A geochemical model for the formation of hydrothermal carbonates on Mars

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It is often argued\(^1\)-\(^3\) that substantially more carbon dioxide and water were degassed from the martian interior than can be found at present in the atmosphere, polar caps and regolith. Calculations have shown that atmospheric escape cannot account for all of the missing volatiles\(^7\). Suggestions that carbon dioxide is stored as marine or lacustrine deposits\(^8\), are challenged by Earth-based and spacecraft remote-sensing data\(^9\). Moreover, recent modelling of the martian atmosphere suggests that rainfall or open bodies of water are in any case unlikely to have persisted for extended periods of time\(^6\). Hydrothermal carbonates therefore provide a possible solution to this dilemma. Using an accessible terrestrial system (Iceland) as a guide to the underlying processes, and a host rock composition inferred from the least-altered martian meteorite\(^9\), we present a geochemical model for the formation of carbonates in possible martian hydrothermal systems. Our results suggest that an extensive reservoir of carbonate minerals—equivalent to an atmospheric pressure of carbon dioxide of at least one bar—could have been sequestered beneath the surface by widespread hydrothermal activity in the martian past.

Hydrothermal systems are an inevitable consequence of igneous activity occurring in the presence of liquid water, and they have presumably existed on Mars, powered by heat from volcanic intrusions and possibly by impact events\(^1\). Direct analysis of martian hydrothermal systems is not possible at present, but the study of active, accessible and diverse terrestrial systems, such as those in Iceland, can considerably expand our understanding of martian systems and influence exploration plans.

In Iceland, hydrothermal circulation systems are deep and widespread. The source of water for systems in the interior of the island is meteoric. This relatively fresh water interacts with basalt host rock at temperatures of at least 340 °C (refs 12, 13). These systems are well characterized chemically, mineralogically and physically, as summarized in Fig. 1, which shows the generalized petrogenetic sequence of the observed alteration minerals found in basalt-hosted systems throughout Iceland as a function of temperature\(^1\). Calcite is present over the entire temperature range of alteration. Hydrothermal carbonate deposits in Iceland range from ~1 to ~50 vol.% of the altered rock, with an average of approximately 4% (ref. 18). Carbonates are found as vein-filling materials and mineral replacements, and are located at least as deep as the deepest well (~2 km below the present surface). The distribution and abundance of the deposits imply that a great deal of carbon dioxide is concealed below the surface as hydrothermal deposits. Assuming 50% alteration to a depth of 5 km and 4 vol.% carbonate in the alteration, we estimate that a likely inventory of CO\(_2\) sequestered within Iceland is ~2.5 mbar or about 6 times the 0.4 mbar of CO\(_2\) in Earth's present atmosphere. This entire amount of CO\(_2\) would have been sequestered over only the past 16 Myr, Iceland's lifetime\(^7\). This calculation demonstrates that hydrothermal systems, even on a small scale, can greatly affect a planet's CO\(_2\) inventory.

To consider the generation of Icelandic deposits in more detail, we have performed series of rock-path calculations\(^19\) involving host rock composition, temperature, water:rock (W/R) ratio, and carbon dioxide fugacity as variables. These calculations start with a system far from equilibrium and use
irreversible thermodynamics to evaluate the geochemical consequences of progress toward an equilibrium state. In the course of the calculations, the effects of fluid interaction with the host rock and subsequent alteration phases are monitored in terms of reaction progress. These theoretical results are independent of spatial and temporal constraints, but can be 'mapped on to' geological systems. In these calculations, conducted with the program EQ3/6 (ref. 20), we used three different Icelandic host rock materials (tholeite basalt, andesite and rhyolite) at three temperatures (50, 150 and 250 °C), and three time-integrated W/R ratios (1.10 and 50 by mass). Results consistent with the deposition of carbonates are found at all temperatures, rock types and W/R ratios; but as temperature increases, the fugacity of carbon dioxide \( f_{\text{CO}_2} \) must be higher to stabilize carbonate minerals.

