Stability of liquid saline water on present day Mars

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[1] Perchlorate salts (mostly magnesium and sodium perchlorate) have been detected on Mars' arctic soil by the Phoenix lander, furthermore chloride salts have been found on the Meridiani and Gusev sites and on widespread deposits on the southern Martian hemisphere. The presence of these salts on the surface is not only relevant because of their ability to lower the freezing point of water, but also because they can absorb water vapor and form a liquid solution (deliquesce). We show experimentally that small amounts of sodium perchlorate ($\sim$ 1 mg), at Mars atmospheric conditions, spontaneously absorb moisture and melt into a liquid solution growing into $\sim$ 1 mm liquid spheroids at temperatures as low as 225 K. Also mixtures of water ice and sodium perchlorate melt into a liquid at this temperature. Our results indicate that salty environments make liquid water to be locally and sporadically stable on present day Mars. **Citation:** Zorzano, M.-P., E. Mateo-Martí, O. Prieto-Ballesteros, S. Osuna, and N. Renno (2009), Stability of liquid saline water on present day Mars, *Geophys. Res. Lett.*, *36*, L20201, doi:10.1029/2009GL040315.

1. Introduction

[2] The presence of liquid water on the Martian surface has important implications for geochemistry, glaciology, mineralogy, geomorphology and climate. It is also important for habitability because liquid water is an essential ingredient for life as we know it. Thus, an important goal of the exploration of Mars is to determine whether liquid water exists there today or existed in the past [*Des Marais et al.*, 2008].

[3] Water ice exists on Mars' polar residual caps [e.g., *Bell*, 2008, and references therein; *Bibring et al.*, 2004 *Kieffer*, 1979; *Kieffer and Titus*, 2001; *Titus et al.*, 2003] and its regolith [e.g., *Boynton et al.*, 2002; *Zent et al.*, 2009; *Fanale et al.*, 1982; *Feldman et al.*, 2002], while trace amounts of water vapor exists in its atmosphere [e.g., *Smith*, 2002; *Encrenaz et al.*, 2005; *Fedorova et al.*, 2004; *Fouchet et al.*, 2007]. The water vapor pressure at the triple point of water ($\sim$600 Pa) is below the present day atmospheric pressure on the lowest regions of Mars, but the low surface temperature ($\sim$180–250 K) and the dry air of these regions inhibits the presence of pure liquid water at the surface on the present day [*Haberle et al.*, 2001]. It has been hypothesized that the presence of salts may depress the freezing point and allow liquid saline water to be sporadically stable on the Martian surface [*Brass*, 1980; *Chevrier et al.*, 2009]. In addition, the low thermal conductivity of hydrated salts might increase the probability of liquid water to be sporadically stable on Mars [*Prieto-Ballesteros et al.*, 2006; *Kargel et al.*, 2007].

[4] Sulfate and chloride salts have been detected on rocks and soils of Meridiani and Gusev by the APXS instrument on the MER rovers [*Campbell et al.*, 2008; *Schmidt et al.*, 2008, *Clark et al.*, 2005], and chlorides have also been detected on the southern hemisphere by the THEMIS instrument on the Mars Odyssey orbiter [*Osterloo et al.*, 2008]. More recently, perchlorate salts, probably mostly magnesium and sodium perchlorates, have been found in significant quantities ($\sim$1 wt %) on the Mars arctic by the MECA instrument on the Phoenix lander [*Hecht et al.*, 2009]. Furthermore, imaging and meteorological measurements made by the Phoenix lander suggest that liquid saline water may be stable at its landing site [*Renno et al.*, 2009]. On Earth, perchlorate salts are found in significant quantities (0.03 to 0.6 wt %) in arid regions such as the Atacama Desert, west Texas and Bolivian Playas [*Parker*, 2009; *Catling et al.*, 2009]. It has been suggested that perchlorate forms when chlorides are subject to high levels of ultraviolet (UV) irradiance [*Kang et al.*, 2006] in dry and oxidizing environments such as those found on Mars and the terrestrial analogues mentioned above [*Catling et al.*, 2009; *Zorzano and Cordoba-Jabonero*, 2007]. Thus, since chlorides seem to be distributed globally on Mars, the perchlorate salts discovered in soil samples of the Martian arctic might be ubiquitous. The presence of chloride and perchlorate salts on the Martian surface is not only relevant because of their ability to lower the freezing point of water [*Chevrier et al.*, 2009], but also because they can absorb water vapor and deliquesce [*Zhang et al.*, 2005].

