

ISOTOPICALLY HEAVY CARBON IN THE ALLENDE METEORITE - NEW OR PREVIOUSLY RECOGNISED PHASES ?

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Interstellar heavy carbon has been studied extensively in residues from CM2 meteorites by gas source mass spectrometric methods since its discovery by Swart et al (1). At least two components have been recognised with a high $\delta^{13}\text{C}$ - (i) $\text{C}\alpha$ believed to be the host of Ne-E(L), which a coarse grained fraction from Murchison suggests has a $\delta^{13}\text{C}$ of ca +338‰ (2) and (ii) $\text{C}\beta$, carrier of s-Xe and thought to be SiC (3) with a $\delta^{13}\text{C}$ of at least 1100‰ (4). In contrast the interstellar component in the type 3 carbonaceous chondrite Allende, is primarily $\text{C}\delta$, diamond with an isotopically light ($\delta^{13}\text{C} < -38\%$) signature. The method of concentrating the isotopically exotic phases has usually depended on wet-chemical removal of isotopically normal carbon using oxidising agents (eg. 1,4) but at least one, $\text{C}\alpha$, may be unstable when using harsh reagents (4). Herein we consider a new approach involving application of stepped combustion, the method previously employed in residue analysis, as a preparative technique for enriching minor components. Initial experiments have been conducted with Allende which has a carbon content dominated by the isotopically normal amorphous carbon ($\text{C}\gamma$).

Allende fragments were treated alternately with 9M HF-1M HCl and 1M HCl at $\sim 20^\circ\text{C}$ until evaporation of the decanted liquids afforded no residue. During each treatment the mixture was dispersed ultrasonically to aid silicate dissolution. To remove sulphur and possibly some isotopically normal carbon, the residue was heated (under IR) for the only time during its preparation with 16M HNO_3 and washed with water then acetone and dried under vacuum to yield a residue CIII containing 38.2 wt % C with a $\delta^{13}\text{C}$ of -16.2‰. High resolution stepped combustion of this sample indicates the presence of a maximum in the $\delta^{13}\text{C}$ of +152‰ at 750°C which confirms the impression we gained from study of a much more highly processed Allende residue (5) that the meteorite contains a small amount of heavy carbon.

The sample CIII is dominated by considerable quantities of $\text{C}\gamma$ and must contain around 25000 ppm of diamond (6) both of which burn at temperatures lower ($< 550^\circ\text{C}$) than the heavy carbon, and are isotopically light. If combustion of $\text{C}\gamma$ or $\text{C}\delta$ exhibits a "tailing" effect, then superposition on the heavy carbon is masking its true isotopic composition. As we do not know the chemical stability of the heavy carbon or whether it is embedded in another mineral, either carbonaceous or oxide, we attempted to remove interfering $\text{C}\gamma$ in the first instance by carrying out a prolonged precombustion of a specimen of CIII at a "safe" temperature from $390\text{--}410^\circ\text{C}$, stopping at intervals to remove a small aliquot for detailed stepped combustion. The first session of precombustion reduced the carbon content to ca 10 wt % but two subsequent treatments, even though they were continued for over 24 hr periods, had less effect. At this stage analytical electron microscopy is unable to distinguish anything other than spinel and other oxide grains embedded in a matrix of fibrous amorphous carbon in an extensively precombusted residue. At its most processed the residue contains 7.1 wt % carbon.

Although not yet complete, the experiment is already demonstrating its potential. Firstly, the detailed stepped combustion of removed aliquots reveal that the $\delta^{13}\text{C}$ maximum for the $700\text{--}750^\circ\text{C}$ extraction step has progressively risen in the sequence 152,205,281,340‰. Correspondingly, the total carbon has dropped and the tailing effect reduced as evidenced from the measured yield for the appropriate steps 92,79,50,28 (in ppm) respectively. Secondly, and more surprisingly, another maximum in the $\delta^{13}\text{C}$ profile has developed in the region between $900\text{--}1100^\circ\text{C}$ with measurements rising from only +7‰ in CIII to 446‰ in the most precombusted sample. It is difficult to rationalise this second isotope peak by the elimination of tailing but it cannot be ruled it out. No guidance is forthcoming from the yield data since the absolute amounts of carbon are very small, ca 1 to 2 nanograms, and thus difficult to quantify and subject to a blank contribution. An alternative worth considering is that the molecular oxygen used in the precombustion is etching a mineral which acts as a secondary host to the carbon containing

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species. There are several grounds from previous studies which make this seem plausible (i) $\delta^{13}\text{C}$ for heavy carbon in CM2 maximises and the temperature of peak release is lowest in residues which have been subject to wet-chemical oxidation, (ii) CM2 HCl residues heated overnight in a muffle furnace to remove organics had higher $\delta^{13}\text{C}$ values in high temperature steps than samples not so treated (7), (iii) a Si-O containing phase possibly produced by degradation of some nitride with anomalous Si isotope ratios has been seen in ion probe experiments on residues from Murray (3) and (iv) the spinel family of minerals are all oxygen deficient and potentially could break down to constituent element oxides during exhaustive combustion.

The identities of the heavy carbon components discovered here pose some interesting questions. Considering the higher temperature one first. The combustion temperature of *ca* 1000°C can be matched by a component repeatedly encountered in CM2 samples, although its isotopic composition still falls far short of the limiting values reached by Murray samples (4). Current thinking dictates that this component is SiC, either C β or C ϵ (host of Ne-E(H)), with preference given to the former because C ϵ seems to be marginally more stable to combustion (8). S-process Xe(9), the noble gas most diagnostic of C β and Ne-E(H)(10) have both been occasionally glimpsed in Allende.

The lowest temperature component is more problematic. On the grounds of isotopic composition it is tempting to equate this component ($\delta^{13}\text{C} > +340\text{‰}$) with C α (+338‰). The Allende heavy carbon burns sharply in interval 700-750°C; only in the most processed sample is the maximum $\delta^{13}\text{C}$ seen at 725°C. We have encountered carbon burning very specifically around this temperature only once before in an Orgeuil residue (unpublished data). In contrast our studies of C α , the Ne-E(L) host, suggest that this form of amorphous carbon burns between 600 and 650°C in Murchison residue 2C10c (2). This sample had a minimal total carbon content of only 3 wt % and was almost certainly devoid of C δ . Thus its $\delta^{13}\text{C}$ could be close to maximised whereas the component recognised in Allende may still undergo further purification and show a yet higher ^{13}C content. Perhaps a definitive test will be to treat the final precombustion residue with boiling perchloric acid, which should destroy C α ; we are reluctant to perform this experiment until it becomes unavoidable. On this particular score, our first hint of heavy carbon burning at 750°C in Allende came from residue CC1 (5) which had already experienced drastic HClO₄ oxidation, this must argue against a C α identification. Additionally, there is no specific report of Ne-E(L) having been found in CV3 chondrites. Until such time as we have more conclusive evidence, we suggest naming the heavy carbon combusting at 700-750°C C *aleph* (C λ) to imply a possible C α affinity.

C λ exists in Allende in amounts not greater than 1 ppm; the high temperature heavy carbon C β or C ϵ occurs at an abundance *ca* 100 times less. Notwithstanding the power of noble gas measurements and the recent advances in ion probe techniques, stepped combustion still has a vital part to play in the search for and classification of interstellar components in meteorites.

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