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On the Isotopic Chemistry of Carbon at the Martian Surface [and Discussion]

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On the isotopic chemistry of carbon at the Martian surface

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A brief overview is presented concerning the possibilities of using meteorites, that are thought to have a Martian origin, to learn something about Mars itself. The main reasons for believing the samples are of Martian descent are also given. As an example of the sorts of information that can be obtained by analysing Martian meteorites, previously unpublished results from a study of the carbon in shock-produced glass from one particular sample are discussed. The experimental data are used to give an insight into the potential of using isotopic data to comprehend the carbon cycle on Mars.

1. Introduction

There are many ways to study the evolution of Martian surface processes. Observations with a simple telescope allow dust storms to be monitored, or the extent of the polar caps to be determined. A more advanced study might use either ground-based, or airborne, spectroscopic telescopes to elucidate the chemistry of the present surface. The clarity of the picture is then improved by comparing the results of these 'remote sensing' operations with data from the Viking programme, acquired from *in situ* analyses of the atmosphere and surface of Mars. Furthermore, using the excellent close-up photographs taken by the Viking orbiters, along with images from the earlier Mariner 9 mission, it is possible to look in detail at some of the ancient surface features of the planet. Finally, the results of these investigations are tied together by using supercomputers to produce theoretical models of the evolution of Mars.

Future space missions to the red planet will include some, or all, of the following: Mars-94/Mars-96 (Russia), the Mars Environmental Survey (U.S.A.), and Inter–Marsnet (ESA). Additional possibilities include exploration of the polar regions, the use of balloons for atmospheric investigations, and mechanical rovers for surface studies. However, there are at present no firm plans to acquire samples of surface materials (rocks, soils, gases) and return them to Earth for analysis. In part this is due to a new realism that has swept through the community of planetary scientists; the complexities, financial ramifications and potential pitfalls associated with a sample-return mission to Mars are enormous. It is apparent that the ever increasing expectations associated with space missions have meant a higher degree of risk and, ultimately, a greater chance of failure. Witness the untimely demise of Mars Observer, a space programme upon which the careers of a whole generation of planetary scientists have been built. However, as if to

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Table 1. *The presently known SNC meteorites*

group	meteorite	date of collection	country of collection
shergottites	Shergotty	Fall, 1865	India
	Zagami	Fall, 1962	Nigeria
	ALH A77005	Find, 1975	Antarctica
	EET A79001	Find, 1979	Antarctica
	LEW 88516	Find, 1988	Antarctica
nakhlites	Nakhla	Fall, 1911	Egypt
	Lafayette	Find, 1931	USA
	Governador Valadares	Find, 1958	Brazil
chassignites	Chassigny	Fall, 1815	France
(?	ALH 84001	Find, 1984	Antarctica)

counterbalance this rather unfortunate event, Nature has been kind enough to have delivered samples of Mars to us, at what is effectively no cost.

Ten individual samples of Mars are currently available for study on Earth (see McSween 1985, for a review). These fell through the Earth's atmosphere to be collected as interlopers among a vast population of asteroidal fragments known as meteorites. Theories on how the relevant pieces of rock were removed from Mars generally involve ejection following an impact event (Melosh 1987), rather than invoking some sort of explosive volcanism. Since impact processes are such a common feature of the Solar System, it is no surprise to record that a number of lunar meteorites have also been recognized. Now that the notion of orbiting planetary debris has been accepted, it is possible to look back through existing collections of meteorites and identify pieces of rock that had origins either on Mars or the Moon.

2. Characteristics of the Martian meteorites

Ironically, one of the main criteria used for preliminary identification of a Martian sample is that, superficially at least, it should look like a meteorite. Indeed, four of the ten known Martian samples were recognized as bona fide meteorites, not only because they were observed to fall, but also because of apparent affinities with an established group known as basaltic achondrites. Two further samples, collected as finds rather than falls, were then linked with one of the four, on the basis of obvious similarities. Within this group of six samples, there are three distinctive types of meteorite, known as shergottites, nakhlites and chassignites (collectively these are referred to as SNC meteorites, from the first letters of the three groupings). The cast, as it stands presently, is given in table 1.

