

FURTHER STUDIES ON THE ISOTOPIC COMPOSITION OF INTERSTELLAR GRAINS IN ALLENDE: 1. DIAMONDS. J.W. Arden*, R.D. Ash, M.M. Grady, I.P. Wright and C.T. Pillinger. Planetary Sciences Unit, Department of Earth Sciences, The Open University, Milton Keynes, MK7 6AA. *Department of Earth Sciences, University of Oxford, Oxford, OX1 3PR.

Microcrystalline diamond was the first type of interstellar grain to be completely isolated and unambiguously identified in primitive chondritic meteorites (1). The discovery of this form of carbon, for a long time referred to by the non-committal name C₈, owes a great deal to the fact that it acts as a host for Xe(HL) enriched in heavy and light isotopes and nitrogen which contains far from normal complement of ¹⁴N (2). Although the techniques for obtaining a "pure" separate of interstellar diamond are now well defined (1), the isotopic compositions of carbon and nitrogen quoted (3) for this material are still the values which were obtained on samples prepared in much earlier investigations. For example, the δ¹³C value of -38‰ is that measured by Swart et al. (4) during a stepped combustion of Murchison residue 2C10 of a sample which is known to contain a number of other forms of carbon. Similarly the δ¹⁵N of -375‰ was obtained during the re-analysis of an Allende fraction CC1 by Ash et al. (5), full details of the experiment in which the data were obtained have never been published. We are currently performing a detailed investigation of the interstellar dust complement in Allende meteorite (6-9); this study allows us to re-appraise the isotopic composition of Allende diamond and to provide appropriately constrained measurements.

Two samples of C₈ were prepared for the study. The first was isolated from 0.039g the HF/HCl residue ARCIII (9) by the following sequence of treatments: (i) chromic acid (0.4N Cr₂O₇²⁻ in 2N H₂SO₄), 30 hours at 75°C; (ii) perchloric acid, 16 hours heated by IR lamp; (iii) 1M HCl-9M HF; 48 hours, 1M HCl; (iv) 3M NH₃ centrifugation at 2100 r.p.m. Acidification of the ammonia solution afforded 0.00148g of ARCIII D1 (i.e. 149 ppm with respect to the original Allende sample) which was shown to be diamond by X-ray diffraction. The solid residue ARCIII S1 weighed 0.00947g (952 ppm of the original meteorite). ARCIII D1 was considered to be inappropriate for definitive nitrogen isotope measurements because it had experienced treatment with nitrogen containing reagents twice during its preparation. Consequently a second C₈ residue was isolated. Allende IVC, the fine matrix fraction of a fresh sample of the meteorite, produced by gently crushing 0.5 to 1 cm chips, was used to obtain ARCIVC. The major difference in the isolation method (compared to ARCIII) being that CS₂ instead of nitric acid was employed to remove sulphur. ARCIVC DS1, 490 ppm of the original sample, was processed almost exactly as ARCIII D1 except that the colloidal separation in ammonia was eliminated so that nitrogen isotopic measurements should not be compromised.

Samples ARCIII D1 and ARCIVC DS1 have been analysed for carbon and nitrogen, using stepped combustion methods and static vacuum stable isotope mass spectrometry. The temperature increments in both types of experiment were small, not greater than 25°C and in many instances only 10°C, over the regions where diamond was known to combust. The protocol for the stepped combustion for carbon and nitrogen release is not quite identical because the procedure for purifying nitrogen requires an additional step.

ARCIII D1 is 89.37 wt % carbon, in keeping with its identification as diamond, and has a bulk isotopic composition of -29.5‰. A small proportion (1.3 wt %) of the carbon burns at high temperature with a positive δ¹³C but the majority (89.9%) is liberated between 400 and 500°C in three steps which define a plateau in δ¹³C of -31.3 ± 1.6‰. Almost all the remaining carbon 7% was liberated in the two steps either side of the major release. Nitrogen isotopic measurements on the 2572 ppm of nitrogen in ARCIII D1 did not define a plateau but dropped from around 0‰ at 400°C to a single minimum of -310‰ in the 500 to 525°C temperature increment. Such a release pattern strongly implies a two component mixture between contamination and indigenous light nitrogen. It was conspicuous that both the maximum nitrogen yield and the minimum δ¹⁵N occurred at one temperature step higher than the peak

carbon yield. An exactly similar situation was observed by Ash et al. (5) for CC1 and led to the suggestion that the true light nitrogen bearing phase might have a high C/N ratio. To investigate this possibility samples of 0-2 μm terrestrial diamond powder were step combusted in a similar fashion to the meteorite specimens; during these experiments nitrogen release lagged about 30°C behind carbon implying that the apparent decoupling of C and N in ARCIII D1 is an artefact.

The nitrogen release from ARCIVC DS1 is considerably sharper than for ARCIII D1. Over the temperature regime 200-400°C no single step releases more than 2% of the nitrogen whereas 75% of the total is liberated in two steps between 475 and 510°C. Another 14% is accounted for by the immediately adjacent steps either side of the main release. More importantly $\delta^{15}\text{N}$ measurements afford a well defined plateau value of $343.8 \pm 3.4\text{‰}$ for three steps between 475 and 520°C. Lower $\delta^{15}\text{N}$ values can be found at higher temperatures but these are for very small amounts of the total N.

Carbon measurements on ARCIVC DS1 showed virtually no carbon (<0.4 wt % of the carbon present) is released above 520°C. Although one $\delta^{13}\text{C}$ value was lost there is every indication that the average $\delta^{13}\text{C}$ below 520°C is a few ‰ lighter than the diamond $\delta^{13}\text{C}$ measured for ARCIII D1 indicating the presence of a second lighter carbon component in ARCIVC DS1. The impression is confirmed by comparison of the N and C yields from the two residues; the former suggest diamond is diluted in the ratio 1:3 in ARCIVC DS1 whereas carbon suggests only a 1:2 dilution; clearly an additional carbon component exists in the non-colloidally separated residue.

In summary, we conclude that the isotopic signatures assigned to C_8 , angstrom sized diamond crystals from Allende, should be $\delta^{13}\text{C} = -31.1 \pm 1.6\text{‰}$ and $\delta^{15}\text{N} = -348.8 \pm 3.4\text{‰}$. Lighter values given for both elements in previous papers indicate the presence of impurities whose investigation as indigenous components of the Allende meteorite is worthy of further study (10).

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