

CARBON RESERVOIRS ON MARS: CONSTRAINTS FROM MARTIAN METEORITES. Monica M. Grady¹ and I. P. Wright², ¹Dept. of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD, U.K. (mmg@nhm.ac.uk), ²PSSRI, The Open University, Walton Hall, Milton Keynes, MK7 6AA, U.K. (i.p.wright@open.ac.uk).

Introduction: The search for life on Mars is a subject of enormous scientific and public interest; it is anticipated that remote missions to Mars over the coming few years will garner the requisite data that will allow the presence, or otherwise, of martian biological carbon to be determined. The only previous attempt to detect the presence of life in martian soil, made by instruments on the *Viking* landers of 1976, yielded ambiguous results [1]. In the three decades since *Viking*, analysis of carbon in martian meteorites has given insight to the complexities of carbon in martian rocks: it is clear that carbon from several reservoirs (mantle, crust, atmosphere) is present. Unless we have a full understanding of these reservoirs, their relative abundances and isotopic compositions, then interpretation of data acquired directly at Mars' surface will be difficult to interpret.

Carbon in martian rocks: There are several contributions to the carbon budget in martian meteorites (not including potential martian biological material): primary indigenous carbon dissolved in minerals (silicates, phosphates); secondary carbonates produced by surficial aqueous activity; atmospheric CO₂ trapped during ejection from the martian surface; spallogenic carbon produced during irradiation in space and organic contamination following arrival on Earth. It is assumed that the first two of these components will be present in martian rocks analysed *in situ*; it remains to be seen whether there is an additional reservoir emanating from a martian biosphere.

Many measurements have been made of the abundance and stable isotopic compositions of secondary carbonates in martian meteorites, particularly in ALH 84001 and Nakhla, the two specimens in which they can most readily be identified. Broadly speaking, several tens to hundreds of ppm ¹³C-enriched carbonate ($\delta^{13}\text{C}$ up to around +60‰) occur in ALH 84001 and the nakhlites [2]. Carbon dioxide in Mars' atmosphere is also ¹³C-enriched, although its actual $\delta^{13}\text{C}$ value is poorly-defined: measurements of the upper atmosphere made by *Viking* have large errors ($\delta^{13}\text{C} \sim 0 \pm 50\%$; ref. 3), and data from martian meteorites only gives a lower limit ($\delta^{13}\text{C} > 30\%$; ref. 4). The occurrence of ¹³C-enriched carbon in the atmosphere and in secondary carbonates led to the interpretation that the carbonates were produced by low temperature aqueous processes on Mars' surface, by dissolution of atmospheric CO₂ in

percolating fluids [4, 5]. Thus a link between two reservoirs, crustal and atmospheric, has been established. In contrast, identification of magmatic (mantle) carbon in martian meteorites is even less well-constrained than that of crustal or atmospheric carbon. This is because planetary igneous rocks contain only low levels of primary magmatic carbon. Attempts to measure magmatic carbon in martian meteorites by combustion are hampered because the temperature at which it is thought to combust is between that at which carbonate decomposes and that at which trapped atmospheric CO₂ is released.

Method: It is against this backdrop that we have continued our programme of analysis of carbon in martian meteorites by high resolution stepped combustion-mass spectrometry (HR-SC-MS). We are aiming to produce an internally consistent and complete suite of data from as many individual martian meteorites as possible, spanning the complete range of compositions and crystallization histories. Sample preparation involves washing whole-rock powders in HCl; this not only removes carbonates (both martian and from terrestrial weathering), but etches the silicates and reduces contributions from spallogenic carbon and trapped atmospheric CO₂. The washed grains are then analysed by HR-SC-MS, using the recently refurbished MS-86 static vacuum system at the Open University. Typical blanks run on the system are less than 10 ng carbon, with $\delta^{13}\text{C}$ around -20‰.

Results and Discussion: We have started the programme with analyses of meteorites from the most numerous sub-group of martian samples, the shergottites. The past five years have seen a tripling of the number of martian meteorites recognized on Earth; by far the most rapid increase in numbers has been in the basaltic sub-group of shergottites. As of 31st December 2002, there were 14 individual shergottites, 10 of which are classified as basaltic. The increasing number of shergottites has also increased the number of ejection events from Mars' surface; dating of the shergottites indicates that lava flows with a range of crystallization ages (approx. 165 - 475 Myr) are being sampled [6]. As well as constraining the isotopic composition of carbon reservoirs on Mars, a goal of the current research is to look at the abundance and isotopic composition of magmatic volatiles in martian rocks, in order

to obtain a picture of whether Mars' volatile inventory has evolved over the past 500 million years or so.

Preliminary carbon isotope results from six shergottites are given in Figure 1. Abundance data are not plotted, but are approx. 10-20 ppm. The isotope data are more tightly constrained than previous reports for magmatic carbon in martian meteorites [7]. Even so, the primary carbon reservoir on Mars still appears to be isotopically light, and similar to basalts from the Moon and the HED parent-body. It is the Earth that seems to be the outlier. This distinction between Earth and Mars reinforces the idea that martian rocks retain the signature of primordial carbon, whilst terrestrial mantle rocks have been contaminated through many millennia of crustal recycling.

