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Using the phase diagram of liquid water to search for life

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The correlation between liquid water and life may be our most reliable tool in the search for extraterrestrial life. To help develop this tool, we explore the complex relationship between liquid water, partial pressure, and solute freezing point depression on Earth and Mars and discuss the conditions under which liquid water is metastable on Mars. We establish the physical conditions for the existence of saline aqueous solutions in the pores of the martian near surface substratum. We find that thin films of near subsurface liquid water on Mars at ~–20°C could provide a viable niche for terrestrial psychrophilic halophiles. Since some martian salts can suppress the freezing point of aqueous solutions with minimal suppression of the water activity, some martian liquid water environments with a water activity above ~0.6 may also be able to support terrestrial life at temperatures as low as −30°C, ~10°C lower than the limit of terrestrial life.

KEY WORDS: water, phase diagram, Mars, biosphere.

INTRODUCTION

Since all terrestrial life requires liquid water during some phase of its life cycle (Rothschild & Mancinelli 2001), the correlation between liquid water and the presence of life may be our most reliable tool in our search for life. Thus, NASA has adopted a 'follow the water' approach in its search for life elsewhere in the Solar System and on potentially habitable exoplanets (Hubbard *et al.* 2002). Although other liquids have been suggested as a basis for extraterrestrial life (e.g. Bains 2004) liquid water is the most abundant liquid at the surface or in the subsurface of terrestrial planets (Baross 2007). Active searches for life in our Solar System involve the search for liquid water beneath the surface of Mars and the exploration of the liquid water ocean beneath the icy surface of Jupiter's moon Europa.

Although H_2O is probably the most common triatomic molecule in the universe, liquid water is far less abundant in the universe than H_2O in its vapour or ice phase. This is because a relatively narrow range of pressure and temperature is required to keep H_2O in its liquid phase. For the past few years we have been using pressure–temperature (P–T) phase diagrams of H_2O as a tool to find the regions of a planet where pressures and temperatures are consistent with the existence of liquid water. For example, in Jones & Lineweaver (2010), we superimposed a P–T diagram of inhabited terrestrial environments onto a P–T diagram of liquid water and onto a P–T diagram of all terrestrial environments (Figure 1). Thus, we were able to identify the regions of P–T phase space on Earth where liquid water is present. Among the environments where there is liquid water, we could distinguish the inhabited water from the uninhabited water (Figure 1). We are investigating the application of this technique to Mars. However, there are complexities involved with using a P–T diagram to search for life. Here we explore some of those complexities such as thin films, partial pressures, hydrological cycles, solute freezing point depression and water activity on Earth and Mars.

The y-axis on the right hand side of Figure 1 refers to the total pressure (P_{tot}). However, to understand the sublimation of ice, evaporation of metastable water and the martian hydrological cycle, we need to distinguish between partial pressure (P_{part}), saturation pressure (P_{sat}) and total pressure.

Figure 2 shows the ranges of the partial pressures of H_2O at the surface of Earth and Mars, bounded on the right by the maximum surface temperatures on these planets. For example, the total pressure on a glass of water at room temperature is represented by point 'B' in Figure 2 while the partial pressure is point 'D.' If the relative humidity of the air increased to 100%, then P_{part} would increase to its maximum P_{sat}, and P_{part} would be on the dotted vapour curve, directly below point 'D.'

The hydrological cycle of the Earth is driven by the evaporation of oceans and the precipitation of freshwater (rain and snow) that resupplies rivers, lakes, near subsurface aquifers and polar caps. The hydrological cycle of Mars is driven by the sublimation and condensation of polar caps and subsurface ice in contact with the large fluctuations in the partial pressure of H_2O in the martian atmosphere (see Table 1). Evaporation,

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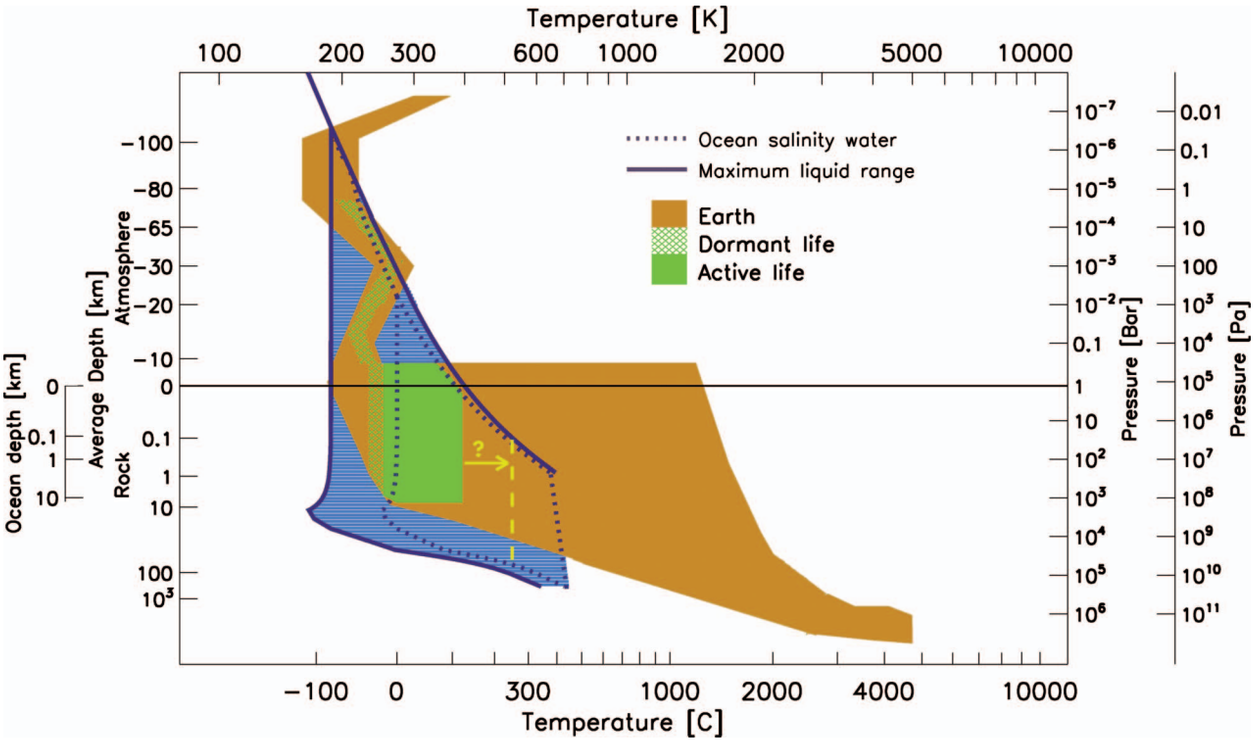

