International Journal of Astrobiology 2 (3): 213–216 (2003) Printed in the United Kingdom
DOI: 10.1017/S1473550403001617 © 2003 Cambridge University Press

Unfrozen subsurface water on Mars: presence and implications

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Abstract: It has been concluded from measurements, recently made by Mars Odyssey experiments, that there is water in the upper few metres of the Martian surface at mid- and equatorial latitudes with regionally high contents of up to about 9 wt%. This Martian subsurface water is shown to be in the form of adsorption (or sorption) water. The adsorptive bond of water molecules is about twice as strong on mineral surfaces compared with on water ice. Therefore, evaporation of adsorption water in porous soil happens on time scales, which exceed those of sublimation of water ice by orders of magnitude. Consequently, sorption water can have survived in the near-surface layers of the Martian soil at mid- and equatorial latitudes over geological time scales, where ice must have been lost by sublimation. Sorption water is unfrozen, i.e. liquid-like, down to temperatures of -40 °C and below. It must, at least regionally and temporarily, be an important and not a trace constituent of the upper-surface Martian soil. The presence of liquid-like sorption water on Mars is also discussed in view of exobiological implications.

Received 30 June 2003, accepted 4 August 2003

Key words: adsorption water, hydrated minerals, liquid-like water, Martian subsurface water content, Martian surface chemistry, unfrozen water.

Introduction

Liquid-like water is a precondition for life of terrestrial-type forms. The often postulated absence of liquid-like water on present-day Mars therefore seems to exclude the possibility that life has survived from the earlier and probably wetter and warmer conditions on Mars. Liquid bulk water can indeed at present not stably exist on and in the upper surface of Mars. Under Martian conditions evaporation will effectively cause a loss of possible water accumulations at pressures and temperatures above the triple point of water. Furthermore, sublimation of water ice is responsible for a complete loss over geological time scales of ice at and in the upper metres of the Martian surface at mid- and equatorial latitudes. Therefore, the upper metres of the present Martian surface are generally assumed to be dry (Squyres *et al.* 1992) . This is not necessarily the case.

In the lower layers above the microscopic surfaces of sorbent minerals, adsorption water has a much stronger bond to these surfaces than water ice. This is the reason for the much longer survival time for adsorption (or sorption) water in porous materials, compared with ice. The water-related results of the Mars Odyssey (Boynton *et al.* 2003; Feldman *et al.* 2003; Mitrofanov *et al.* 2003) experiments are a strong support in favour of the proposed model of a 'sorption-wetted' upper Martian surface. It is the aim of this paper to describe these physical effects in more detail in view of current Martian thermo-dynamical conditions and of the properties of the porous Martian soil minerals. It is finally concluded that there are new challenges for studying physical properties, low-pressure and low-temperature 'sorption-water-triggered' chemical processes and exobiological aspects of a sorption-wetted upper Martian surface.

Sorption and adsorption enthalpies

Adsorption water forms at solid surfaces due to the attraction between the polar water molecule and the surface forces (van der Waals forces). The range of the surface forces is typically about 0.5 nm. The thickness of one layer of adsorption water is about 0.3 nm. Thus, complete pore volumes can be filled by water in the case of micro- and nano-sized pores or interfacial spaces, which can be filled by adsorption. The term 'sorption' has been introduced to describe the combined surface and volume effects of adsorption and absorption, respectively.

The bond of water molecules on sorbent surfaces can be described in terms of adsorption enthalpies, as they are used in describing the dependence of vapour pressure $p(T)$ on the energetic bond of the molecules on the surface and on temperature. This can for water ice be described in the temperature range of $-65 < T < 0$ °C by

$$p\ [\mathrm{Pa}] = 611.2 \exp\left[\frac{22.46(T-273.15)}{T-0.53}\right] \quad (1)$$

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(Sonntag 1990). For temperatures $T \gg 0.53$ K this takes the form

$$p\ [\mathrm{Pa}] = 3.47 \times 10^{12}\ \mathrm{e}^{\Delta H_{\mathrm{ice}}/kT[\mathrm{K}]}, \quad (2)$$

as also follows from the Clausius–Clapeyron relation for constant enthalpy of sublimation ΔH_{ice}. In the case of sublimation, this enthalpy is the heat (i.e. the external energy), which is necessary for the phase change from ice to vapour. It follows with the values of equation (1) for ice that $\Delta H_{\mathrm{ice}} = 8.4662 \times 10^{-20}$ W s $= 0.529$ eV $= 50.78$ kJ mol^{-1}. This adsorption enthalpy is a measure for the energetic bond of water molecules, which are adsorbed on the surface of water ice.

