (1979) Chemical analysis of Martian surface material: status report. 10th Lunar Planet. Sci. Conf. 215-217
- 14 Clark BC, van Hart DC (1981) The salts of Mars. Icarus 45: 370-378
- Clifford SM, Hillel D (1983) The stability of ground ice in equatorial regions of Mars. J. Geophys. Res. 88: 2456-2474
- 16 Clifford SM, Fanale FP (1985) The thermal conductivity of the Martian dust. J. Geophys. Res. Suppl. 90: D144-D145
- 17 Clifford SM (1993) A model for the hydrologic and climatic behavior of water on Mars. J. Geophys. Res. 98(E16): 10973-11016
- 18 Coleman NM (2003) Aqueous flows carved the outflow channels on Mars. J. Geophys. Res. 108(E5): 5039, 10.1029/2002JE001940
- 19 Costard FM (1988) Thickness of sedimentary deposits of the mouth of outflow channels. 19th Lunar Planet. Sci. Conf. 211-212
- 20 Costard FM (1989) The spatial distribution of volatiles in the Martian hydrolithosphere. Earth Moon Planets 45: 265-290
- 21 Croft SK (1979) Impact craters from centimeters to megameters. Ph.D. Thesis, Univ. of California, Los Angeles
- 22 Croft SK (1984) Scaling of complex craters. 15th Lunar Planet. Sci. Conf. 188-189
- 23 Davies GF, Arvidson RE (1981) Martian thermal history, core separation and tectonics. Icarus 45: 339-346
- 24 Evans N, Rossbacher LA (1980) The last picture show: small-scale patterned ground in Lunae Planum. In Report of Planetary Geology Program, NASA-TM 82385, NASA, Washington, D.C.: 376-378
- 25 Fanale FP (1976) Martian volatiles: their degassing history and geochemical fate. Icarus 28: 179-202

- 26 Fanale FP (1986) The water and other volatiles of Mars. Sci. Technol. Ser. Am. Astronaut. Soc. Publ. 71:157-174
- 27 Fanale FP, Salvail JR, Zent AP, Postawko SE (1986) Global distribution and migration of subsurface ice on Mars. Icarus 67: 1-18
- 28 Farmer CB, Doms PE (1979) Global and seasonal variations of water vapor on Mars and the implications for permafrost. J. Geophys. Res. 84 (B6): 2881-2888
- 29 Feldman WC, Boynton WV, Tokar RL, Prettyman TH, Gasnault O, Squyres SW, Elphic RC, Lawrence DJ, Lawson SL, Maurice S, McKinney GW, Moore KR, Reedy RC (2002) Global distribution of neutrons from Mars: results from Mars Odyssey. Science 297: 75-78
- 30 Gault DE, Greeley R (1978) Exploratory experiments of impact craters formed in viscous-liquid targets: analogs for Martian rampart craters? Icarus 34: 486-495
- 31 Greeley R, Guest JE (1987) Geologic Map of the Eastern Equatorial Region of Mars, scale 1:15,000,000, U.S.G.S. Misc. Inv. Series Map I-1802-B
- 32 Gold LW, Lachenbruch AH (1973) Thermal conditions in permafrost a review of North American literature. In Proc. Permafrost 2nd Internat. Conf., Natl. Acad. Sci.-Natl. Res. Council, Yakutsk, U.S.S.R: 3-25
- 33 Henderson-Sellers A, Meadows AJ (1976) The evolution of the surface temperature of Mars. Planet. Space Sci. 24: 41-44
- 34 Hoffman N (1999) White Mars: a global evolution model for Mars' surface based on CO,. Icarus 146: 326-343
- 35 Hoffman N (2001) Explosive CO₂-driven source mechanism for an energetic outflow "jet" at Aromatum Chaos, Mars. 32nd Lunar Planet. Sci. Conf. 1257
- 36 Horner VM, Barlow NG (1988) Martian craters: changes in the diameters range for ejecta fluidization with latitude. 14th Lunar Planet. Sci. Conf. 505-506
- 37 Ivanov BA (1986) Cratering mechanics. NASA TM-88477 (N87-15662)
- 38 Ivanov BA (1988) Effect of modification of impact craters on the size-frequency distribution and scaling. 19th Lunar Planet. Sci. Conf. 531-532
- 39 Ivanov BA (1996) Spread of ejecta from impact craters and the possibility of estimating the volatile content of the Martian crust. Solar Syst. Res. 30: 43-58
- 40 Jakosky BM, Henderson BG, Mellon MT (1993) The Mars water cycle at other epochs: recent history of the polar cap and layered terrain. Icarus 102: 286-297
- 41 Jankowski DG, Squyres SW (1993) Softened impact craters on Mars: implications for ground ice and the structure of the Martian megaregolith. Icarus 106: 365-379
- Kargel JS, Baker VR, Beget JE, Lockwood JF, Pewe TL, Shaw JS, Strom RG (1995) Evidence of ancient continental glaciation in the Martian northern plains. J. Geophys. Res. 100(E3): 5351-5368
- 43 Kargel JS, Tanaka KL, Baker VR, Komatsu G, MacAyeal DR (2000) Formation and dissociation of clathrate hydrates on Mars: polar caps, northern plains, and highlands. 21st Lunar Planet. Sci. Conf. 1891
- 44 Kieffer HH, Zent AP (1992) Quasi-periodic climate change on Mars. In Kieffer HH, Jakosky BM, Snyder CW, Matthews MS (eds) Mars. Univ. Arizona Press, Tucson: 1180-1220
- 45 Kieffer SW, Ahrens TJ (1980) The role of volatiles and lithology in the impact cratering process. Rev. Geophys. Space Phys. 18: 143-181
- 46 Knauth LP, Burt DM (2002) Eutectic brines on Mars: origin and possible relation to young seepage features. Icarus 158: 267-271

- 47 Komatsu GJ, Kargel JS, Baker VR, Strom RG, Ori GG, Mosangini C, Tanaka KL (2000) A chaotic terrain formation hypothesis: explosive outgas and outflow by dissociation of clathrate on Mars. 31st Lunar Planet. Sci. Conf. 1434
- 48 Kossacki KJ, Markiewicz WJ (2002) Martian seasonal CO₂ ice in polygonal troughs in southern polar region: role of the distribution of subsurface H₂O ice. Icarus 160: 73-85
- 49 Kudryavcev VA, Dostovalov BN (1978) The General Permafrost. Moscow University Press, Moscow
- 50 Kuzmin RO (1977) On possible structure of the Martian cryolithosphere. 8th Lunar Planet. Sci. Conf. 566-568
- 51 Kuzmin RO (1980) Morphology of fresh Martian craters as an indicator of the depth of the upper boundary of the ice-bearing permafrost: a photogeologic study. 11th Lunar Planet. Sci. Conf. 585-586
- 53 Kuzmin RO (1983) The Cryolithosphere of Mars. Nauka Press, Moscow
- 54 Kuzmin RO (1984) Structure of the cryolithosphere on Mars. In 27th Intern. Geol. Congress, Comparative Planetology issue, Moscow: 32-39
- 55 Kuzmin RO, Bobina NN, Zabalueva EV, Shashkina VP (1988) Structural inhomogeneities of the Martian cryolithosphere. Solar Syst. Res. 22: 121-133
- 56 Kuzmin RO, Zabalueva EV (1998) On salt solution of the Martian cryolithosphere. Solar Syst. Res. 32: 187-197 (Astron. Vestnik 32: 212-225)
- 57 Kuzmin RO, Zabalueva EV (2000) Possibility of the seasonal existing of salt solutions in the Martian surface regolith and their morphologic effect. 31st Lunar Planet. Sci. Conf. 2104
- 58 Kuzmin RO, Ershov ED, Komarov IA, Kozlov AH, Icaev VS (2002) The comparative morphometric analysis of polygonal terrains on Mars and the Earth high latitude areas. 33rd Lunar Planet. Sci. Conf. 2030
- 59 Kuzmin RO, Mitrofanov IG, Litvak ML, Boynton W, Saunders RS (2003) Mars: detaching of the spread regions of the free water (ice) signature on the base of HEND/ODYSSEY data and their correlation with some permafrost features from MOC data. 34th Lunar Planet. Sci. Conf. 1369
- 60 Kuzmin RO, Zabalueva EV, Mitrofanov IG, Litvak ML, Boynton W, Saunders RS (2004) Regions of potential existence of free water (ice) in the near-surface Martian ground: results from the Mars Odyssey High-Energy Neutron Detector (HEND). Solar Syst. Res. 38: 1-11 (Astron. Vestnik 38: 3-13)
- 61 Kuzmin RO, Zabalueva EV (2003) Polygonal terrains on Mars: preliminary results of global mapping of their spatial distribution. 34th Lunar Planet. Sci. Conf. 1912
- 62 Lachenbruch AH (1962) Mechanics of thermal contraction cracks and ice-wedge polygons in permafrost. Spec. Pap. Geol. Soc. Am. 70 pp.
- 63 Leighton RB, Murray BC (1966) Behavior of carbon dioxide and other volatiles on Mars. Science 153: 136-144
- 64 Longhi J (2001) Clathrate and ice stability in a porous Martian regolith. 32nd Lunar Planet. Sci. Conf. 1955
- 65 Lucchitta BK (1981) Mars and Earth: comparison of cold-climate features. Icarus 45: 264-303
- 66 Lucchitta BK (1984) Ice and debris in the fretted terrain, Mars. J. Geophys. Res. 89: 409-418
- 67 Lucchitta BK (1985) Geomorphologic evidence for ground ice on Mars. In Klinger J, Benest D, Dollfus A, Smoluchowski R (eds) Ice in the Solar System. D. Reidel Publ., Dordrecht, pp 583-604

- 68 Malin MC, Edgett KS (2001) Mars Global Surveyor Mars Orbiter Camera: interplanetary cruise through primary mission. J. Geophys. Res. 106(E10): 23429-23570
- 69 Mangold N, Allemand P, Peulvast1 J-P (2000) Topography of ice related features on Mars. 31st Lunar Planet. Sci. Conf. 1131
- 70 Mangold N (2003) Geomorphic analysis of lobate debris aprons on Mars at Mars Orbiter Camera scale: evidence for ice sublimation initiated by fractures. J. Geophys. Res. 108(E4): 8021, 10.1029/2002JE001885
- 71 Masaitis VL, Naumov MV, Ivanov BA (1993) Fluidized ejecta of Puchezh-Katunki impact crater: possible implications to rampart craters of Mars. Vernadsky Institute-Brown University Microsymposium 18: 45-56
- 72 Masaitis VL (1999) Impact structures of northeastern Eurasia: the territories of Russia and adjacent countries, Meteorit. Planet. Sci. 34: 691-711
- 73 Masson P, Carr MH, Costard F, Greeley R, Hauber E, Jaumann R (2000) Geomorphologic evidence for liquid water. In Space Sciences Series of ISSI 12: 333-364
- 74 Max MD, Clifford SM (2001) Initiation of Martian outflow channels: related to the dissociation of gas hydrate? Geophys. Res. Lett. 28: 1787-1790
- 75 Mellon MT, Jakosky BM (1993) Geographic variations in the thermal and diffusive stability of ground ice on Mars. J. Geophys. Res. 98(E2): 3345-3364
- 76 Mellon MT, Jakosky BM (1995) The distribution and behavior of Martian ground ice during past and present epochs. J. Geophys. Res. 100(E6): 11781-11799
- 77 Mellon MT (1997) Small-scale polygonal features on Mars: seasonal thermal contraction cracks in permafrost. J. Geophys. Res. 102(E11): 25617-25628
- 78 Mellon MT, Jakosky BM, Postawko SE (1997) The persistence of equatorial ground ice on Mars. J. Geophys. Res. 102: 19357-19369
- 79 Mellon MT, Feldman WC, Prettyman TH (2003) Theory of ground ice on Mars and implications to the neutron leakage flux. Sixth Int'l. Conf. Mars. abstr. 3142
- 80 Melosh HJ (1989) Impact Cratering. A Geologic Process. Oxford Univ. Press, New York
- 81 Miller SM, Smithe WD (1970) Carbon dioxide clathrate in the Martian ice cap. Science 170: 531-533
- 82 Milliken RE, Mustard JF, Goldsby DL (2003) Viscous flow features on the surface of Mars: observations from high-resolution Mars Orbiter Camera (MOC) images. J. Geophys. Res. 108(E6): 5057, 10.1029/2002JE002005
- 83 Milton DJ (1974) Carbon dioxide hydrate and floods on Mars. Science 183: 654-656
- 84 Mitrofanov IG, Anfimov, Kozyrev A, Litvak ML, Sanin A, Tret'yakov V, Krylov A, Shvetsov V, Boynton W, Shinohara C, Hamara D, Saunders RS (2002) Map of subsurface hydrogen from the High Energy Neutron Detector, Mars. Science 297: 78-81
- 85 Mouginis-Mark PJ (1979) Martian fluidized crater morphology: variations with crater size, latitude, altitude, and target material. J. Geophys. Res. 84: 8011-8022
- 86 Mouginis-Mark PJ (1981) Ejecta emplacement and modes of formation of Martian fluidized ejecta craters. Icarus 45: 60-76
- 87 Musselwhite DS, Swindle TD, Lunine JI (2001) Liquid CO₂ breakout and the formation of recent small gullies on Mars. Geophys. Res. Lett. 28: 1283-1285
- 88 Mutch TA, Arvidson RE, Binder AB, Guinness EA, Morris EC (1977) The geology of the Viking 2 landing site. J. Geophys. Res. 82: 4452-4467
- 89 Naumov MV (1999) Hydrothermal-metasomatic mineral formation. In Masaitis VL, Pevzner L (eds) Deep Drilling in the Puchezh-Kutunki Impact Structure. Spec. Publ. VSEGEI Press: 276-286 (in Russian)

- 90 Phillips CJ, Davies RH (1991) Determining rheological parameters of debris flow material. Geomorphology 4: 101-110
- 91 Rieder R, Economou T, Wänke H, Turkevich A, Crisp J, Brückner J, Dreibus G, McSween HY Jr. (1997) The chemical composition of Martian soil and rocks returned by the Mobile X-ray mode. Science 278: 1771-1774
- 92 Reiss D, Jaumann R (2003) Debris flows on Mars: global distribution and their correlation to present day maximum surface pressures and temperatures. 34th Lunar Planet. Sci. Conf. 1821
- 93 Romanovskiy NN (1977) Formation of ice-wedge structures. Science Press, Novosibirisk
- 94 Rossbacher LA, Judson S (1981) Ground ice on Mars: inventory, distribution and resulting landforms. Icarus 45: 39-59
- 95 Rossi AP, Komatsu G, Kargel JS (2000) Rock glacier-like landforms in Valles Marineris, Mars. 31st Lunar Planet. Sci. Conf. 1587
- 96 Schultz PH, Gault DE (1979) Atmospheric effect on Martian ejecta emplacement. J. Geophys. Res. 84: 7669-7687
- 97 Schultz PH, Gault DE (1984) On the formation of contiguous ramparts around Martian impact craters. 15th Lunar Planet. Sci. Conf. 732-733
- 98 Scott DH, Tanaka KL (1986) Geologic Map of the Western Equatorial Region of Mars, scale 1:15,000,000, U.S.G.S. Misc. Inv. Series Map I-1802-A
- 99 Sharbattyan AA (1974) Experimental estimations in geothermy and geocryology. Nauka Press, Moscow
- 100 Seibert NM, Kargel JS (2001) Small-scale Martian polygonal terrain: implications for liquid surface water. Geophys. Res. Lett. 28: 899-902
- 101 Shoji H, Higashi A (1978) A deformation mechanism map of ice. J. Glaciol. 85: 419-427
- 102 Squyres SW (1978) Martian fretted terrain: flow of erosional debris. Icarus 34: 600-613
- 103 Squyres SW (1979) The distribution of lobate debris aprons and similar flow on Mars. J. Geophys. Res. 84: 8087-8096
- 104 Squyres SW, Carr MH (1986) Geomorphic evidence for distribution of ground ice on Mars. Science 231: 249-252
- 105 Squyres SW (1989) Water on Mars. Icarus 79: 229-288
- 106 Squyres SW, Clifford SW, Kuzmin RO, Zimbelman JR, Costard FM (1992) Ice in the Martian regolith. In Kieffer HH, Jakosky BM, Snyder CW, Matthews MS (eds) Mars. Univ. Arizona Press, Tucson, pp 523-554
- 107 Smoluchowski R (1968) Mars: retention of ice. Science 159: 1348-1350
- 108 Stewart ST, Nimmo F (2002) Surface runoff features on Mars: testing the carbon dioxide formation hypothesis. J. Geophys. Res. 107(E9): 5069, 10.1029/ 2000JE001465
- 109 Stewart ST, O'Keefe JD, Ahrens TJ (2004) Impact processing and redistribution of near-surface water on Mars. Submitted to Nature.
- 110 Stoffler D, Gault FE, Wedekind J, Polkowski G (1975) Experimental hypervelocity impact into quartz sand: distribution and shock metamorphism of ejecta. J. Geophys. Res. 80: 4062-4077
- 111 Toksöz MN, Hsui AT (1978) Thermal history and evolution of Mars. Icarus 34: 537-547
- 112 Toon OB, Pollack JB, Ward W, Burns JA, Bilski K (1980) The astronomical theory of climatic change on Mars. Icarus 44: 552-607

- 113 Toulmin P, Baird AK, Clark BC, Keil K, Rose HJ Christian RP, Evans PH, Kelliher WC (1977) Geochemical and mineralogical interpretation of the Viking inorganic chemical results. J. Geophys. Res. 84: 4625-4634
- 114 Turtle EP, Pathare AV, Crown DA, Hartmann WK, Greenham JC, Hartness N (2003) Modeling the formation of lobate debris aprons on Mars by creep of ice-rich permafrost. 34th Lunar Planet. Sci. Conf. 1891
- 115 Ward WR (1992) Long term orbital and spin dynamics of Mars. In Kieffer HH, Jakosky BM, Snyder CW, Matthews MS (eds) Mars. Univ. of Arizona Press, Tucson, pp 298-320
- 116 Washburn AL (1973) Periglacial Process and Environments. Edward Arnold, London
- 117 Willliams PJ, Smith MW (1989) The Frozen Earth. Cambridge Univ. Press., Cambridge
- 118 Wohletz KH, Sheridan MF (1983) Martian rampart crater ejecta: experiments and analysis of melt-water interaction. Icarus 56: 15-37
- 119 Yoshikawa K (2000) Contraction cracking and ice wedge polygons in Mars. Second Mars Polar Sci. Conf.: 186-187
- 120 Zent AP, Fanale FP (1986) Possible Mars brines: equilibrium and kinetic considerations. J. Geophys. Res. 91: 439-445

8 Water Cycle in the Atmosphere and Shallow Subsurface

Tetsuya Tokano

The global water cycle on Earth constitutes one of the most relevant components of the terrestrial ecosystem. While the vast majority of terrestrial water is stored in the world oceans, the perpetual cycle of water between ocean, atmosphere and land in all three phases is recognised as one basic feature that characterises the Earth, and is contrasted to the rest of the Solar System. On the other hand, Mars is devoid of a liquid hydrological cycle in the atmosphere and on the surface in the form of rainfall, rivers or oceans, which favour life on Earth's surface. However, a subtle water cycle does exist on present Mars and elucidating the details of the water cycle is crucial in understanding the global water inventory.

This chapter illustrates the various forms of water observed in the atmosphere and the shallow subsurface and discusses the state of atmospheric water and the cycle between the different reservoirs from a climatological point of view. Many aspects of the Martian water cycle are compared with the terrestrial counterpart to emphasise analogies and differences.

8.1 Observations of Atmospheric Water

8.1.1 Water Vapour

Mars is covered by a thin atmosphere composed mainly of CO_2 . The mean atmospheric pressure at the surface is only about 6 hPa (= mbar), roughly 150 times less than on Earth, but varies by 25 % with the seasons because a part of the atmosphere condenses out and is deposited at the poles in their respective winter. Due to the larger distance to the Sun compared to the Earth and the lack of a substantial greenhouse effect, the mean surface temperature is only 210 K, about 80 K lower than on Earth. Since a thin atmosphere can rapidly respond to solar heating both the seasonal and diurnal variation of the air temperature are large. Diurnal temperature variations of more than 100 K are common at low latitudes. Characteristic of the Martian atmosphere is also the large susceptibility of the atmospheric structure to the amount and distribution of suspended dust.

Water vapour is one of the trace species of the atmosphere with a volume fraction of the order of 10^{-4} , and was first detected by spectroscopic measurements from Earth-based telescopes [59]. Atmospheric water vapour was systematically mapped by the Viking Orbiter in the 1970s. The Viking Orbiter was equipped with a spectrometer termed MAWD (Mars Atmospheric Water Detector Experiment)

T. Tokano, Water Cycle in the Atmosphere and Shallow Subsurface. In: *Water on Mars and Life*, Tetsuya Tokano (ed.), Adv. Astrobiol. Biogeophys., pp. 191–216 (2005) springerlink.com © Springer-Verlag Berlin Heidelberg 2005 devoted to the measurement of the global water vapour amount from the intensity of water absorption lines in the near-infrared spectra [26]. Similar measurements of the vapour abundance have recently been conducted by the Mars Global Surveyor Thermal Emission Spectrometer (TES) as well [57, 58]. The global and seasonal map of the column vapour abundance (vertically integrated amount of vapour at a given place) acquired by MAWD and TES represent the most complete picture of the temporal and spatial variation of atmospheric water, and are the basic data in the assessment of the global water cycle. (The TES results are shown in Fig. 8.1). The column vapour abundance is expressed in precipitable micrometres (pr μ m = 10⁻³ kg m⁻²), which gives the height of precipitation that would result on the surface if it entirely condenses out. In general MAWD data are biased towards lower values than the TES data because the MAWD spectra were more susceptible to scattering by dust.

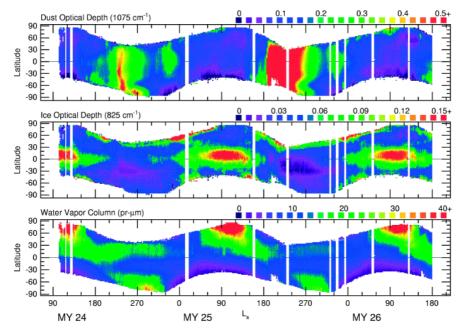


Fig. 8.1 Latitudinal and seasonal variation of the dust optical depth, water ice cloud optical depth and atmospheric water vapour column abundance (in pr μ m) retrieved by TES reprinted from Smith [58] (reprinted with permission from Elsevier). The data cover more than two Mars years and L_s is the areocentric longitude of the Sun (season on Mars) beginning with 0° (northern vernal equinox).

On an annual average the Martian atmosphere contains a global vapour amount of 2×10^{11} kg -2.3×10^{12} kg, with a substantial seasonal variation [57]. This is more than 10^4 times less than the terrestrial atmospheric water content. To a first approximation the atmospheric vapour content on Mars varies with season and latitude and the basic feature does not differ much from year to year. The most

apparent feature is the annual maximum of about 100 pr µm observed near the north pole shortly after the summer solstice. A further characteristic feature is the tongue-like feature which extends from the north pole southward with progressing season. For any given latitude in the northern hemisphere the peak water vapour column abundance occurs progressively later in the season for lower northern latitudes. The annual peak also decreases towards the equator. The seasonal variation in the southern hemisphere is not an exact mirror image of the northern counterpart. The annual maximum vapour abundance at the south pole is also found shortly after the southern summer solstice, but is substantially smaller. The southern maximum was 40 pr µm in the TES data [57] and only 10 pr µm in the MAWD data [26]. This is the most significant interannual variability concerning the atmospheric water content. Further interannual variability is discernible in southern summer when planet-encircling dust storms develop. The annual-mean vapour abundance is largest between the equator and 30°N, not near the north pole. This is because the vapour abundance in the polar region drops to almost zero in polar winter, while the equatorial region holds water year-round without any large seasonal variation.

The vertical distribution of water vapour is a critical factor in models of photochemistry and aeronomy (see also Section 8.2.4). Remote observations indicate that the water vapour is uniformly distributed up to 20–25 km, but rapidly diminishes above 25 km [53]. However, the observation from the Martian surface by the IMP (Imager for Mars Pathfinder) suggests that water vapour is more concentrated near the surface [66]. This difference may be a seasonal one. There are also some diurnal variations of the vapour amount, with a maximum in the early afternoon and a minimum in the morning and late afternoon [60, 65]. The diurnal variation is more pronounced in the vicinity of large volcanoes. Besides seasonal and latitudinal variations there is also some longitudinal variation of the annual-mean vapour abundance (Fig. 8.7 and [57, 58]).

The atmosphere of Mars is dry not only in terms of its absolute moisture content, but also with respect to its relative humidity. Under the given temperatures and air pressures the equatorial region could contain 200 times more vapour than is actually observed. It is also quite unlike the Earth in that the atmospheric water content does not steadily decrease towards the poles. However, models indicate that the vapour amount and the vigour of the atmospheric water cycle in general may dramatically increase during repeatedly occurring epochs of high obliquity because the polar cap sublimation enhances [39, 49].

8.1.2 Ice Clouds

Clouds on Mars have been documented for at least 200 years by telescopic observations [23], but they were identified as water ice only 30 years ago [12]. Nowadays, Martian clouds can be detected by visual observation, spectral mapping (MGS TES (shown in Fig. 8.1), Mars Odyssey THEMIS) and laser (MGS MOLA). On Mars both H_2O and CO_2 clouds are possible, but they can be distinguished from each other if the temperature is known. Morphologically, many clouds resemble thin high-altitude clouds on Earth, which appear faint on weather

satellite images. Ice clouds consist of particles with radii of $1-4 \ \mu m [12, 46]$, which are comparable to those of terrestrial ice cloud particles or ice fog, but are substantially smaller than terrestrial snow. Ice particles typically settle with velocities of less than 5 cm s⁻¹ for about one day before they sublime [29]. In many respects the Martian ice particles are considered similar to the so-called diamond dust in the clear Antarctic sky.

A prominent cloud feature is the cloud belt that extends over all longitudes within the $10^{\circ}S-30^{\circ}N$ latitude region in late northern spring and early northern summer (Figs. 8.1 and 8.2) [10, 46, 56, 58, 63, 64, 70]. These clouds are referred to as the equatorial cloud belt or aphelion cloud belt [10] because they form near the equator when Mars approaches its aphelion, the farthest point from the Sun on the orbit of Mars. These bright clouds have optical depths of 0.2–0.6 and are visible, e.g. on images taken by the Hubble Space Telescope. In the initial phase the cloud belt looks fibrous, but later on it contains more convective clouds [70]. A further persistent feature is the grey, opaque polar hood, which is more ubiquitous in the north than in the south. The polar hood sometimes extends south of 60°N due to the action of storm systems in winter [46, 63]. Sometimes there are also large spiral clouds at the edge of the north polar cap. They are virtually the Martian counterparts of the eastward-travelling mid-latitude storm systems on Earth.

Otherwise, relatively more clouds are observed in the vicinity of large mountains such as Olympos Mons, Tharsis volcanoes, Alba Patera or Elysium as well as over the Hellas basin [5, 28, 45, 58, 63]. Orographic clouds are more frequent in (cold) northern summer, and undergo diurnal variations, with thickest clouds observed in the afternoon. Clouds over the summits of volcanoes are the most opaque and highest ones observed on Mars. On the other hand, vertically extensive clouds such as thunderstorms do not develop on Mars because the humidity is too low. A detailed cloud catalogue was created based on images acquired by Mariner 9 and Viking Orbiters [17]. Many of the clouds have analogies on Earth such as wavelike lee waves in the lee of large obstacles, periodical cloud streets or irregular streaky clouds.

The cloud base altitude (condensation level, hygropause) depends on the temperature and water vapour profile, and varies mainly with season rather than with latitude [57]. The cloud base becomes highest (40 km) at perihelion near the northern winter solstice and drops to as low as 10 km at aphelion near the northern summer solstice. The presence of clouds does not imply saturation of the air below the cloud down to the surface because downward transport of water by precipitation considerably lowers the relative humidity of the air [51].

A special type of cloud is the surface fog that develops during the night in some regions and seasons on Mars (Fig. 8.3). The fog was first imaged by the Viking Orbiter [7]. The inflection in the time series of the near-surface air temperature, i.e. an anomalous temperature drop for about an hour in the night, was also interpreted as radiative cooling caused by fog [54].

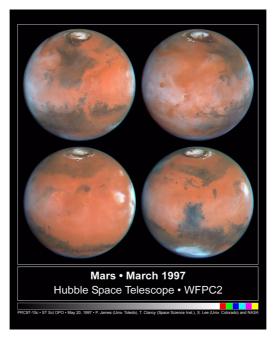


Fig. 8.2 Mars in early northern summer/southern winter imaged by the Hubble Space Telescope (STScI-PRC1997-15C, courtesy of STScI) on 30 March 1997. A faint aphelion cloud belt is visible near the equator. Also visible are thick clouds over volcanoes near the equator.



Fig. 8.3 False-colour image of morning fog in northern spring near 53°N, 65°W imaged by the Mars Orbiter Camera on 4 June 1998 (MOC2-52, courtesy of NASA/JPL/Malin Space Science Systems). North is up and illumination is from the right.

Fogs on Mars are frequent in topographic depressions, particularly in the large basins Hellas and Argyre [17]. Laser observations reveal that surface fogs of H_2O ice are prevalent along the edges of the seasonal polar cap at night [43].

8.2 Aspects of the Atmospheric Water Cycle

The atmospheric and shallow subsurface water cycle of Mars consists of various components as illustrated in Fig. 8.4. Each of them will be discussed in this section. Atmospheric escape processes discussed in Chap. 2 by Lammer et al. are only relevant on geological time scales, so they are totally negligible in the consideration of the present global water cycle.

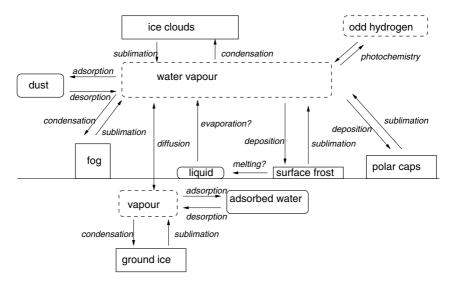


Fig. 8.4 Schematic diagram showing the different reservoirs of exchangeable water in the atmosphere and shallow subsurface as well as the fluxes between them. The magnitudes of the fluxes are not shown because of large uncertainties.

8.2.1 Exchange with the Polar Caps

The accumulation of water in polar caps (ice sheets) is a characteristic feature in cold climates, and is also expected to have prevailed to some extent on Earth during the ice ages. In such climates atmospheric water does not readily precipitate out as rain, but it is transported to the poles where it is finally trapped. Mars represents such a state and the polar caps indeed involve the largest water reservoirs on the surface.

On present Mars the sublimation of the H_2O polar cap in summer after the retreat of the seasonal CO₂ cap overlying the H_2O cap provides the largest seasonal source of atmospheric water [3, 49]. The total vapour amount released in one summer may be $10^{11}-10^{12}$ kg. At the north pole the sublimation begins near the northern summer solstice and continues until late summer. The vapour emission rate is controlled by the cap surface temperature, the total area of the exposed cap (poleward of about 82° N) and the wind speed near the surface [18]. The water vapour amount over the cap suddenly increases with the onset of the cap sublimation and becomes largest in early summer with 100 pr µm. The maximum is found when the polar cap attains the annual maximum temperature (205 K). This implies that the vapour amount in the polar region in summer would sensitively vary if the polar cap peak temperature changes for some reason, e.g. a change of insolation pattern as a result of secular variation of astronomical parameters or a change of the polar cap albedo as a result of variable dust deposition.

Until recently the southern polar cap was not considered a major seasonal source of atmospheric water, in contrast to the northern cap. However, recent observations with the Mars Odyssey THEMIS detected the exposure of H_2O ice in a small part of the southern polar cap in late southern summer [67]. Mars Express OMEGA more directly confirmed the presence of perennial water ice in the southern polar cap [80]. In accordance with this, the water vapour abundance over the south polar cap recently acquired significantly increases in this season, albeit the maximum is only 40 pr μ m, about 60 % less than in the north [57]. This smaller maximum may indicate that either the summer peak temperature of the south polar cap is lower or the actual extent of the exposed H_2O cap is smaller.

The polar caps are not only an important source of atmospheric water, but also a sink. Atmospheric water in the polar region provided in early summer by sublimation of the polar cap is deposited again to the polar cap in late summer when the temperature drops [3]. In this way much (but not all) of the water from the polar cap is recycled within one season. Presently, (only) the centre of the polar cap is a net sink of atmospheric water [4]. More detailed discussions of the polar caps are given in Chap. 6 by Hvidberg.

8.2.2 Water Vapour Transport

Water vapour in the atmosphere is subject to transport by the wind. The wind system on Mars relevant for the north-south transport consists of several components [e.g. 15, 19, 62, 71] (Fig. 8.5). The first component is the so-called Hadley circulation, which is forced by the global imbalance of solar heating and infrared cooling of the atmosphere. Air is forced to lift in the warm summer hemisphere, flows to the winter hemisphere, descends and flows back to the summer hemisphere near the surface. The circulation pattern reverses twice per Mars year. The Hadley circulation on Mars is about six times stronger than the terrestrial counterpart, and is particularly strong in southern summer when global dust storms develop, with wind speeds of several tens of m s⁻¹. The second component is the so-called CO₂ condensation flow, which develops as a result of a

periodical cycle of condensation and sublimation of a quarter of the total atmosphere at both poles. Air flows from the spring/summer pole, where the air pressure increases with the CO_2 sublimation, to the autumn/winter pole, where the situation is reversed. This flow is strongest (some tens of cm s⁻¹) at the edge of the polar cap and is significant because the Hadley circulation in this region is weak. Otherwise, the condensation flow is insignificant in comparison with the Hadley circulation. The third component is the atmospheric wave activity generated by inherent atmospheric instabilities and external forcing such as topography or strong solar heating (thermal tide). Atmospheric instabilities are caused by strong horizontal temperature variations and wind shear, and are analogous to the weather systems at mid latitudes of the Earth. They manifest themselves in short-term disturbances of wind and temperature.

The role and intensity of the transport processes for the global water budget as compared to sources and sinks cannot be assessed by the analysis of the observational data alone. Water transport depends on the direction and speed of winds and on the spatial gradient of the water vapour amount. One approach to investigating the atmospheric water transport is to implement water vapour and clouds as prognostic variables in numerical climate models (general circulation models). Typically, model results are verified by comparing the predicted and observed seasonal and latitudinal variation of the vapour abundance. However, some caution is necessary in the interpretation of such numerical models. Different water cycle models seemingly have been able to reproduce the observation only if a strong seasonal exchange of water between the atmosphere and soil is included [24, 25], while other models do not require such exchange at all [49, 51].

The latter model [51] without any water exchange across the surface suggests that the atmospheric transport is one major mechanism in the global water cycle. The condensation flow in northern summer accounts for the southward transport of water vapour released from the northern cap. As the volume of air increases towards the equator, water vapour becomes diluted by longitudinal redistribution. The southward transport is efficient because the latitudinal vapour gradient is particularly large in this season and much of the northern tongue-like shape in Fig. 8.1 is attributed to the equatorward transport. A similar transport pattern is also found in the southern hemisphere. The weather systems in the northern subpolar region cause a strong mixing of water vapour. In late summer this strong mixing brings much water back into the polar region. At lower latitudes the transport is mainly by the Hadley circulation, and is directed from the summer to winter hemisphere. The Hadley circulation is also crucial for the upward transport and subsequent cross-equatorial transport of water at high altitudes.

The net annual interhemispheric transport of water in the atmosphere is likely to be northward. This may partly be due to the astronomically forced asymmetric heating pattern of the hemispheres, but it is also suggested that the global dichotomy of the Martian topography (southern highlands versus northern lowlands) may be responsible for the asymmetric transport pattern [50, 62].

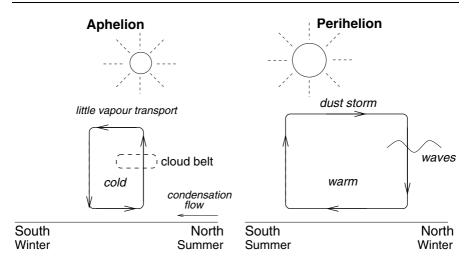


Fig. 8.5 Simplified scheme of the global vapour transport on Mars in two different seasons.

8.2.3 Influence of Clouds and Fogs

Despite their relatively small amount, ice clouds on Mars have a significant effect on the global water cycle. The most important aspect is the aphelion cloud belt near the equator [10]. This cloud belt begins to form when Mars approaches the aphelion, so the equatorial temperatures generally drop. Due to the lower air temperature condensation sets in at lower altitudes than otherwise. In this season the rising branch of the Hadley circulation is located at low northern latitudes, so water vapour in this region is efficiently carried upward and encounters condensation [51]. This gives rise to the observed aphelion clouds, which typically form at altitudes between 5 and 10 km (Figs. 8.2 and 8.5). The cloud belt disappears in late northern summer when the temperature increases. In northern late spring and early summer the cross-equatorial wind is northward near the surface but southward further above. If water vapour were able to enter these high altitudes, it would be transported southward. However, the cloud formation efficiently limits the upward transport of vapour, so water remains relatively near the surface and cannot be transported to the southern hemisphere. A similar reversed feature does not occur near the perihelion because then the air temperature is higher and no cloud belt forms that would otherwise limit the northward transport across the equator in southern summer. Besides this particular aphelion feature, condensation and subsequent sedimentation of ice particles always act to concentrate water vapour near the surface, especially in late northern summer.

Another cloud feature of importance for the water cycle is the thick polar hood that develops along the edge of the polar night. The latitudinal extent and the thickness of the polar hood is controlled by the actual vapour amount, the location of the interface between the polar and subpolar air masses (polar front) and the water transport efficiency across this polar front [51]. The polar hood is likely to act as a seasonal reservoir of atmospheric water in the cold polar winter in which almost no water vapour can exist.

Although clouds on Mars are optically thin, they are able to affect the temperature profile of the thin Martian atmosphere. The first hint on the radiative effect of clouds came from the vertical temperature profile measured at the Mars Pathfinder site [34]. During the night the temperature profile showed a marked inversion up to 20 km altitude, which could not be explained by atmospheric waves or night-time cooling under clear sky. Infrared cooling by the cloud during the night creates a large temperature inversion of 5-10 K near the cloud top, initiating further cloud formation and cooling [11]. Moreover, clouds reduce the amount of sunlight arriving at the surface during the day, lowering the surface other exchange temperature. On the hand. heat associated with condensation/dissipation of clouds is negligible on Mars because of the tiny cloud mass. Otherwise, clouds are excellent markers of the atmospheric motion, and often reveal the circulation pattern or turbulence in the atmosphere, although the clouds are of minor meteorological importance compared to dust.

The formation mechanism of fog is qualitatively different from the clouds observed near the summit of Martian volcanoes, although both show a marked diurnal behaviour. The diurnal temperature near the surface is quite large, so the relative humidity can vary between less than 1 % to 100 % within a Martian day [55, 76]. The fog begins to form in the evening or at night and disappears soon after sunrise. It may extend from the surface up to a height of several tens of metres. In contrast, orographic clouds usually develop in the afternoon when the upslope wind transports water vapour to higher, colder regions where water vapour encounters saturation. The optical depth of the surface fog is anticorrelated to the surface temperature [74], indicating that the temperature variation is the main driver for the fog formation and dissipation.

The surface fog is a temporary night-time reservoir of atmospheric water that cannot be accommodated in the vapour phase. It is light enough to remain suspended the whole night without precipitation to the surface, except very near the surface.

8.2.4 Photochemistry Related to Water

Water vapour is subject to photolysis which produces odd hydrogen (e.g. OH, H, HO_2), a catalytic driver of carbon and oxygen chemistry on Mars [42]. The decomposition of water molecules in the atmosphere is a prerequisite of all the atmospheric escape processes discussed in Chap. 2 by Lammer et al., although on the time scales discussed in this chapter the atmospheric loss of water to space can safely be neglected.

In most parts of the Martian atmosphere the water vapour abundance is not sensitive to photochemistry [42]. On the other hand, the budget of several other species, particularly in the upper atmosphere, is controlled by the varying abundance and vertical distribution of water.

One important species whose abundance is very sensitive to water is ozone (O_3) . Photochemical models predict that atomic H reacts with O_2 , thereby reducing the amount of O_2 available to reform O_3 from collisions between O and O_2 [e.g. 42]. Odd hydrogen chemistry accounts for the destruction of O_3 and as a whole O_3 and water vapour abundance are expected to be anti-correlated. For instance, the reduction in H-atom densities above the hygropause as a result of water condensation can permit higher O_3 densities [9]. However, since the altitude of the hygropause varies with season (Section 8.1.2) the ozone number density at 10–40 km altitude is predicted to vary by an order of magnitude in the course of a Martian year. Simultaneous telescopic observations of the global ozone and water distribution are quite useful in this context and they are beginning to confirm some of these predictions [44].