Figure 1 Pressure–temperature diagram of all terrestrial environments (brown), liquid water (blue) and inhabited terrestrial environments (green). The P–T range for 'Ocean salinity water' is nearly identical to the P–T range for freshwater, but is much more restricted than 'Maximum liquid range' whose freezing temperature can be as low as –100°C. See figure 5 of Jones & Lineweaver (2010) for details.

Table 1 Average pressures and temperatures on Earth and Mars.

Environment	Total pressure (bar)	Partial pressure (bar)	Temperature (°C)	Reference
Earth surface	1 (0.3–1.2)	10^{-1} to 10^{-3}	15	Dziewonski & Anderson (1981)
Mars surface	6×10^{-3} (7×10^{-4} to 1.2×10^{-2})	10^{-5} to 10^{-7}	−50	Melchiorri *et al.* (2007, 2009); Barlow (2008)

sublimation and condensation can be most easily understood in the context of the variation in the partial pressure of H_2O in the atmospheres of Earth and Mars, as shown in Figure 2.

The distribution of water ice on the martian surface and in the shallow subsurface is predominantly determined by the diffusion of water vapour. Early modelling indicated that the depth of the subsurface ice table on Mars (10–100 cm) is located where the annual average partial pressure of water vapour in pore spaces is less than the partial pressure of water vapour near the surface (Mellon & Jakosky 1993, 1995). These models were later shown to be generally consistent with ice tables derived from remote sensing (Mellon *et al.* 2008). Hence, the concentrations of subsurface water ice are dependent on the pressure of water vapour in the martian atmosphere. A higher partial pressure on the surface will cause vapour to diffuse into the soil and condense as ice; a lower partial pressure will cause subsurface ice to sublimate into the atmosphere (Sizemore & Mellon 2006). The partial pressure of water vapour on Mars undergoes large fluctuations with the seasonal sublimation of the polar cap (Haberle & Jakosky 1990) and with diurnal temperature gradients (Clifford 1993; Mellon & Jakosky 1993; Clifford & Parker 2001). Hence, surface and shallow water ice on Mars cycles seasonally and even diurnally if exposed to the atmosphere. This has consequences for the habitability of the shallow martian subsurface. Despite the improved understanding of the stability of water ice on Mars, the complexities of the potential formation of surface liquid water, the possible time-scales of its existence, and the effect of salts are poorly understood. For example, the locations of putative liquid water features on the martian surface, gullies (Heldmann & Mellon 2004), correspond generally to low concentrations of shallow subsurface ice (Figure 3). Shallow liquid water on Mars (from the melting of condensed water frost) is linked to the cycling of water vapour described above and is illustrated in Figure 4. However, if liquid water is present on Mars it may be saline, as a variety of salts (Table 2) have been detected (Squyres *et al.* 2004) and are expected to be present (Brass 1980) in the martian regolith. Salts not only lower the freezing temperature of liquid water but also retard its evaporation rate (Levin & Levin 1998). This effect can greatly increase the lifetime of any liquid water that forms on the surface.

