

ALTERATION OF THE NAKHLITE LAVA PILE: WAS WATER ON THE SURFACE, SEEPING DOWN, OR AT DEPTH, PERCOLATING UP? EVIDENCE (SUCH AS IT IS) FROM CARBONATES. Monica M. Grady^{1,3}, M. Anand^{2,3}, M. A. Gilmour¹, J. S. Watson¹ and I. P. Wright¹ ¹PSSRI, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK (m.m.grady@open.ac.uk), ²Dept. of Earth Sciences, The Open University, Walton Hall, Milton Keynes MK7 6AA, UK, ³Dept. of Mineralogy, The Natural History Museum, London, SW7 5BD, UK.

Introduction: the petrogenesis of the nakhlites is thought to be as a lava flow, or series of flows extruded onto the surface of Mars some 1300 million years ago [1]. The close similarities in mineralogy and mineral chemistry amongst the nakhlites imply that they all come from the same magma body, whilst petrographic variations suggest that they are derived from different depths within a cumulate pile. The extent of equilibration within individual ferromagnesian silicate grains has been recognised as a marker for crystallization depth [2, 3], and on that basis, since MIL 03346 contains the least equilibrated of all silicates, it is assumed to derive from the outermost edge of the intrusion, perhaps even a chill margin [4]. Alteration by fluids on the surface of Mars has also affected the nakhlites. There are at least two populations of martian weathering products: (1) clay minerals formed *in situ* within olivines, by the alteration and hydration of silicates and (2) precipitation of carbonates and sulphates within cracks. Weathering has affected the nakhlites to different extents, leading to the suggestion that formation of secondary minerals indicates progressive deposition from an evaporating brine [5]. This conclusion was based on examination of Nakhla, Governador Valadares and Lafayette; since it was undertaken, the number of nakhlites has more than doubled. We have examined two Antarctic nakhlites (MIL 03346 and Y 000593) and a Saharan nakhlite (NWA 998) to see if they too exhibit the effects of martian weathering, and if so, whether they can be fitted into the sequence defined by [5]. The first phase of the work was to investigate carbonates within the nakhlites, as their carbon isotopic composition is diagnostic of the martian (rather than terrestrial) origin of the weathering [6, 7].

Method: Analysis of carbonates in martian meteorites is not easy: with the exception of ALH 84001, the carbonates are small, and generally mixed with clay minerals in cracks within primary silicates. Because it is difficult to analyse carbonates *in situ*, the favoured technique is to dissolve whole rock meteorite in 100% H₃PO₄, following the method employed for terrestrial carbonates. There has been a reasonable degree of success in determining the abundance and isotopic composition of carbonates in martian meteorites [e.g., 7], ever since the first measurement demonstrated that they were enriched in ¹³C, and thus presumably produced from solution of mar-

tian atmospheric CO₂ in surface water [6]. However, because copious sulphur-bearing species are also generated by the acid dissolution procedure, there are often problems associated with producing pure CO₂ for isotopic analysis. We report here data acquired following a new gas clean-up procedure, one that passes the product gases through a gas chromatograph (Thermo TraceGC Ultra, at a column flow rate of 2.5ml/min through a 30m x 0.32mm J&W GS-Q Plot column) to separate CO₂ from other species, prior to isotope analysis in a Thermo 253 mass spectrometer. The minimum amount of carbon dioxide that could be analysed was about 20 nmole; at this level, errors on the isotopic measurements were around ±2‰.

Results: are given in the table, and plotted in Figure 1. In agreement with previous studies, the carbonates are ¹³C-enriched. However, because the acid reaction was carried out in a single stage at 72°C, we cannot identify the mineralogical composition of the carbonate. Petrographic work, though, has indicated that the carbonates are predominantly sideritic. Results for NWA 998 are omitted – this sample contained abundant calcite, with a carbon isotopic composition characteristic of terrestrial weathering, thus any martian carbonates were impossible to distinguish. There are almost two orders of magnitude difference in carbonate abundance within the five samples, from MIL 03346 (the least) to Y 000593 (most). Carbonates in MIL 03346 also have the least ¹³C-enriched isotopic composition, implying that some of the carbonates might have a terrestrial origin. This is confirmed by their oxygen isotopic composition, which is much lower than carbonates in the other nakhlites.

Sample	Depth ¹	Yield ²	δ ¹³ C (‰)	δ ¹⁸ O (‰)
MIL 03346	1	1	+10.3	+18.7
Y 000593	2	60	+42.0	+26.6
Nakhla	3	27	+51.5	+33.6
GV	4	26	+24.6	+31.3
Lafayette	5	17	+24.8	+29.1

¹On the basis of annealing or equilibration of olivine composition [2, 3], and assigned a relative value, where 1 is the fastest cooling rate (most shallow crystallization depth). The depth scale is not linear. ²These are NOT yields for absolute carbonate abundances in ppm, but are values normalized to the amount of carbonate measured in MIL 03346.

Discussion: The plot in Figure 1 indicates a loose correlation between increasing carbonate abundance and carbon isotopic composition ($r = 0.7$; $n=5$). In a terrestrial environment, as a pool of brine evaporates, the $\delta^{13}\text{C}$ value of the remaining bicarbonate solution gradually increases, as isotopically lighter carbon escapes. Carbonate precipitated in equilibrium with this fluid will therefore also gradually increase in $\delta^{13}\text{C}$ value. The data plotted in Figure 1 indicate that the same fractionation process occurs on Mars, albeit at the enhanced level of ^{13}C -enrichment characteristic of the martian atmosphere.