Another major product of water vapour photolysis is H_2O_2 (hydrogen peroxide). H_2O_2 is produced by reaction of two HO_2 radicals and is rapidly destroyed by photodissociation, and its abundance strongly correlates with the water vapour abundance [13]. Observations seem to indicate that H_2O_2 is substantially lower at aphelion than at perihelion, reflecting the well-known fact that there is less water vapour in the upper atmosphere at aphelion compared to perihelion as a result of the aphelion cloud belt. This species was suggested as a possible candidate oxidant in the Martian soil because H_2O_2 can condense to the surface [36] or diffusion of gaseous H_2O_2 may be possible [8]. However, see Chap. 2 by Lammer et al. for an alternative, more likely oxidant (superoxides) in the soil.

8.2.5 Surface Frost

Viking 2 Lander observed an accumulation of a white thin layer on the surface in winter, which was interpreted as surface frost composed of H_2O [21, 61]. The images (Fig. 8.6) themselves do not reveal whether this frost was composed of H_2O or CO_2 . It is also unknown whether this ice fell as snow or formed *in situ* as surface frost. Since the surface temperature at this site and season was not low enough to form and retain CO_2 ice, the frost was assumed to be H_2O ice.

Basically, surface frost forms when the near-surface air gets saturated with respect to H_2O ice. However, this is not a self-evident process, as fog formation is an alternative process in such a situation. The formation (condensation) and retreat (sublimation) of the frost critically depend on the surface thermal balance and transport efficiency of vapour near the surface. Condensation begins when water vapour comes into contact with the cold surface. This may be favourable, e.g. in the shadow of large rocks [61]. The long survival of the frost is possible because water vapour near the surface is not readily transported away unlike the fog, so it can be re-deposited on the surface during the winter many times.

The surface frost formation/sublimation is considered a regular process in several atmospheric water cycle models and to account for a part of the seasonal water cycle [24, 49]. The thickness of the surface frost depends on season, and increases with latitude in both hemispheres. Maximum surface frost coverage of about 150 pr μ m in polar winter is predicted. On the other hand, observations seem to indicate that the frost may be much thinner [46]. The frost deposition at the poles is ultimately responsible for the net accumulation of the polar cap, and simulating this process is an important but difficult task.



Fig. 8.6 Surface frost observed by Viking 2 Lander in Utopia Planitia (47.7°N, 48°W) in May 1979 (image reference: PIA00533, NASA Planetary Photojournal). At other landing sites (Viking 1 Lander, Mars Pathfinder) located at lower, warmer latitudes no surface frost was observed.

The frost deposition in autumn and the sublimation in spring may constitute a small temporary sink and source of atmospheric water at mid and high latitudes. As the leading edge of the seasonal ice cap is sublimed, water that is released into the atmosphere has some chance of being mixed poleward over the nearby seasonal ice cap [49]. This process is continually repeated, allowing surface frost to creep poleward. This mechanism has been suggested to explain the moderate vapour abundance maximum near the south pole in summer, i.e. a southern H_2O cap would not be required.

8.2.6 Liquid Water?

Present Mars is obviously devoid of an ocean and not a single standing or flowing body of liquid water has ever been observed on the surface of Mars with certainty. In 1980 it was speculated that there was a seasonal appearance of liquid water in the near-surface soil in the Solis Lacus region (14–22°S, 84–100°W) because of an unusually high radar reflectivity in southern summer [79]. This feature was interpreted as evidence of brines formed by the melting of ice at depths of a few tens of centimetres. However, this interpretation has been strongly questioned because such brines in the shallow subsurface would be severely out of equilibrium and would barely survive even a single freeze-thaw cycle [78]. Instead, the anomalous radar reflectivity was probably caused by some combination of unique scattering properties of some yet unidentified process other than ice melting [78]. Moreover, recent fast neutron data of Mars Odyssey indicate that this region belongs to the driest places on Mars with water contents of only 2 wt % or so (Fig. 5.8 bottom in Chap. 5). There is also no coincidence at all with the locales of gullies observed by [35].

Recent detection of small surface runoff features (gullies) within the walls of some impact craters at mid latitudes [35] gave rise to reconsideration of the transient occurrence of liquid water. The phase diagram of H₂O dictates that liquid water is thermodynamically stable if the temperature and air pressure are above the triple point (6.11 hPa, 273.16 K), but at the same time below the boiling point, which increases with air pressure. Since the maximum surface pressure on Mars does not exceed 12 hPa, the maximum boiling point on Mars is only 283 K, in stark contrast to 373 K on Earth at sea level. At most places the boiling point is even lower. In a nutshell, a surface pressure higher than 6.11 hPa and a surface temperature slightly above 273 K would be required for pure liquid water to be stable. Because of the low temperature and low air pressure on Mars the applicable range is very limited.

Due to the large diurnal temperature variation this cannot be achieved for an extended period. Nevertheless, certain regions of Mars fulfil this criterion for a total of a few days within a Martian year [20, 33]. This applies to the Hellas and Argyre basin at southern mid latitudes and a large portion between the equator and 40°N. In the presence of salts in the soil the applicable area further extends because of the freezing point depression, depending on the concentration and composition of the salts.

It is important to point out that on real Mars liquid water could temporarily exist even it is not stable according to the phase diagram. For energetic reasons both evaporation and freezing of liquid water would be sluggish on Mars [22, 31]. Water is then said to be metastable. Once ice melts, liquid water may persist for a longer period than would be expected. Whether melting can actually occur depends on the surface heat balance, which significantly varies from place to place due to differences in meteorology, topography or geology, but it may occur on slopes nearly anywhere on Mars [22] (see also Chap. 9 by McKay et al.).

The global map of liquid water stability on the surface of Mars is not invariant, but changes due to astronomically caused precession ([69], see also Section 8.4). If the perihelion occurs in another season than is the case presently, the insolation pattern and hence the surface temperature change. This causes a substantial change in the liquid water stability. For instance, when the perihelion occurs in northern summer, the liquid water stability disappears in the southern hemisphere except for in the equatorial canyon systems, while in large parts of the northern lowlands the stability increases. This result illustrates that the thermal condition favouring the existence of Mars may substantially change over time scales of 50000 years, even have done so in the recent past. The highest liquid water stability throughout the precession cycle is achieved in the Hellas basin, the southern rim of Amazonis Planitia, Chryse Planitia and southeast of Elysium.

With the exception of the Hellas basin, the stability is always higher in the northern hemisphere.

The presence of liquid water, however, not only requires the right temperature and pressure range at the surface, but also the availability of abundant water at these places at the right time. It turns out that higher liquid water stability is always accompanied with low soil water content because of the high temperature. Therefore, the open question is whether there is a mechanism to bring water from somewhere to these places (see Chap. 9 by McKay et al. and Chap. 10 by Cabrol and Grin).

In the context of the global atmospheric water cycle it is only important whether occasional liquid water on the surface would affect the water cycle. The volume of liquid water that would have been required to carve the 120 observed gullies is conservatively estimated to 2500 m^3 ($2.5 \times 10^6 \text{ kg}$) per gully [35]. A more detailed analysis yielded an estimated volume of 60000 m³ ($6 \times 10^7 \text{ kg}$) per gully [72]. While this may appear to be a big local source of water, even a simultaneous and rapid evaporation of all the liquid water is still tiny compared to the present total vapour abundance (10^{12} kg). This comparison shows that the analysis of the seemingly tiny cycle of water vapour is more important in the consideration of the long-term global water cycle.

8.2.7 Exchange with the Soil

The atmosphere is bounded on its bottom by the planetary surface, which provides the interface between a gaseous and solid/liquid medium. In principle, water can be exchanged across the surface, changing the water content both in the atmosphere and subsurface. On Earth this exchange mostly takes place in the form of rainfall, infiltration, evaporation from the ocean or land surface. Snow does not enter the subsurface unless it melts. By this mechanism the atmospheric water on Earth is recycled within about 9 days [47].

The lack of liquid water in the atmosphere of Mars greatly reduces the efficiency of surface water exchange. Nevertheless, some exchange is supposed to take place because otherwise the present global distribution of subsurface water would be difficult to explain [68].

There is so far no *in situ* measurement of the water exchange at the Martian surface that could confirm such a mechanism. The observed temporal variation of the atmospheric water vapour content can certainly set an upper limit on the exchange rate, but we have to ascertain that the vapour content simultaneously changes due to many other effects, so the relative significance of the surface exchange is not readily estimated.

One basic reason to suggest the exchange of water at the surface is the dependence of the water holding capacity of the soil on basic climatological parameters such as temperature or vapour amount [14]. Mineral grains in the soil have the ability to attach water vapour by van der Waals forces between the negatively charged mineral grains and dipolar water molecules. The attached water molecules form a thin film of adsorbed water around the grains [41].

Adsorbed water does not form a crystal lattice, so it is unfrozen. As a general rule the amount of adsorbed water increases with the atmospheric vapour amount adjacent to the mineral grains and decreases with temperature (see Fig. 4.5 in Chap. 4), and depends on the mineralogy. The mineralogical composition of the Martian soil and its global distribution is not well known (see Chap. 4 by Bishop), but it is likely that hydrated minerals include montmorillonite (smectite) or zeolites. The adsorptive capacity of Na-montmorillonite and palagonite under Mars-like conditions has been experimentally determined [75]. The adsorptive capacity of montmorillonite (a clay mineral) or zeolites is much larger than that of palagonite (coating observed on alterated basaltic glass) because of the much larger specific surface area, i.e. there is more space for water molecules. Zeolites can retain more water than smectites at temperatures higher than 200 K for a given vapour pressure, but also at very low atmospheric vapour pressures typical for Mars [6]. Water can be reversibly exchanged between the cavities and channels within the zeolite structure and the atmosphere. Zeolites are suggested as one likely component of the dust particles as well as of the dust mantle on the surface.

The exchange of water between the soil and atmosphere requires not only adsorption and desorption, but also transport of water molecules. As liquid water usually does not exist on the surface of Mars and no infiltration of liquid water takes place, the transport of water in the shallow subsurface takes the form of diffusion of water vapour through narrow soil pores. The vapour diffusion can be upward or downward, depending on the actual vertical gradient of vapour density. The amount of water transported in this way is incredibly tiny in comparison with water percolating in Earth's soil. The vapour diffusion may be limited if the soil is cemented, e.g. by salts or ice, the latter probably being the case in the polar region. Migration of the adsorbed water film itself is negligible under Martian conditions [37].

One could assume that in the warm daytime or in warm seasons the adsorptive capacity of the soil decreases, so the water molecules released as vapour would diffuse to the atmosphere and enter the soil again as the air gets colder in the afternoon or in autumn. In arid regions of the Earth the diurnal variation of the water vapour adsorption by the soil indeed affects the soil water content on diurnal time scales, particularly in clayey soils [30]. In sandy soils (dune), however, the diurnal cycle is due to the evaporation and condensation of liquid water and the diffusive exchange of water vapour between the atmosphere and soil rather than adsorption and desorption of water [73].

However, in the case of Mars there is considerable uncertainty as to whether a substantial exchange of water across the surface takes place on seasonal or even diurnal time scales. Some models support a strong seasonal exchange [24, 25], while others discard it [3, 49]. Similarly, some studies suggest a substantial diurnal exchange [6, 27, 65], while others do not consider this to be significant [55, 68, 75, 76, 77].

The first uncertainty concerns the time required for the adsorption and desorption of water molecules. For kinetic reasons, the adsorption of H_2O by smectites is a relatively slow process, which typically takes several days until equilibrium is achieved [77]. On the other hand, zeolites hydrate and dehydrate quickly (on time scales of an hour) [6]. Therefore, it is possible but not certain that

the water contents of minerals in the Martian soil change on diurnal time scales. Another concern is that water desorbed from minerals has to be transported within the soil and into the atmosphere and vice versa. The efficiency of this process depends on properties of the soil, the near-surface air (boundary layer) and the actual amount of water vapour near the surface. The vapour amount near the surface can simultaneously vary by surface frost deposition/sublimation, surface fog formation/dissipation, horizontal and vertical transport and vapour flux into and out of the soil, so the temporal variation of the vapour amount near the surface alone cannot be automatically attributed to the water exchange with the soil.

Enhanced diurnal exchange of water with the surface by adsorption/desorption in the Tharsis region was suggested on the basis of previous measurements as reviewed by [65], but it was not clear why this should be unique to Tharsis [77]. Recent GCM simulation of the atmospheric water cycle [51] reproduced substantial thickening of clouds in the Tharsis region, as observed, without any water exchange with the surface. The Tharsis clouds were ascribed to the regional daytime upward motion and radiative cooling in the vicinity of Tharsis, giving rise to an intensive cloud activity and water accumulation there. The enhanced water vapour abundance at this place is likely to be caused by the sublimation of these clouds.

The positive and negative arguments for the significance of seasonal or diurnal water exchange between the soil and atmosphere are mostly based on the ability or inability of the numerical models under consideration to reproduce the observation. It is fair to state that no model has been able to consider all the relevant details for the surface-atmosphere water exchange and, more importantly, the knowledge about the thermodynamic behaviour of hydration and dehydration of minerals and of the global distribution of minerals is tentative.

8.2.8 Impact of Dust on the Water Cycle

Dust is a ubiquitous, non-volatile component of the Martian atmosphere with a huge impact on the meteorology. In principle the dust particles are weathering products of the soil, and are readily suspended if the wind speed at the surface exceeds some threshold. The dust content in the atmosphere is quite variable, and mainly depends on season, but varies dramatically from year to year.

The atmospheric water cycle is affected by dust in several important ways. Dust particles are likely to act as condensation nuclei for H_2O ice. Without such nuclei either the vapour amount would have to become much higher or the temperature must drop much more strongly to initiate ice condensation and cloud formation at all. If there had been no ice condensation due to the lack of dust particles, the global distribution of water vapour would have been more uniform than it is today, as can be imagined from the previous discussion in this chapter. However, ions and micrometeorites may be alternative condensation nuclei, although their abundance in the Martian atmosphere is less uncertain than that of dust [38].

If the surface can adsorb water molecules, dust particles should be able to adsorb water as well. Evidence for such a mechanism came from the simultaneous observation of the diurnal cycle of dust and water vapour in southern summer [16]. While the water vapour content increases in the morning and decreases in the afternoon, the dust opacity decreases in the morning and increases in the afternoon, i.e. the diurnal cycle of dust and vapour is anti-correlated. This behaviour is best understood by adsorption/desorption of water molecules by the dust particles added to the atmosphere, causing a decrease/increase of the water vapour content. The increase of the dust opacity in the afternoon is probably induced by the convective instability near the surface, which gives rise to suspending of a large number of dust particles from the surface. Water adsorption by suspended dust ought to be easier than by soil because water vapour need not be transported into or out of the regolith. Hence, this may be regarded as a possible mechanism to account for the observed diurnal cycle, in addition to the surface fog formation. The attachment of water molecules by the dust particles may also be important for the global water cycle, considering the intensity of planet-encircling dust storms, but has not yet been quantified.

Furthermore, the occurrence of large dust storms affects the water transport substantially. Since dust raises the temperature, ice clouds dissipate and the dust particles no longer transport water with themselves (see also Fig. 8.1). At the same time, dust strengthens the Hadley circulation. The northward transport of water vapour is greatly increased in years with strong dust storms [52, 68]. The amount of water transported each year across the equator may vary from year to year as with the intensity of the dust storms themselves.

8.3 Variability of the Soil Water Content

8.3.1 Influence of the Water Cycle on the Soil Moisture

One important message of Mars Odyssey is that the water content in the Martian soil varies considerably from place to place. This is described exhaustively in Chap. 5 by Mitrofanov, so only aspects related to the global water cycle will be discussed here. As can be seen from Fig. 5.8 in Chap. 5, water is not only present in the polar region in the form of ground ice, but also at low and mid latitudes. Remarkably, considerable regional variability of water contents within the low and mid latitudes has been derived: for instance, Arabia Terra ($20^{\circ}S-30^{\circ}N$, $0^{\circ}-45^{\circ}E$) and Memnonia ($0-25^{\circ}S$, 180–200^{\circ}E) are characterised by an enhanced water content (typically 10 wt %) underneath a thin dry layer (2 wt % water content), while Solis Planum ($16-53^{\circ}S$, $246-293^{\circ}E$) has a water content of only ~2 wt %. (However, the accuracy of the absolute values suffers from the inaccurate *in situ* measurements by the Viking landers used as reference [2].) It is not possible to derive from the Mars Odyssey neutron data alone in what form the water exists in these sites, but this water content may generally comprise adsorbed

water on mineral grains including that at interlayer and extraframework sites of minerals as well as bound water and structural OH in hydrated minerals. Even the presence of ice cannot be entirely ruled out *a priori*, although this would be unexpected given the long-term thermal instability of ground ice at these latitudes (see Chap. 7. by Kuzmin).

Basically, the observed spatial variability could be explained by the present environmental condition and soil properties or by the aqueous history (e.g. possible presence of liquid bodies of water) in the geological past.

The present environmental condition is relevant for the amount of adsorbed water because it is in loose contact with the atmosphere. Relevant parameters include the soil temperature, surface pressure and atmospheric vapour abundance, which all change both in space and time (season, daytime and astronomical epoch). It turns out that some of the observed spatial inhomogeneity of the soil water content can be qualitatively explained by these factors [68]. Among the various surface parameters the annual maximum surface temperature shows the highest linear correlation with the near-surface water content represented by the depression of fast neutrons of HEND [69]. This implies that the input of high energy into the soil controls the water content very close to the surface. This behaviour is in contrast to the distribution of ground ice in deeper layers, which is mainly controlled by the annual mean temperature (see Chap. 7 by Kuzmin). The reason for this difference is that the enthalpy of hydration of minerals is sufficiently higher than that of sublimation of ice [6], so the annual maximum temperature is required to further desiccate the already dry soil. Under the present climate the southern low and mid latitudes experience the highest maximum temperature, so the soil can retain the least amount of water for any globally uniform soil properties. Moreover, the larger atmospheric vapour abundance in the northern hemisphere [57] prevents desiccation of the soil in the north as compared to the south.

The pronounced longitudinal variation of the soil moisture indicates that besides the astronomically caused north-south asymmetry of the insolation pattern, some other factors must be playing a role as well. The thermal inertia is one important factor controlling the annual maximum temperature [68]. This quantity is a measure for the tardiness of the response of the soil temperature to heating or cooling. The thermal inertia of the Martian surface varies by more than an order of magnitude. For instance, Chryse Planitia (landing site of Viking 1), Isidis Planitia or Solis Planum exhibit a much higher thermal inertia than Arabia Terra. Generally, a lower thermal inertia amplifies the diurnal surface temperature variation, but depresses the mean surface temperature. The lower the mean surface temperature, the higher the equilibrium adsorbed water content for a given atmospheric vapour amount.

The topography of Mars can also affect the adsorbed water content to some extent [68]. Topographic depressions have inherently higher surface pressures, so the atmospheric vapour column abundance therein has to be greater as long as the air is well mixed. The deepest place on Mars is the Hellas basin with a mean surface pressure of 10 hPa, which is twice as high as outside the basin. The observed annual-mean vapour column abundance is indeed high (18 pr μ m) compared to 9 pr μ m outside the basin (Fig. 8.7 top). The equilibrium adsorbed

water content near the surface is higher at higher vapour pressures. Indeed a part of the Hellas basin contains an enhanced water content near the surface (fast neutrons) in comparison with the surroundings (Fig. 5.8 bottom). However, the pressure-dependence of the adsorbed water content is significantly smaller than the temperature-dependence, so it is probably not the dominating effect.

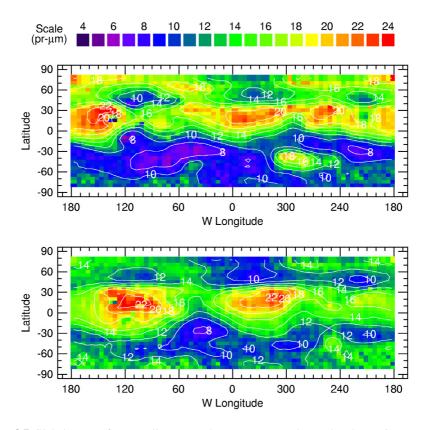


Fig. 8.7 Global maps of seasonally averaged water vapour column abundance (in pr μ m) [57] (courtesy of M.D. Smith, reprinted with permission from AGU). The upper panel shows the measured data, while in the lower panel the data are divided (surface pressure/6.1 hPa) to remove the effect of topography. The vapour abundance is high within the Hellas basin (40°S, 290°W) because of the topographic depression (upper map).

In all these considerations the exchange of shallow subsurface and atmosphere is a prerequisite for this spatial inhomogeneity. This indicates that the atmospheric water cycle may have an influence on the soil moisture on long time scales, even if the soil moisture does not strongly affect the seasonal or diurnal water cycle in the atmosphere.

In addition to the present environmental condition, soil properties which have been created in the geological past or by more recent dust redistribution on the surface can also affect the content of both adsorbed and bound water [2, 40]. One potentially important parameter controlling the adsorbed water content is the specific surface area, which gives the surface area of minerals exposed to air per unit of mass. The adsorptive capacity is directly proportional to this quantity. The only *in situ* value for the specific surface area is 1.7×10^4 m² kg⁻¹ at the Viking Lander 1 site [1, 41]. This particular value is small and is more typical of palagonite than of montmorillonite. On the other hand, from chemical analyses the Viking 1 site is inferred to contain much more clay minerals than palagonite. Unfortunately, it is unclear whether this value is representative of Mars. The specific surface area generally decreases with increasing mineral particle size and the particle size correlates with the thermal conductivity, which is one major factor controlling the thermal inertia of the soil [48]. As the thermal inertia shows a huge geographical variability, the specific surface area and hence adsorptive capacity is also likely to vary from place to place.

More discussion on this topic can be found in Chap. 5 by Mitrofanov. A definite explanation for the obvious geographic variability of the soil water content outside the polar region can only be given after the soil mineralogy and porosity are better constrained and the form of water (adsorbed, bound or ice) is determined by future *in situ* measurements.

8.3.2 Secular Variation of the Near-Surface Water Content

The high correlation between the annual maximum surface temperature and the near-surface water content implies that the water content should change when the maximum surface temperature changes for some reason [69]. The surface temperature of Mars is largely governed by the insolation pattern, which basically varies for astronomical reasons. While the global distribution of ground ice is believed to change by the obliquity cycle because of its effect on the annual mean soil temperature (see Chap. 7 by Kuzmin), the water content of the dry (ice-free) soil near the surface may vary over a shorter period, i.e. the climatic precession cycle (51000 years) as a result of the precession of the Mars' spin axis and the precession of the axis to the orbital plane causing the secular migration of the season at which perihelion occurs. This precession cycle seems to be evidenced by the observation of the stratigraphic structure of the northern polar layered terrain [32]. Presently the perihelion passage occurs shortly before the southern summer solstice. Due to the relatively large eccentricity of Mars, the season of perihelion has a huge impact on the maximum surface temperature. When the perihelion passage occurs in northern summer, the maximum temperature obviously becomes higher in the northern hemisphere, unlike at present.

One major consequence of this would be the secular variation of the soil water content near the surface by a few wt % [69]. While presently the southern hemisphere is more desiccated in comparison with the northern counterpart, this distribution is likely to reverse with the climatic precession cycle. The exchange of water between the hemispheres is likely to take place via atmospheric transport

and hydration/dehydration in the soil. Given the large area of the dry low and mid latitudes, the amount of water exchanged in this time scale may be considerable. However, the global sum of the near-surface soil water cannot always be equal and some exchange of water with the polar caps is likely to account for the global water balance. In the present epoch, in which the annual maximum temperature in the north is decreasing, the northern hemisphere is likely to become wetter, while the southern hemisphere is being desiccated. Mars Odyssey neutron data indicate that at northern high latitudes ground ice extends up to the surface, while at southern high latitudes ground ice is covered by a thin dry layer (see Chap. 5). It would be interesting to consider whether this feature is evidence of this evolution.

8.4 Conclusions

In spite of the cold and dry state, the Martian atmosphere represents an important medium for redistributing the planetary water inventory as illustrated in Fig. 8.4. As is characteristic of cold climates, the Martian hydrology is generally sluggish and subtle. The atmospheric water content is tiny by terrestrial standards, but the total amount of 10^{12} kg is still sufficiently larger than, e.g. the water amount necessary to create the observed gullies. Elucidating several details of the atmospheric water cycle discussed in this chapter is thus important in the assessment of the long-term evolution of the subsurface water content, its spatial variability or the origin of different water reservoirs. It may also be of relevance for the theoretical consideration of a possible "snowball Earth" (where the global oceans are completely frozen at their surface) in the past, which is generally considered to be devoid of a hydrological cycle.

The present seasonal water cycle in the atmosphere seems to be controlled by the polar caps and the atmospheric vapour transport by the global circulation, and is not strongly affected by the soil. On the other hand, the soil is an important reservoir of water and much of the water outside the polar region ought to be adsorbed on mineral grains. Given the large area of low and mid latitudes compared with the polar region, water in or on minerals near the surface may represent a second type of subsurface water, in addition to the ground ice in the polar region. The near-surface soil water content is controlled by the annual maximum surface temperature, reflecting the higher enthalpy of hydration of minerals in comparison with the sublimation enthalpy of ice.

It is uncertain on which time scales water is exchanged between the soil and atmosphere, but in the long-term the soil water content may vary as a result of climate changes for instance by a variation of orbital parameters of Mars. The season of perihelion associated with the climatic precession cycle may have a larger impact on the near-surface soil humidity than the obliquity cycle because of the importance of the annual maximum temperature, while for atmospheric water and ground ice at high latitudes the opposite is true.

To some extent the observed spatial variability of the soil water content is consistent with the long-term or short-term interaction of water between the subsurface and atmosphere. Additionally, some regional variability of the soil water could be ascribed to the aqueous or geological history since the adsorbed water content can be controlled by the soil properties as well and the abundance and distribution of hydrated minerals may be a result of geological processes.

A complete understanding of the atmospheric water cycle in the present and past will require monitoring of the spatial and temporal variation of *all* water forms in the atmosphere, on the surface and in the subsurface and of the environmental parameters, as well as mapping of the soil properties, particularly of the mineralogy.

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8.5 References

- 1 Ballou EV, Wood PC, Wydeven T, Lehwalt ME, Mack RE (1978) Chemical interpretation of Viking 1 life detection experiment. Nature 271: 644-645
- 2 Basilevsky AT, Litvak ML, Mitrofanov IG, Boynton WV, Saunders RS, Head JW (2003) Search for traces of chemically bound water in the Martian surface layer based on HEND measurements onboard the 2001 Mars Odyssey spacecraft. Sol. Syst. Res. 37: 387-396 (Astron. Vestnik 37: 423-434)
- 3 Bass DS, Paige DA (2000) Variability of Mars' north polar water ice cap II. Analysis of Viking IRTM and MAWD data. Icarus 144: 397-409
- 4 Bass DS, Herkenhoff KE, Paige DA (2000) Variability of Mars' north polar water ice cap I. Analysis of Mariner 9 and Viking Orbiter imaging data. Icarus 144: 382-396
- 5 Benson JL, Bonev BP, James PB, Shan KJ, Cantor BA, Caplinger MA (2003) The seasonal behavior of water ice clouds in the Tharsis and Valles Marineris region of Mars: Mars Orbiter Camera observations. Icarus 165: 34-52
- 6 Bish DL, Carey JW, Vaniman DT, Chipera SJ (2003) Stability of hydrous minerals on the Martian surface. Icarus 164: 96-103
- 7 Briggs G, Klaasen K, Thorpse T, Wellman J, Baum W (1977) Martian dynamical phenomena during June-November 1976: Viking Orbiter imaging results J. Geophys. Res. 82 (B28): 4121-4150
- 8 Bullock MA, Stoker CR, McKay CP, Zent AP (1994) A coupled soil-atmosphere model of H₂O₂ on Mars. Icarus 107: 142-154
- 9 Clancy RT, Nair H (1996) Annual (perihelion-aphelion) cycles in the photochemical behavior of the global Mars atmosphere. J. Geophys. Res. 101(E5): 12785-12790
- 10 Clancy RT, Grossman AW, Wolff MJ, James PB, Rudy DJ, Billawala YN, Sandor BJ, Lee SW, Muhleman DO (1996) Water vapor saturation at low altitudes around Mars aphelion: a key to Mars climate? Icarus 122: 36-62
- 11 Colaprete A, Toon OB (2000) The radiative effects of Martian water ice clouds on the local atmospheric temperature profile. Icarus 145: 524-532

- 12 Curran RJ, Conrath BJ, Hanel RA, Kunde VG, Pearl JC (1973) Mars: Mariner 9 spectroscopic evidence for H₂O ice clouds. Science 182: 381-383
- 13 Encrenaz T, Greathouse TK, Bézard B, Atreya SK, Wong AS, Richter MJ, Lacy JH (2002) A stringent upper limit of the H_2O_2 abundance in the Martian atmosphere. Astron. Astrophys. 396: 1037-1044
- 14 Fanale FP, Cannon WA (1971) Adsorption on the Martian regolith. Nature 230: 502-504
- 15 Forget F, Hourdin H, Fournier R, Hourdin C, Talagrand O (1999) Improved general circulation models of the Martian atmosphere from the surface to above 80 km. J. Geophys. Res. 104(E10): 24155-24176
- 16 Formisano V, Grassi D, Ignatiev NI, Zasova L (2001) IRIS Mariner 9 data revisited: water and dust daily cycles. Planet. Space Sci. 49: 1331-1346
- 17 French RG, Gierasch PJ, Popp BD, Yerdon RJ (1981) Global patterns in cloud forms on Mars. Icarus 45: 468-493
- 18 Haberle RM, Jakosky BM (1990) Sublimation and transport of water from the north residual polar cap on Mars. J. Geophys. Res. 95 (B2): 1423-1437
- 19 Haberle RM, Pollack JB, Barnes JR, Zurek RW, Leovy CV, Murphy JR, Lee H, Schaeffer J (1993) Mars atmospheric dynamics as simulated by the NASA Ames general circulation model 1. The zonal-mean circulation. J. Geophys. Res. 98(E2): 3093-3123
- 20 Haberle RM, McKay CP, Schaeffer J, Cabrol NA, Grin EA, Zent AP, Quinn R (2001) On the possibility of liquid water on present-day Mars. J. Geophys. Res. 106(E10): 23317-23326
- 21 Hart HM, Jakosky BM (1986) Composition and stability of the condensate observed at the Viking Lander 2 site on Mars. Icarus 66: 134-142
- 22 Hecht MH (2002) Metastability of liquid water on Mars. Icarus 156: 373-386
- 23 Herschel FW (1784) On the remarkable appearances of the polar regions of the planet Mars, the inclination of its axis, the position of its poles, and its spheroidical shape; with a few hints relating to its real diameter and atmosphere. Philos. Trans. R. Soc. London 24: 233-273
- 24 Houben H, Haberle RM, Young RE, Zent AP (1997) Modeling the Martian seasonal water cycle. J. Geophys. Res. 102(E4): 9069-9083
- 25 Jakosky BM (1983) The role of seasonal reservoirs in the Mars water cycle II. Coupled models of the regolith, the polar caps, and atmospheric transport. Icarus 55: 19-39
- 26 Jakosky BM, Farmer CB (1982) The seasonal and global behavior of water vapor in the Mars atmosphere: complete global results of the Viking atmospheric water vapor detector experiment. J. Geophys. Res. 87(B4): 2999-3019
- 27 Jakosky BM, Zent AP, Zurek RW (1997) The Mars water cycle: determining the role of exchange with the regolith. Icarus 130: 87-95
- 28 James PB, Bell JF III, Clancy RT, Lee SW, Martin LJ, Wolff MJ (1996) Global imaging of Mars by Hubble Space Telescope during the 1995 opposition. J. Geophys. Res. 101(E8): 18883-18890
- 29 Kahn RA (1990) Ice haze, snow, and the Mars water cycle. J. Geophys. Res. 95(B9): 14677-14694
- 30 Kosmas C, Danalatos NG, Poesen J, van Wesemael B (1998) The effect of water vapour adsorption on soil moisture content under Mediterranean climate conditions. Agric. Water Mgmt. 36: 157-168

- 31 Kuznetz LH, Gan DC (2002) On the existence and stability of liquid water on the surface of Mars today. Astrobiology 2: 183-196
- 32 Laskar J, Levrard B, Mustard JF (2002) Orbital forcing of the Martian polar layered deposits. Nature 419: 375-377
- 33 Lobitz B, Wood BJ, Averner MA, McKay CP (2001) Use of spacecraft data to derive regions on Mars where liquid water would be stable. Proc. Nat. Acad. Sci. 98: 2132-2137
- 34 Magalhães JA, Schofield JT, Seiff A (1997) Results of the Mars Pathfinder atmospheric structure investigations. J. Geophys. Res. 104(E4): 8943-8956
- 35 Malin MC, Edgett KS (2000) Evidence for recent groundwater seepage and surface runoff on Mars. Science 288: 2330-2335
- 36 McDonald GD, de Vanssay E, Buckley JR (1998) Oxidation of organic macromolecules by hydrogen peroxide: implications for stability of biomarkers on Mars. Icarus 132: 170-175
- 37 Mellon MT, Jakosky BM (1993) Geographic variations in the thermal and diffusive stability of ground ice on Mars. J. Geophys. Res. 98(E2): 3345-3364
- 38 Michelangeli DV, Toon OB, Haberle RM, Pollack PB (1993) Numerical simulations of the formation and evolution of water ice clouds in the Martian atmosphere. Icarus 100: 261-285
- 39 Mischna MA, Richardson MI, Wilson RJ, McCleese DJ (2003) On the orbital forcing of Martian water and CO₂ cycles: a general circulation model study with simplified volatile schemes. J. Geophys. Res. 108(E6): 5062, 10.1029/2003JE002051
- 40 Mitrofanov IG; Litvak ML, Kozyrev AS, Sanin AB, Tret'yakov VI, Boynton WV, Shinohara C, Hamara D, Saunders S, Drake DM (2003) Search for water in Martian soil using global neutron mapping by the Russian HEND instrument onboard the US 2001 Mars Odyssey spacecraft. Sol. Syst. Res. 37: 366-377 (Astron. Vestnik 37: 400-412)
- 41 Möhlmann DTF (2003) Unfrozen subsurface water on Mars: presence and implications. Int. J. Astrobiol. 2: 213-216
- 42 Nair H, Allen M, Anbar AD, Yung YL, Clancy RT (1994) A photochemical model of the Martian atmosphere. Icarus 111: 124-150
- 43 Neumann GA, Smith DE, Zuber MT (2003) Two Mars years of clouds detected by the Mars Orbiter Laser Altimeter. J. Geophys. Res. 108(E4): 5023, 10.1029/2002JE001849
- 44 Novak RE, Mumma MJ, DiSanti MA, Dello Russo N, Magee-Sauer K (2002) Mapping of ozone and water in the atmosphere of Mars near the 1997 aphelion. Icarus 158: 14-23
- 45 Parker DC, Beish JD, Troiani DM, Joyce DP, Hernandez CE (1999) Telescopic observations of Mars, 1996-1997: results of the Marswatch program. Icarus 139: 3-19
- 46 Pearl JC, Smith MD, Conrath BJ, Bandfield JL, Christensen PR (2001) Observations of Martian ice clouds by the Mars Global Surveyor Thermal Emission Spectrometer: the first Martian year. J. Geophys. Res. 106 (E6): 12325-12338
- 47 Peixoto JP, Oort AH (1992) Physics of Climate. American Institute of Physics, New York
- 48 Presley MA, Christensen PR (1997) The effect of bulk density and particle size sorting on the thermal conductivity of particulate materials under Martian atmospheric pressures. J. Geophys. Res. 102(E4): 9221-9229

- 49 Richardson MI, Wilson RJ (2002a) Investigation of the nature and stability of the Martian seasonal water cycle with a general circulation model. J. Geophys. Res. 107(E5): 10.1029/2001JE001536
- 50 Richardson MI, Wilson RJ (2002b) A topographically forced asymmetry in the Martian circulation and climate. Nature 416: 298-300
- 51 Richardson MI, Wilson RJ, Rodin AV (2002) Water ice clouds in the Martian atmosphere: general circulation experiments with a simple cloud scheme. J. Geophys. Res. 107(E9): 5064, 10.1029/2001JE001804
- 52 Rizk B, Haberle RM, Hunten DM, Pollack PB (1995) Meridional transport and water reservoirs in southern Mars during 1988-1989. Icarus 118: 39-50
- 53 Rodin AV, Korablev OI, Moroz VI (1997) Vertical distribution of water in the nearequatorial troposphere of Mars: water vapor and clouds. Icarus 125: 212-229
- 54 Ryan JA, Sharman RD (1981) H₂O frost point detection of Mars? J. Geophys. Res. 86(C1): 503-511
- 55 Savijärvi H (1995) Mars boundary layer modeling: diurnal moisture cycle and soil properties at the Viking Lander 1 site. Icarus 117: 120-137
- 56 Smith MD, Bandfield JL, Christensen PR, Richardson MI (2003) Thermal Emission Imaging System (THEMIS) infrared observations of atmospheric dust and water ice cloud optical depth. J. Geophys. Res. 108(E11): 5115, 10.1029/2003JE002115
- 57 Smith MD (2002) The annual cycle of water vapor on Mars as observed by the Thermal Emission Spectrometer. J. Geophys. Res. 107(E11): 5115, 10.1029/JE001522
- 58 Smith MD (2004) Interannual variability in TES atmospheric observations of Mars during 1999-2003. Icarus 167: 148-165
- 59 Spinrad H, Münch G, Kaplan LD (1963) The detection of water vapor on Mars. Astrophys. J. 137: 1319-1321
- 60 Sprague AL, Hunten DM, Doose LR, Hill RE (2003) Mars atmospheric water vapor abundance: 1996-1997. Icarus 163: 88-101
- 61 Svitek T, Murray B (1990) Winter frost at Viking Lander 2 site. J. Geophys. Res. 95(B2): 1495-1510
- 62 Takahashi YO, Fujiwara H, Fukunishi H, Odaka M, Hayashi Y, Watanabe S (2003) Topographically induced north-south asymmetry of the meridional circulation in the Martian atmosphere. J. Geophys. Res. 108(E3): 5018, 10.1029/2001JE001638
- 63 Tamppari LK, Zurek RW, Paige DA (2000) Viking era water-ice clouds. J. Geophys. Res. 105(E2): 4087-4107
- 64 Tamppari LK, Zurek RW, Paige DA (2003) Viking-era diurnal water-ice clouds. J. Geophys. Res. 108(E7): 5073, 10.1029/2002JE001911
- 65 Titov DV (2002) Water vapour in the atmosphere of Mars. Adv. Space Res. 29(2): 183-191
- 66 Titov DV, Markiewicz WJ, Thomas N, Keller HU, Sablotny RM, Tomasko MG, Lemmon MT, Smith PH (1999) Measurements of the atmospheric water vapor on Mars by the Imager for Mars Pathfinder. J. Geophys. Res. 104(E4): 9019-9026
- 67 Titus TN, Kieffer HH, Christensen PR (2003) Exposed water ice discovered near the south pole of Mars. Science 299: 1048-1051
- 68 Tokano T (2003a) Spatial inhomogeneity of the Martian subsurface water distribution: implication from a global water cycle model. Icarus 164: 50-78
- 69 Tokano T (2003b) Precession-driven migration of water in the surficial layers of Mars. Int. J. Astrobiol. 2: 155-170

- 70 Wang H, Ingersoll AP (2002) Martian clouds observed by Mars Global Surveyor Mars Orbiter Camera. J. Geophys. Res. 107(E10): 5078, 10.1029/2001JE001815
- 71 Wilson RW, Hamilton K (1996) Comprehensive model simulation of thermal tides in the Martian atmosphere. J. Atmos. Sci. 53: 1290-1326
- 72 Wynn-Williams DD, Cabrol NA, Grin EA, Haberle RM, Stoker CR (2001) Brines in seepage channels as eluants for subsurface relict biomarkers on Mars? Astrobiology 1: 165-184
- 73 Yamanaka T, Yonetani T (1999) Dynamics of the evaporation zone in dry sandy soils. J. Hydrol. 217: 135-148
- 74 Zasova L, Formisano V, Grassi D, Ignatiev N, Maturilli A (2002) Martian winter atmosphere at north high latitudes: Mariner 9 IRIS data revisited. Adv. Space Res. 29(2): 151-156
- 75 Zent AP, Quinn RC (1997) Measurement of H₂O adsorption under Mars-like conditions: effects of adsorbent heterogeneity. J. Geophys. Res. 102(E4): 9085-9095
- 76 Zent AP, Haberle RM, Houben HC, Jakosky BM (1993) A coupled surface-boundary layer model of water on Mars. J. Geophys. Res. 98(E2): 3319-3337
- 77 Zent AP, Howard DJ, Quinn RC (2001) H_2O adsorption on smectites: application to the diurnal variation of H_2O in the Martian atmosphere. J. Geophys. Res. 106(E7): 14667-14674
- 78 Zent AP, Fanale FP, Roth LE (1990) Possible Martian brines radar observations and models. J. Geophys. Res. 95(B9): 14531-14542
- 79 Zisk SH, Mouginis-Mark PJ (1980) Anamalous region on Mars: implications for nearsurface liquid water. Nature 44: 735-738
- 80 Bibring J-P, Langevin Y, Poulet F, Gendrin A, Gondet B, Berthé M, Soufflot A, Drossart P, Combes M, Bellucci G, Moroz V, Mangold N, Schmitt B, the OMEGA team (2004) Perennial water ice identified in the south polar cap of Mars. Nature doi:10.1038/nature02461

9 Polar Lakes, Streams, and Springs as Analogs for the Hydrological Cycle on Mars

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The extensive fluvial features seen on the surface of Mars attest to the stable flow of water on that planet at some time in the past. However the low erosion rates, the sporadic distribution of the fluvial features, and computer simulations of the climate of early Mars all suggest that Mars was quite cold even when it was wet. Thus, the polar regions of the Earth provide potentially important analogs to conditions on Mars during its wet, but cold, early phase. Here we review studies of polar lakes, streams, and springs and compare the physical and geological aspects of these features with their possible Martian counterparts. Fundamentally, liquid water produced by summer melts can persist even when the mean annual temperature is below freezing because ice floats over liquid and provides an insulating barrier. Life flourishes in these liquid water habitats in Earth's polar regions and similarly life may have been present in ice-covered lakes and permafrost springs on Mars. Evidence for past life on Mars may therefore be preserved in the sediments and mineral precipitates associated with these features.