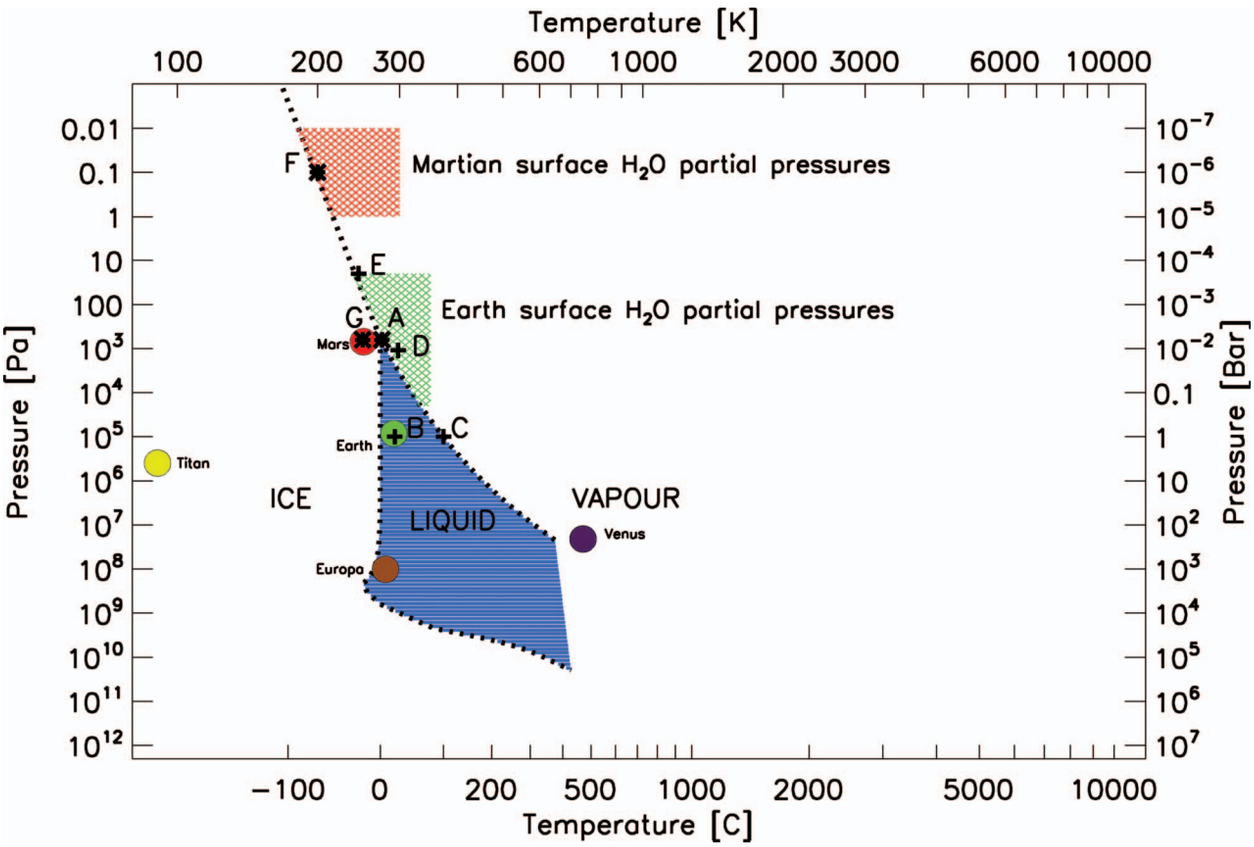

Figure 2 Phase diagram of pure liquid water showing the range of unstable and metastable conditions for liquid water on Earth and Mars. Pressures are P_{part} unless indicated otherwise. A=triple point, also boiling point at zero elevation on Mars (P_{sat}); B=sea-level Earth (P_{tot}); C=boiling point at sea-level Earth (P_{sat}); D=typical indoor environment; E=dry Antarctic conditions; F=typical frost point on Mars; G=zero elevation on Mars (P_{tot}). Pure liquid water is never stable on the martian surface as the partial pressures (red hatched) are less than the triple point pressure of pure water. Despite the large range in terrestrial surface partial pressures (green hatched) less than the triple point partial pressure, only extremely cold and extremely dry environments will have P_{part} less than the vapour curve. The shape of the hatched regions are bounded on the left by the vapour and sublimation curves. The remainder of the hatched regions correspond to the range of P_{part} of water vapour at the temperatures encountered on the surface of Mars and Earth. This figure is a modified version of figure 2 of Jones & Lineweaver (2010).

STABILITY OF LIQUID WATER ON MARS

The metastability of liquid water is an important factor on Mars. The P_{part} of water vapour in the atmosphere is always less than the triple point pressure (6 mbar) of pure water (Haberle *et al.* 2001; Richardson & Mischna 2005). In the martian atmosphere P_{part} varies between $\sim 10^{-7}$ and 10^{-5} bar (Melchiorri *et al.* 2007, 2009; Figure 2) but is typically $\sim 10^{-6}$ bar (Jakosky & Phillips 2001; Carr 2006). For comparison a typical P_{part} at sea-level on Earth is 3 mbar (Goody & Belton 1967). The P_{tot} in many locations on the surface of Mars is less than the pressure at the triple point of water (Carr 2006), but P_{tot} is greater than the pressure at the triple point in some regions such as Hellas Basin. Liquid water is able to exist in a metastable state (time-scale discussed below) on Mars where water ice is present and P_{tot}–T is within the liquid regime (Haberle *et al.* 2001).

