

THE ROLE OF CO₂ IN AQUEOUS ALTERATION OF ULTRA-MAFIC ROCKS AND THE FORMATION OF MG-, FE-RICH AQUEOUS SOLUTIONS ON EARLY MARS. P.B. Niles¹, M.Yu. Zolotov², and L.A. Leshin³,

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Introduction: An adequate understanding of water on Mars that moves beyond the simplistic “warm-wet” vs. “cold-dry” dichotomy must include strong constraints on the variables: water/rock ratio, time, temperature, and chemical composition. By constraining these variables first on local, then regional and global scales we will be capable of precisely targeting landed missions to definitively understand the history of water on Mars and the possible existence of life.

Data from remote sensing of Mars, landed missions, and martian meteorites indicate that secondary minerals formed from aqueous fluids on Mars are predominately Fe- and Mg-rich. The unique Mg-, Fe-rich carbonates in the ALH 84001 meteorite provide an excellent opportunity to provide strong constraints on an Fe-, Mg-rich aqueous system on early Mars. This work seeks to use the unusual chemical compositions of the ALH 84001 carbonates as a constraint for the composition of their formation fluid. These constraints can be used to better understand aqueous processes at a critical time in martian history.

Methods: The chemical composition of the fluid that formed the ALH 84001 carbonates can be understood if we assume that they formed from a single fluid according to the mechanism described by previous experimental [1] and theoretical work [2]. This mechanism uses the fact that carbonate solutions typically precipitate carbonate minerals that are more Ca-rich than the bulk chemical composition of the fluid. This process then drives the fluid to more and more Mg-rich values as Ca is removed through precipitation of carbonate. Thus the variation in chemical composition observed in the ALH 84001 carbonates can place constraints on the chemical composition of the fluid. These constraints can then be used to evaluate the possibility that the chemical composition of the fluid was derived through interaction with rocks similar to ALH 84001.

A series of potential fluid compositions were calculated using equilibrium thermodynamic modeling of the reaction of a rock with similar composition to the ALH 84001 meteorite with varying amounts of water and CO₂ gas, at a variety of temperatures. We used the GEOCHEQ program [3] to calculate chemical equilibria. Since sulfur is not a significant component in ALH 84001 we did not include it in our calculations. To simulate low temperature kinetic inhibitions antigorite, talc, tremolite, Mg anthophyllite, magnesite, dolomite, siderite, graphite, and methane were excluded at tem-

peratures <50°C. At temperatures between 50°-100°C antigorite, talc, graphite, and methane are excluded from the calculations. At temperatures >100°C, graphite and methane are the only species excluded. A variety of water/rock ratios are combined with different temperatures and CO₂ fugacities to evaluate the effect of each variable on the system. Water/rock ratios can be viewed as a proxy for reaction progress with the highest ratios (water>>rock) signifying very small amounts of rock reacting with a fixed amount of water, and the lowest ratios (water~rock) indicating large amounts of rock reacting with the same volume of water [4].

Results: The minimum initial molar Mg/Ca ratio of the formation fluid is dictated by the bulk chemistry of the carbonates and especially the Mg-rich nature of the final phases. If the initial Mg/Ca ratio of the fluid is less than that of bulk carbonates precipitated then it will inevitably drive the fluid to lower Mg/Ca ratios, which is inconsistent with the chemical composition of the carbonates that show an ever-increasing Mg/Ca ratio as precipitation proceeds. Thus, the initial fluid must at least have an Mg/Ca ratio that is greater than the Mg/Ca ratio of the bulk carbonates which is ~5.0 [5].

Similarly, the Fe/Ca ratio of the bulk composition of the ALH84001 carbonates (~2.5 [5]) can be used as a guide for the initial Fe/Ca ratio of the fluid. Since the composition of the carbonates initially increases in Fe and then decreases, it is likely that the fluid composition became depleted in iron as the reaction progressed. Since a significant portion of the Ca in the fluid must be consumed by carbonate precipitation in order to significantly change the Mg/Ca ratio in the fluid, the Fe/Ca ratio of the bulk carbonates is a good constraint on the amount of iron in the solution.

Some of the results of equilibrium thermodynamic modeling are displayed in Figure 1 which shows the effects of CO₂ content, water-rock ratio, and temperature. The constraints on the Mg/Ca and Fe/Ca ratio of the precipitating fluid posed by the empirical model discussed above are met at low temperatures (<100°C) and P_{CO2} levels greater than 0.1 bar. Water-rock ratios only become important at high values (>10,000) where the solutions are very dilute and reflect the chemistry of the rock.

Discussion: The results of the equilibrium modeling show that in order to create Fe-,Mg-rich solutions through interactions with an ultra-mafic rock, the flu-

ids must have a lower pH (< 7) and a low temperature ($< 100^\circ\text{C}$). In this system, which eventually precipitates carbonates, the low pH is probably due to a relatively large partial pressure of CO_2 . At higher temperatures and pH the iron and magnesium are lost from the solution through the precipitation of serpentine, siderite and Fe-rich clays. Thus a low temperature, CO_2 -rich aqueous system is necessary to create an Fe-, Mg-rich solution through a simple interaction with an ALH 84001 type host rock.

