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Hypothesis Paper

Adsorption Water-Related Potential Chemical and Biological Processes in the Upper Martian Surface

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ABSTRACT

Mars Odyssey has given strong evidence for the existence of water in the upper martian surface at equatorial latitudes. The water content, which corresponds to the hydrogen in the soil, can regionally reach values up to about 15%. This water is mainly in the form of structurally and partially irreversibly bound "crystal" water, and of reversibly bound and partially unfrozen adsorption water. This adsorption water, which has "liquid-like" properties as a two-dimensional fluid or film, can trigger—in the presence of ultraviolet light and in concentrations similar to what has been measured on Mars—photocatalytic processes that are important for martian surface chemistry. The consequences of the diurnally variable presence of adsorption water on the chemistry and hypothetical biological processes at and in the upper martian surface at equatorial and mid-latitudes are discussed in terms of water-related environmental aspects for chemical and hypothetical life processes on Mars. Key Words: Liquid-like adsorption water—Martian surface—Adsorption water-triggered chemistry—Adsorption water-based life processes. Astrobiology 5, 770–777.

INTRODUCTION

THE MARTIAN SURFACE IS, at middle and low latitudes, not dry (Feldman *et al.*, 2002; Mitrofanov *et al.*, 2002). The water content in the upper surface, as estimated by Feldman *et al.* (2004), can regionally reach values of 10% by weight and more (Fig. 1). This water is present in the upper meter of the martian surface in the form of irreversibly bound "crystal water," which contributes to the structure of minerals and salts (Bish *et al.*, 2003). It is also present in the form of adsorption water, which participates in the reversible processes of temporary adsorption and desorption during the course of diurnally variable atmosphere–surface interactions. The content of adsorption water in the upper millimeter-to-centimeter-thick surface layer ("surface skin") ranges from multiple monolayers of adsorption water, when the atmosphere is saturated, to less than one monolayer when the atmosphere is dry (Möhlmann, 2004). Here, a monolayer refers to a single molecular layer of water molecules, which may not be a continuous film but may—in the case of "less than one"–consist of local water "islands." At greater depths, the content of adsorption water tends to become stable at about two monolayers.

The energetic bond "e_{ads}" per molecule of adsorption water on the surface of a mineral is

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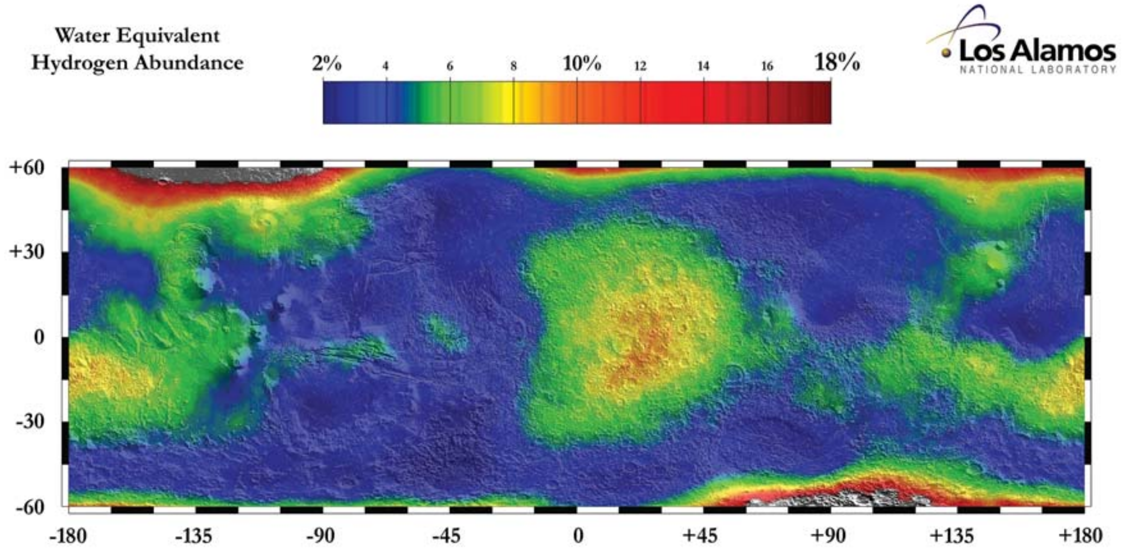