Shergotty and Zagami are two examples of meteorites that were originally classified erroneously as basaltic achondrites. The misidentification is clearly the result of petrographic similarities – shergottites are coarse-grained basalts. The nakhlites, on the other hand, were always recognized as anomalous because of their mineralogical composition, which is mainly pyroxene. Nakhla has achieved a certain amount of notoriety because one of the 40 stones that constituted the shower fall supposedly killed a dog (see information in Graham *et al.* 1985). Lafayette also has a rather colourful history being observed to fall and subsequently donated to a university, but not recognized as a meteorite until some time later (see Nininger 1935). A few years ago there were thought to be two chassignites; however, following a reclassification, there is currently only a single example, Chassigny, which is a rock type known as a dunite. The other 'chassignite', Brachina, was originally linked to Chassigny on the basis of chemical and mineralogical similarities (Floran *et al.* 1978). Subsequently, that most incontrovertible evidence of all, oxygen isotopic composition, has been used to distinguish the two meteorites (Clayton & Mayeda 1983), even though for a time it looked like the isotopic compositions of the two samples might be similar (e.g. see datum for Chassigny in Wood & Ashwal 1981, and compare with results for Brachina in Clayton & Mayeda 1983).

In addition to the six samples discussed above, three more shergottites have been identified in collections of meteorites returned from Antarctica by the US-led *Antarctic Search for Meteorites*. These samples, which have been instrumental in helping to constrain the origins of SNC meteorites, are ALH A77005, EET A79001 and LEW 88516 (note that extensive reference will be made to EET A79001 herein; for brevity it will be referred to henceforth as 'E1'). The closely related ALH A77005 and LEW 88516, which are rock types known as feldspathic harzburgites, represent the complementary residues of the source magmas that produced the basaltic shergottites. From information gained from these samples it is possible to derive a thorough understanding of the melting processes that occurred on Mars. E1 comprises two distinctive sorts of igneous rock (differing mainly in grain size), referred to as lithologies A and B. The different lithological types are not the result of brecciation, which is common among meteorites, but are two separate sorts of volcanic rock joined by an igneous contact (E1 was the first meteorite in which this phenomenon was documented). E1 also contains within it small pockets of a shock-produced glass (known as lithology C) thought to have been formed when the sample was ejected from the surface of Mars. Upon analysis this glass is found to contain gases that have many similarities to those in the Martian atmosphere (more of this below).

A further sample collected from Antarctica, ALH 84001, although collected in the 1984–85 field season, has only just been recognized as an SNC meteorite. The reason for this is that it represents a totally new rock type, known as an orthopyroxenite, and so it was not obviously related to the other samples (hence the difficulty of placing it in table 1). There is a cruel irony here in that at about the same time that planetary scientists faced dejection over the loss of Mars Observer, an exciting new sample of the Martian crust was recognized on Earth. This sample may hold yet further vital clues to the origin and evolution of surface processes on Mars.

3. Establishing the origin of Martian meteorites

Schmitt & Smith (1963) remarked upon the similarity in rare-earth element fractionation between nakhlites and terrestrial basalts. Perplexed by this finding the authors suggested, in accordance with an earlier idea of Urey (1959) on the origin of meteorites in general, that nakhlites may have had a lunar origin (recall that this was prior to the return of lunar samples). Eventually it was shown that the nakhlites had young formation ages, of about 1.4×10^9 years (Podosek 1973; Papanastassiou & Wasserburg 1974; Gale *et al.* 1975), an observation at odds with other meteorites, having ages around 4.5×10^9 years. Early interpretations of the young ages considered the possibilities of igneous or metamorphic events on asteroidal bodies, but these were at odds with all other theories of Solar System evolution. The problems of assigning the nakhlites to a particular sort of parent body were dealt with by Reid & Bunch (1975). An origin on the Moon was firmly dispelled with the application of oxygen isotope analyses to both SNC meteorites and returned lunar samples.