9.1 Polar Hydrology

There are several regions on Earth where mean annual temperatures are well below freezing and yet liquid water persists in these locales. Such polar regions provide an excellent analog to study the hydrological cycle under conditions that have prevailed in the polar desert environment of Mars. In this review we will focus on two areas including Axel Heiberg Island in the Canadian High Arctic and the McMurdo Dry Valleys of Antarctica. In both locations the mean annual air temperatures are extremely low and range from -15° C to -20° C on Axel Heiberg Island and from -15° C to -30° C at the dry valley bottoms in Antarctica [1, 2]. At both the Arctic and Antarctic sites the precipitation is low creating desert conditions. The site on Axel Heiberg Island lies within a region of thick, continuous permafrost and two sets of springs flow throughout the year with constant temperature and flow rates. In the McMurdo Dry Valleys of Antarctica, summer streams of glacial meltwater create large perennially ice-covered lakes. Important lessons regarding the search for life on Mars, past or present, are gleaned from studies of these terrestrial ecosystems.

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9.1.1 Arctic Springs

There are two sets of cold saline springs on Axel Heiberg Island located at approximately 79°N, 90°W [3] (Fig. 9.1). One group, located at the base of Colour Peak, consists of approximately 20 spring outlets 30–40 m above sea level that flow via a series of mineralized pipes and troughs down the south-facing slope of Colour Peak into Expedition Fiord. The second group is located at the base of Gypsum Hill 11 km east of Colour Peak. At Gypsum Hill the springs and seeps discharge from approximately 40 outlets along a band nearly 300 m long and 30 m wide and flow onto the Expedition River floodplain. The individual spring outlets are tens of centimeters in diameter.

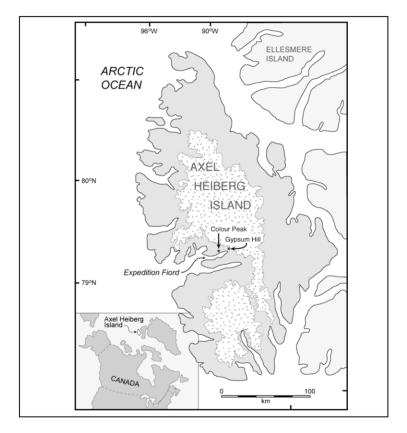


Fig. 9.1 Study site location map for the Axel Heiberg spring sites.

The mean annual air temperature in the vicinity of the springs is -15° C and the region is characterized by thick, continuous permafrost reaching depths of nearly 600 m [1, 4]. Despite the cold conditions, the spring water flows at a constant temperature and rate all year (as shown in Fig. 9.2) discharging an anoxic brine with a near neutral pH and vent temperatures varying between -4° C and 7° C [3].

The combined flow of all outlets at Gypsum Hill and Colour Peak is 10-15 l/sec and 20-25 l/sec, respectively [3]. During the winter the Colour Peak discharge flows into the waters of the Expedition Fiord whereas the Gypsum Hill flow emerges from the springs and flows onto the Expedition River floodplain. Below freezing temperatures result in the formation of a residual icing that has reached $300,000 \text{ m}^2$ in size and the growth of numerous seasonal frost mound structures in the vicinity of the vents [3, 5]. Salts associated with the brine are deposited as a result of evaporative and freeze fractionation. During the summer months when air temperatures are above freezing the icing and mineral deposits are removed almost entirely by runoff and deflation.

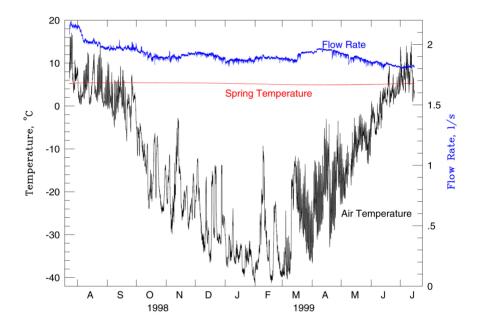


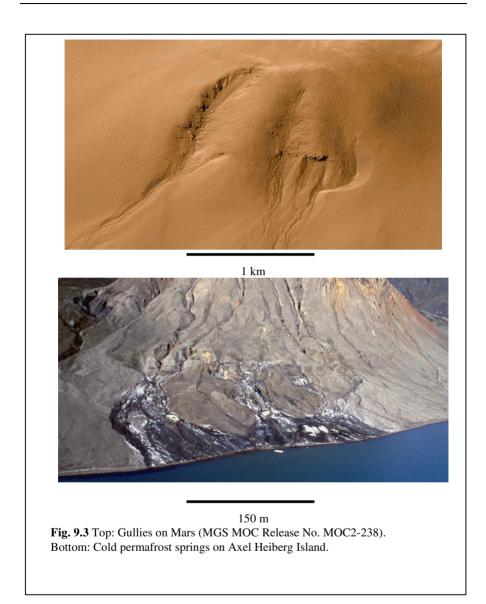
Fig. 9.2 Temperature and flow rate of the cold saline springs on Axel Heiberg Island. Air temperature is shown as well [1].

Analysis of the dissolved gases and bubbles in the spring water indicates that the source of the water is a combination of subglacial melt and lake water. Two nearby glacially dammed alpine lakes, Phantom Lake and Astro Lake, provide large reservoirs of water and have basins residing upon gypsum-anhydrite piercement structures [1, 6]. Lake water is transported into the subsurface via permeable strata associated with the piercement structures. The water continues to flow along the subsurface salt strata and is transported to the spring sites. The water accumulates dissolved salts as it flows through this subsurface layer and emerges with a salinity value about five times that of seawater. The composition of dissolved gases in the springs indicates that only 50 % of the water comes from lake water and that the other 50 % comes from glacial ice that has melted while isolated from the atmosphere [6]. The dissolved gases in lake water reflect the equilibrium with the atmosphere based on the relative solubility of each gas. In contrast, air trapped in glacial ice has an atmospheric composition other than for Ne and He. These latter two gases are soluble in ice and would therefore be expected to diffuse through the ice. As an example, the ratio of N_2/Ar in lake water in equilibrium with the atmosphere is 37 while for air it is 84.

Interestingly, the springs on Axel Heiberg Island flow all year with little variation in their temperature and are not associated with volcanic activity [1]. Andersen et al. [1] show that this can be explained by considering the flow through the subsurface salt layers. The flow enters the subsurface via the permeable strata associated with the salt diapirs that reside beneath the lakes, glaciers and ice-cap. At this depth the groundwater temperature is 0°C. The flow then proceeds below the surface to depths of at least 600 m and is warmed by the local geothermal gradient to temperatures up to 6°C. The flow rate to the surface is rapid enough that the temperature of the emerging groundwater does not change significantly from its initial value at depth.

Fluvial spring systems in a polar desert environment likewise may exist on Mars (Fig. 9.3). Geologically young small-scale features resembling terrestrial water-carved gullies were observed by the Mars Global Surveyor (MGS) Mars Orbiter Camera (MOC) and first reported by Malin and Edgett [7]. The superposition of the gullies on geologically young surfaces such as dunes and polygons as well as the extreme scarcity of superposed impact craters indicate the relative youth of the gullies, suggesting that the gullies formed within the past few million years [7, 8, 9]. These features exhibit a characteristic morphology indicative of fluid-type erosion of the surficial material and liquid water has been suggested as a likely fluid [7, 9–22]. The gullies are found exclusively poleward of 30° latitude in both the northern and southern hemispheres [8, 18]. These regions correspond with the areas of ground ice stability on Mars [23], suggesting that gully formation may be intrinsically tied to the presence of subsurface ice in the Martian polar desert environment.

Generally, gully morphology can be divided into alcove, channel, and depositional apron regions [7]. The theater-shaped alcove generally tapers downslope and may represent a fluid source region. The channels typically begin at the base of the alcove. Channels appear incised into the slope surface, having steep walls with a distinctive V-shaped cross section [7, 18]. Near the alcove-channel transition there is sometimes evidence of channels streamlining around obstacles and anastomosing channel patterns [7, 18]. The depositional aprons typically have a triangular shape which broadens downslope. The aprons appear smooth on a decameter scale but smaller swells and swales are observed that are oriented downslope along the long axis of the gully [7, 18]. The aprons sometimes extend beyond the base of the gully slope, and channels sometimes cut into the apron structure [7, 18].



Numerous models have been proposed which invoke various physical processes, as well as various agents of erosion, to explain the origin of the Martian gullies and the origin of the erosive agents. Musselwhite et al. [24] proposed that a liquid CO_2 aquifer could form capped by a dry-ice barrier which seasonally breaks out rapidly releasing the liquid CO_2 from the side of the slope. Malin and Edgett [7] and Mellon and Phillips [21] suggested that a shallow aquifer several hundred meters deep could be the source of liquid water that ultimately carves the gully

features, while Gaidos [13] argued for a deep aquifer. Costard et al. [12] likewise proposed liquid water as the principle agent of erosion, but suggested that melting shallow ground ice is the source of the water. Gilmore and Phillips [14] also rely on the melting of near-surface ground ice and proposed that meltwater would percolate to an impermeable layer that dips towards an exposed slope wall. Lee et al. [20], Hartmann et al. [15] and Christensen [11] suggested that the gullies may be formed by liquid water from dissipating snowpacks. In addition, Treiman [25] proposed that mass-wasting is also a candidate mechanism of gully formation.

However, a thorough analysis of Mars Global Surveyor (MGS) spacecraft data from the Mars Orbiter Camera (MOC), Mars Orbiter Laser Altimeter (MOLA), and Thermal Emission Spectrometer (TES), as well as an analysis of terrestrial springs in polar desert environments suggests that liquid water emanating from an underground aquifer is the most robust explanation regarding the formation of the Martian gullies [18]. A shallow aquifer can occur where competent rock layers can trap water below ground upslope from a ridge, while maintaining an overlying dry and thermally insulating soil layer. The dry insulating overburden allows geothermal heat to maintain liquid water within the confined aquifer at only a few hundred meters depth [18]. An ice-cemented-soil plug between the aquifer and slope surface develops where ground ice is generally stable. Freezing cycles induced by obliquity variations cause increased fluid pressure in the aquifer to fracture the ground ice plug and allow liquid water to emerge from the side of a slope to create the gully [21].

9.1.2 Antarctic Lakes

The McMurdo Dry Valleys of Antarctica are the largest ice-free region on the continent. Mean annual valley bottom temperatures range from -15 to -30° C and summer maximum temperatures are a few degrees above freezing [2]. The precipitation is low at 1–2 cm water equivalent and occurs almost entirely as snow. This is the most Mars-like environment on Earth. Despite these conditions there is an active hydrological cycle in these valleys which supports the presence of large ice-covered lakes with rich microbial communities on the lake bottom [26–29], in the water column [27, 30] and within the ice cover [31, 32]. A few percent of the light incident on the surface of the lake penetrates the ice cover [33, 34] but this is adequate for photosynthesis. The perennial ice cover inhibits the exchange of gases between the water column and the atmosphere. As a result gases carried into the lake in solution in the meltwater are concentrated, including O₂ [35], N₂[36], and Ar [37] and biologically produced gases such as O₂ [38] and N₂O [39].

The hydrological cycle in the dry valleys begins with snow carried in primarily from the coast. The snow that falls at low elevations sublimes away without creating any appreciable flow. At high elevations the snow accumulates and then flows downward as glaciers, as can be seen in Fig. 9.4. These glaciers provide the source of meltwater in the summer when air temperatures rise above freezing. With air temperatures above freezing, and of course with total pressure well above the triple point of water, the flow from the glaciers can travel a considerable distance. This process has formed the Onyx River in Antarctica (Fig. 9.4). The rivers and streams flow into the lowest point in the valleys and form lakes. Due to the lower temperatures the lakes are perennially ice-covered. However the lakes are not frozen solid. Indeed the ice covers are only 4–5 m thick and overlie 30–70 m of the water column. The thickness of the ice cover was explained by McKay et al. [40] by a simple annually averaged energy balance shown schematically in Fig. 9.5. The energy balance equation is

$$kdT/dz = (1-r)(1-a)Se^{-z/h} + Fg + vL\rho,$$
 (1)

where k is the thermal conductivity of the ice cover, T is the temperature, z is the depth measured downward, r is the fraction of the surface covered by dirt, a is the albedo of the ice cover, S is the solar energy reaching the surface, h is the extinction length for light, Fg is the geothermal flux, v is the rate of ablation from the top of the ice cover, L is the latent heat of fusion for water, and ρ is the density of ice. For the dry valley lakes [40, 41] the nominal values of these parameters are r = 0.1, a = 0.3, S = 90 W m⁻² but considering only the visible portion of the sunlight which is capable of penetrating the ice cover S = 45 W m² [41], Fg is negligible at ~0.08 W m⁻², v = 30 cm/year. If Eq. 1 is integrated across the ice cover, the steady state annual average thickness of the ice can be computed and agrees with the observed ice cover thickness on the lakes.

The primary energy input into the lake is the latent heat carried by the inflowing meltwater. This latent heat is released when the water freezes at the bottom of the ice cover. In steady state the rate of freezing at the bottom of the ice cover equals the rate of ablation from the top of the ice cover (ν). The ice cover thickness then adjusts so that, in steady state, the energy loss by conduction balances the energy input.

The key to the existence of such ice covered lakes is summer temperatures above freezing. In the dry valleys the value of the yearly degree days above freezing varies from 40 to 90°C-days [2, 42, 43]. If the temperature in the dry valleys were to fall such that the summer temperature no longer rose above freezing then the lakes would no longer be resupplied with liquid and would sublime away, maintaining liquid water under an ice cover of approximately the same thickness.

The energy balance model of the ice cover has also been applied to the thick ice cover of Lake Vida (19 m) [41]. There the ice is sealed and no meltwater flows below the ice cover in the summer. The ice cover overlies a brine solution and so the temperature of the bottom of the ice is not constant at 0°C as is the case for the other dry valley lakes. Instead the ice-brine interface varies with the concentration of the brine.

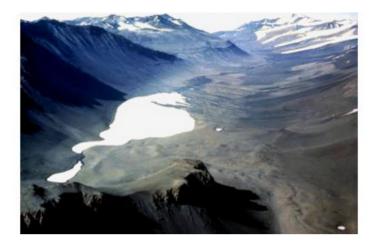


Fig. 9.4 Perennially ice-covered Lake Vanda in Wright Valley, Antarctica. The Onyx River flows into the lake for a few weeks each summer. The lake is about 5 km across. Photo by J. Robie Vestal.

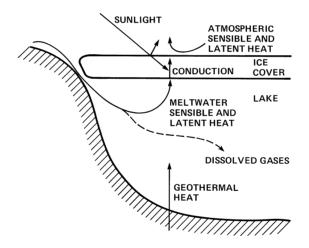


Fig. 9.5 Energy balance of the ice cover on dry valley lakes.

When the ice becomes thicker the underlying brine becomes more concentrated, which lowers the equilibrium temperature at which the brine and ice coexist. The lowering of the temperature at the lower boundary of the ice decreases the steady state thickness of the ice. The net result is a negative feedback which stabilizes the ice cover thickness [41].

9.2 Martian Hydrology: Rivers and Lakes Without Rain

McKay and Davis [44] have applied this model to predict the existence of perennially ice-covered lakes on early Mars. For example, Gusev Crater may have once been an ice-covered lake (Fig. 9.6) (see also Chap. 10 by Cabrol and Grin). On Mars there would be seasonal variations even at the equator due to the relatively high eccentricity (0.1) of the Martian orbit. At higher latitudes the obliquity and eccentricity both cause seasonal effects. When the obliquity is at its maximum (45°) and perihelion occurs at summer then daily average temperatures above freezing can occur even if mean annual temperatures are as low as -40°C [44]. The modeling results suggest that ice-covered lakes on Mars could have persisted up to 500 Ma after mean annual temperatures fell below freezing. Indeed, even if mean annual temperatures on Mars were never above freezing and there was never any rain on Mars, large ice-covered lakes could have existed replenished by a snow-based hydrological cycle. As in Antarctica, these lakes could have provided a habitat for life (see Fig. 9.7). Moore et al. [45] developed a plausible regional scale hydrological cycle in the Chryse region of Mars patterned after the dry valleys. In their model moisture, which evaporated from the ice, covered northern plains accumulates to form glaciers which provide a source of meltwater. The biological perspective on the history of water on Mars [46] suggests that the evidence for life accessible on the surface would be in sediments from such lake deposits [47].

It is important to note that such lakes cannot exist on Mars today due to the low pressure. The pressure on Mars is close to the triple point pressure of water (610 Pa). At these low pressures meltwater is not generated from the heating of glacial ice and instead the ice sublimes [48, 49]. There are regions on Mars where conditions would allow for liquid water [50, 51] but no ice is present at these locations.

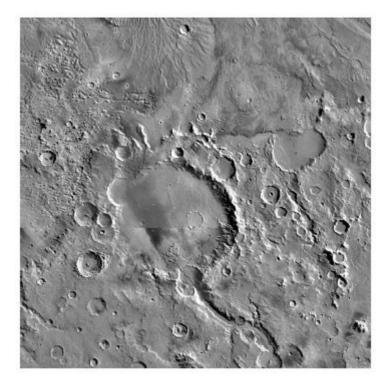


Fig. 9.6 Gusev Crater on Mars could have been an ice-covered lake similar to those seen in the dry valleys of Antarctica. A river, Ma'adim Vallis, has entered the crater from the lower right. The heavily cratered terrain surrounding Gusev is inconsistent with rain - rivers and lakes without rain.



Fig. 9.7 Benthic microbial mat communities beneath the ice covers of Lake Vanda (top) and Lake Hoare (bottom) in the McMurdo Dry Valleys. Microbial communities similar to these played a major role in shaping Earth's earliest biosphere. Similar communities may have evolved on Mars during a more clement period when liquid water was stable at the surface.

9.3 Conclusions

Even when Mars was wet it was probably cold. Thus the hydrological cycle in the coldest regions on Earth provides the best analogs for the possible Martian hydrology. From studies of springs, rivers and lakes in the polar regions we have developed quantitative models that show how liquid water could have persisted on Mars even if mean annual temperatures were below freezing. The fact that ice floats and the existence of even transient temperatures above freezing are the keys to liquid water, and possibly life, on Mars.

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9.4 References

- 1 Andersen DT, Pollard WH, McKay CP, Heldmann, JL (2002) Cold springs in permafrost on Earth and Mars. J. Geophys. Res. 107(E3): 10.1029/2000JE001436
- 2 Doran PT, Priscu JC, Lyons WB, Walsh JE, Fountain AG, McKnight DM, Moorhead DL, Virginia RA, Wall DH, Clow GD, Fritsen CH, McKay CP, Parsons AN (2002) Antarctic climate cooling and terrestrial ecosystem response. Nature 415: 517-520
- 3 Pollard WH, Omelon C, Andersen DT, McKay CP (1999) Perennial spring occurrence in the Expedition Fiord area of Western Axel Heiberg Island, Canadian High Arctic. Canadian J. Earth Sci. 36: 1-16
- 4 Doran PT, McKay CP, Adams WP, English MC, Wharton RA, Meyer MA (1996) Climate forcing and thermal feedback of high Arctic residual ice covers. Limnol. Oceanogr. 41: 839-848
- 5 Heldmann JL, Pollard WH, McKay CP, Andersen DT, Toon OB (2003) Annual development cycle of an icing deposit and associated perennial spring activity on Axel Heiberg Island, Canadian High Arctic. Arct. Antarct. Alpine Res.: submitted
- 6 Andersen DT (2004) Perennial springs in the Canadian High Arctic: analogs of Martian hydrothermal systems. Ph.D. Thesis, McGill University, Montreal
- 7 Malin MC, Edgett KS (2000) Evidence for recent groundwater seepage and surface runoff on Mars. Science 288: 2330-2335

- 8 Edgett KS, Malin MC, Williams RME, Davis SD (2003) Polar and middle-latitude Martian gullies: a view from MGS MOC after two Mars years in the mapping orbit. 34th Lun. Planet. Sci. Conf. 1038
- 9 Malin MC, Edgett KS (2001) The Mars Global Surveyor Mars Orbiter Camera: interplanetary cruise through primary mission. J. Geophys. Res. 106(E10): 23429-23570
- 10 Bridges NT, Hecht MH (2002) Mars polar gully modification and possible formation from condensed volatiles. Eos 83: 47
- 11 Christensen PR (2003) Formation of recent Martian gullies through melting of extensive water-rich snow deposits. Nature 422: 45-48
- 12 Costard F, Forget F, Mangold N, Peulvast JP (2002) Formation of recent Martian debris flows by melting of near-surface ground ice at high obliquity. Science 295: 110-113
- 13 Gaidos EJ (2001) Cryovolcanism and the recent flow of liquid water on Mars. Icarus 153: 218-223
- 14 Gilmore MS, Phillips EL (2002) The role of aquicludes in the formation of the Martian gullies. Geology 30: 1107-1110
- 15 Hartmann WK (2002) Comparison of Icelandic and Martian hillside gullies. 33rd Lun. Planet. Sci. Conf. 1904
- Hartmann WK (2001) Martian seeps and their relation to youthful geothermal activity. Space Sci. Rev. 96: 405-410
- 17 Hecht MH (2002) Metastability of liquid water on Mars. Icarus 156: 373-386
- 18 Heldmann JL, Mellon MT (2004) Observations of Martian gullies and constraints on potential formation mechanisms. Icarus 168: 285-304
- 19 Knauth LP, Burt DM (2002) Eutectic brines on Mars: origin and possible relation to young seepage features. Icarus 158: 267-271
- 20 Lee P, McKay CP, Matthews J (2002) Gullies on Mars: clues to their formation timescale from possible analogs from Devon Island, Nunavut, Arctic Canada. 33rd Lun. Planet. Sci. Conf. 2050
- Mellon MT, Phillips RJ (2001) Recent gullies on Mars and the source of liquid water.
 J. Geophys. Res. 106(E10): 23165-23179
- 22 Stewart ST, Nimmo F (2002) Surface runoff features on Mars: testing the carbon dioxide formation hypothesis. J. Geophys. Res. 107 (E9): 5069, 10.1029/2000JE001465
- 23 Mellon MT, Jakosky BM (1995) The distribution and behavior of Martian ground ice during past and present epochs. J. Geophys. Res. 100(E6): 11781-11799
- 24 Musselwhite DS, Swindle TD, Lunine JI (2001) Liquid CO₂ breakout and the formation of recent small gullies on Mars. Geophys. Res. Lett. 28: 1283-1285
- Treiman AH (2003) Geologic settings of Martian gullies; implications for their origins.
 J. Geophys. Res. 108(E4): 8031, 10.1029/2002JE001900
- 26 Hawes I, Schwarz AM (1999) Photosynthesis in an extreme shade environment: benthic microbial mats from Lake Hoare, a permanently ice-covered Antarctic lake. J. Phycology 35: 448-459
- 27 Parker BC, Simmons GM, Seaburg KG, Cathey DD, Allnutt FTC (1982) Comparative ecology of plankton communities in seven Antarctic oasis lakes. J. Plank. Res. 4: 271-286
- 28 Parker BC, Simmons GM, Love FG, Wharton RA, Seaburg KG (1981) Modern stromatolites in Antarctic dry valley lakes. BioScience 31: 656-661

- 29 Wharton RA, Parker BC, Simmons GM, Seaburg KG, Love FG (1982) Biogenic calcite structures forming in Lake Fryxell, Antarctica. Nature 295: 403-405
- 30 Wharton RA, Simmons GM, McKay CP (1989) Perennially ice-covered Lake Hoare, Antarctica: physical environment, biology and sedimentation. Hydrobiologia 172: 305-320
- 31 Fritsen CF, Adams EE, McKay CP, Priscu, JC (1998) Liquid water content of permanent ice covers on lakes in the McMurdo dry valleys. In: Priscu JC (ed) Ecosystem Dynamics in a Polar Desert: The McMurdo Dry Valleys, Antarctica, Antarctic Research Series 72, American Geophysical Union, Washington D.C., pp 269-280
- 32 Priscu JC, Fritsen CF, Adams EE, Giovannoni SJ, Paerl HW, McKay CP, Doran PT, Gordon DA, Lanoil BD, Pinckney JL (1998) Perennial Antarctic lake ice: an oasis for life in a polar desert. Science 280: 2095-2098
- 33 McKay CP, Clow GD, Andersen DT, Wharton RA (1994) Light transmission and reflection in perennially ice-covered Lake Hoare, Antarctica. J. Geophys. Res. 99: 20427-20444
- 34 Palmisano AC, Simmons GM (1987) Spectral downwelling irradiance in an Antarctic lake. Polar Biol. 7: 145-151
- 35 Wharton RA, McKay CP, Simmons GM, Parker BC. (1986) Oxygen budget of a perennially ice-covered Antarctic lake. Limnol. Oceanogr. 31: 437-443
- 36 Wharton RA, McKay CP, Mancinelli RL, Simmons GM (1987) Perennial N₂ supersaturation in an Antarctic lake. Nature 325: 343-345
- 37 Andersen DT, McKay CP, Wharton RA (1998) Dissolved gases in perennially icecovered Antarctic lakes of the McMurdo Dry Valleys. Antarct. Sci. 10: 124-133
- 38 Craig H, Wharton RA, McKay CP (1992) Oxygen supersaturation in ice-covered Antarctic lakes: biological versus physical contributions. Science 255: 318-321
- 39 Priscu JC, Downes MT, McKay CP (1996) Extreme supersaturation of nitrous oxide in a poorly ventilated Antarctic lake. Limnol. Oceanogr. 41: 1544-1551
- 40 McKay CP, Clow GD, Wharton RA, Squyres SW (1985) The thickness of ice on perennially frozen lakes. Nature 313: 561-562
- 41 Doran PT, Fritsen CH, McKay CP, Priscu JC, Adams EE (2003) Formation and character of an ancient 19 m ice cover and underlying trapped brine in an "ice-sealed" east Antarctic lake. Proc. Nat. Acad. Sci. 100: 26-31
- 42 Clow GD, McKay CP, Simmons GM, Wharton RW (1988) Climatological observations and predicted sublimation rates at Lake Hoare, Antarctica. J. Climate 1: 715-728
- 43 Doran PT, McKay CP, Clow GD, Dana GL, Fountain AG, Nylen T, Lyons WB (2002) Valley floor climate observations from the McMurdo dry valleys, Antarctica, 1986-2000. J. Geophys. Res. 107(D24): 10.1029/2001JD002045
- 44 McKay CP, Davis WL (1991) Duration of liquid water habitats on early Mars. Icarus 90: 214-221
- 45 Moore JM, Clow GD, Davis WL, Gulick VC, Janke DJ, McKay CP, Stoker CR, Zent AP (1995) The circum-Chryse region as a possible example of a hydrologic cycle on Mars: Geologic observations and theoretical evaluation. J. Geophys. Res. 100: 5433-5447
- 46 McKay CP, Friedmann EI, Wharton RA, Davis WL (1992) History of water on Mars: a biological perspective. Adv. Space Res. 12: 231-238

- 47 Doran PT, Wharton RW, DesMarais D, McKay CP (1998) Antarctic paleolake sediments and the search for extinct life on Mars. J. Geophys. Res. 103(E12): 28481-28493
- 48 Ingersoll AP (1970) Mars: occurrence of liquid water. Science 168: 972-973
- 49 Kahn R (1985) The evolution of CO, on Mars. Icarus 62: 175-190
- 50 Haberle RM, McKay CP, Schaeffer J, Cabrol NA, Grin EA, Zent AP, Quinn R (2001) On the possibility of liquid water on present-day Mars. J. Geophys. Res. 106 (E10): 23317-23326
- 51 Lobitz B, Wood BL, Averner MA, McKay CP (2001) Use of spacecraft data to derive regions on Mars where liquid water would be stable. Proc. Nat. Acad. Sci. 98: 2132-2137

10 Ancient and Recent Lakes on Mars

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The search for life on Mars is guided by our knowledge of the environments occupied by terrestrial biota. Geology and atmospheric models converge to show that Mars habitability potential was higher during the first 500 Ma of its history. Rivers and lakes, possibly an ocean, started to decline around 3.5 Ga. There is evidence that they may have occurred again in later geological periods but episodically and as lower magnitude events, their formation possibly driven by magmatic pulses and/or obliquity changes. This chapter focuses on Martian lakes and their environmental conditions through time. Paleolakes on Mars were identified first at Viking resolution in basins, impact craters, and volcanic regions. The Mars Global Surveyor (MGS) Mars Orbiter Camera (MOC) and Mars Orbiter Laser Altimeter (MOLA) provided additional geological evidence to support the existence of past lakes and showed that the magnitude of the Martian lacustrine activity was much greater than unraveled by Viking. These new data allow the precise definition of watersheds, paleochannel courses and basins and show that lakes abounded on early Mars. Later in the planet's history, environmental conditions likely included: episodic water supply; increasing evaporation due to the thinning of the atmosphere leading to chemical, pH, and salinity changes in the lakes; high-UV radiation; cool temperatures with seasonal, then perennial icecover; and short to long-term hydrothermal activity for impact and volcanic crater lakes. Evidence for recent water activity through gullies and glaciers opens the possibility for modern short-term ponds as well. Understanding how these conditions could have affected putative life is of paramount importance to assess adaptation and survival potential on a changing Mars.

10.1 Early Mars: The Lake Planet

10.1.1 Water as a Prerequisite

Whether on Mars or on Earth, ancient lakes are Rosetta stones and key paleoenvironments to explore. Their waterlain sediments retain the record of seasonal and orbital changes, the variations in hydrological regimes of the channels, and the main hydrogeological events that punctuated the history of their catchment areas. Lacustrine environments are of the utmost importance from an astrobiological perspective as well [7, 8, 16]: Terrestrial lakes host abundant and diversified biota. They facilitate its inception and expansion through complex food webs. Lacustrine life follows the temporal fluctuations of the environment through climate and hydrological changes, which in time lead to pathways of evolution or

extinction. Subtle or dramatic modifications in the spatial distribution of life can occur at very small-scale (cm to m) within the margins of a lake triggered by the variations of water influx (e.g., clusters of hydrothermal springs of various temperatures, water salinity and chemistry). Lakes are equally unique in their ability to preserve the record of life: when organisms die, they accumulate on lakebeds and are covered under regularly deposited sediments. Rapid burial allows the generation of anoxic conditions favoring the formation of fossils by preventing oxidation and decay.

It is not known yet if life appeared on Mars and left a fossil record [32, 33] but past and current missions are providing supporting evidence that ponding over extended geological periods might have happened, generating both perennial and ephemeral lakes [9, 10, 12]. Commonly, the term *lake* refers to water as being the ponding fluid for terrestrial features, while "lava" lakes specifically designate a fluid from volcanic origin. However, no unambiguous evidence exists so far about the nature of the fluid involved in the formation of flow features on Mars. If we search for life as we know it, water is a prerequisite. Cold temperatures, thin atmosphere, abundance of CO_2 , and spatial distribution of recent gullies in an environment that does not allow water to flow at the surface anymore, have led to suggest that CO_2 [50, 72], exotic flows (e.g., cryovolcanism and clathrates [36] – although contested [59]) and not H₂O [66, 69] were responsible for carving recent flow features. Those would generate ponds, if any, of a very different nature than their terrestrial counterparts.

Some go farther. Recent studies proposed that CO, is the more likely fluid not only for the gullies but for all Martian flow features (valley networks, outflows, gullies), whether recent or ancient [49]. Highly debated, this model encounters many difficulties. It lacks an explanation of how large CO, reservoirs could have accumulated and subsisted near the surface for thousands of years under unstable conditions (e.g., magmatic activity and impact-induced tectonic) especially in warmer sub-tropical to mid-latitudes (30°S-45°S) where gullies are also observed in abundance [66]. Moreover, this model is not consistent with the morphological observations and mineralogical measurements performed recently by the MOC and TES instruments. Although conditions at sub-polar latitudes would allow liquid CO, to be theoretically stable at depths corresponding to the location of the gully sources, the gully morphology does not support this hypothesis. CO, is liquid at -56.4°C and 5.1 bars. It is potentially stable at depth in its liquid phase but would become instantaneously unstable at contact with the surface where the pressure of 6 mbars is ~1000 times lower than required for its liquid phase. The outcome of surface exposure would be at best a sudden outburst followed by immediate sublimation. Gullies are characterized by terraced ravines, debris aprons, and channels narrowing from upstream to downstream suggesting a regular evaporation consistent with that of water. The presence of some percentage of briny material in the water would have allowed flow at freezing temperatures [62, 90].

The hematite deposits discovered by TES [23] may be additional evidence for past water activity. Large-scale hydrothermal systems (magma and water/ice

interactions) or precipitation in a shallow lake were suggested for its formation. Both hypotheses involve water at some time in the Martian past and cannot be explained by CO, processes. The observation of massflows [2, 13, 15, 55] with morphologies inconsistent with CO₂-driven processes at latitudes where *currently* ground ice is stable near the surface [76], and in an environmental domain shared with the gullies, is a very strong support of the H₂O-based hypothesis. Mars Odyssey (MO) has cast an even larger shadow on the CO, model by delivering a global epithermal neutron map of Mars [34]. This map shows the distribution of hydrogen abundance as ice and hydrated minerals at global scale and is consistent with a large reservoir of H₂O ice even today in the very near subsurface. From about 55° latitude to the poles, the Odyssey data show an average of 50% water by mass. Closer to the equator, this value is 2-10% beneath several centimeters of dry soil. See Chap. 5 by Mitrofanov for more details. Moreover, climatic models indicate that liquid water can form in localized transient events today, although it would not be in equilibrium with the environment [44]. The following sections, therefore, discuss lakes on Mars assuming that the most likely fluid associated with their formation is water.

10.1.2 Abundance and Diversity

The generation, abundance and distribution of lakes on early Mars would directly result from the initial physical and climatic conditions of the planet during the Noachian era (e.g., warm and wet *vs.* cold and dry) [86]. Far from being resolved, the debate about these early conditions is currently being revived in light of MGS and MO new data.

The abundance of valley networks and channels is consistent with Mars being a water-rich planet in its early times [20]. The distribution of hydrogen abundance as a current reservoir of ice and hydrated minerals shown by MO could indicate that Mars still has some significant water/ice resources and could have started with a H₂O reservoir proportionally larger than the Earth's. The morphology of the majority of valley networks and channels [65] and the lack of large carbonate deposits [3] are also consistent with a planet which was never much warmer than at the present time. Although Mars was likely warmer during the Noachian because of a thicker CO, atmosphere [43, 57], possible greenhouse effects, and an increased internal heat flux, current data may be showing that "warmer" might define at best a periglacial climate. Morphological, geological, and mineralogical evidence point to an early cold and wet Mars, with enough moisture in the cold atmosphere to generate snow precipitation [53]. Impacts have been presented as possible agents for local rainfalls forming hydrographic systems [84], although the drainage maturity of Martian valley networks provides little support to this hypothesis [11]. In a cold and wet scenario, lakes could still have been generated through various processes, including seasonal melt, subglacial flow, and groundwater circulation locally associated with hydrothermal activity. They formed in a variety of physical and geographical environments comparable to their counterparts on Earth. The combination of both climatic, geographical, and

physical conditions would have led to a diversity of types, whose classification is likely as complex as that of terrestrial basins. Lakes on Mars were neither accidental occurrences nor rare [9, 10, 29, 31, 37, 74, 83]. Because Viking data lacked resolution and altimetric precision, the first attempt at identifying and classifying Martian lakes [9] used the very confined limits of structural impact crater basins as identification criteria, leading to define a physical classification of open, closed, and lake-chain basins. About 200 impact crater lakes were identified, mostly Hesperian, with some occurrences in the Amazonian [10]. Since, MOC images and the MOLA altimetry have finally made it possible to identify topographic basins as well. Much smaller and older lakes are now accessible and their number is, as expected, orders of magnitude more elevated than perceived with Viking. For instance, the Ma'adim Vallis watershed region alone counts at least as many lakes, ponds, and larger basins (topographic and impact-related) as the total number identified at global scale with Viking data [63]. High-resolution allows access to smaller surface areas of eroded geological units (e.g., Noachian) and ultimately will lead to the reassessment of the timing of the maximum peak of lacustrine activity. As unravelled by MGS and MO, early Mars could be defined as the "Lake Planet". Lacustrine basins of varied dimensions and types were numerous and widely spread over the entire globe, possibly contemporaneous with the largest of all basins: the northern ocean.

The diversity of early Mars lacustrine activity is best characterized by the many methods that can be used to define it. Except for the biological activity, which often defines lakes on Earth but still has to be demonstrated on Mars, terrestrial criteria could be valid classifiers, with possibly the exception of plate-tectonic induced basins which may or may not be applicable to early Mars [6]. MGS and MO data show the potential for a much more diverse classification than Viking allowed, with classifiers which could encompass: the origin of the water source, the hydrologic regime of the systems supplying the lakes, associated climatic conditions; the origin of the topography of the basin itself (e.g., tectonic, structural, volcanic); its dynamics (open, closed, lake-chain); and its relative lifetime (perennial, ephemeral). At a high level, lakes can be characterized using only one of these criteria (e.g., volcanic) or they could be more precisely defined using a suite of criteria, such as a perennial, closed, impact crater lake. Some criteria directly result from data interpretation: they are *inductive* classifiers (e.g., closed, open, impact crater, tectonic basins) and should be used as the foundation for the classification of Martian lakes as they rely on observation. Deductive classifiers result from analytical and logical processes that are not necessarily directly supported by observation. For instance, the presence of a large paleobasin showing evidence of shorelines, terraces, and a delta may lead to the assessment that the basin was occupied by a perennial lake. Although normally an inductive classifier on Earth, perennial is deductive on Mars. Because it comes in this particular case as a deduction from a series of direct observations, it can be defined as a strong hypothesis and be used as a classifier. The more the deductive process relies on pure logic and departs from observation, the more the end result will lean toward speculation which should never be used for classification. For instance, "brackish" cannot be used at this stage to classify Martian paleolakes, although intuitively one can assume that brackish lakes were common [24, 58]. The situation is complicated on Mars by the fact that ground-truth is rare (surface missions). Thus, even direct observations (especially image interpretation) rely most of the time on *analogy* with Earth. In all fairness, "direct" classifiers should be considered hypotheses. Therefore, the following classification proposed in Table 10.1, revised compared to the Viking-based one [9] uses classifiers resulting from strong analogies and strong hypotheses.

Classifier	Origin	Characteristics
Glacial	Snowfall	One major water/sediment input peak during melt
		season. Latitude/altitude dependent.
	Glacial Melt ¹	Lakes at the front of glaciers. Maximum peak at melt season.
	Permafrost	Large-scale thawing of ice-rich permafrost
Hydrologic	Rainfall	Limited to warmer latitudes. Seasonal peak(s)
	(if any)	depends on geographical location. Role of asteroid impacts?
	Groundwater	Volcanic/Hydrothermal. Input follows activation of volcanic centers.
		Polar Basal Melting. Circulation varies in time with
		location and extent of polar caps, and depends on pore
		space availability.
		Regional/Local subsurface circulation. Lakes and
		ponds supplied by local groundwater reservoir (e.g., residual perched aquifers).
Karstic	Solution	Formed by dissolution of soluble rock by percolating water. See also permafrost for cryokarstic lakes.
Structural /Volcanic	Fault/Ridges	Compression or extension of the Martian crust traps water circulating in surface and subsurface.
	Volcanic	Lakes in craters, maars, cinder cones, calderas, and collapsed lava tubes
	Impact Craters	Lakes in impact basins
Topographic	Basins	Lakes in local to regional low topography (e.g.,
		inside valleys, between high-relief).
Dynamics	Physiography	Lakes can be open, closed, linked in chains
Temporal	Duration	Perennial or ephemeral (relative lifetime)
Biologic	Life	TBD

^T Separation between glacial melt and snowfall: glacier morphologies are observed in MOC images. If glaciers, they resulted from snow accumulation but glacial melt can still occur while glaciers are receding at the end of wet climate episodes.