FIG. 1. Water equivalent hydrogen abundances in the upper meter of the martian surface (Feldman *et al.*, 2004), which are interpreted as a measure of the content of water molecules.

stronger than the energetic bond e_{ice} per molecule of adsorption water on ice by a factor of $\exp[(e_{\text{ads}} - e_{\text{ice}})/kT]$ (Möhlmann, 2004). For Mars, water adheres 10^5–10^7 times more strongly to mineral surfaces than to ice [$e_{\text{ice}} = 0.5$ eV per water molecule and $e_{\text{ads}} = 0.8$ eV (and larger) per water molecule]. Thus, adsorption water is expected to persist on mineral surfaces in the upper martian surface at middle and low latitudes over geological time scales. There is no permanent ice; only "young" or temporary water ice could be expected to occur in these regions since water ice sublimates effectively at these latitudes.

Adsorption water exists also in terrestrial permafrost in a liquid-like state at temperatures at and below −40°C. This is the so-called "unfrozen water" in permafrost (Anderson and Tice, 1972). Soil with unfrozen water has modified physical, chemical, and biological properties in comparison with dry frozen soil. These are discussed in the following sections with regard to possible chemical and hypothetical biological processes in the upper martian surface, which could be driven or facilitated by adsorption water.

ADSORPTION WATER IN THE UPPER MARTIAN SURFACE

Adsorption of water on surfaces of grains is a common phenomenon in the presence of atmospheres with water vapor. This happens on Mars as well, where the water content of the atmospheric column is between about 10 pr μm and 100 pr μm (Smith, 2002). Here, pr μm stands for the height of water if all of the atmospheric water were precipitated, and is measured in "precipitable micrometers."

The amount of adsorption water depends on the properties of the surface (as energetic bond and specific surface) of the "adsorbent," and on the humidity of the atmosphere. Mikhail and Robens (1983) have shown, by summarizing numerous experimental results, that for most natural minerals at room temperature (and at lower temperatures) there is less than one monolayer on mineral surfaces. The number of monolayers of adsorption water increases with humidity to about eight layers when the atmospheric water content is saturated. This is taken into account by an analytical approximation of the relation $n(a_W)$ between the number "n" of monolayers and the normalized relative humidity or water activity $a_W = p(T)/p_0(T)$, where p_0 is given by $p_0 = a \exp[-b/(kT)]$. Here, p and T are water vapor pressure and temperature, respectively, k is Boltzmann's constant, and the water-related constants are for water vapor above ice $a = 3.47 \times 10^{12}$ Pa and $b = 8.4662 \times 10^{-20}$ Ws (Möhlmann, 2004).

The number of monolayers $n(a_W)$ depends only weakly on relative humidity in the range up to about two to three monolayers. This is due to the fact that the first two to three monolayers above the surface of the adsorbent are most strongly

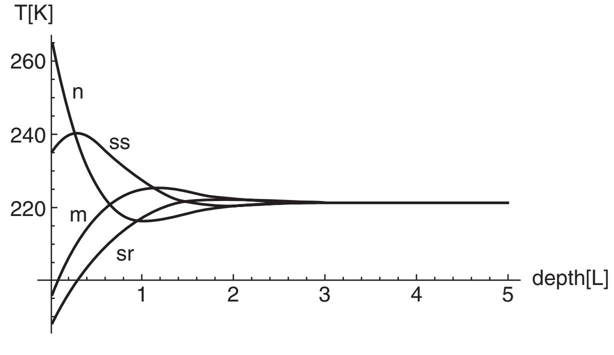

FIG. 2. Depth profiles of the diurnal temperature variation on Mars. The depth is given in units of the diurnal penetration depth $L_T \approx 4.4$ cm. The curves refer to the diurnal temperature variation at noon (n), sunrise (sr), sunset (ss), and midnight (m).

bound to this surface, whereas the monolayers beyond them display properties increasingly similar to that of bulk water (*e.g.*, they may freeze at low temperatures). The first two to three monolayers will remain unfrozen down to temperatures of about 140 K (Pearson and Derbyshire, 1974). It is this liquid-like property that makes adsorption water important for chemical (and possibly biological) processes at temperatures below 0°C.

