

**Calculating the Effects of Hydrothermal Alteration on Mars:** Laura L. Griffith, Everett L. Shock, and Raymond E. Arvidson, Department of Earth and Planetary Sciences, McDonnell Science Center, Washington University, St. Louis, MO 63130.

Hydrothermal systems on Mars could have pervasively altered the crust on a regional basis, greatly modified the volatile budget, and generated channels, chaotic terrain, and other surface features. An example of the relevance of hydrothermal systems is the observation that hydrothermal carbonates provide a plausible reservoir for carbon dioxide on Mars. Our model results indicate that hydrothermal carbonate formation is likely under a wide range of possible Martian conditions. Subsurface deposition of carbonate would provide an explanation for the apparent lack of surface expression of carbonates on Mars. Locating and identifying surface manifestations of hydrothermal systems may be more easily accomplished by looking for a general alteration assemblage, such as quartz-chlorite-tremolite-albite-carbonate-magnetite-augite, rather than restricting a search specifically to carbonates.

A consensus viewpoint about the volatile inventory of Mars is that there should be more volatiles present than can currently be accounted for in the atmosphere, polar caps, and regolith. Specifically, carbon dioxide is "missing" in an amount between ~100 mbars up to ~20 bars [1]. One approach often taken to account for this discrepancy is to assume that marine or lacustrine carbonates account for the "missing" CO<sub>2</sub> [2]. While there have been many attempts to detect massive surficial carbonate deposits, no conclusive identifications have been made [3,4]. This leaves the dilemma of the "missing" CO<sub>2</sub> unresolved, and leads to evaluating another prevalent terrestrial process involved in the carbon dioxide cycle: hydrothermal systems. In this process most of the carbonate is deposited below the surface in a dispersed nature in veins, vugs, or as mineral replacements. Any surficial deposits would tend to be relatively localized, like terrestrial hot spring deposits. This behavior explains the lack of evidence for massive surficial carbonate deposits, and is consistent with recent studies of carbonate in an SNC meteorite [5].

To better understand hydrothermal carbonate depositional patterns, a well studied terrestrial analog, Iceland, was examined in detail. Iceland was chosen for a variety of reasons, including: pervasive, fresh-water, basaltic hydrothermal systems (both extinct and active), island-wide calcite production, a wealth of data available in the literature, some remote sensing data already collected over the island, and accessibility. While the island straddles the Mid-Atlantic Ridge, the majority of the activity is due to hot-spot volcanism. The island is mostly composed of high-iron basalts, a sizable percentage being intrusives that help fuel the extensive hydrothermal systems [6]. At depths accessible to drilling, these systems reach temperatures of at least 340°C, and most are of meteoric or glacial meltwater origin [7]. Although atmospheric CO<sub>2</sub> is sufficient to produce calcite in most systems, our modeling indicates that the hottest systems must have an additional source of CO<sub>2</sub> to stabilize their calcite.

The modeling we have done involves closed-system mass transfer calculations [8]. These calculations predict an alteration assemblage starting from initial rock and fluid compositions, and use water to rock ratio (W/R), temperature, and the overburden carbon dioxide pressure (PCO<sub>2</sub>) as variables. With the calculations we can match a general alteration assemblage found in Iceland for a basaltic host rock at temperatures of ≥ 150°C. Below this temperature kinetic factors become increasingly important and closed-system calculations are inappropriate. At 250°C, with a low PCO<sub>2</sub> (atmospheric = 0.4 mbars) and W/R=1, we obtain a quantitative match to the assemblage: albite, epidote, quartz, chlorite, tremolite, prehnite, and biotite. In this simulation there is not enough CO<sub>2</sub> to stabilize calcite. By raising the overburden PCO<sub>2</sub> to 2 bars, calcite is stabilized and usurps prehnite in the alteration assemblage. Alternating layers of a prehnite assemblage and a calcite assemblage can be found in high temperature Icelandic wells [9]. We believe this indicates cycling of CO<sub>2</sub> through the system; when an area is volcanically quiescent, the systems exhibit a low PCO<sub>2</sub> and produce prehnite bearing assemblages; when an area is active, the CO<sub>2</sub> is entrained in the water and the PCO<sub>2</sub> rises, stabilizing calcite. A process such as this could have operated on Mars, where volcanic activity, particularly intrusive activity, fueled extensive hydrothermal systems supplied by melt-water from above and additional CO<sub>2</sub> from below (volcanic outgassing).

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Considering this possibility, we have done preliminary calculations for several Martian scenarios. In these calculations we vary several parameters, including host rock type,  $PCO_2$ , and temperature. The basis for host rock types is taken from the SNC meteorites. The SNC's, however, are restricted to mafic and ultramafic compositions; therefore, to consider more acidic rocks, we have extrapolated from Icelandic andesites and rhyolites. The  $PCO_2$  in the calculations has been allowed to vary over a wide range, along with the temperature. Whereas in some of the Icelandic cases the water to rock ratio was allowed to become quite high (50), the Martian scenarios were limited to W/R of 1 due to a possible lower availability of water for extended cycling on Mars.

Preliminary calculations indicate that the alteration assemblages for the Martian basaltic case would look very similar to Icelandic assemblages. At 250°C a typical Martian basaltic alteration assemblage could consist of albite, tremolite, quartz, chlorite, calcite, magnetite, and augite. Due to the higher iron content of the Martian host rocks, the oxygen fugacity tends to be slightly lower than the Icelandic cases, and the alteration assemblage often includes magnetite rather than epidote. Because epidote contains both ferric iron and calcium, its stability affects the stability of calcite and other calcium carbonate phases. Since it is doubtful that Mars is entirely one rock type, variation is to be expected over the planet. Calculations using more siliceous rocks obviously produce more silicic alteration phases, but also indicate lower calcium concentration in the fluid, as well as pH and oxygen fugacity values which are outside the range of carbonate saturation, restricting carbonate formation. However, our calculations also indicate that carbonate may form more readily under Martian conditions than Icelandic conditions due to the differences in initial host rock. In the Martian scenarios the pH and oxygen fugacity reach carbonate saturation at earlier stages of reaction progress than in Icelandic simulations, allowing formation of more carbonate.

Theoretically, Mars should have readily formed hydrothermal systems and sequestered carbonate in a dispersed nature. It is this process that makes detecting hydrothermal systems difficult by means of remote sensing. Even in Iceland, a highly altered area, the average volume percent of calcite is ~4%, below the detection limit of most instruments. Locally the percentage can exceed 25, but only in very small areas. This calls for a systems approach to testing this idea on Mars. Perhaps, looking for the signature of the entire alteration assemblage might prove more fruitful. Also, specifically targeting areas that have exposed the subsurface (e.g. crater walls, chasma walls, and outflow channels) or are surface expressions of hydrothermal areas (e.g. hot springs) may increase the detection possibility.

Deciphering the possibility of marine/lacustrine carbonates vs. hydrothermal ones is not only an issue of their detectability. The two processes are of fundamentally different origin. Marine/lacustrine deposits develop in a sedimentary environment, driven by solar energy. Hydrothermal carbonates are deposited in alteration zones, driven ultimately by radioactive decay. At present, there is no evidence to completely exclude either process, or to suggest that both processes did not function simultaneously. Finally, if hydrothermal systems did operate on Mars, the question of the origins of life as it pertains to Mars may become relevant and play a part in future landing site selections.

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