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Magmatic carbon in Martian meteorites: attempts to constrain the carbon cycle on Mars

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Abstract: One of the current goals of Martian exploration is to find evidence for extinct (or even extant) life. Carbon (an essential ingredient of life on Earth) is known to occur on Mars as CO_2 in the atmosphere and frozen in the polar caps; it is inferred to be present as carbonates in the Martian crust and soils. We are attempting to define and quantify the different carbon reservoirs on Mars, so that we can follow Mars' carbon cycle. This paper discusses a primordial magmatic component that could be the starting point of such a cycle. The nature, distribution and isotopic composition of carbon was measured in a suite of Martian meteorites, comprising Chassigny and 11 shergottites. Other Martian meteorites were not included, as they sample rocks that have been altered by fluids at Mars' surface. Our results, obtained by high-resolution stepped combustion and mass spectrometry, show that the magmatic component has a very variable abundance of 1–100 ppm, with $\delta^{13}C \sim -20 \pm 4\,‰$. This value is close to magmatic carbon determined for Moon and for Vesta (the parent body of the HED basaltic meteorites), but very different from that of Earth.

Introduction

The search for life on Mars is a subject of enormous scientific and public interest, and has received a great deal of publicity following the success of recent missions (Mars Odyssey, Mars Express, Spirit, Opportunity, etc.), and also the disappointment of others (Mars 96, Polar Lander, Nozomi, Beagle 2). All but one of the latest series of missions based their search for life on a search for water, or water-lain salts, in Mars' surface rocks, since water is assumed to be a necessity for life (e.g., Brack 2002). However, water is merely the solvent that facilitates biological processes; a more pertinent parameter may be the elemental signature of the potential biotic processes themselves. If we believe that extraterrestrial life has arisen by similar mechanisms from similar starting materials to life on Earth, then documenting the occurrence of carbon might be a useful way to investigate whether or not Mars once supported life. Unfortunately, however, the presence of carbon or carbon-bearing components is not, by itself, sufficient to indicate living organisms – all carbonaceous materials can have an abiological as well as a biological origin.

We know from the geological record on Earth that carbon from ancient biospheres is often not preserved: biological entities can be lost through dehydration and diagenesis. Even when organisms are preserved, as fossils, the original carbon is often replaced by, for example, silica. For carbon to indicate life, its presence has to be taken within the context of all carbonaceous components, their speciation (organic, carbonate, etc.), molecular chirality and isotopic composition. One of the main objectives of the Beagle 2 probe was to search for signs of extinct (or even extant) life on Mars by determining the abundance and isotopic composition of carbon in rocks and soil on Mars' surface, as well as in the atmosphere (Wright *et al*. 2000). This would have been the first direct measurement of carbon isotopic composition in Martian rocks: the only other attempt to detect carbon in Martian soil was made by instruments on the Viking landers of 1976. The Viking mass spectrometers measured carbon, but not its isotopic composition, and the results were ambiguous in terms of evidence for life (Klein 1978).

In the three decades since Viking, we have learnt a great deal more about Martian soil and surface–atmosphere interactions, partly through data from orbiters and landers, but mainly through the study of Martian meteorites (which had not been recognized at the time of the Viking mission). Analysis of carbon in Martian meteorites has given insight into 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. The aim of this study was to measure the abundance and isotopic composition of magmatic carbon present in a suite of Martian meteorites. This parameter is a proxy for the juvenile carbon reservoir on Mars; eventually, when coupled with measurements on carbonates and trapped gases in Martian meteorites, its determination will allow us to build up a carbon cycle for Mars. Any such a cycle could have analogies to that in operation on Earth, and we will be able to model the extent of potential biogenic input or influence.

There is still a secular carbon cycle operating on Mars – the seasonal effects of polar cap warming transfers CO_2 to the atmosphere, which then condenses in colder regions. This is, at best, a very abbreviated 'carbon cycle'. Herein, we are concerned with a more complete picture of the carbon cycle which includes processes operating over geological time and over regional scales; in principle, we wish to understand how the distribution of carbon today is related to the original partitioning of the element at the time that Mars was first formed. To a first approximation, following planet formation, carbon may have been degassed from the interior of the body into the atmosphere and surface layers. Long-term atmospheric processes may then have acted to change the surface environment in a rather monotonic way. A previous (or even extant) biosphere may have acted upon the surficial carbon reservoirs, early plate tectonics may have caused large-scale recycling of materials, cryospheric processes may facilitate relatively deeper trapping of volatiles that were formerly in evidence at the very surface, the processes of volcanism may continue to add primitive magmatic gases to the surface environment even today, and so on. It is against this backdrop that we have determined magmatic carbon in a suite of Martian rocks, as an attempt to define more thoroughly the primordial platform onto which a carbon cycle has been superimposed.