To determine the number of adsorption layers $n[p(T)/p_0(T)]$ on surfaces in the surface skin of Mars, it is necessary to know the dependence of the temperature field $T(x,t)$ with time t and depth x. Figure 2 gives a corresponding example for martian equatorial conditions during northern spring. The diurnal thermal penetration depth $L_T = \lambda P/\rho c$ depends upon the surface material of mass density ρ, heat conductivity λ, specific heat c, and daily rotation period $P = 88{,}642$ s. Typical numerical values are $\rho = 3{,}000$ kg m^{-3}, $\lambda = 0.1$ Wm^{-1} K^{-1}, and $c = 1{,}500$ Ws kg^{-1}.

The typical scale-length L_T follows by replacing depth z and time t in the heat diffusion equation $\partial T/\partial t = (\lambda/\rho c)\partial^2 T/\partial z^2$ by the dimensionless coordinates $\tau = Pt$ and $x = L_T z$, and using the descaled equation $\partial T/\partial \tau = \partial^2 T/\partial x^2$.

It can be seen in Fig. 2 that a rather constant temperature of about 220 K develops with increasing depth, while the diurnal variations are most efficient in the upper surface parts of up to about 3 L_T.

Temperature governs the normalized relative humidity or "water activity" $a_W(T) = p(T)/p_0(T)$. Thus, the number of adsorption layers on mineral grains in the upper martian surface is a function of the diurnal variation of the surface and subsurface temperatures. This is described in Fig. 3 for: the temperature field of Fig. 2; the $n(a_W)$ relation, as given by Fig. 4; and an atmospheric water content of 10 pr μm (Smith, 2002) or 3×10^{19} water molecules m^{-3}.

In Fig. 3, it can be seen that the variability of the number of adsorption layers is restricted to the upper parts of the martian surface at depths of only a few L_T. Adsorption is strongest during night and morning hours. Exchange with the atmospheric water is restricted to the uppermost millimeter-to-centimeter-thick skin layer (Möhlmann, 2004). A drier "transition layer" evolves below the temporarily wet skin layer. A constant content of adsorption water (with $n \approx 2$) that develops at greater depths is referred to as the "permanent layer."

The diurnal variation of the number of monolayers n at the surface is shown in Fig. 5 for two different seasons.

ADSORPTION WATER AND MARTIAN SURFACE CHEMISTRY

Liquid-like water can act as a solvent as transport processes become more effective. Chemical processes that are triggered by adsorption water have experimentally been shown to be effective under martian conditions (Möhlmann, 2004). With ultraviolet (UV)-visible radiation as the energy source, highly oxidizing $OH^{\bullet}$ radicals can be

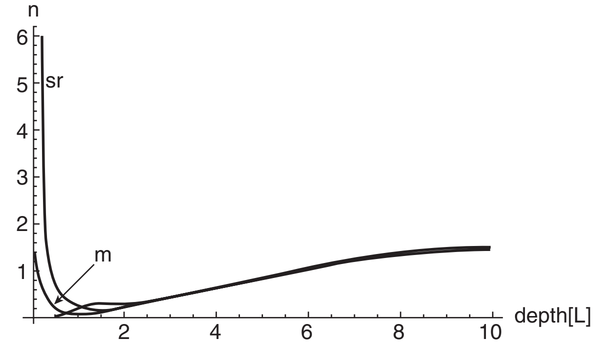

FIG. 3. Variation of the depth dependence of the number n of monolayers of water in the upper martian surface for the temperature model, as is described by Fig. 2. Depth is given in units of L_T. The curves refer to sunrise (sr) and midnight (m). n is ≤1 for noon and sunset.

