

CARBONATE PRECIPITATION DRIVEN BY CLAY LEACHATES ON EARLY MARS. M. Melwani Daswani¹, S. P. Schwenzer¹, M. H. Reed², I. P. Wright¹ and M. M. Grady¹, ¹Department of Physical Sciences, Open University, Walton Hall, Milton Keynes MK7 6AA, UK (mohit.melwani-daswani@open.ac.uk), ²Department of Geological Sciences, University of Oregon, Eugene, OR 97403-1272.

Introduction: Secondary carbonate minerals produced by low temperature aqueous processes [1] in the martian meteorite ALH 84001 are evidence of an early active hydrosphere on Mars when they were formed ~3.9 Ga ago [2]. Further evidence for an early hydrosphere includes orbital and surface observations of diverse alteration mineral assemblages [e.g. 3-5] and fluvial geomorphology [6]. While carbonates are observed in ALH 84001, unusually, there is no evidence of secondary phyllosilicates associated to low temperature aqueous alteration of the meteorite, and there is a lack of textural evidence for intensive fluid interaction [7]. We have used geochemical modelling techniques to show that the carbonates in ALH 84001 can be produced in a two stage process in which low temperature fluids percolate and leach clay-bearing layers prior to encountering the unweathered host of ALH 84001.

Modelling: We carried out thermochemical models with CHIM-XPT [8], limiting the temperature to 15, 20 and 25 °C, consistent with CO₂ clumped isotope thermometry of the formation of the carbonates in ALH 84001 [1]. The initial fluid used to alter the meteorite's host rock was in equilibrium with 1 and 2 bar pCO₂, in accordance with estimates of the early martian atmosphere [9]. In contrast to previous models (which then varied the amount of rock relative to the amount of fluid in the system and observed the resulting chemical and mineralogical changes [10, 11]), we first allowed the fluid to percolate through phyllosilicate minerals detected on the surface of Mars (Table 1), and then altered the parent rock of ALH 84001 with these fluids.

Finally, we modelled the isothermal evaporation of water from the system and observed the mineralogical changes generated.

Table 1. Martian phyllosilicates used in the model

| Phyllosilicate | Detection |
|-----------------|----------------------------------------------------|
| Montmorillonite | MER "Spirit" in Columbia Hills, Gusev crater [13]. |
| Celadonite | Possible detection by MRO CRISM [14]. |
| Saponite | Analysis in Lafayette martian meteorite [15]. |
| Nontronite | Detection by MEx OMEGA [4]. |

Results: Without first leaching Ca, Mg, Fe, Na, etc. from the phyllosilicates, carbonates of similar composi-

tion to those in ALH 84001 cannot be formed without also significant amounts of phyllosilicates being produced (Fig. 1), comparable to the models presented in [10, 11].

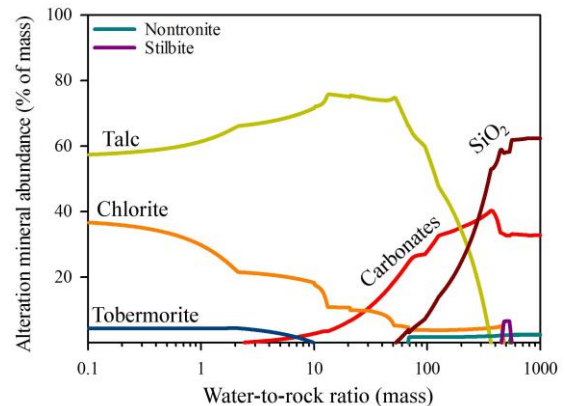


Figure 1. Minerals produced in the alteration of the ALH 84001 host rock by a fluid at 20 °C and in equilibrium with a 1 bar pCO₂ atmosphere.

Leachates from the phyllosilicates, on the other hand, at W/R of ~ 500 formed carbonates in contact with the ALH 84001 parent rock while minimising the production of alteration phases not observed in the meteorite (Fig. 2). Moreover, carbonate compositions produced this way approximated the compositions measured in the meteorite and followed the compositional zonation observed (Fig. 3, cf. composition from [16]).