Meteorites from Mars

It is now two decades since meteorites from Mars were first recognized on the basis of their young crystallization ages (Wasson & Wetherill 1979; Wood & Ashwal 1982) and the gases trapped within them (Bogard & Johnson 1983). Originally, there were only six specimens and the group was known as the SNCs, on the basis of sub-division into three types (shergottites, nakhlites and Chassigny). As of 30th June 2004, there were 53 numbered meteorites, representing 30 separate individuals. The most up-to-date listing of Martian meteorites is maintained at http://www2.jpl.nasa.gov/snc/; the most comprehensive bibliography is the Mars Meteorite Compendium at http://wwwcurator.jsc.nasa.gov/curator/antmet/mmc/mmc.htm. As the number of Martian meteorites increases, so has their sub-classification into separate types become more specific. All of the Martian meteorites are igneous rocks; in terms of terrestrial nomenclature, they would be designated as dunite (Chassigny), orthopyroxenite (ALH 84001), basalt, lherzolite and picrite (shergottites) and clinopyroxenite (nakhlites). Each type has a different petrogenetic history. The most numerous of the 30 separate Martian meteorites are shergottites, 22 in total, eight of which are classified as basaltic, six lherzolitic and eight olivine-phyric. Dating of the shergottites indicates that lava flows with a range of crystallization ages (approximately 540–165 Myr, or between Cambrian and Jurassic, using designations from the terrestrial geological record) are being sampled (Nyquist *et al.* 2001). Chassigny and nakhlites, at around 1300 Myr old, would be regarded as Precambrian, whilst the oldest of all, ALH 84001, is older than any samples on Earth and with an age of 4500 Myr would have belonged to the Hadean era. With the increasing numbers of Martian meteorites that have been discovered has come the increasing realization that the number of ejection events from Mars' surface has become more commonplace. Cosmic-ray exposure ages have suggested that at least six ejection events must be responsible for the meteorites (Nyquist *et al.* 2001; Eugster *et al.* 2002).

Carbon in Martian rocks

There are several contributions to the carbon budget in Martian meteorites: primary indigenous carbon dissolved in minerals (silicates, phosphates); secondary carbonates produced by surficial aqueous activity; atmospheric CO_2 trapped during ejection from the Martian surface; spallogenic carbon produced during irradiation in space and organic contamination following arrival on Earth. It remains to be seen whether there is an additional reservoir emanating from a Martian biosphere, although evidence for Martian organics materials has been presented previously (e.g., Wright *et al.* 1989).

Many measurements have been made of the abundance and stable isotopic compositions of secondary and tertiary carbon components in Martian meteorites. Carbonates are relatively abundant in ALH 84001 and nakhlites: several tens to hundreds of ppm ^{13}C-enriched carbonate (δ^{13}C up to around $+60$‰; Wright *et al.* 1992; Jull *et al.* 1995). Carbon dioxide in Mars' atmosphere is also ^{13}C-enriched, although its actual δ^{13}C value is poorly defined: measurements of the upper atmosphere made by Viking have large errors (δ^{13}C $\sim 0 \pm 50$‰; Nier *et al.* (1976)), and data from Martian meteorites only give a lower limit (δ^{13}C > 30‰; Carr *et al.* (1985)). The occurrence of ^{13}C-enriched carbon in the atmosphere and in secondary carbonates led to the interpretation that low-temperature aqueous processes on Mars' surface produced the carbonates, by dissolution of atmospheric CO_2 in percolating fluids (Carr *et al.* 1985; Romanek *et al.* 1994). Thus a link between two reservoirs, crustal and atmospheric, has been established. It is, therefore, clear that nakhlites and ALH 84001 have been altered by Martian water – they contain abundant carbonates and other salts (e.g., Bridges & Grady 2000), as well as demonstrating incipient degeneration of primary silicates into clay minerals. In contrast, identification of magmatic (mantle) carbon in Martian meteorites is 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 CO_2 is released. Because we wished to concentrate our study on primary magmatic phases and not secondary aqueous alteration, we selected only the dunite Chassigny and a range of shergottites, omitting the carbonate-bearing nakhlites and ALH 84001.

