

**Introduction:** In spite of the view, widely held over a long period of time, that large deposits of carbonate should be present on Mars, conclusive evidence has not been forthcoming. Spectral remote sensing data is either negative or controversial. *In situ* measurements by the Sojourner rover's APX reported no detection, with a current upper limit on C of 0.7% [1]. Yet, the so-called "missing carbonates" issue has been singled out as one of the major conundrums of martian science [2].

**Basis for Carbonates:** In order to explain planet-wide conditions that previously would have permitted abundant liquid at the surface to create the numerous morphological features, there are two possibilities.

- (1) The first is that CO<sub>2</sub> pressures were much higher than now, and the more efficient capture of solar energy by this greenhouse gas resulted in higher mean temperatures over the planet. If salts were in the water, it would not be necessary for temperatures to be above the triple point of pure H<sub>2</sub>O.
- (2) The second possibility is that some more extreme freezing-point depressor enabled liquid water even under conditions not far from the present state.

The first possibility implies that large deposits of carbonates are now sequestered in the martian regolith. The second allows for lesser quantities of missing CO<sub>2</sub>, with significant amounts possibly being accommodated as adsorbed molecules on regolith fines.

**Roles for Sulfuric Acid:** We shall now turn to the roles that sulfuric acid and related sulfur compounds could play in the potential answer to these two possibilities.

*Obscuration of Massive Carbonates.* Let us first suppose that large carbonate reservoirs are present in the regolith. Why are they observed neither by *in situ* measurements of the soil and rocks, nor with confidence by spectral studies using remote sensing observations? Soil compositions at the two Viking and the Pathfinder landing sites are remarkably similar, reinforcing the generalization that martian soil could be ancient and ubiquitously uniform to a large degree. As fines are being constantly redistributed over the surface by eolian action, they necessarily come into intimate and repeated contact with atmospheric gas constituents. Even if carbonates had at some time formed in the soil, either concurrently with the origi-

nal weathering of source rock, or as a later modification, it seems unavoidable that they have been scrubbed out by subsequent episodes of S-containing gases from volcanism and other magmatic outgassing. This is because all plausible major carbonate species in the fines (Mg, Ca, Na, K, Fe) are thermodynamically unstable with respect to their corresponding sulfates. As shown some time ago [3], even under contemporaneous martian conditions of cold and low dew point, the displacement reactions can occur extremely rapidly under UV irradiation (hours, not centuries). CO<sub>2</sub> is released back to the atmosphere. In oxidizing environments, such as in the martian atmosphere, any S-gases will be rapidly converted to SO<sub>2</sub>, and eventually SO<sub>3</sub>. The latter reacts strongly with any H<sub>2</sub>O molecule it encounters to form H<sub>2</sub>SO<sub>4</sub>.

The problem could be constrained just at this point. Martian fines are ubiquitous, and cover and coat many rocks (e.g., Big Joe's crown of soil, and the rocks partially buried in drift deposits at the Viking-1 site; soil covers on flat-topped rocks at Pathfinder, plus the finding that nearly all rock surfaces were obscured with varying amounts of adhering dust). If carbonate rocks or bedded deposits exist on Mars, they may be simply covered by regolith fines to obscure their carbonate signatures in the IR spectral regions used to search for their presence.

However, the destruction of carbonates is assuredly even more widespread. If carbonate materials exist at a surface location, they too will be subjected to weathering reactions. Adsorbed H<sub>2</sub>O is present on most mineral surfaces on Mars due to the cold environment and high energy of adsorption, in spite of the low ambient H<sub>2</sub>O partial pressure of about 1 microbar. Any SO<sub>3</sub> molecule in the atmosphere will also condense out, but has a very strong affinity for the H<sub>2</sub>O molecule. Once H<sub>2</sub>SO<sub>4</sub> forms, it also is extremely hygroscopic and can take up more H<sub>2</sub>O molecules to make a more dilute sulfuric acid with a very low freezing point. Sulfuric acid is highly reactive, but reactions with igneous minerals can be slowed by the cold temperatures and subsequent armoring by a very thin weathering layer. These factors could allow the acidic solution to persist until it can migrate to a mineral grain with which it has an almost immediate reaction, viz., a carbonate grain. However, this being a superficial process, it may proceed only skin-deep. Modification of all exposed carbonate minerals at the surface of Mars seems unavoidable. IR spectral measure-

ments are sensitive only to micrometer depths. Hence, there is little likelihood of a strong carbonate signature being found even if the carbonate minerals were originally directly positioned face-up at the atmosphere-surface interface.

