

PTX PHASE EQUILIBRIA IN THE H₂O-CO₂-SALT SYSTEM AT MARS NEAR-SURFACE CONDITIONS. R.J. Bodnar¹, ¹Fluids Research Laboratory, Department of Geological Sciences, Virginia Tech, Blacksburg, VA 24061 email: bubbles@vt.edu.

Introduction: Beginning with the earliest observations in the 18th century, various surface features of Mars have been attributed to the effects of water [1]. While it is generally accepted that liquid water was present on Mars early in its history, there is still considerable debate concerning the presence of liquid water today, or in the recent past. This debate was brought to the forefront last year when gullies observed in images obtained from the Mars Global Surveyor Mars Orbital Camera (MGS-MOC) were interpreted to be geologically-recent erosional features produced by flowing liquid water [2].

Many workers have addressed the issue of the possibility of present-day liquid water on or near the martian surface. Most of these studies have focussed on the importance of the mean annual surface temperature on Mars, which ranges from about 150K at the poles to about 215K at the equator [3], temperatures that are well below the triple point of pure water (273.16K) (Fig. 1). To explain this dilemma, other workers have considered saline brines [4,5], carbon dioxide [6], or water-carbon dioxide mixtures [7] as the fluid responsible for producing the observed erosional features on Mars. While each of these is a possible erosional agent on Mars, none are universally accepted by the scientific community. Here we present PTX phase diagrams for the system H₂O-CO₂-salt, with emphasis on compositions that are stable at Mars near-surface conditions.

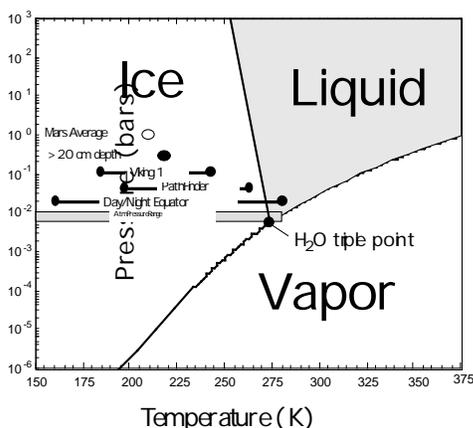


Fig. 1. P-T diagram showing the stability field for liquid water, compared to the measured and estimated temperatures on or near the martian surface. Also shown is the range of atmospheric pressures measured at the Pathfinder site.

Phase Equilibria:

H₂O-salt. Addition of salt to water causes the triple point to migrate to lower temperatures and lower pressures. While many workers have studied the depression of the freezing temperature when salt is added to water, there are relatively few studies of the vapor pressures over water-salt solutions at low temperatures, and these are summarized on Figure 2. To a first approximation, the vapor pressure at the triple point is controlled by the vapor pressure of water ice at that temperature. At the H₂O-CaCl₂ eutectic temperature (223K) the vapor pressure is about 40 mbar. Stated differently, a calcium chloride-rich brine is stable at any temperature and pressure above 223K and 40 mbar, and much of the range martian surface P-T conditions falls within the liquid stability field for a calcium chloride brine (Fig. 2).

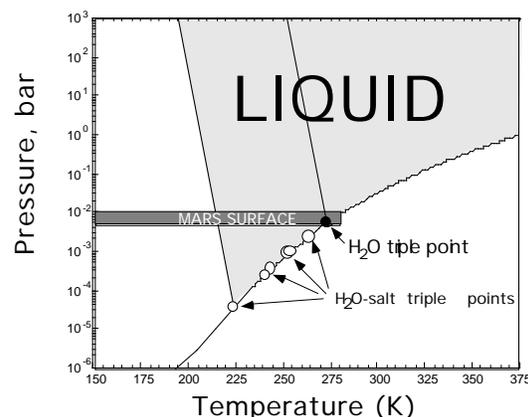


Fig. 2. P-T diagram showing the stability field for liquid brines, compared to the estimated temperature-pressure conditions on the martian surface (shaded horizontal box). Note that much of the range of surface P-T conditions falls within the liquid field.