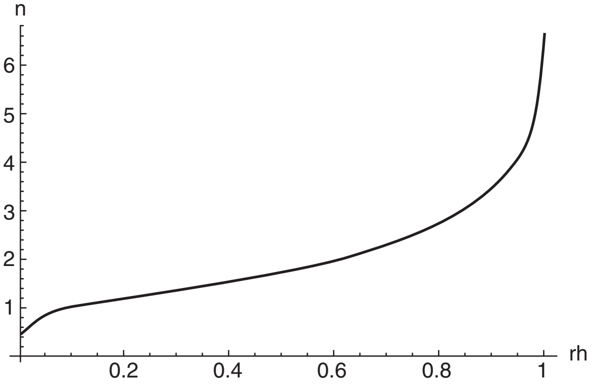

FIG. 4. **Dependence of the number *n* of monolayers on water activity a_W [based on experimental data of Mikhail and Robens (1983)].**

generated in the presence of hematite (Fe^{3+}) and adsorption water in the uppermost martian surface layer. This adsorption water-driven photochemical process is described by

$$\mathrm{Fe^{3+}_{aq}} + \mathrm{H_2O} \xrightarrow{h\nu} \mathrm{Fe^{2+}_{aq}} + \mathrm{H^+} + \mathrm{OH^{\bullet}} \qquad (1)$$

("photo-Fenton reaction"). It has been shown experimentally (cf. Fig. 6) that even a few percent by weight of adsorption water are sufficient for this reaction to become effective (Möhlmann, 2004).

The results of an experiment shown in Fig. 6 indicate that the $OH^{\bullet}$ radical, measured by CO_2 production, was the result of the oxidizing action of the $OH^{\bullet}$ radical on isopropanol, which was continuously blown over the UV-irradiated sample of wetted hematite. The content of wetting adsorption water was about 3% and 5% by weight. UV light was switched on at $t = 0$, and switched off after 40 min. The UV lamp became effective after about 10 min. The CO_2 production rate increased within these first 10 min, then decreased slowly because of drying of the sample until $t = 40$ min, followed by a stronger decrease after the UV source was switched off.

When this experiment (production of $OH^{\bullet}$ radicals by the photo-Fenton reaction with wetted hematite) was repeated within an atmosphere of methane (instead of blowing isopropanol over the UV-irradiated and wetted hematite), formaldehyde was produced as a result of the OH-forced oxidation of methane. The gas chromatography record of this experiment is shown in Fig. 7. The results of this experiment may be important in light of the Mars Express PFS experiment, which detected methane (Formisano, 2004) and formaldehyde (V. Formisano, personal communication) in the martian atmosphere.

In this context, it is interesting to note that the same experiment (UV, wetted hematite) performed within a CO_2 atmosphere resulted in the direct formation of formaldehyde, which was likely produced because of photocatalytic redox processes. A better understanding of martian photochemistry that is driven or made possible by adsorption water is a current challenge with regard to a better understanding of the upper martian surface.

The results of these preliminary experiments suggest that the presence of adsorption water in the upper martian surface may be a key to understanding the high degree of oxidation of martian surface materials. Furthermore, the known presence of SO_3 in the martian surface (Banin *et al.*, 1992) will, together with adsorption water, generate sulfuric acid that will lead to the formation of sulfate on the surfaces of carbonate particles. Surface coatings of sulfates will prevent the detection of carbonates by spectrometric remote sensing methods.

A photo-Fenton-like process on mineral surfaces that releases hydroxyl radicals and, thus, that oxidize any organic molecules may be responsible for the lack of organics of meteoritic origin in martian soil of the upper surface, as was concluded from the results of Viking mission experiments.