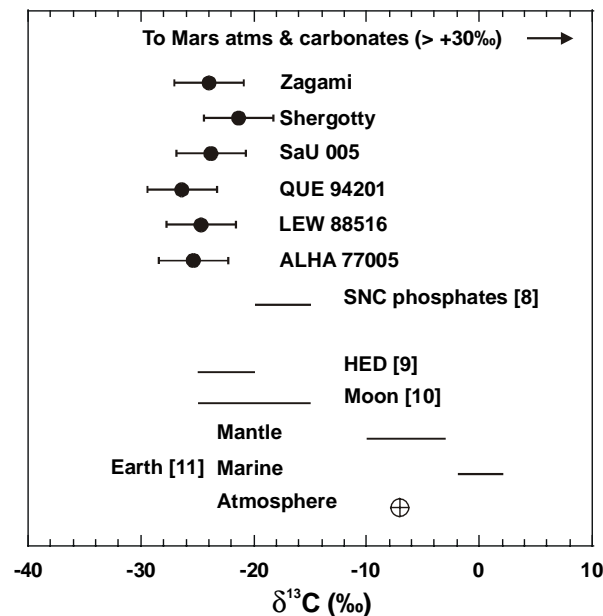


Fig. 1. The isotopic composition of carbon in various Solar System reservoirs. Martian meteorite data are for acid-washed whole-rock powders, determined by HR-SC-MS; error bars are $\pm 1\sigma$. References for the other ranges are given below.

The same carbon isotope data are plotted against crystallisation age (where known) in Figure 2. There is potentially a relationship of decreasing $\delta^{13}\text{C}$ with increasing age, but it is not well-defined, and we do not, as yet, attach any significance to it. However, additional analyses of older rocks might serve to define the relationship if magmatic degassing was a significant process during Mars' history. On the limited dataset currently available, there does not appear to be any difference in carbon isotopic composition (or carbon abundance) between the basaltic and lherzolitic shergottites, perhaps indicating the homogeneity of the

martian mantle, despite the lack on convective tectonics.

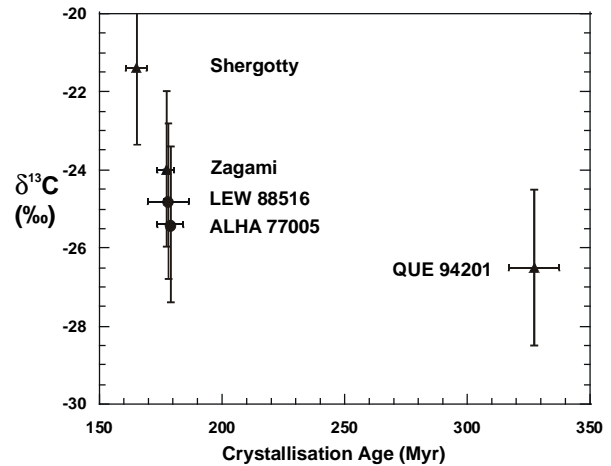


Fig. 2. Relationship between crystallisation age (from ref. 6) and the isotopic composition of magmatic carbon in shergottites. Symbols: triangle, basalt; circle, lherzolite.

Summary: primordial carbon in basalts that crystallised in the latest epoch of Mars' history are more ^{12}C -enriched than their terrestrial counterparts. This is rather unfortunate from an experimental viewpoint, as it places the data firmly in the range exhibited by terrestrial organisms. We are satisfied that our experimental technique is capable of distinguishing between residual terrestrial contamination and martian magmatic carbon. However, if martian organisms have a similar carbon isotopic composition to their terrestrial relatives, then without a complete understanding of the interrelationships between different carbon reservoirs on Mars, interpretation of data acquired at Mars' surface might be problematic.

References: [1] Klein H. P et al. (1976) *Science*, 194, 99-105. [2] Jull A. J. T. et al. (1995) *Meteoritics*, 30, 311-318. [3] Nier A. O. et al. (1976) *Science*, 194, 68-70. [4] Carr R. H. et al. (1985) *Nature*, 314, 248-250. [5] Romanek C. S. et al. (1994) *Nature*, 372, 655-657. [6] Nyquist L. E. et al. (2001) *Sp. Sci. Rev.*, 96, 105-164. [7] Grady M. M. et al. (1997) *JGR*, E102, 9165-9173. [8] Goreva J. et al. (2002) *LPS XXXIII*, Abstract #2014. [9] Grady M. M. et al. (1997) *MAPS*, 32, 863-868. [10] Des Marais D. J. (1983) *GCA*, 47, 1769-1781. [11] Hoefs J. (1987) *Stable Isotope Geochemistry*, Springer 3rd Ed.