The goal of the current research is to look at the abundance and isotopic composition of magmatic carbon in Martian rocks, in order to obtain a picture of whether Mars' volatile inventory has evolved over the past 500 million years or so. Results from this work also form part of a broader initiative, to investigate the carbon cycles of Mars and to compare these with what is known on Earth, whereby carbon is transferred from the atmosphere into the hydrosphere and lithosphere then back into the atmosphere through tectonic cycling. We hope to determine and measure effects resulting from the two major differences between Earth's cycle and that of Mars (lack of plate tectonics and a greatly reduced (if not absent or extinct) biosphere).

Experimental methods

The analytical technique employed was that of high-resolution, stepped-combustion, mass spectrometry (HR-SC-MS), undertaken using the Open University's refurbished MS86 static vacuum system (Yates *et al.* 1992). Stepped combustion is a unique way of separating different carbonaceous or carbon-bearing components from each other on the basis of thermal stability under oxygen. Since the first application of stepped combustion to extraterrestrial materials (Swart *et al.* 1983), we have been instrumental in developing the technique and can now recognize the temperature ranges characteristic of the combustion of different materials (e.g., Grady *et al.* 2002). Thus volatile compounds (such as simple organic species or adsorbed gases) combust or are released at low temperatures, generally less than $\sim 300\,°C$. Slightly more refractory organic species (complex molecules, amorphous carbon) combust up to $\sim 500\,°C$. Carbonates decrepitate between $400\,°C$ and $700\,°C$ (depending on major element chemistry), whilst well-crystallized graphite is oxidized at $700–800\,°C$. Magmatic carbon (i.e. carbon coating or occluded within primary silicates, or trapped in vescicles) is exposed for oxidation when the silicates start to soften, at $\sim 800–950\,°C$. At the highest temperatures of all, when silicate lattices break down, spallogenic carbon (i.e. that produced from other elements, such as oxygen in silicates, by cosmic irradiation during exposure in space) starts to combust. These temperature ranges are indicative, since interpretation of stepped-combustion data is based not just on combustion temperature, as that can be related to grain size, sample size and oxygen pressure. By coupling combustion temperature with carbon isotopic composition, it is possible to model end-member abundances and isotopic compositions

for several components. We are aiming to produce an internally consistent suite of data from as many individual shergottites as possible, spanning the complete range of compositions and crystallization histories.

Sample preparation involved washing whole-rock powders in HCl to remove carbonates (both Martian and from terrestrial weathering). The acid wash and rinsing also reduced the level of terrestrial organic contaminants, along with any indigenous soluble Martian organics. Small chips (~ 100 mg) of each meteorite were crushed to a coarse powder and then suspended in 0.1 M HCl at room temperature for 24 hours; the samples were subject to intermittent gentle agitation. After decanting the acid, the powders were rinsed until neutral with high-purity water and then dried at $70\,°C$ overnight. Weight losses on acid dissolution were variable, between 1 and 50%; samples suffering the highest weight losses were the weathered desert meteorites, which are highly fractured and contain visible alteration veins that include carbonates.

Following the HCl wash, grains (~ 20 mg) were wrapped in degassed high-purity platinum foil for analysis by HR-SC-MS. After introduction into the extraction system, each sample was heated in incremental steps from room temperature to $1400\,°C$. An individual heating step lasted for the same fixed time and took place in the presence of excess oxygen gas derived from the equilibrium decomposition of copper (II) oxide. A hot platinum catalyst within the combustion vessel ensured that volatile species were fully combusted to CO_2, even at the lowest temperature steps of the experiment. By-products of combustion (N_2, SO_2, H_2O, etc.) were separated from the CO_2 by a series of cold traps and fingers, following which the CO_2 was quantified and isotopic composition determined. Carbon abundance was measured by two methods: using a capacitance manometer within a known volume, and also from calibration of the MS86 ion beam current, to ± 0.2 ng. Carbon isotopic compositions were determined ($\delta^{13}C$ to ± 0.5‰) relative to a laboratory CO_2 standard gas calibrated against NBS standard materials; results are quoted in parts per thousand (per mil; ‰) relative to the international Pee Dee formation belemnite (PDB) standard. Typical blanks were 5–10 ng carbon, with $\delta^{13}C$ around -20‰.

Results

A summary of the results obtained from HR-SC in the temperature range $600–1000\,°C$ for 11 shergottites and Chassigny is given in Table 1 and Fig. 1; henceforth, we refer to these results as representing magmatic carbon. All abundance data are corrected for weight loss and given relative to whole rock. Data were also corrected for system blank.

