

AN INVESTIGATION INTO THE ASSOCIATION OF ORGANIC COMPOUNDS WITH CARBONATES IN ALH 84001. I.P.Wright¹, M.M.Grady^{1,2} and C.T.Pillinger¹. ¹Planetary Sciences Research Institute, Open University, Walton Hall, Milton Keynes MK7 6AA, UK (i.p.wright@open.ac.uk); ²Natural History Museum, Cromwell Road, London SW7 5BD, UK (m.grady@nhm.ac.uk).

Abstract: The carbonate minerals in ALH 84001 are not only extremely aesthetic in appearance but also provide us with an interesting and as yet unresolved scientific challenge - how did they form? Their importance has recently been promoted following revelations that they may have been implicated in past biological activity on Mars. Since, in this regard, it is the overall carbon budget of the sample that is relevant, we have attempted to study the relationship of the carbon in both the carbonates and the major, non-carbonate form, namely organic compounds. To this end we have used an acid-dissolution procedure to remove carbonates selectively (by reaction to give CO₂ gas), followed by analysis of the reclaimed residues.

Carbonate minerals in the ALH 84001 martian meteorite (hereafter A84) were first documented by Mittlefehldt [1], who determined on the basis of mineral chemistry that they were formed at about 700°C. Subsequent investigations of stable isotopic compositions, on the other hand, suggest formation temperatures of 0-80°C [2]. Furthermore, the presence of Zn sulfides constrains temperatures to <300°C [3]. And yet there remains a dichotomy in the assessments of formation temperatures with other work seeming to show a high-temperature origin [e.g. 4,5]. Clearly the carbonates in A84 are intriguing and warrant further study.

The treatment of various fractions of A84 with acids to liberate CO₂ for carbon and oxygen isotope analyses has previously been carried out in two separate studies. In the first [2], hand-picked carbonate grains were analysed - on the basis of reaction kinetics and extractions after different time intervals, it was proposed that the Ca,Fe-rich carbonates were slightly depleted in ¹³C relative to the Mg-rich varieties (i.e. $\delta^{13}\text{C} = +39.5$ versus $+41.8\%$). In a further study, whereby bulk samples of A84 were studied [6], a range of carbon isotopic compositions was obtained, suggesting the presence of different generations of carbonates. In a refinement of this work it transpires that indigenous carbonates may have $\delta^{13}\text{C}$ values as low as -10.6% [7]. This is in contradistinction to the dominant form of carbonates, which appear to have $\delta^{13}\text{C}$ of around $+40\%$ [8].

Since the carbon isotope results from acid-dissolution studies of A84 are somewhat anarchic it was decided to perform a new series of experiments to

try and shed light on the subject. Starting with 50.52 mg of crushed A84,106 (i.e. bulk material from the "crushed" zone) this was treated with 100% orthophosphoric acid for 18 hours at 25°C. Evolved CO₂ was analysed and the residue reclaimed in order to determine the remaining carbon by stepped combustion [9] and static mass spectrometry [10]. 46.072 mg of residual material was reclaimed, of which 41.315 mg were treated with acid for a second time, at 75°C. Evolved CO₂ was analysed twice, after 18 and 36 hours (after which, 38.714 mg of residue was retrieved). The CO₂ evolved after the first treatment had $\delta^{13}\text{C}$ of $+6.8\%$. Note that $\delta^{18}\text{O}_{\text{SMOW}}$ of the corresponding carbonate (assuming calcite) was $+15.1\%$, which is within the range of Romanek et al. [2] and implies a relatively low formation temperature. Carbon dioxide from the two subsequent extractions had $\delta^{13}\text{C}$ values of -5.6 and -2.0% . These results were somewhat surprising since a stepped combustion analysis of the starting material (i.e. bulk A84,106) had already shown that a component believed to be carbonate, on the basis of decomposition temperature, had an average $\delta^{13}\text{C}$ of about $+40\%$.

In trying to understand the present results we consider just that of the first extraction. Here it should be noted that the $\delta^{13}\text{C}$ values obtained from the preliminary etches of Jull et al. [7] were $+2.4$, $+9.3$ and $+9.8\%$ for three separate samples (two of which gave values of $+39$ to $+41\%$ upon extended etching). Thus, having low $\delta^{13}\text{C}$ values from short-term acid-dissolutions of bulk A84 should not be considered a surprise. Of more concern is the fact that the yield of carbon as CO₂ from the first extraction herein was only 12.8 ppm - the overall carbon content of the original crushed A84,106 sub-sample was 546.5 ppm, approximately 50% of which was due to carbonate (according to stepped combustion results; compare with previously reported data [8]). Upon analysis of the reclaimed residue it was apparent that the equivalent of 332.9 ppm carbon had been "lost" during the phosphoric acid treatment, including most of the ¹³C-enriched carbonates. We can be fairly confident at this point that this was not due to a lapse in procedure since at the same time we were analysing carbonaceous chondrites, as part of another study, and obtained results compatible with previous data. As a working hypothesis we believe that during the acid treatment of

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A84, carbonate grains became physically detached from their original locations within the bulk powder. These grains, being relatively small in size (i.e. compared to the overall size of the grains making up the crushed powder), were subsequently removed when the acid was separated from the residue. Since the grain size of the crushed material is probably of the order of 10-50 μm , and that of individual carbonate grains might be 10-100 nm (if, for instance, they are like the ovoids observed by McKay et al. [11]) then physical loss appears to be a possibility, especially when the viscosity of phosphoric acid is taken into consideration (i.e. making recovery of the residue difficult).

It is noteworthy that when treating a bulk sample of A84 with orthophosphoric acid at 25°C, as little as 2.7% of the total carbonates are etched within the first 26 hours [7]; i.e., it would appear that the carbonates are extremely slow to react. In contrast, 56.4% of the total carbon released from the hand-picked carbonates was released within 4 hours when using orthophosphoric acid at 75°C [2]. Unfortunately, because the starting mass of carbonate in this experiment was not determined it is difficult to assess the significance of the carbon yield. However, extended reaction of the sample (beyond that in [2]) liberated very little extra carbon and so we can be confident that about 50% of the carbonates reacted within 4 hours.

We can explain the results herein and those of other studies as follows. In the case of the hand-picked grains [2] one of the selection criteria was their orange color. Since orange-colored carbonates are found in the cores of globules [which are described in 1,11] the minerals analysed are not representative of carbonates as a whole. In contrast, the bulk samples analysed herein and by Jull et al. [6,7] represent all types of

carbonates (including the cores and rims of globules, and the fine-grained varieties dispersed over fracture surfaces throughout the central crushed zone of the sample). In the Jull et al. work the samples were left to react over extended periods, with no attempt to remove the acid - in which case, all carbonates probably reacted eventually (giving rise to carbon yields of expected magnitudes). In the present study, reaction was stopped after 18 hours; fine-grained carbonates in suspension in the acid were then inadvertently removed from the sample. A question remains: if the carbonates dislodged by the acid treatment were extremely fine-grained, as proposed, why did they not react? This is potentially explicable if they had a Mg-rich composition, but may also be because the individual crystals are coated with something that is acid-resistant (magnetite, sulfides, etc.). In this regard it is noteworthy that as well as carbonates being lost, a substantial amount of organic materials were removed as well. Perhaps individual carbonate grains (which become physically dislodged during the extraction) are in fact surrounded by a thin layer of acid-resistant organic materials (a biofilm?).

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