DENSE EUTECTIC BRINES ON MARS: THEY COULD BE BOTH COMMON AND CA-RICH. D. M. Burt[1], L. P. Knauth[2], and S. Klonowski[2], [1]Visiting Scientist, LPI (Lunar and Planetary Institute, 3600 Bay Area Blvd., Houston TX 77058-1113; Burt@lpi.usra.edu), [2]ASU (Dept. of Geological Sciences, Arizona State University, Box 871404, Tempe AZ 85287-1404; Knauth@asu.edu; Klonowski@asu.edu).

Introduction: The recent, somewhat controversial observation of young gullies apparently related to seepage or flow of liquid water on Mars [1] has raised the question of whether the fluids responsible (if any) might be concentrated, $CaCl_2$-rich brines, which alone among aqueous fluids have the low vapor pressures and depressed freezing points [2,3] to be stable at the intermediate to high latitudes at which the distinctive gullies have been observed. The gullies invariably originate high on slopes, implying a perched aquifer. Even if the cause of these gullies is not brines (and *many* other possibilities have been suggested), we submit that dense, eutectic, $CaCl_2$-rich brines would still be expected deep in the basaltic martian regolith, as a natural consequence of the presumably wet early history of Mars, followed by devolatilization, freeze-down, and water-rock interaction.

Evidence Against $CaCl_2$-rich Brines:

*Mars apparently lacks evaporites***.** No evaporite deposits have yet been unambiguously observed on Mars [4]. However, evaporite minerals are difficult or impossible to detect if etched, coated with dust, or mixed with lithic or soil materials. Large evaporite deposits on Earth form in shallow basins on the edges of continental platforms, mainly as a result of plate tectonic processes [5], an environment presumably lacking on Mars. About 90% evaporation is needed before halite precipitates from terrestrial sea water; by the time this degree of evaporation had occurred on Mars, brines could have disappeared into the regolith.

*Mars has sulfate-rich soils and a CO_2-rich atmosphere***.** The Viking and Pathfinder missions to Mars both performed chemical (but not mineralogic) analyses of soils in the vicinity of the landers. The soils, particularly an indurated soil called duricrust, are S-rich, with less Cl [e.g., 6]. The S was assumed to be sulfate, which forms insoluble salts (gypsum or anhydrite) with Ca, apparently ruling out Ca-rich brines. Although Mg forms soluble sulfates, its carbonates (like those of Ca) are insoluble, and the Mars atmosphere is CO_2-rich. The implication is that Mars brines could contain neither Ca nor Mg [7]. This result, widely accepted for the past 20 years, is based on two assumptions that are probably erroneous. These are 1) that a subsurface brine must be in equilibrium with the atmosphere, and 2) that the salt composition of the duricrust reflects that of a subsurface brine. The first assumption is patently false for virtually any terrestrial groundwater (e.g., those that deposit supergene sulfides in ore deposits). In reference to the second, duricrust forms not by simple quantitative evaporation of brine, but by water rising to the surface by capillary action. Terrestrial duricrust typically contains the least soluble salts (e.g., calcite and gypsum); its composition therefore need not reflect the content of the more soluble salts (i.e., chlorides) that remain in solution at depth.

*Mars can be modeled as a closed system***.** Simple evaporation or freezing models subtract the compositions of first H_2O (as vapor or ice), then H_2O plus crystallizing salts; the system is a sealed, inert bathtub, open to the atmosphere. Ca is removed early as sulfates or carbonates, and therefore is predictably absent in the last brine to freeze, at the eutectic point [8]. The problem is that once a brine has sunk into the regolith, or is covered with a layer of ice or of low-density fresh water, it is out of equilibrium with the atmosphere. Furthermore, its container is not inert, but is highly reactive, Ca-rich (basaltic) regolith, consisting of a brecciated mixture of impact melts, volcanic rocks, and other fines. Given the billions of years available, the brine will certainly exchange Na or Mg for some of the Ca in the rocks, making it Ca-rich. Similar reactions are common on Earth, both in Ca-rich brines that have reacted with sediments [9], and in seawater that has circulated through mid-ocean ridge basalts [10].