From the phase diagram of water (Figures 2, 5) at the mean P_{part} on the martian surface (10^{-6} bar) the transition from solid to vapour occurs at 200°K, −73°C (F in Figure 2). This point is referred to as the martian frost point. From the variation in P_{part} on the martian surface in Figure 2 (red hatched), the frost point temperature varies between ∼190 and 210K (−83 to −63°C). At a temperature above the frost point any ice exposed to the atmosphere will not be stable and will sublimate (Mellon & Phillips 2001). The water activity of an aqueous solution (discussed further below) is the ratio of P_{part} over the solution, to P_{part} over pure water (Blandamer *et al.* 2005). A solution with low water activity will have a lower P_{part} at a given temperature than a solution with higher water activity (Altheide *et al.* 2009). The rate of evaporation of water on the martian surface depends on the relative humidity. Also, low activity water will evaporate more slowly than high activity water (Altheide *et al.* 2009). Hence, the concentration and precipitation of salts affects the evaporative process. From modelling and laboratory experiments in Mars simulated atmospheres, the mean evaporation rate at 0°C and 7 mbar is on the order of 0.7 mm/h for liquid water and 0.1–0.4 mm/h for ice (Sears & Moore 2005 and references therein; Levin & Weatherwax 2003). For example, if $\sim 10^3$ m^3 of water carved a typical martian gully (Christensen 2003) and pooled to a thickness of

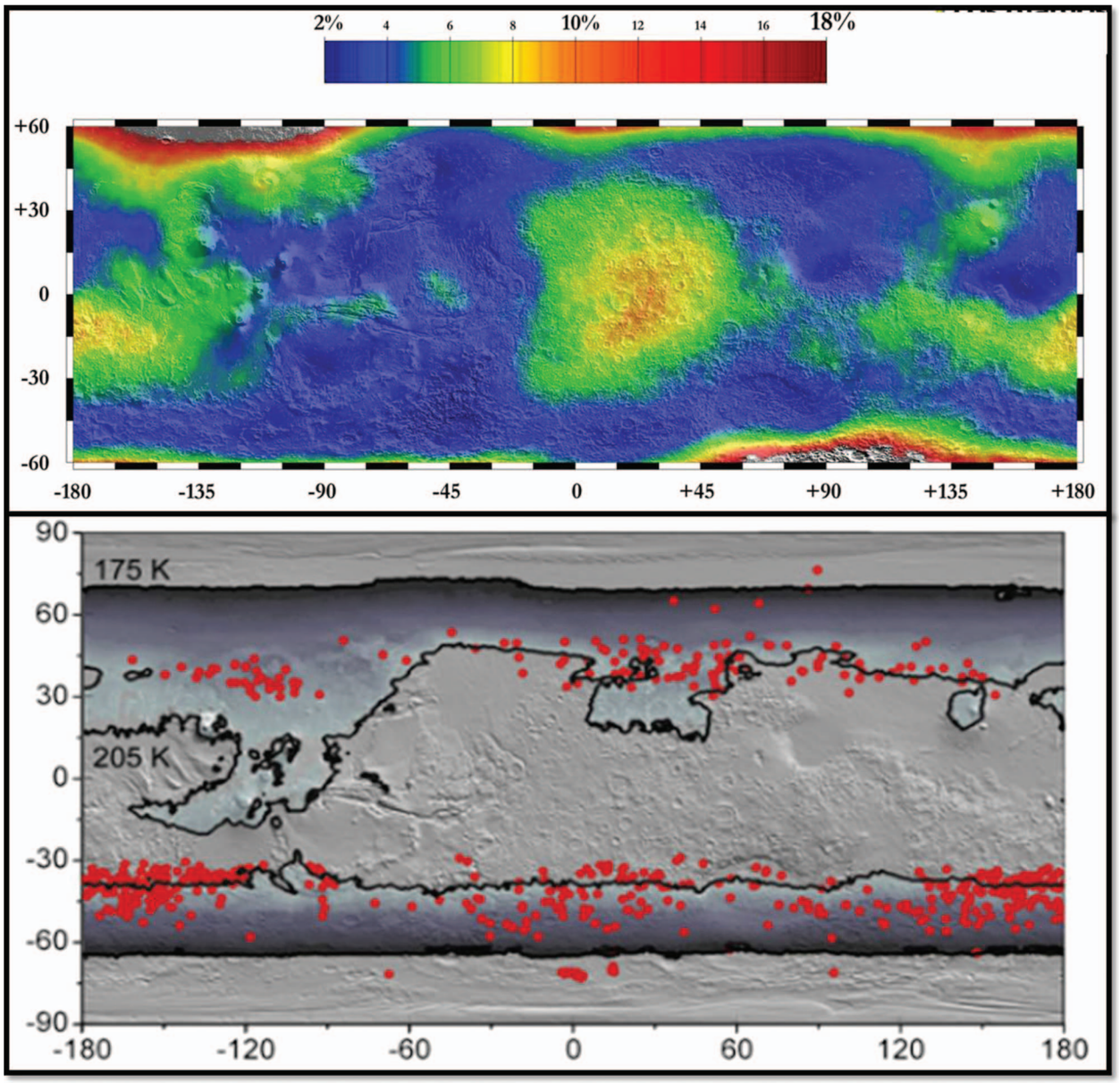

Figure 3 Deep and shallow putative water features on Mars. The top image is the Gamma-Ray Spectrometer water equivalent hydrogen abundance map (Feldman *et al.* 2004) sensitive to the top ~2 m of the martian subsurface. The bottom image shows the observed locations of martian gully systems (Chevrier & Altheide 2008), which form on slopes at alcove depths of 0–2 km beneath the local surface (Heldmann & Mellon 2004). Gully systems are generally found in the driest regions of the shallow subsurface, suggesting that many of the gullies may form from either >2 m deep liquid aquifers or seasonal meltwater from surface frost.