There have been many studies of magmatic carbon in terrestrial rocks (e.g., DesMarais & Moore 1984; Mattey *et al.* 1984, 1989; Mathez 1987; Des Marais 2001); stepped combustion analysis techniques indicate that this component is released from terrestrial rocks between 600 and $1000\,°C$. Accordingly, this is the temperature range across which

Table 1. *Magmatic carbon in shergottites and Chassigny.*
Abundance and isotopic data for carbon released between
600 °C (below which organic contamination is prevalent) and
1000 °C (above which trapped atmospheric CO_2 is released)

Sample	Type	HCl wash	[C] (ppm)	$\delta^{13}C$ (‰)	Age[1] (Myr)
Los Angeles	BS	Y	6.5	−24.3	170
QUE 94201	BS	Y	1.3	−23.1	327
Shergotty	BS	N	4.3	−19.4	165
Zagami	BS	N	52.8	−22.7	177
DaG 476	OS	Y	6.0	−22.1	474
Dhofar 019	OS	N	109.4	−21.7	550
NWA 1183	OS	N	19.7	−14.8	185
SaU 005	OS	Y	8.2	−16.4	
ALHA 77005 (uncorrected)[2]	LS	Y	1.7	−21.4 (−10.5)[2]	179
LEW 88516	LS	Y	1.8	−20.2	178
Y 793605	LS	N	2.6	−14.9	212
Chassigny	C	N	2.1	−20.8	1340

[1] Crystallization ages are as listed by Meyer (2003) and mainly drawn from Nyquist *et al.* (2001).
[2] Data for ALHA 77005 were skewed by the release of trapped Martian atmosphere at around 800 °C (see Fig. 2(b)). They were corrected by assuming a $\delta^{13}C$ value for the atmosphere of +50‰ and an abundance similar to that found in EETA 79001 (Carr *et al.* 1985); uncorrected data are given in brackets.

we have assumed Martian magmatic carbon combusts. However, determination of this component was not straightforward: other carbon-bearing species are present and have the potential to interfere. Most carbonates decrepitate at $T < 600$ °C (Grady *et al.* 2002) and were in any case removed by the acid wash; spallogenic carbon is not released until temperatures in excess of 1200 °C, so neither of these species should interfere.

Generally, CO_2 from Mars' atmosphere trapped in glass during shock excavation does not appear until temperatures in excess of 1000 °C. However, if the component is particularly abundant, it can be released at temperatures as low as 800 °C. Since Martian CO_2 is enriched in ^{13}C (with $\delta^{13}C > +30$‰; Carr *et al.* (1985)), its presence would act to raise the apparent $\delta^{13}C$ of the magmatic component.

Figure 2 shows the full stepped-combustion release profile for two of the samples, SAU 005 and ALHA 77005. Results for the former (Fig. 2(a)) are fairly typical of most of the meteorites: the largest yield of carbon is released at temperatures below 600 °C from organics (mostly terrestrial, but possibly a small component of Martian). Above 1000 °C, $\delta^{13}C$ rises, as trapped Martian atmosphere is liberated. In contrast, ALHA 77005 (Fig. 2(b)) contains abundant trapped atmospheric gases that are liberated at 900 °C, interfering with the magmatic component. In fact, the data given here represent the highest $\delta^{13}C$ value yet obtained for a sample of Martian atmosphere (released from a meteorite), rising to +40‰ at 1200 °C. For the data given in Table 1, we have attempted to correct for the presence of atmospheric gases in ALHA 77005 by assuming a $\delta^{13}C$ value of +50‰ for the atmosphere and an abundance similar to that found
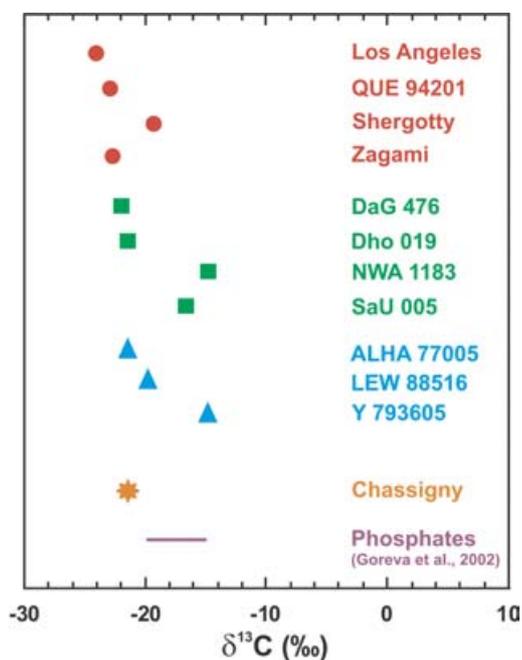