By the late 1970s, scientists were beginning to discuss seriously the possibility that SNC meteorites could have a planetary, rather than asteroidal, origin. In this regard, it is clear that potential parent bodies are not entirely limitless. However it is difficult to find any convictions in printed format, other than vague references to a 'possible planetary origin'. A good review of the status of SNC meteorite research by the end of the 1970s is given by Wood & Ashwal (1981) who also show, by a logical process of deduction, that Mars is the most likely candidate for the parent body. This prompted Fallick *et al.* (1983) to investigate SNC meteorites for their carbon, nitrogen and hydrogen stable isotopic compositions, in an attempt to assess whether any evidence of a possible planetary origin could be uncovered. However, it is the work of Bogard & Johnson (1983) and Becker & Pepin (1984) which is the most widely regarded as providing the best evidence for a Martian origin. In the former work, noble gas measurements, and in the latter additional nitrogen isotope determinations, have been used to demonstrate striking similarities between gases trapped in the E1 meteorite, and the Martian atmosphere as analysed by the Viking landers (Owen *et al.* 1977).

4. The carbon chemistry of Martian meteorites

It might have been anticipated that the carbon chemistry of basaltic SNC meteorites would be of limited value having a bearing, perhaps, only on magmatic events. As it transpires, however, the carbon constituents of SNC meteorites are much more complicated than would be expected intuitively (Wright *et al.* 1986, 1992). For instance, SNC meteorites have experienced processes of low-temperature weathering, which has resulted in the formation of a variety of salts such as carbonates, sulphates, phosphates, aluminosilicates, and possibly nitrates (see, among others, Gooding *et al.* 1988; Grady *et al.* 1993). Furthermore, the processes that trapped gases from the Martian atmosphere also resulted in the dominant constituent (CO_2) being captured (Carr *et al.* 1985). Somewhat more speculatively, a component of carbon in E1 has been ascribed to organic materials (Wright *et al.* 1989), possibly of pre-terrestrial origin.

With the diverse set of carbonaceous materials that are present in SNC meteorites, determinations of stable isotopic compositions should enable a reasonable attempt at deriving models of the Martian carbon cycle. Unfortunately the typical carbon contents of the least contaminated SNC meteorites (i.e. falls, or samples collected from Antarctica) are only 100–300 p.p.m., and of this a large proportion is most probably terrestrial in origin. It is not a simple matter to perform a physical separation of an SNC meteorite so as to extract its constituent carbon-bearing components. Consider that restricted sample availability limits the extent to which separation procedures can be carried out; furthermore, there is an inherent danger that too much sample handling in the laboratory could cause contaminants to be inadvertently added to the samples. For these reasons the isotopic chemistry of carbon in SNC meteorites has been studied using a technique known as stepped combustion (Swart *et al.* 1983; Wright & Pillinger 1989). In this method a single piece of material, or a representative powder, is heated from room temperature to *ca.* 1300 °C in successive increments (e.g. 25 °C, 50 °C or 100 °C) in an atmosphere of pure oxygen (at a pressure of typically 10–100 torr). Carbonaceous materials of varying stabilities then combust, or simply decrepitate, to form CO_2 over a range of different temperatures. At the same time any CO_2 gas that is physically trapped in the material is released at a temperature that is diagnostic of the confining phase. So, for instance, organic materials burn to form CO_2 at 200–500 °C, carbonates decompose from 400–700 °C, and CO_2 trapped in silicate glass is released at more than 1000 °C. If a stepped combustion experiment is performed with extreme care then, even with components that have overlapping release temperatures, it is possible to document the carbonaceous components present.