[5] In order to determine the upper limit to the eutectic temperature of perchlorate salts likely to be found on Mars, we investigate experimentally, in the Planetary Atmospheres Simulation Chamber (PASC) [*Mateo-Martí et al.*, 2006] (see Text S1 in the auxiliary material), the stability of sodium perchlorate under Martian atmospheric conditions.[3] Mixtures of sodium perchlorate with other salts such as magnesium and calcium perchlorates would further reduce the eutectic temperature of their mixtures [*Brass*, 1980].

2. Deliquescence of Sodium Perchlorate Under Martian Conditions

[6] A sample of sodium perchlorate was placed on PASC's cold finger and images in the visible wavelengths (Figure 1) and infrared (IR) spectroscopy (Figure 2) were used to study the hydration level and phase changes of the sample. We found that dehydrated sodium perchlorate at

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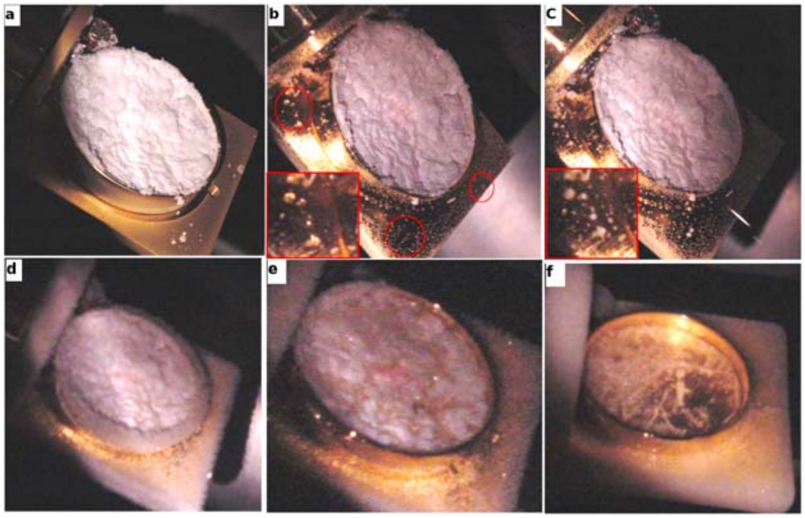

Figure 1. Sequence of images of deliquescing dehydrated sodium perchlorate in a simulated Martian atmosphere at pressure of 700 Pa at temperature of 225 K (Figures 1a–1e) and 240 K (Figure 1f). The sample holder is made of gold and has a diameter of 4 cm. (a) The sample of dehydrated sodium perchlorate (about 8 g) is stable under dry Martian atmospheric conditions. When water vapor is added to the chamber's atmosphere with the sample holder at 225 K, (b) small amounts (~1 mg) of salts deliquesce and grow into liquid spheroids of ~1 mm of diameter (see the enlarged square inset and circulated areas), which (c) freeze as they grow and get diluted. (d) As more vapor is added to the chamber, frost forms on the sample holder and the cold finger. (e) Then, in a few minutes the sample partially deliquesces, its temperature increases spontaneously from 225 K to 232 K, and frost disappears from the edge of the sample holder. (f) Finally, the sample deliquesces completely when the temperature of the cold finger is increased to 240–250 K.

the atmospheric conditions of Phoenix landing site (CO_2 at 700 Pa) increases its volume and changes phase by deliquescing at temperatures as low as 225 K.

