

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. 25-150°C) 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 Nakhla and Lafayette samples.

Techniques: Whole rock samples of Nakhla (BM 1911, 369) and Lafayette (BM 1959, 755) were powdered using an agate mortar and pestle. We also used Nakhla pyroxene separates (>95% pure) and olivine-enriched samples of lower purity.

Samples for Li-isotope analysis were dissolved in HF/HNO₃, and passed through a cation exchange column to separate Li [3]. Li-isotope ratios were measured using a Nu instruments multicollector ICP-MS [4]. A sub-sample of Nakhla was subjected to sequential leaching procedure: the sample was ultrasonicated in water to dissolve soluble salts, and the residue was then leached with weak (1N) acetic acid. The residue from this procedure was dissolved in HF/HNO₃. Li isotope ratios are reported as $\delta^7\text{Li}$, where

$$\delta^7\text{Li} \text{‰} = \left\{ \left[\frac{(^7\text{Li}/^6\text{Li})_{\text{SAMPLE}}}{(^7\text{Li}/^6\text{Li})_{\text{STANDARD}}} \right] - 1 \right\} * 1000.$$

Carbon yield and isotopes of whole samples of Nakhla (7.85 mg) and Lafayette (6.63 mg) were analysed by stepped-combustion mass spectrometry [5]. Samples were heated to 1300°C in 100°C steps from 0-500°C and 1000-1300°C. Heating between 500-1000°C was in 50°C steps. The same procedure was applied to Nakhla olivine-rich (10.44 mg) and pyroxene (10.55 mg) samples. Lafayette was heated in 50°C steps from 300-500°C and 25°C steps from 500-700°C. In order to remove traces of carbonates in the pyroxene sample an aliquot (9.53 mg), was washed in 0.1M HCl prior to combustion.

Powders of both meteorites were pyrolysed using a combined thermogravimetric and evolved gas analysis system in a He carrier gas from 20-1000°C, with CO₂ release monitored.

Results: *Li-Isotopes.* Table 1. shows our results which include the first bulk $\delta^7\text{Li}$ values for martian meteorites. The $\delta^7\text{Li}$ value for bulk Nakhla is within error of that for bulk Lafayette, and similar to those of terrestrial ultramafic rocks [6]. The Nakhla water-leach (+14.2 ‰) reflects the $\delta^7\text{Li}$ of soluble salts known to be in this meteorite. However, the Nakhla acid-leach has a similar composition to the igneous

phases implying that the siderite does not contain fractionated Li-isotopes. The detectable fractionation between Nakhla pyroxene and olivine-rich samples (0.5‰) suggests that the olivine contains a ⁷Li-rich alteration phase, which may be the nontronite-like clay present in cracks e.g. [1] or intramineral fractionation [6].

Table 1. Li-isotopes in Nakhlite Samples

	$\delta^7\text{Li}$ ‰	1 σ error
Nakhla bulk	4.5	0.2
Nakhla px	3.7	0.3
Nakhla ol-rich	5.1	0.3
Lafayette bulk	4.1	0.3
Nakhla water leach	14.2	0.5
Nakhla acid leach	3.7	0.5
Nakhla bulk (after leaches)	3.8	0.2

$\delta^7\text{Li}$ is reported relative to the NIST L-SVEC standard [7].

Carbon. Our results (Fig. 1a-c) show the bulk of carbon released <400°C, which in addition to terrestrial contamination may include some martian organics [8,9]. The $\delta^{13}\text{C}$ excursions at ~450°C mark the combustion of siderite [10]: with Lafayette wr showing $\delta^{13}\text{C} = -12$ ‰ at this point and the Nakhla olivine-rich sample $\delta^{13}\text{C} = +22$ ‰. This suggests a difference of approximately 35‰, between the siderite compositions within the Nakhla 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 $\delta^{13}\text{C}$ values from acid-extracts of Nakhla 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 Nakhla (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 175-600°C. 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 Nakhla 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 Nakhla 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:

$$\alpha (\text{mineral-fluid}) = 0.997-0.990 \quad [12]$$

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 α 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 $\delta^{13}\text{C} = +35\text{‰}$ [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 $\text{CO}_2(\text{g})$ 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_2O system but the relatively ^{13}C -poor siderite

in Lafayette suggests more than one carbon source was sampled.

References: [1] Bridges J. C. and Grady M. M. (2000) *EPSL*, 176, 267-279. [2] Bridges J. C. et al. (2001) *Space Science Reviews*, 96, 365-392. [3] James R. H. and Palmer M. R. (2000) *Chem. Geol.*, 166, 319-326. [4] Kisakurek B. et al. (2004) *Chem. Geol.*, 212, 27-44. [5] Wright I. P. and Pillinger C. T. (1989) *USGS Bull.*, 1890, 9-34. [6] Seitz H-M. et al. (2004) *Chem. Geol.*, 212, 163-177. [7] Flesch G. D. et al. (1973) *Int. J. Mass Spectrom. Ion Process.*, 12, 265-272. [8] Jull A. J. T. et al. (2000) *GCA*, 64, 3763-3772. [9] Sephton M. A. et al. (2004) *Astrophysical Journal*, 612, 588-591. [10] Wright I. P. et al. (1992) *GCA*, 56, 817-826. [11] Jull A. J. T. et al. (1995) *Meteoritics*, 30, 311-318. [12] Rudnick R. L. et al. (2004) *Chem. Geol.*, 212, 45-57. [13] Romanek C. S. et al. (1994) *Nature*, 372, 655-657. [14] Carr R. H. et al. (1985) *Nature*, 314, 248-250. [15] Chacko T. et al. (1991) *GCA*, 55, 2867-2882.

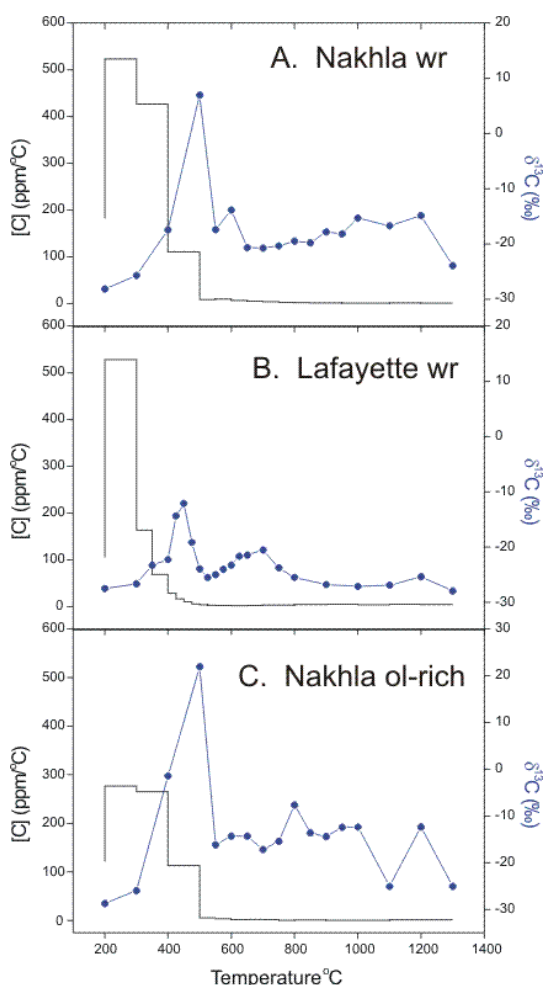


Fig. 1. Stepped Combustion Carbon Analyses.