5. Analysis of carbon in a shock-produced glass sample

To demonstrate the capability of the stepped combustion technique an analysis of lithology C from E1 is presented. A single piece of material (subsample E1,149) was taken for analysis, consisting predominantly of shock-produced glass, but also remnants of crystalline lithology A. It is known from other studies (Gooding *et al.* 1988) that the glassy materials of E1 contain small grains of calcium carbonate enclosed within the glass, which is good evidence that the carbonates are of pre-terrestrial origin and not merely weathering products formed in Antarctica.

Figure 1 shows the stepped combustion plot of 5.5494 mg of E1,149; the experiment was performed using the instrument and techniques of Prosser *et al.* (1990) and Yates *et al.* (1992). The sample has a total carbon content of 58.2 p.p.m. and an overall (average) $\delta^{13}C$ value† of −17.8‰. The carbon content is lower than the typical value for SNC meteorites – this is because (*a*) the meteorite was collected in Antarctica and has suffered only minimal levels of organic contamination; (*b*) the subsample was removed from several centimetres depth, from a surface cut under clean conditions; (*c*) since the subsample is a relatively rare occurrence of shock-produced glass, containing trapped Martian atmospheric gases, it has been handled at all times with utmost care; (*d*) the glassy nature of the material means it is relatively coherent, i.e. less prone to contamination; and (*e*) the analysis was carried out on a single chip, rather than a powder, in order to keep sample processing, and thus contamination, to a minimum.

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† $\delta^{13}C$, in units of ‰ (parts per thousand), is given by

$$\left(\frac{{}^{13}C/{}^{12}C_{\text{sample}}}{{}^{13}C/{}^{12}C_{\text{PDB}}} - 1\right) \times 1000,$$

where PDB is the international reference material, which is known to have a ${}^{13}C/{}^{12}C$ ratio of 0.0112372.

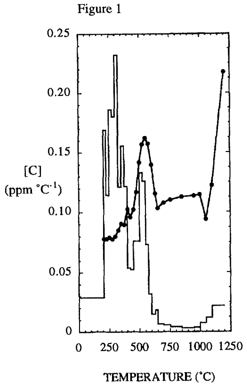

Figure 1. Stepped combustion data acquired from EET A79001,149. The histogram represents the yield of carbon dioxide obtained from each temperature step. The left-hand y-axis is calibrated in p.p.m. carbon $^{\circ}\mathrm{C}^{-1}$ (normalization to 1 °C is done because not all temperature steps are of an equal increment). The right-hand y-axis is a measure of $\delta^{13}\mathrm{C}$ in ‰ (or parts per thousand); the dots joined by the straight line shows the variation in $\delta^{13}\mathrm{C}$ versus temperature.

From figure 1 it can be derived that between room temperature and 450 °C, 39.7 p.p.m. of carbon are released with a $\delta^{13}\mathrm{C}$ value that gradually increases from -29 to -19‰ across the temperature range. This phenomenon is observed in all analyses of SNC meteorites that have been conducted using temperature increments of 25 °C. The carbon released below 450 °C arises from two distinct sources of organic materials, which have been non-committally referred to as LC1 and LC2 (for Low-temperature Carbon components 1 and 2; see Wright *et al.* 1993). That the trend in $\delta^{13}\mathrm{C}$ across the < 450°C range is not an intrinsic property of a single organic constituent is demonstrated by the fact that the ratio of LC1/LC2 varies between different meteorites (or different samples of individual meteorites). In samples where LC2 is prevalent, the $\delta^{13}\mathrm{C}$ values attain a plateau above *ca.* 300 °C, at around -20‰. On the basis of its isotopic composition, and its low temperature of release, LC1 is considered to be atmospheric hydrocarbon contamination (e.g. alkanes, polycyclic hydrocarbons, etc.), which is only very loosely adsorbed on to the surfaces of any particular sample. LC2, on the other hand, is a more refractory form of carbon and has been tentatively ascribed to airborne particulates, such as pollen and spores. As far as E1,149 is concerned it would seem that the sample contains 27.1 p.p.m. of carbon in the form of LC1 ($\delta^{13}\mathrm{C} = -28.1 \pm 1.1$‰) and 12.6 p.p.m. carbon as LC2 ($\delta^{13}\mathrm{C} = -22.0 \pm 2.3$‰).