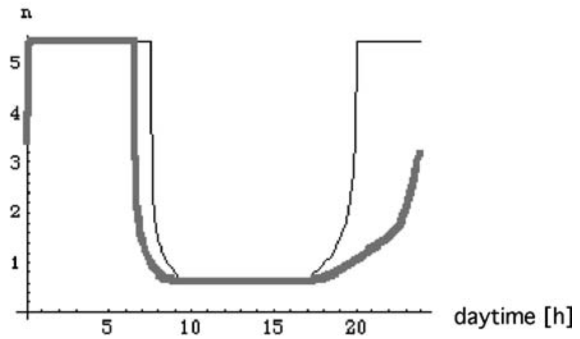

FIG. 5. **Diurnal variation of the number of water adsorption layers for grains at the martian surface during the winter (thin line) and summer solstices (cf. Möhlmann, 2002).** The uppermost surface is comparatively drier during warmer summer conditions.

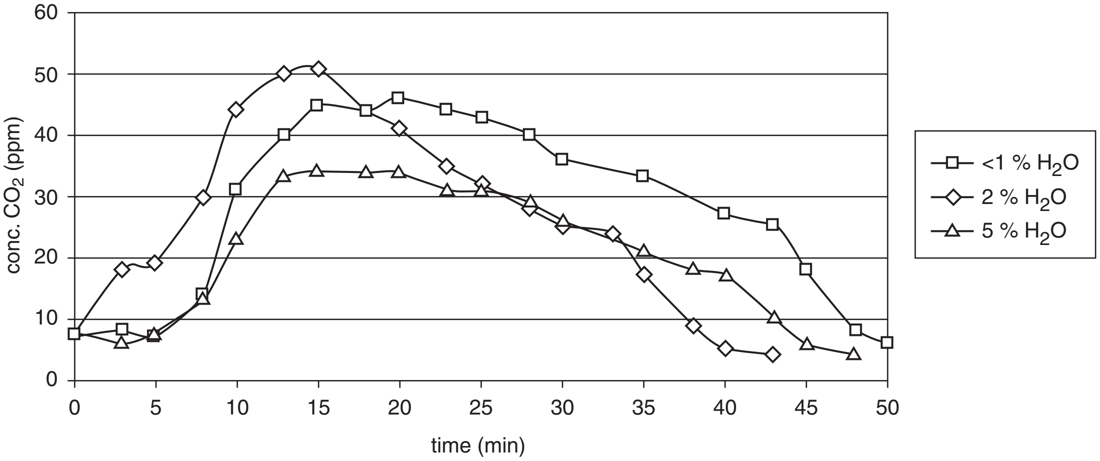

FIG. 6. Time dependence of the CO_2 production in the course of the photo-Fenton reaction in UV-VIS-irradiated hematite, which was wetted by adsorption and additional water (<1%, 2%, and 5% by weight). Courtesy of DLR-TT, Cologne, Germany.

ADSORPTION WATER-BASED HYPOTHETICAL BIOLOGICAL PROCESSES ON MARS

Given that aqueous chemistry is facilitated by the presence of adsorption water on Mars, one can hypothesize that it could support biologic processes. As noted previously, the photo-Fenton reaction reduces, in the presence of UV and adsorption water, ferric to ferrous iron. Ehrenreich and Widdell (1994) demonstrated that, in the presence of photons (visible light), CO_2, and (adsorption) water, terrestrial bacteria are able to oxidize ferrous to ferric iron.

The presence of such bacteria along with the surface chemistry that results from photocatalyzed processes in adsorption water could provide a first example of the iron–carbon cycle shown in Fig. 8, which was proposed by Nealson and Stahl (1997). Under martian conditions, the photo-Fenton reaction must proceed in the uppermost surface layer, where all of the UV light is absorbed. If iron-oxidizing permafrost bacteria live beneath the uppermost surface layer, which can be reached by visible light only, they could account for part A in the iron–carbon cycle at depth. Visible-light photons are used under anaerobic conditions for the fixation of CO_2 to organic carbon $(CH_2O)_n$. Alternatively, the oxidizing biogenic reaction could occur in the uppermost surface layer if the bacteria evolved a UV-protecting "mantle."

