

FURTHER STUDIES ON THE ISOTOPIC COMPOSITION OF INTERSTELLAR GRAINS IN ALLENDE: 2. CARBON ASSOCIATED WITH SPINELS R.D. Ash, J.W. Arden*, 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, OX1 3PR.

From their oxygen isotopic composition, spinel grains in primitive meteorites may be recognised as important components in the early solar system (1). In CM2 chondrites, these minerals have shown that they are important secondary hosts of isotopically anomalous carbon components which can be released by phosphoric acid dissolution and may be varieties of interstellar grains. For example, Murchison spinels contain (i) up to 14 wt % of C θ , an easily combusted form of carbon with a $\delta^{13}\text{C}$ of $-49.9 \pm 1.1\%$ (2), (ii) C ϵ , SiC the host of NeE(H) (3). More recently (4,5,6) it has been suggested that prolonged combustion at temperatures around 400-500°C (preparative precombustion) is able to unlock Allende spinels to reveal minor isotopically anomalous components which may differ from those encountered in CM2 meteorites. One of these, C λ , is an extremely light form of carbon $\delta^{13}\text{C} < -261\%$, another, C κ , is isotopically heavy $> +527\%$. Here we consider preparative precombustion data obtained from various Allende acid residues and look at the implications that such investigations have in terms of recognising carbon components which are trapped within or associated with spinels.

Preparative precombustion (6) is a two stage experiment whereby relatively large acid residues are burned in unlimited oxygen at fixed temperatures for extended periods. At any time the carbon dioxide liberated may be removed, quantified and isotopically measured. Similarly the precombustion may be temporarily suspended and a representative specimen of the sample removed and subjected to a full analysis over the temperature scale employed for stepped combustion (room temps. to 1300°C). By looking only at the latter data we were able to discover the components C λ and C κ referred to above. The yield and isotopic data from the two experiments may be combined to follow the progress of the experiment through material balance considerations. If $\delta^{13}\text{C}_{\text{sc}}$ is the bulk isotopic composition of the solid at any stage of the reaction and $\delta^{13}\text{C}_{\text{pc}}$ is the cumulative isotopic composition of the gas phase since the last stop, then at any time $\delta^{13}\text{C}_{\text{sc}}$ and $\delta^{13}\text{C}_{\text{pc}}$ should lie on opposite sides of bulk isotopic composition of the solid which was last analysed by full stepped composition. For the most part during the precombustion of ARCIII this is true, but over the time period 80-108 hours there is a clear indication from $\delta^{13}\text{C}_{\text{sc}}$ that the residue contains some light carbon which was previously unavailable to the stepped combustion. We conclude that the extended (*ca.* 108 hours) treatment with oxygen at temperatures between 400 and 450°C has degraded some mineral(s) in ARCIII which are able to protect carbon from combustion even at high temperatures (up to 1300°C) provided the exposure time is short. Since the mineral content of ARCIII is dominated by spinels it seems reasonable to suspect these oxide grains. From the stepped combustion of the residue from the 80-108 hours precombustion it is apparent that the extraneous carbon burns in the temperature interval 400-550°C but its abundance and isotopic composition cannot be distinguished because of large amounts of carbon already in this temperature interval. Purely on circumstantial grounds (i.e. trapped nature, isotopically light, and combustion temperature), it is easy to speculate that precombustion is liberating a C θ component in Allende spinels.

A second preparative precombustion has commenced using Allende sample ARCIII S1 which is the coarse grained fraction left after diamond has been removed from the residue of ARCIII after oxidation with Cr₂O₇²⁻ and HClO₄ (7). A straightforward stepped combustion (room temperatures to 1300°C) shows that ARCIII S1 contains between 0.44 and 0.55 wt % carbon which is dominated by a release between 350 and 500°C (peak release 400-450°C) with an isotopic composition of $-38.1 \pm 1.5\%$. This component must be the carbon which led to

C δ (diamond) being assigned an erroneously low $\delta^{13}\text{C}$ value (7). We cannot identify this carbon but since it has survived a variety of wet chemical oxidation procedures it is not C θ . It may be the light component recognised by Swart et al. (8) in the very first series of stepped combustion experiments involving Allende; this species manifested itself as a sharp negative spike around 450°C in a region of normally monotonically increasing $\delta^{13}\text{C}$.

The preparative precombustion of ARCIII S1 has now been in progress for 101 hours at 400°C; the carbon release and its isotopic composition being continuously monitored. The release defines a clear exponential decay with the combustion rate having declined to <2ng/hour after a cumulative yield of 0.46 wt % at -37.7‰. Discarding the first 400°C step, which can be expected to have some blank/contamination contribution, the next four steps liberating one third of combusted carbon have a $\delta^{13}\text{C} = -38.2 \pm 1.4$. The fact that the low temperature light carbon has been almost completely removed has been confirmed by the full stepped combustion of an aliquot PC(a) removed from the precombusted ARCIII S1. The amounts of carbon burning up to 400°C and its isotopic composition are at typical blank levels. There is a small amount of carbon burning from 400 to 650°C which could be residual C κ (4, 5, 6). More interesting however, is the sharp dip in isotopic composition at 700°C (possibly indicative of C λ) (5) and the rise in $\delta^{13}\text{C}$ to +102‰ at 800°C suggesting that corrosion of mineral grains is beginning to make C κ available for combustion (6). Most surprising in the experiment is the sudden release at 1200°C of 107 ppmC (the largest yield by a factor of three for an individual step) with an isotopic composition of -35.5‰. It is possible to speculate that protecting minerals in ARCIII S1 are virtually on the point of decomposition and that this high temperature light carbon is that which manifested itself in the 80-108 hour step of the precombustion experiment on ARCIII.

Studies are now in progress to continue the precombustion of ARCIII S1 for longer times and at higher temperatures. We are also considering acid treatment of precombusted residues.

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