With abundant rocks, and hence large amounts of igneous minerals available to weathering processes, there are ample cations available to form both sulfates and carbonates in abundance. Carbonate deposits may well exist but have been completely scrubbed out of the soils, and the older rocks and bedrock deposits have been modified just where we try to sense them, at the atmosphere-solid boundary.

What, then are the prospects or strategies for finding such deposits? Deep drilling is one obvious approach, but selection of a suitable and promising site may be difficult, and will in any event be extremely expensive because of the complexity of the approach. Gamma ray and neutron spectroscopy of surface material may be candidates for searching for buried carbonate deposits. However, these methods are not highly definitive for C, and their penetration is only some tens of centimeters into typical regolith.

The most likely location for detection of carbonates sequestered normally at depth is in the ejecta from fresh craters, whose age is so recent that sulfurous magmatic emissions have not had the opportunity to interact and destroy the carbonate surfaces. Another possibility is that a carbonate deposit has been protected from the atmosphere by soil deposition, which has "recently" been deflated by changing weather patterns or the actions of dust devils. In the case of the fresh crater, the probability is that it is very small (crater size-age distribution effect). Likewise, a newly deflated region is also likely to be relatively small (streaks and pits). Thus, in order to detect such new outcroppings of carbonates, the ground track of an orbiter-borne IR instrument would have to be very small, preferably much smaller than the TES instrument on MGS (3 x 3 km) and preferably smaller than the THEMIS instrument on the MSP-01 orbiter.

*Major Freezing Point Depressant.* With respect to the second possibility, the phase diagram of aqueous sulfuric acid solutions is quite instructive. Although pure H<sub>2</sub>SO<sub>4</sub> itself freezes at 283 K, its aqueous solutions have extraordinarily depressed freezing points. Of great potential consequence for Mars is that the eutectic aqueous solution of 39% H<sub>2</sub>SO<sub>4</sub> does not freeze until about 200 K, well below the diurnally-averaged temperatures at all latitudes on contemporaneous Mars during local summer (except on residual ice deposits). Eutectics form by freeze-out of end-member or intermediate products. Thus, precipitation of ice or acid hydrates drive the residual liquid toward

the eutectic point so that some liquid remains even at very low temperatures. Viscosity will be higher because of the lower temperatures. Erosion and sapping processes will still occur due to the transport properties of the fluid, augmented in part by increased density (1.3 g/cm<sup>3</sup> at the eutectic). Analogs on Earth are difficult to come by, although erosive lavas and mud flows may represent better analogies than the extremes of fresh water or glacier ice.

Acidity will be neutralized by weathering reactions. Some minerals will be more susceptible to weathering than others, but reaction rates vary enormously as a function of temperature and H<sub>2</sub>O availability. Susceptible materials, such as olivines, glass, or carbonates, will be readily attacked, while pyroxenes, feldspars, and Fe / Ti oxides will be much more resistant. The mineral assemblages of shergottite meteorites are in the second category.

Chemical armoring and sediment sealing of lake beds can form a barrier to further loss of acidity. Infall of eolian transported debris will provide new material, but settling rates, grain size, composition-dependent reaction rates all affect the acid neutralization rate. If Mars' dominant soluble anion is SO<sub>4</sub><sup>2-</sup>, then strong freezing-point depressors such as CaCl<sub>2</sub> would not be available for salt brines because of spontaneous reaction to form poorly-soluble CaSO<sub>4</sub>. A pervasive drawdown of atmospheric volatiles would result from chemical reaction with abraded and comminuted surface materials and may be the key to climatological evolution and desertification on Mars.

**References:** [1] Brueckner et al. (1999) *LPSC XXX*, #1250. [2] Carr, M. (1998) *LPSC XXIX*, Special Plenary Session, Masursky Lecture. [3] Clark B.C. et al. (1979) *J. Molec. Evol.*, 14, 91-102.