Fig. 1. Magmatic carbon in shergottites and Chassigny. Red circles, basaltic shergottites; green squares, olivine-phyric shergottites; blue triangle, lherzolite shergottites; orange star, Chassigny. Data for ALHA 77005 are corrected for trapped Martian atmosphere (see footnote to Table 1). Data for phosphates from shergottites measured by ion microprobe (Goreva *et al.* 2002) are given for comparison.

in EETA 79001 (Carr *et al.* 1985). Both corrected and uncorrected data are given in the table. Two other meteorites (Y 793605 and NWA 1183) are also outliers in Fig. 1. NWA 1183 is a heavily weathered desert meteorite; unfortunately, only whole-rock (i.e. not acid-washed) data are available for this specimen and its isotopic composition is undoubtedly affected by the presence of terrestrial carbonates. Data for Y 793605 were also affected by premature release of trapped atmosphere, but since the amounts measured are close to the background for the specimen, correction was considered unnecessary. With these provisos about carbon data, we now see that carbon abundance is very variable (Table 1), from 1–100 ppm, the same range and variability as terrestrial basalts (Des Marais 2001). At a $\delta^{13}C$ of -20 ± 4‰, isotope data are slightly better constrained than previous reports for magmatic carbon in Martian meteorites (Grady *et al.* 1997a), and encompass the range for phosphates (Goreva *et al.* 2002).

Magmatic carbon on Earth: a framework for primary Martian carbon

Carbon on Earth is partitioned into four reservoirs: atmosphere, biosphere, hydrosphere and lithosphere. Carbon in the last of these can be sub-divided into that associated with surface, crustal or mantle rocks. The abundance of carbon in mantle rocks is greater than in any of the other reservoirs and sub-reservoirs in which carbon is present on Earth
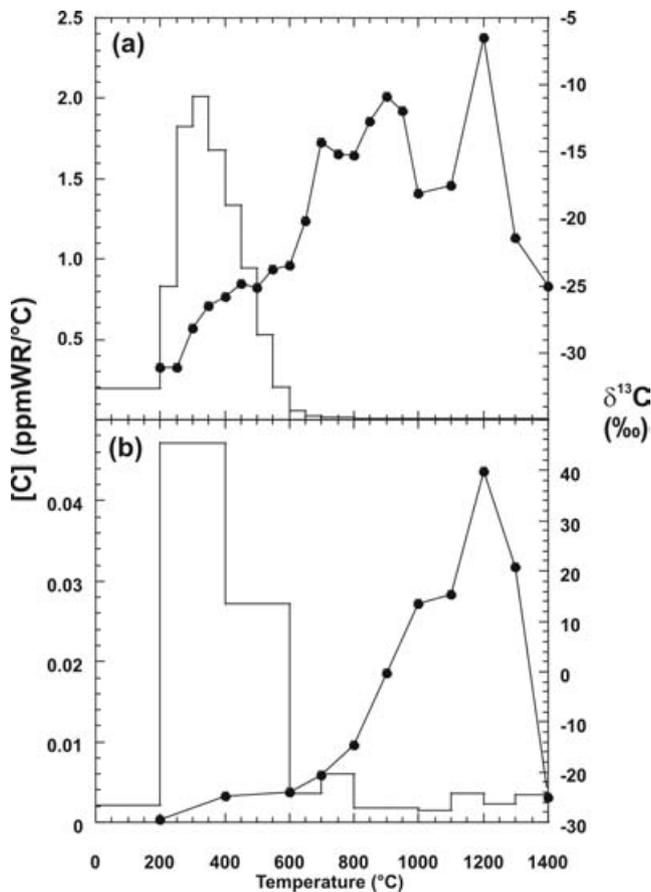
Fig. 2. Stepped combustion of (a) SAU 005 and (b) ALHA 77005.
The yield of carbon released at each step of the experiment, in
ppm of the whole rock per °C, is given as a histogram; the
corresponding isotopic composition is plotted as dots joined by a
line. Errors in $\delta^{13}C$ are less than the size of the symbol. Note the
difference in scales between the two plots.