Mars is often assumed to be too dry for life

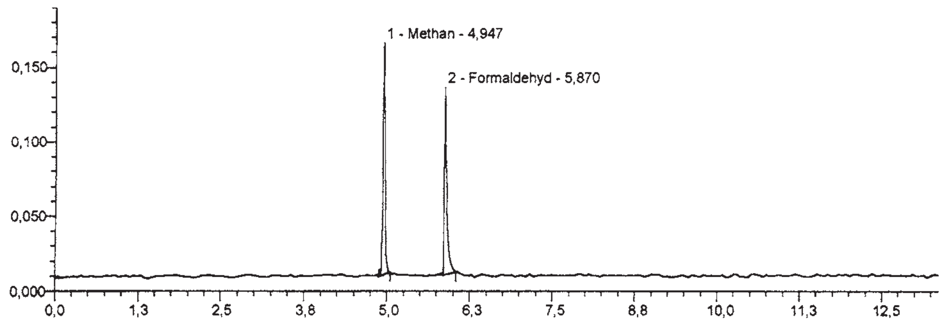

FIG. 7. Gas chromatographic record of methane and its oxidation product formaldehyde in an atmosphere of methane. Oxidizing $OH^{\bullet}$ radicals have been released by the photo-Fenton reaction from wetted hematite (5% by weight of water). The relative signal strength (in mV) is shown in dependence on the retention time (in minutes). Courtesy of Institute of Non-classical Chemistry, Leipzig, Germany.

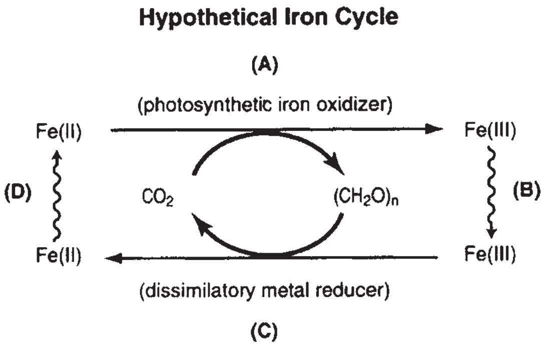

FIG. 8. Iron–carbon cycle proposed by Nealson and Stahl (1997). Reaction A is realized (on Earth) by iron-oxidizing permafrost bacteria; reaction C happens (also on Mars) by the photo-Fenton reaction.

processes that require environments with a "water activity" $a_W = p(T)/p_0(T)$ of, at minimum, between 0.9 and 0.8 (Leonovich, 1987; Troller, 1987). But this is not necessarily true if the humidity is not constant and the microorganisms have some way of harvesting and controlling water from thin films that form during temporary saturation at low temperature. This is not a capability known in life on Earth but may be postulated for martian life.

The ideas presented in this paper lead to a testable hypothesis: The temporary existence of adsorption water in the uppermost layers of the martian surface (with a diurnal average water activity of less than 0.8) could support organisms by allowing them to accumulate adsorption water at night and in the morning. The possibility for such life processes depends on the properties and presence of adsorption water only a few monolayers thick on the surfaces of microorganisms.

It is also possible that martian microbes could have evolved specialized surface structures that would enhance their ability to "capture" adsorption water. For example, aquaporins, *i.e.*, water channel proteins (cf. de Groot and Grubmüller, 2001), located in the cell wall could establish a mechanism to transport liquid-like adsorption water into cells and thereby support the type of metabolism represented in Fig. 9. The aquaporins could work in a temperature-dependent mode by opening inward for water transport at low temperatures (of saturation) and closing to prevent an outward loss of water when warmer daytime conditions prevailed. In other words, metabolism would become more active during warmer daytime conditions after the accumulation of "cold" water at night.

Note that adsorption water remains liquid-like during the colder martian nights. Thus, this process would be favored thermodynamically if the concentration of water in the liquid water film at the cell wall surface were higher than the water concentration inside the cell. Osmotic effects would control this gradient.