Adsorption enthalpies of minerals

The enthalpies of adsorption (or sorption) can for natural minerals, such as clays, overcome up to a factor of about 2 or more the enthalpy of sublimation of ice. Sondi & Pravdic (1998) have shown that clays (montmorillonites) can have a 'wetting enthalpy' of about 0.7 eV (147 J g^{-1}). The microscopic surfaces of terrestrial natural minerals are to be characterized by local irregularities and micro-scale 'roughness'. These are dependent on the peculiar history of each of these micro-surfaces, as they have been formed during the course of the interaction of the micro-surfaces within the physically and chemically active terrestrial environment. This is one of the reasons for the fact that there are only a few adsorption enthalpies known precisely for natural minerals, and that measurements with values up to 1 eV and more show large differences. As an example, Fubini *et al.* (1989) report experimental adsorption energies for a water molecule on a metal ion at an oxide surface between 0.7 and 1.24 eV. Carey & Bish (1996) have shown that zeolithes (clinoptilolites) with their more regular micro-surfaces have 'hydration enthalpies' of up to $\Delta H_{\mathrm{hyd}} = 0.8$ eV (77 kJ mol^{-1}) and above. Here, further and more detailed experimental investigations are required to study quantitatively the sorption and wetting properties of natural minerals, especially under low-pressure and low-temperature conditions.

To have a quantitative estimate, a vapour pressure relation of sorption water of the form $p_{\mathrm{s}}\ [\mathrm{Pa}] = 3.47 \times 10^{12}\ \mathrm{e}^{\Delta H_{\mathrm{s}}/kT[\mathrm{K}]}$ shall be used in the following with two exemplary sorption enthalpies of $\Delta H_{\mathrm{s}} = 0.75$ and 0.85 eV.

Unfrozen water

The stronger bond of the surface forces up to distances of about 0.5 nm above the surface indicates that the physical properties of the two lower monolayers of adsorption water are governed by the surface forces of the sorbent mineral. Therefore, the few lower monolayers of adsorption water must be more resistant to desorption, and the properties of the higher water monolayers become increasingly similar to those of liquid bulk water with an evaporation enthalpy at 0 °C of $\Delta H_{\mathrm{eva}} = 45.054$ kJ mol$^{-1} = 0.45$ eV. The physics of adsorption water with only one or a few monolayers differs from that of bulk water. Materials with only a few monolayers of adsorption water therefore differ in their properties compared to more wetted materials with multiple monolayers. As an example, ice can form at temperatures $T < 0$ °C in the bulk water above the lower few monolayers, which remain liquid-like down to much lower temperatures.

The phenomenon of 'unfrozen water', as it is known to exist in terrestrial permafrost down to temperatures of −40 °C and below, can be explained by the combined action of capillary forces and of the above-mentioned surface forces. This liquid-like unfrozen water must be expected to exist in Martian soil. The physics behind this is that, as described above, at solid surfaces, in general a few physisorbed layers of water ('adsorption water') are in a liquid-like state (Stillinger 1980; Thiel & Madey 1987; Staszczuk 1995; Henderson 2002). The comparatively strong bond of water molecules to the solid surface reduces the vapour pressure and shifts evaporation towards higher temperatures. Further freezing point depression is caused in bulk water by surface tension caused by capillary effects. Chemicals in the water can additionally cause a decrease of the freezing point temperature.

It is this liquid-like property of unfrozen sorption water in Martian soil that extends the importance of Martian subsurface water to a large number of physical, chemical and possibly also biological aspects.

It has been discussed by Möhlmann (2002) that the existence of at least two mono-layers of liquid-like adsorption water in Martian soil could help us to understand the water content in the upper Martian surface as observed by Mars Odyssey experiments (Boynton *et al.* 2003; Feldman *et al.* 2003; Mitrofanov *et al.* 2003). This conclusion has recently been supported by Bish *et al.* (2003), who have shown that the possible existence of hydrated clinoptilolites on Mars can help to explain the water content as found by Mars Odyssey. The approach of Bish *et al.* is based on the concept of hydrous minerals. This is similar and complementary to the description in terms of processes of sorption (adsorption) of unfrozen water with liquid-like properties in porous soil.

Survivability of unfrozen sorption water and ice on Mars

The evaporation rate E [molecules m^{-2} s^{-1}] of a plane layer of adsorption water (into vacuum) can be described by $E = (N/4)v_{\mathrm{th}}$, where N is the number density of the evaporated water molecules at the evaporating surface and $v_{\mathrm{th}} = \sqrt{8kT/\pi m}$ is the mean thermal velocity of the water molecules of mass m. It follows for an ideal gas with $p = NkT$ that $E = 3.47 \times 10^{12}\ \mathrm{e}^{-\Delta H_{\mathrm{s}}/kT}/\sqrt{2\pi m k T}$. The sublimation rate of ice is described by the same relation, but with the sublimation enthalpy $\Delta H_{\mathrm{ice}} = 0.529$ eV. The ratio $S = Z/E = \exp[(\Delta H_{\mathrm{s}} - \Delta H_{\mathrm{ice}})/kT]$ of the sublimation rate Z of ice and the evaporation rate E of adsorption water are a direct measure of the longer lifetime of evaporating adsorption water compared with that of sublimating water ice. Fig. 1 illustrates this behaviour. The temperature range is typical for the upper Martian subsurface layers at depths of one