A further component of low-temperature carbon observed in SNC meteorites, LC3, is known to burn above 400 °C, and has a characteristically low $\delta^{13}\mathrm{C}$ value of *ca.* -30‰ (Wright *et al.* 1993). It is presently not clear whether LC3 is a contaminant or indigenous. Regardless, it is not observable in E1,149 because, over the temperature range 450–625 °C, there is a discrete release of $\mathrm{CO_2}$ from the decrepitation of calcium carbonate. The maximum $\delta^{13}\mathrm{C}$ recorded during stepped heating of the carbonate is $+4.9$‰; failure to achieve a plateau in $\delta^{13}\mathrm{C}$ during the experiment is evidence that the carbon isotope data have been compromised, most probably from the simultaneous liberation of $\mathrm{CO_2}$ from the combustion of LC3. As such, the maximum recorded $\delta^{13}\mathrm{C}$ for the carbonates is a lower limit.

Returning to figure 1, it can be seen that between 625 and 1100 °C the $\delta^{13}\mathrm{C}$ values define what looks like a plateau at around -15‰. Intuitively this represents carbon from a single distinctive source; however, note that the release is very broad with no well-defined maximum. Furthermore, careful examination of the 'plateau' shows the existence of a shallow slope with δ^{13}C values rising from -18.7‰ (at 650 °C) to -14.2‰ (at 1000 °C). This could be interpreted as resulting from isotopic fractionation incurred when CO_2 diffused out of the sample during the extraction. However, it is more likely to be controlled in some way by a mixing of indigenous carbon and system blank (as explained by Wright & Pillinger 1989).

The mathematics involved with deriving a satisfactory correction procedure for the effects of system blank is a straightforward application of algebraic formulae. However, quantifying the behaviour of the system blank is problematic, partly because the level of blank is low (typically less than 1 ng carbon as CO_2 per step) and so it is difficult to measure accurately its yield and isotopic composition. A way around this problem is to apply a model blank correction, the characteristics of which can be defined in terms of the following two components: (1) a time-dependent build-up of CO_2 (experienced when the extraction system is isolated from the pumps) which, because the step duration is fixed, can be considered a constant component, and (2) a temperature-dependent, i.e. variable, component, manifested as an enhancement in the carbon yield over the range 300–500 °C. Of interest here is that above a certain temperature, the quantities of system blank decrease exponentially with increasing temperature (i.e. exhibit a 'tail' in the carbon release; note also that any organic contamination from the sample itself also displays the same trend).

For the analysis of E1,149 the result of applying a blank correction for both the constant and variable components is shown in figure 2. From 625–950 °C, five consecutive data points define a plateau with δ^{13}C of -7.3 ± 1.3‰. The variation in the data for the three steps from 950 to 1100 °C is probably the result of the correction procedure. For simplicity it is considered that all the carbon released from 625–950 °C arises from a single component (equivalent to 1.9 p.p.m. carbon). Before considering the origin of this component it is appropriate to describe the results from the ultimate step of the experiment at 1100–1200 °C (2.19 p.p.m. carbon as CO_2 with δ^{13}C of $+27$‰, corrected to 2.1 p.p.m. and $+30$‰). This component represents trapped Martian atmospheric CO_2 (Carr *et al.* 1985) which, at the time of incorporation into E1, had a δ^{13}C of at least $+27$‰ (a conclusion reached by analysing 12 ng of carbon from an SNC meteorite!).

