PHYSICAL AND THERMODYNAMICAL EVIDENCE FOR LIQUID WATER ON MARS? Nilton O. Renno[1], Brent J. Bos[2], David Catling[13], Benton C. Clark[3], Line Drube[4], David Fisher[5], Walter Goetz[6], Stubbe F. Hviid[6], Horst Uwe Keller[6], Jasper F. Kok[1], Samuel P. Kounaves[7], Kristoffer Leer[4], Mark Lemmon[8], Morten Bo Madsen[4], Wojciech Markiewicz[6], John Marshall[9], Christopher McKay[10], Manish Mehta, Miles Smith[11], Peter H. Smith[12], Carol Stoker[10], Suzanne M. M. Young[7], [1]Department of Atmospheric, Oceanic, and Space Sciences, University of Michigan, Ann Arbor, MI 48103, [2]NASA Goddard Space Flight Center, Greenbelt, MD 20771, [3]Space Science Institute, Boulder, CO 80301, [4]Niels Bohr Institute, University of Copenhagen, Copenhagen 302100, Denmark, [5]Geological Survey of Canada, University of Ottawa, Ottawa K1A 0Y3, Canada, [6]Max Planck Institute for Solar System Research, Max-Planck-Str. 2, Katlenburg-Lindau 37191, Germany, [7]Department of Chemistry, Tufts University, Medford, MA 02155, [8]Texas A & M University, College Station, TX 77843, [9]Carl Sagan Center, SETI Institute, Mountain View, CA 94043, [10]NASA Ames Research Center, Mountain View, CA 94035, [11]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, [12]Department of Planetary Sciences, University of Arizona, Tucson, AZ 85721, [13]University of Washington, Seattle, WA 98195.

Introduction: The objective of the Phoenix Mars mission is to determine if Mars' polar region can support life. Since liquid water is a basic ingredient for life as we know it, an important goal of the mission is to determine if liquid water exists at the landing site. It is believed that a layer of soil preserves ice by forming a barrier against high temperatures and sublimation, but that exposed ice sublimates without the formation of the liquid phase [1, 2]. Here we show independent physical and thermodynamical evidence that besides ice, liquid saline-water exists in areas disturbed by the Phoenix lander. Moreover, we show that the thermodynamics of freeze-thaw cycles ranging from diurnal to geological time-scales leads to the formation of saline solutions with freezing temperatures much higher than current summer ground temperatures where surface ice exists near the surface [3-4]. Thus, we hypothesize that liquid saline-water is common on Mars. This finding has important implications for the stability of liquid water, weathering, mineralogy, geochemistry, and the habitability of Mars.

Deliquescent materials, mostly salts, absorb large amounts of water when exposed to the atmosphere, and form liquid solutions when the relative humidity is above a threshold value known as the deliquescence relative humidity, RH_D. However, the solutions usually remain liquid until the relative humidity falls below a much lower value known as the efflorescence relative humidity, RH_{EF} [5]. The RH_D of mixture of salts is always lower than that of the individual salts and can be smaller than 0.1 [5]. Besides absorbing water, salts depress the freezing point temperature and reduce the vapor pressure of aqueous solutions, lowering their boiling point pressure. This is important because, on Mars, the atmospheric pressure is of the order of the vapor pressure at the triple point of water. The lowest temperature at which aqueous saline solutions freeze, known as their eutectic temperature, can be lower than 200 K [5]. For a given salt, the solution with this minimum freezing temperature, known as a eutectic mixture, usually has salt mass fraction $\chi_{Eut} \sim 0.3$-0.5. The freezing point depression ΔT_{Eut} of saline solutions depends on their composition. Above the eutectic temperature only deliquescence is possible, but below it, aqueous solutions can be supersaturated with respect to ice, and therefore both deliquescence and ice formation are possible [5]. Indeed, it has been shown that even NaCl solutions remain partially liquid at temperatures as low as 230 K and that cooling can increase their concentration by more than an order of magnitude [6].

The formation of brines and salt layers: Brine layers are observed near the surface when seawater freezes, and at about 2-10 cm below the surface in Antarctica's Dry Valleys, a good Mars analogue [7, 8]. The presence of brines on Mars is consistent with the evidence of aqueous alteration in Mars meteorites while they were on Mars [8]. Finally, brines have a large dielectric constant that can cause attenuation of radar signals as that measured by Mars orbiters. Fig. 1 shows a sketch of the phase diagram of a generic single-salt solution with the climate process postulated to produce eutectic solutions indicated. The phase diagram for the multi-component solutions expected in nature is more complex, but this simple diagram illustrates the thermodynamical process that leads to the formation of eutectic solutions. The green double arrow labeled ΔT_{Clim} indicates the amplitude of the temperature variation during an arbitrary cycle ranging from diurnal to geological time-scales. We postulate that eutectic solutions form when the soil temperature oscillates around the eutectic temperature T_{Eut}. When this happens, ice precipitates from solutions with salt concentration smaller than χ_{Eut} and water molecules from it diffuse into deliquescent salts if any is present in the soil. This drives the concentration of the solution toward the eutectic value. This is consistent with the discovery of 2-10 cm deep salt layers in soils of Antarctic Dry Valleys. Phoenix's wet chemistry laboratory (WCL) found large amounts of perchlorates and magnesium ions in the soil of the landing site, probably from calcium and magnesium perchlorates (see article by Hecht *et al.*). Thus, T_{Eut} is $\Delta T_{Eut} \sim 70$ K below the freezing point even for single salts discovered at the

