

AN INTERPRETATION OF ^{14}C MEASUREMENTS OF WEATHERING PRODUCTS IN SNC METEORITES; I.P.Wright¹, M.M.Grady^{1,2} and C.T.Pillinger¹, ¹Dept. of Earth Sciences, Open University, Walton Hall, Milton Keynes MK7 6AA, UK; ²The Natural History Museum, Cromwell Road, London SW7 5BD, UK.

Abstract: Apparent elevations in the ^{14}C contents of carbonate weathering products in SNC meteorites would, at face value, appear to require a terrestrial origin for at least some of the minerals in the samples. However since the data are acquired by treating whole-rock meteorites with orthophosphoric acid, there exists the possibility that the ^{14}C arises from sources within the meteorites other than carbonates. In this regard, stepped combustion experiments have already shown that the carbon chemistries of SNC meteorites are quite complex; indeed, a major proportion of the total carbon in any sample could be organic in nature. Some, if not all, of this carbon is of terrestrial origin and would have a ^{14}C signature indicative of the time when it was introduced to the sample. If this carbon is liberated during acid-dissolution it may potentially enhance the measured ^{14}C contents without affecting the $\delta^{13}\text{C}$ values (or it might disturb both).

Investigations of SNC meteorites have shown the existence of weathering products, such as carbonates, in these samples [e.g. 1,2,3]. Carbon and oxygen stable isotopic compositions of the carbonates have been used to place constraints on formation conditions and evolutionary processes on Mars [a good recent review of how SNC meteorites are used to infer conditions on Mars can be found in ref. 4]. Jull et al. [5,6] reported measurements of ^{14}C for the weathering products and concluded that the results demonstrate the presence of two forms of carbonate, one indigenous and one of terrestrial origin. The evidence for this hypothesis comes from an anti-correlation of $\delta^{13}\text{C}$ with ^{14}C concentration, suggesting a mixture of martian carbonates (high $\delta^{13}\text{C}$ and low ^{14}C content) and others of presumed terrestrial origin (characterised by high ^{14}C contents). In the case of ALH 84001, the distinction between martian and terrestrial carbonates seems clear because the minerals that are indigenous to the meteorite have quite extreme $\delta^{13}\text{C}$ values [7]. On the other hand, for EET A79001 the results are more difficult to interpret since both types of carbonate appear to have similar $\delta^{13}\text{C}$ values, in the range +3 to +9‰ [2,5,8].

The technique usually employed to measure carbon and oxygen isotopic compositions (i.e. $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $[^{14}\text{C}]$) of carbonates in SNC meteorites is to subject a whole-rock sample to orthophosphoric acid-dissolution, a technique originally used to analyse carbonaceous chondrites [9,10]. The basic premise of the method is that the acid selectively attacks the carbonate minerals to liberate carbon dioxide gas, which is then collected and purified. The gas is admitted directly to a mass spectrometer for stable isotope measurement ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$), and then may be converted to graphite for ^{14}C determination by accelerator mass spectrometry. The use of such techniques has undoubtedly been successful in many ways and has opened up the possibility of employing SNC meteorites to study processes such as atmosphere-surface reactions on Mars, on evolutionary time-scales [e.g. 11,12]. However, there may potentially be a problem with using orthophosphoric acid for the analysis of SNC meteorites. Consider that when the technique is used for geological studies on Earth, e.g. analyses of foraminifera to derive records of palaeotemperature, it is commonplace to treat the samples with oxidising agents, gas-phase oxidation, roasting etc., to remove the small quantities of organic materials present. The protagonists that advocate these procedures believe them to be obligatory. However, there are considerable differences of opinion regarding the exact nature of the pre-treatments, or indeed, whether they are necessary or not. Regardless, in some quarters at least, the presence of relatively minor quantities of organic materials is considered to exert considerable influence on isotopic measurements. Without wishing to join the debate

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regarding pre-treatment, two possible problems are evident: the orthophosphoric acid (i) reacts with certain constituents of the organic materials to form carbon dioxide, which then interferes directly with the isotopic measurements, or (ii) partially degrades the organic materials, thereby producing volatile fragments which may cause direct, or indirect interference. It is possible that both stable isotope and ¹⁴C determination would be affected; however, for the second possibility it is conceivable that just the ¹⁴C measurement would suffer.

We have previously alluded to the potential problems of using orthophosphoric acid to liberate carbon dioxide from whole-rock SNC meteorite samples [2]. Our caution stemmed from observations during analyses of EET A79001 and Nakhla that the $\delta^{13}\text{C}$ values measured by orthophosphoric acid dissolution were lower than the maxima recorded during stepped combustion experiments. For example, in EET A79001, $\delta^{13}\text{C}$ from acid-dissolution was +6.8‰ while the most extreme value from the combustion extraction was +8.9‰. The disparity becomes even greater when consideration is made of the $\delta^{13}\text{C}$ value of +3‰ made using orthophosphoric acid by Jull et al. [5]. The reason for concern is that SNC meteorites contain, in addition to carbonates, carbon of low thermal stability, which is almost certainly organic in nature [e.g. 13,14]. Furthermore, the relative proportion of this reduced carbon is comparatively high (and may exceed carbonate carbon). Thus if orthophosphoric acid liberates volatiles from components other than carbonates, the isotope results may be compromised. By extension, the interpretation of Jull et al. [6] that there are both terrestrial and martian carbonates in SNC meteorites may be incorrect; in fact there may be only indigenous minerals present. Of course, if such a hypothesis is true then the high levels of ¹⁴C could be ascribed to the organic compounds, which in turn would seem to indicate a terrestrial origin for these materials.

There are a number of ways that the problems outlined above could be overcome. For instance, it may be possible to treat whole-rock SNC meteorites with oxidising agents prior to acid-dissolution, in order to remove organic materials. Alternatively, pre-treatment involving heating in air may suffice. Perhaps the most satisfactory approach is that adopted by Romanek et al. [7] who, in a sophisticated isotopic study of the carbonates in ALH 84001, hand-picked individual carbonate grains for analysis. Thus, it was not necessary to use a whole-rock sample of the meteorite. The efficacy of the approach is demonstrated by the fact that $\delta^{13}\text{C}$ measurements made by acid-dissolution are compatible with stepped combustion data. Importantly, the study has shown that there are two generations of carbonates, characterised by differences in isotopic compositions, but both are martian in origin. Unfortunately, hand-picking of grains is not possible for all SNC meteorites due to the low abundance of carbonates in most samples. However, the approach could probably be used to explore further the carbonates in EET A79001, one of the most important samples of the group, and for which there are lingering doubts regarding the origin(s) of the weathering products.

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