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Leachates formed carbonates in ALH84001 and on early Mars

M. Melwani Daswani, M. M. Grady, S. P. Schwenzer and I. P. Wright
The Open University, Milton Keynes, UK (mohit.melwani-daswani@open.ac.uk)

Abstract

1. Introduction

Evidence abounds for liquid water existing on Mars prior to the late heavy bombardment (LHB) $\sim$ 3.9 Ga ago and physicochemically interacting with rocks to form distinct geomorphological landforms and mineralogical alteration products (e.g. [3, 4, 8, 14]). ALH84001, the oldest ($\sim$4.5–4.1 Ga [11, 13]) known martian meteorite, contains secondary carbonate minerals formed on Mars $\sim$3.9–4.0 Ga ago [5], roughly contemporaneous to the LHB. Recent isotopic evidence supports their formation at low temperature ($\sim$18 °C [9]) and also by fluids derived from aqueous weathering in the Noachian/Phyllosian, due to the elevated ^{87}Sr/^{86}Sr ratios in the carbonates and bulk rock of ALH84001 [1].

2. Methods

In order to understand the chemistry and origin of the alteration fluid, we have thermochemically modelled the system that produced the secondary phases in ALH84001 with the modelling program CHIM-XPT [15]. Prior efforts to model the system at low temperature disagree on the process of formation of the carbonates, which range from dissolution and reprecipitation at low CO_2 pressures (consistent with modern Mars or Earth) [10], precipitation through degassing of CO_2-rich fluids [12] and formation in an environment with dynamically changing CO_2 [2]. These previous models all start with pure water equilibrated with an amount of CO_2 prior to interacting with the host rock, but do not account for an initial alteration fluid that likely contained inherited leached components.

2.1. Leaching

We derived the composition of the alteration fluid used to form the carbonates in ALH84001 firstly by leaching clays (themselves products of alteration) observed on the surface of Mars by orbital spectrometers and rover instruments [4, 6, 14]. Leaching was modelled at high $p\mathrm{CO}_2$ (1–2 bar) and low T (20 °C). Reported here are the leaching scenarios tested with the clays celadonite, nontronite and montmorillonite.

2.2. Alteration

We extracted the initial alteration fluid to alter the host rock of ALH84001 from the leaching scenarios in which more carbonates were produced relative to other minerals. Water-to-rock ratios (W/R) varied from 0.1–10^4, $p\mathrm{CO}_2$ was kept elevated (1–2 bar) and T was low (15, 20 and 25 °C).

2.3. Evaporation and replenishment

We modelled the extraction of (pure) water from the system by simulating isothermal evaporation. Evaporating water at certain W/R and replenishing the fluid yielded a method to fix and vary the composition of the carbonates respectively, replicating the layering of the compositionally distinct carbonate phases in ALH84001.

3. Results

Models of aqueous alteration of ALH84001 resulted in the precipitation of upto 10 % carbonate by mass relative to other alteration phases at 20 °C and 2 bar $p\mathrm{CO}_2$, but the carbonates were compositionally different to those found in the meteorite (Fig. 1). At the other low temperatures and $p\mathrm{CO}_2$ tested, the alteration phases were predominantly hydrous silicates (serpentines, chlorite, smectites and talc) and amphiboles (e.g. Fig. 2), which are not observed in the meteorite.

Leaching the clays celadonite, nontronite and montmorillonite and using the fluids derived to alter ALH84001 resulted in more compositionally diverse carbonates (Fig. 1). From the leaching scenarios reported here, only montmorillonite-leaching fluids produce carbonate-dominated (>60 % carbonate) secondary mineral assemblages in the ALH84001 host, containing only trace amounts of hydrous silicates

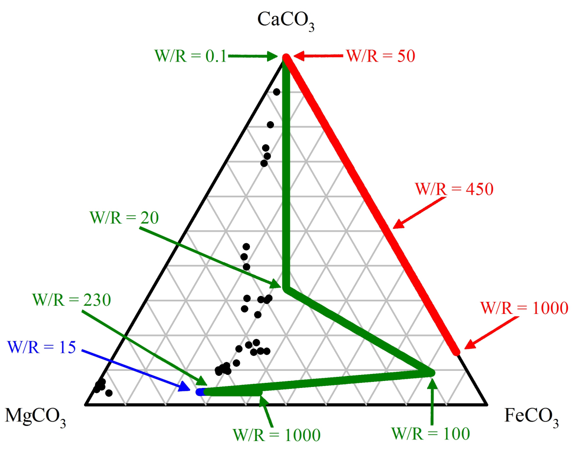

Figure 1: Carbonate composition changes plotted on a carbonate endmember triangle. Red: alteration with water and 2 bar pCO_2. Green: alteration of the host after leaching montmorillonite at 20 °C and pCO_2 = 1 bar. Blue: evaporation from W/R = 230 to 15 after leaching montmorillonite and alteration of the ALH84001 host. Black dots are compositions of carbonates sampled from ALH84001 [7].

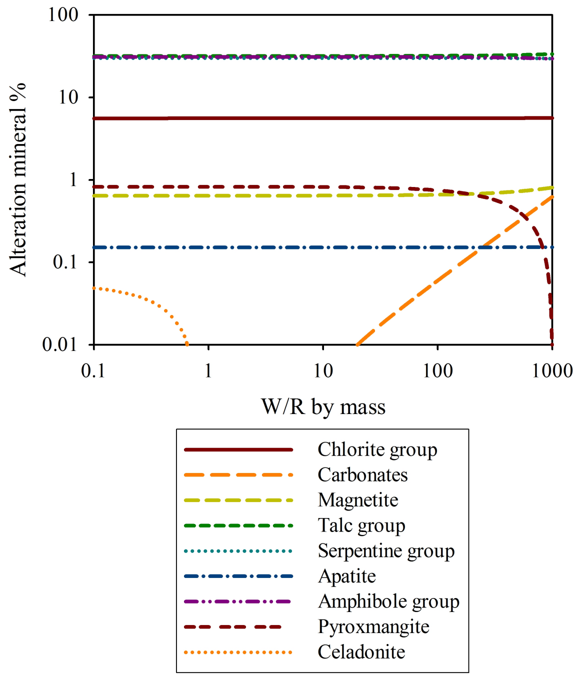

Figure 2: Secondary minerals precipitated from aqueous alteration of the ALH84001 host rock at 25 °C and with pCO_2 = 2 bar.

(upto 2 %). Isothermally evaporating water from the montmorillonite derived leachate alteration system from W/R ≈ 230 to ∼15 fixes the composition and mass of the secondary carbonates produced, and only slightly changes the alteration assemblage to a more magnesitic composition as opposed to sideritic (Fig. 1). Alternating evaporation and fluid replenishment can therefore explain the observed compositional zoning of the carbonates.

4. Discussion and conclusions

Thermochemical modelling of phyllosilicate derived leachate interaction with the ALH84001 host resulted in in alteration of similar composition to the observed assemblage in the rock. In particular, montmorillonite-derived leachate produced the most similar assemblage at 20 °C and 1 bar atmospheric pCO_2. This result, as well as the unaltered nature of the host rock and the Sr isotope evidence [1], coupled with the fact that aqueous alteration models of the host did not produce a comparable alteration to ALH84001's at the T, pCO_2 and W/R ranges tested, strongly supports that the alteration assemblage in ALH84001 incorporates a non-indigenous component into the host introduced by a fluid.

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