CARBON STABLE ISOTOPE ANALYSES OF ANTARCTIC MICROMETEORITES;

G. A. Graham[1,2], I. P. Wright[1], M. M. Grady[1,2], M. Perreau[3], M. Maurette[4] and C. T. Pillinger[1], [1]Planetary Sciences Unit, Open University, Walton Hall, Milton Keynes MK7 6AA, UK; [2]Department of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD, UK; [3]LEM, CNRS-ONERA, BP 72, 92322 Châtillon Cedex, France; [4]CSNSM, Batiment 108, 91406 Campus-Orsay, France.

Abstract: Micrometeorites exhibit a range of carbon contents, which can reach up to 13 x CI1 [1]. The carbon abundance of several Antarctic micrometeorites (AMMs) might be up to 2 x CI1 [2]. One AMM, extracted from a 100-400 μm size fraction and identified by EELS as having a high carbon content, was analysed by stepped combustion-mass spectrometry. The combustion temperature of the major carbonaceous component (400-600°C) implied that it was an amorphous or poorly-crystalline phase, with a $\delta^{13}C$ (-18‰) similar to that of the major carbonaceous component in carbonaceous chondrites. In addition, there was some evidence for the presence of a small quantity of a ^{13}C-rich component which combusts around 1000°C.

There is currently a great deal of interest in the carbon present in micrometeorites: in a few samples it is in higher relative abundance than in CI1 chondrites. In IDPs, the carbon content ranges from 0.3-13 x CI1 [1], thus some IDPs are the most carbon-rich of any extraterrestrial material. Most of the carbon appears to occur as amorphous or poorly-crystalline material, although carbonates have also been identified [1,3]. There have been many attempts to determine the stable isotopic composition of the carbon present in micrometeorites by techniques of stepped combustion-mass spectrometry [4-9], with varying degrees of success. Those samples selected from deep-sea sediments often appear to be contaminated, or otherwise weathered [4,5], whilst those from Greenland cryoconite are contaminated with algae [6,7]. Isotopic analysis of the carbon in IDPs by conventional techniques has proved difficult, on account of the small sample size and potential contamination with silicone oil [8,9], and ion probe analyses are subject to large errors [10]. Antarctic micrometeorites (AMMs) appear to offer the best hope but preliminary studies of these failed to produce unambiguous signals [6,7]. Large (i.e. >100 μm) AMMs have been shown (by EELS) to contain carbon that is up to 2 x CI1 in abundance [11], and contain an unidentified minor carbon-rich phase dubbed "COPS" [12]. This phase has also been identified in the fusion-crust of Murchison [12]. In contrast, smaller AMMs have lower carbon abundances lower than CI1s. Although larger samples, having been subjected to higher degrees of heating (and possibly melting) during atmospheric infall, they appear not to have lost carbon by volatilisation, or even reaction (i.e. combustion) with atmospheric oxygen. This would appear to be in keeping with preliminary results obtained by flash heating of micrometeorite analogue material. We report here a study of the isotopic composition of the carbon in these large AMMs, in an attempt to identify the characteristics of the carbon-bearing components present.

The sample selected for preliminary study was 93-05-05 from the 100-400 μm fraction collected during the 1993 Antarctic field season. EELS analyses of individual grains (~0.1 μm) found within the sample gave C/O values of 0.00, 0.08, 0.08, 0.21 and 0.48, measurements that span the C/O values of bulk Murchison (0.21) and Orgueil (0.35) [2]. A large fraction of the sample (amounting to ~ 5 μg in mass) was loaded into a platinum foil packet within clean laboratories at LEM. The foil had been cleaned at the Open University (OU) by combustion at 1000°C for several hours, followed by supercritical fluid extraction with CO_2. A blank packet was also cleaned in the same way, and transported to LEM and back, along with the sample.

After return to the OU, both the blank platinum foil packet and that containing the sample, were analysed by stepped combustion and isotope ratio determination using static mass spectrometry. The blank contained 84.5 ng carbon, 84% of which was released below 300°C. The sample, on the other hand, released 344.4 ng carbon during the extraction; at very least this implies about 250 ng of indigenous carbon (amounting to perhaps 5% by weight, or about 1 x CI1 abundance). The major release of carbon was from 400-600°C, a combustion temperature consistent with identification of the phase as either poorly-crystalline carbon, or carbonate, both of which have been identified in micrometeorites [3]. However, the $\delta^{13}C$ of -18‰ is very similar to that of the major form of carbon in carbonaceous chondrites [13], and completely different from the $\delta^{13}C$ of carbonates in CI and CM chondrites ($\delta^{13}C$ ~ +20‰ - +80‰; ref 14). The combustion temperature and $\delta^{13}C$ of the component is also distinct from common terrestrial organic contaminants [15]. Between 600-1000°C, $\delta^{13}C$ rose to -13‰. Only very minor quantities of carbon were released up to this temperature, but applying an appropriate blank correction leads to the inference that relatively refractory ^{13}C-rich material might also be present in AMMs. On the basis of $\delta^{13}C$, we conclude that there are at least two carbon-bearing components in 93-05-05. It is not yet possible to say if either is associated with the "COPS" phase.

The stepped combustion profile suggests that AMM sample 93-05-05 contains amorphous or poorly-crystalline carbon analogous to that in Allende, rather than the highly complex cross-linked organic material present in CI and CM chondrites. We do not know the thermal history of this particle, but it is apparent from the carbon release profile that it was not significantly heated above 400°C during atmospheric entry, otherwise the carbon would have vaporised or reacted. It is, however, possible that the particle originally contained macromolecular-type material that has been slightly metamorphosed during atmospheric heating, to carbon with a higher degree of cross-linking, a process which would raise its combustion temperature.

References: [1] Thomas K. L. et al. (1995) *Meteoritics, 30,* 587-588; [2] Perreau M. et al. (1993) *Lunar Planet. Sci., XXIV,* 1125-1126; [3] Keller L. P. et al. (1993) *Lunar Planet. Sci., XXIV*, 785-786; [4] Wright I.P. et al. (1988) *Meteoritics, 23,* 339-347; [5] Yates P.D. et al. (1994) *Trends in Chem. Geol.*, 1, 215-225; [6] Yates P.D. et al. (1988) *Meteoritics, 23,* 313; [7] Yates P.D. et al. (1991) *Meteoritics, 26,* 412; [8] Carr R.H. et al. (1984) *Lunar Planet. Sci., XV*, 137-138; [9] Carr R.H. et al. (1986) *Meteoritics, 21,* 344-345; [10] McKeegan K. D. et al. (1985) *Geochim. Cosmochim. Acta* 49 1971-1987; [11] Perreau M. et al. (1992) *Meteoritics, 27,* 274; [12] Engrand C. et al. *Lunar Planet. Sci., XXIV,* 441-442; [13] Kerridge J. F. (1985) *Geochim. Cosmochim. Acta* 49 1707-1714; [14] Grady M. M. et al. (1988) *Geochim. Cosmochim. Acta* 52 2855-2866; [15] Swart P. K. et al. (1983) *Meteoritics* 18 137-154.