MARS AS A SALT-, ACID-, AND GAS-HYDRATE WORLD. J.S. Kargel[1] and Giles M. Marion[2], [1]USGS Astrogeology (2255 N. Gemini Dr., Flagstaff, AZ 86001, jkargel@usgs.gov), [2]Desert Research Inst. (Reno, NV)

Introduction: The widespread occurrence, abundance, and major geologic roles of water on Mars (occurring in all three pure phases) are now accepted after more than a century of speculation and increasing observations. Imaging indicates diverse water- and ice-mediated geologic processes, especially at high and middle latitudes in geologically recent times and globally long ago. Neutron/gamma-ray spectroscopy has confirmed hydrogen in amounts that (1) at the poles can only be ice, and (2) at lower latitudes suggest hydrates as the chief hydrogen host [1]. Here I report on the stability of hydrates and possible processes involving them.

Why should hydrates be abundant? With aqueous processes having been active on Mars, solutes should be important in those aqueous systems, as they are on Earth and carbonaceous chondrites. Mars should have a diversity of salts and secondary alteration phases. However, the rarity on Mars of large-scale surface runoff and aquifer flow due to precipitation recharge in geologically recent times means that the upper crust has not been thoroughly leached and that solutes largely remain in soils and rocks, ready for leaching.

Low temperatures in the Martian upper crust will stabilize many substances, including highly hydrated salts, acids, and gases (clathrates, [2]), which on Earth would be transported to the sea or atmosphere. Mars' surface and upper crust rarely exceed 273, except in high heat-flow, hydrothermal areas; pure ice is rarely apt to melt. Consequently, many hydrated phases melt at eutectics and incongruently at peritectics. Less concentrated brines may evolve to eutectics by evaporative or cooling-driven fractional or equilibrium crystallization.

Geologic roles of hydrates. Salts and other solutes are expected to be critical in permafrost annual and diurnal active layers; in evaporitic duricrusts; and shallow groundwater aquifers. A high abundance of hydrated sulfates and chlorides is expected in bedded sedimentary evaporite deposits and frozen lakes; in sublimation-pumped evaporative duricrusts; in late-stage igneous pegmatite-like dikes; in frozen groundwater and hydrothermal brines; in aqueous alteration and contact metamorphism zones adjacent to silicate igneous dikes and sills and lava-baked soil horizons; in vesicle fillings, trapped fluid inclusions, and other pore spaces in volcanic flows and impact breccias; and in permafrost lenses and wedges. Vast marine evaporitic platforms and thick evaporitic basin sequences may be less common than on Earth (or absent), but substantial masses of evaporitic and freeze-precipitated salt beds, lenses, nodules, and dikes are expected to be very common in Martian permafrost, in frozen debris flows, around volcanoes and in soil horizons baked by lava flows, and in many other circumstances.

As seen in many permafrost localities on Earth, but even more so, spring waters on Mars are expected to be highly saline, containing an abundance of chlorides and, in warmer brines, sulfates. Eutectic or quasi-eutectic brines should be the rule. Ice-salt eutectics should be common, but at lower latitudes, where ice may be absent, water-poor eutectics involving lower hydrates may be common.

Copious gases (e.g., CO_2 and SO_2) may be vented by volcanic activity or high mantle heat flow and degassing, lower crustal burial metamorphism of evaporites, or sulfide oxidation. These gases would form clathrate phases in the crustal aquifer or cryosphere. In an oxygenated aqueous environment SO_2 would form sulfuric acid, as it does on Earth. An acidic aqueous environment would mobilize iron [3] and could help produce an oxidized surface.

Extreme aqueous liquids: Sulfuric acid brines

Much attention has been given by the Mars community to a role of multiply saturated chloride brines. This is appropriate, since chlorine is known to be important in Martian rocks and soils, and chloride brines provide eutectics down to 225-251 K, which approaches the mean annual temperature (shallow upper crustal temperature) in the warmest parts of Mars. However, in looking for the limits of aqueous processes on Mars, acid systems provide for even colder eutectics (Fig. 1) under conditions of water vapor partial pressure and temperature that could marginally allow stable surface liquid. Figure 2 shows the case for the binary system H_2SO_4-H_2O. Additional salt and acid components would bring a set of eutectics fully into conditions where they would exist stably at the surface. Extreme acid-brine marshes (without grasses!) and cryogenic brine springs, the waters formed through fractional crystallization at low crustal temperatures, are likely.

The *Spirit* rover may have landed in an acid-salt marsh. The soil is cohesive and fluid-like in some respects (Fig. 3); the upper soil layers could be weakly bonded by acidic brine and salt precipitates. This working hypothesis is outrageous, speculative, and probably incorrect. The more likely culprit is dry cohesion of fine-grained air-fall dust. But if this hypothesis is correct, it carries intriguing scientific implications for aqueous geochemistry and astrobiology, but it also forebodes danger for *Spirit* investigations and future astronaut investigations.

Geologic roles of hydration/dehydration. Mean annual conditions of surface temperature and surface atmospheric fH_2O cross key hydration/dehydration boundaries of many salt hydrates. The case of epsomite-kieserite represents a particularly likely boundary [1]. These salts are expected not only on the surface of Mars but, like ice at higher latitudes, through much of the upper crust.