(e.g., Des Marais 2001). Carbon present in diamonds and
outgassed from volcanoes, generally has $\delta^{13}C$ around -5‰
(e.g., Deines 1980; Mattey et al. 1984, 1989; Mathez 1987),
and is taken as the isotopic composition of primary mantle
carbon. Des Marais (2001) calculates the terrestrial abun-
dance of magmatic carbon as 27×10^{21} moles, by far the
largest of any of the terrestrial carbon reservoirs, by several
orders of magnitude. There is a portion of carbon in igneous
rock that is isotopically light, with $\delta^{13}C$ between -30 and
-10‰ (with an abundance about 0.04% that of the
magmatic abundance; Des Marais (2001)). This component,
which is thought to be reduced in nature, has been produced
by thermal metamorphism during subduction and recycl-
ing of crustal sedimentary carbon, which contains organic
carbon produced through biological processes at Earth's
surface. It has been argued (Mozjsis et al. 1996) that the low
$\delta^{13}C$ values occurring in Archaean rocks might be the results
of anaerobic biological activity.

On Earth, magmatic carbon may either come from a deep
primordial reservoir (and so potentially constraining the
original source of the rocks), or may tap an intermediate

level reservoir that has been contaminated by input of sedi-
ments from Earth's surface. Sediments contain carbon from
carbonates (with $\delta^{13}C \sim 0 \pm 2$‰) and organic materials ($\delta^{13}C$
typically around -25‰) and, when mixed together in the
approximate proportions of their relative surface abundance,
produce carbon with $\delta^{13}C \sim -5$‰, i.e. indistinguishable, at
least in isotopic composition, from primordial magmatic
carbon. A rock could contain both primordial carbon from
the deep mantle and carbon from higher levels in the crust
(assimilated during magma ascent); oxidized carbon might
be trapped as gases in fluid inclusions ($\delta^{13}C \sim -5$‰) whilst
reduced carbon ($\delta^{13}C \sim -25$‰) is present along grain
boundaries and on grain surfaces.

The currently accepted value for magmatic carbon on
Earth is determined from fresh basaltic glasses and, as noted
above, is generally around -5‰. Looking backwards
through the geological record, the mantle signature is re-
tained in carbonatites and diamonds, rather than in typical
basalts. The $\delta^{13}C$ of mantle carbon from carbonatites is
still between -6 and -0.5‰ in specimens of 50 to 1000
million years in age (Nelson et al. 1988). Thus it appears that
there has been no significant evolution of terrestrial mantle
carbon over a significant part of Earth's active magmatic
history. In other words, input from sediment subduction
has had no effect over this, vastly bigger, carbon reservoir.