Using isotope data acquired from SNC meteorites Wright *et al.* (1990) and Jakosky (1991) have attempted to describe certain aspects of the evolution of the Martian atmosphere. These studies utilize carbon isotopic differences between atmospheric and magmatic reservoirs to constrain long-term processes of CO_2 loss to outer space. Clearly, data from SNC meteorites have the potential to delimit the isotopic composition of the atmosphere. As far as the magmatic reservoir is concerned, Wright *et al.* (1990,1991) have postulated that δ^{13}C is probably in the range -20 to -30‰. However, this is at odds with mantle carbon from the Earth, which has a δ^{13}C of -5 to -7‰. It is difficult to envisage how two planetary-sized bodies, formed in close proximity on a Solar System scale, should exhibit such differences in their δ^{13}C values. Herein, a carbon component uncovered in E1, which is released at a temperature compatible with interpretation as a magmatic species, has δ^{13}C of about -7.3‰. It is tempting to ascribe the δ^{13}C value of -7.3‰ to Martian magmatic carbon (and conclude that the previous

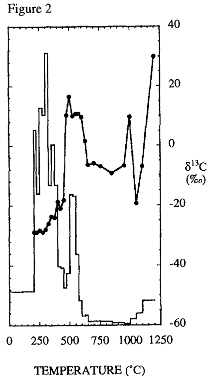

Figure 2. The same data shown in figure 1, but each step corrected for the effects of a constant blank of 0.6 ng carbon with a δ^{13}C of −30‰. In addition, results above 450 °C have been corrected for a variable blank contribution (i.e. an exponentially decreasing tail, with δ^{13}C of −30‰).

assessment of −20 to −30‰ was in error). However, caution is necessary because during glass formation, magmatic and atmospheric volatiles might have become mixed and distributed throughout the material (i.e. dissolved in the glass, or as small vesicles), in which case the δ^{13}C of −7.3‰ could represent a mixing of atmospheric and magmatic volatiles (with δ^{13}C values of +30‰ and −20‰ respectively).

It would seem that a complete understanding of the E1,149 sample probably requires determination of other entrapped species, such as nitrogen and noble gases, in addition to CO_2. Constraining magmatic carbon will have to rely on analyses of unshocked SNC meteorites, such as Nakhla (although note that this is one such sample wherein magmatic carbon would appear to have δ^{13}C of −20‰, or less; clearly a more detailed analysis of this meteorite is required along with an appropriate model blank calculation as performed herein).

Note in figure 2 that from 450–600 °C, the temperature range where carbonates are expected to decompose, there are six consecutive steps that show similar δ^{13}C values. The integrated data correspond to $\delta^{13}\text{C} = +11.1 \pm 2.0$‰ (with most of the uncertainty due to just one of the six points). It is considered that the calculated δ^{13}C value is a far better reflection of the carbonate minerals than the maximum recorded in the raw experimental data (+4.9‰). If the modelling is valid then the sample contains 9.3 p.p.m. carbon as carbonate (which would be equivalent to 77.5 p.p.m. calcium carbonate).

6. Summary and conclusions

From a single stepped combustion analysis of shock-produced glass from an SNC meteorite it is possible to recognize five distinct carbon-bearing materials (table 2). The first two, which amount to 75% of the total carbon, are probably terrestrial organic contaminants (demonstrating the difficulties associated with an investigation of this kind). The carbonate is a secondary component, added by weathering of the sample when it resided at the Martian surface. Previous measurements of magmatic carbon in SNC meteorites have yielded δ^{13}C values in the range −20 to −30‰. The new data presented here suggest that δ^{13}C could

Table 2. *The carbon components in EET A79001,149*

component	[C] p.p.m.	δ^{13}C (‰)
LC1	27.1	-28.1 ± 1.1
LC2	12.6	-22.0 ± 2.3
carbonate	9.3	$+11.1 \pm 2.0$
magmatic carbon(?)	1.9	-7.3 ± 1.3
atmospheric CO_2	2.1	$> +27.0$

be as high as −7.3‰, but further high-quality measurements of unshocked SNC meteorites will be needed to substantiate this. Trapped Martian atmospheric CO_2 has been found to have δ^{13}C of at least +27‰.