To date, although suggested [35] no evidence for evaporite or large carbonate deposits has been detected. This may reflect paleoclimate conditions [3] or result from surface global dust cover or resolution and specification of the instruments [60]. However, if/when detected, mineralogical clues will be the very first true

inductive classifiers. They will give deeper insights into Martian lacustrine evolution. They will broaden the classification to mineralogy, chemistry (e.g., fresh, brackish), physics (e.g., stratification, fractioning), and will give a better assessment of a lake's lifetime. The Mars Exploration Rover (MER) Spirit should provide for the first time such a mineralogical ground-truth while testing a paleolake hypothesis in Gusev crater [18].

10.2 Identification of Ancient Lakes

To understand the nature and structure of a lake, it is essential to collect data about its formation and history. The evolution of a standing body of water depends on many factors, including: how it was formed, the shape of the basin in which it was resting and its dimension, the topography, the chemistry and mineralogy of its watershed, and the climate evolution during its lifetime. If life evolved on Mars, it will be essential to consider ancient local biological communities in the future as well. Unfortunately, many of these factors, even more so the latter, are still poorly known or unknown. The identification of ancient lakes and the reconstruction of their history have to rely on morphological and physical clues, and the resolution and accuracy of instruments and datasets through which the planet is perceived. Morphological and topographical data are to-date the best assets in the interpretative and modeling toolbox.

10.2.1. Diagnosis Evidence

Morphological clues of the presence of ancient lakes abound planetwide with the highest density in the southern uplands. Dry basins at the termini of fluvial valley networks are the first indicators of the plausible presence of an ancient lake [9, 29, 37, 81, 83, 89]. Other evidence includes the existence of deltas, terraces, shorelines, evaporite deposits, and layers [12, 67, 75]. On a first order approach, none of these indicators constitute on its own an unambiguous proof of a lacustrine environment. For instance, a delta and an alluvial fan may in some cases display transitioning morphologies from one form to the other that can be mistakenly interpreted. The former develops in water while the latter on dry land. Both are present on Mars but deltaic landforms are the critical ones to survey for a better understanding of ancient lacustrine environments.

Deltas- Terrestrial deltas provide clues to assess the environmental conditions under which the Martian landforms were created. Candidate-deltas were already identified at Viking resolution and 75 of them were used to generate a first classification into three main types: fan-like, elongate, and lobate [10]. Transitional forms were observed for each of these types. With MOC, more deltas and more fine-scale morphological details are now accessible. Deltaic morphologies give indirect information about the grain-size composition, the characteristics of the water flowing into the basin, and the physical environment of the delta while it was forming (e.g., sub-glacial, free water, subaerial). Some landforms on Mars provide enough converging evidence to suggest that they could be massive deltas covering large surface areas (e.g., Ma'adim Vallis delta: 250 km^2) [38, 40]. Their dimension is an important indicator of the relative stability of the environment in which they were formed. On Earth, such large landforms take thousands of years to form. Assuming a comparable time scale for Mars, their presence indicates that large lakes at some point in the early times could have been sustained at the surface of the planet. A spectacular delta located in a small crater north of the large Holden basin (Fig. 10.1) unfolds a complete fluvio-lacustrine story in its sedimentary record.

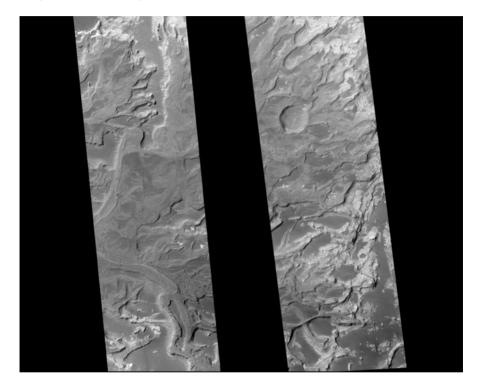


Fig. 10.1 Delta in a crater north of Holden basin (24.07°S/33.88°W). Left, MOC E1800401 showing the channel inverted relief, cut-offs and oxbows, distributary channels and deltaic topset and foreset (3.60 m/pixel, width: 3.68 km). Right, MOC E1701341(2.95 m/pixel, width: 3.02 km) centered on the delta and distributary channels which are inverted.

Channel and delta are clearly associated. The evidence is unambiguous because the dark and light tone layering of the delta is directly traced to the layering in the channel. It shows possible cycles (e.g., sediment grain-size change due to seasonal, secular cycles) that could have resulted from the dynamics of the channel itself, or from other regional cyclic activity (e.g., volcanic, aeolian – massive dust storms) while the channel was active. This activity was sustained long enough that cut-off meanders and distributary channels are observed in the residual delta. Subsequent erosion has inverted the channel's topography which appears now as a positive relief. In this particular example of a mature delta and long-term fluvial activity, there is clear evidence for a stable fluvio-lacustrine environment over a significant duration, which makes this site an outstanding astrobiological target to search for past habitats and life.

Terraces- They are ambiguous in basins as they can result from two processes: one is tectonic and does not involve any water action, whereas the other is sedimentary, requires water and is evidence for erosional and/or depositional processes. When resolution fails, fractures breaching impact craters and tectonic terraces can be mistakenly interpreted and used as supportive evidence for a lacustrine hypothesis.

Shorelines- They are fragile environments whose rapid erosion limits their identification or makes it difficult. Recently, MOLA altimetry has proven to be a helpful tool in the hunt for isometric contour lines that signal the potential for shorelines in a basin [21,48] and for following stratigraphic units from paleolake beds to the channels upstream [18].

Layered deposits- Except in cases where layers can be traced back directly to a fluvial channel (such as in Fig. 10.1) they, too, can be ambiguous. A typical example was given by the massive layers observed throughout Mars by MGS [67]. Even at MOC resolution, when layers cannot be connected to channels they should not be considered a priori evidence for lacustrine activity. With few exceptions, such as flash floods with rapid deposition of large quantities of poorly sorted sediments, lacustrine sedimentation generally produces very thin banded layers (mm to cm) piling up with time on top of each other. This type of layering (e.g., varves) cannot be captured by the MOC camera resolution. Massive deposits are likely to represent the deposition of large events such as volcanic eruptions and climate changes. However, on Earth as on Mars, reality is more complex and layers of different natures are often observed together. A typical case on Mars is Gale crater, where the total volume of layered sediment is much larger than the total volume of sediment that could have been extracted from the channel entering the basin to the south [14]. However, MOC images show that at least some of these layered sediments are connected to the south channel. They should be considered fluvial and/or lacustrine in origin. In other places, like the northern region of the crater, a fossil channel was exhumed from within the deposits. Although there is no clear connection to the main south channel, it indicates a fluvial component for at least some of the neighboring sediments (Fig. 10.2).

10.2.2 Early Northern Ocean and/or Great Lakes?

In addition to morphological evidence, precision altimetry is proving a critical complementary diagnosis tool. It is at the center of the debate about the existence of the Martian northern ocean. MOLA has shown that one third of the surface area of Mars is being covered by the northern lowlands, which could have been occupied by the largest of the standing bodies of water: the northern ocean (Fig. 10.3).

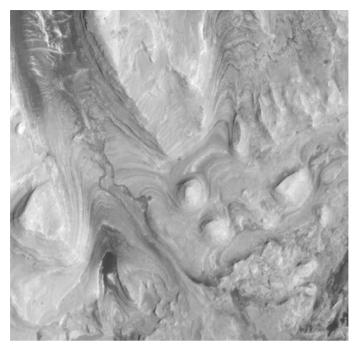


Fig. 10.2 North Gale crater in the Aeolis region (4.88°S/222.88°W). This MOC image M0301521 subframe shows that the layering extends over the entire sedimentary deposits. In the center, a residual channel filled with sediments is supportive evidence for the presence of fluvial and/or lacustrine material in this region of the crater. Image resolution: 3.49 m/pixel; scale width: 2.94 km.

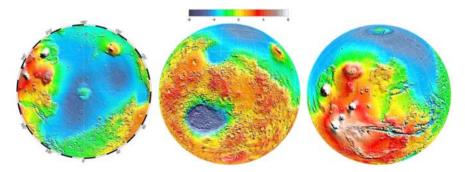


Fig. 10.3 GSFC/NASA MOLA topographic map of Mars showing the distribution of the basins. If one ocean, the body of water would have covered the northern plains (left). The other hypothesis is that a series of large lakes occupied sub-depressions in the Isidis and Elysium regions (center) and the Chryse and Amazonis regions (right).

An ocean would have been essential as a possible crucible for life on Mars as it was on Earth, and as a regulator of the Martian climate. According to general circulation models (GCMs), its presence would have saturated the atmosphere of the northern hemisphere with water vapor clouds. Precipitation would result from these clouds being transported over the highlands through the atmospheric general circulation [44]. This mechanism provides water/ice to watersheds. It initiates a hydrological cycle, charging aquifers, creating valley networks and lakes in the southern hemisphere, which in turn generate more potential habitats.

The existence of such a large body of water is supported by several direct observations that were made during Viking and revisited recently by MGS. Viking images clearly showed that six large outflows (Mawrth, Ares, Tiu, Simud, Maja, and Kasei Valles) emptied in Chryse Planitia [1, 71, 83]. Morphological analysis of the contact between the highlands and the lowlands suggested the existence of a series of shoreline levels [77, 78], but a positive conclusion was impossible at low resolution. MOLA provided new evidence. The putative shoreline contours were revisited and a Contact 1 at $-3,500 \text{ m} \pm 500 \text{ m}$ and a Contact 2 at $-4000 \text{ m} \pm 300 \text{ m}$ were established [48]. However this evidence is still controversial and it was proposed that there might not have been an ocean at anytime on Mars, but rather a series of large lakes occupying a series of northern sub-depressions (Amazonis, Utopia, Elysium, Chryse, Isidis, and the North Polar basin) at various times [21].

There are issues with the discontinuity of some contour lines reflected by the range of elevations provided for Contact 1 and Contact 2, as the hypothesis of a large ocean relies heavily on altimetric data. Meanwhile, distinguishing shoreline breaks on Mars as contacts from global layering, mass sliding, and a succession of depositional events is a difficult challenge without ground-truth. The geomorphic expression of shoreline formations resulting from repeated erosion by coastline current waves breaking on shallow offshore platforms is equivocal. On Earth, dry lakes and sea paleoshorelines display an array of curvilinear bands that reflect the reduction of the body of water over time. Bands of various brightness caused by sorting of the material through wave action (or a succession of progression and regression episodes) are typical of this type of coastline. Several factors complicate this interpretation on Mars: one is time. The northern ocean, if any, was at its peak activity in early history. The succession of geological events and climate changes probably conspired to obscure its record. Another factor is the climate under which the putative ocean was formed. There is mounting evidence of an early cold Mars. As a result, standing bodies of water would tend to be quickly covered by ice with critical implications for their geomorphic record. An ice cover prevents the generation of pelagic formations usually observed in temperate climate. Instead, ice covering water and pushing on contact with land creates scour marks and boulder lines. If the cold Mars hypothesis is verified for early times, these are the types of geomorphic evidence to search for. These fragile formations, if very old, might still elude high-resolution scrutiny [64] because they are eroded away or covered.

Provided that the volume of water for an early ocean can be reconciled with the volume of the original potential reservoirs of water [25, 34] the hypothesis of one ocean and that of great lakes would not necessarily exclude each other. Early, more water might have been available to create an ocean [20]. Later, episodic

underground water discharges through outflow activity that may have decreased in intensity over the aeons, and generated large lakes which occupied subdepressions of the former northern ocean. Their formation and evolution likely contributed to obscure the record of oceanic shorelines.

The potential for great lakes exists all around the Martian globe at the lowland/upland contact. While the outflows of Lunae Planum and Oxia Palus debouching in Chryse Planitia are the most often referenced, the large system of Mangala Valles in Memnonia could have contributed to a putative large Amazonis Lake [83] and that of Granicus Valles to the Elysium basin [80]. Formations at the mouth of Mangala were interpreted as possible deltaic and estuarine formation [39]; in the Casius region, the large and deep Auqakuh and Huo Hsing Valles empty in the northen plains. In Syrtis Major, valley networks enter the Isidis Basin [28]; during its early activity, Ma'adim eroded the northern rim of Gusev crater and might have continued to the east of Apollinaris Patera to enter the Elysium Basin where the existence of an estuary was proposed [39].

If the hydrological activity of Mars was mainly triggered by orbital parameter changes [53], it is thus possible that many of these channels and basins all around the upland/lowland contact were active at the same time. The question is to know whether or not the water reservoir was sufficient, whether conditions lasted long enough to release enough water, and for water to pond still and form a northern ocean in the lowlands. If not an ocean, it is still conceivable that great lakes formed by large outflows and valley networks were generated at the same time during favorable climatic episodes [1].

10.3 Modern Lakes and Ponds: Conditions of Formation on a Changing Planet

The geological record shows that the end of the Noachian marked a fundamental change on Mars [47] due to the loss of a significant fraction of its atmosphere. Fluvial and lacustrine activity would never in the following eras develop with the same intensity. Previous work at Viking resolution [10] indicated that the transition might not have been necessarily abrupt as lakes still formed (although more locally and episodically) during the Hesperian and the Amazonian. However, the MGS and MO data point to new evidence that may reshape this previous assessment. Preliminary observations show that: (1) the Noachian episode is of much stronger magnitude than perceived through Viking. If the numbers of paleolakes observed in the Ma'adim watershed [52, 63] alone can be expanded to all the hydrologically active regions of Mars during the Noachian, then, the number of early lakes could be in the hundreds of thousands, extremely diverse in dimension and origin. Obtaining a clear picture of the consequences of the atmosphere loss will require the Hesperian and early Amazonian populations to be reassessed; and (2) a massive climate change occurred in modern times on Mars [2, 13, 15, 55, 66, 73], the evidence of which was completely missed during the Viking era because of poor image resolution. This episode left behind clear evidence of a morphoclimatic continuum consistent with periglacial to glacial conditions, see Fig. 10.4.

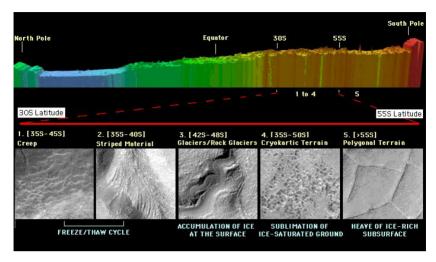


Fig. 10.4 Morphological continuum inherited from the recent climate change [15]. A typical succession of landforms is observed from the sub-tropical to the high latitudes: periglacial features requiring freeze/thaw cycles are concentrated between 35°S and 45°S; glacial landforms (e.g., debris-covered glacial) are observed between 42°S and 48°S.; pitted terrain (cryokarst) covers both hemispheres between 35°S and 50°S. Large polygons are present in regions also saturated in ice but at latitudes where ice is still stable near the surface. This continuum shows the standard transitions from periglacial to glacial environment as it could be encountered on Earth. The setting of such continuum requires (a) a voluminous amount of subsurface ice and (b) surface ice, likely through snowfalls (see Fig. 10.5).

Fresh landforms including gullies, massflows, debris-covered glaciers, stripped valleys, pitted surfaces and patterned ground are spread planetwide following a specific latitudinal distribution. The lack of impact cratering and the pristine state of these landforms suggests that they could be extremely young. The term "modern" is used in the following sections to define this most recent part of the Martian history and its associated features. Age estimates vary from a few millions to tens of thousands of years [2, 15, 66, 73]. It has been suggested that some gullies might still be active [13]. These observations have fundamental implications on our understanding of the climatic, geological, and potentially biological evolution of Mars that are far greater than the scope of this chapter. However, they also show that this climate change might have brought the necessary conditions for the formation of modern temporary ponds and lakes.

Amongst the evidence of recent water/ice activity, gullies and glaciers, along with the polar caps, are the most promising primary sources of water in modern times. The lifetime of putative associated basins would be once again very much related to the environmental conditions at the time of their formation. Although the causes for a climate change of the observed magnitude still have to be understood, it is unlikely that global conditions on Mars were drastically different in the recent past from what they are today, thus preventing a long-term direct exposure of water at the surface. When formed, ponds or lakes likely faced rapid evaporation that could have been balanced and/or prevented only by continuous water discharge higher than the evaporation rate, and by the protection of the standing bodies of water under an ice cover [19, 68, 71].

Indirect clues about these environmental conditions are given by modern landform morphologies. Glaciers need snowfall and a wetter climate to form (Fig. 10.5). Stripped valleys, rock glaciers, mudflows, and patterned ground require freeze/thaw cycles to activate, implying higher mean temperatures than those of today. On Mars, as on Earth, massflows (e.g., rock glaciers) reflect non-steady-state environmental conditions. Earth's rock glaciers require a mean annual temperature of below -2° C for interstitial ice to exist and above -15° C for ice to deform [27]. Around -15° C, rock glaciers can only form where precipitation is too low to generate glaciers [45]. The upper limits of annual precipitation for rock glacier formation are 2500 mm y⁻¹ at -2° C, and 400 mm y⁻¹ at -15° C. Although these values may differ for Mars, the presence of rock glaciers and glaciers necessarily implies higher mean temperatures compared to the present.

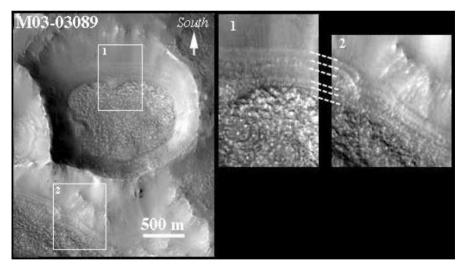


Fig. 10.5 Evidence of snow and/or ice accumulation in the mid-latitudes in recent times. The depression and the impact crater are isolated from each other by the crater rim. However, the same slope marking and spacing is observed in the crater and in the depression. The texture of the material is the same as that observed in debris-covered glaciers. We interpret those markings as snow or ice accumulation lines. MOC 03-03089 located 32.45°S/332.45°W. Resolution: 2.80 m/pixel; scale width: 2.86 km.

The increased exchange between surface and atmosphere at global scale through precipitation and evaporation of surface, subsurface ice (as shown by the pitted terrain) and water could have raised the atmospheric pressure a fraction higher than its current value. However, it was not necessary for the pressure to be significantly higher than today to allow temporary ponding. GCMs have demonstrated that water is metastable on Mars today for several hours per day and several days per year in specific regions [44]. As a result, while unstable, ponds and lakes were likely to form during that period because of the environmental conditions reflected by surface landforms. Their lifetime would have been highly dependent on their primary water source, how fast water was covered by ice and dust, and where they formed (in or out of water metastability regions). Primary sources for modern ponds and lakes could have included, to various extents, water flow from gullies, glaciers, and hydrothermal groundwater circulation associated with late heat sources which produced the most recent lava flows [4], and with impact cratering in a volatile-rich subsurface [74].

Modern lakes of significant size through gully flow is improbable mostly because of the flow dynamics associated with gully formation as reflected by their morphology. Their channels narrow down from upstream to downstream. This is clearly indicative of the dynamics of an evaporating fluid with a short erosion phase near the spring rapidly transitioning to deposition (incapacity to transport sedimentary loads any further). Well-developed alluvial fans without cut banks indicate their formation and evolution on a dry surface. Therefore, they did not enter a standing body of water at any time during their development. In such a process, the fluid has no time to pond before it evaporates. Another factor is the origin of the water carving the gullies. Several hypotheses have been presented. The most favorable case for the formation of a standing body of water would be the rapid generation of a group of gullies in close proximity caused by the sudden emergence of large subsurface aquifers [66, 69]. Enough water may then reach the bottom of a depression and pond before freezing and disappearing. The presence of dissolved salts [24] could have played a role by lowering the melting point and reducing the equilibrium vapor pressure considerably, favoring both water flow and residence time. Dissolved salts are likely because the Martian soil is estimated to contain 8-25% weight salts [62, 90]. These occurrences may be better defined as puddles or pools rather than ponds or lakes and they might not have lasted more than a few hours to a few days (Fig. 10.6). However, ice lenses might have resulted from their surface exposure, and if rapidly covered by dust and debris, could have lasted much longer. If this activity has continued until recent times or is still ongoing, ice lenses might still be present today in these depressions under a cover of debris.

If the melting of snowpacks on valley and crater slopes [22] is at the origin of the gullies, it is unlikely that any puddle or pond were ever generated through that process. Current models predict that up to 10 meters of snow could fall on Mars every 50,000 to 500,000 years following obliquity changes [44, 53]. Snow would provide thermal protection (local greenhouse effect) and delay evaporation. It would allow melting and flow even at temperatures below freezing. However, the flow envisioned through this process is more a trickle leading at best to some infiltration if pore space is still available and not already closed by ice.

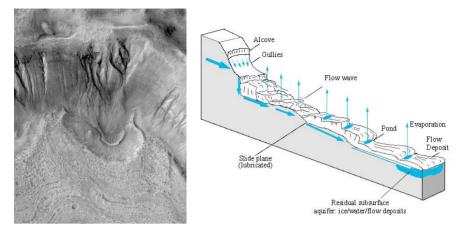


Fig. 10.6 MOC 0804758 of a 7.3 km impact crater at 40.54°S/142.22°W (resolution: 3.42 m/pixel; scale width: 2.85 km). Large system of gullies, debris aprons, push-ridges forming plastic flow waves regularly spaced creating terracettes. The ridges progress toward the center of the basin in large folds, which supports the hypothesis of a volatile-rich material. At the contact between the ridges, strings of small depressions could be the expression of the evaporation of water/ice forced out by compaction. The morphology is consistent with creep and gelifluction and has analogs in terrestrial permafrost environments. Right: scheme of the process.

The most unfavorable scenario for the generation of ponds would be that of dry avalanches, which were also considered as a mechanism to form the gullies. Often the alluvial fans are dissected by small, braided and terraced, channels which are typical signatures of a fluid. Several types of avalanches were proposed, including rock, dust, and CO_2 snow and ice which defrost in spring and would generate brief avalanches of CO_2 -lubricated debris as snowpacks sublime and collapse down-channel [49]. This process might be possible in the sub-polar regions at most but cannot explain the mid-latitude gullies.

Glaciers provide the most favorable environment for the formation of modern lakes and ponds of significant size and duration. Pristine modern landforms resembling terrestrial glaciers are abundant on Mars. Their density is higher in the southern mid-latitudes $(30^{\circ}-47^{\circ}S)$ but they are found in the northern hemisphere, too [2, 15, 55, 56]. The current climate does not allow for snow precipitation at these latitudes, therefore they are generally considered to be the relics of the latest climate change. However, their morphology suggests that ice possibly still persists under a cover of debris. They occur on steep slopes (valley and crater walls) with a typical accumulation area, a flow section, moraine-like debris and a distal margin marked by tongue-shaped material deposits (Fig. 10.7). On Earth, lakes form at the distal margin of glaciers as a result of ice melt, and within the flow section of the glacier itself. They can be gouged out, kettle lakes, or moraine-dammed lakes. Kettle lakes are created when an isolated mass of glacial ice detaches from the main glacier and is left behind when the glacier melts. It is

surrounded by outwash debris and when the ice melts, it leaves a depression (kettle) that can be filled with meltwater.

If ice has persisted in the debris-covered glaciers, it can be speculated that the large mass of a glacier and its debris would keep meltwater forming at the contact with the ground from evaporating. However, these ponds or lakes would not be visible from the surface and would need shallow penetration radar to prove their existence. However, there is more than these theoretical hidden bodies of water to support the hypothesis of modern glacial and subglacial lakes on Mars. Several MOC images show modern landforms that present striking analogies to glacial and sub-glacial lakes now dry (Fig. 10.8) [13, 70].

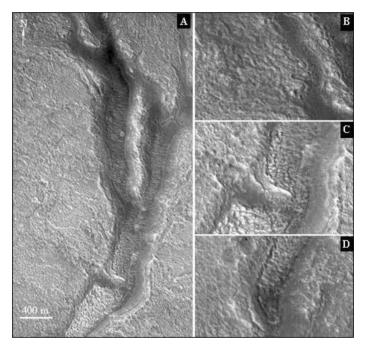


Fig. 10.7 A: source area of dark albedo material and merging of voluminous masses of material in the valleys. Long ridges border the flow. They are also observed near the source areas. The wavelength between the ridges suggests both steep slope and volatile-rich material. Both lateral marking and valley size suggest regression. B: sinuous lateral ridges near the source area. C: local overtopping of the valley material by slope material which originates from slump lobes developed on the slope. D: distal end of a second flow in the same crater. The tongue of material is lobate and narrows downhill. Lateral, frontal ridges, and lobate tongue material are all consistent with a glacier hypothesis. (Detail of MOC 1201450 centered at 35.04°S/322.94°W. Resolution: 4.19m/pixel; scale width: 2.81 km.)

Other images suggest that a few ice-covered lakes might still exist on Mars. If they are current lakes, their location will give critical clues about the origin of the water and the boundary conditions that keep them at the surface. The most striking ones are located in the Hellas basin (see Fig. 10.9).

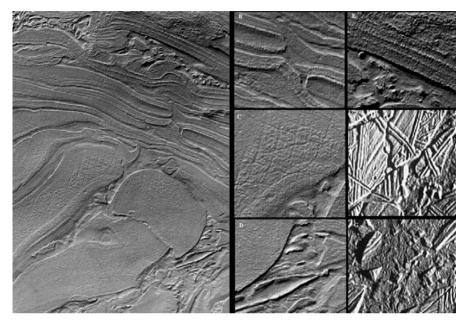


Fig. 10.8 A: subframe of MOC 2001277. Hellas basin at 39.7°S/306.7°W showing rafted plates and interconnecting folded ridges and troughs. The space between plates and ridges is filled with smooth material. The current hypotheses for this formation encompass mudflows and a (now dry) ice-covered lake. B-E: details of the subframe at larger scale. Scour marks visible on B are consistent with a body of ice having pushed on a softer surface. The overall morphology of the formation strikingly resembles that of Europa's surface (F-G, Galileo images) for which the main hypotheses is that of an ice-covered body of water [61, 85]. (Scale width: 2.67 km.)

Because of its depth, the Hellas basin is probably the most favorable place on Mars to search for current metastable bodies of water. Hellas is a sink for volatiles. The atmospheric pressure at the level of its floor is the highest on Mars and could still maintain standing bodies of water temporarily. In Hellas, the radio experiment onboard MGS has reported pressures of 10.13 mbars at -7066 m at $34^{\circ}S/302^{\circ}W$ in mid-summer (source: NASA web data archive: MGS Radio Experiment). Moreover, large volcanic edifices surrounding the basin argue for significant past magmatic activity. Although speculation at this stage, it cannot be totally excluded that heat sources could still exist at depth in Hellas and interact with the subsurface ice. Movement in large fractured polygonal terrain could allow artesian upwelling of water at the surface. Whether current lakes or not (Fig. 10.9), it is critical to survey the evolution of these features with time to better understand their origin. If confirmed, they will become obvious astrobiology targets.

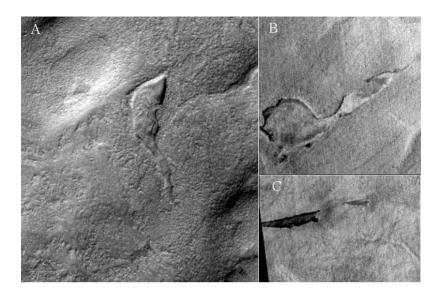


Fig. 10.9 A. MOC 22-00247b (resolution: 4.18m/pixel). Recent activity in NW Hellas (36.63°S/ 306.26°W). A small channel has eroded its way into a 250 m-wide depression and formed a fresh alluvial fan (near the upper tip of the depression). Although the morphology of the fan is not suggestive of a sublacustrine setting, this image shows that water release happened recently (currently?) in Hellas. Provided that the released volumes are substantial, Hellas would be the most favorable place on Mars for ponding to occur in present day. B-C. Details of MOC 10-02815 (resolution 2.80 m/pixel). Current bodies of water in Hellas? Each image is 1.5 km wide and shows large polygons with sharp margins, fractured in place. B shows a circular depression opened and deformed. Its surface material has a high albedo signature and is composed of small (few pixels) to large (~100m) fractured blocks. The elongated depression connecting to the east has a darker albedo signature with lighter-tone blocks. C. About 2 km north of the left image, dark albedo material associated with a fracture. Dust accumulation can result in dark deposit. However, no other dust deposits are observed nearby and the local materials are light-tone. Long projected shadows and water generate dark signatures. A long shadow would have to be explained by the presence of a localized deep crevasse as all other shadows in the image are short. A sinuous feature seems to connect to the dark area. The image was acquired during southern summer and is located at 36.73°S/305°W in a region where relatively high pressures are recorded by MGS radio experiment.

10.4 Conclusion: Habitats for Life

Lakes of all dimensions, possibly an ocean, could have provided life with diverse and favorable habitats on Mars over time [54], which have analogues in terrestrial polar, Alpine and Andean high-altitude lakes [17]. In these analogues, life is thriving. Moreover, the margins of some of these putative bodies of water border sites of major volcanic activity [42]. For instance, the fluvio-lacustrine system of Mangala Valles starts out of a fault emanating from the Tharsis region [30], the same system that runs west into the watershed of Ma'adim Vallis where abundant evidence for ancient lakes exists. The putative Elysium Paleolake borders the Elysium volcanic bulge; Apollinaris Patera could have connected through a dense system of faults and fractures [82] to the Aeolis basins and possibly to the Elysium Paleolake itself. This connection could have been the source for episodic hydrothermal activity over long periods of time.

Other major basins exist on the uplands, Hellas being the largest. Rings of volcanoes of all dimensions and shapes border the basin, which led to suggest volcanic/ice interaction [87]. MOC images revealed geomorphic evidence that has been interpreted as the record of a former, possibly ice-covered, lake in Hellas [15, 70], but could Hellas still harbor lakes? There too water and energy could have been present. Countless smaller scale ancient lake basins are located in regions of faults or near volcanic edifices (e.g., Zephyra Patera in the Durius Valles watershed region). In non-volcanic regions, snow packs and dusty ice covering standing bodies of water are well-known habitats on Earth for microbes and algae [51]. Migration of microbes from the surface into lakes has been documented [79]. If life appeared, it is to be expected that, as on Earth, aeolian activity whether local or global, may have been used as a seeding mechanism to populate new lakes over the entire Martian globe.

On the base of plausible habitats only, Martian lakes as perceived through the current data appear to have been favorable to the evolution of life in early times and could be the last oasis of modern times. The upside is that they were abundant and diverse and have well-known analogues on Earth were life is thriving. The downside, however, is that other environmental factors could have played a major role in preventing or limiting the evolution of life even before it reached these lakes or other standing bodies of water, if those were not the original crucible. One of them, possibly the most critical, is ultraviolet (UV) radiation [5, 17, 26, 46, 88]. Once living organisms reach water, provided that they are mobile and not immobile periphyton, they can escape deadly exposure by populating the deepest waters and use the water column as an efficient UV shielding mechanism. This strategy works well in perennial lakes and could have been used in early Mars with some measure of success. As conditions deteriorated, the atmospheric pressure decreased and evaporation increased. Life in these lakes would have faced mounting difficulty to find effective shielding conditions if they remained in the water.

Very high altitude lakes in the Andes may present currently the best analogues to these critical conditions on Mars 3.5 Ga ago. Brackish lakes (lagunas) were

formed at high-altitudes (4500 m on average or higher) as large fresh water lakes in the Altiplano 18,000 years ago [41]. They were supplied by abundant precipitation of snow and seasonal melt and by local hydrothermal activity sustained by active volcanoes. As the climate changed, dry conditions set in and the lagunas started to quickly recede generating changes in water pH and chemistry. Evaporation has dried out some of them completely, but others are left with extremely shallow bodies of water that can be several times saltier than seawater [17]. At these altitudes and latitudes, UV radiation is 40 % higher than at sea level and the atmospheric pressure is 550 mbars in average. Temperatures vary between -30° C and $+10^{\circ}$ C. In one of these lagunas the water depth is at best 50 cm. Therefore mobile and immobile living organisms are exposed to UV no matter where they are. There, populations of diatoms have been found to show a rate of deformities and abnormalities 10 times higher than in other standing bodies of water [17]. It is not suggested here that diatoms have ever appeared on Mars. They are simply used to exemplify the consequences of exposure to UV radiation for life in receding bodies of water and in environmental conditions close to those of the end of the Noachian on Mars. A higher lake (6014 m, 480 mbars surface pressure and -40°C to +3°C temperatures), which is ice-covered most of the year, does show life and food webs [17]. Cold and low pressure at these altitudes do not appear to prevent life' survival as long as there is enough water column to shield it against UV. This observation is of great importance when thinking about life in ancient or modern Martian lakes, and its potential for survival and adaptation through time. It gives a possible indication of a breaking point in time for life in Martian lacustrine environments, unless life adapted and found protection in sediment

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10.5 References

- Baker VR, Strom RG, Gulick VC, Kargel JS, Komatsu G, Kale VS (1991) Ancient oceans, ice sheets and the hydrological cycle on Mars. Nature 352: 589-594
- 2 Baker VR (2001) Water and the Martian landscape. Science 412: 228-230
- 3 Bandfield JL, Glotch TD, Christensen PR (2003) Spectroscopic identification of carbonate minerals in the Martian dust. Science 301: 1084-1087
- 4 Berman DC, Hartmann WK (2002) Recent fluvial, volcanic, and tectonic activity on the Cerberus Plains of Mars. Icarus 159: 1-17

- 5 Bothwell ML, Sherbot D, Pollock CM (1994) Ecosystem response to solar ultraviolet-B radiation: influence of trophic-level interactions. Science 265: 97-100
- Breuer D, Spohn T (2003) Early plate tectonics versus single-plate tectonics on Mars: evidence from magnetic field history and crust evolution. J. Geophys. Res. 108 (E7): 5072-5085
- 7 Cabrol NA, Grin EA (1995) A morphological view on potential niches for exobiology on Mars. Planet. Space Sci. 43: 179-188
- 8 Cabrol NA, Grin EA (1996) Duration of aqueous sedimentation and favorable environments for life inception on Mars: a case in the Aeolis region. Orig. Life Evol. Biosph. 26: 3-5
- 9 Cabrol NA, Grin EA (1999) Distribution, classification and ages of Martian impact crater lakes. Icarus 142: 160-172
- 10 Cabrol NA, Grin EA (2001) The evolution of lacustrine environments on Mars: is Mars only hydrologically dormant? Icarus 149: 291-328
- 11 Cabrol NA, Grin EA (2001) Composition of the drainage network on early Mars. Geomorphology 37: 269-287
- 12 Cabrol NA, Grin EA (2002) Overview on the formation of paleolakes and ponds in impact craters on Mars. Global Planet. Change 35: 199-219
- 13 Cabrol NA, Grin EA (2002) The recent Mars global warming and/or south pole advance hypothesis: global geological evidence and reasons why gullies might still be forming today. 33rd Lunar Planet. Sci. Conf. 1058
- 14 Cabrol NA, Grin EA, Newsom HE, Landheim R, McKay CP (1998) Hydrogeologic evolution of Gale crater and its relevance for exobiology exploration. Icarus 139: 235-245
- 15 Cabrol NA, Grin EA, Dohm JM (2001) From gullies to glaciers: a morphological continuum supporting a recent climate change on Mars. AGU Fall Assembly, San Francisco. P12E-11
- 16 Cabrol NA, Wynn-Williams DD, Crawford DA, Grin EA (2001) Recent aqueous environments in impact crater lakes on Mars: an astrobiological perspective. Icarus 154: 98-112
- 17 Cabrol NA, Grin EA, Friedmann R, McKay CP, Murbach M, Friedmann I, Chong G, Demergasso C, Tambley C, Escudero L, Kisse K, Grigorszky I, Fike D, Hock A, Grigsby B (2003) Licancabur: exploring the limits of life in the highest lake on Earth. NASA/TM-2003-211862: 64-67
- 18 Cabrol NA, Grin EA, Carr MH, Sutter B, Moore J, Farmer J, Greeley R, Des Marais D, Kramer M, Newsom H, Barber C, Thorsos I, Tanaka K, Barlow N, Fike D, Urquhart M, Grigsby B, Grant F, de Goursac O (2003) Exploring Gusev crater with spirit: review of science objectives and testable hypotheses. J. Geophys. Res. 108(E12): 8076, 10.1029/2002JE002026
- 19 Carr MH (1984) Stability of streams and lakes on Mars. Icarus 56: 476-485
- 20 Carr MH (1996) Water on Mars. Oxford University Press, New York
- 21 Carr MH, Head III JW (2003) Oceans on Mars: an assessment of the observational evidence and possible fate. J. Geophys. Res. 108(E5): 5042, 10.1029/ 2002JE001963
- 22 Christensen P (2003) Formation of recent Martian gullies through melting of extensive water-rich snow deposits. Nature 422: 45–48
- 23 Christensen PR, Bandfield JL, Clark RN, Edgett KS, Hamilton VE, Hoefen T, Kieffer HH, Kuzmin RO, Lane MD, Malin MC, Morris RV, Pearl JC, Pearson

RC, Roush TL, Ruff SW, Smith MD (2000) Detection of crystalline hematite mineralization on Mars by the Thermal Emission Spectrometer: evidence for near-surface water. J. Geophys. Res. 105(E4): 9623-9642

- 24 Clark BC, Van Hart DC (1981) The salts of Mars. Icarus 45: 370-378
- 25 Clifford SM, Parker TJ (2001) The evolution of the Martian hydrosphere: implications for the fate of a primordial ocean and the current state of the northern plains. Icarus 154: 40-79
- 26 Cockell CS (2000) The ultraviolet history of the terrestrial planets implications for biological evolution. Planet. Space Sci. 48: 203-214
- 27 Corte AE (1987) Central Andes rock glaciers: applied aspects. In Giardino JR, Shroder Jr. JF, Vitek JD (eds) Rock Glacier. Unwin Hyman, Boston, pp 289-302
- Crumpler L (2003) MER science goals and testable hypotheses at the Isidis site.
 4th Landing Site Selection Workshop, Jan. 9th
- 29 De Hon R (1992) Martian lake basins and lacustrine plains. Earth Moon Planets 56: 95-122
- 30 Dohm JM, Maruyama S, Baker VR, Anderson RC, Ferris JC (1999) Tharsis superplume (2): earthlike evolution of the Tharsis magmatic complex. Planet. Space Sci. 47: 411-431
- 31 Doran PT, Wharton Jr. RA, DesMarais D, McKay CP (1998) Antarctic paleolake sediments and the search for extinct life on Mars. J. Geophys. Res. 103(E12): 28481-28493
- 32 Farmer JD (1995) Mars exopaleontology. Palaios 10 (3): 197-198
- Farmer JD, DesMarais DJ (1999) Exploring for a record of ancient Martian life. J. Geophys. Res. 104(E11): 26977-26995
- 34 Feldman WC, Boynton WV, Tokar RL, Prettyman TH, Gasnault O, Squyres SW, Elphic RC, Lawrence DJ, Lawson SL, Maurice S, McKinney GW, Moore KR, Reedy RC (2002) Global distribution of neutrons on Mars: results from Mars Odyssey. Science 297: 75-78
- Forsythe RD, Zimbelman JR (1995) A case for ancient evaporite basins on Mars.J. Geophys. Res. 100(E3): 5553-5563
- 36 Gaidos EJ, (2001) Cryovolcanism and the recent flow of liquid water on Mars. Icarus 153: 218-223
- Goldspiel JM, Squyres SW (1991) Ancient aqueous sedimentation on Mars. Icarus 89: 392-410
- 38 Grin EA, Cabrol NA (1997) Limnologic analysis of Gusev crater paleolake, Mars. Icarus 130: 461-474
- 39 Grin EA, Cabrol NA (1998) Ma'adim Vallis estuarine delta in Elysium Basin and its relevance as a landing site for exobiology exploration on Mars. 29th Lunar Planet. Sci. Conf. 1011
- 40 Grin EA, Cabrol NA (2000) Hydrologic and climatic significance of lacustrine deltas in Martian impact craters. 31st Lunar Planet. Sci. Conf. 1299
- 41 Grosjean M, Messerli B, Ammann C, Geyh M, Graf K, Jenny B, Kammer K, Lantoro L, Schreier H, Schotterer U, Schwalb A, Valero-Garcés B, Vuille M (1995). Holocene environmental changes in the Atacama Altiplano and paleoclimatic implication. Bull. Inst. fr. études andines 24: 585–594
- 42 Gulick VC, Baker VR (1990) Origin and evolution of valleys on Martian volcanoes. J. Geophys. Res. 95: 14325-14344
- 43 Haberle RM (1998) Early Mars climate models J. Geophys. Res. 103(E12): 28-46