Phoenix landing site. Because of the large ΔT_{Eut} of these salts, their eutectic solutions can form and remain liquid almost anywhere on Mars. Since it has been shown that even eutectic solutions of single salts with modest freezing point depression such as NaCl (ΔT_{Eut} ~ 20 K) can sporadically be liquid almost anywhere on Mars[5], we argue that liquid eutectic brines are common on Mars.
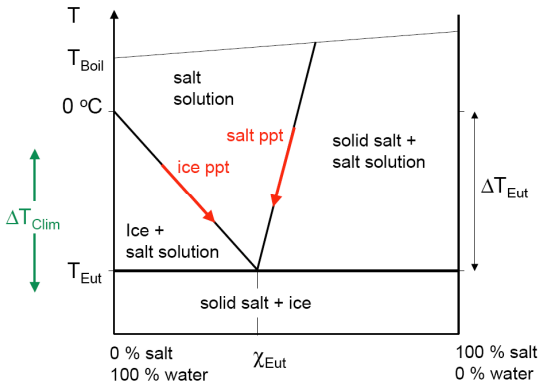

Fig. 1. Sketch of the phase diagram of the aqueous solution of a generic salt. We hypothesize that eutectic solutions form during freeze-thaw cycles. Pure water ice precipitates when dilute mixtures are cooled and their salt concentration increases until the eutectic temperature is reached. Then, the eutectic mixture freezes. On the other extreme, salts precipitate when concentrated mixtures are cooled until the eutectic concentration is reached and the solution freezes.

Evidence of Liquid Water: The impingement of the Phoenix landing thruster plumes on the surface removed the top soil, exposed the subsurface ice, and splashed any brine present above the subsurface ice on struts of the Phoenix leg. However, it might have also altered the local chemistry [9]. Fig. 2 shows physical evidence that various oblate spheroids observed on a strut are liquid solutions that grow by deliquescence on splashed material, likely a mixture of salts with large amounts of perchlorate hydrates. Two spheroids, enclosed by the white circle in Fig. 2, appear to have merged with each other between martian days (Sols) 8 and 31. Most spheroids present substantial growth between Sols 8 and 44, but not between Sols 44 and 90. This suggests that the relative humidity reached a peak value and the spheroids' mid-afternoon salt concentration became small enough for their saturation vapor pressure to reach the atmospheric value, inhibiting further growth during the later period. As the spheroids grow, their salt concentration decreases and their freezing temperature increases. Thus, they might freeze when the temperature falls in the evening and only melt again on the next Sol. The spheroids might also effloresce if the humidity falls below RH_{EF}. The "smoking gun" that spheroids moved and therefore

were liquid is the fact that growth is suppressed only over the material left behind by the spheroid that moved and merged with a neighbor. This suggests that the spheroid that moved carried most of its salts with it. Moreover, the "smoking gun" that the spheroids grow by deliquescence is the fact that they grow only over splashed material, and that their sizes and growth is proportional to their volume. Finally, the spheroidal shape also suggests the presence of liquid phase. The observed growth rates are similar to that predicted by deliquescence (not shown here). The only spheroid that shrank between Sols 8 and 44 was the remainder of one that appears to have moved and partially merged with a neighbor. The diffuse component of scattered power from a wet or icecovered object is reduced by an amount proportional to the inverse of the square of the index of refraction. Since the index of refraction of liquid water is larger than that of water ice, liquefation darkens water substance [10]. This is consistent with what is seen on the images and reinforces the idea that the spheroid liquifed before it moved, and merged with a neighbor [11]. Another independent evidence that spheroids grow by deliquescence is the fact that the exposed subsurface ice on the shadow near the strut sublimates while spheroids grow on the warmer strut.
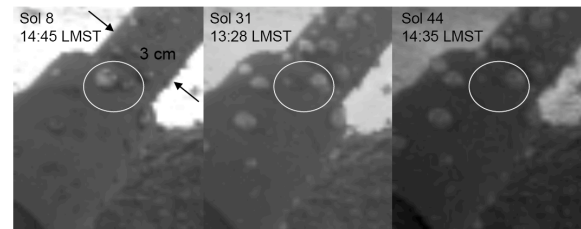

Fig. 2. RAC images of a strut of the strut on Sols 8, 31 and 44. The two spheroids enclosed by the circle appear to merge with each other. The resulting spheroid moves to the right, that is downslope. The "smoking gun" that the spheroids merged is the fact that growth was inhibited in the material left behind. The fact that the spheroid gets darker before it moves is also consistent with the fact that it became liquid [10].

References: [1] C. B. Farmer, *Icarus* **28**, 279 (1976). [2] K. L. Bryson et al., *Icarus* **196**, 446 (2008). [3] R. M. Haberle *et al.*, *JGR.* **106**, 23317 (2001). [4] W. C. Feldman *et al.*, *JGR* **109**, doi:10.1029/2003JE002160 (2004). [5] J. H. Seinfeld, S. N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change* (Wiley, New York, ed. 2, 2006). [6] T. Koop *et al.*, *J. Geophys. Res.,* **105**, 2126393 (2000). [7]W. W. Dickinson, M. R. Rosen, *Geology* **31**, 199 (2003). [8] S. J. Wentworth et al., *Icarus* **174**, 383 (2005). [9] D. H. Plemmons et al. (2008), JGR, 113, doi:10.1029/2007JE003059. [10] K. C. Jezek and G. Koh, Appl. Optics, 26, 5143 (1987). [11] R. E. Grimm, D. E. Stillman, *LPSC XXXIX* (2008).