Results presented here for Iceland are those most easily compared with results from Mars (basaltic host rock, meteoric source water and low W/R ratio). As an example, Fig. 2a, b summarize Icelandic results for basalt alteration at 250 °C with two different CO\(_2\) fugacities. In these calculations, the system is closed for all components except CO\(_2\), which is maintained at a constant fugacity. Models at a constant \( f_{\text{CO}_2} \), equivalent to the present terrestrial atmospheric CO\(_2\) partial pressure (Fig. 2a) are consistent with the formation of prehnite [\( Ca_3Al_2Si_4O_{12}(OH)_2 \)] rather than carbonate [\( Ca(Ca,Mg,Fe)CO_3 \)] (Fig. 2b). With a moderately higher value of \( f_{\text{CO}_2} \), the calculated assemblage includes carbonate (97% CaCO\(_3\)), not prehnite (Fig. 2b). This change is consonant with observations from Iceland, where calcite and prehnite assemblages occur in alternating layers, but not commonly together\(^\text{13}\). We believe that cycling of CO\(_2\) through the Icelandic systems causes this layering effect. During periods of volcanic and/or tectonic activity, released magmatic gases become entrained in the hydrothermal fluids, increasing the \( f_{\text{CO}_2} \) and stabilizing calcite, even at higher temperatures (to at least 340 °C). During periods of quiescence, the \( f_{\text{CO}_2} \) decreases, and calcite does not form, allowing other calcium-rich minerals such as prehnite to precipitate.

Martian hydrothermal systems could be extremely similar to those Icelandic systems where the source of water is meteoric rather than sea water. To test this hypothesis we chose a host rock of shergottite composition (a basaltic SNC meteorite\(^\text{10}\)) for reaction-path calculations using water containing variable amounts of CO\(_2\) (Fig. 2c). The shergottite host was chosen because it appears to be the least altered of the basaltic SNC meteorites and therefore provides a first estimate for a starting composition. Comparison of Fig. 2b, c shows that chlorite, carbonate (96% CaCO\(_3\)), tremolite, albite and quartz are common to both the Icelandic and martian calculated alteration assemblages. The differences between the Icelandic and martian results seen in Fig. 2 are generated by differences in initial bulk composition and mineralogy.

Similar calculations demonstrate that the presence of carbonate is plausible under a wide range of likely Martian hydrothermal temperatures and CO\(_2\) fugacities, as illustrated in Fig. 3, which can be used to estimate the potential production of carbonate minerals (in mol%) for any combination of temperatures.

**Fig. 2.** Predicted alteration assemblages for progressive alteration of Icelandic and martian basalts with water at 250 °C, pressure equal to vapour–liquid equilibrium for H\(_2\)O and a W/R ratio of 1 by mass. a, Icelandic results for \( f_{\text{CO}_2} = 0.4 \) mbar (atmospheric); b, Icelandic results for \( f_{\text{CO}_2} = 2 \) bar; c, martian results for \( f_{\text{CO}_2} = 1 \) bar. Reaction-path calculations monitor reaction progress, which is a quantitative measure of the extent to which equilibrium has been reached (see ref. 19). These plots show logarithmic values of the reaction progress variable, which is calculated from the mass of rock that has been altered. A value of \(-7\) pertains to a system of unaltered rock, water and the indicated \( f_{\text{CO}_2} \), and a value of 0 denotes the equilibrium state as a result of hydrothermal alteration. Numbers at the right give mass percentages of the minerals in the equilibrium assemblages. The following phases are solid solutions with compositions that may change during the course of reaction progress: albite, augite, biotite, carbonate, chlorite, epidote and tremolite.
FIG. 3 Carbonate production capacity from a shergottite composition (W/R = 1) as a function of temperature and constant f_{CO2} (in bar). The surface represents mol percentages of CO₂ incorporated in equilibrium alteration assemblages as carbonate minerals: calcite solid solution containing variable minor amounts of magnesium and iron and/or dolomite. At higher temperatures a higher f_{CO2} is required to reach the value of dissolved CO₂ necessary to stabilize carbonate, consistent with the decreasing solubility of carbonate minerals with increasing temperature. The step-like appearance of this surface results from the interplay between the stabilities of the calcite solid solution and dolomite, which are in turn influenced by reactions involving other calcium-, magnesium- and iron-bearing minerals. The third step from the bottom is due to the appearance of dolomite.