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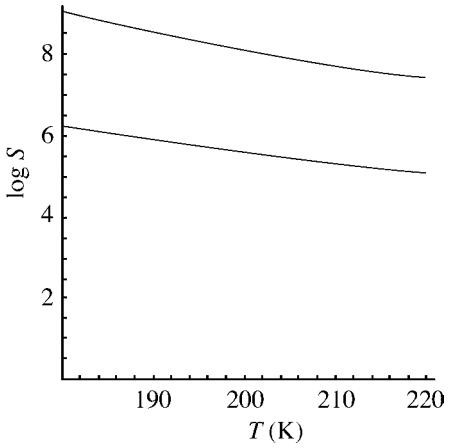


Fig. 1. Logarithm of the ratio $S = Z/E$ of sublimation rates of ice and evaporation rates of adsorption water versus temperature and the sorption enthalpy ΔH_s (upper curve, $\Delta H_s = 0.85$ eV; lower curve, $\Delta H_s = 0.75$ eV).

or a few metres (cf. Carr 1996; Helbert & Benkhoff 2003). It can be seen that sorption water with enthalpies of the above given values will survive at these temperatures about 10^6–10^8 times longer than ice. In other words, water ice must have completely been sublimated over geological time scales in the upper Martian surface while sorption water could have survived over billions of years in the upper few metres of Martian mid- and equatorial latitudes until the present.

This fact can help us to understand the Mars Odyssey observations of near-surface subsurface water on Mars. Of course, the amount of sorption water in the porous Martian soil depends on temperature and on the specific surface (or sorption capacity) of the soil.

The content of sorption water

The amount of adsorption water in porous matter depends on the internal surface A of the adsorbing porous material. Usually, this is described in terms of the specific surface S_M with respect to the dry mass. A Viking-1 based value of $S_M = 1.7 \times 10^4$ m² kg^{-1} has been published by Ballou *et al.* (1978). Unfortunately, this is the only known value of direct relevance to Mars. The accuracy and range of validity of this local value are unknown. Terrestrial minerals have comparable values of $S_M = 1 \times 10^4$ m² kg^{-1} for well-crystallized kaolinite clays on the one hand, and of $S_M = 8.2 \times 10^5$ m² kg^{-1} for montmorillonite (Arizona, Cheto) on the other hand (van Olphen & Fripiat 1979). Terrestrial natural zeolithes have specific surfaces of the order of 10^6 m² kg^{-1}.

The content of adsorption water depends on the value of the surface mass density Σ of a monolayer of adsorption water. Here, a value of $\Sigma = 3 \times 10^{-7}$ kg m^{-2} will be used. The mass m of adsorbed water is given by $m = n\Sigma A$, where n is the number of adsorption layers. The mass M of the corresponding soil of dry mass density ρ_S and of internal surface A follows with $M = \rho_S V = A/S_M$. The mass ratio of adsorption water with respect to soil mass is then described by $m/M = n\Sigma S_M$.

Thus, a content of 1 wt% (with respect to the dry mass) of adsorption water in Martian soil of a specific surface of $S_M = 1.7 \times 10^4$ m² kg^{-1} is equivalent to the presence of about two monolayers ($n = 1.96$). A content of adsorption water of 9 wt%, as has been derived for regions at equatorial latitudes from the above-mentioned Mars Odyssey measurements requires a specific surface of $S_M = 1.5 \times 10^5$ m² kg^{-1} in the case of two liquid-like monolayers. Given the range of specific surfaces of terrestrial minerals this cannot be excluded at present.

Adsorptive exchange in the uppermost surface

The content of water vapour of the lower Martian atmosphere of $hp = 10$ pr μm (where pr μm denotes precipitable microns of water, cf. Ryan *et al.* 1982) of a mass density of water of $\rho_W = 1000$ kg m^{-3} is equivalent to a surface mass density of $m/F = \rho_W V/F = \rho_W hp = 10$ g m^{-2} at the Martian surface area F. It follows with $m/M = n\Sigma S_M$ for a height h of soil volume $V = hF$ that $h = V/F = M/(\rho_S F) = (m/F)/(n\Sigma\rho_S S_M)$. The depth h of this soil layer would be $h = 1.31$ mm if a content of 10 pr μm (with $m/F = 10^{-2}$ kg m^{-2}) of atmospheric water was adsorbed in the case of only one monolayer at the surfaces of Martian soil minerals of specific surface $S_M = 1.7 \times 10^4$ m² kg^{-1} and a dry soil mass density of $\rho_S = 1500$ kg m^{-3}. This thickness will decrease in the case of larger specific soil surfaces.