H₂O-CO₂-salt Carbon dioxide is the most abundant volatile in the martian atmosphere, and would interact with any other fluids that might be present in the near-surface environment. The stability field for carbon dioxide liquid is at pressures that are well above those that might be encountered in the near-surface (Fig. 3). However, carbon dioxide reacts with water to form the solid phase carbon dioxide clathrate with the composition CO₂ · 5.75 H₂O, and the decomposition of this phase produces carbon dioxide gas (or liquid at higher pressure) in equilibrium with liquid water. If the ice

plus clathrate mixture contains any salt, melting will begin at the water-carbon dioxide-salt eutectic point, which for NaCl corresponds to approximately 262K. If the salt is calcium-rich, initial melting would occur at approximately 230K. The initial brine produced will have the eutectic composition, and will be in equilibrium with carbon dioxide gas.

The decomposition of clathrate to produce brine plus gas would generate considerable mechanical (PV) energy owing to the large volume change associated with this reaction. The reaction of clathrate dissociating to produce gas plus brine is analogous to the process that occurs in silicic volcanic eruptions on earth, whereby water dissolved in the melt exsolves to form a separate fluid phase. The large difference between the molar volume of the exsolved fluid (water) and the partial molar volume of water dissolved in the silicate melt provides the energy for explosive volcanic eruptions. A similar process associated with the breakdown of carbon dioxide clathrate on Mars may provide the energy to move large volumes of regolith material to produce the characteristic erosional features that are observed on the martian surface.

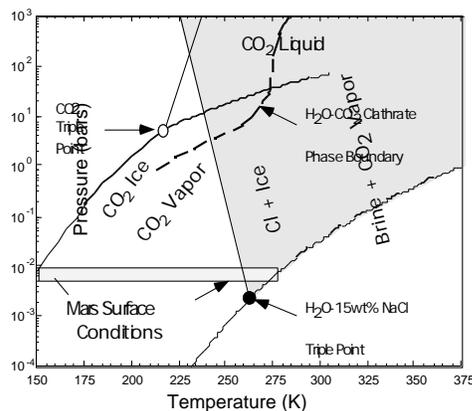


Fig. 3. P-T diagram showing the stability field for a brine containing 15 wt.% salt (shaded region), along with the stability fields for carbon dioxide liquid, vapor and ice. Also shown is the region where ice and carbon dioxide clathrate would dissociate to form brine in equilibrium with carbon dioxide gas. Note that the region of brine plus gas equilibrium overlaps the upper temperature portion of Mars surface conditions.

Summary:

High quality and high resolution images being obtained by the Mars Global Surveyor provide remarkable evidence for recent erosion of the martian landscape by fluvial processes. These features are similar to those produced on earth by flowing liquid water, but

liquid water has been discounted as a potential fluid candidate on Mars owing to the low ambient temperatures, which are well below the stability field for liquid water. While brines have been proposed in the past as the potential fluid responsible for producing erosion on Mars, this model has received little support because satisfactory explanations have not been provided for generating large volumes of brines. Moreover, while (pure) liquid water is a necessary component for life to develop and evolve, it is thought that such occurrences would be less likely in the presence of high salinity brines. However, some previous workers did not consider the fact that very high salinity brines can be produced from eutectic melting of ice-hydrate mixtures with a low bulk salinity. Thus, eutectic melting of an ice-hydrate phase with a bulk salinity comparable to modern terrestrial seawater (about 3.5 wt.% TDS) would produce a brine with a salinity of about 24 wt.%. If the phase that is melting is carbon dioxide hydrate, this mechanism not only provides a reasonable means of generating aqueous solutions that are stable at current martian surface conditions, but also provides an energy source to produce large amounts of erosion from relatively small amounts of fluid.

References: [1] Carr, M.H. (1996) *Water on Mars*, Oxford University Press. [2] Malin, M.C. & Edgett, K.S. (2000) *Science*, 288, 2330-2335. [3] Kieffer, H.H., Martin, T.Z., Peterfreund, A.R. and Jakosky, B.M. (1977) *J. Geophys. Res.*, 82, 4249-4291. [4] Brass, G.W. (1980), *Icarus*, 42, 20-28. [5] Knauth, L.P. (2000), *Geol. Soc. Am. Abstr. w/Prog.*, 32, no. 7, A303. [6] Hoffman, N. (2000) *Icarus*, 146, 326-342. [7] Draper, D.S., Jones, J. & Longhi, J. (2000) *EOS*, 81, F777. [8].