1 m, it could have taken ~60 martian days to evaporate at 0°C, 7 mbar. A typical annual average evaporation rate of open water on Earth is ~15 cm/60 Earth days (Penman 1948).

Saturation occurs on Mars when the temperature decreases at a given P_{part} (Smith *et al.* 2009). At the highest martian surface pressures (P_{tot}) there is at most 7 degrees between the solid and vapour lines of pure water (Kuznetz & Gan 2002; Levin & Weatherwax 2003) and hence less than 7°C between freezing and boiling. The condition for boiling is $P_{\mathrm{tot}} = P_{\mathrm{part}}$ with T on the vapour curve, which in general does not occur on Mars so water cannot boil. Boiling can occur however if the P_{part} at the surface increases faster than the P_{part} away from the surface, due to the slow diffusion of the vapour and mixing with the atmosphere (Hecht 2002; Schorghofer *et al.* 2002; Levin & Weatherwax 2003).

The relationship of subsurface liquid water pressure with depth is complex as it depends on how the liquid water is confined and whether it is in contact with the surface P_{part}. JL10 used the approach of equating the maximum pressure of subsurface water to the pressure due to the overburden of rock (calculated by density of rock × gravity × depth) in the crust and upper mantle of the Earth and Mars. This approach is useful because:

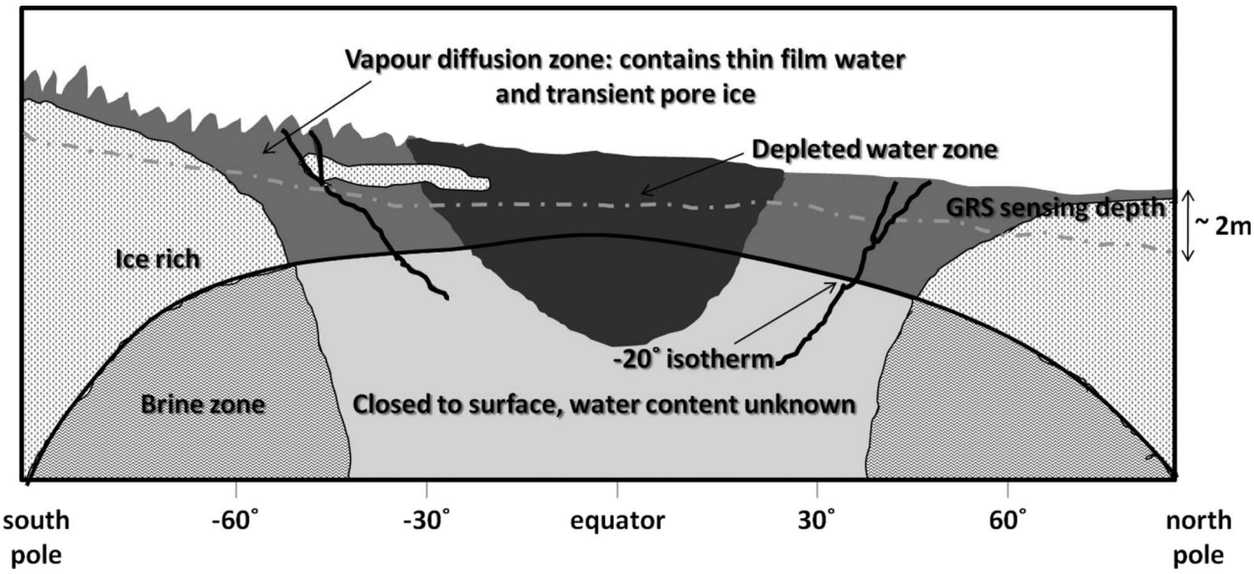

Figure 4 Schematic showing different subsurface water zones on Mars. The depth of the ice table is shown by the dotted ice-rich region where ice is perennially stable. At low latitudes, water ice is unstable, but patches of water ice have been excavated by impact craters (Byrne *et al.* 2009). Water frost and shallow pore ice are observed on the surface both at high and low latitudes (Carrozzo *et al.* 2009) due to vapour diffusion in the top $\sim$10 cm of soil. The hydrogen map produced by the Gamma Ray Spectrometer and High Energy Neutron Detector (top panel of Figure 3) has a sensing depth of $\sim$2 m which intersects with the ice-rich terrain at latitudes higher than $\sim \pm 60^{\circ}$. A -20°C isotherm is shown. Beneath this isotherm, temperatures are higher, and the pore space may be filled with brine (brine zone, middle grey) if there is a source of liquid water present. At latitudes lower than $\pm 30^{\circ}$, subsurface water ice has most likely been depleted due to the warm equatorial surface temperatures in the current obliquity. This would be consistent with the lack of observed low latitude gullies (see bottom panel of Figure 3). Two examples of plausible gully systems are shown in bold—one due to meltwater from seasonal shallow subsurface water ice; the other due to the upward movement of putative liquid water beneath the -20°C isotherm. The vertical axis is not to scale.

1. there are many examples (Orr & Kreitler 1985) of terrestrial confined aquifers (1–3 km deep) whose pressures are given by or exceed hydrostatic pressure (calculated by density of water $\times$ gravity $\times$ depth); and
2. the density of rock in both the Earth's and Mars' crust and upper mantle is at most three times the density of subsurface water (Dziewonski & Anderson 1981). This factor of three has a minimal effect on the pressure calculations in JL10 at the large depths involved.