Ice or frost can develop at this uppermost surface in the case of a temporary formation of multiple adsorption layers in the course of saturation-caused adsorption during cool Martian night and morning hours. The upper and more bulk-water-like layers of this adsorption water can freeze at these temperatures. The Viking-Landers have indeed observed the temporary deposition of frost at the Martian surface.

The above estimates indicate that a direct adsorptive diurnal exchange between the water in the Martian atmosphere and in the upper Martian surface will be most effective at and in the upper millimetres of the surface only. The sorption water at the soil particles at larger depths has a sufficiently strong bond to the particle surfaces, which reduces the ability of this unfrozen subsurface water to effectively participate in a diurnal exchange with the atmosphere.

Possible implications of sorption water in the Martian surface

Unfrozen, i.e. liquid-like, water is partially different in its molecular structure (formation of ice-like or polymeric clusters, preferential orientations, the water is more ordered) compared with bulk water. It exhibits anomalous physical and chemical properties (viscosity, transport processes at the surface such as electric and thermal conductivity, optical and spectral properties, sound velocities, rate enhancement by catalysis, chemisorption or chemical reactions such as corrosion, solution of parts of the solid and foreign species present on the surface, etc.). The presence of unfrozen water in Martian granular soil must therefore have an influence on

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physical and rheological properties such as viscosity, acoustic velocities, electric (including spectral) and thermal properties (such as conductivities) of the upper Martian surface.

Furthermore, adsorption and sorption water is to be characterized by the interaction with and the influence of the adsorbing solid surface. Chemical processes will take place in layers of adsorption water, which directly interact with the solid surface, and catalytic and structural ordering effects are to be expected. These processes will have small reaction rates at Martian temperatures, but nevertheless, they can become effective over longer (i.e. geological) time scales. Thus, Martian surface chemistry has to be revised in view of 'sorption-water-triggered' low-temperature chemistry.

Despite the comparatively low temperatures, the ultraviolet (UV) insolation at the Martian surface is an effective energy source for chemical processes on Mars. One example is the photo-Fenton reaction (Spacek *et al.* 1995), which becomes effective in acidic aqueous solution:

$$Fe^{3+}_{aq} + H_2O \xrightarrow{h\nu} Fe^{2+}_{aq} + H^+ + OH^{\cdot}.$$

Hydroxyl radicals have a large oxidation potential. They cause chemical oxidation reactions very effectively. Thus, the presence of adsorption water may be a key to understanding the reasons for the high degree of oxidation of Martian surface materials. Hydroxyl radicals oxidize most organic compounds completely, forming carbon dioxide, water and minerals.

A photo-Fenton-like process, triggered by adsorption water on Mars, may well be responsible for the lack of organics of meteoritic origin in Martian soil, as became apparent from the Viking life sciences experiments. (The photo-Fenton reaction is used in technical chemistry on Earth to clean waste waters, which are contaminated by organics.)

Furthermore, sulphur is present at and in the Martian surface. The concentration of SO_3 is estimated to be of about 7.3% (Banin *et al.* 1992). SO_3 forms sulphuric acid in the presence of liquid-like adsorption water. Possibly existing carbonates will form sulphates at their surfaces. Thus, the carbonates in these sulphate-covered substances are not observable directly by remote spectroscopic methods. This may be related to the fact that the spectroscopic search for Martian carbonates has failed so far.

Finally, it has to be noted that unfrozen sorption water is one of the most essential environmental parameters in view of studying biological processes under Martian subsurface conditions. This available type of liquid-like water could support the metabolism of living organisms. The current presence of liquid-like unfrozen sorption water in Martian subsurface soil is therefore a challenge to exobiological *in situ* experiments on Mars. Terrestrial Mars simulation experiments can help to answer the question of the survival and adaptation capabilities of microbial organisms under 'sorption-water-wetted' Martian subsurface conditions.

Recommendations

Future work is necessary to substantiate more quantitatively the consequences of the present existence of an up to about 10 wt% wet Martian subsurface at mid- and low latitudes. The resulting tasks span a field of broad activities of:

- measuring the hydration and wetting properties of natural 'Mars-relevant' minerals by laboratory experiments;
- studying the influence of wetting of granular and Mars-relevant materials on physical (mechanical, electrical, optical and spectral) parameters;
- investigating the importance of a low-pressure and low-temperature 'sorption-water-triggered' chemistry of granular materials of Mars relevance;
- Mars simulation experiments to study the adaptation and the survival potential of organisms in a wet Mars-subsurface-like environment under Martian thermophysical conditions and with Mars-analogue minerals.

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