ON THE ^{14}C AND AMINO ACIDS IN MARTIAN METEORITES. I.P.Wright[1], M.M.Grady[1,2] and C.T.Pillinger[1]. [1]Planetary Sciences Research Institute, Open University, Walton Hall, Milton Keynes MK7 6AA, UK (i.p.wright@open.ac.uk); [2]Natural History Museum, Cromwell Road, London SW7 5BD, UK (m.grady@nhm.ac.uk).

Two recent papers in *Science* [1,2] seem to cast yet more doubt on the conclusions from a study of ALH 84001, which has suggested there is evidence for past life on Mars [3]. While the jury is out it is appropriate to scrutinise the new results just to be sure there are no ambiguities remaining.

Firstly we need to consider the development of certain ideas relating to martian meteorites. Thus, from an appreciation more than 20 years ago that Nakhla contained water-bearing minerals of presumed low-temperature origin [4] it subsequently became apparent that martian meteorites such as Nakhla and EET A79001 (hereafter E79) also contained carbonates [5]. Indeed, it now appears that all martian meteorites contain carbonates to some extent [6] and these are considered to be largely low-temperature components introduced by weathering reactions at the martian surface (although in detail, there could be another generation of carbonates, possibly magmatic in origin). During a detailed investigation of carbonate minerals in E79 [7,8] it became apparent that these were accompanied by organic compounds. These were considered to be present in amounts that far exceeded what could be ascribed to terrestrial contamination [9]. With the discovery of ALH 84001 (hereafter A84) and its rather obvious complement of chemically zoned carbonates [10] it transpired again that organics were associated with the carbonates [11] and that the carbonates were predominantly low-temperature in origin [12].

So, at least 2 of the 12 martian meteorites contain petrographically observable carbonates which are associated with organics. Unfortunately both samples, E79 and A84, were recovered from Antarctica and so there exists the inevitable possibility that weathering/contamination over the 12-13,000 years since their falls to Earth [2] could have lead to alteration of the low-temperature constituents of the samples. In other words, the carbonates, or some fractions thereof, could be terrestrial origin (or, at least, have been altered on Earth); furthermore, the associated organics could actually have been added to the meteorites as a consequence of fluid flow through the samples. The latest results suggest that amino acids associated with carbonates in A84 are (largely) terrestrial in origin [1]. This is on the basis of a similarity in the distribution of amino acids between the meteorite and the local ice, and also, low D/L values which suggest the action of terrestrial-like biology. Clearly there are some philosophical issues here, not least of all the fact that biology on another planet could produce effects that are similar to equivalent processes on Earth. This is a debate that is unlikely to be answered through meteorite research alone. However, we draw attention to two things: (i) The D/L ratio of alanine in Antarctic ice is 0.22 [13] - in contrast, equivalent D/L ratios in A84 are variable, ranging from 0.05 up to 0.33 (taking the results from [1] at face value). As such, Antarctic ice is unlikely to be the sole source of alanine in A84. Evidently there exists the possibility that amino acids in A84 might represent mixed biological and abiological sources, or differing degrees of racemisation. (ii) As described earlier [14] to get the observed concentrations of amino acids in E79 requires relatively large quantities of meltwater to flow through the samples. Whilst this issue has been addressed [15] and taken to reflect an efficient concentration mechanism of amino acids in ice at the Antarctic surface (incidently, an interesting hypothesis that should be easily testable) we doubt its operation since the surfaces of Antarctic meteorites would then be expected to be highly contaminated. From our work, analyses of total carbon in a fusion crust sample of A84 shows there to be about the same as in the interior. Since DL-serine in one particular sample of A84 is present at the level of 7.1 ppm [1], this would require about 13 litres of meltwater (based on DL-serine content of ordinary Allan Hills ice, [13]) to have flowed through this half-gram piece of the meteorite, if indeed, meltwater is the source of the amino acids. Even if this water did not affect the oxygen isotopic composition of the primary silicates in the rock, it would surely have begun to convert them to phyllosilicates. Whilst a veritable army of petrographers are currently searching for phyllosilicates (because of the importance such minerals may have in constraining martian processes), scant evidence for their presence in A84 is forthcoming. That indigenous water-bearing minerals exist in A84 is not in doubt since elevated δD values have been obtained during stepped heating [16]. It would perhaps be surprising that any vestige of an original deuterium enrichment would be preserved under the torrent of Antarctic meltwater which is proposed may have flowed through A84 (equivalent to about 50,000 litres of water integrated over the entire meteorite sample!).

Next we consider the ^{14}C data [2], concentrating on results from E79. We recall here that in 1989 we published results from E79 [9] showing an association of organics and carbonate in one particular sub-sample of the meteorite (E79,239); the overall carbon content was 4,680 ppm and δ^{13}C was +1.2‰. The high carbon content reflects our ability to analyse small samples of material selected on the basis of petrographic criteria (E79,239 weighed 0.594 mg, and was chosen for analysis because of its obvious enrichment in carbonates). In contrast, the low abundance of ^{14}C necessarily requires analysis of much larger samples (between 300 and 400 mg in [2]). In which case the results from ^{14}C studies are more reasonably compared with analyses of bulk E79 (e.g. bulk lithology A) rather than specific hand-picked materials analysed in detail. In this regard it should be stated that we have always maintained that martian meteorites (apart from the terrestrial finds) contain a background level of organic contamination, at around 100-200 ppm C (see for instance [17]). The new data from E79 have carbon at 309 and 325 ppm in two separate samples. While these are somewhat higher than would be expected we note that the analyses were made on powders. This in itself is a risky business; the act of crushing may result in the inadvertent addition of contamination. For instance, in the case of the Antarctic shergottite, LEW 88516, whilst uncrushed chips (,8 and ,9) were found to contain 76 and 91 ppm of carbon, small samples of a crushed powder prepared from 1.66 g of bulk meteorite [18] contained between 1200 and 1600 ppm C! [19]. It seems inescapable that crushing can introduce contaminants into meteorite samples.

Something else to note about the new data [2] is that on the basis of the stepped combustion results there are perhaps at most 30-50 ppm C as carbonate, with the balance from organics. E79,239, on the other hand, contained 3810-3140 ppm C as carbonate and 870-1540 ppm C as organics [9]. Thus, while the ratio of $[C]_{organic}$ to $[C]_{carbonate}$ was about 1:5 to 1:10 in the radiocarbon study, it was about 2:1 to 4:1 in the E79,239 analysis. Again this argues for a relatively large input of contaminant organics in the ^{14}C study, and this is borne out by the radiocarbon measurements. Something that may be more difficult to explain away are the apparently high levels of ^{14}C in the carbonates [2]. However, it should be pointed out that the measured δ^{13}C values for the carbonate are -3 to -5‰, which are a long way removed from the true value of about +9‰ [9], and suggests that the carbon extracted as carbonate in [2] is severely compromised by organic materials (and by extension, the measured ^{14}C must also be in error, appearing to be terrestrial because of the presence of organic contamination).

In conclusion we are a long way from having the kind of detailed and definitive data which can unambiguously constrain the origin and sources of organics in martian meteorites. Also, it is clear that as we progress with this work it is essential to keep an open mind about the results. Given that life on another planet may ultimately utilise the same kinds of organic compounds as life on Earth, and may impart isotopic imprints equivalent to terrestrial processes, we may have to work overtime to untangle the evidence. One potential way forward is to study meteorites which are not from Antarctica - in this way we can remove at least one potential problem, that of long term, low-temperature weathering in the Antarctic environment. We have already taken steps in this direction via a study of Nakhla [20].

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