Analyses of carbon from meteorites of Martian origin can be used to construct global-scale models of the evolution of surface processes on Mars. However, the samples that are currently available for study are probably not ideal materials for this task. They have been collected and curated because they look like meteorites. But samples of a Martian origin in the broadest sense will be more like terrestrial rocks than meteorites. And here lies an awful possibility for meteorite curators past and present; how many times have they been accosted by the proud owners of materials that were allegedly observed to fall from the sky, but which in all other respects did not look like conventional meteorites? Consider that on Mars it has been proposed, on the basis of theoretical calculations, that there could in places be kilometre-thick deposits of carbonates (i.e. limestones) present on the planet's surface; furthermore, it is conceivable that ancient fluvial activity on Mars would have acted to produce, what on Earth at least, would be categorized as sedimentary rocks. It is fairly certain that should rocks of this nature be ejected from Mars, transported to Earth and found as meteorites, their origin would not easily be accepted. Even dedicated meteorite hunters, or collection teams searching in desert environments and constituted from experts, would probably not be able to distinguish some of the common Martian rock types from analogous terrestrial materials. Thus, unless the elusive materials are observed to fall from the sky by a credible witness, the only hope of finding some of the Martian rocks on Earth is to perform a systematic search of a desert environment (preferably a location in Antarctica) and collect *every* rock within a certain area. Prospective Martian materials would then have to be distinguished on the basis of geochemical criteria. Although this might sound like a very tedious proposition, it is of course considerably less expensive than a Martian sample return mission. Furthermore, the work could start tomorrow.

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Discussion

D. C. Tozer (*Physics Department, University of Newcastle-upon-Tyne, U.K.*). Regarding the question of unusual or novel types of Martian material being found on the Antarctic ice cap, is it possible, perhaps by careful selection of the collection site, to be in a position to say that virtually anything one finds in masses that could not be blown around is extraterrestrial in origin?

M. M. Grady (*Natural History Museum, London, U.K.*). It is indeed true that many of the blue ice regions in Antarctica are far from rocky outcrops, e.g. the Allan Hill icefields. In these localities, practically all the rocks collected are meteorites. However, the glaciers wich flow over these fields have a ‘catchment area’ of several tens (or hundreds) of square miles, thus ‘terrestrial’ rocks can become entrained with the ice and carried for many miles before the surface of the ice is ablated and the rocks liberated.

M. K. Wallis (*University of Wales, Cardiff, U.K.*). If SNCs are part of the surface spall from bolide impacts, one would surely expect many or most of them to show evidence of shocks. Is this so, or is it more plausible to assume they come from surface rocks blown off in the impact’s blast waves, as most efficiently occurs with low inclination impactors?

I. P. Wright. Certainly it is plausible that SNC meteorites could have been ejected by low-inclination impactors – the existence on the Martian surface of so-called ‘butterfly’ craters is testimony to glancing impacts. The meteorites might also have been ejected through a mechanism of blow-off following an impact into permafrost, or by a process of stress-wave interference resulting in the ejection of a thin surface layer of materials. Clearly there are a range of possibilities. Interestingly, some of the SNC meteorites show evidence for shock (peak pressures up to 80 GPa), while others do not. It is probable that the range of shock features present in SNC meteorites results from variable conditions during ejection, which could argue for a number of impacts of different types.

R. Hutchison (*Mineralogy Department, Natural History Museum, London, U.K.*). I comment on the suggestion that abundant carbonate rocks may locally be present on the surface of Mars, so we might expect rare limestone meteorites. As the curator of a major collection of meteorites for 20 years, I have inspected numerous limestone ‘meteorites’ sent by interested enquirers. Identifiable fossils were present in many of the ‘meteorites’ and none appeared to be extraterrestrial.

We may, however, be conditioned into believing that we can with certainty identify a rock as terrestrial. True meteorites may therefore be overlooked and discarded. Nininger and Huss made this point several times. Huss (1977, p. 143) stressed that a blue ice area in Antarctica may provide 'a more or less complete collection of infalling material', where all the material on the ice should be collected. 'The most important study to be undertaken is... (of the stones) ... which do not conform to our present criteria for the recognition of meteorites'. Although Huss may have been over optimistic in assuming the total absence of terrestrial rocks in some blue ice areas, his point is well taken. We must continue to look out for 'new' types of meteorite, some of which may resemble terrestrial rocks.