Carbon on Earth is processed through the interconnected
carbon cycles on a variety of timescales, from very rapid
(atmosphere–hydrosphere interactions; tens of years) to
crustal–mantle subduction (many millions of years). Re-
cycling is powered and controlled by plate tectonics. Mars, of
course, is completely different. There is now no significant
operation of plate tectonics; cycling of carbon between res-
ervoirs may at best be sluggish or even impossible. This
situation has not necessarily pertained throughout Mars'
history: the identification of 'magnetic reversals' in Martian
surface rocks has indicated that a Martian tectonic cycle
was possibly in operation for the first 500 Myr of the
planet's history (Connerney et al. 1999). How, though, can
we relate our observations of magmatic carbon in Martian
rocks to that in terrestrial basalts? Assuming that the carbon
abundances we measure in Martian meteorites (1–100 ppm)
are representative of the abundance of magmatic carbon in
Mars' mantle, then Mars' mantle contains between about
5 and 500×10^{17} kg of igneous carbon. This is between 5 and
15% of the Earth's abundance (3240×10^{17} kg; Des Marais
(2001)). We observed previously that the terrestrial igneous
carbon reservoir was so much greater than other reservoirs
that its isotopic composition remained unchanged by sedi-
ment recycling. Can we draw the same inferences for Mars?
Most of the data for all the shergottites (no matter what
age or petrogenetic origin) and Chassigny show that igneous
carbon has a $\delta^{13}C$ of between -24 and -16‰. Whilst this
is within the same range as buried and metamorphosed
carbon in terrestrial rocks, it is not yet possible to infer that
this carbon represents buried and metamorphosed carbon
on Mars. We do not, as yet, have accurate abundances or
isotopic compositions for Mars' sedimentary reservoirs – that
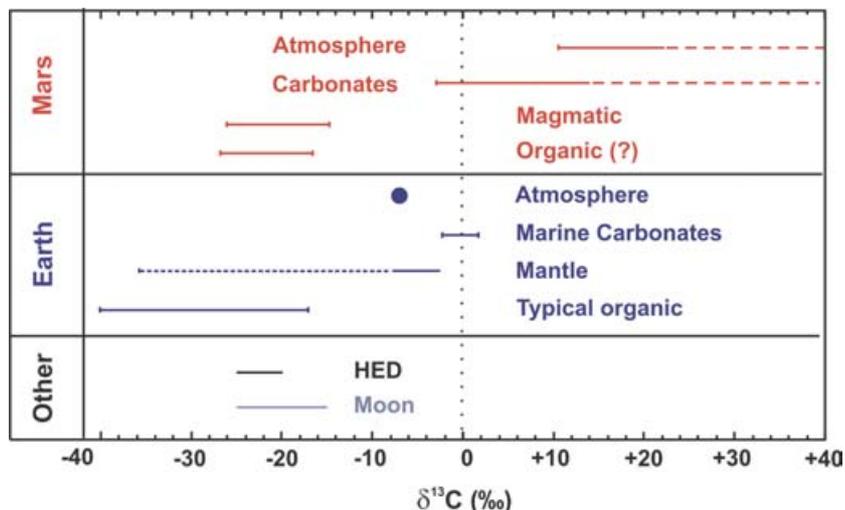
Fig. 3. Isotopic composition of carbon from various Solar System reservoirs. HEDs are basaltic meteorites thought to come from Vesta or Vesta-like asteroids. Data are taken from several sources: Mars atmosphere (Carr *et al*. 1985); Martian carbonates (Wright *et al*. 1992; Romanek *et al*. 1994; Jull *et al*. 1995); magmatic carbon (this study); Martian organics (Wright *et al*. 1989); terrestrial reservoirs (summarized in Des Marais 2001); HED (Grady *et al*. 1997b); Moon (Des Marais 1983).

must wait for better analyses of the organic component in Martian meteorites and its separation from terrestrial contaminants. However, as discussed by Wright & Pillinger (1994), it would seem logical that the bulk $\delta^{13}C$ of Earth and Mars were similar (they, after all, formed from the same protoplanetary dust, at the same time and through the same accretion and differentiation processes). So we might be led to infer that the $\delta^{13}C$ of Martian magmatic carbon should be around $-5‰$. Such a component was identified in EETA 79001 (Wright & Pillinger 1994), but not in other studies (e.g., Grady *et al*. 1997b) or, indeed, in the study reported here. We are, therefore, left with a number of possible interpretations.

1. The bulk $\delta^{13}C$ of Mars ($-20\pm4‰$) is different from that of Earth ($\delta^{13}C \sim -5‰$).
2. Magmatic carbon observed in Martian meteorites is generally influenced by processes of isotopic fractionation during emplacement, with large-scale loss of a primordial component with $\delta^{13}C \sim -5‰$.
3. Martian meteorites contain a component of carbon that has been influenced by surface processes and subsequently recycled (in which case, the carbon could, in principle, reflect the operation of biological processes).
4. Although it would seem unlikely, perhaps the $-5‰$ signal observed on Earth is not representative of its primordial value. There appears to be a similarity in magmatic carbon isotopic composition (Fig. 3) between Mars (or at least Martian meteorites), Moon (Apollo samples) and Vesta (HED meteorites); if anything, it would seem that, in Solar System terms, it is the Earth that is unusual.

Magmatic history of Mars

Evidence for significant magmatic episodes on Mars is not difficult to find: ever since the first high-resolution images of
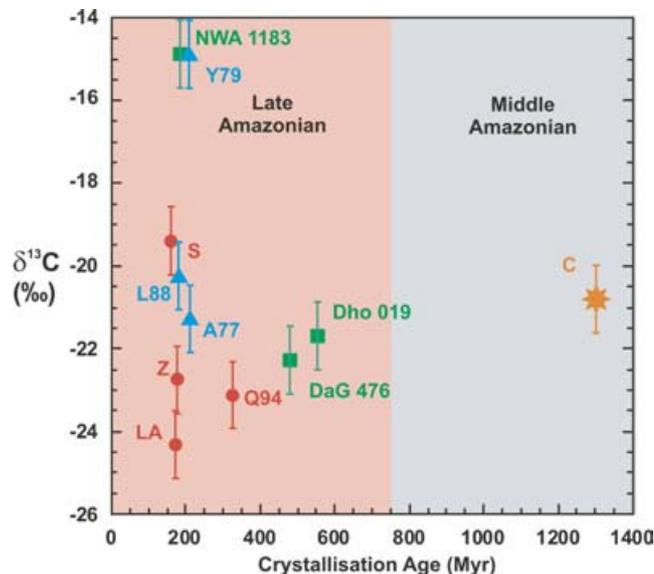
Fig. 4. Relationship between crystallization age and isotopic composition of magmatic carbon. Red circles, basaltic shergottites; green squares, olivine-phyric shergottites; blue triangle, lherzolite shergottites; orange star, Chassigny. Error bars are $\pm1\sigma$. Crystallization ages are as listed by Meyer (2003) and mainly drawn from Nyquist *et al*. (2001). Dates of Amazonian stages are from Hartmann & Neukum (2001).