A liquid-like water film is expected to persist for several hours during the night. One monolayer of adsorption water consists of about 10^{19} molecules m^{-2}, or about 10^9 molecules on the surface of a cell with a surface area of about $(10\ mm)^2$. Under thermodynamic equilibrium conditions, a liquid-like water would be supplied continuously from the vapor phase. The rate of flow of water molecules from the vapor phase to the adsorbed water film on a cell at $T = 200$ K and a partial water vapor pressure of 10^{-1} Pa would be about 6×10^{21} molecules $m^{-2}\ s^{-1}$, or 6×10^{11} molecules [of $(10\ \mu m)^{-2}$] s^{-1}. Thus, a single cell with a surface area of about $(10\ \mu m)^2$ under martian nighttime conditions could extract, at most, 10^{15} water molecules over 3 h, a volume of fluid equivalent to $3 \times 10^{-14}\ m^3$, which exceeds the volume of the microbial cell.

Liquid-like adsorption water and solar photons are present simultaneously at the martian surface for several hours after sunrise, while liq-

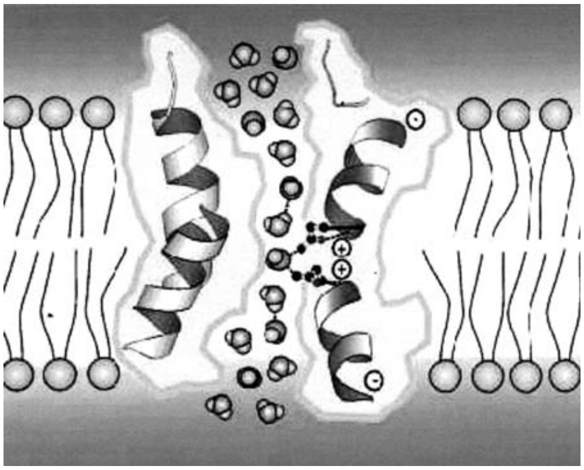

FIG. 9. Aquaporins in cell walls can transport liquid-like water through the cell wall into the cellular body. Courtesy of http://ntmf.mf.wau.nl/aquaporin/images/mechan._aqpl.jpg. (After Murata *et al.*, 2000.)

uid-like adsorption water persists during night and morning hours as well. Thus, hypothetical martian organisms that live at the surface would need to have developed a UV-protective "mantle" that could support the accumulation of adsorption water as a result of its large specific surface and a high adsorption enthalpy or energetic bond for adsorption water. Zeolithic structures that, according to Ruff (2004), exist on Mars are a good example of structures characterized by a large specific surface area and a strong energetic bond between its surface and adsorbed water molecules. A large adsorption enthalpy (energetic bond) has the additional effect of heating the adsorbent during adsorption, which would temporarily support life processes at low temperatures when the maximum amount of water vapor is adsorbed during atmospheric saturation.

CONCLUSIONS

Liquid-like adsorption water exists in the comparatively warmer middle and low latitude upper (down to decimeter depths) martian surface, and may be present during late night and morning hours in the upper millimeter-thin "surface skin."

Adsorption water may trigger numerous chemical processes, especially photocatalytic chemical processes such as OH-driven oxidation of organics and sulfate covering of carbonates on Mars. Adsorption water could also support some biological processes. A better understanding of chemical processes that are driven or facilitated by adsorption water is a challenge in view of the chemistry of the upper martian surface.

Given the temporary existence of adsorption water in the uppermost layers of the martian surface and the fact that microorganisms can adsorb water on their surfaces, a testable hypothesis is presented: Microorganisms could, during night and morning hours under martian atmospheric conditions, survive by utilizing this adsorption water. A possible mechanism for transporting adsorption water into microbial cells is by temperature-controlled aquaporins, which would open at lower temperatures ("drinking phase") and close during warmer and drier daytime conditions.

To survive in the uppermost martian surface layer, microorganisms that survive via the iron–carbon cycle must have developed a UV-protecting "mantle." This mantle is likely to support the accumulation of adsorption water as a result of its large specific surface (as porous mantle material would be characterized by a large adsorption enthalpy).

The current challenge is to determine whether there are adsorption water-driven microbial life processes on Earth and Mars.

ACKNOWLEDGMENTS

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ABBREVIATIONS

pr μm, precipitable micrometers; UV, ultraviolet.

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