If subsurface pore space water on Mars is in vapour contact with the atmosphere, its pressure will be significantly less than hydrostatic pressure. However, as ice on Mars condenses into near-surface pores it will seal water in the deeper crust from any contact with the atmosphere (Clifford 1993; Clifford & Parker 2001). The P_{part} of water vapour in the pore space is then assumed to be in equilibrium with water ice and adsorption surfaces in the pore. When water ice is not present in the pore space, the vapour density must maintain equilibrium with the adsorbant soil surface (Mellon & Jakosky 1993). Therefore, it is possible for subsurface liquid water to be stable within a subsurface pore space if the P_{part} of water vapour is equal to the saturation pressure within the pore space. This could occur when solar insolation or geothermal heat increases the temperature of the ice in the pore space (while the shallow ice-plug remains intact and the pore space remains isolated from the atmosphere). Additionally, at km scale depths, it is possible that ancient martian liquid water remains, under high pressure, beneath the martian cryosphere (Clifford 1993; Gaidos 2001).

EXPANDING THE LIQUID RANGE

The phase diagram in Figure 5 shows the P–T region of pure water and a maximum liquid range on Earth. Two mechanisms expand the range of P–T conditions at which liquid water is stable: lowering the freezing temperature and elevating the temperature of boiling.

Solute effect

The presence of a solute, such as salt, is often an effective freezing point depressor of water. Table 2 shows the lowest temperature of the liquid saline solutions of some common terrestrial and Mars candidate salts (in order of plausible abundance on Mars with sulfates > chlorides > carbonates and nitrates; King *et al.* 2004).

An example of the effect of freezing point depression by a solute was observed on the Phoenix Lander in the northern martian arctic (68°N). Spherical droplets photographed on the lander's struts have been interpreted as a liquid saline solution formed by perchlorate salts, $(2\mathrm{Mg},\mathrm{Na})\mathrm{ClO}_4$ (Table 2) absorbing water vapour

Table 2 Eutectics and water activity of saturated aqueous solutions of some common terrestrial salts and Mars candidate salts.

Salt	Eutectic (°C) (ref.)	a_w of saturated solution at/near 0°C [temperature if not 0°C] (ref.)	Percentage of salt in terrestrial seawater (by mass out of 35 g/l of salt) (11–13)
$MgSO_4$[a]	−5 (5)	0.1 [22] (6)	3.5
Na_2SO_4[a]	−5 (18)		
$CaSO_4$[a]			
K_2SO_4[a]		0.99 (7)	
$FeSO_4$[a]	−68 (17)		
$FeCO_3$[a]			
NaCl[a]	−21 (4)	0.76 (7)	82
$MgCl_2$[a]	−33 (1)	0.34 (3, 7)	8
$CaCl_2$[a]	−54 (1)	0.26 [20] (3,14)	4
KCl	−11 (10)	0.89 (7)	2.5
$MgCO_3$[a]			
$(2Mg,Na)ClO_4$[a] perchlorate	−69 (15)	≪0.6 (16)	
$Mg(NO_3)_2$	−32 (1)	0.60 (7)	
$NaNO_3$	−18 (8)	0.79 [5] (7)	
KNO_2	−40.2 (1)		
$MgBr_2$	−42.7 (1)		
$CaBr_2$		0.22 [10] (7)	
NaBr	−29 (1,9)	0.64 [5] (2,7)	
KBr	−13 (10)	0.86 [5] (7)	

[a]Mars candidate salts. (1) Morillon *et al.* (1999); (2) Negi & Anand (2004); (3) Siegel & Roberts (1966); (4) Grant (2004); (5) Pillay *et al.* (2005); (6) Zhang & Chan (2000); (7) Greenspan (1977); (8) Van der Ham *et al.* (1998); (9) Tang *et al.* (2003); (10) Steele *et al.* (1969); (11) Lewis & Schwartz (2004); (12) Duedall & Weyl (1967); (13) Millero (1969); (14) Bui *et al.* (2003); (15) Zorzano *et al.* (2009); (16) Besley & Bottomley (1969); (17) Chevrier *et al.* (2009); (18) Williams & Robinson (1981).

from the atmosphere until the salts dissolve in solution (Renno *et al.* 2009). Perchlorate salts, analogous to those found at the site, form a saline aqueous solution at martian pressures down to a temperature of −69°C (Zorzano *et al.* 2009). This phenomenon may also occur anywhere that salts with a low eutectic are present, and the relative humidity is high (Renno *et al.* 2009).

A number of terrestrial and martian candidate salts are given in Table 2. Sampling by the Opportunity Rover at Meridiani Planum and remote sensing by OMEGA and CRISM revealed concentrations of Mg, Ca, K and Na sulfates (Squyres *et al.* 2004; Gendrin *et al.* 2005; McLennan *et al.* 2005), Fe and Mg carbonates (Ehlmann *et al.* 2008), Na, Mg and/or Ca chlorides (Clark *et al.* 2005; McLennan *et al.* 2005) in martian terrains. Furthermore, the Phoenix Lander found perchlorate salts in the arctic soil (Hecht *et al.* 2009; Smith *et al.* 2009).

