

# The nakhlite alteration and habitability – mobility and quantification of essential elements

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## Abstract

The nakhlite Martian meteorites contain alteration mineral assemblages, which reveal detailed information about their formation conditions; Thermochemical modeling allows the assessment of factors not observable in the rocks, such as temperature and fluid chemistry at the time of mineral formation. Combining observation and thermochemical modeling leads to the conclusion that ~4 g CO<sub>2</sub> are sequestered per 10 g of altered Lafayette in the presence of 1 kg of water. 27 x 10<sup>-9</sup> g of P and 0.06 g of S are available in the fluid after mineral precipitation. Other cations important for habitability, e.g., Na, K, Ca, and Mg, are present in solution.

## 1. Introduction

For habitability the availability of essential elements and energy are critical (e.g., [1,2]). Of main concern thereby are the elements C, N, P, and S, but also cations such as Fe, Ca, K, and Na. To assess the availability of these elements we take a two way approach, combining mineralogical observations of the nakhlite Martian meteorites [3] and thermochemical modeling [4,5].

### 1.1 Alteration minerals and processes

Martian alteration minerals can be observed at the greatest level of detail in the nakhlite Martian meteorites, where precipitation of a carbonate–smectite–gel succession is found ([3], and references therein) after dissolution of mostly olivine [3,6]. The hydrothermal system was short lived, leading to a dispersed network of veinlets, and the temperature gradient between the carbonate and clay formation was steep, suggesting an impact-generated hydrothermal origin of the assemblages [3,5].

## 1.1 Modeling

Using thermochemical modeling we suggested a four stage process formed Lafayette alteration, potentially linked to impact-generated hydrothermal processes on Mars: inhomogeneous dissolution favouring olivine and mesostasis is followed by carbonate precipitation at temperatures between 150 and 200 °C. Upon reduction of CO<sub>2</sub> partial pressure and cooling to about 50 °C, smectite (saponite) formation occurs, followed by gel precipitation [3,5,7]. In contrast, for ALH 84001 low-temperature carbonate formation is proposed [8,9].

## 2. Method

Thermochemical modeling for this work was carried out with CHILLER [10] and details are presented in [5]. CHILLER, now followed by CHIM-XPT [11], but results from both are comparable for Martian rock compositions [12]. For starting conditions we calculated the host rock chemistry from Lafayette whole rock and olivine [13] and Lafayette mesostasis (new SEM-EDX data) in an iterative process that allows for the observed alteration minerals to form [3]. Various amounts of CO<sub>2</sub>, ranging from 10 (in early carbonate-rich part of fluid's history) to 0.1 mole/kg water, were added to explore the carbonate formation parameter space.

## 3. Results

Results presented here build on the models and results that led to the characterization of the Lafayette alteration assemblage formation and the brine(s) in equilibrium with that assemblage [5]. We take the 'mixed source' model of [5] as example, and use 0.1 mole CO<sub>2</sub> and T=50 °C at W/R of 100. Main minerals precipitated are nontronite (77 %), carbonate (14 %), quartz (5 %) and kaolinite (4 %). All concentrations below are for 1000 g (or 55.5 moles) of water and 10 g of dissolved host rock.

### 3.1 Carbon

In our models we can only directly observe the pathways and sinks of carbon, which is added to the system as CO<sub>2</sub>. In the investigated case, 0.097 moles of CO<sub>2</sub> (= 4.27 g CO<sub>2</sub>) are sequestered out of the system, 0.003 moles stay in solution, mainly as HCO<sub>3</sub><sup>-</sup>. Thus, with the dissolution of 10 g of dissolved Lafayette, 0.097 moles of carbonate (chemically 3.55 g of dolomite and 4.58 g of magnesite) are precipitated. We next need to estimate the degree to which Lafayette is altered. From observation Changela and Bridges [5] concluded that ~1% of Lafayette reacted to form the vein material. This is equivalent to 1.16 g C (or ~8 g carbonate) being sequestered per kg of dissolved Lafayette. If we deduce that 1% of the top 1 km of the Martian crust (3.3x10<sup>20</sup> kg) were altered in that way, this is equivalent to ~0.22 bar of CO<sub>2</sub> partial pressure. This is too high for direct exchange with the Amazonian atmosphere, showing that the nakhlite hydrothermal fluid was derived from a crustal CO<sub>2</sub>-H<sub>2</sub>O ice reservoir. This implies uncertainties in the C/N and noble gas/C ratios which will not be equal to the current atmospheric values.

### 3.2 S and P

Sulfur and phosphorous are contained in the sulphides and phosphates of the unaltered Lafayette rock, making up 0.02 (FeS) and 0.06 (P<sub>2</sub>O<sub>5</sub>) wt.-% of the starting composition. After alteration, 89 % of the S (molar) is contained in the precipitate; and almost all P is precipitated with the solid phases. The S in solution is dominantly oxidized compared to the sulphides in the host rock.

### 3.3 Fe, Ca, et al.

Cations such as K, Na, Ca, and Mg are essential elements for life. While bound to rock forming, magmatic minerals, they are not or not easily available to metabolic processes. Hydrothermal dissolution concentrates the most soluble cations in solution (100 % of Na and K, equal to 0.004 and 0.001 moles of Na and K, respectively). Elements such as Ca and Mg are precipitated with the carbonates and silicates, but 1.4 % of Ca (0.0003 mole), and 3.3 % of Mg (0.003 moles) are available in dissolved form. Iron is especially interesting because of its two valence states, but is almost quantitatively precipitated.

## 4. Discussion

Using a specific example, we can quantify the sinks and mobility of key elements during Lafayette alteration. Applying this example in greater detail to the case discussed in [5] leads to a quantification of element mobility in this Martian system. This allows the assessment of key parameters for habitability in an observed Martian alteration assemblage at a time when the surface of Mars was cold, dry and hostile to life.

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