the planet were returned by Mariner 9 in 1971, we have been astonished by the extent of the volcanoes of the Tharsis bulge in Mars' western hemisphere. Martian history is divided into three epochs (Noachian, Hesperian and Amazonian), whose relative chronology can be inferred through comparison with crater counts on the Earth and Moon. This allows age limits to be placed on the epochs, but until we can either link specific Martian meteorites to a specific impact crater, or

measure the age of the Martian surface *in situ*, we will not have absolute ages for Martian igneous provinces. Each epoch is associated with volcanism to a varying extent, with the main episodes associated with active volcanism taking place in the Hesperian epoch (3–3.7 billion years ago). We do not (yet) have any Martian meteorites from this period – the most ancient Mars meteorite is ALH 84001, with a crystallization age of ~ 4.5 Gyr, or Noachian. Chassigny (and the nakhlites) is early Amazonian, a time of under-surface emplacement of dykes and sills. In contrast, shergottites (of every petrogenesis) are Late Amazonian, when the final surface flows were generated. Figure 4 plots the crystallization age of Martian meteorites (where known) against the isotopic composition of magmatic carbon. The rocks that we have analysed have not been altered to any significant extent by flowing water. Looking at Fig. 4 with the eye of faith distinguishes a potential relationship of decreasing $\delta^{13}C$ with younger ages, but the relationship is so weak and ill-defined that it is difficult to attach any significance to it. If the rocks were all from one source region, we could cast any potential relationship between age and carbon isotopic composition in the framework of an evolving magma chamber, with continual assimilation of fresh, volatile-rich material (otherwise, in a closed system, the source would gradually become heavier in isotopic composition with increasing time). Unfortunately, however, although lherzolitic shergottites maybe parental to the olivine-phyric shergottites, they are not all derived from the same magma body. With such an abbreviated rock suite available for study (and a rock suite with no known field relations to each other), cooling dynamics and carbon isotope evolution are broadly inferred to show that assimilation of crustal rocks during magma ascent has not been a significant process in Mars' most recent past. 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 basaltic, olivine-phyric and lherzolitic shergottites, perhaps indicating the homogeneity of the Martian mantle, despite the lack of convective tectonics.

Recognition of potential signatures of life on Mars?

Primordial carbon in basalts that crystallized in the latest epoch of Mars' history is 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. It is also clear that determination of carbon *in situ* in Martian rocks and soil will be very technically challenging. Carbon abundance is low and its measurement will require an extremely sensitive instrument. Analysis of primary magmatic carbon dissolved in silicate minerals requires temperatures up to 1000 °C; this is difficult. Return of Martian samples to Earth is still fraught with the problems of terrestrial contamination.

Conclusions

We have determined the abundance and isotopic composition of carbon in a suite of shergottites plus Chassigny. Carbonates (terrestrial and Martian) were removed by washing in HCl; subsequent HR-SC-MS allowed distinction between primary magmatic carbon and tertiary carbon implanted during shock or by irradiation. The primary carbon is present as reduced, quite well crystalline carbon, presumably on grain surfaces and occluded within silicates. Its $\delta^{13}C$ of $-20 \pm 4 ‰$ is much lighter than primary magmatic carbon from terrestrial basalts. We suggest four possible reason for this: (1) the bulk $\delta^{13}C$ of Mars is genuinely different from Earth; (2) Martian meteorites contain a primary form of reduced carbon, with $\delta^{13}C$ established by isotopic fractionation during emplacement; (3) Martian meteorites contain a recycled component that could, in principle, reflect a Martian biological signature; or (4) although unlikely, perhaps the $\delta^{13}C$ of $-5 ‰$ on Earth does not represent the bulk planet.

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