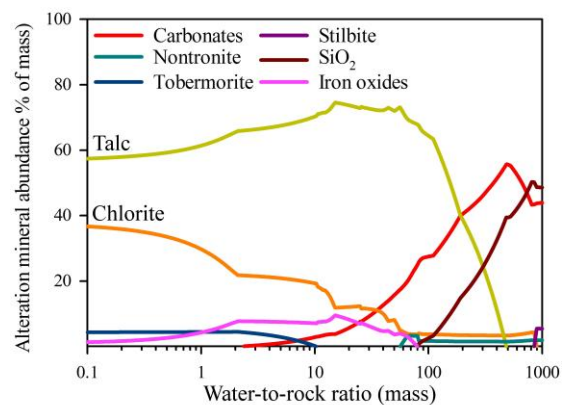


Figure 2. Minerals produced in the alteration of the ALH 84001 host rock by a montmorillonite leachate at

20 °C and in equilibrium with a 1 bar pCO₂ atmosphere.

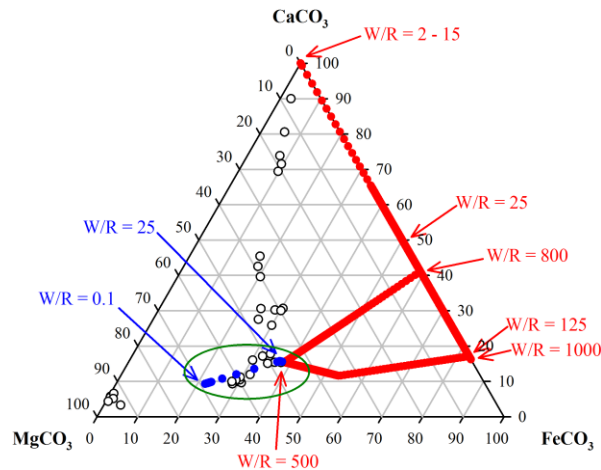


Figure 3. Carbonate compositions (normalised and omitting Mn-rich endmember, which is typically < 1% mass) produced in the alteration of the ALH 84001 host rock by a montmorillonite leachate at 20 °C and 1 bar pCO₂. Red: change in carbonate composition with water-to-rock ratio. Blue: change in carbonate composition with isothermal evaporation of the water from the system. Empty circles: representative compositions measured in the meteorite [16]. Green oval: overlap in calculated and observed compositions.

The post-alteration, isothermal evaporation of water from the system further increased the carbonates relative to other alteration phases, and brought the carbonate composition closer to the magnesite-rich component found in the outer layers of the carbonates in ALH 84001 (Fig. 3).

Not all leachates from the phyllosilicates produced significant carbonates relative to other alteration phases, or a carbonate composition that matched the observations in ALH 84001. Montmorillonite, saponite and celadonite leachates were more successful, whereas the nontronite leachate was less successful.

Discussion: The low temperature formation of the carbonates in ALH 84001 in equilibrium with the martian atmosphere is intensified (relative to alteration phases not found in the meteorite, e.g. phyllosilicates) by an appropriate alteration fluid. A combination of a relatively high pCO₂ atmosphere and available cations in the fluid here facilitates the formation of the carbonates with minimal interaction with the parent rock (apparent in the high water-to-rock ratios needed to produce the carbonates, and consistent with precipitation in voids).

Phyllosilicates lend bound cations to a leaching fluid more readily than the parent rock of ALH 84001

does, which otherwise also precipitates substantial amounts of SiO₂ when altered (Fig. 1).

Conclusion: Clay minerals preceding the carbonates in ALH 84001 and leading to the formation of the latter via leaching fluids is consistent with the elevated ⁸⁷Sr/⁸⁶Sr in the carbonates and bulk of the meteorite [12]. The results here indicate that weathering, clay-forming conditions existed very early on the surface of Mars, prior to the formation of the carbonates (> 3.9 Ga ago). The evaporation of the alteration fluid drove the carbonate composition in the model closer to the actual composition of carbonates in ALH 84001. The carbonates in ALH 84001 could have formed in a similar environment to Gale crater, where clay minerals were precipitated by diagenetic fluids that also formed later mineral phases, such as gypsum [5, 17].

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