- Haberle RM, McKay CP, Cabrol NA, Grin EA, Schaeffer J, Zent AP, Quinn R
 (2001) On the possibility of liquid water on present day Mars. J. Geophys. Res. 106(E6): 23317-23326
- 45 Haeberli W (1985) Creep of mountain permafrost: internal structure and flow of alpine rock glaciers. Hydrol. Glaziol. 77: 1-142
- 46 Häder DP (1993) Risks of enhanced solar ultraviolet radiation for aquatic ecosystems. Prog. Phycol. Res. 9: 1-45
- 47 Hartmann WK, Neukum G (2001) Cratering chronology and evolution of Mars. Space Sci. Rev. 96: 165-194
- 48 Head III JW, Hiesinger H, Ivanov MA, Kreslavsky MA, Pratt S, Thomson BJ (1999) Possible ancient oceans on Mars: evidence from Mars Orbiter Laser Altimeter data. Science 286: 2134-2137
- 49 Hoffman N (2000) White Mars: a new model for Mars' surface and atmosphere based on CO₂. Icarus 146: 326-343
- 50 Hoffman N, Knauth P, Klonowski S, Burt D, Saunders RS, Zurek RW, Doran PT, Forman SL (2000) Ideas about the surface runoff features on Mars. Science 290: 711-714
- 51 Hoham RW, Duval B (2001) Microbial ecology of snow and freshwater ice with emphasis on snow algae. In: Jones JG, Pomeroy JW, Walker DA, Hoham RW (eds). Snow Ecology: An Interdisciplinary Examination of Snow-Covered Ecosystems. Cambridge University Press, Cambridge, pp 168-228
- 52 Irwin III RP, Maxwell TA, Howard AD, Craddock RA, Leverington DW (2002) A large paleolake basin at the head of Ma'adim Vallis, Mars. Science 296: 2209-2212
- 53 Jakosky BM, Carr MH (1995) Possible precipitation of ice at low latitudes on Mars during periods of high obliquity. Nature 315: 559-561
- 54 Jakosky BM, Shock EL (1998) The biological potential of Mars, early Earth, and Europa. J. Geophys. Res. 103(E8): 19359-19364
- 55 Kargel JS (2001) New evidence for ancient glaciation and modern debris-covered nonpolar glaciers on Mars. 32nd Lunar Planet. Sci. Conf. 2079
- 56 Kargel JS, Strom RG (1992) Ancient glaciation on Mars. Geology 20: 3-7
- 57 Kasting JF (1991) CO₂ condensation and the climate of early Mars. Icarus 94: 1-13
- 58 Kempe S, Kazmierczak J (1997) A terrestrial model for an alkaline Martian hydrosphere. Planet. Space Sci. 45: 1493-1499
- 59 Kieffer HH (2000) Clathrates are not the culprit. Science 287: 1753-1754
- 60 Kirkland EE, Herr KC, Adams PM (2003) Infrared stealthy surfaces: Why TES and THEMIS may miss some substantial mineral deposits on Mars and implications for remote sensing of planetary surfaces. J. Geophys. Res. 108(E12): 5137, 10.1029/2003JE002105
- 61 Kivelson MG, Khurana KK, Russell CT, Volwerk M, Walker RJ, Zimmer C (2000) Galileo Magnetometer measurements: a stronger case for a subsurface ocean at Europa. Science 289: 1340-1343
- 62 Knauth L, Burt D, Klonowski S (2000) Dense, eutectic, valley-forming, intermediate latitude brines on Mars. Geol. Soc. Am. 32(7): A303
- 63 Kramer M, Sletten R, Cabrol NA, Grin EA, Carr MH, Potter C, DesMarais DJ (2003) Ice/snow melt surface water features and closed basins in Ma'adim Vallis watershed: a source for episodic lacustrine activity in Gusev Crater. Nature. Submitted

- 64 Malin MC, Edgett KS (1999) Oceans and seas in the Martian lowlands: high resolution imaging tests of proposed shorelines. Geophys. Res. Lett. 26: 3049-3052
- 65 Malin MC, Carr MH (1999) Groundwater formation on Martian valleys. Nature 397: 589-591
- 66 Malin MC, Edgett KS (2000) Evidence for recent groundwater seepage and surface runoff on Mars. Science 288: 2330-2335
- 67 Malin MC, Edgett KS (2000) Sedimentary rocks of early Mars. Science 290: 1927-1937
- 68 McKay CP, Clow SS, Wharton Jr. RA, Squyres SW (1985) Thickness of ice on perenially frozen lakes. Nature 313: 561-562
- 69 Mellon MT, Phillips RJ (2001) Recent gullies on Mars and the source of liquid water. J. Geophys. Res. 106(E10): 23165-23180
- 70 Moore JM, Wilhelms DE (2001) Hellas as a possible site of ancient ice-covered lakes. 32nd Lunar Planet. Sci. Conf. 1446
- 71 Moore JM, Clow GD, Davis WL, Gulick VC, Janke DR, McKay CP, Stoker CR, Zent AP (1995) The circum-Chryse region as a possible example of a hydrologic cycle on Mars: geologic observations and theoretical evaluation. J. Geophys. Res. 100(E3): 5435-5447
- 72 Musselwhite DS, Swindle TD, Lunine J (2001) Liquid CO breakout and the formation of recent small gullies on Mars. Geophys. Res. Lett. 28: 1283-1285.
- 73 Mustard JF, Cooper CD, Rifkin MK (2001) Evidence for recent climate change on Mars from the identification of youthful near-surface ground ice. Nature 412: 411-414
- 74 Newsom HE, Britelle GE, Hibbitts CA, Crossey LJ, Kudo AM (1996) Impact crater lakes on Mars. J. Geophys. Res. 101(E6): 14951-14955
- 75 Ori GG, Marinangeli L, Baliva A. (2000) Terraces in Gilbert-type deltas in crater lakes in Ismenius Lacus and Memnonia (Mars). J. Geophys. Res. 105(E7): 17629-17643
- 76 Paige DA. (1992) The thermal stability of near-surface ground-ice on Mars. Nature 356:43-45
- 77 Parker TJ, Gorcine DS, Saunders RS, Pieri DC, Schneeberger DM (1993) Coastal geomorphology of the Martian northern plains. J. Geophys. Res. 98: 11061-11078
- 78 Parker TJ, Grant JA, Rice JW, Franklin B (2001) A comparison of proposed Martian shore morphology with coastal landforms of the Bonneville basin, Utah. 97th Annual Meeting Pacific Section, Am. Assoc. Petr. Geol.
- 79 Price PB (2000) A habitat for psychrophiles in deep Antarctic ice. Proc. Nat. Acad. Sci. 97(3): 1247-1251
- 80 Scott DH, Chapman MG (1991) Mars Elysium basin: geologic and volumetric analyses of a young lake and exobiologic implications. 21st Lunar Planet. Sci. Conf. 669-677
- 81 Scott DH, Rice Jr. JW, Dohm JM (1991) Martian lacustrine basins and reassessment of fluvial history: exobiologic implications. Orig. Life Evol. Biosph. 21: 189-198
- Scott DH, Dohm JM, Applebee DJ (1993) Geological Map of Science Study Area
 8, Apollinaris Patera Region of Mars. U.S. Geol. Surv. Misc. Inv. Series, 1:500,000. Map I-2351
- 83 Scott DH, Dohm JM, Rice JW (1995) Map of Mars showing channels and possible paleolakes. U.S. Geol. Surv. Misc. Inv. Series, Map I-2461

- 84 Segura TL, Toon OB, Colaprete A, Zahnle K. (2002) Environmental effects of large impacts on Mars. Science 298: 1977-1980
- 85 Spaun NA, Head III JW (2001) A model of Europa's crustal structure: recent Galileo results and implications for an ocean. J. Geophys. Res. 106(E4): 7567-7576
- 86 Squyres SW, Kasting JF (1994) Early Mars: how warm and how wet? Science 265: 774-749
- 87 Squyres SW, Wilhems DE, Moosman AC (1987) Large scale volcano-ground ice interactions on Mars. Icarus 70: 385-408
- 88 Vinebrook RR, Leavitt PR (1996) Effects of ultraviolet radiation on periphyton in an alpine lake. Limnol. Oceanogr. 41(5): 1035-1040
- 89 Wharton RA, Crosby JM, McKay CP, Rice JW (1995) Paleolakes on Mars. J. Palaeolimnol. 13: 267-283
- 90 Wynn-Williams DD, Cabrol NA, Grin EA, Haberle RM, Stoker CR (2001) Brines in seepage channels as eluents for sub-surface relict biomolecules on Mars? Astrobiology 1: 165-184

11 Impact Craters, Water and Microbial Life

Charles S. Cockell and Darlene S.S. Lim

Because of the lack of recent plate tectonics, the surface of Mars has abundant, well-preserved impact structures. Impact structures can localize water in a number of ways including: 1) circulation of water into hydrothermal systems, 2) ponding of water in the hydrologic depression of the crater. This ponding can occur because of excavation below the water table, filling of the crater by rivers that breach the crater rim, penetration of deep, confined aquifers or by collection of precipitation in the form of rain and snow, 3) entrapment of water in the fractures of shocked rocks and 4) melting of existing frozen water sources by the heat of impact. The local enhancement of water availability provides a potential mechanism for the local enhancement of microbial communities compared to regions outside of craters, provided that an energy source and other nutrient requirements for life are present. We discuss some examples of microbial communities in terrestrial impact structures that are associated with some of these mechanisms of water enhancement and we discuss the importance of impact structures as places suitable for microbial life on other rocky planets, specifically Mars

11.1 Introduction

The enormous kinetic energies associated with the collision of asteroids and comets with the Earth's surface have the effect of rearranging the local geology of the affected area and thus, its hydrologic cycle [1]. As life depends upon a source of liquid water to grow, among other factors, it is not surprising that as well as the obvious consequence of destroying life, impact events also influence the distribution of life in the area well after the first major environmental effects have abated. In many impact structures today, the influence of impact processing of the local target material on the distribution of microbial life can be seen millions of years after impact, most conspicuously in the form of intra-crater lakes.

We can understand how profound impacts can be for potential microbial habitats by briefly reviewing the major changes that occur after the instant in time at which an asteroid or comet first touches the Earth's surface [2].

The collision of the bolide excavates a 'transient' crater, a process that occurs in less than about 2 minutes after impact. The upper zone of the crater is made up of material ejected at sufficient velocity to throw it out of the crater as an ejecta blanket and in large impacts, even to distribute it globally. In the lower part of the crater, material is displaced downward and outward. Pressures transmitted by the shock wave during the initial 'compression' stage, when the bolide first touches the ground, can exceed many tens of gigapascals and temperatures can exceed many hundreds of degrees centigrade, depending on the distance from ground zero and the origin of the material, causing rocks to fracture and even to melt.

In the case of an impact that forms a crater of less than ~2-4 km in diameter (this diameter depends on the gravity of the planet being considered), the transient crater leads to the formation of a simple crater bowl. Heated, fractured and brecciated rocks fill part of the crater to form a breccia lens as well as those ejected outside of the crater to form the ejecta blanket. In the case of larger or 'complex' craters, gravity causes slumping and faulting around the rims of the crater. Thus, the final crater diameter can be significantly larger than the transient cavity excavated during impact. These changes occur during the phase of postimpact 'modification'. In complex craters other features such as a central uplift or uplift rings are formed within the crater, giving the crater a complex morphology. All of these profound geological changes cause a severe perturbation of the local hydrologic cycle. For a more detailed discussion of the processes of impact crater formation the reader is referred to [1, 2].

In this chapter we will describe some of the ways in which impact events can change the local hydrology, and so the distribution of microbial life (Fig. 11.1). We will give some examples of present-day terrestrial impact structures in which we can see these features represented and we will speculate on the implications for abodes for life on Mars-like planets.

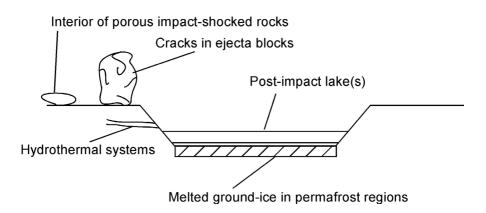


Fig 11.1 Some microbial habitats associated with enhanced water availability within impact structures. Each of these micro-habitats is associated with different periods in the crater history (see text for discussion).

We note for the reader that this chapter will specifically focus on microorganisms and will not discuss the colonization of craters by metazoans. The record of such colonization events, particularly inferred from intra-crater lake sediments, is rich and the reader is referred to other papers for this material (some review of this material and references can be found in [3]).

11.2 Hydrothermal Systems

11.2.1 The Environment for Microbes Immediately After Impact – A Plausible Picture

The first obvious hydrologic consequence of impact is the formation of hydrothermal systems. The energy delivered by the impactor will heat the target rocks, generating a transient thermal anomaly [e.g., 4]. Water from deep confined aquifers penetrated by the impact, precipitation, groundwater and other sources of water can be heated and vaporized. In ice-rich regions ground-ice may be melted.

Hydrothermally-precipitated minerals have now been recognized in a number of structures including the Ries [4], Haughton [5], Manson [6] and Chicxulub [7]. Osinski et al. examined the hydrothermal alteration within localized hydrothermal pipes in the Haughton impact structure's fault systems and within the polymict impact breccia that filled the crater after impact 23 million years ago [5]. The first stage they recognize in this process is an early stage where quartz is precipitated and temperatures are above 200°C, well above the currently defined upper temperature limit for life (113°C). In the main stage that follows they recognize the precipitation of calcite, barite, marcasite and other minerals. During this stage temperatures are between 100° and 200°C. At this stage, temperatures within some of these systems are appropriate for hyperthermophiles, whose growth temperatures are above 80°C. During the late stage temperatures drop below 100°C and selenite is formed.

The authors estimate that it took some tens of thousands of years for the crater to cool below 50°C [5], making the phase of the hydrothermal anomaly a geologically short-lived event, but a long-term event when considered in context of biological colonization (new volcanic lakes, for example, can be colonized in a matter of months). Once temperatures are reduced to below 50°C the environment becomes suitable for prokaryotic mesophiles (organisms that grow best between 25 and 40°C) and eukaryotes (which have not been found above ~55°C).

In terms of understanding how these phases of water temperature affect microbial life, it is important to try to picture the real physical environment. The mineralogical signatures from Haughton suggest that hydrothermal activity occurred for many thousands of years and theoretical models give convenient curves of crater cooling over time that are uniform, but it is unlikely that these observations and calculations apply to the *entire* crater with the uniformity that they suggest.

For example, one can imagine a large ejecta block thrown onto the rim of a crater, isolated from the melt sheet and exposed to the wind. On the surface of such a block temperatures might have dropped to below 50°C within days. Similarly, the surface of some outlying regions of melt rocks isolated from hydrothermal pipes may have cooled down more quickly than hydrothermal systems being continuously supplied with heated water/steam from the base of the

melt sheet. Osinski et al. have mapped the hydrothermal pipes in Haughton and found them to be associated with the edges of the crater, suggesting that they flowed out around the faults of the crater and were localized features.

In the Manson structure, hydrothermally-altered minerals are localized to the central uplift [6] and in this case alteration may have been dominated by geothermal heating from the uplifted material. As the subsurface heats at approximately 30°C per kilometre depth, an uplift of ~2-3 kilometres would expose material from the subsurface whose surface temperatures would be suitable for thermophiles and hyperthermophiles.

So what would such an environment look like to a field microbiologist? The microbiological view across a new crater is speculative, but we can imagine it to be heterogeneous. A plausible analogue of the environment around the edges of the crater days to months after impact may be the hot springs found in a hydrothermal region such as Yellowstone National Park [8]. Here there are hot springs with temperatures in excess of 90°C, but areas of cooled terrain in between lead to a patchwork environment fit for mesophiles, thermophiles and hyperthermophiles that varies on spatial scales of tens of metres. Changes in plumbing from subsurface geologic activity might now and then change the location of the springs. This is a microbiologically diverse environment, where water comes in the form of hydrothermally heated sources, rain and maybe snow and cool groundwater feeding into hydrologic depressions.

In the centre of a newly-formed crater, the melt sheet might sustain more homogeneous temperatures if it is uniformally heated during impact. In the 25 kmdiameter Ries structure, the initial temperature of the suevite is estimated as ~550°C [4]. Degassing pipes suggest that cooling could have begun quite rapidly. Alteration products within the pipes suggest temperatures below 100-130°C [4]. Osinski et al. estimate temperatures of 650-700°C during the emplacement of the Haughton melt sheet [5]. Draining of water into the crater and the formation of pond(s) and lake(s) would have further caused localized rapid reductions of surface temperature, first resulting in steam, but when the temperature was reduced to below 100°C, causing convective cooling. Thus, very quickly, regions of the suevite would have become suitable for microbial colonization.

Hydrothermal systems are significant on Mars, not so much as a source of hot water, but as a source of any water at all [9]. The phase of hydrothermal activity presents the possibility of melting subsurface ground ice that could provide a rare source of sustained liquid water for life [10]. The impact-induced thermal anomaly may delay the freezing of lakes and furthermore, the heat gradient would drive convection with the lake [9], mixing warm water and any potential nutrients. The recent detection of substantial ground ice on Mars [11] suggests that this is a potentially important process in the Martian post-impact environment with potentially relevant exobiological implications. However, one important factor militates against too much biological optimism. Just because liquid water is formed does not mean there are any organisms to colonize it. On Earth, the dogma, 'where there is water, there is life' holds true because of the substantial microbial biosphere that covers the planetary surface. Usually, the transient

presence of water leads to colonization by airborne microorganisms or those leached from the ground. On Mars, the lack of an aerial biota or substantial surface microbiota sustained by a photosynthetic biosphere means that it is more plausible to imagine transient *sterile* bodies of water. Nevertheless, the thermal pulse generated by impact increases biological *potential* and so it is a phenomenon of exobiological interest on any planet, regardless of the presence of life or not.

11.2.2 Evolutionary Significance of the Duration of Hydrothermal Systems

At any given time in the history of Earth, volcanic hydrothermal systems have existed. In Hawaii alone, new lava flows, for instance, have existed continuously for the last 70 million years [12], suggesting the continuity of post-volcanic habitats over geologic time periods. Can the same be said of impact-induced hydrothermal systems? Clearly it cannot, as there is no hydrothermal system associated with a fresh crater on Earth today. The mean impact interval required to allow for almost continuous hydrothermal post-impact crater habitats can be estimated. Osinski et al. estimate the period of hydrothermal temperatures greater than 50°C in the Haughton structure to be 'several tens of thousands of years' [5]. The current interval of impact events on this scale is once every $\sim 10^7$ years [13], much longer than the period of hydrothermal activity. Events with much longer hydrothermal durations are correspondingly less frequent. A bolide of 10 km size may have two orders of magnitude more energy than Haughton (such as the impactor that formed the Chicxulub structure at the so-called K/T boundary, the geologic boundary between the Crataceous and Tertiary) and so its hydrothermal phase could plausibly last for ~1 million years, but the corresponding frequency is once every 100 million years.

From the microbiological point of view we can therefore say that for presentday impact fluxes, microbial colonization of hot springs at the sites of fresh craters depends on a source of propagules from non-impact hydrothermal systems, such as those associated with volcanoes or subsurface geothermally-heated habitats. The exception to this statement may be when multiple impacts occur, as might happen after fragmentation of the bolide. In this case, cross-contamination of the craters could potentially occur. Also, although the *mean* interval may be greater than the duration of hydrothermal systems, statistically it is still possible today to have two impacts occur whose hydrothermal systems overlap in time, although this would be rare.

During the Archaean (3.8 to 2.5 Ga ago) impact fluxes were much higher than today, possibly two to three orders of magnitude more [13]. At this period in Earth's history the interval between large impact events would be very similar to the period of their hydrothermal phases (perhaps one million years between 10-km-sized bolides with a similar duration of their hydrothermal systems). Cross-contamination of post-impact hydrothermal systems could conceivably have occurred for craters formed from completely different bolides. Concomitantly, however, volcanic hydrothermal systems were probably much more common on

early Earth. Although Archaean Earth may have been a place of interaction between post-impact hydrothermal systems, volcanic hydrothermal systems, like today, were the dominant and most abundant habitats for heat-loving microorganisms.

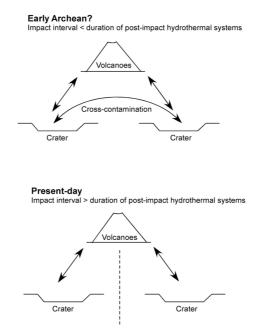


Fig 11.2 During the Archaean it is plausible that the mean interval between impact events was less than the duration of hydrothermal systems, in which case cross-inoculation of impact hydrothermal systems might have been common. Today, most new impact crater hydrothermal systems require a source of thermophiles and hyperthermophiles from non-impact hydrothermal systems such as volcanoes. Exceptions would be multiple impact events caused by fragmentation of the bolide and rare occasions when the impact interval was less than the duration of the hydrothermal system.

As the history of the impact flux on Mars is similar to that on the Earth we can postulate the same constraints on the cross-contamination of post-impact hydrothermal systems there.

In summary, impact fluxes today do not provide for hydrothermal systems that offer a consistent planetary habitat for heat-loving organisms. The maintenance of such forms of life on planets with impact fluxes similar to those of the present-day requires the sustained presence of other hydrothermal habitats such as those formed by geothermal or volcanic processes (Fig. 11.2).

11.3 Ponding of Water in the Crater

The hydrologic depression within the impact structure caused by excavation is likely to fill with water, forming pond(s) and lake(s). This may not always be the case. Small impacts in arid desert environments, for example, can form a crater devoid of water, but these are rarer [3]. A diversity of impact structures contain lakes today, some of them many millions of years after impact, demonstrating that the re-arrangement of the hydrologic system is by no means a transient phenomenon from the point of view of the longevity of the resulting microbial habitat.

The formation of the lake may overlap with the hydrothermal phase. In the Boltysh impact structure in Russia, hydrothermally altered sediments have been found in the lower parts of the stratigraphic sequence [14], suggesting that like volcanic calderas, there may have been an interaction of the lake with the post-impact hydrothermal system. In this case microbial communities within the lake obtain the advantage of hydrothermal warming of the lake waters and possibly an improved availability of nutrients caused by convective mixing of the lake waters.

11.3.1 Present-Day Ponding

The microbiota within the lake will be influenced by the climatic regimen in which the impact occurs. As the crater depression will remain in place for millions of years, the lake biota will be influenced by long-term changes in the planetary climate. Thus, generalized comments on the microbial content of impact lakes are not possible. It depends both on time and location and indeed, on the scale of the impact, which will influence the size of the resulting water bodies.

A number of impact lakes have been examined and their present-day microbial ecosystems characterized, although infrequently these studies have been related to post-impact colonization. To provide contrast we will discuss two intra-crater lakes in two very different climates. First, Lake El'gygytgyn in northeastern Siberia, a crater-lake characteristic of a tundra biome and second, the intra-crater lake of the Tswaing impact structure in South Africa, a lake typical of highveld summer rainfall zone. The purpose of this brief review is to illustrate the diverse physical and chemical environments associated with intra-crater bodies of water.

Lake El'gygytgyn is a 12 km-diameter lake situated within a complex impact structure formed ~ 3.6 Ma ago [15] (Fig. 11.3 left). The total diameter of the crater is ~18 km with a well-defined rim. The crater-lake is fed by a catchment area of just under 300 km² and the major outflow from the lake is a river that runs from the south of the crater.

The lake is situated in a dry, cold, tundra biome above the tree line, with less than 400 mm of rain each year. At $67^{\circ}10$ 'N and $172^{\circ}05$ 'E, the crater-lake experiences frigid winters with temperatures below -30° C in January and rising to a maximum of 8°C in July. Because of these low temperatures the lake is ice-covered for most of the year.

Because of its biologically depauperate setting and extreme weather conditions, the lake has low organic carbon concentrations. The Secchi disk depth is 19 m (a Secchi disk is a 20 cm-diameter disk with alternating black and white quadrants. It is lowered into a lake until the observer can no longer see it. This depth of disappearance is called the Secchi disk depth). Recent studies of the lake show the physical and chemical characteristics to be quite constant through its depth [15]. The temperature through the 175 m deep lake is approximately 3.3° C, with a pH just less than 6.8. The oxygen concentration is 12 mg Γ^{-1} through most of the lake. Below 140 m it becomes slightly more anoxic. At the bottom of the lake oxygen concentrations are about 10 mg Γ^{-1} .

The microbiological study of this lake is limited to the diatom flora. A diverse diatom flora is recorded. 113 diatom taxa were found in the lake, although one species, *Cyclotella* sp. dominated the flora, accounting for over 95% of the planktic community [15].

The near constancy of the physical and chemical conditions in the lake suggests complete mixing, probably caused by the high winds of this extreme location. Because the electrical conductivity is low ($12 \ \mu S \ cm^{-1}$), it is suggested that the lake is mainly supplied by meltwater from snow and ice. This would also explain the high Secchi disk depth and the apparent lack of organics. In summary, therefore, this lake is a cold, mixed, nutrient-poor environment [15].



Fig 11.3 The 12 km-wide El'gygytgyn crater-lake in Siberia within the 18-km diameter complex crater (left) and the much smaller Tswaing crater-lake in the 1.13 km-diameter simple crater in South Africa (right).

By contrast, the Tswaing crater at 25°24'S, 28°04'E is a very different limnetic environment [16–18] (Fig. 11.3 right). The intra-crater lake is set within a simple 1.13 km-diameter impact structure formed about 200,000 years ago. The craterlake is set below the treeline in a region of vegetation of the South African bushveld. The crater is heavily colonized by vegetation such as *Acacia* spp. By contrast to the tundra environment of El'gygytgyn, the rainfall is 400–750 mm a year. Mean summer temperatures vary between 14.2 and 35.2°C in December and January (summer) and between 3.6 and 15.6°C in June and July (winter). Unlike El'gygytgyn, the lake is never ice-covered. Because of the rich vegetation and warm temperatures, organic and nutrient inputs from the soil are high. The Secchi disk depth of the lake is a mere 7 cm (contrast this to 19 m for El'gygytgyn).

Unlike El'gygytgyn, the lake is highly stratified, even though it is only 0.49 m deep at its lowest point and up to 2.85 m deep at high water in winter. Temperatures at the surface can exceed 35°C, but drop to 25°C at the bottom of the lake. The lake is hypersaline, with a salinity of 10 % at the top increasing to >35% at the bottom of the lake. This is partly caused by the warm climate and the high rates of evaporation. The saltpan has been classified as a Na-Cl-CO₃-type brine. The pH was found to vary from 8.8 at the surface to 9.2 at the bottom with some variation up to 10.4 in between. Oxygen concentrations also varied considerably from ~20 mg Γ^1 near the surface to < 0.1 mg Γ^{-1} below 30 cm and they varied depending on the time of day. The electrical conductivity, because of the high salinity, is several orders of magnitude higher than in El'gygytgyn.

The very different chemical and physical regimen to be found in the hypersaline Tswaing crater compared to El'gygytgyn drives a very different microbial composition. The lake is inhabited by cyanobacterial benthic microbial mats that grow around the edges of the lake. A rich diversity of planktonic algae and bacteria inhabit the surface waters where light is available. A 5–6 cm deep plate of photosynthetic bacteria (*Chlorobium* sp.) is formed just below the zone of maximum temperature [16]. The lake also hosts a diatom flora [19]. Eleven species of diatom were examined, but in many of the samples *Nitzschia* sp. comprised over 70 % of the diatom population.

In view of the very different climatic regimens, the differences in the chemical, physical and thus biotic conditions between the intra-crater lakes at El'gygytgyn and Tswaing are not surprising (similar differences would be seen in lakes within depressions caused by other agents such as glacial scouring). However, they demonstrate to the reader unfamiliar with the microbiota of lakes that the ponding of water within a crater depression can lead to very different microbiological consequences depending on the setting, despite the fact that the mechanism of formation (formation of a hydrologic depression by impact excavation) is the same [3].

In some cases the chemistry of the intra-crater materials can influence lake chemistry. Lim and Douglas [20] report that the high sulfate concentrations of two lakes within the Haughton structure are caused by the underlying melt rocks. Their data suggest that intra-crater lakes cannot simply be considered as ponding associated with a large hole in the ground, but that impact-processing may influence the subsequent chemical interactions between the intra-crater materials and intra-crater bodies of water. Impact crater lakes must therefore be examined within the context of knowledge of the effects of impact on the target materials.

In some craters the rate of evaporation in desert climates may be so high as to transform the intra-crater lake into a playa deposit, examples being Wolfe Creek crater in the Australian desert and Monturaqui in the Atacama desert of Chile.

The colonization of Martian impact crater lakes by a biota is completely speculative. Whilst there is no climate on Earth that can truly be described as 'analogous' to Mars, the ultra-oligotrophic, ice-covered lake of El'gygytgyn with its poor nutrient regimen and its low organic content represents the type of nutrient and physical environment that would be close to that expected in early Martian lakes, albeit they would be expected to also be anoxic and high in ultraviolet radiation, because of the lack of an ozone shield on Mars.

11.3.2 The Fossil Record

In the previous section we showed the great contrast in the physical and chemical characteristics and thus, micro-biota that can exist in even present-day intra-crater lakes. Perhaps the most exobiologically relevant link between impact structures and Mars is the search for fossil life within intra-crater lake sedimentary deposits.

The coring of intra-crater lake sediments on Earth has revealed remnants of past microbial communities. An 89.95 m core was removed from the Tswaing impact crater in South Africa [21]. Extending from the floor of the lake through to the fractured basement granite, the 200,000 years of sequence could be divided into a number of well-defined parts. The top 34 m consisted of evaporites and muds, similar to the sediments being deposited today, with a high concentration of NaCl (halite). Below 30 m to the base of the sequence the core is dominated by calcium carbonate and within this sequence is abundant biological debris. Two segments within the core record a drop in pollen concentrations, suggesting xeric, desert-like, periods and illustrating how the record in impact lake cores can be used to derive a picture of post-impact climatic changes since the beginning of deposition. Other craters have been examined for their sedimentary records, notable examples being the Haughton impact structure and the Ries structure [22, 23].

In a previous publication we used the published information on the fossil record of microbial life in impact structures to postulate a sequence for the exobiological study of impact craters on Mars [3]. First, the crater rim might be examined for macroscopic signs of fossil life. An obvious analogy here is the fossil bioherms associated with the Ries crater in Germany [24] and with the central uplift of its postulated twin, the Steinheim crater. These outcrops of visibly laminated structures would present the most obvious signs of life in a post-impact lake. The bioherms are associated with the edges of the crater where they had a surface on which to grow, but light levels were sufficient for photosynthesis. In the absence of such biota, the surface of the playa/sedimentary deposits might be examined for signs of life. In the case of Martian craters, the interface between the dust layer from the Martian regolith and the beginning of sedimentary sequences could be examined for microscopic signatures of life. The terrestrial analogy here would be the surfaces of sediments such as those found in the Haughton structure in the high arctic. In the absence of a signature here, then the third step is to drill into the sedimentary deposits and seek signs of life buried within the deposits and fossilized. Analogues here include the drilling efforts into a diversity of craters, including the Ries and Lappajärvi structures, whose cores have revealed the presence of pre- and post-impact micro-fossils [e.g. 25]. Finally, deep drilling into the sediments to collect a complete core from the earliest stages of post-impact colonization might be attempted. In the case of Martian impact structures, the phase of liquid water availability might be transient and so drilling to the interface

between the first sedimentary deposits and the crater floor may yield the most trustworthy answer to the question of whether microbial life used the post-impact lake habitat.

11.4 Water in Impact-Shocked Rocks

The fracturing of rocks by the pressure wave generated during impact and the brecciation of target materials creates micro-environments in which water can be preferentially trapped or circulated.

Precambrian basement gneiss shocked to > 10 Ga from the Haughton impact structure is found to contain cyanobacterial communities and abundant heterotrophic communities as well [26, 27]. The porosity of this rock is increased substantially by impact-shock such that the surface area of pores greater than 1 micron in diameter is increased by approximately 25 times [26]. These pores and inter-connected fractures provide access points for microorganisms and surfaces for them to form biofilms. We have recently shown that after rain, exposed shocked rocks can retain water for many days, presumably on account of it leaching into the micro-fractures [28]. This water can provide moisture for the microorganisms within the rock after the surfaces have been wind-dried, allowing them to grow in an otherwise dry polar desert for longer periods than epilithic communities that inhabit the surface of rocks.

Similarly, the fracturing of large blocks of dolomite also provides spaces for cyanobacteria to grow into the cracks as chasmoliths (Fig. 11.4). After rains, water leaches into these cracks and provides moisture to the communities. We have observed moist zones within these cracks four to five days after the surfaces of the shocked blocks have been wind-dried, illustrating how impact fracturing of rocks can provide preferential availability of water to microbial communities growing within the fractures.

Because impact fractures also provide a refugium from ultraviolet radiation and can provide a thermally improved environment, with temperatures up to 10°C higher than air temperatures [28], impact-shocked rocks are a potentially intriguing model for micro-habitats suitable for life on Mars.

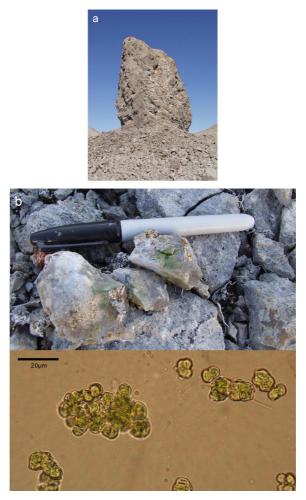


Fig 11.4 Cyanobacteria colonize impact-induced fractures in a large block of shocked dolomite of circumference 15.3 m in the Haughton impact structure (75°24.4'N, 89°49.90'W) shown in (a). The cyanobacteria grow as 'chasmoliths', forming biofilms within the fractures (b) that were formed by the pressure wave during impact. In this microhabitat water is preferentially trapped while the surface of the dolomite is wind-blown and dry. The micro-habitat also provides UV protection.

The significance of this habitat from the point of view of water availability and microbial life is that it can be sustained for potentially hundreds of millions of years and even in excess of a billion years (Fig. 11.5). Provided the rocks containing the impact-induced fractures are not completely eroded away, the preferential leaching or movement of water by capillary action into impact fractures will provide micro-environments suitable for microbial life long after

impact. The preferential colonization of the impact-induced fractures within the shocked gneiss and dolomite at Haughton, for instance, is still occurring 23 million years after impact, long after the lake(s) have drained away. Impact-induced fracturing is still evident at the Vredefort structure, South Africa, 2 billion years after impact. Thus, impact cratering should be seen not just as a geologic process, but also as a truly biologic process, yielding improved micro-habitats for micro-organisms over geologic time periods (Fig. 11.5).

Hydrothermal systems											
Impa	mpact crater-lakes										
Imp	act fractu	ired rock	S								
0	10 ⁰	10 ¹	10 ²	10 ³	10 ⁴	10 ⁵	10 ⁶	10 ⁷	10 ⁸	10 ⁹	
				Durati	on (yrs)						

Fig 11.5 Approximate duration (years) of habitats and micro-habitats within a typical 20 km-diameter impact structure on Earth in which there is enhanced liquid water availability.

11.5 Conclusions

Asteroid and comet impact events substantially alter the localized availability and flow of liquid water, thus influencing the biogeographical distribution of microbial life. In this chapter we have reviewed for the reader just some of the principal ways in which this is manifested and the major microbiological consequences that can be expected. We have related these phenomena to the exobiological potential of Mars, but note that they apply to extrasolar planets as well (impact events are a universal process and so habitats for simple life must exist in craters on extrasolar planets too). From the onset of high temperature hydrothermal activity to the sustained existence of crater lakes over millions of years and water-containing impact-fractures for potentially billions of years, craters can provide locally enhanced sources of liquid water for microbes long after their formation, representing an important extraterrestrially-mediated mechanism of microbial habitat formation.

11.6 References

- 1 Melosh HJ (1989) Impact Cratering. A Geologic Process. Oxford University Press, Oxford
- 2 French B (1998) Traces of Catastrophe. Lunar and Planetary Institute Publication, Houston

- 3 Cockell CS, Lee PC (2002) The biology of impact craters. Biol. Rev. 77: 279-310
- 4 Newsom HE, Graup G, Sewards T, Keil K (1986) Fluidization and hydrothermal alteration of the suevite deposit at the Ries crater, West Germany, and implications for Mars. J. Geophys. Res. 91: 239-251
- 5 Osinski GR, Spray JG, Lee P (2001) Impact-induced hydrothermal activity within the Haughton impact structure: generation of a transient, warm, wet oasis. Meteorit. Planet. Sci. 36: 731-745
- 6 McCarville P, Crossey LJ (1996) Post-impact hydrothermal alteration of the Manson impact structure. In Koeberl C and Anderson RR (eds) The Manson Impact Structure, Iowa: Anatomy of an Impact Crater. Geol. Soc. America Special Paper, Denver, pp 347-376
- 7 Kring DA, Zurcher L, Hörz F (2003) Impact lithologies and post-impact hydrothermal alteration exposed by the Chicxulub scientific drilling project, Yaxcopoil, Mexico (abstract) Third International Conference on Large Meteorite Impacts, Nördlingen, Germany
- 8 Brock T (1978) Thermophilic Micro-Organisms and Life at High Temperatures. Springer-Verlag, Berlin, Heidelberg, New York
- 9 Rathbun JA, Squyres SW (2002) Hydrothermal systems associated with Martian impact craters. Icarus 157: 362-372
- 10 Newsom HE (1980) Hydrothermal alteration of impact melt sheets with implications for Mars. Icarus 44: 207-216
- 11 Mitrofanov I, Anfimov D, Kozyrev A, Litvak M, Sanin A, Tret'yakov V, Krylov A, Shvetsov V, Boynton W, Shinohara C, Hamara D, Saunders RS (2002) Maps of subsurface hydrogen from the high energy neutron detector. Science 297: 78-81
- 12 Thornton IWB (1984) Psocoptera of the Hawaiian islands, Part III. The endemic *Ptycta* complex (Psocidae): systematics, distribution and evolution. Int. J. Entomol. 26: 1-128
- 13 Chyba CF, Owen T, Ip W-H (1994) Impact delivery of volatiles and organic molecules to Earth. In Gehrels T (ed) Hazards due to Comets and Asteroids. University of Arizona Press, Tucson, pp 9-58
- 14 Gurov EP (1996) The Boltysh impact crater: lake basin with a heated bottom (abstract) International Tunguska Workshop, Tunguska '96, Bologna, Italy
- 15 Cremer H, Wagner B (2003) The diatom flora in the ultra-oligotrophic Lake El'gygytgyn, Chukotka. Polar Biol. 26: 105-114
- 16 Ashton PJ (1999) Limnology of the Pretoria Saltpan Crater-Lake. In Partridge TC (ed) Tswaing. Investigations into the origin, age and paleoenvironments of The Pretoria Saltpan Council for Geoscience. Geol. Survey of South Africa. Memoir 85. Pretoria
- 17 Ashton PJ, Schoeman FR (1988). Thermal stratification and the stability of meromixis in the Pretoria Salt Pan, South Africa. Hydrobiologia 158: 253-265
- 18 Ashton PJ, Schoeman FR (1983) Limnological studies on the Pretoria Salt Pan, a hypersaline maar lake. 1. Morphometric, physical and chemical features. Hydrobiologia 99: 61-73
- 19 Schoeman FR, Ashton PJ (1982). The diatom flora of the Pretoria Salt Pan, Transvaal, Republic of South Africa. Bacillaria 5: 63-99
- 20 Lim, DSS, Douglas, M (2003) Limnological characteristics of 22 lakes and ponds in the Haughton crater region of Devon Island, Nunavut, Canadian High Arctic. Arct. Antarct. Alpine Res. 35: in press

- 21 Partridge TC, Kerr SJ, Metcalfe SE, Scott L, Talma AS, Vogel JC (1993) The Pretoria saltpan: a 200,000 year southern African lacustrine sequence. Palaeogeogr. Palaeoclimatol. Palaeoecol. 101: 317-337
- 22 Hickey LJ, Johnson KR, Dawson MR (1988) The stratigraphy, sedimentology, and fossils of the Haughton formation: a post-impact crater-fill, Devon Island, N.W.T., Canada. Meteoritics 23: 221-231
- 23 Pohl J, Stoffler D, Gall H, Ernston K (1977) The Ries impact crater. In Roddy DJ, Pepin RO, Merrill RB (eds) Impact and Explosion Cratering. Pergamon, New York, pp 343-404
- 24 Riding R (1979) Origin and diagenesis of lacustrine algal bioherms at the margin of the Ries crater, Upper Miocene, Southern Germany. Sedimentology 26: 645-680
- 25 Uutela A (1990) Proterozoic microfossils from the sedimentary rocks of the Lappajärvi impact crater (Finland). Bull. Geol. Soc. Finland 62: 115-120
- 26 Cockell CS, Lee P, Osinski G, Horneck G, Broady P (2002) Impact-induced microbial endolithic habitats. Meteorit. Planet. Sci. 37: 1287-1298
- 27 Fike D, Cockell CS, Pearce D, Lee P (2003) Heterotrophic colonization of impactshocked rocks from the Haughton impact crater, Canadian High Arctic. Int. J. Astrobiol. 1: 311-323
- 28 Cockell CS, McKay CP, Omelon C (2003) Polar endoliths anticorrelation of climatic extremes and microbial biodiversity. Int. J. Astrobiol. 1: 305-310

12 Microbial Life in Brines, Evaporites and Saline Sediments: The Search for Life on Mars

Rocco L. Mancinelli

When water on a planet begins to evaporate the dissolved minerals become more concentrated, form a brine, eventually precipitating out of solution and forming evaporite deposits. The brines and evaporites form a highly saline environment that is hostile to most life forms, but provides an ideal habitat for organisms that are osmophilic, or halophilic. Halophiles are salt "loving" organisms that inhabit environments with salt concentrations ranging from 15 % to saturation. On Earth, representatives of halophiles occur in all three domains of life, the *Archaea*, *Bacteria* and *Eukarya*.