These conclusions are further supported by other studies of the ALH 84001 carbonates that suggest minimal water-rock interaction [6], low carbonate formation temperatures [7, 8], and CO_2 rich fluids through the presence of siderite [9].

While many investigators have attributed the origin of CO_2 -rich fluids to a dense CO_2 atmosphere on early Mars, the stable isotopic compositions of the ALH 84001 carbonates suggest that the fluid itself underwent significant isotopic changes during carbonate

precipitation, which cannot be accomplished by simply sitting on the surface in equilibrium with the atmosphere [7, 10]. The isotopic changes can be explained if the fluids obtained their CO_2 -rich character in the subsurface, and the isotopic changes occurred when this CO_2 -rich subsurface fluid was exposed to a sparse, arid atmosphere which prompted rapid evaporation, CO_2 degassing, and carbonate precipitation.

The source of the subsurface CO_2 gas is not clear, although the $\delta^{13}\text{C}$ composition of the ALH 84001 carbonates indicates that it is not magmatic. We suggest that it might be buried $\text{H}_2\text{O}-\text{CO}_2$ clathrates which are consistent with the $\delta^{13}\text{C}$ and $\Delta^{17}\text{O}$ compositions of the carbonates and have been hypothesized to have existed in the martian subsurface [11-14].

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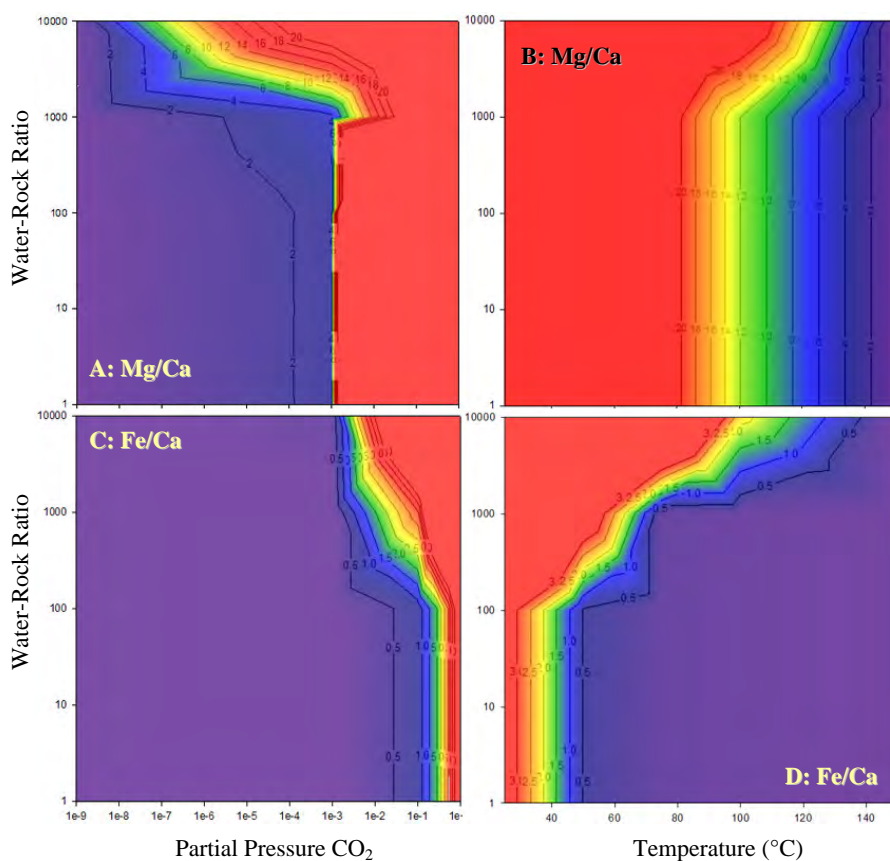


Figure 1: **A)** Calculated Mg/Ca molar ratio (contour lines) of fluid in equilibrium with an ALH 84001 type rock at a constant temperature of 25°C and variable P_{CO_2} . The warmer colors indicate fluids that are consistent with the empirical constraints ($\text{Mg}/\text{Ca} > 5$). **B)** A similar graph of Mg/Ca ratio (contour lines) of a fluid in equilibrium with an ALH84001 type rock at a constant P_{CO_2} of 0.5 bar. Again warmer colors indicate fluids that are consistent with empirical constraints ($\text{Mg}/\text{Ca} > 5$). **C)** Similar plot calculated Fe/Ca molar ratio (contour lines) of fluid at 25°C and variable P_{CO_2} . Warmer colors show fluids that meet empirical constraints ($\text{Fe}/\text{Ca} > 2.5$). **D)** Fe/Ca ratio (contour lines) at constant P_{CO_2} of 0.5 bar and variable temperature.