Lithium and carbon isotopic fractionations between the alteration assemblages of Nakhla and Lafayette

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LITHIUM AND CARBON ISOTOPIC FRACTIONATIONS BETWEEN THE ALTERATION ASSEMBLAGES OF NAKHLA AND LAFAYETTE. J. C. Bridges1, R. H. James2, V. K. Pearson1, L. Baker1, A. B. Verchovsky1 and I. P. Wright1 1PSSRI, Open University, Milton Keynes MK7 6AA, UK j.bridges@open.ac.uk, 2Dept. of Earth Sciences, Open University, Milton Keynes MK7 6AA, UK.

The nakhlites experienced a fluid alteration event on Mars leading to the rapid crystallization at low temperature (e.g. 25-150ºC) of siderite, clay and other salts in fractures within olivine and interstitial sites [1-2]. In order to help constrain the origin and evolution of the brine we present new Li-isotopic, C and Thermal Gas Analysis data for Nakhlite and Lafayette samples.

Techniques: Whole rock samples of Nakhlites (BM 1911, 369) and Lafayette (BM 1959, 755) were powdered using an agate mortar and pestle. We also used Nakhlite pyroxene separates (>95% pure) and olivine-rich meteorites. The acid-leach (+14.2 ‰) reflects the terrestrial ultramafic rocks [6]. The Nakhlite water-leach has a similar composition to the igneous phases implying that the siderite does not contain fractionated Li-isotopes. The detectable fractionation between Nakhlite pyroxene and olivine-rich samples (0.5‰) suggests that the olivine contains a "Li-rich alteration phase, which may be the nontronite-like clay present in cracks e.g. [1] or intraminal fractionation [6].

Table 1. Li-isotopes in Nakhlite Samples

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>δ7Li ‰</th>
<th>1σ error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nakhlite bulk</td>
<td>4.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Nakhlite px</td>
<td>3.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Nakhlite ol-rich</td>
<td>5.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Lafayette bulk</td>
<td>4.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Nakhlite water leach</td>
<td>14.2</td>
<td>0.5</td>
</tr>
<tr>
<td>Nakhlite acid leach</td>
<td>3.7</td>
<td>0.5</td>
</tr>
<tr>
<td>Nakhlite bulk (after leaches)</td>
<td>3.8</td>
<td>0.2</td>
</tr>
</tbody>
</table>

δ7Li is reported relative to the NIST L-SVEC standard [7].

Carbon. Our results (Fig. 1a-c) show the bulk of carbon released <400ºC, which in addition to terrestrial contamination may include some martian organics [8,9]. The δ13C excursions at ~450ºC mark the combustion of siderite [10]: with Lafayette showing δ13C = -12 ‰ at this point and the Nakhlite olivine-rich sample δ13C = +22‰. This suggests a difference of approximately 35‰, between the siderite compositions within the Nakhlite olivine (which contains siderite along veins) and Lafayette (wr) but exact differences cannot be determined without Lafayette mineral separates. However Jull et al. [11] have reported δ13C values from acid-extracts of Nakhlite of up to +50‰ that was thought to be carbonate and similarly Wright et al. [10] reported an acid extract in Lafayette of +1‰.

Acid-washed pyroxene from Nakhlite (not plotted here) contains low C yields (<6 ppm C per temperature step) indicating the removal of almost all terrestrial and martian C-bearing phases.

Pyrolysis. CO2 is released from both meteorites between 175-600ºC. Variations in release temperature may reflect textural and chemical differences between the siderite of the 2 meteorites. Organic components will also have been pyrolysed within this range but were indistinguishable with the sample sizes available.

Discussion: Lafayette siderite has 22-27 mol% CaCO3 whereas Nakhlite is 0.1-6 mol% [1,2]. This reflects the passage of a brine through fractures in the nakhlite parent rocks, with Lafayette near the heat and fluid source and Nakhlite closer to the surface with final
evaporation products (e.g. less Ca-rich siderite and more soluble salts) of the brine. This relationship between the 2 meteorites provides the context for interpreting the Li-and C-isotopic fractionations.

In a low-T, rapidly precipitated system such as found in the nakhlite secondary assemblage we assume that it can be considered a closed system for Li because it is unlikely that multiple crustal sources could easily exchange with the fluid. Variation in the Li-isotope ratios of different components thus reflect Rayleigh fractionation. Taking Nakhla pyroxene as the starting crustal composition and a range of likely isotopic fractionation factors for Li:

$$\alpha_{\text{mineral-fluid}} = 0.997-0.990$$ [12]

With 90% brine evaporation (f=0.1), minerals with $\delta^{7}\text{Li}$ of +11 to +27 ‰ would be precipitated across the range of likely $\alpha$ values. For f=0.5, $\delta^{7}\text{Li} = +6$ to +11 ‰. The f=0.1 values are consistent with the Nakhla water-leach composition and the presence of late-stage, water-soluble crystallisation products from the evaporating brine that are present in Nakhla but not found in Lafayette [1].

Although the mineral compositions and Li-isotopes may be modelled as the result of Rayleigh fractionation associated with progressive evaporation such a mechanism is inconsistent with an increase in $\delta^{13}\text{C}$ values from Lafayette to Nakhla [13]. This difference might simply reflect a drop in brine T from Lafayette to Nakhla (e.g. 150 to 25°C) within a system open to CO$_2$ exchange between atmosphere and brine. Carbonate compositions in equilibrium with an atmosphere of $\delta^{13}\text{C} = +35$‰ [14] would be +37‰ at 150°C and +45 ‰ at 25°C [15]. Clearly this does not explain the magnitude of the actual $\delta^{13}\text{C}$ isotopic differences between the meteorites and the apparent lack of such $^{13}$C-rich siderite in Lafayette. We have assumed that the source of the carbon is predominantly atmospheric, either through direct exchange of CO$_2$(g) with the brine or through dissolution of pre-existing evaporitic deposits. However in order to explain the presumed light C-isotopic compositions of the Lafayette siderite it may be necessary to invoke the incorporation and mixing of other less $^{13}$C-rich material. One possible source could be organics carried in the fluid although we have not been able to characterize it isotopically or by pyrolysis.

Conclusions: Mineral compositions and Li-isotopic values are consistent with the progressive fractionation of a brine from Lafayette to Nakhla. Lafayette was nearest the fluid and heat source, which may have been impact, associated with fracturing in the nakhlites. C-isotopic compositions were partially influenced by falling T in an open CO$_2$ ($^{13}$C-rich atmosphere)-H$_2$O system but the relatively $^{13}$C-poor siderite in Lafayette suggests more than one carbon source was sampled.


Fig. 1. Stepped Combustion Carbon Analyses.