The presence of sulfates and perchlorates in the martian soil suggests that saline solutions may exist in the martian substratum (e.g. Clark & Van Hart 1981). The composition of a subsurface martian brine would vary locally but, given the information in Table 2, it may be expected to be dominated by magnesium sulfate, sodium chloride and calcium sulfate (Jagoutz 2006; Tosca *et al.* 2008; Marion *et al.* 2009), with typical martian soil (from Viking measurements) containing between 8 and 25% salt by mass (Clark & Van Hart 1981). It is likely that a martian brine would have a weakly depressed freezing point from sulfates (~10°C). A saturated solution of NaCl will freeze at −21°C and saturated calcium chloride brine at −54°C but these brines may be uncommon on Mars (a $CaSO_4$ brine is more likely—Marion *et al.* 2009). Additionally although perchlorates produce a strong freezing point depression their concentration in the subsurface is not known.

The freezing point of a brine on Mars will depend on the ratios of ions in the system and the complex equilibrium relationship between multiple phases of fluid–solid–vapour (Jagoutz 2006). Subsurface liquid water on Mars that is not in contact with the atmosphere may be highly saline as it may not be recharged by fresh liquid water or water vapour. Although a freezing point of anywhere between −10 and −60°C would be plausible, a freezing point around ~−10 to −20°C would be most likely. Furthermore, weakly saline liquid water is consistent with modelling of channel lengths of martian gullies (Heldmann *et al.* 2004, 2007). Despite this, some authors (e.g. Lobitz *et al.* 2001; Andersen *et al.* 2002) invoke brines as necessary to explain martian gullies and Chevrier & Altheide (2008) and Chevrier *et al.* (2009) suggest aqueous ferric sulfate as a candidate solution (supported by Howe *et al.* 2009).

Thin-film effect

The second mechanism of freezing point depression is liquid water adsorption. Thin films of unfrozen water can exist at the contact between ice–ice or ice–soil grains at very low temperatures (Price 2000) as cold as −130°C (Mazur 1980). The water remains unfrozen as a result of van der Waals forces due to the close proximity of grain boundaries (Möhlmann 2008). This causes a change in the energy state of the water molecules resulting in the stability of the water at temperatures significantly below 0°C (Davis 2001). The thickness of these films is governed by temperature, with the films decreasing to a thickness of around two to three water molecules at temperatures below −20°C (Anderson & Tice 1972; Jakosky *et al.* 2003). Although not precisely 'liquid water' these films have fluid-like properties, particularly for water separated by more than two monolayers (a monolayer is one water molecule thick) from the grain contact (Möhlmann 2008).

Freezing-point depression is important for understanding the minimum temperature of liquid water that could support active life.

LIQUID WATER ACTIVITY

An important consideration for biology is the availability of liquid water in its environment, which is quantified through the water activity (Grant 2004). Water activity provides a measure of the availability of water for reactions (such as biological processes). Studies into brine environments where life is present only in a dormant, unmeasurably low metabolising state—such as the $CaCl_2$ concentrated brine in Don Juan

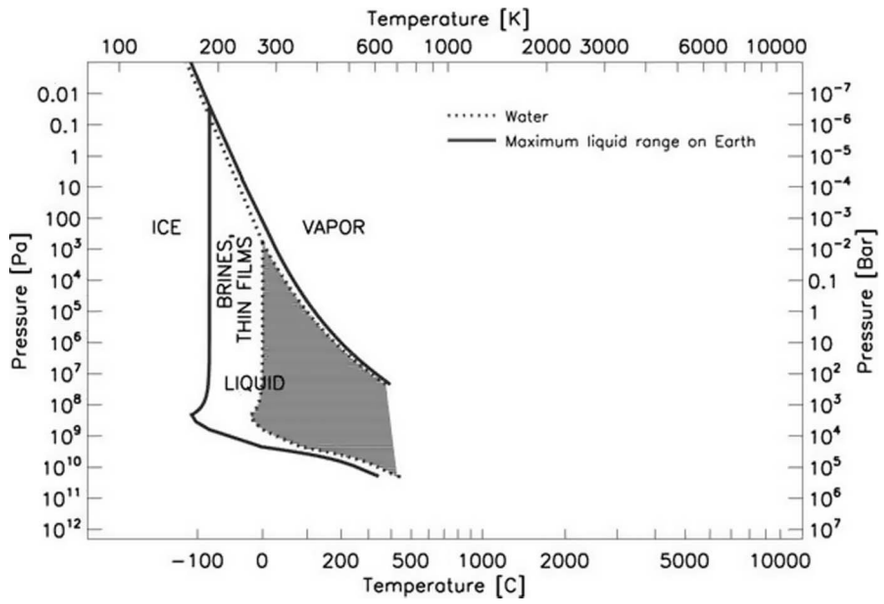

Figure 5 Expanded liquid range, comparing the phase diagram of pure water with the maximum liquid range on Earth; −89°C is the minimum possible temperature of terrestrial liquid water (could be encountered in Vostok, Antarctica; see table 2 of JL10).

Pond (Siegel *et al.* 1979) and $MgCl_2$ saturated bitterns (Bolhuis *et al.* 2006)—have indicated that there may be a low water activity limit to life. Currently an a_w of 0.6 is recognised as the lower limit to life (Grant 2004; life in hypersaline lakes with $MgCl_2$ brines) as below this cutoff the availability of free water molecules does not appear sufficient to sustain metabolising life (Rothschild *et al.* 1994). Mazur (1980) found that decreasing water activity from 1 to 0.2 decreased the cell water content of yeast to 1% of normal and resulted in death.