Data from recent Mars missions suggest that Mars almost certainly had abundant liquid water on its surface at some time in the past, which was eventually lost. The loss of water probably occurred when Mars lost its atmosphere causing the water to evaporate, or recede into the subsurface. As the water evaporated, the dissolved minerals became more concentrated, forming brine pockets and evaporites within the permafrost.

Because data suggest that it may be relatively easy for halophilic, or osmophilic type organisms to evolve, if there were any life on Mars in water, then there should have been the evolution of some type of osmophile, or halophile. Brine pockets containing high concentrations of dissolved salts would have selected for the survival of osmophiles, or halophiles. These brine pockets may either be "oases" for an extant Martian biota, or the last refuge of an extinct Martian biota.

12.1 What Are Halophiles?

Halophiles are microorganisms that live in hypersaline environments that have salt concentrations ranging from 15 % to saturation. All three domains of life, the *Archaea*, the *Bacteria* and the *Eukarya* have halophilic representatives (Fig. 12.1). These organisms are abundant in hypersaline environments forming populations so dense that the red color associated with hypersaline lakes and ponds is due to the pigmentation of the halophilic *Archaea* and the eukaryote *Dunaliella* (Fig. 12.2). Although these lakes and ponds contain populations of halophilic bacteria and other members of the Eukarya they go unnoticed to the naked eye because they are not pigmented.

Halophiles fall into two categories, extreme halophiles requiring 15 % salt to saturation, or moderately halophilic organisms living in saline environments ranging from seawater to 15 %. Organisms that are halotolerant prefer non-saline environments, but can grow from essentially no salt to nearly 10 % salt.

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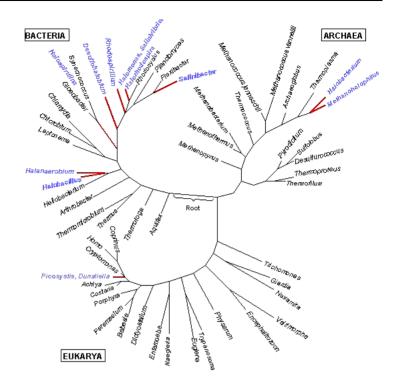


Fig. 12.1 Phylogenetic tree depicting common genera in the three domains of life: *Bacteria, Archaea* and *Eukarya*. Halophiles are indicated in blue.

12.1.1 The Place of Halophiles in the World

Halophiles are everywhere in the world where there is salt. They represent a physiologically, evolutionarily, and ecologically diverse group of organisms. Most halophiles are found interspersed among non-halophiles in the phylogenetic tree (Fig. 12.1). They encompass heterotrophs, autotrophs, and some possess light harvesting pigments either for photosynthesis, or for energy production via rhodopsin. They live in cold, or hot environments, wet environments (e.g. lakes and ponds), dry environments (e.g. soils and salt crusts), alkaline as well as neutral environments. They can be aerobes, anaerobes, or facultative anaerobes. Some have true cell walls (*Bacteria* and *Eukarya*) and some do not (*Archaea*). They even differ with respect to their modes of osmotic adaptation. The one characteristic they have in common is their ability to live in hypersaline environments.

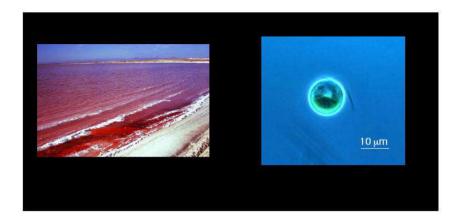


Fig. 12.2 A salt evaporation pond (left frame) containing red pigmented halophiles including the eukaryotic alga Dunaliella (right frame).

12.1.2 The Halophilic Archaea

Within the domain *Archaea* halophily can be found in the *Halobacteriaceae*, the *Methanospirillaceae* and the *Mahanosarcinaceae*. Unlike the *Methanospirillaceae* and the *Mahanosarcinaceae* which have few halophilic representatives, all members of the family Halobacteriaceae are extreme halophiles. Many new species of halophilic *Archaea* have been isolated and characterized during the past 25 years representing diverse morphologies and physiologies. The order Halobacteriales [38] forms a branch within the Euryarchaeota. Halobacteriales consists of one family, the Halobacteriaceae that is divided into 15 genera with 44 species.

The *Halobacteriaceae* are basically aerobic heterotrophs. They are all chemoheterotrophs, and some are photoheterotrophs using bacteriarhodopsin to generate energy. Autotrophic growth, however, has never been demonstrated. Denitrification, that is anaerobic respiration, the reduction of nitrate to either N_2O or N_2 occurs in several species [e.g. 71, 48]. In comparison, the *Methanospirillaceae* and the *Mahanosarcinaceae* are anaerobic methanogens that use methylated amines or methanol for substrates.

The morphology of the organisms in the *Halobacteriaceae* includes rods, cocci, pleomorphic cells, square cells, as well as triangular and trapezoid shaped cells. These shapes are determined by the properties of the organism's cell wall and membrane. The unusual shapes such as triangles, and squares are possible because the cells do not possess significant turgor pressure [114], so shapes that may not be feasible for other types of organisms are feasible for these halophiles.

Most Archeael halophiles do not possess a true rigid cell wall, but rather what is called an S-layer that consists of large subunits of a large glycoprotein that depends on a high salt concentration for structural stability. When these organisms are placed in a hypotonic solution they lyse, but lysis is due to denaturation of the glycoproteins rather than osmotic pressure [61]. The exceptions are members of the genera *Halococcus* and *Natronococcus* who do possess a rigid cell wall that does not depend on high salt for structural stability. *Halococcus* has a wall consisting of a heteropolysaccaride [102], while *Natronococcus* has a wall made of repeating units of poly(L-glutamine) [77]. None of the Archaeal halophiles possess the classical cell wall components such as D-amino acids and teichoic acid.

The cell membranes of the Archaeal halophiles are composed of lipids and proteins. However, unlike other microbes they are primarily composed of branched C20 and C25 carbon chains bound to glycerol by ether bonds that form polar and neutral lipids only found in the Archaea [56].

Classification of the genera and species of the Halophilic *Archaea* is based primarily on cellular morphology, growth characteristics, membrane lipid composition, and 16S rDNA sequence data [e.g. 84].

12.1.3 The Halophilic and Halotolerant Bacteria

Halophiles are spread throughout the phyla and orders, within the domain *Bacteria*. Halophilic *Bacteria* vary widely in their physiological properties, and include aerobic and anaerobic chemoheterotrophs, photoautotrophs and photoheterotrophs, as well as chemolithotrophs [80, 81].

Oxygenic photosynthetic *Bacteria*, i.e. the Cyanobacteria, are present in hypersaline environments. Cyanobacteria inhabiting microbial mats in salterns containing up to 25 % salt [53] and in evaporitic salts [98] are extreme halophiles. Examples of halophilic cyanobacteria include the species of *Halospirulina* [79], *Microcoleus Cyanothese*, *Aphanothece*, *Chroococcidiopsis*, and *Myxobactron* [35]. The taxonomy of the cyanobacteria is not well defined, resulting in diverse physiological types grouped together in one genus. Thus, not all species of the above named cyanobacteria are halophilic.

Halophilic anoxygenic photosyntesizers are sulfur *Bacteria*. They include two genera and range from the extremely halophilic genus *Halorhodospira* to the moderately halophilic *Ectothiorhodospira* [51, 108, 112].

Unlike the halophilic *Archaea*, the halophilic and halotolerant *Bacteria* are metabolically diverse. The physiological types include aerobic and anaerobic heterotrophs, oxygenic and anoxygenic photoautotrophs, photoheterotrophs and chemolithotrophs.

The *Halomonadaceae* family of the *Bacteria*, made up of the genera *Halomonas* and *Chromobacter*, are metabolically versatile aerobic moderate halophiles that have few non-halophiles among them [111]. Most of the halophilic anaerobic *Bacteria* form a phylogenetically coherent group within the order Haloanaerobiales [92].

Much less is known about the details of the cellular structures of the halophilic and halotolerant *Bacteria* than the Archaeal halophiles. However, the halophilic *Bacteria* have much in common with the non-halophilic *Bacteria*. Their cell wall appears to contain peptidoglycan much like the non-halophilic *Bacteria*. The cell wall of most halophilic *Bacteria* that have been studied contain some type of hydrophobic protein [85]. The cell membranes are made of proteins and lipids as are non-halophilic *Bacteria*. They differ from their non-halophilic counterparts in that the membrane is regulated by the outside salt concentration to adjust ion permeability and the activity of the integral proteins [100].

12.1.4 The Halophilic and Halotolerant Eukarya

The halophilic *Eukarya* are not as diverse as the *Bacteria*, and represent a small fraction of the domain Eukarya. The few types that do exist, however, contribute significantly to the biomass of hypersaline environments. Species of the green algae *Dunaliella* and *Picosystis salinarum* can grow in environments ranging from slightly brackish to saturated brines [85]. While most diatoms cannot grow in hypersaline environments, a few, mostly members of the genera *Annphora*, *Nitzschia* and *Entomoneis* can grow in saline environments containing 15 % salt [19]. Protozoa also have members that are halophilic, most notably several genera of the ciliates, sarcodines and zooflagellates. Certain groups of fungi also thrive in hypersaline environments, and contribute significantly to the biomass of these environments [42].

Relatively little is known about the specifics of the physiology of the halophilic and halotolerant *Eukarya*. They do, however, encompass photoautotrophs, as well as heterotrophs.

The *Eukarya* in general have more complex cellular structures than either the *Archaea*, or the *Bacteria*. *Dunaliella* do not possess a rigid cell wall allowing them to swell and shrink as an immediate reaction to changes in the salinity of their environment. The cytoplasmic membrane can rapidly either take up, or efflux large molecules such as dextrans [37]. It is thought that this ability is what enables the organisms to swell, or shrink in response to rapid changes in salt concentration in the environment. *Dunaliella* contain β -carotene in the inter-thylakoid space within the chloroplast. Sterols are a major component of the lipids in the fungi.

12.1.5 Halophily and Osmophily – Is There a Difference?

Osmophily refers to the osmotic aspects of life at high salt concentrations, especially turgor pressure, cellular dehydration and desiccation. Halophily refers to the ionic requirements for life at high salt concentrations. Although these phenomena are physiologically distinct, they are environmentally linked because increasing salt concentrations lead to increases in osmolarity. Because of the environmental link between osmolarity and salt concentration, a halophile must be able to physiologically compensate for the osmolarity that accompanies its

optimum salt concentration requirement. Under normal growth conditions the osmotic aspect of the high salt requirement cannot be clearly separated from the solute aspect, making it difficult to study the physiology of osmophily separately from halophily.

Many microorganisms respond to increases in osmolarity by accumulating substances, termed osmotica, in their cytosol. Osmotica protect organisms from cytoplasmic dehydration and desiccation [9, 116]. With the exception of the Halobacteriaceae and the Haloanaerobiales, which use K^+ as their osmoticum [66], glycine-betaine is the most common osmoticum in most prokaryotes [32, 64, 67] including the cyanobacterium *Synechococcus* (Nägeli) [69, 93; reviewed in 50]. Studies of the osmoticum in halophilic eukaryotes has centered around *Dunaliella* and to a lesser extent *Asteromonas* species. It appears that halophilic eukaryotes use glycerol as their osmoticum while maintaining very low intercellular ionic concentrations [e.g. 5].

The osmoticum used by halophiles belong to different chemical classes with little structural similarity. The general properties they have in common are that they are very soluble, have no net charge, and exhibit very limited interaction with proteins. These compounds are all strong water structure formers and as such they are excluded from the hydration shell of proteins. This exclusion most likely defines their function as effective stabilizers of the hydration shell of proteins and other cytoplasmic structural elements [34, 109]. The phenomenon of preferential hydration of proteins favors a more compact protein conformation. It also opposes an increase in surface area and, because unfolding usually results in surface area increase, it favors the native structure of the protein. It is therefore primarily free water, as opposed to bound water, that responds to osmotic changes in the environment, and the compatibility of osmotic solutes is based on the fact that they specifically adjust the osmotic equilibrium of the free water fraction. Exclusion of compatible solutes from the hydration sphere of proteins is consistent with a decrease in entropy of the system (higher ordering). This entropically unfavorable condition in turn causes minimization of the excluded volume and subsequently stabilizes the conformation of a protein [33].

12.2 Evolution of Halophiles

It is clear from the above discussion that halophiles form a phylogenetically diverse group. They occur in all three domains of life. No correlation has been found between an organism's place in the tree of life and its ability to grow at high salt concentrations. Halophiles occur amid non-halophiles in several instances in the tree of life.

Adaptation to life at high salt concentrations can be achieved in different ways, as previously discussed. The most commonly occurring strategy involves the accumulation of organic osmotic solutes without the need for specialized adaptation of intracellular proteins to high salt. This mechanism occurs in all three domains of life. The second option is the intracellular accumulation of high concentrations of K^+ . This strategy, unlike the use of organic solutes, requires

extensive adaptation of the intracellular enzymatic machinery for it to be functional in the presence of high ionic concentrations. This mechanism is used by a minority of the known halophiles. This minority is represented by the Halobacteriales of the *Archaea* and Haloanaerobiales of the *Bacteria*. The great diversity in strategies used by the halophiles to cope with the high salinity in their environment coupled with the fact that halophily occurs throughout the tree of life in all three domains suggests that adaptation to life at high salt concentrations evolves easily, and has probably occurred many times during the evolution of life.

12.3 Where Do Halophiles Live?

12.3.1 Lakes

Lake environments are numerous and diverse ranging from fresh non-saline to hypersaline, from acidic to alkaline, and cold to hot. Lakes comprise a complex and diverse array of ecosystems. Hypersaline lakes regardless of their other environmental attributes serve as habitats for halophiles. Hypersaline lakes fall into two categories: thalassohaline and athalassohaline.

Thalassohaline lakes are those that originated by evaporation of seawater having an ionic composition reflecting that of seawater, that is with Na⁺ as the dominant cation and Cl⁻ as the dominant anion, followed by $SO_4^{2^-}$, with a pH near neutral. It should be noted, however, that as evaporation of seawater proceeds, different minerals precipitate out of solution before NaCl. These include CaCO₃ as well as gypsum (CaSO₄⁻2H₂O). Therefore, changes in the ionic composition of the water in the brine occurs as evaporation proceeds. For example there are ocean intertidal areas where evaporation occurs causing the salts to precipitate. When this occurs the organisms in the water are trapped in the salt. This environment seems to select for halophilic cyanobacteria (Fig. 12.5) [117]. An example of a thalassohaline lake is the Great Salt Lake in the Western United States.

Athalassohaline environments are natural brines that have ionic compositions different from that of seawater. Examples include soda lakes that are depleted in Mg^{2+} and Ca^{2+} , but contain high concentrations of carbonate and bicarbonate and have a pH greater than 10. Another example is the Dead Sea, which lies on the border between Jordan and Israel, and is slightly alkaline with higher concentrations of Mg^{2+} and Ca^{2+} than Na^+ and K^+ . In general hypersaline athalassohaline lakes occur world-wide with a wide range of ionic compositions.

Due to this wide variation in ionic composition the microbes that inhabit one type of saline environment may not be well adapted to live in a different environment where the salinity is due to different ions, including non-halides. Halides are a group of minerals whose principle anions are halogens. Halogens are a special group of elements that usually have a charge of negative one when chemically combined. The halogens that are found commonly in nature include fluorine, chlorine, iodine and bromine. The typical halide mineral is soft, can be transparent, is generally not very dense, has good cleavage, and often has bright colors. There are only a few common halide minerals. The most common halide mineral is halite (NaCl).

In the broadest sense if organisms live in salts that are not halides, then the organisms are truly not halophilic, but still retain the osmotic adaptation and requirement for high salt. So, such organisms are more generally and correctly termed osmophiles. If brines exist on Mars, they may or may not be halide brines. In general then, the organisms living on Mars in brines would be osmophiles, but may not be halophiles.

Cold Hypersaline Lakes

Many of the cold saline and hypersaline lakes of the world that have been studied are in Antarctica. The high salt content of hypersaline lakes depresses the freezing point of the water allowing them to be liquid at much colder temperatures than they otherwise would be. Among the most studied hypersaline lakes in Antarctica are those in the Vestfold hills, including Organic Lake, Ekho Lake, and Deep Lake (Fig. 12.3). These lakes are relictual seawater catchments that became isolated form the sea about 6000 years ago. Organic Lake is a 7.5 m deep meromictic lake (permanently stratified where the bottom layer and top layer of water do not mix) with an oxycline (steep oxygen gradient) between 4–5 m. The surface waters are moderately saline having a salt concentration of 8 g Γ^1 , with a seasonal average temperature variation ranging from –14 to + 15°C. The bottom of the lake, however, is much more saline with a salt concentration of 210 g Γ^1 and an average temperature of -7° C. Ekho Lake is a 42 m deep meromictic lake with a surface salinity of 14 g Γ^1 that increases with depth to 190 g Γ^1 . The bottom of the lake is a near constant 15°C. Deep Lake is an aerobic meromictic lake, 36 m deep with a salt concentration of 320 g Γ^1 and temperatures reaching down to -18° C.

The microbiota inhabiting these lakes include representatives of all three domains of life. However, it appears that the majority of the organisms are psychrophilic and psychrotolerant members of the *Bacteria* and the *Archaea*. Representatives of the genera *Halomonas* and *Psychroflexus* were the dominant *Bacteria* identified and *Halorubrum* the dominant Archaeal representative [e.g. 31, 52, 63].

Hot Hypersaline Lakes

One of the most studied warm hypersaline lakes is Solar Lake, a 5 m deep lake situated on the Sinai peninsula along the Gulf of Aqaba. During the summer, the lake is completely aerobic and has a salinity of approximately 180–200 g Γ^{-1} . During the winter, the lake becomes stratified due to seawater seepage from the Gulf and occasional influx of rainwater. During stratification the top layer becomes less saline having a salt content of 60 g Γ^{-1} , whereas the bottom remains saline at 180–200 g Γ^{-1} . The bottom layer quickly becomes anaerobic, sulfide rich [55] and reaches temperatures greater than 60°C as a result of heliothermal heating (heat from solar radiation) [20, 21, 23, 59].

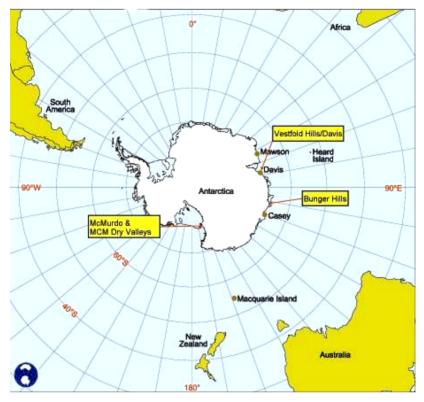


Fig. 12.3 Map of Antarctica showing the location of the Vestfold Hills.

During the summer the water column does not contain a rich dense microbiota, rather it is inhabited by a few photosynthetic microbial communities, most of which are cyanobacteria. During the winter the population within the water column is extremely sparse. In contrast, the bottom water layer of the lake is densely populated with communities of photosynthetic microbes. Most of these microbes are sulfide utilizing anaerobic phototrophs belonging to the *Bacteria* [22].

12.3.2 Solar Salterns

Solar salterns are artificial shallow ponds designed for the production of NaCl by evaporation from seawater. The process occurs in stages. Seawater is transferred into ponds where the water evaporates. When a certain salinity is reached, the water is transferred to another pond where further evaporation occurs and the salinity increases again (Fig. 12.4). This process is continued until the dissolved salts reach saturation and begin precipitating out of solution (Fig. 12.5). CaCO₃ is one of the first salts to precipitate. NaCl precipitates when the total salt concentration increases to just above 300 g l⁻¹. After the NaCl precipitates, the concentrated brine contains primarily Mg²⁺, K⁺, Cl⁻, and SO₄²⁻ [53, 54, 83].



Fig. 12.4 Aerial view of the Cargill salt concentrating ponds in Newark, California, USA

The biota inhabited by these ponds include the full range of halotolerant to extremely halophilic microbes, depending on the salinity of the pond. As the salinity increases, typically microbial mats form that are dominated on the surface by cyanobacteria [6, 24, 53, 82]. As the salinity approaches saturation the ponds typically turn red from the pigmented Archaeal halophiles and *Dunaliella*, although the microbiota is comprised of halophiles from all three domains of life. These brines can easily contain more than 10^7 microbes per ml.

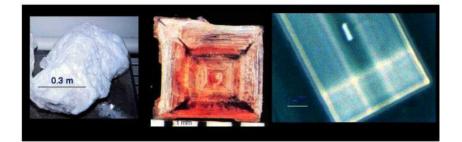


Fig. 12.5 Halophiles as they naturally occur in a large NaCl crystal (left frame). A population of a species of Haloarcula, an extreme halophile belonging to the domain Archaea, shown in a dry NaCl crystal (center frame).

12.3.3 Deep-Sea Brines and Hydrothermal Vents

Deep-sea hypersaline brines have been detected throughout the world, including the Gulf of Mexico, the Red Sea and the Mediterranean Sea [85]. These areas range from 2–2.5 km deep, are anoxic, have a pH range of 5.3 to 6.2, a temperature range from 56°C to 24°C and a salinity range between 210 and 310 g of salt per liter [8, 26, 75].

Little is known about the microbiology of the deep-sea brines. Studies suggest that the number of microbes in the Red Sea brines number approximately 10^5 cells ml⁻¹ [57]. More recently, 16S rDNA studies have shown that both *Archaea* and *Bacteria* inhabit the brine [25, 26], but more definitive studies must be done to truly characterize the biota. Microbiological analyses of the deep-sea brines of the Mediterranean Sea using 16S rDNA analyses reveal that they are inhabited by *Bacteria* and *Archaea* [101, 110]. Biomass measurements using ATP extracted from the water suggest that microbes also inhabit the deep-sea brines in the Gulf of Mexico [65].

Species of *Halomonas* and *Marinobacter*, both *Bacteria*, have been isolated from hydrothermal vent systems [58, 107]. Using 16S rDNA analyses, sequences belonging to the Archaeal genus *Haloarcula* were found in association within black smoker chimneys [107]. A more comprehensive discussion of microbes in hydrothermal vents is presented in Chap. 13 of this volume by Prieur.

12.3.4 Hypersaline Soils

Few studies have been undertaken to determine the microbiology of hypersaline soils at the surface, or beneath the surface of the Earth. Studies have found soils to be inhabited by both Bacterial and Archael halophiles [91, 111].

12.3.5 Can Halophiles Live in Permafrost?

Viable microbes have been found in Arctic permafrost that is 1 to 3 million years old [36, 94, 103, 113], and in permafrost that is probably older in Antarctica [115]. These microbes are psychrotrophs and psychrotolerant mesophiles.

Permafrost, permanently frozen soil, contains unfrozen water [29, 76] allowing mass transfer of ions [87]. This transfer is greatest in microzones with low ice contents and least at sites where the ice content is high or in solid ice [87]. Thus, the physical structure of permafrost makes metabolic activity possible. Using incorporation of ¹⁴C-labeled acetate into lipids by samples of a natural population of bacteria from Siberian permafrost [95] showed that microbes could metabolize in permafrost down to -20° C. Mancinelli et al. (in press and unpublished data) have shown that halophiles can survive freezing in a liquid brine, dried in salt, as well as freeze-thaw cycles.

12.4 Mars

Mars is a cold dry planet bombarded with UV radiation. Overall, it is currently considered inhospitable to life. Yet, Mars is considered the most likely planet, next to Earth, to either harbor life now in protected oases, or to have done so sometime during its past. It is thought that all of the constituents for life are present on the planet, and that the radiation regime would not have precluded the origin and evolution of life [4, 72]. The one factor that would preclude life on Mars at any stage is the lack of liquid water sometime during its past.

12.4.1 History of Water on Mars

The surface of Mars today exhibits carved features such as outflow channels, valleys and lahars that date back to its early history [2, 13, 16, 105, 106]. These features have led many planetary geologists to hypothesize that liquid water once flowed across the Martian surface [1, 2, 13, 14, 16, 17, 68, 74, 89, 90, 105, 106]. A thorough review of water on Mars and its history is presented elsewhere in this volume.

12.4.2 Evaporites on Mars

Evaporite deposits consisting primarily of halite (NaCl), gypsum (CaSO₄ 2H₂O), or anhydrite (CaSO₄) and containing bacterial and algal assemblages are well known in the fossil record and are still geographically widespread. [E.g. 98, 78] showed that microorganisms entrapped in fluid inclusions of growing NaCl crystals may be motile for three weeks, and may remain viable for up to six months. Rothschild et al. [98] demonstrated that microorganisms inhabiting gypsum halite crusts perform carbon and nitrogen fixation while inside the dry

crystals of the crust for at least a year. Although highly controversial, bacteria might survive for millions of years in the fluid inclusions of salt deposits including evaporites [103].

Several studies have speculated on the presence of evaporite deposits on Mars [e.g. 18, 97]. However, the presence of evaporitic deposits has not been confirmed. The potential for evaporites to occur on Mars and their relationship to liquid water and life has been reviewed by Rothschild [97].

12.4.3 Water and Life on Mars

A key question for life is, did water exist on the surface of Mars to allow life to originate and evolve? Current attempts to answer this question are based, among others, on the interpretation of photographs from recent missions to Mars. The valley networks in the southern highlands suggest that water flowed across the Martian surface early in the history of the planet. Recently revealed gullies may be sites of present day near surface liquid water [70, 15] (see also Chaps. 9 and 10). Photographs of Holden Crater show apparent layers that may be remnants of former shorelines of a standing body of water on Mars [e.g. 88]. The change in albedo observed near Schiaparelli Crater may be due to evaporites [e.g. 10].

Data collected during landed missions to Mars, as well as from analyses of the Martian meteorites suggest that all of the necessary chemical constituents for life existed on Mars during its early history [e.g. 4]. Further, it has been suggested that the environmental conditions on early Mars would not preclude the origin and evolution of life on that planet [72]. A primary habitat for any life that may have evolved on Mars would have been water, which would certainly have contained various dissolved minerals. Mars is thought to have lost most of its atmosphere as time progressed (see Chap. 2 by Lammer et al.). As this process continued, the water on the planet's surface would have frozen and evaporated, and although none have been found, high saline brine pockets and evaporite deposits would have formed. These brine pockets would most likely occur deep beneath the surface and may be an oasis for an extant biota, or the last refuge for an extinct Because brine pockets would have a high osmolarity, the most likely biota. organisms to survive in a brine pocket, or an evaporite are osmophiles that could be halophiles if the salt is halide.

The presence of osmophiles and halophiles has been documented in terrestrial systems, such as in gypsum-halite crusts in intertidal areas of the ocean (Fig. 12.6) [98], and in NaCl crystals [86, 99] (Fig. 12.5).

Water in the liquid state serves as the solvent for many biogenic compounds and mediates important geochemical (abiotic), prebiotic and biological reactions. Liquid water is important to the reactions necessary for the origin of life and its continued evolution because it is the primary intracellular solvent. As a consequence, the temperature regime of at least some portion of a planet must be above the triple point of water for life to have evolved.



Fig. 12.6 Naturally occurring gypsum halite crusts along the coast of the Pacific Ocean near Guerrero Negro, Baja California, Mexico. The right panel shows a green band of a population of halophilic cyanobacteria that live in the salt.

During the past 30 years numerous microbiological investigations have been conducted on Antarctic Dry Valley soils, some in preparation for the Viking mission to Mars [7, 11, 12, 47, 49]. The data from these investigations indicated that the number of viable microorganisms in the soil of the Antarctic Dry Valleys declined as a function of soil moisture (more negative water potential). The data suggest that water is the factor limiting microbial activity in the soil rather than temperature [49]. The same would be true for Mars if life existed on that planet.

Investigations were undertaken during the 1960s and 1970s to determine the effect of freeze-thaw cycles at one atmosphere and at reduced atmospheric pressures. For example, it was demonstrated that a variety of soil microorganisms survived being subjected to freeze-thaw cycles using temperature ranges from +25 to -60° C [30, 39, 45, 46, 62, 117], low atmospheric pressures down to 10 mbar [30, 43, 62, 96, 104], and levels of moisture in soils of ~0.5 wt % [46, 59]. The results of these studies suggest that the most important factor for the survival and growth of life is the availability of liquid water.

It is known that changes in water content of soils have profound effects on microbial activity [41], which result in changes in soil microbial populations [40]. Water potential is the free energy of water in a system, relative to the free energy of a reference pool of pure, free water. Pure free water has, by definition, zero water potential, and for example, the potential energy of water in unsaturated soils is negative. The tendency for water for microbes in the soil as the potential is lowered. The water potential of a microbial cell in soil is likely to be near equilibrium with its microenvironment within the soil (see e.g. [28] for a review). The prospects for the origin of life on Mars would only have been favorable if the water potential was higher than it is today. Due to the necessity of liquid water, life undoubtedly arose in liquid water. Thus, life on Mars would be located in association with water-laden deposits, aquifers or soils that were once saturated with liquid water.

12.5 Conclusions

Although the Viking mission found no evidence of life on the Martian surface (reviewed by [60, 73]) the search for extant and extinct life on Mars continues. There is mounting evidence from missions to Mars that there was liquid water on the surface of the planet early in its history [e.g. 70]. Additionally, there may be occasional liquid water on the surface today resulting from melting snow fields [15]. Further, data from recent missions suggest that evaporites exist on Mars [10, 18, 27, 97].

Halophily/osmophily is not rare and probably evolves easily, and arose many times. If life evolved on Mars, then osmophily probably evolved as well. Osmophiles are best suited for life in brines and evaporites. As discussed previously, halophiles/osmophiles are found in a variety of cold environments. Studies have shown that microbes can metabolize in permafrost [94]. Halophiles/osmophiles are better adapted than other organisms to survive in brines, drying and freeze-thaw cycles, as may have occurred on Mars.

The last vestiges of an extinct Martian biota, or an extant biota could be present in a cold, desiccating environment, perhaps in brine pockets within permafrost. Therefore, it is possible that the last organisms to survive on the Martian surface were osmophiles, and that any near surface extant life on Mars may be osmophiles.

12.6 References

- 1 Anders E, Owen T (1977) Mars and Earth: origin and abundance of volatiles. Science 198: 453-465
- 2 Baker VR, Milton DJ (1974) Erosion by catastrophic floods on Mars and Earth. Icarus 23: 27-41
- 3 Baker VR (1982) The Channels of Mars. Univ. of Texas Press, Austin
- 4 Banin A, Mancinelli RL (1995) Life on Mars? I. The chemical environment. Adv. Space Res. 15(3): 163-170
- 5 Ben-Amotz A, Grunwald T (1981) Osmoregulation in the halotolerant alga *Asteromonas gracilis*. Plant Physiol. 67: 613-616
- 6 Bauld J (1981) Occurrence of benthic microbial mats in saline lakes. Hydrobiologia 81: 87-111
- 7 Benoit RE, Hall CL (1970) The microbiology of some Dry Valley soils of Victoria Land, Antarctica. In Holdgate MW (ed) Antarctic Ecology, Vol. 3. Academic Press, New York, pp 697-701
- 8 Brooks JM, Bright TJ, Bernard BB, Schwab CR (1979) Chemical aspects of a brine pool of the East Flower Garden bank, northwestern Gulf of Mexico. Limnol. Oceanogr. 24: 735-745
- 9 Brown AD (1976) Microbial water stress. Bacteriol. Rev.40: 803-848
- 10 Cabrol NA, Grin EA (1999) Evolution of lacustrine environments on Mars and their significance: the case for the Brazos Lakes and East Terra Meridiani Basins as landing

sites for Surveyor 2001. Workshop on Mars 2001: Integrated Science in Preparation for Sample Return and Human Exploration, p 25

- 11 Cameron RE (1972) Microbial and ecologic investigations in Victoria Valley, southern Victoria Land, Antarctica. In Lano GA (ed) Antarctic Terrestrial Biology, Antarctic Research Series 20: 195-210, American Geophysical Union, Washington, DC
- 12 Cameron RE, King J, David CN (1970) Microbiology, ecology and microclimatology of soil sites in dry valleys of southern Victoria Land, Antarctica. In Holdgate MW (ed) Antarctic Ecology, Vol. 2, Academic Press, New York, pp 702-716
- 13 Carr MH (1981) The Surface of Mars. Yale Univ. Press, New Haven
- 14 Carr MH (1986) Mars: speculations on a water-rich planet. Icarus 68: 187-216
- 15 Christensen PR (2003) Formation of recent Martian gullies through melting of extensive water-rich snow deposits. Science 422: 45-47
- 16 Christianson EH (1989) Lahars in the Elysium Region of Mars. Geology 17: 203-206
- 17 Clark BC, Baird AK (1979) Volatiles in the Martian regolith. Geophys. Res. Lett. 10: 811-814
- 18 Clark BC, van Hart DC (1981) The salts of Mars. Icarus 45: 370-378
- 19 Clavero E, Hernández-Mariné M, Grimalt JO, Garcia-Pichel F (2000) Salinity tolerance of diatoms from thalassic hypersaline environments. J. Phycol. 36: 1021-1034
- 20 Cohen Y, Krumbein WE, Shilo M (1975) The Solar Lake: limnology and microbiology of a hypersaline, monomictic heliothermal heated sea-marginal pond (Gulf of Aquaba, Sinai). Rapp. Comm. Int. Mer. Medit. 23: 105-107
- 21 Cohen Y, Krumbein WE, Goldberg M (1977a) Solar Lake (Sinai) I: physical and chemical limnology. Limnol. Oceanogr. 22: 597-608
- 22 Cohen Y, Krumbein WE, Shilo M (1977b) Solar Lake (Sinai) II: distribution of photosynthetic microorganisms and primary production. Limnol. Oceanogr. 22: 609-620
- 23 Cytryn E, Miinz D, Oremland RS, Cohen Y (2000) Distribution and diversity of Archaea corresponding to the limnological cycle of a hypersaline stratified lake (Solar Lake, Sinai, Egypt). Appl. Environ. Microbiol. 66: 3269-3276
- 24 Davis JS, Giordano M (1996) Biological and physical events involved in the origin, effects, and control of organic matter in solar saltworks. Int. J. Salt Lake Res. 4: 335-347
- 25 Eder W, Jahnke LL, Schmidt M, Huber R (2001) Microbial diversity of the brineseawater interface of the Kebrit Deep, Red Sea, studied via 16S rRNA gene sequences and cultivation methods. Appl. Environ. Microbiol. 67: 3077-3085
- 26 Eder W, Ludwig W, Huber R (1999) Novel 16S rRNA gene sequences retrieved from highly saline brine sediments of Kebrit Deep, Red Sea. Arch. Microbiol. 172: 213-218
- 27 Edgett KS, Parker TJ (1998) "Bright" aeolian dunes on Mars: Viking Orbiter observations. 29th Lunar Planet. Sci. Conf. 1338
- 28 Elliott LF (1981) Water Potential Relations in Soil Microbiology. Soil Science Society of America, Madison
- 29 Ershov ED (1998) General Geocryology. Cambridge Univ. Press, Cambridge, United Kingdom
- 30 Foster TL, Winans L Jr, Casey RC, Kirschner LE (1978) Response of terrestrial microorganisms to a simulated Martian environment. Appl. Environ. Microbiol. 35: 730-737

- 31 Franzmann PD (1991) The microbiota of saline lakes of the Vestfold Hills, Antarctica. In Rodriguez-Valera F (ed) General and Applied Aspects of Halophilic Bacteria. Plenum Publishing, New York, p 9-14
- 32 Galinski EA, Trüper HG (1982) Betaine, a compatible solute in the extremely halophilic phototrophic bacterium *Ectothiorhodospira*. Eur. J. Biochem. 149: 135-139
- 33 Galinski EA (1993) Compatible solutes of halophilic eubacteria: molecular principles, water-solute interactions, stress protection. Experientia 49: 487-496
- Galinski EA (1995) Osmoadaptation in bacteria. Adv. Microbial Physiology 37: 273-328
- 35 Garcia-Pichel F, Prufert-Bebout L, Muyzer G (1996) Phenotypic and phylogenetic analyses show *Microcoleus chtonoplastes* to be a cosmopolitan cyanobacterium. Appl. Environ. Microbiol. 62: 3284-3291
- 36 Gilichinsky D, Wagener S (1995) Microbial life in permafrost: a historical review. Permafrost Periglacial Processes 6: 243-250
- 37 Ginzburg M, Ginzburg BZ, Wayne R (1999) Ultrarapid endocytotic uptake of large molecules in *Dunaliella* species. Protoplasma 206: 73-86
- 38 Grant WD, Larsen H (1989) Extremely halophilic archaeobacteria, order Halobacteriales ord. nov. In Staley JT, Bryant MP, Pfennig N, Holt JG (eds) Bergey's Manual of Systematic Bacteriology, Vol. 3. Williams & Wilkins, Baltimore, pp 2216-2233
- 39 Green RH, Taylor DM, Gustan EA, Fraser SJ, Olson RL (1971) Survival of microorganisms in a simulated Martian environment. Space Life Sci. 3: 12-24.
- 40 Griffin DM (1972) Ecology of Soil Fungi. Chapman and Hall, London.
- 41 Griffin DM (1981) Water potential as a selective factor in the microbial ecology of soils. In Elliott LF (ed) Water Potential Relations in Soil Microbiology. Soil Science Society of America, Madison, pp 141-151
- 42 Gunde-Cimerman N, Zalar P, de Hoog S, Plemenitas A (2000) Hypersaline waters in salterns – natural ecological niches for halophilic black yeasts. FEMS Microbiol. Ecol. 32: 235-240
- 43 Hagen CA, Jones R (1963) Life in extraterrestrial environments. Quarterly Stat. Report, Sept.-Nov. NASr 22: IITRI Proj. C194
- 44 Hagen CA, Hawrylewicz EJ, Ehrlich R (1967) Survival of microorganisms in a simulated Martian environment. II. Moisture and oxygen requirements for germination of *Bacillus cereus* and *Bacillus subtilis* var., *niger* spores. Appl. Microbiol. 15: 285-291
- 45 Hawrylewicz EJ, Hagen CA, Ehrlich R (1965) Survival of microorganisms in a simulated Martian environment. Life Sci. Space Res. III, 64
- 46 Hawrylewicz EJ, Hagen CA, Ehrlich R (1966) Survival and growth of potential microbial contaminants in severe environments. Life Sci. Space Res. IV, 166
- 47 Hirsch P, Hoffmann B, Gallikowski CA, Mevs U, Siebert J, Sittig M (1988) Diversity and identification of heterotrophs from Antarctic rocks of the McMurdo Dry Valley (Ross Desert). Polarforschung 58: 261-269
- 48 Hochstein LI (1991) Nitrate reduction in the extremely halophilic bacteria. In Rodriguez-Valera F (ed) General and Applied Aspects of Halophilic Microorganisms. Plenum Press, New York, pp 129-137
- 49 Horowitz NH, Cameron RE, Jubbard JS (1972) Microbiology of the dry valleys of Antarctica. Science 176: 242-245