Fig. 1. *$CaCl_2$-rich Don Juan Pond, Antarctica (from Ed Stump slide A68-13, taken January, 1983).*

Evidence in Favor of $CaCl_2$-rich Brines:

*Chlorine is incompatible***.** Cl doesn't fit in most silicate structures and is expelled as HCl during planetary degassing and volcanism. HCl reacts with rocks to form salts that dissolve in the early hydrosphere [11].

*Mars is more Cl-rich than Earth***.** Available evidence (mainly from SNC meteorites) and planetary accretion models indicate that Mars is more Cl-rich than Earth [12]. Late cometary volatile input on either planet would probably have been equally Cl-rich.

*Mars soils are Cl-rich and somewhat Ca-depleted***.** Given that Cl forms highly soluble salts, the Cl contents in the martian soils are high, possibly owing to impact dispersal of early brines or wind disperal of dried evaporite dust. Ca, on the other hand, appears somewhat depleted relative to Si [13], indicating that it could have been leached into brines.

SNC meteorites are Cl-rich. Many of these basaltic meteorites, presumably impact-ejected from Mars, appear to have interacted with Cl-rich brines before leaving Mars [14].

*Basalt-brine interactions leach Ca***.** See above discussion of closed system models and [10].

Freezing will concentrate $CaCl_2$ in brines. During the eutectic freezing process, the components that depress the freezing point the most are those that are inevitably concentrated in the residual brine, until the eutectic point is reached, and everything crystallizes. Of the common cations (i.e., excluding exotic brine components such as LiCl or $ZnCl_2$), $CaCl_2$ exhibits the greatest freezing point depression [2], and therefore is the most likely to be concentrated in residual liquid.

Don Juan Pond, a Possible Mars Brine Analog: Don Juan Pond in the Wright Valley of Antarctica is the type locality for antarcticite, $CaCl_2 \cdot 6H_2O$ [15]. It is the saltiest and most sterile of Antarctic saline lakes, and is the only one with wholly internal drainage. Geologically, it is a playa, and its salts (including gypsum) appear to be dispersed by the wind at about the same rate that they are deposited on a salt pan by evaporation of the brine [16]. It is small, 100 x 300 m, only 10 cm deep on average, and evaporates completely at times. Although its shallow depth means that it is always at ambient temperatures, it rarely freezes, because it is essentially a eutectic brine of H_2O, $CaCl_2$, and NaCl, with a F.P. of –52°C (221°K) [17], and a density approaching 1.4. The lake appears to be fed from below by brine springs in equilibrium with a sill of Ferrar Dolerite, a fractured basaltic rock constituting a confined aquifer [16]. This basaltic aquifer, and the extremely cold, dry conditions, possibly make Don Juan Pond an acceptable analog for Mars brines. The highly visible white salt deposits surrounding the lake (**Fig. 1**) are a feature not seen on Mars images.

Two Implications for Mars:

Eutectic compositions could be common. Especially at intermediate latitudes, episodes of temperature cycling, caused by variations in the martian seasons (on the surface) or long-term orbit (in the shallow subsurface), should assist the attainment of eutectic brine compositions (a process analogous to refining in chemical engineering.) On heating, any mixture of salts and ices will first melt at the unique eutectic composition (partial melting); on cooling, any initial brine compostion will migrate towards the unique eutectic composition (fractional crystallization). In other words, eutectic brines, despite their special compositions, could be common, not rare, for most of the same reasons that granite and basalt are common igneous rock types. On the other hand, if subsurface liquid water is sufficiently abundant [18], then deep brine bodies will be dilute, not eutectic. They should still become Ca-enriched, however.

*Brines should segregate by density***.** Eutectic brines are dense liquids, denser than ice or liquid water, but less dense than crystalline salts (or rocks of the regolith). Brine density increases with salinity. When ice freezes out on top of a brine, a more concentrated brine is formed that sinks; still denser salts can then crystallize out only towards the base of the brine body. As long as liquid brine is present to promote mass transfer, the eventual result in the regolith cements should be a "brine sandwich", with ice on top and salts underneath. This simple geometry, if preserved in a perched aquifer (or frozen paleoaquifer), provides one explanation for the typical appearance of the young gullies of [1]. Also, if brines sink into the megaregolith before freezing, crystallization of soluble salts *beneath* the brines provides a simple explanation for the apparent lack of evaporite minerals on the surface of Mars. Of course, impact or magmatic processes (or salt diapirism) could complicate this simple picture, as would simple lateral flow of the brine away from the crystalline phases.

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