

CARBON AND NITROGEN STUDIES OF CARBONACEOUS AND UNEQUILIBRATED ORDINARY CHONDRITES. P.K. Swart, M.M. Grady, S.J. Norris, I.P. Wright and C.T. Pillinger. Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, U.K.

Recently the existence of large enrichments of ^{13}C have been discovered in small portions of the Murchison C2 chondrite. Values of $\delta^{13}\text{C}$ of up to $+1100\text{‰}$ ($^{12}\text{C}/^{13}\text{C}=42$) have been found for carbon oxidisable at high temperatures in two separates, 2C10m and 2C10f (1) known to contain s-process noble gases and Ne-E (2,3). A smaller proportion of the same heavy carbon seems also to be present in Allende (1). In sample 2C10f, the heavy carbon seemed associated with nitrogen having a maximum $\delta^{15}\text{N}$ (-14‰) which was quite normal (4). Equally important, the presence of an isotopically light carbon component (-38‰) associated with the CCFXe rich samples 2C10f of Murchison and B1B of Allende has been recognised (2). However in this case, the $\delta^{15}\text{N}$ of nitrogen released from appropriate temperature fractions of 2C10f (3) is exceptionally low (ca -273‰). A number of primitive meteorites, both carbonaceous and unequillibrated ordinary chondrites, have been demonstrated to be highly enriched in deuterium (5,6,7) possibly through ion-molecule reactions in interstellar clouds.

The separated noble gas host phases so far studied for light elements are characterised by the following correlations: (i) s-process noble gases or Ne-E with heavy carbon, normal nitrogen and (ii) CCFXe with light carbon and light nitrogen. No link between noble gases, the light elements and high deuterium contents has yet been established. Correlated isotopic anomalies are important for constraining the astrophysical and nucleosynthetic history of the interstellar medium (8), therefore, it is necessary to confirm their existence and to establish the frequency of their occurrence. For this reason we have continued to survey carbon and nitrogen in primitive meteorites in the hope that the characteristic isotope signatures will point the way to future studies.

Isotopically heavy carbon: There is evidence that the occurrence of isotopically heavy carbon is fairly widespread. A clue to its existence in Murchison was provided by the stepped combustion of a residue left after treatment of the bulk sample with H_3PO_4 to remove (Ca,Mg,Fe) carbonates, long known (9) to be isotopically heavy (up to $+45\text{‰}$) on a more modest scale. Phosphoric acid residues from other C1 and C2 carbonaceous chondrites have now been studied by a similar technique. Two of the meteorites involved, Orgueil and Banten, although different petrologic groups, show essentially the same carbon release pattern as Murchison with the majority of the carbon combusting at below 600°C . After 900°C the $\delta^{13}\text{C}$ for successive small amounts of carbon rises steeply to maxima of $+90\text{‰}$ and $+560\text{‰}$ for Orgueil and Banten respectively in the 1200°C step. The presence of high temperature ($1100\text{--}1200^\circ\text{C}$) heavy carbon ($+40\text{‰}$) has also been detected in a step-combusted bulk sample of the C2R meteorite Renazzo, where it is quite distinct from carbonate which decomposes at much lower temperatures ($600\text{--}700^\circ\text{C}$). In contrast, however, a phosphoric acid residue from another C2R sample, Al-Rais, gave no $\delta^{13}\text{C}$ value above -12‰ , even in high temperature steps. In all four samples studied here, the vast majority of carbon, however, is combustible below 600°C with normal $\delta^{13}\text{C}$ values between -10 and -20‰ . Knowing heavy carbon with a low combustibility exists in Allende, it is possible to rationalise the bulk sample stepped combustion pattern. Thus, the rise in $\delta^{13}\text{C}$ values from -20‰ to -10‰ and above during the latter stages of bulk combustion is probably due to small amounts of heavy carbon being liberated. In this respect, it is interesting that ALHA 77003, a type C03 carbonaceous chondrite which has an