- 50 Imhoff JF (1988) Halophilic phototrophic bacteria. In Rodriguez-Valera R (ed) Halophilic Bacteria. CRC Press, Boca Raton, pp 85-108
- 51 Imhoff JF (2001) True marine and halophilic anoxygenic phototrophic bacteria. Arch. Microbiol. 176: 243-254
- 52 James SR, Burton HR, McMeekin TA, Mancuso CA (1994) Seasonal abundance of Halomonas meridiana, Halomonas subglaciescola, Flavobacterium gondwanense, and Flavobacterium salegens in 4 Antarctic Lakes. Antarct. Sci. 6: 325-332
- 53 Javor B (1989) Hypersaline Environments. Microbiology and Biogeochemistry. Springer-Verlag, Berlin, Heidelberg, New York
- 54 Javor BJ (2002) Industrial microbiology of solar salt production. J. Ind. Microbiol. Biotechnol. 28: 42-47
- 55 Jorgensen BB, Cohen Y (1977) Solar Lake (Sinai). 5. The sulfur cycle of the benthic cyanobacterial mats. Limnol. Oceanogr. 22: 657-666
- 56 Kamekura M, Kates M (1999) Structural diversity of membrane lipids in members of Halobacteriaceae. Biosci. Biotechnol. Biochem. 63: 969-972
- 57 Karbe L (1987) Hot brines and the deep sea environment. In Edwards AJ, Head SM (eds) Key Environments. Red Sea. Pergamon Press, Oxford, pp 70-89
- 58 Kaye JZ, Baross JA (2000) High incidence of halotolerant bacteria in Pacific hydrothermal-vent and pelagic environments. FEMS Microbiol. Ecol. 32: 249-260
- 59 Kirkland DW, Bradbury JP, Dean WE (1983) The heliothermic lake a direct method of collecting and storing solar energy. Arch. Hydrobiol. Suppl. 65: 1-60
- 60 Klein HP (1979) The Viking mission and the search for life on Mars. Rev. Geophys. Space Phys. 17: 1655-1662
- 61 Kushner DJ (1964) Lysis and dissolution of cells and envelopes of an extremely halophilic bacterium. J. Bacteriol. 87: 1147-1156
- 62 Kuzurina LA, Yakashina VM (1970) Behavior of certain soil microorganisms in the "artificial Mars" chamber. In Imshenetskii AA (ed) Extraterrestrial Life and its Detection Methods, NASA TTF-710
- 63 Labrenz M, Hirsch P (2001) Physiological diversity and adaptations of aerobic heterotrophic bacteria from different depths of hypersaline, heliothermal and meromictic Ekho Lake (East Antarctica). Polar Biol. 24: 320-327
- 64 Lai M-C, Hong T-Y, Gunsalus PR (2000) Glycine betaine transport in the obligate halophilic archaeon *Methanohalophilus portucalensis*. J. Bacteriol. 182: 5020-5024
- 65 LaRock P, Lauer RD, Schwarz JR, Watanabe KK, Wiesenberg DA (1979) Microbial biomass and activity distribution in an anoxic, hypersaline basin. Appl. Envrion. Microbiol. 37: 466-470
- 66 Larsen H (1967) Biochemical aspects of extreme halophilism. Adv. Microb. Physiol. 1: 97-132
- 67 Le Rudulier D, Bouillard L (1983) Glycine betaine, an osmotic effector in *Klebsiella pneumonia* and other members of the Enterobacteriaceae. Appl. Environ. Microbiol. 46: 152-159
- 68 Lewis JS (1972) Metal/silicate fraction in the Solar System. Earth Planet. Sci. Lett. 15: 286-290
- 69 Mackay MA, Norton RS, Borowitzka LJ (1984) Organic osmoregulatory solutes in cyanobacteria. J. Gen. Microbiol. 130: 2177-2191
- 70 Malin MC, Edgett KS (2000) Sedimentary rocks of Early Mars. Science 290: 1927-1937

- 71 Mancinelli RL, Hochstein LI (1986) The occurrence of denitrification in extremely halophilic bacteria. FEMS Microbiol. Lett. 35: 55-58
- 72 Mancinelli RL, Banin A (1995) Life on Mars? II. Physical restrictions. Adv. Space Res. 15(3): 171-178
- 73 Mancinelli RL (1998) Prospects for the evolution of life on Mars: Viking 20 years later. Adv. Space Res. 22(3): 471-477
- 74 McElroy MB, Kong TY, Yung YL (1977) Photochemistry and evolution of Mars' atmosphere: a Viking perspective. J. Geophys. Res. 82: 4379-4388.
- 75 Miller AR, Densmore CD, Degens FT, Hathaway JC, Manheim FT, McFarlin PF, Pocklington R, Jokela A (1966) Hot brines and recent iron deposition in deeps of the Red Sea. Geochim. Cosmochim. Acta 30: 341-359
- 76 Nersesova ZA, Tsytovich NA (1966) Unfrozen water in frozen soils. In Permafrost: Proc. International Conference. National Academy of Sciences, Washington, D.C., pp 230-234
- 77 Niemetz R, Kärcher U, Kandler O, Tindall BJ, Kønig H (1997) The cell wall polymer of the extremely halophilic archaeon *Natronococcus occultus*. Eur. J. Biochem. 249: 905-911
- 78 Norton CF, Grant WD (1988) Survival of halobacteria within fluid inclusions in salt crystals. J. Gen. Microbiol. 134: 1365-1373
- 79 Nübel U, Garcia-Pichel F, Muyzer G (2000) The halotolerance and phylogeny of cyanobacteria with tightly coiled trichomes (*Spirulina* Turpin) and the description of Halospirulina tapeticola gen. nov., sp. nov. Int. J. Syst. Evol. Microbiol. 50: 1265-1277
- 80 Ollivier B, Caumette P, Garcia J-L, Mah, RA (1994) Anaerobic bacteria from hypersaline environments. Microbiol. Rev. 58: 27-38
- 81 Oren A, Ventosa A, Gutierrez MC, Kamekura M (1999) *Haloarcula quadrata* sp. nov., a square, motile archaeon isolated from a brine pool in Sinai (Egypt). Int. J. Syst. Bacteriol. 49: 1149-1155
- 82 Oren A (2000a) Salts and brines. In Whitton, BA Potts M. (eds) Ecology of Cyanobacteria: Their Diversity in Time and Space. Kluwer Academic Publishers, Dordrecht, pp 281-306
- 83 Oren A (2000b) Life at high salt concentrations. In Dworkin M, Falkow S, Rosenberg E, Schleifer K-H, Stackebrandt E (eds) The Prokaryotes. A Handbook on the Biology of Bacteria: Ecophysiology, Isolation, Identification, Applications. 3rd ed. Springer-Verlag, Berlin, Heidelberg, New York (electronic publication)
- 84 Oren A (200a) The order *Halobacteriales*, In Dworkin M, Falkow S, Rosenberg E, Schleifer K-H, Stackebrandt E (eds) The Prokaryotes. A Handbook on the Biology of Bacteria: Ecophysiology, Isolation, Identification, Applications. 3rd ed. Springer-Verlag, Berlin, Heidelberg, New York (electronic publication)
- 85 Oren A (2002a) Halophilic Microorganisms and their Environments. Kluwer Academic Publishers, Norwell
- 86 Oren A (2002b) Diversity of halophilic microorganisms: environments, phylogeny, physiology and applications. J. Ind. Micorbiol. Biotechnol. 28: 56-63
- 87 Ostroumov VE, Siegert C (1996) Exobiological aspects of mass transfer in microzones of permafrost deposits. Adv. Space Res. 18(12): 79-86
- 88 Parker TJ, Clifford SM, Banerdt WB (2000) Argyre Planitia and the Mars global hydrologic cycle. 31st Lunar Planet. Sci. Conf. 2033
- 89 Pieri D (1980) Martian valleys: morphology, distribution, age, and origin. Science 210: 895-897

- 90 Pollack JB, Black DC (1979) Implications of the gas compositional measurements of Pioneer Venus for the origin of planetary atmospheres. Science 205: 56-59
- 91 Quesada E, Ventosa A, Rodriguez-Valera F, Ramos-Cormenzana A (1982) Types and properties of some bacteria isolated from hypersaline soils. J. Appl. Bacteriol. 53: 155-161
- 92 Rainey FA, Zhilina TN, Boulygina ES, Stackebrandt E, Tourova TP, Zavarzin GA (1995) The taxonomic status of the fermentative halophilic anaerobic bacteria: description of Halobacteriales ord. nov., *Halobacteroidaceae* fam. nov., *Orenia* gen. nov. and further taxonomic rearrangements at the genus and species level. Anaerobe 1: 185-199
- 93 Reed RH, Chudek JA, Foster R, Stewart WDP (1984) Osmotic adjustment in cyanobacteria from hypersaline environments. Arch. Microbiol. 138: 333-337
- 94 Rivkina E, Gilichinsky D, Wagener S, Tiedje J, McGrath J (1998) Biogeochemical activity of anaerobic microorganisms from buried perma-frost sediments. Geomicrobiol. J. 15: 187-193
- 95 Rivkina EM, Friedmann EI, McKay CP, Gilichinsky DA (2000) Metabolic activity of permafrost bacteria below the freezing point. Appl. Environ. Microbiol. 66: 3230
- 96 Roberts TL (1963) Studies with a simulated Martian environment. J. Astronaut. Sci. 10: 65-74
- 97 Rothschild LJ (1990) Earth analogs for Martian life. Microbes in evaporites, a new model system for life on Mars. Icarus 88: 246-260
- 98 Rothschild LJ, Giver LJ, White MR, Mancinelli RL (1994) Metabolic activity of microorganisms in gypsum-halite crusts. J. Phyc. 30: 431-438
- 99 Rothschild, LJ, Mancinelli RL (2001) Life in extreme environments. Nature 409: 1092-1101
- 100 Russell NJ (1993) Lipids of halophilic and halotolerant microorganisms. In Vreeland RH, Hochstein LI (eds) The Biology of Halophilic Bacteria. CRC Press, Boca Raton, pp 163-210
- 101 Sass AM (2003) Novel microorganisms from deep-sea hypersaline anoxic basins of the Eastern Mediterranean Sea. Abstract for the Annual Meeting of the German Microbiologist Association, March 23-26, Berlin
- 102 Schleifer KH, Steber J, Mayer H (1982) Chemical composition and structure of the cell wall of *Halococcus morrhuae*. Zbl. Bakt. Hyg. 1 Abt. Orig. C 3: 171-178
- 103 Shi T, Reeves RH, Gilichinsky DA, Friedmann EI (1997) Characterization of viable bacteria from Siberian permafrost by 16S rDNA se-quencing. Microb. Ecol. 33: 169-179
- 104 Silverman GJ, Davis SN, Beecher N (1963) Resistivity of spores to ultraviolet and gamma radiation while exposed to ultra high vacuum or at atmospheric pressure. Appl. Microbiol. 15: 510-515
- 105 Squyres SW (1984) The history of water on Mars. Ann. Rev. Earth Planet. Sci. 12: 83-106
- 106 Squyres SW, Carr MH (1986) Geomorphic evidence for the distribution of ground ice on Mars. Science 231: 249-25.
- 107 Takai K, Komatsu T, Inagaki F, Horikoshi K (2001) Distribution of archaea in a black smoker chimney structure. Appl. Environ. Microbiol. 67: 3618-3629
- 108 Thiemann B, Imhoff, JF (1996) Differentiation of *Ectothiorhodospiraceae* based on their fatty acid composition. Syst. Appl. Microbiol. 19: 223-230

- 109 Timasheff SN (1992) A physiochemical basis for the selection of osmolytes by nature. In Somero GN, Osmond CB, Bolis CL (eds) Water and Life. Springer-Verlag, Berlin, Heidelberg, New York, pp 70-86
- 110 Van der Wielen PWJJ, Brons JK, Bolhuis H (2003) Novel archaeal and bacterial divisions from Mediterranean deep hypersaline anoxic basins. Abstract for the spring meeting of the Dutch Society for Microbiology, April 15-16, Arnhem
- 111 Ventosa A, Nieto JJ, Oren A (1998) Biology of moderately halophilic aerobic bacteria. Microbiol. Mol. Biol. Rev. 62: 504-544
- 112 Ventura S, Viti C, Pastorelli R, Giovannetti L (2000) Revision of species delineation in the genus *Ectothiorhodospira*. Int. J. Syst. Evol. Microbiol. 50: 583-591
- 113 Vorobyova E, Soina V, Gorlenko M, Minkovskaya N, Zalinova N, Mamukelashvili A, Gilichinsky D, Rivkina E, Vishnivetskaya T (1997) The deep cold biosphere: facts and hypothesis. FEMS Microbiol. Rev. 20: 277-290
- 114 Walsby AE (1971) The pressure relationships of gas vacuoles. Proc. R. Soc. London B 178: 301-326
- 115 Wilson GS, Braddock P, Forman SL, Friedmann EI, Rivkina EM, Chanton JP, Gilichinsky DA, Fyodorov-Davidov DG, Ostroumov VE, Sorokovikov V, Wizevich MC (1998) Coring for microbial records of Antarctic climate. Antarct. J. U. S. 1996 Review 31 (2): 83-86
- 116 Yancey PH, Clark ME, Hand SC, Bowlus RD, Somero GN (1982) Living with water stress: evolution of osmolyte systems. Science 217: 1214-1216
- 117 Young RS, Deal PH, Whitfield O (1968) The response of spore-forming vs. non-sporeforming bacteria to diurnal freezing and thawing. Space Life Sci. 1: 113-117

13 Microbiology of Deep-Sea Hydrothermal Vents: Lessons for Mars Exploration

Daniel Prieur

A large proportion of the Earth (70 %) is covered by seas and oceans. Oceanic waters below one kilometre depth constitute the deep-sea, which represents 75 % of the total volume of the oceans [20]. However, even if it was estimated that these water masses might represent 62 % of the Earth's biosphere, ocean bottoms were regarded as low animal density ecosystems until 1977.

The reason for this is that sunlight does not penetrate water layers below a few hundred metres depth, where total darkness prevails. This lack of light prevents photosynthesis, and consequently primary production (organic matter synthesis by autotrophic algae). Also, deep oceanic environments are cold with an average temperature of 2°C, exposed to elevated hydrostatic pressure (10 MPa per km), and, from a trophic point of view, depend on the upper ocean layers: only corpses, debris or feces from organisms living in the photic zones, or what remains after in route bacterial degradation, may reach the bottom through sedimentation processes [20].

The discovery of deep-sea hydrothermal vents in 1977 in the Galápagos area greatly increased our knowledge about deep oceanic environments [10]. Two years later, the discovery of the "Black Smokers" led to the description of novel species within the Bacteria and Archaea domains that thrive in very extreme conditions, using a variety of organic and mostly inorganic compounds. These examples of extremophilic chemosynthetic life forms constitute novel references for life detection in the Solar System and particularly on Mars.

In this last chapter we dive into such deep-sea hydrothermal vents where microbial life flourishes, and think about the implications for Mars.

13.1 Deep-Sea Hydrothermal Vents

13.1.1 Discovery

The hydrothermal system at the ocean bottom is a consequence of plate tectonics of the Earth's crust. Plates are bordered by submarine chains of mountains (oceanic ridges) for a total distance of 60 000 km. Analysis of the water column above certain ridge segments revealed seawater anomalies such as slight increases in temperature, and manganese or methane concentrations. To explain these anomalies a hydrothermal circulation was hypothesised: after penetration through cracks of the ocean floor, seawater is heated when it approaches the magma chamber, becomes enriched with chemical elements and vents out because of its low density [10].

This hypothesis was confirmed after a series of dives organised in 1977 in the Galápagos area at 2000 m depth, using the manned deep-sea submersible "Alvin". But the great surprise for Alvin passengers and pilot was the discovery of unexpected luxuriant animal communities around warm water springs. Two years later, in 1979, again on the East-Pacific Rise, Alvin passengers discovered spectacular mineral constructions named "black smokers", venting out high-temperature (350°C) particle-rich fluids.

These findings were the starting point for novel expeditions and discoveries of hydrothermal vents in numerous tectonically active zones of the sea floor (ridges, back-arc) basins located in the Pacific, Atlantic and Indian Oceans at depths ranging from 800 m to 3600 m.

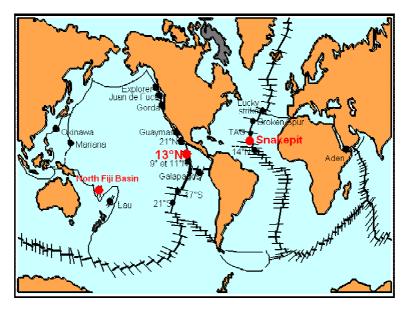


Fig. 13.1 Locations of hydrothermal vents on Earth. Courtesy of Y. Fouquet (Ifremer).

13.1.2 Vent Geochemistry

Physicochemical processes that occur at deep-sea hydrothermal vents have been well documented [15]. Hydrothermal circulation occurs in areas exposed to tectonic activity. There, seawater penetrates through cracks of the oceanic crust down to depths of several kilometres below the sea floor, where it interacts with hot basaltic rocks. The seawater becomes an acidic solution enriched with minerals and metallic elements. This superheated solution (kept liquid because of the high hydrostatic pressure) rises up through cracks to the ocean floor. When this solution mixes with cold oxygenated seawater, minerals and particularly calcium sulphate and polymetallic sulphides ("black smoke") precipitate. Parts of these precipitates build up the black smokers from which fluids vent at temperatures up to 350°C. However, hot fluids may mix with cold water before reaching the sea bottom. In this case, fluids vent out at lower temperatures (10–30°C), and surrounding areas may be colonised by invertebrate communities [10].

Table 13.1 Chemical composition of standard seawater and hydrothermal fluids from the mid-Atlantic Ridge (adapted from Charlou et al. [36], reprinted with permission from Elsevier). If two values are given, they indicate the possible range. mM, μ M and nM stand for millimolar (1/1000 of a mole per litre), micromolar and nanomolar concentration. PDB is a standard unit to express the isotopic composition.

	Standard	Logatchev	Mark-1/2	TAG
	seawater	(14°45'N)	(23°N)	(26°N)
Depth (m)		3000	3460	3670
Temp. (°C)	2	347/352	335/350	321/290
pН	7.8	3.3	3.9/3.7	3.1
$Si(OH)_4$ (mM)	<0.2	8.2	18.2/18.3	22.0
Cl (mM)	546	515	559/559	659
Br (µM)	838	818	847	880/1045
SO_4 (mM)	26.2	0	0	0
Na (mM)	464	430	510/559	584
Li (µM)	26	245	843/849	411
K (mM)	9.8	21.9	23.6/23.9	18.0
Rb (µM)	1.3	27.7	10.5/10.8	10
Cs (nM)	2.3	385	177/181	110
Mg (mM)	53	0	0	0
Ca (mM)	10.2	27.3	9.9/10.5	26.0
Sr (µM)	87	138	50/51	99
Ba (µM)	0.14	>4.5	>4.3	>19
Fe (µM)	< 0.001	2500	2180/1832	1640
$Mn (\mu M)$	< 0.001	330	491/493	1000
Cu (µM)	0.007	15/50	17/10	150
Zn (µM)	0.01	25/30	50/47	46
Gases				
H ₂ S (mM)	0	0.5/0.8	5.9/5.9	6.7
$CO_{2}(mM)$	2.3	10.1	5.2/6.7	2.9/3.4
$\delta^{13}C(CO_2)$	-5.1/-5.9	-4.3	-	-8.4/-10.0
(‰ PDB)				
CH_4 (mM)	0.0003	2.1	0.023/0.062	0.124/0.147
$\delta^{13}C(CH_{A})$	-	-13.6	-	-8.0/-9.5
(‰ PDB)				
CO (nM)	0.3	-	-	-
Ar (µM)	16	12	17/35 20/40	
N ₂ (mM)	0.59	3.0	1.20/3.37	0.90/0.89
H_{2} (mM)	0.0004	12.0	0.19/0.48	0.15/0.37

Table 13.1 (continued)

	Broken Spur	Rainbow	Lucky Strike	Menez Gwen
	(29°N)	(36°14'N)	(37°17'N)	(37°50'N)
Depth (m)	3200/3300	2300	1700	850
Temp. (°C)	356-364	365	170/364	275/284
pH	-	2.8	3.5/3.7	4.2/4.3
$Si(OH)_4$ (mM)	-	6.9	11.5/16.3	7.7/11.6
Cl (mM)	460	750	442/533	357/381
Br (µM)	749/765	1178	735/924	666/710
SO_4 (mM)	0	0	0	0
Na (mM)	419/422	553	347/446	312/319
Li (µM)	1006/1033	340	278/357	238/274
K (mM)	18.1/19.6	20.4	21.1/26.7	22.1/23.8
Rb (µM)	13.0/13.6	36.9	22.7/39.1	20.3/29.4
Cs (nM)	139/146	333	200/280	330
Mg (mM)	0	0	0	0
Ca (mM)	11.8/12.8	66.6	31.3/38.2	29.7/33.1
Sr (µM)	42.9/48.0	200	67/119	100/111
Ba (µM)	>12.9/>21.3	>67	10/52	>12
Fe (µM)	1684/2156	24050	30/863	<2/18
Mn (µM)	250/260	2250	84/446	59/71
Cu (µM)	28.3/69.6	121/162	4/26	0.6/3
Zn (µM)	40.8/88.0	115/185	5/57	2.4/4.3
Gases				
$H_2S(mM)$	8.5/11.0	1.2	2.5/3.0	<1.5
$CO_{2}(mM)$	6.9/7.1	16	13/28	17/20
$\delta^{13}C(CO_2)$	-9.0	-3.15	-7.2/-10.6	-6.8/-9.1
(‰ PDB)				
CH_4 (mM)	0.065/0.13	2.5	0.50/0.97	1.35/2.63
$\delta^{13}C(CH_{4})$	-18/-19	-15.8	-12.7/-13.7	-18.8/-19.6
(‰ PDB)				
CO (nM)	-	5000	_	_
Ar (µM)	-	-	11/30	11/38
N_2 (mM)	-	1.8	0.61/0.97	0.60/1.90
H, (mM)	0.43/1.03	16	0.02/0.73	0.024/0.048

Vent fluids have a chemical composition different from seawater, and are characterised by a low pH, and a high concentration of dissolved gases (hydrogen sulphide H_2S , methane CH_4 , sometimes carbon monoxide CO (only in Rainbow), carbon dioxide CO_2 , hydrogen H_2) and minerals (silicons, iron, manganese, zinc, etc). The fluid composition, temperature and emission speed (several cm/s to 2 m/s) may vary depending on the vent site location and its geological context, and they consequently influence the mineral composition of the smokers. Among the compounds present in the fluids, H_2S , CH_4 , iron or manganese show very elevated concentrations (Table 13.1), while all these compounds are not detected in seawater. Also, copper and zinc reach high concentrations (Table 13.1) with an enrichment factor of 1500 and 4000, respectively, with respect to seawater. On the

contrary, magnesium and sulphate ions present in seawater are absent in vent fluids [15].

13.2 Microbial Communities

Several components are frequently distinguished among deep-sea vent microbial communities: free-living and surface-bound bacteria in the warm and cold areas, invertebrate symbionts, thermophilic (and hyperthermophilic) organisms.

13.2.1 Free Living and Attached Bacteria in Warm and Cold Vent Areas

When approaching an active vent side with a manned-submersible, it is very common to observe bacterial mats on the sea bottom that can sometimes reach a thickness of several centimetres. The bacteria constituting these mats showed various morphotypes and metabolic types as well [19], but sulphur-oxidising bacteria showing filamentous forms (*Beggiatoa, Thiotrix*) seem to be dominant within these communities. In cold and warm seawater, at a short distance from the vents, bacterial densities are similar to those found in coastal marine waters, and range from 6×10^4 to 10^9 cells/ml. Autotrophic organisms may account for 10 to 2.2×10^6 cells/ml, the highest concentrations being unusual in common oceanic waters. However, measurements of autotrophic activities showed that the biomass production of free-living autotrophic bacteria was too low to sustain the invertebrate biomass present at the vent sites [23].

From the surface-bound and free-living communities, a variety of metabolic types (autotrophs, heterotrophs, sulphur-oxidisers, methane-oxidisers, nitrifyers, denitrifyers, sulphate reducers, etc.) has been reported [30]. Specific to the vent sites are the autotrophic and heterotrophic sulphur-oxidisers that gain their energy from aerobic oxidation of reduced sulphur compounds and particularly hydrogen sulphide, which is quite abundant in the vent fluids [14]. To a smaller extent, manganese-oxidising bacteria have also been reported [13] from the vent environment and the plumes. It must be noted that mesophilic halotolerant (16 % to 27 % NaCl) bacteria have been found in different vent plume samples collected at the Juan de Fuca Ridge, where they may form up to 28 % of the total microbial community, as estimated by means of MPN (most probable number method) viable counts [18]. Several isolates have been assigned to the genus *Halomonas* and *Marinobacter*, but they have not been fully identified. These organisms may have originated from sub sea-floor brine environments.

A few species have been isolated in pure culture and fully characterised. They are listed in Table 13.2. These strains do not reflect the real biodiversity of freeliving mesophiles, but were obtained from experiments dedicated to autotrophy and sulphur oxidation, artificial surface colonisation or specific enrichment and screening for exopolysaccharide production [33].

Genus	Species	Metabolism	Temperature	References
			range	
Thiomicrospira	Crunogena	sulphur-oxidiser	mesophilic	38
Thibacillus	Hydrothermalis	sulphur-oxidiser	mesophilic	39
Hyphomicrobium	Hirschiana	heterotroph	mesophilic	40
Hyphomicrobium	Jannaschiana	heterotroph	mesophilic	40
Alteromonas	Macleodii/jijiensis	heterotroph	mesophilic	41
Alteromonas	Infernus	heterotroph	mesophilic	42
Vibrio	Diabolicus	heterotroph	mesophilic	43

Table 13.2 Mesophilic bacterial species isolated from deep-sea hydrothermal vents.

13.2.2 Invertebrate Symbionts

The discovery of abundant animal communities (unknown species of tube worms, bivalves, polychaetes, shrimps, etc.) in the close vicinity of warm $(10-30^{\circ}C)$ water emissions was totally unexpected. How can we explain such animal (primary consumers) concentrations when the total darkness prevents photosynthetic primary production? Tissues of tube worms (Vestimentifera) and bivalves were examined with SEM (scanning electron microscope) and TEM (transmission electron microscope), and it was shown that they contained abundant bacterial cells. Further biochemical analyses indicated that these endosymbiotic bacteria were able to gain their energy from aerobic oxidation of hydrogen sulphide, and to fix carbon dioxide into organic matter [7].

Vestimentifera

Riftia pachyptila is the most spectacular tube worm from the eastern Pacific vent environments. It lives within a tube made of chitin and proteins from which a plume of red gills appears, and the biggest individuals can reach a height of 2 metres. This organism does not have a digestive tract (no mouth or anus) but a specific organ called the trophosome which is full sulphur-oxidising bacteria [6]. Nutrients required for bacterial life, such as carbon dioxide as a carbon source, hydrogen sulphide as an energy source and molecular oxygen as an electron acceptor, are collected from the environment by the worm and provided to the bacteria through blood transportation. Oxygen and hydrogen sulphide are transported towards the trophosome endosymbionts on two distinct sites of a blood pigment, which is rather similar to haemoglobin [16].

Molluscs

Vent molluscs (bivalves and gastropods) also harbour symbionts. The large bivalve *Calyptogena magnifica*, which lives in several eastern Pacific vent sites, has a digestive tract that is probably not functional. The symbionts are sulphur-oxidisers and are located in specific cells within the gill filaments. Mussels such as *Bathymodiolus* are present with different species in all vent sites explored so far. They have a functional digestive tract but they still have symbionts within their gill filaments [25].

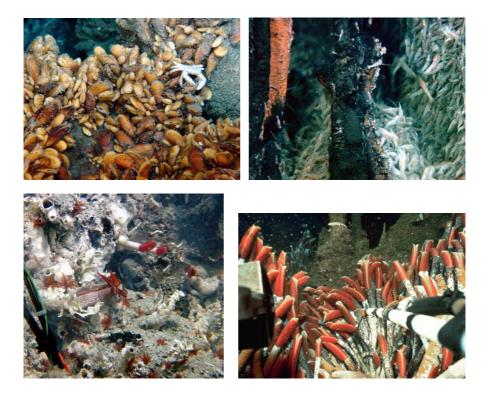


Fig. 13.2 Invertebrates from deep-sea hydrothermal vents with endo- and ecto-symbionts. Upper left: *Bathymodiolus azorensis* and Bythograeid crab (*Segonzacia*) in Menez Gwen (850 m depth); upper right: swarms of *Rimicaris exoculata* on chimney walls in the Rainbow hydrothermal vent field near the Azores Islands (2300 m depth); lower left: *Alvinella pompejana* and *Paralvinella grasslei* at 13°N on the East Pacific Rise (2630 m depth); lower right: *Riftia pachyptila* (Siboglinidae) at 13°N on the East Pacific Rise (2630 m depth). Courtesy of Ifremer/Atos, Ifremer/Phare and Ifremer/Hydronaut.

It has been reported that particularly by *Bathymodiolus* species possess methanotrophic symbionts [8], and dual symbiosis (methane-oxidising bacteria

and sulphur-oxidising bacteria within the same host) have been described for certain mid-Atlantic Ridge mussel populations. Despite many attempts, no symbiont has been cultured in a laboratory so far. Their physiology has been deduced from detection of enzymes involved in sulphide oxidation and autotrophic carbon dioxide fixation, or by analysing their rRNA (5S, 16S) sequences which demonstrated that they belong to the gamma subdivision of Proteobacteria [12] (see phylogenetic tree, Fig. 12.1 in Chap. 12).

In the western Pacific, several species of gastropods inhabit active vent sites. Although less studied, these snails also harbour autotrophic bacteria within their gill filaments.

An important question for these symbionts is the problem of transmission along their life cycles. Molecular techniques based on amplification (PCR) of genes encoding for 16S rRNA, and in situ hybridisation showed that a direct (vertical) transmission exists for the bivalve *Calyptogena magnifica* through their oocytes [4]. However, in the case of the tube worm *Riftia*, symbionts probably come from the environment and infest the worm after its metamorphosis.

Polychaetous Annelids

While Bivalve and Vestimentifera live in moderate temperature areas, other invertebrates thrive close to smoker walls and hence are exposed to elevated temperatures. This is the case for the polychaetous annelid *Alvinella pompejana* (Fig. 13.2), whose one individual has even been photographed [9] while twisted around a temperature probe at 100°C! These animals build the tube in which they live onto the outer walls of active smokers from the eastern Pacific. The temperature of their environment is most probably in the range 40–60°C. *Alvinella* is probably one of the most thermotolerant metazoans. These animals harbour a very dense epibiotic microbial community on their integuments, and some epibionts are inserted at very precise locations, as confirmed by structural modification of the worm's cuticule. SEM observations [7] showed various morphotypes (filaments, rods, cocci, twisted and stalked forms), and some of them have been successfully cultured in the laboratory, showing their rather high metabolic diversity [30].

However, the dominant morphotypes that consist of filaments that are visible to the naked eye again escaped culturing. Analysis of their 16S rRNA revealed that they belong to the epsilon subdivision of Proteobacteria, a phylogenetic lineage whose cultured known members are microaerophilic or anaerobic and metabolise sulphur compounds [5]. (See Fig. 12.1 in Chap. 12 for the phylogenetic tree.)

Crustaceans

According to their geographic location, vent invertebrate communities are characterised by specific assemblages (tube worms and Alvinellid worms in the eastern Pacific, Gastropods in the western Pacific, for instance). Atlantic vents are unique because of their spectacular clouds of shrimps swarming around active smokers. These shrimps belong to several genera, and the genus *Rimicaris* is one of the most abundant and most studied. Mouth parts of these shrimps are enlarged

and covered by epibiotic filamentous and rod-shaped bacteria. Using molecular techniques, it was demonstrated that these ectosymbionts also belong to the epsilon subdivision of Proteobacteria [28]. They are not dependent on their host because they have been also found on sulphide rocks, even with no shrimps around. The trophic role of the epibiotic bacteria has not been clearly demonstrated for either annelid or crustacean symbiosis.

13.2.3 Thermophiles and Hyperthermophiles

Among the physical parameters influencing life, temperature is probably the most studied. For centuries, heat has been used (and is still being used) for bacterial decontamination and sterilisation. The first thermophilic organism (living optimally above 60°C) was discovered in the late 1960s. *Thermus aquaticus* was isolated by T. Brock [3] from a hot spring in Yellowstone National Park (USA). More than 30 years later, the enzyme DNA polymerase from *Thermus aquaticus* made DNA amplification possible through the polymerase chain reaction (PCR) with applications in basic biology, medical sciences, food microbiology and even criminology. In 1977, T. Brock isolated *Sulfolobus acidocaldarius*, the first hyperthermophilic organism (the optimal temperature for growth is above 80°C), a member of the third domain of life discovered the same year by C. Woese: the Archaea [34].

Novel Hydrothermal Vent in the Bacteria Domain

The occurrence of hot fluids venting at temperatures up to 350°C certainly influenced the search for hyperthermophilic organisms, with the aim of discovering organisms growing at above 100°C (the temperature of boiling water under atmospheric pressure). However, enrichment cultures of hydrothermal chimney samples at temperatures below 60°C allowed isolation of several organisms [1] from the Bacteria domain (Table 13.3). The first microorganisms isolated were strict anaerobes of the genus Thermotoga and Thermosipho fermenting organic matter. Moreover, among anaerobes, an autotrophic organism, Desulfurobacterium thermolithotrophum, which utilises hydrogen as the electron donor and thiosulphate as the electron acceptor, was described. Later, aerobic thermophiles were also described for the genera Thermus and Bacillus. These organisms were not the first found because the thermal gradient is very steep: only a few decimetres may be separating the hot anaerobic zone from the cold oxygenated deep water, and the border line between anaerobiosis and aerobiosis is at about 30°C. However, certain hydrothermal chimneys have a porosity that allows cold water intake and results in an internal circulation of warm water, slightly oxygenated at temperatures around 70°C. Further, relative genera such as Oceanothermus, Vulcanithermus, Caldithrix, Caloranaerobacter were isolated and described. Thermophilic sulphate-reducers such as Thermodesulfator indiensis, or iron-reducers such as Deferribacter abyssi have also been described recently.

In order to improve the knowledge about the diversity of vent Prokaryotes, molecular approaches (PCR amplification of 16S rRNA genes) were also used. For the Bacteria domain, this approach revealed the importance of the epsilon subgroup of Proteobacteria. Furthermore, culture methods allowed isolation of novel members from this lineage, belonging to the genera *Nautilia, Caminibacter* or *Sulfurospirillum*. These organisms are anaerobes or microaerophilic, and may use nitrate and/or sulphur as electron acceptors.

Novel Hydrothermal Vent in the Archaea Domain

Two lineages are distinguished for Archaea: Euryarchaeota and Crenarchaeota. The first lineage gathers organisms from various metabolic types (Table 13.4). The most frequently isolated lineages from deep-sea hydrothermal vents are Thermococcales, with the genera Pyrococcus and Thermococcus, for a total of about 15 abyssal species [1]. All are hyperthermophilic, grow optimally above 80°C, ferment organic compounds and particularly peptides. Most of them require elemental sulphur or a sulphur-containing amino-acid (cystein) in the culture medium, and produce hydrogen sulphide. The dominance of Thermococcales in collections of hydrothermal microorganisms does not necessarily correspond to the natural situation. Although the number of species described certainly corresponds to a real diversity, it must be noticed that these organisms are relatively easy to grow in the laboratory. These organisms are strict anaerobes, but may resist oxygen exposure if this occurs at low temperatures (< 20°C), or under organic carbon starvation [26]. All these observations could explain why they apparently dominate in enrichment cultures and consequently strain collections. Recently, a third Thermococcales genus, Paleococcus ferrophilus was described. This organism requires ferrous iron as the electron acceptor in the absence of elemental sulphur.

Among the Euryarchaeota, two sulphate-reducing species were described within the genus *Archaeoglobus*. Close to these sulphate-reducers, the genus *Geoglobus*, which is able to use ferric iron as electron acceptor was recently isolated. Methanogens (producing methane from hydrogen and carbon dioxide) belonging to the genera *Methanococcus*, renamed *Methanocoaldococcus*, *Methanothermococcus* and *Methanopyrus* were currently isolated. For several years, *Methanopyrus kandleri* remained the most thermophilic organism on Earth, growing optimally at 106°C, with a maximum temperature for growth at 110°C.

Crenarchaeota constitute the second main lineage for Archaea (a third lineage, Korarchaeota, only known from 16S rRNA sequences). is All are hyperthermophilic organisms metabolising sulphur or sulphur containing compounds. Several species have been isolated from deep-sea hydrothermal vents. They are strictly anaerobic, but show various metabolic types. They belong to the genera Desulfurococcus, Staphylococcus, Ignicoccus, Pyrodictium and Pyrolobus. The last genus includes the species Pyrolobus fumarii, which grows optimally at 110°C, with a maximum at 113°C. This is the most thermophilic organism presently known on Earth. Moreover, it can survive 2 hours exposure in an autoclave (120°C).

An additionnal lineage has been proposed within the Archaea with the discovery of *Nanoarchaeum equitans*, a small sized-organism (400 nm) living in very close association with *Ignicoccus* cells.

Comparison of thermophilic and hyperthermophilic genera isolated from deepsea hydrothermal vents and other hot environments shows rather few differences. Acidophilic hyperthermophiles such as *Sulfolobus* have not been reported from deep-sea vents. Although hydrothermal fluids are acidic, they are quickly diluted into neutral (pH = 8) seawater. Consequently, a hot (less than 113°C) and acidic (pH < 5–6) biotope has not been reported yet at a vent site. Certain species such as *Staphylothermus marinus* have been reported from shallow and deep hot springs, and probably have a ubiquitous distribution. For most of these hyperthermophiles, a novelty was found at the species level as confimed by the numerous species called "*profundus*", "*abyssi*" or "*hydrothermalis*". However, several genera, particularly for the thermophilic Archaea recently described, seem to be only present in deep-sea vents (*Pyrolobus, Paleococcus, Desulfurobacterium, Nautilia, Caminibacter*, etc.). However, it is not firmly proven that they only thrive in deep environments, and perhaps shallow vent species are still waiting to be detected.

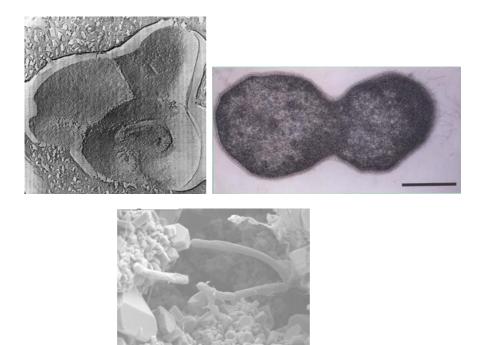


Fig. 13.3 Novel micro-organisms from deep-sea hydrothermal vents. Upper left: *Pyrolobus fumarii*, the most thermophilic organism known on Earth (reprinted from Blöchl et al. [37] with permission from Springer-Verlag), size 2.9 µm; upper right: *Pyrococcus abyssi*; lower: *Desulfurobacterium thermolithotrophum*.

Table 13.3 Novel Bacteria from deep-sea hydrothermal vents. (A: autotroph; H: heterotroph; F/S° : fermentative, elemental sulphur required; in the energy column, compounds on the left of "," are electron donors, compounds on the right of "/" are electron acceptors; μO_2 : microaerophilic; OC: organic carbon).

Lineage	Genus	Species	Carbon source	Energy	Optimal T (°C)	Ref.
Aquificales	Persephonella	Marina	А	$\begin{array}{c} H_2/NO_3^{2-} \\ S^{\circ}, \mu O_2 \\ S_2O_3^{2-} \end{array}$	70	44
		Guayma- sensis	A	H_2/NO_3^{2-} S°, μO_2 S ₂ O ₂ ²⁻	80	44
		Hydrogeno- Phila	А	$\begin{array}{c} H_2/NO_3^{2-} \\ \mu O_2 S_2O_3^{2-} \end{array}$	70	45
Desulfuro- bacteriales	Desulfuro- bacterium	Thermolitho- trophum	А	H ₂ /S°	70	46
		Crinifex	А	H_2/NO_3^{2-} S°	60–65	47
Thermo-	Marinitoga	Camini	Н	F/S°	55	48
togales		Piezzophila	Н	F,S°	65	49
	Thermotoga	sp.	Н	F	80	50
	Thermosipho	Melanensis	Н	F/S°	70	51
		Japonicus	Н	F/S°	72	52
Thermo- desulfuro- bacteriales	Thermo- desulfuro- bacterium	Hydrogeno- Philum	А	H ₂ /S°	75	53
Thermus/	Thermus	sp.	Н	OC/O ₂	70-80	54
Deino- coccus		Thermo- philus GY1211	Н	OC/O ₂	75	55
	Marinithermus	Hydro- thermalis	Н	OC/O ₂	67	56
	Vulcanithermus					57
	Oceanithermus	Profundus	H/A	$H_2, OC/O_2$ μO_2	60	58
Deferri- bacteriales	Deferribacter	Desulfurican s	Н	OC/S° NO^{3-} , As	60–65	59
		abyssi		110 , AS		60

Firmicutes	Bacillus	sp.	Н	O ₂ /F	60-80	61
	Caloranaero-	azorensis	Н	F	65	62
	bacter					
	Caminicella	sporogenes	Н	F	55-60	63
Proto-	Caminibacter					64
bacteria	Nautilia					65
	Sulfospirrilum					66
	Thermodesul-					67
	fatator					
Novel	Caldithrix	abyssi	H/A	acetate,	65	62
lineage				H_2/NO_3^-		
				F		

Table 13.3 (continued)

 Table 13.4 Novel Arachaea from deep-sea hydrothermal vents.