Where salt hydrates are major constituents, dehydration and hydration changes and attendant volume changes can drive geologic processes, such as salt-wedge polygon formation (akin to permafrost ice wedging); karst formation; sedimentary heave and thrust tectonics; and mud volcanism and diapirism.

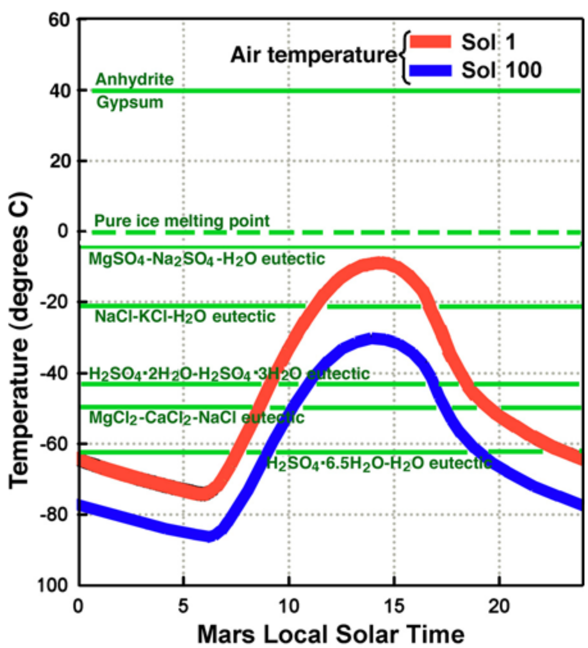

Fig. 1. Key melting, dehydration, and incongruent melting thresholds are indicated on a plot of diurnal temperature variations at sol 1 (summer) and sol 100 (autumn) at the *Spirit* landing site (Mars data courtesy of NASA/MER team). Salt and acid assemblages could undergo diurnal and annual freeze-thaw. The warmer assemblages, however, would first dehydrate and form a less-hydrated duricrust; needed water then would be unavailable for melting.

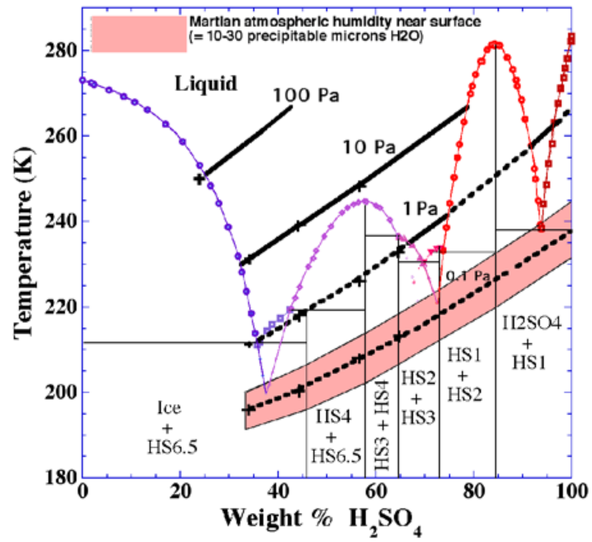

Fig. 2. Phase equilibria in the system H_2O-H_2SO_4 (data of Gable, Betz, and Maron 1950, reinterpreted by Hornung, Brackett, and Giaque 1956). Labelled isobars show H_2O partial pressure derived from Zhang et al. 1993. The coincidence of eutectics and metaeutectics under conditions similar to atmospheric temperature-humidity of the Martian surface allows the existence of sulfuric acid liquid brines directly on the surface.

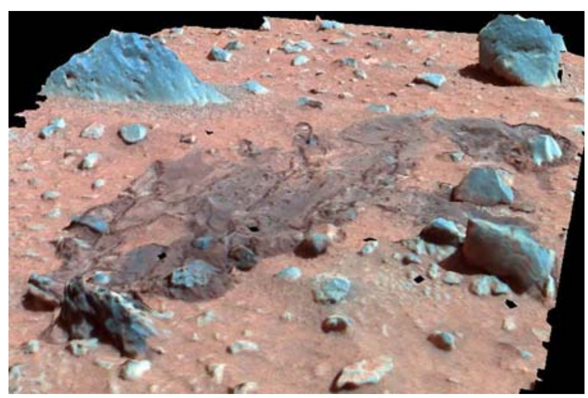

Fig. 3. The "magic carpet" at the *Spirit* landing site, produced where landing airbags were retracted and dragged over the surface. The disturbed soil has a muddy, fluid/cohesive appearance. The flatness of the fine matrix and its embayment relations with larger rocks, also suggests or allows deposition and smoothing by brine or slurry. Although most likely due simply to cohesion of fine dust and silt, a possibility is that it is soil dampened by acid-salt brine, which would be stable during the day. 3-D image courtesy of NASA/MER team.

References. [1] Abstract by Feldman, W., et al., this meeting. [2] Kargel, J. et al., 2000, *Lunar Planet. Sci.* **XXXI**, abstract #1891 (CD-ROM). [3] Marion, G.M. et al., 2003, *Geochim. Cosmochim. Acta*, **67**, 4251-4266.