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unusually high bulk $\delta^{13}\text{C}$ ($-8^{\circ}/\text{oo}$) releases about 120ppm of carbon (8% of the total) over the temperature interval 800-1200°C with a $\delta^{13}\text{C}$ up to $+7^{\circ}/\text{oo}$. Isotopically light carbon: CCFXe has been recognised in C1, CM2, CV3, C03 and unequilibrated ordinary chondrites (10). During stepped combustion analyses of a suite of the latter group of meteorites, we have come across two specimens giving unusually light $\delta^{13}\text{C}$ values; unfortunately neither has been the subject of detailed noble gas measurements. Firstly, the isotope pattern of Sharps shows the existence of a small amount of carbon released at 600°C with a $\delta^{13}\text{C}$ of $-38^{\circ}/\text{oo}$. This carbon is distinct from the graphite in graphite magnetite matrix (known to be in Sharps and thought by some (11) to be a primitive condensate) both isotopically and in terms of its combustion characteristics. Secondly, an H_3PO_4 residue of one of the least equilibrated ordinary chondrites, Semarkona, contains a substantial fraction of carbon having a $\delta^{13}\text{C}$ value as low as $-60^{\circ}/\text{oo}$.

Nitrogen isotope measurements: It was anticipated that the characteristically low $\delta^{15}\text{N}$ which is associated with the CCFXe host might be a good indicator of the occurrence of this phase even in bulk samples. However, a stepped pyrolysis study of Orgueil, Al-Rais and Renazzo provided no evidence for any light nitrogen. All the nitrogen liberated from these samples is isotopically heavy; $\Sigma\delta^{15}\text{N}$ values are $+31^{\circ}/\text{oo}$, $+53^{\circ}/\text{oo}$ and $+170^{\circ}/\text{oo}$ respectively. In each case the peak release of nitrogen occurs in the range 800-1000°C and a corresponding peak in $\delta^{15}\text{N}$ is encountered in the same temperature interval ($+51^{\circ}/\text{oo}$, $+73^{\circ}/\text{oo}$ and $+178^{\circ}/\text{oo}$ respectively). The nitrogen isotopic ratios observed here thus correlate with δD of the same sample. In this context, it is very interesting that stepped pyrolysis of Semarkona also releases only heavy nitrogen, $\Sigma\delta^{15}\text{N}=+36^{\circ}/\text{oo}$ with a maximum of $+60^{\circ}/\text{oo}$ in the 800°C temperature step. Semarkona shows higher D enrichments but lower $\delta^{15}\text{N}$ than Renazzo. However, if the low $\delta^{13}\text{C}$ found for Semarkona is indicative of a CCFXe host with associated light nitrogen, then the bulk Semarkona $\delta^{15}\text{N}$ could be lowered accordingly. There is every reason to expect that deuterium enrichment would be correlated to nitrogen since the interstellar molecules showing the highest D abundance are HCN and HNC (12). Thus, a third pattern of correlated isotopic compositions might be normal carbon with heavy nitrogen and high deuterium - if the phase arose from polymerisation of small molecules in the interstellar medium, it might not be expected to carry other than normal planetary noble gases.

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References:

- (1) Alaerts, L. et al., *Geochim. Cosmochim. Acta*, **44**, 189-209 (1980)
- (2) Swart, P.K. et al., *Science*, in press
- (3) Lewis, R.S. et al., This volume
- (4) Wright, I.P. et al., This volume
- (5) Kolodny, Y. et al., *EPSL*, **46**, 149-158 (1980)
- (6) McNaughton, N.J. et al., *Nature*, **294**, 639-641 (1981)
- (7) Robert, F. and Epstein, S., *Geochim. Cosmochim. Acta*, **46**, 81-95 (1982)
- (8) Schramm, D.N. and Dearborn, D.S.P., *Science* submitted
- (9) Clayton, R.N., *Science*, **140**, 192-193 (1963)
- (10) Anders, E., *Proc. Roy. Soc. Lond. A*, **374**, 207-238 (1981)
- (11) Scott, E.R.D. et al., *Lunar Planet. Sci.* XII, 955-957 (1981)
- (12) Brown, R.D., *Nature*, **270**, 39-41, (1977)