[7] In a dry Martian atmosphere at 225 K, the sample of dehydrated sodium perchlorate (Figure 1a) exhibits the flat spectrum characteristic of anhydrous salts (Figure 2, curve a). When water vapor is added to the chamber's atmosphere, small amounts (~1 mg) of sodium perchlorate on the sample holder grow by deliquescence into small dark spheroids (diameter of ~ 1 mm) (Figure 1b) before frost forms on it. The reflectance of the spheroids to visible light increases when they become diluted enough to freeze (Figure 1c) (about 3 minutes later). As the amount of water vapor in the chamber's air is increased (about 30 minutes later), frost forms completely covering the sample and the sample holder (Figure 1d) at 255 K. At this point the water vapor partial pressure has reached 4 Pa, its value at this frost point temperature. Then, within 5 minutes, certain areas of the sodium perchlorate on the sample holder darken indicating the occurrence of deliquescence (Figure 1e). The IR spectrum confirms the presence of the liquid phase on the sample (Figure 2, curve e). Because the deliquescence of sodium perchlorate is an exothermic process, the sample temperature increases from 225 K to 232 K and the frost disappears from it as can be seen by comparison of Figures 1d and 1e. Finally, after roughly 5 minutes, at 240–250 K only the liquid phase is present on the sample (Figures 1f and 2, curve f).

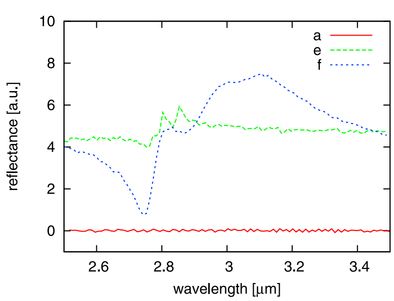

Figure 2. Infrared spectra of the sample of sodium perchlorate at 700 Pa at different stages of the experiment illustrated in Figure 1. The labels (a, e, and f) refer to the corresponding images in Figure 1. At 225 K the dehydrated sodium perchlorate sample shows a flat spectrum (a). When water vapor is added to the chamber's atmosphere, the sample partially deliquesces (e). When the sample temperature is increased to 240–250 K deliquescence becomes complete (f).

3. Stability of Liquid Brines Under Martian Conditions

[8] We also conducted an independent experiment to study the hydration and changes of phase of sodium perchlorate solutions subject to thermal cycles. A sample of aqueous solution of sodium perchlorate was placed inside the chamber and its temperature was lowered to 150 K for the solution to freeze. The IR spectrum of the frozen solution is shown in Figure 3. It suggests a mixture of hydrated salt (double absorption band at ~2.78–2.83 μm) and water ice (absorption band at ~3.10 μm). Then, dry Martian air was circulated through the chamber while the temperature was slowly raised from 150 to 250 K. At 225 K the water ice band disappeared indicating that only the liquid phase and bi-hydrated sodium perchlorate were present. At 250 K only the single absorption band of the

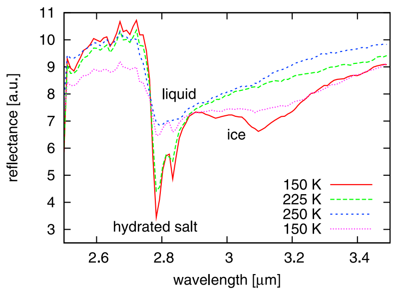

Figure 3. Infrared spectra of a saturated solution of sodium perchlorate through a thermal cycle at dry Martian atmospheric conditions. At 225 K, mixtures of water ice and sodium perchlorate deliquesces into the liquid phase (see text for details).

asymmetric stretch mode of liquid water at ~2.80 μm was observed indicating that only the liquid solution was present. When the temperature was lowered back to 150 K the ice and double hydrated salt signatures were recovered, although with smaller amplitude because of the loss of water to the dry chamber's atmosphere. These temperatures are lower by about 10 K than the theoretically calculated values for sodium perchlorate at terrestrial sea level pressure [*Chevrier et al.*, 2009].

4. Discussion

[9] We have proven that the deliquescence of sodium perchlorate can form liquid aqueous solutions at temperatures as low as 225 K in a simulated Martian atmosphere at 700 Pa by absorbing water vapor from the atmosphere. We show that the deliquescence of sodium perchlorate is an exothermic reaction that increases the temperature of the sample significantly, and can mitigate freezing at ambient temperatures lower than 225 K. We also find that at Martian atmospheric conditions, mixtures of water ice and salt deliquesce at temperatures as low as 225 K.