I. P. WRIGHT. That identifiable fossils were found in many, rather than all, 'meteorites' means that some samples contained unidentifiable fossils, or indeed, no fossils at all. In which case, what criteria were used to assess the origin of the samples? Consider the Martian basalts, in the form of SNC meteorites, look superficially like terrestrial basalts. It is only the presence of a well-defined fusion crust, or the fact that the samples were observed to fall from the sky, that gives a preliminary indication of an extraterrestrial origin. Since a Martian limestone will probably have features in common with analogous terrestrial rocks, coupled with the fact that the passage through the Earth's atmosphere will not result in a 'traditional' looking fusion crust, preliminary identification is very difficult. Absolute proof may require geochemical analyses; a fairly straightforward approach would be to make carbon and oxygen isotope measurements (i.e. Martian carbonates appear to be distinct from typical terrestrial samples in this regard).

I am indebted to Dr Hutchison for alerting me to the existence of the Bleckenstad stone, the first documented example of a 'calcarite' (limestone meteorite). It would seem that the sample is probably terrestrial in origin, but nevertheless material has now been procured for the purpose of making some geochemical analyses.

M. KAULA (*UCLA, U.S.A.*). Has Dr Wright created a calcium oxide fusion crust in the laboratory? How would it differ in appearance from an olivine fusion crust?

I. P. WRIGHT. In principle a synthetic calcium oxide fusion crust could be easily prepared by flash-heating the surface of a piece of calcium carbonate to temperatures of about 1000 °C (either in vacuum or in air). The flame from a hydrogen/oxygen gas torch would be useful for this purpose. However, this will probably not help us to learn to recognize the surface of a limestone meteorite. Consider that calcium oxide has a melting point of 2850 °C; in other words, it might be expected that beyond a certain point, a fusion crust would effectively shield the original sample against further thermal degradation. In reality a limestone would include features resulting from the formation process, such as bedding planes, high degrees of porosity, etc. Such phenomena might enable the entire sample to become calcined upon atmospheric entry. Furthermore, once on the ground, the calcium oxide fusion crust would react with water (atmospheric vapour, rain, surface fluids, etc.) to form calcium hydroxide. This in turn would then absorb carbon dioxide from the air, resulting in the formation of calcium carbonate. It is thus extremely difficult to know exactly what the exterior surface of a limestone meteorite would look like.

T. OWEN (*University of Hawaii, U.S.A.*). Would not most Martian meteorites be basaltic rather than limestone? Therefore should we not expect them to be recognized as meteorites? It does seem that the best approach would be to go to a ‘blue ice’ area in Antartica and bring everything everything (all rocks you find) back for examination.

I. P. Wright. While it is true that the majority of Martian bedrock is basaltic in nature, the ejecta released from the planet following an impact even will be comprised predominantly of surface materials. Some of these are demonstrably fresh basaltic samples (e.g. the SNC meteorites). However, the surface of Mars is known to be covered with highly weathered materials (showing affinities with palagonite, scapolite, nanophase hematite, etc.) and various sediments (aeolian, fluvial, ?lacustrine, ?marine, etc.). In addition it is known from theoretical studies than an initial 10–20 bar pressure of atmospheric carbon dioxide could result in a planet-wide deposit of carbonates 0.5 km thick. Finally, the upper layers of the martian crust (1–2 km depth, or more) may have been subjected to sub-surface processes associated with hydrothermal alteration. In other words, the type of rocks likely to be present at the Martian surface are generally unlike what has been recovered on Earth in the form of SNC meteorites. The problem for meteorite hunters and curators alike is one of identification: how do you recognize a sedimentary rock from Mars?

Additional reference

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