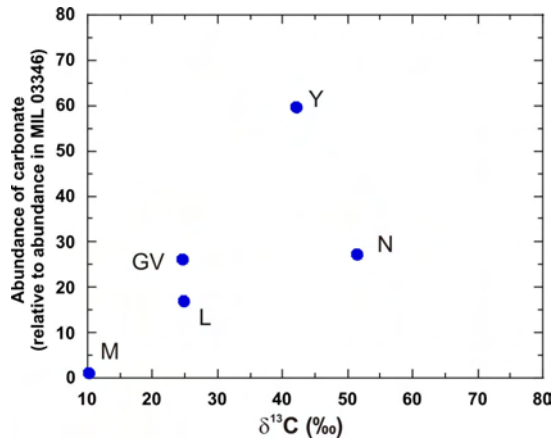


Figure 1: variation of the carbon isotopic composition of martian carbonates with abundance.

Plotted in Figure 2 is the variation in both relative carbonate yield and $\delta^{13}\text{C}$ value with crystallization depth (taken from olivine composition; ref 2, 3). If the carbonates were produced at different depths within a single magma flow, one might anticipate some relationship between the amount of carbonate produced and the extent of aqueous penetration, with samples close to the surface experiencing a greater alteration. It is clear that there is not a monotonic decrease in carbonate yield with crystallization depth. MIL 03346 stands out as being different from the other nakhlites. It contains almost no carbonate, and that which is present has a $\delta^{13}\text{C}$ value much lower than in the other nakhlites. It is altered by fluids, because the olivines (large in size but low in abundance) are broken by clay-filled veinlets.

Figure 3 is a cartoon to illustrate a potential fluid alteration scenario for the nakhlites, assuming they derive from a single magma flow. The low carbonate abundance in MIL 03346 might be because it has not been exposed at the surface of Mars, but is from the chill margin at the bottom of the intrusion, not the top. It has been suggested [8] that there are two populations of carbonates in martian meteorites, with an isotopically-light carbonate (present in Chassigny,

with $\delta^{13}\text{C}$ around -4‰) produced from groundwaters that have not been in extensive contact with the surface, and thus the martian atmosphere. The carbonates in MIL 03346 might be a mixture of the two populations. Alternatively, MIL 03346 might be from the upper chill margin of a separate magma flow. The carbon (and oxygen) isotopic composition of the carbonates might then be a more true reflection of the Antarctic residence of the meteorite than its martian heritage.

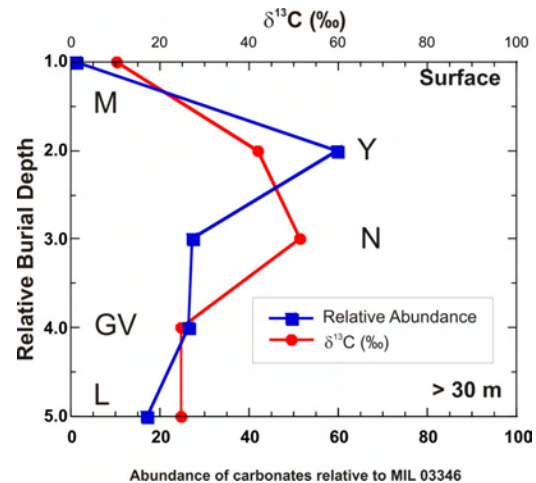


Figure 2: variation of carbonate abundance and carbon isotopic composition with depth in nakhlites.

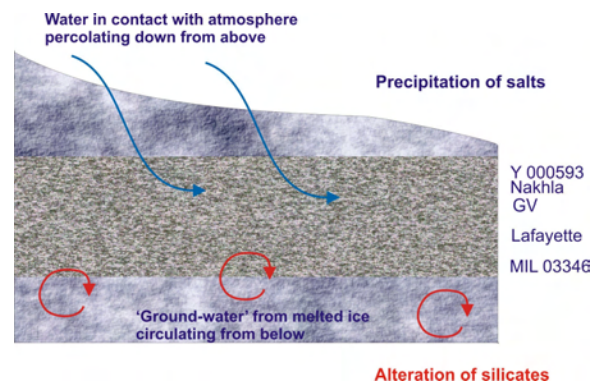


Figure 3: Alteration of the nakhlite flow. MIL 03346 is depicted as being from the basal chill margin of the flow, in defiance of other authors [2,3].

References: [1] Lentz R. et al. (1999) *Meteoritics & Planet. Sci.*, 34, 919-932. [2] Harvey R. P. and McSween H. Y. Jr. (1992) *Earth Planet. Sci. Lett.*, 111, 467-482. [3] Mikouchi T. et al. (2003) *Ant. Met. Res.*, 16, 34-57. [4] Day J. M. D. et al. (2006) *Meteoritics & Planet. Sci.*, 41, 581-608. [5] Bridges J. C. and Grady M. M. (2000) *Earth Planet. Sci. Lett.*, 176, 267-279. [6] Carr R. H. et al. (1985) *Nature*, 314, 248-250. [7] Jull et al. (1995) *Meteoritics*, 30, 311-318. [8] Wright I. P. et al. (1992) *GCA*, 56, 817-826.