(from 50 to 250 °C) and f_{CO₂} (from 10⁻⁶ to 1 bar). As an example, it can be seen that carbonate can precipitate at temperatures ≤150 °C at f_{CO₂} equal to that in the current martian atmosphere (10⁻⁶ bar = 6 mbar). Amounts of carbonate predicted at 150 °C and log f_{CO₂} = -2.2 are small (~1 mol%), but would increase considerably at equilibrium if the temperature of alteration were lower for the same f_{CO₂}. If the temperature of alteration exceeds 150 °C, then a higher f_{CO₂} is required for carbonate precipitation, as shown in Fig. 3. As in Iceland, locally higher f_{CO₂} values on Mars may be attained through magmatic outgassing and CO₂ entrainment.

There are several applications of mass-transfer calculations to the study of the evolution of Mars. For example, combining model calculations with petrologic and isotopic studies of martian rocks, including the SNC meteorites, may lead to a better understanding of the sequence of events leading to the present appearance of these rocks. But it is not our aim in this work to explain the petrogenesis of the SNC meteorites. In the future, combination of more comprehensive theoretical calculations with analytical studies may help to constrain alteration temperatures, scenarios and carbonate production in the SNC meteorites. Our present calculations produce anywhere from minute to massive amounts of carbonate (Fig. 3), but smaller amounts seem more consistent with the few samples of the martian surface currently accessible. Although the calculated assemblages are not directly reflected in these few samples, this is not an argument against the plausibility of hydrothermal systems having strongly influenced martian volatile processing. Because it is possible that most hydrothermal activity occurred early in Mars’ history, samples from that era would be revealing. Unfortunately, only one old sample (ALH84001 : > 3 Gyr (ref. 22)) is currently recognized. This particular sample has had an extremely complex history and has left Mars researchers with the problem of trying to piece together the planet’s early history from one very confusing example22. The carbonate in this specimen is very rich in magnesium and iron, and may reveal much about the composition of martian fluids once the history of the meteorite is better understood.

Finally, these theoretical calculations allow first-order estimation of the amount of CO₂ that could be hidden as hydrothermal carbonate in Mars. We estimate that a maximum of 5 bar of CO₂ could be sequestered in the martian crust owing to hydrothermal alteration. This requires ~2.5% carbonate globally dispersed throughout the upper 5 km of crust. Crustal storage of 1 bar of CO₂ would require an average of only 0.5% carbonate in the upper 5 km or 1% in the upper 2 km. Thus we submit that hydrothermal deposits could account for a considerable amount of the carbon dioxide released by volcanic activity on Mars, with many implications for understanding the inventory of martian volatiles. Because magmatic activity was more frequent on Mars in the first half of geological time, we surmise that the effectiveness of hydrothermal systems for sequestering CO₂ has changed dramatically with time. Hydrothermal processes would have been particularly important if Mars did not have a hydrologic cycle with extensive rainfall and runoff, that is, if surface temperatures and pressures did not reach the triple point of water.

In areas where the water table intersected the surface, warm, CO₂-laden fluids should have degassed to produce locally extensive travertine units. These sites provide a test of the hydrothermal carbonate hypothesis. Because most of the activity in hydrothermal systems occurs at depth, investigations of the subsurface at eroded channels, chasma walls, and craters furnish additional areas of observation and testing of this hypothesis. Hydrothermal systems on another planet offer new probabilities for the synthesis of organic compounds and the possible emergence of life23,24.


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