Lineage	Genus	Species	Carbon source	Energy	Optimal T (°C)	Ref.
Eury- archaeota						
Methano-	Methano-	jannaschii	А	H ₂ /CO ₂	85	69
coccales	caldo-	infernus	А	H ₂ /CO ₂	85	70
	coccus	vulcanius	А	H,/CO,	80	71
	Methano- thermo-coccus	okinawensis	А	H ₂ /CO ₂	60–65	72
Methano- pyrales	Methano-pyrus	kandleri	А	H ₂ /CO ₂	98	73
Thermoco-	Thermo-coccus	guaymensis	Н	F,S°	88	74
ccales		aggregans	Н	F,S°	88	74
		barossi	Н	F,S°	82	75
		fumicolans	Н	F,S°	85	76
		hydrothermalis	Н	F,S°	85	77
		peptonophilus	Н	F,S°	85-90	78
		siculi	Н	F,S°	85	79
		chitonophagus	Н	F,S°	85	80
		barophilus	Н	F,S°	85	81
		atlanticus	Н	F,S°	85	82
		gammatolerans	Н	F,S°	88	83
	Pyrococcus	abyssi	Н	F,S°	96	84
		glycovorans	Н	F,S°	95	85
		horikoshii	Н	F,S°	98	86
	Paleococcus	ferrophilus	Н	F,S° Fe ⁺⁺⁺ required	83	87

Archaeo- globales	Archaeo- globus	profundus	H,A	H ₂ ,OC/ SO ²⁻	82	88
giobales	groous	veneficus	H,A	$H_2,OC/$ SO_3^{2-} $S_2O_3^{2-}$	75–80	89
	Geoglobus	ahangari	H,A	H ₂ ,OC/ Fe ³⁺	88	90
Cren- archaeota						
Desulfuro-	Ignicoccus	pacificus	А	H ₂ /S°	90	91
coccales	Staphylo- thermus	marinus	Н	F/S°	85–92	92
	Pyrodictium	abyssi	Н	F/S°	97	93
	Pyrolobus	fumarii	A	H_2/NO^{3-} $\mu O_2,$ $S_2O_3^{2-}$	106	37
"Nano- archaeota"	Nano- archaeum	equitans	A?	?	90	94

Table 13.4 (continued)

The existence of very hot fluids certainly drove the search for hyperthermophiles into deep-sea hydrothermal vents. However, the upper temperature limit for life (113°C) reported for a deep vent organism (*Pyrolobus fumarii*) exceeds the maximum growth temperature of *Methanopyrus kandleri*, isolated also from a 100 m deep vent in Iceland, or of *Pyrodictium occultum* isolated from shallow vent at Vulcano Island (Sicily, Italy) only by 3°C.

Carbon, Energy Sources and Electron Acceptors

In the absence of light, deep-sea microorganisms gain their energy from oxidoreduction reactions. A variety of electron donors and acceptors has been found to be used by thermophiles and/or hyperthermophiles (Tables 13.3, 13.4). From these reactions, they obtain energy to fix carbon dioxide or to use organic compounds as carbon sources. Almost all metabolic types already known for chemotrophic Prokaryotes have been found and most of the biogeochemical cycles may function in the vent environment: carbon, sulphur, iron, etc. However, the nitrogen cycle does not seem to function at elevated temperatures. If nitrate and nitrite may be used as electron acceptors by several organisms, they apparently cannot be oxidised at elevated temperature, although aerobic nitrification was reported for moderate thermophiles. Anaerobic nitrication has been recently demonstrated for organisms of the Planctomycetales lineage [2], which utilise nitrite as the electron acceptor to oxidise ammonium. The search and discovery of such organisms in the hyperthermophilic range would definitely establish that an ecosystem can fully function at elevated temperatures.

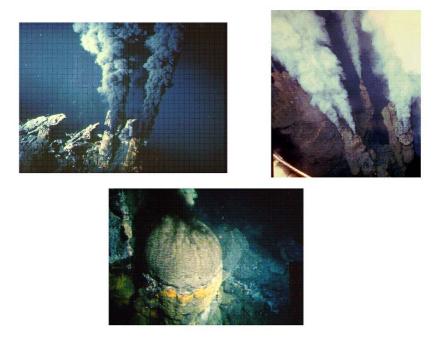


Fig. 13.4 Hydrothermal chimneys. Courtesy of Y. Fouquet (Ifremer).

13.2.4 Specific Adaptations

Fluctuations of Environmental Conditions

At deep-sea hydrothermal vents, several parameters may fluctuate and affect the physiology of microorganisms. This is the case for oxygen and nutrient concentrations. Hyperthermophiles are mostly anaerobic and sensitive to exposure to oxygen. This situation may occur *in situ* as a result of a decrease of venting activity. Using *P. abyssi* as a model strain, it was shown that, although oxygen was toxic for this strain at growth temperature, *P. abyssi* was able to survive for several weeks at 4°C in the presence of oxygen. Similarly, this organism was not affected by starvation in a minimal medium (no organic carbon) for at least one month at 4°C, and only minimally at 95°C for several days [26]. Furthermore, cells were more resistant to oxygen under starvation conditions. These results may indicate that at least *Pyrococcus*, but probably also other vent organisms, are adapted to fluctuations occurring in vent environments, and may be disseminated from one vent field to another.

Hydrostatic Pressure

Among all physical parameters mentioned above, the hydrostatic pressure (of the water column) is the one which is characteristic of all deep vent sites. Responses to an elevated hydrostatic pressure have first been studied in microorganisms from cold deep environments [24, 29, 35]. Piezophilic and even obligate piezophilic organisms have been described, and their physiology and adaptations studied at the molecular level. However, much less is known for deep-sea vent thermophiles. One of the reasons is that during the collection of a black smoker sample, using a retaining-pressure collecting device is not so easy: a single very small metallic particle (frequent in the vent plume) may cause a leak in the sampler. For this reason, all the samples studied were decompressed when brought up to the surface. All enrichment cultures that lead to the isolation of organisms described above were carried out under atmospheric pressure, or a slightly hyperbaric pressure to avoid boiling of culture media for temperatures close to or above 100°C.

Hence, the question of the effect of elevated hydrostatic pressure on deep-sea thermophiles is still open. Several microbiologists exposed deep-sea thermophilic organisms isolated under atmospheric pressure to elevated hydrostatic pressure, using pressurised bioreactors. Several responses were observed: some organisms were baro-sensitive, and showed a slower growth rate under pressure; others were barotolerant, and their growth was not affected by pressure. However, most of the species studied appeared to be barophiles, and their growth rates were enhanced by hydrostatic pressure. Moreover, their optimal growth temperatures increased by a few °C. For instance, for Pyrococcus abyssi, while the maximum growth temperature under atmospheric pressure is 102°C, it reached 105-106°C under elevated hydrostatic pressure. Similarly, the optimum growth temperature increased from 96 to 100°C. Similar observations reported by several authors were compiled and discussed by Deming and Baross [11], who noted that for all barohyperthermophiles, the pressure allowing optimal growth was always above the pressure existing at the capture depth (for an organism isolated from a sample collected at 2000 m depth, the optimum pressure for growth was 40 MPa). This point is very remarkable since for baro-psychrophiles the optimum pressure for growth was always below the pressure existing at the capture depth.

Another experimental approach consisted in isolating hyperthermophilic organisms from enrichment cultures (and subcultures) under elevated hydrostatic pressure. This method allowed isolation of a novel Archaea species (Thermococcus barophilus) and a novel Bacteria species (Marinitoga *piezzophila*). For both organisms, which are not real taxinomic novelties, but only novel species, growth rates were enhanced under hydrostatic pressure, but growth remained possible under atmospheric pressure. In the case of Marinitoga, cell divisions were very slow under atmospheric pressure and cell morphology was clearly modified. As observed for other microorganisms, the maximum growth temperature was increased, but the optimal growth temperature was not affected by pressure increases. Further information was obtained from a study of total proteins of T. barophilus cultured under elevated hydrostatic pressure or atmospheric pressure [27]. Under hydrostatic pressure, an unknown 35 kDa protein was expressed. Under atmospheric pressure, a 60 kDa protein was expressed, which corresponded to a stress protein already known for other hyperthermophilic Archaea. All these data confirm that this *Thermococcus* species is a true baro-thermophile.

Heavy Metals

Several heterotrophic strains (Acinetobacter, Alteromonas, Pseudomonas, Vibrio) have been isolated from alvinellid Polycheates living on the chimney walls, and appeared resistant (or multi-resistant) to heavy metals such as cadmium, zinc, silver, arsenate and particularly copper [21]. This feature confirmed the adaptation of at least a part of the worm's microflora to the elevated metal concentrations existing in the vent environment. About 20 % of the strains studied harboured one or several plasmids (up to five) of sizes ranging from 4.6 to 157 kb. The occurrence of plasmids with some similarities for strains belonging to different phyla could suggest the existence of genetic transfers in the vent environments. Further studies involving a thermophilic Bacillus from deep-sea vents showed that exposure to cadmium and copper induce the expression of proteins including a manganese superoxide dismutase. Experiments with *E. coli* demonstrated that superoxide dismutase is involved in the defence against oxidative stress mediated by heavy metals, but the possibility that superoxide dismutase might also reduce metal toxicity by some process of metal storage was not excluded.

Ionising Radiation

Several hyperthermophilic Archaea have been shown to resist ionising radiation, but not as much as *Deinococcus radiodurans*, the most radioresistant microorganism known so far. In the vent environment, it was reported that invertebrates living on black smoker were exposed to natural radiation one hundred times above that received by Man on Earth. For this reason, responses of the Archaeon *Pyrococcus abyssi* to ionising radiation have been studied. It was observed that this organism did not show any loss of viability until 2 kGy of γ -irradiation. It was then established that *P. abyssi* did not have a DNA protection mechanism that could explain its radioresistance although the chromosomic DNA was fully restored, under optimal growth conditions, within 2 hours following gamma irradiation. Experimental data indicated that strategies used by *P. abyssi* included an uncoupling of DNA repair and DNA synthesis, and a prevention of accumulation of genetic mistakes by exporting damaged DNA.

In order to isolate more radioresistant hyperthermophiles, enrichment cultures under conditions designed for growth of Thermococcales were exposed to elevated doses of radiation (20 to 30 kGy), and then processed for strain isolation [22]. Three radioresistant strains were obtained, and the most radioresistant (about the same range as *Deinococcus radiodurans*) was fully described as a novel species: *Thermococcus gammatolerans*.

13.3 Implications for Mars

It is widely accepted that life on Earth arose in liquid water, and for this reason water is considered as one of the conditions necessary for life on any planet. Mapping of Mars by several spacecraft clearly led to the conclusion that liquid water existed on or even below the surface of Mars, but was most probably restricted to the early history of Mars, at least on the surface, as discussed in previous chapters of this book.

However, liquid water is not enough to support life, and no organism can thrive in pure water. All life processes and especially nutrition and growth require energy and nutrients. On Earth living organisms utilise light (photosynthesis) and/or chemical (chemosynthesis) energy sources, the photo-autotrophic organisms being presently responsible for the primary production of organic matter.

It is most probable that on early Earth chemosynthesis by anaerobic lithotrophic organisms (utilisation of inorganic energy sources in the presence of an oxidant different from molecular oxygen; for instance dihydrogen and elemental sulphur) preceded photosynthesis. Such energetic metabolisms, although known for a long time, were re-discovered with the exploration of deep-sea hydrothermal vents and their mesophilic or thermophilic microbial communities.

As a consequence of plate tectonics, submarine volcanism enables the circulation of water in hydrothermal systems created by cracks in cooling volcanic rocks. This circulating water is heated, chemically reacts with the rocks and vent out at elevated temperatures, enriched with various compounds. Some of these compounds may serve as energy sources, but it was also demonstrated that some organic matter synthesis was possible under hydrothermal conditions [31, 32].

Similar phenomena also occur at the surface of Earth (solfatara, geysers, etc). Basically, these forms of hydrothermalism are not so different from the deep-sea systems. However at the surface, photosynthetic life occurs and strongly competes with chemosynthetic life. Consequently, in the deepest and darkest part of the Earth, chemosynthetic microorganisms dominate exclusively and may show a high diversity at a single site. Probably, neither plate tectonics nor deep oceans occurred on Mars. However, if hydrothermal systems existed there, chemosynthetic life might have arisen and existed for a certain time in the underground compartments of these environments.

Deep-sea hydrothermal vent microorganisms showed various adaptations to the extreme conditons of their environments, and this indicates that life may resist or even thrive optimally in biotopes that are hostile for human beings. From what is known about past environmental conditions on Mars, and from physicochemical limits for life on Earth, there is no reason to exclude the possibility that life might have existed on Mars.

The possibility that life arose on Earth in environments resembling the present hydrothermal vents has been supported by several authors. Consequently the presence of liquid water on early Mars but also volcanic activity should inevitably lead to hydrothermal systems. Also crustal heating from heavy impacts could have produced hydrothermal systems. Although volcanic activity and consequently energy produced through hydrothermalism has been estimated to be several hundred times less than on early Earth, recent calculations [95] lead to the conclusion that "there was sufficient geochemical energy available that life may have arisen independently on Mars". Consequently, to explore signatures of past life on (in) Mars locations where fossil hydrothermal systems or hot springs presumably have existed should be selected.

13.4 Conclusions

Experiments carried out by the Mars Viking landers were designed to detect energetic metabolisms that presently dominate at the surface of the Earth: oxygenic photosynthesis and aerobic respiration. A few years later, exploration of deep-sea hydrothermal vents by microbiologists pointed out that litho-autotrophic microorganisms are very abundant, utilise a variety of energy sources and electron acceptors (in the absence of molecular oxygen), grow optimally under unexpected physicochemical conditions (temperature, pressure), and resist severe conditions in terms of heavy metal concentrations or high doses of ionising radiation. In parallel, it was well established that hydrothermal conditions were favourable for synthesis of organic compounds that may serve as carbon sources for lithotrophic organisms.

At the beginning of the 21st century, when a series of orbiting and landing missions to Mars have been launched, planned, scheduled or are in preparation, it is obvious that exploration of deep oceans on Earth may provide lessons for astrobiology in and outside the Solar System.

Glossary

acidophilic	low pH-loving
aerobic	requires O ₂
anaerobic	cannot tolerate O_2
autotrophic	traps energy from physical or chemical sources
barophilic	weight-loving
barotolerant	tolerates weight
chemotrophic	utilising the energy obtained from the oxidation of hydrogen sulphide
ectosymbionts	symbiotic organisms living on the surface of other organisms
endosymbionts	symbiotic organisms living in the digestive tract
epibiotic	reproductive structure is on the outside of the substrate or host cell
heterotrophic	relies upon molecules created by other organisms
hyperthermophilic	growing at >80°C
lithotrophic	utilising inorganic energy sources
mesophilic	growing at 15–60°C
microaerophilic	tolerates some O ₂
piezophilic	pressure-loving
psychrophilic	growing at <15°C
thermotolerant	tolerates high temperatures

13.5 References

- 1 Alain K (2003) Approches culturales et moléculaires des assemblages microbiens associées aux Polychètes hydrothermaux de la famille Alvinellidae. Thèse Doctorat de l'Université de Brest (France). 219p
- 2 Brochier C, Philippe H (2002) A non hyperthermophilic ancestor for Bacteria. Nature 417: 244
- 3 Brock TD (1985) Life at high temperatures. Science 230: 545-550
- 4 Cary SC, Giovannoni SJ (1993) Transovarial inheritance of endosymbiotic bacteria in clams inhabiting deep-sea hydrothermal vents and cold seeps. Proc. Natl. Acad. Sci. USA 90: 5695-5699
- 5 Cary SC, Cottrell MT, Stein JL, Camacho F, Desbruyères D (1997) Molecular identification and localization of filamentous symbiotic bacteria associated with the hydrothermal vent annelid alvinella pompejana. Appl. Environ. Microbiol. 63: 1124-1130
- 6 Cavanaugh CM, Gardiner SL, Jones ML, Jannasch HW, Watrebury JB (1981) Prokaryotic cells in the hydrothermal vent tube worm *Riftia pachyptila* Jones: possible chemoautotrophic symbionts. Science 213: 340-341
- 7 Cavanaugh CM (1983) Symbiotic chemoautotrophic bacteria in marine invertebrates from sulphide-rich habitats. Nature 302: 58-61
- 8 Cavanaugh CM, Wirsen CO, Jannasch HW (1992) Evidence for methylotrophic symbionts in a hydrothermal vent mussel (Bivalvia Mytilidae) from the Mid-Atlantic Ridge. Appl. Environ. Microbiol. 58: 3799-3803
- 9 Chevaldonné P, Desbruyères D, Childress JJ (1992) Some like it hot... and some even hotter. Nature 359: 593-594
- 10 Corliss JB, Dymond J, Gordon LI, Edmond J, von Herzen RP, Ballard RD, Green K, Williams D, Bainbridge A, Crane K, van Andel TH (1979) Submarine thermal springs on the Galapagos Rift. Science 203: 1073-1083
- 11 Deming JW, Baross JA (1993) Deep-sea smokers: windows to a subsurface biosphere. Geochim. Cosmochim. Acta 57: 3219-3230
- 12 Distel DL, Lane DJ, Olsen GJ, Giovannoni SJ, Pace B, Pace NR, Stahl DA, Felbeck H (1988) Sulfur-oxidizing bacterial endosymbionts: analysis of phylogeny and specificity by 16S rRNA sequences. J. Bacteriol. 170: 2506-2510
- 13 Durand P, Prieur D, Jeanthon C, Jacq E (1990) Présence et activité de bactéries hétérotrophes mangano-oxydantes associées aux Alvinellidés (Annelides polychètes) dans un site d'hydrothermalisme profond de la dorsale du Pacifique Oriental. C.R. Acad. Sci. Paris, t.310, Série III: 273-278
- 14 Durand P, Benyagoub A, Prieur D (1994) Numerical taxonomy of heterotrophic sulfuroxidizing bacteria isolated from South-West Pacific hydrothermal vents. Can. J. Microbiol. 40: 690-697
- 15 Edmond J, Van Damm K, MacDuff R, Measures C (1982) Chemistry of hot springs on the East Pacific Rise. Nature 297: 187-191
- 16 Felbeck H (1985) CO₂ fixation in the hydrothermal vent tube worm *Riftia pachyptila* Jones. Physiol. Zool. 58: 272-281
- 17 Gaill F, Desbruyères D, Prieur D (1987) Bacterial communities associated with "Pompei worms" from the East Pacific Rise hydrothermal vents: Sem, TEM observations. Microbiol. Ecol. 13: 129-139

- 18 Holden JF, Summit M, Baross JA (1998) Thermophilic and hyperthermophilic microorganisms in 3–30°C hydrothermal fluids following a deep-sea volcanic eruption. FEMS Microbiol. Ecol. 25: 33-41
- 19 Jannasch HW, Wirsen CO (1979) Chemosynthetic primary production at East Pacific Rise sea floor spreading centers. Bioscience 29: 592-598
- 20 Jannasch HW, Taylor CD (1984) Deep-sea microbiology. Ann. Rev. Microbiol. 38: 487-514
- 21 Jeanthon C (2000) Molecular ecology of hydrothermal vent microbial communities. Antonie van Leeuwenhoek 77: 117-133
- 22 Jolivet E, Corre E, L'Haridon S, Forterre P, Prieur D (2003) *Thermococcus gammatolerans* sp. Nov., a hyperthermophilic archaeon from deep-sea hydrothermal vent that resists ionizing radiation. Int. J. Syst. Evol. Microbiol. 53: 847-851
- 23 Karl DM, Wirsen CO, Jannasch HW (1980) Deep-sea primary production at the Galapagos hydrothermal vents. Science 207: 1345-1347
- 24 Kato C (1999) Barophiles (piezophiles). In Horikoshi K, Tsujii K (eds) Extremophiles in Deep-sea Environments. Springer-Verlag, Berlin, pp 91-111
- 25 Le Pennec M, Prieur D (1984) Observations sur la nutrition d'un Mytilidae d'un site actif de la dordale du Pacifique oriental. C. R. Acad. Sci. Paris. 298: 493-498
- 26 Marteinsson VT, Moulin P, Birrien JL, Gambacorta A, Vernet M, Prieur D (1997) Physiological responses to stress conditions and barophilic behaviour of the hyperthermophilic vent Archaeon *Pyrococcus abyssi*. Appl. Environ. Microbiol. 63: 1230-1236
- 27 Marteinsson VT, Reysenbach AL, Birrien JL, Prieur D (1999) A deep-sea barophilic hyperthermophile *Thermococcus barophilus* induces a stress protein when grown under atmospheric pressure. Extremophiles 3: 277-282
- 28 Polz MF, Cavanaugh CM (1995) Dominance of one bacterial phylotype at a Midatlantic Ridge Hydrothermal vent site. Proc. Natl. Acad. Sci. USA 92: 7232-7236
- 29 Prieur D, Marteinsson VT (1998) Prokaryotes living under elevated hydrostatic pressure. Adv. Biochem. Engineer. Biotechnol. 61: 23-35
- 30 Prieur D, Benbouzid-Rollet N, Chamroux S, Durand P, Erauso G, Jacq E, Jeanthon C, Mevel G, Vincent P (1989) Distribution de divers types métaboliques bactériens sur un site hydrothermal profond (Dorsale de Pacifique Oriental à 13°N). Cahiers de Biol. Mar. 30: 515-530
- 31 Shock EL (1990) Geochemical constraints on the origin of organic compounds in hydrothermal systems. Orig. Life Evol. Biosph. 20: 331-367
- 32 Shock EL (1997) High-temperature life without photosynthesis as a model for Mars. J. Geophys. Res. 102(E10): 23687-23694
- 33 Vincent, P, Pignet P, Talmont F, Bozzi L, Fournet, B, Guezennec J, Jeantho C, Prieur D (1994) Production and characterization of an exopolysaccharide excreted by a deep-sea hydrothermal vent bacterium isolated from the Polychaete Annelid, *Alvinella pompejana*. Appl. Environ. Microbiol. 60: 4134-4141
- 34 Woese C (1987) Bacterial evolution. Microbiol. Rev. 51: 221-271
- 35 Yayanos AA (1986) Evolution and ecological implications of the properties of deepsea barophilic bacteria. Proc. Natl. Acad. Sci. USA 83: 9542-9546
- 36 Charlou JL, Donval JP, Fouquet Y, Jean-Baptiste P, Holm N (2002) Geochemistry of high H₂ and CH₄ vent fluids issuing from ultramafic rocks at the Rainbow hydrothermal field (36°14'N, MAR). Chemical Geol. 191: 345-359

- 37 Blöchl E, Rachel R, Burggraf S, Hafenbradl D, Jannasch HW, Stetter KO (1997) *Pyrolobus fumarii*, gen. and sp. nov., represents a novel group of archaea, extending the upper temperature limit for life to 113°C. Extremophiles 1: 14-21
- 38 Wirsen CO, Brinkhoff T, Kuever J, Muyzer G, Molyneaux S, Jannasch HW (1998) Comparison of a new *Thiomicrospira* strain from the Mid-Atlantic Ridge with known hydrothermal vent isolates. Appl. Environ. Microbiol. 64: 4057-4059
- 39 Durand P, Reysenbach A-L, Prieur D, Pace N (1993) Isolation and characterization of *Thiobacillus hydrothermalis* sp. nov., a mesophilic obligately chemolitotrophic bacterium isolated from a deep-sea hydrothermal vent in Fiji Basin. Arch. Microbiol. 159:150639-150644
- 40 Weiner RM, Devine RA, Powell M, Dagasan L, Moore RL (1985) *Hyphomonas oceantitis* sp. nov., *Hyphomonas hirschiana* sp. nov., and *Hyphomonas jannaschiana* sp. nov. Int. J. Syst. Bacteriol. 35: 237-243
- 41 Raguénès G, Pignet P, Gauthier G, Pérès A, Christen R, Rougeaux H, Barbier G, Guézennec J (1996) Description of a new polymer-secreting bacterium from a deep-sea hydrothermal vent, *Alteromonas macleodii* subsp. *Fijiensis* and preliminary characterization of the polymer. Appl. Environ. Microbiol. 62: 67-73
- 42 Raguénès GHC, Pérès A, Ruimy R, Pignet P, Christen R, Loaec M, Rougeaux H, Barbier G, Guézennec JG (1997a) *Alteromonas infernus* sp. nov., a new polysaccharide-producing bacterium isolated from a deep-sea hydrothermal vent. J. Appl. Microbiol. 82: 422-430
- 43 Raguénès G, Christen R, Guézennec J, Pignet P, Barbier G (1997b) *Vibrio diabolicus*, sp. nov., a new polysaccharide-producing bacterium isolated from a deep-sea hydrothermal vent polychate annelid, *Alvinella pompejana*. Int. J. Syst. Bacteriol. 47: 989-995
- 44 Godz D, Banta A, Beveridge TJ, Rushdi AI, Simoneit B, Reysenbach AL (2002) Persephonella marina gen. nov., nov. and Persephonella guaymasensis sp. nov., two novel, thermophilic, hydrogen-oxidizing microaerophiles from deep-sea hydrothermal vents. Int. J. Syst. Evol. Microbiol. 52: 1349-1359
- 45 Nakagawa S, Takai K, Horikoshi K, Sako Y (2003) *Persephonella hydrogeniphila* sp. nov., a novel thermophilic, hydrogen-oxidizing bacterium from a deep-sea hydrothermal vent chimney. Int. J. Syst. Evol. Microbiol. 53: 863-869
- 46 L'Haridon S, Cilia V, Messner P, Raguénès G, Gambacorta A, Sleytr UB, Prieur D, Jeanthon C (1998) *Desulfurobacterium thermolithotrophum* gen. nov., a novel autotrophic, sulphur-reducing bacterium isolated from a deep-sea hydrothermal vent. Int. J. Syst. Bacteriol. 48: 701-711
- 47 Alain K, Rolland S, Crassous P, Lesongeur F, Zbinden M, Le Gall C, Godfroy A, Page A, Juniper SK, Cambon-Bonavita MA, Duchiron F, Quérellou J (2003) *Desulfurobacterium crinifex* sp. nov., a novel thermophilic, pinkish-streamers forming, chemolithoautotrophic bacterium isolated from a Juan de Fuca ridge hydrothermal vent. Emendation of the genus *Desulfurobacterium*. Extremophiles 7: 361-370
- 48 Wery N, Moricet J, Cueff V, Jean J, Pignet P, Lesongeur F, Cambon-Bonavita M, Barbier G (2001b) *Caloranoaerobacter azorensis* gen. nov., sp. nov., an anaerobic thermophilic bacterium isolated from a deep-sea hydrothermal vent. Int. J. Syst. Evol. Microbiol. 51: 1789-1796
- 49 Alain K, Marteinsson VT, Miroshnichenko ML, Bonch-Osmolovskaya EA, Prieur D, Birrien JL (2002a) *Marinitoga piezophila* sp. nov., a rod-shaped, thermo-piezophilic

bacterium isolated under high hydrostatic pressure from a deep-sea hydrothermal vent. Int J Syst Evol Microbiol **52** : 1331-1339.

- 50 Marteinsson VT, Birrien JL, Prieur D (1997b) *In situ* enrichment and isolation of thermophilic microorganisms from deep-sea vent environments. Can. J. Microbiol. 43: 694-697
- 51 Antoine E, Cilia V, Meunier JR, Guezennec J, Lesongeur F, Barbier G (1997) *Thermosipho melanesiensis* sp. nov., a new thermophilic anaerobic bacterium belonging the *Thermotogales*, isolated from deep-sea hydrothermal vent in the southern Pacific ocean. Int. J. Syst. Bacteriol. 47: 1118-1123
- 52 Takai K, Sugai A, Itoh T, Horikoshi K (2000) Palaeococcus ferrophilus gen. nov., sp. nov., a barophilic, hyperthermophilic archaeon from a deep-sea hydrothermal vent chimney. Int. J. Syst. Evol. Microbiol. 50 Part 2 : 489-500
- 53 Jeanthon C, L'Haridon S, Reysenbach AL, Vernet M, Messner P, Sleytr UB, Prieur D (1998) *Thermodesulfobacterium hydrogeniphilium* sp. nov., a thermophilic, chemolithoautotrophic, sulfate-reducing bacterium isolated from a deep-sea hydrothermal vent at Guaymas Basin, and emandation of the genus Thermodesulfobacterium. Int. J. Syst. Evol. Microbiol. 52: 765-772
- 54 Marteinsson VT, Whiteley AS, Griffiths RI, Bailey MJ (2002) First isolation of thermophilic aerobic non-sporulating heterotrophic bacteria from deep-sea hydrothermal vents. FEMS Microbiol. Ecol. 18: 163-174
- 55 Marteinsson VT, Birrien JL, Raguénès G, Da Costa MS, Prieur D (1999a) Isolation and characterization of *Thermus thermophilus* Gy1211 from a deep-sea hydrothermal vent. Extremophiles 3: 247-251
- 56 Sako Y, Nakagawa S, Takai K, Horikoshi K (2003) *Marinithermus hydrothermalis* gen. nov., sp. nov., a strictly aerobic, thermophilic bacterium from a deep-sea hydrothermal vent chimney. Int. J. Syst. Evol. Microbiol. 53: 59-65
- 57 Miroshnichenko ML, L'Haridon S, Nercessian O, Antipov AN, Kostrikina NA, Tindall BJ, Schumann P, Spring S, Stackebrandt E, Bonch-Osmolovskaya EA, Jeanthon C (2003c) *Vulcanithermus mediatlanticus* gen. nov., sp. nov., a novel member of the family *Thermaceae* from a deep-sea hot vent. Int. J. Syst. Evol. Microbiol. 53: 1143-1148
- 58 Miroshnichenko ML, L'Haridon S, Jeanthon C, Antipov AN, Kostrikina NA, Tindall BJ, Schumann P, Spring S, Stackebrandt E, Bonch-Osmolovskaya EA (2003b) *Oceanithermus profundus* gen. nov., sp. nov., a thermophilic, microaerophilic, facultatively chemolithoheterotrophic bacterium from a deep-sea hydrothermal vent. Int. J. Syst. Evol. Microbiol. 3: 747-752
- 59 Takai K, Kobayashi H, Nealson KH, Horikoshi K (2003b) *Deberribacter desulfuricans* sp. nov., a novel sulfur-, nitrate- and arsenate-reducing thermophile isolated from a deep-sea hydrothermal vent. Int. J. Syst. Evol. Microbiol. 53: 839-846
- 60 Miroshnichenko ML, Slobodkin AI, Kostrikina NA, L'Haridon S, Nercessian O, Spring S, Stackebrandt E, Bonch-Osmolovskaya EA, Jeanthon C (2003d) *Deferribacter abyssi* sp. nov., an anaerobic thermophile from deep-sea hydrothermal vents of the Mid-Atlantic Ridge. Int. J. Syst. Evol. Microbiol. 53: 1637-1641
- 61 Marteinsson VT, Birrien JL, Kristjansson JK, Prieur D (1995) Numerical taxonomic study of thermophilic *Bacillus* isolated from three geographical separated deep-sea hydrothermal vents. FEMS Microbiol. Ecol. 21: 255-266
- 62 Wery N, Moricet J, Cueff V, Jean J, Pignet P, Lesongeur F, Cambon-Bonavita MA, Barbier G (2001b) *Caloranaerobacter azorensis* gen. nov., sp. nov., an anaerobic

thermophilic bacterium isolated from a deep-sea hydrothermal vent. Int. J. Syst. Evol. Microbiol. 51: 1789-1796

- 63 Alain K, Pignet P, Zbinden M, Quillévéré M, Duchiron F, Donval JP, Lesongeur F, Raguénès G, Crassous P, Quérellou J, Cambon-Bonavita MA (2002c) *Caminicella sporogenes* gen. nov., sp. nov., a novel thermophilic spore-forming bacterium isolated from an East-Pacific Rise hydrothermal vent. Int. J. Syst. Evol. Microbiol. 52: 1621-1628
- 64 Alain K, Quérellou J., Lesongeur F, Pignet P, Crassous P, Raguénès G, Cueff V, Cambon-Bonavita MA (2002d) *Caminibacter hydrogeniphilus* gen. Nov., sp. Nov., a novel thermophilic, hydrogen-oxidizing bacterium isolated from an East Pacific Rise hydrothermal vent. Int. J. Syst. Evol. Microbiol. 52: 1317-1323
- 65 Miroshnichenko ML, Kostrikina NA, L'Haridon S, Jeanthon C, Hippe H, Stackebrandt E, Bonch-Osmolovskaya EA (2002) *Nautilia lithotrophica* gen. nov., sp. nov., a thermophilic sulfur-reducing epsilon-proteobacterium isolated from a deep-sea hydrothermal vent. Int. J. Syst. Evol. Microbiol. 52: 1299-1309
- 66 Campbell BJ, Cary SC (2001) Characterization of a novel spirochete associated with the hydrothermal vent polychaete annelid, *Alvinella pompejana*. Appl. Environ. Microbiol. 67: 110-117
- 67 Moussard H, L'Haridon S, Tindall BJ, Banta A, Schumann P, Stakebrandt E, Reysenbach AL, Jeanthon C (2004) *Thermodesulfatator indicus* gen. nov., sp. nov., a novel thermophilic chemolithoautotrophic sulfate-reducing bacteria isolated from the Central Indian Ridge. Int. J. Syst. Evol. Microbiol. 54: 227-233
- 68 Miroshnichenko ML, Kostrikina NA, Chernyh NA, Pimenov NV, Tourouva TP, Antipov AN, Spring S, Stackebrandt E, Bonch-Osmolovskaya EA (2003) *Caldithrix abyssi* gen. nov., sp. nov., a nitrate-reducing, thermophilic, anaerobic bacterium isolated from a Mid-Atlantic Ridge hydrothermal vent, represents a novel bacterial lineage. Int. J. Syst. Evol. Microbiol. 53: 323-329
- 69 Jones WJ, Leigh JA, Mayer F, Woese F, Woese CR, Wolfe RS (1983) *Methanococcus jannaschii* sp. nov., an extremely thermophilic methanogen from a submarine hydrothermal vent. Arch. Microbiol. 136: 254-261
- 70 Jeanthon C, L'Haridon S, Reysenbach AL, Vernet M, Messner P, Sleytr UB, Prieur D (1999) *Methanococcus infernus* sp. nov., a novel hyperthermophilic lithotrophic methanogen isolated from a deep-sea hydrothermal vent. Int. J. Syst. Bacteriol. 48: 913-919
- 71 Jeanthon C, L'Haridon S, Cueff V, Banta A, Reysenbach AL, Prieur D (2002) *Methanococcus vulcanius* sp. nov., a novel hyperthermophilic methanogen isolated from East Pacific Rise, and identification of *Methanococcus* sp. DSM 4213 (T) as *Methanococcus fervens* sp. nov. Int. J. Syst. Bacteriol. 49: 583-589
- 72 Takai K, Inoue A, Horikoshi K (2002) Methanothermococcus okinawensis sp. nov., a thermophilic, methane-producing archaeon isolated from a Western Pacific deep-sea hydrothermal vent system. Int. J. Syst. Evol. Microbiol. 52: 1089-1095
- 73 Kurr M, Huber R, König H, Jannasch HW, Fricke H, Trincone A, Kristjansson JK, Stetter KO (1991) *Methanopyrus kandleri*, gen. and sp. nov. represents a novel group of hyperthermophilic methanogens, growing at 110°C. Arch. Microbiol. 156: 239-247
- 74 Canganella F, Jones WJ, Gambacorta A, Antranikian G (1998) *Thermococcus guaymasensis* sp. nov. and *Thermococcus aggregans* sp. nov., two novel thermophilic archea isolated from the Guaymas Basin hydrothermal vent site. Int. J. Syst. Bacteriol. 48: 1181-1185

- 75 Duffaud GD, Dhennezel OB, Peek As, Reysenbach AL, Kelly RM (1998) Isolation and characterization of *Thermococcus barossii*, sp. nov., a hyperthermophilic Archeon isolated from a hydrothermal vent flange formation. Syst. Appl. Microbiol. 21: 40-49
- 76 Godfroy A, Meunier JR, Guézennec J, Lesongeur F, Raguénès G, Rimbault A, Barbier G (1996) *Thermococcus fumicolans* sp. nov., a new hyperthermophilic archaeum isolated from deep-sea hydrothermal vent in North Fiji bassin. Int. J. Syst. Bacteriol. 46: 1113-1119
- 77 Godfroy A, Lesongeur F, Raguénès G, Quérellou J, Antoine E, Meunier JR, Guézennec J, Barbier G (1997) *Thermococcus hydrothermalis* sp. nov., a new hyperthermophilic Archeon isolated from dep-sa hydrothermal vent. Int. Syst. Bacteriol. 47: 622-626
- 78 Gonzalez JM, Kato C, Horikoshi K (1995) *Thermococcus peptonophilus* sp. nov., a fast-growing, extremely thermophilic archaebacterium isolated from deep-sea hydrothermal vents. Arch. Microbiol. 164: 159-164
- 79 Grote R, Li LN, Tamaoka J, Kato C, Horikoshi K, Antranikian G (1999) *Thermococcus siculi* sp. nov., a novel hyperthermophilic archaeon isolated from a deep-sea hydrothermal vent at the Mid-Okinawa Trough. Extremophiles 3: 55-62
- 80 Huber H, Stöhr J, Honenhaus S, Rachel R, Burggraf S, Jannasch HW, Stetter KO (1995) *Thermococcus chitonophagus* sp. nov., a novel, chitin-degrading, hyperthermophilic archaeum from a deep-sea hydrothermal environment. Arch. Microbiol. 164: 255-264
- 81 Marteinsson VT, Reysenbach AL, Birrien JL, Prieur D (1999c) A stress protein is induced in the deep-sea barophilic hyperthermophile *Thermococcus barophilus* when grown under atmospheric pressure. Extremophiles 3: 277-282
- 82 Cambon-Bonavita MA, Lesongeur F, Pignet P, Wery N, Lambert C, Godfroy A, Quérellou J, Barbier G (2003) *Thermococcus atlanticus* sp. nov., a hyperthermophilic Archaeon isolated from a deep-sea hydrothermal vent in the Mid-Atlantic Ridge. Extremophiles 7: 101-109
- 83 Jolivet E, L'Haridon S, Corre E, Forterre P, Prieur D (2003) *Thermococcus gammatolerans* sp. nov., a hyperthermophilic Archaeon from a deep-sea hydrothermal vent that resists ionizing radiation. Int. J. Syst. Evol. Microbiol. 53: 847-851
- 84 Erauso G, Reysenbach AL, Godfroy A, Meunier JR, Crump B, Partensky F, Baross JA, Marteinsson V, Barbier G, Pace NR, Prieur D (1993) *Pyrococcus abyssi* sp. nov., a new hyperthermophilic archaeon isolated from a deep-sea hydrothermal vent. Arch. Microbiol. 160: 338-349
- 85 Barbier G, Godfroy A, Meunier JR, Quérellou J, Cambon MA, Lesongeur F, Grimont PAD, Raguénès G (1999) *Pyrococcus glycovorans*, sp. nov., a hyperthermophilic archaeon isolated from the East pacific Rise. Int. J. Syst. Bacteriol. 49: 1829-1837
- 86 Gonzalez JM, Masuchi Y, Robb FT, Ammeramn JW, Maeder DL, Yanagibayashi M, Tamaoka J, Kato C (1998) *Pyrococcus horikoshii* sp. nov., a hyperthermophilic archaeon isolated from hydrothermal vent at the Okinawa Trough. Extremophiles 2: 123-130
- 87 Takai K, Sugai A, Itoh T, Horikoshi K (2000) Palaeococcus ferrophilus gen. nov., sp. nov., a barophilic, hyperthermophilic archaeon from a deep-sea hydrothermal vent chimney. Int. J. Syst. Evol. Microbiol. 50 Part 2: 489-500
- 88 Burggraf S, Jannasch HW, Nicolaus B, Stetter KO (1990) Archaeoglobus profundus, sp. Nov., represents a new species within the sulfate-reducing archaebacteria. Syst. Appl. Microbiol. 13: 24-28

- 89 Huber H, Jannasch H, Reinhard R, Fuchs T, Stetter KO (1997) Archaeoglobus veneficus, sp. nov., a novel facultative chemolithoautotrophic hyperthermophilic sulfite reducer, isolated from abyssal black smokers. Syst. Appl. Microbiol. 20: 374-380
- 90 Kashefi K, Tor JM, Holmes DE, Gaw Van Praagh CV, Reysenbach AL, Lovley DR (2002) *Geoglobus ahangari* gen. nov., sp. nov., a novel hyperthermophilic archaeon capable of oxidizing organic acids and growing autotrophically on hydrogen with FE (III) serving as the sole electron acceptor. Int. J. Syst. Evol. Microbiol. 52: 719-728
- 91 Huber H, Burggraf S, Mayer T, Wyschkony I, Rachel R, Stetter KO (2000b) *Ignicoccus* gen. nov., a novel genus of hyperthermophilic, chemolithoautotrophic Archaea, represented by two new species, *Ignicoccus islandicus* sp. nov. and *Ignicoccus pacificus* sp. nov. Int. J. Syst. Evol. Microbiol. 50: 2093-2100
- 92 Fiala G, Stetter KO, Jannasch HW, Langworthy TA, Madon J (1986) *Staphylothermus marinus* sp. nov. represents a novel genus of extremely thermophilic submarine heterotrophic archaeabacteria growing up to 98°C. Syst. Appl. Microbiol. 8: 106-113
- 93 Pley U, Schipka J, Gambacorta A, Jannasch HW, Fricke H, Rachel R, Stetter KO (1991) *Pyrodictium abyssi* sp. nov. represents a novel heterotrophic marine archaeal hyperthermophile growing at 110°C. Syst. Appl. Microbiol. 14: 245-253
- 94 Huber H, Hohn MJ, Rachel R, Fuchs T, Wimmer VC, Stetter KO (2002a) A new phylum of Archaea represented by a nanosized hyperthermophilic symbiont. Nature 417: 63-67
- 95 Jakosky BM, Shock EL (1998) The biological potential of Mars, the early Earth, and Europa. J. Geophys. Res. 108(E8): 19359-19364

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