[10] Deliquescence has been recently proposed as a plausible explanation for spheroids (4–10 mm in diameter) observed on a strut of the Phoenix leg at temperatures of ~225–250 K and atmospheric pressures of ~750 Pa [*Renno et al.*, 2009]. In our experiments at 225 K, small particles of sodium perchlorate become darker and spheroidal (~1–2 mm in diameter) when they increase their volume and change into the liquid phase by deliquescing (Figure 4a). Their reflectance to visible light increased after they became diluted enough to freeze (Figure 4b). This is similar to the changes of reflectance observed on the Phoenix spheroids. A plausible mechanism for the formation and growth of these spheroids is deliquescence of perchlorate salts ejected during the Phoenix landing on Mars; see Figures 4c and 4d. Liquid water has low reflectance and thus appears as dark in visible images, whereas ice is bright in the visible range due to its high reflectance [*Perovich et al.*, 2002]. Since the reflectance of the liquid brine to visible light is lower than that of water ice sodium perchlorate darkens when it absorbs water from the atmosphere and deliquesces and becomes brighter when it freezes. This scenario is supported by our laboratory experiments results.

[11] During our deliquescence experiment, as the flux of water vapor into the chamber was slowly raised from 0 to 10–20 mg/hour, deliquescence was first observed on small sodium perchlorate particles on the sample holder at 225 K (see Figure 1b). Since the deliquescence relative humidity of small sodium perchlorate particles is about 44% [*Zhang et al.*, 2005], this indicates that the partial pressure of water vapor in the chamber at the moment of deliquescence just reached about 1.8 Pa. It is interesting that this is the daytime (from 8 to 20 local solar time) value of the water vapor partial pressure at the Phoenix landing site on the Martian pole. Indeed, *Smith et al.* [2009] and *Hudson et al.* [2009] show that the daytime averaged water vapor pressure was approximately constant throughout the Phoenix mission (Ls 76 to 147) at 1.8 Pa.

[12] Our results demonstrate that deliquescent salts such as sodium perchlorate can form liquid water solutions on Mars on locations where salts are in contact with water vapor from the atmosphere or ice reservoirs. These results suggest a water cycle on Mars in which atmospheric vapor deliquesces salt particles into liquid solutions, freezes and sublimates. A terrestrial analog of this water cycle occurs at the Atacama Desert, a cold and extremely dry environment where the hygroscopic chloride salt "halite" (NaCl) absorbs water vapor from the atmosphere and deliquesces [*Davila et al.*, 2008]. The deliquescent properties of perchlorate salts may thus play a significant role in controlling soil and atmospheric water content [*Hecht et al.*, 2009]. The possible presence of liquid saline water on the surface of Mars has important implications for the interpretation of Martian data, the selection of landing sites for future missions, mission planning, planetary protection and our understanding of local water cycles [*Zorzano and Vázquez*, 2006; *Gómez-Elvira et al.*, 2009].

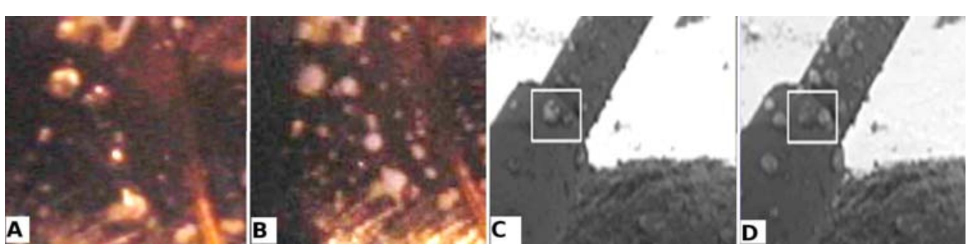

Figure 4. (a and b) Comparison of the images in the visible range from the spheroids observed in our experiments on PASC (see insets in Figures 1b and 1c) and those observed by RAC on the strut of the Phoenix leg on sols (c) 8 and (d) 31 (photo credit: NASA-JPL/Caltech-University of Arizona-Max Planck Institute). Liquid water brines have low reflectance and appear as dark or transparent in visible images, whereas ice is bright in the visible range.

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