Water activity of brines

The maximum water activity of saturated salt solutions is achieved at temperatures near zero as the water activity can be modelled by $\ln(a_w) = \frac{k_1}{T} - k_2$, where k_1 and k_2 are constants that depend on the salts present and are obtained experimentally (Kitic *et al.* 1986). At subzero temperatures, the water activity of saline solutions generally decreases steeply with decreasing temperature (Morillon *et al.* 1999). The equation assumes that the moisture content of the system remains constant (Sahin & Sumnu 2006). The water activity of a saturated saline solution near zero will vary with each brine (Table 2). Some of the salts in Table 2 are present in seawater at the concentrations shown in the fourth column. The remainder are found in inland salt lakes (Nissenbaum 1975; Krumgalz & Millero 1982; Benison & Laclair 2003) and groundwater (Davis *et al.* 1980).

If liquid water is present on Mars, salts may play an important role in depressing the temperature at which it freezes. The most likely martian brines—sulfates and chlorides—have weak to moderately depressed freezing points and generally have low water activity at temperatures below 0°C. This generally makes them poor candidates for supporting biology. A possible exception is a solution of K_2SO_4, which has a high activity at 0°C and is present in the martian soil; however we can find no data on its eutectic. Salts such as magnesium nitrate and sodium bromide may also be able to support terrestrial life at temperatures as low as −30°C (from Table 2); however these salts may not be present on Mars.

Water activity of thin films

The thickness of water films is governed by temperature, with the films decreasing to a thickness of around two to three water molecules at temperatures below −20°C (Anderson & Tice 1972; Jakosky *et al.* 2003). Experimental data summarised in Möhlmann (2005) show that a_w drops below 0.6 when a thin film is less than 3 monolayers thick, as would be the case at such extremely low temperatures.

LIQUID WATER FOR LIFE

From the discussion above, the minimum temperature for terrestrial life may be −30°C (for example in a magnesium nitrate or sodium bromide brine) as no common terrestrial salt or thin-film adsorption effects can maintain water activity >0.6 at colder temperatures.

Möhlmann (2005) hypothesised, however, that this limit may not be valid in environments with changing humidity, as some micro-organisms may have adapted the ability to harvest thin film water when saturation occurs and use it to sustain themselves during periods of lower water activity. It is unknown whether life requires immersion in high a_w liquid water or whether equilibrium with water vapour can be sufficient for some organisms (Mazur 1980). For example, Lange *et al.* (1970) found that lichens in the Negev Desert which survive through desiccated $a_w < 0.6$ conditions during the day absorb enough water vapour at night from the atmosphere to photosynthesise the next morning. This suggests that small amounts of high activity liquid water can be sufficient.

The water-activity cutoff for life is likely linked to the increase in osmotic pressure across the cellular membrane that is required to maintain cellular respiration in cells in low activity water (Walter *et al.* 1987; Ponder *et al.* 2008). When a cell experiences osmotic stress, its energy is directed primarily towards restoring a favourable osmotic pressure, before the secondary needs of growth and division (Vriezen *et al.* 2007; Ponder *et al.* 2008; Amato & Christner 2009). Brown (1990) suggests that a fundamental limit to water activity within the cell occurs at 0.53 when RNA polymerase and metabolism cease. There may be examples of psychrophiles and halophiles that can remain metabolising and active in water of activity >0.53 but <0.6.

If the water-activity limit for terrestrial life is found to be lower than the current limit, then there may be many low temperature liquid water environments that can support terrestrial-like life. Thin films are the state in which water exists in soil below -20°C (Jakosky *et al.* 2003). There is some controversy as to whether the films of liquid water present at these temperatures would be sufficient for life (Gilichinsky *et al.* 2003; Jakosky *et al.* 2003) and it is likely that there would be a size restriction on microbes existing in these films (Gilichinsky *et al.* 2003). However, it is possible that these films can allow both the diffusion of ions (Anderson 1967) and the movement of some microbes. Hence, these environments are a potential ecological niche for psychro- and halo-tolerant organisms such as *Methanosarcina* (Franzmann *et al.* 1997). In laboratory conditions *Methanosarcina* can survive down to temperatures of -78.5°C for an extended period of time and high NaCl concentrations of 6M (Morozova *et al.* 2007; Morozova & Wagner 2007).

CONCLUSIONS

We have discussed the distinction between total pressure and partial pressure in the context of the phase diagram of water and the stability of liquid water. Liquid water on Mars is unstable in many locations due to the low surface total pressure but can be metastable in the higher pressures of low altitude environments or under the surface. Liquid water in pore space will be metastable on Mars when the pore space atmosphere is saturated with water vapour, the temperature is above zero, the total atmospheric pressure is above 6.1 mbar, and ice is present. The -20°C limit to terrestrial life is most likely related to the low water activity of terrestrial brines and thin films below that temperature. Liquid water may however be able to support terrestrial-like life down to temperatures as low as -30°C if dissolved salts such as magnesium nitrate and sodium bromide allow the water activity to remain above 0.6.

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