

AMORPHOUS CARBON GRAINS IN THE MURCHISON METEORITE. A. King^{1,4,5}, T. Henkel¹, S. Chapman¹, H. Busemann¹, D. Rost¹, C. Guillermier², M.R. Lee³, I.A. Franchi² and I.C. Lyon¹, ¹School of Earth, Atmospheric and Environmental Sciences, University of Manchester, Manchester M13 9PL, ²Planetary and Space Sciences Research Institute, The Open University, Milton Keynes, MK7 6AA, ³School of Geographical and Earth Sciences, University of Glasgow, Glasgow, G12 8QQ, ⁴present address: Department of Geophysical Sciences, University of Chicago, Chicago, IL 60637, ⁵Chicago Center for Cosmochemistry. (ajking@uchicago.edu)

Introduction: During a search for presolar graphite grains gently separated [1] from the Murchison (CM2) meteorite, we discovered a set of micron-sized amorphous carbonaceous grains. The presence of amorphous carbon has previously been reported in insoluble organic matter (IOM) [2], interplanetary dust particles (IDPs) [3] and cometary samples [4], as well as carbon flakes, nano-tubes and nano-globules [5,6]. However, it is still unclear as to how this amorphous carbon was formed and became incorporated into a wide range of primitive solar system materials.

Experimental: Material from three size and density aliquots, referred to as B4a, B4b (both containing grains 7–20 μm and 2.15–2.26 gcm^{-3}), and C4a (1–7 μm , 2.15–2.26 gcm^{-3}), were deposited onto separate Au-foils. Carbonaceous grains were located on the foils using a secondary electron microscope (SEM) and energy dispersive X-ray analysis. Ten carbonaceous grains were found in sample B4a, 14 in B4b and 9 in C4a (Figure 1).

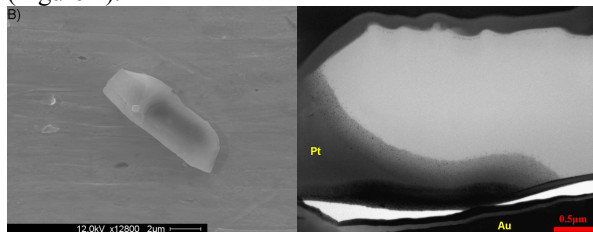


Figure 1. SEM image of carbonaceous grain B4a-X-1 (left) and a bright-field TEM image of the same grain confirming its amorphous nature (right).

TOFSIMS. Six carbonaceous grains from B4a, and all from C4a, were measured for $^{12}\text{C}/^{13}\text{C}$, $^{14}\text{N}/^{15}\text{N}$ and $^{16}\text{O}/^{18}\text{O}$ using a time-of-flight secondary ion mass spectrometer (TOFSIMS). Carbon and N isotopes were determined by measuring CN^- . Mass fractionation was corrected by measuring terrestrial graphite.

NanoSIMS. The $^2\text{D}/^1\text{H}$, $^{12}\text{C}/^{13}\text{C}$, $^{14}\text{N}/^{15}\text{N}$ and $^{16}\text{O}/^{18}\text{O}$ ratios of all carbonaceous grains from B4b were acquired using the NanoSIMS 50L at the Open University. In the first round of measurements negative secondary ions of C, O and CN were collected. During a second round of measurements negative ^1H and ^2D ions were collected, along with ^{12}C as a control on grain position. Mass fractionation was corrected using well characterized IOM samples [7].

Raman Spectroscopy. Raman analyses were performed after SIMS measurements, except for two

grains that were not analyzed by SIMS. Spectra were obtained using a Horiba Scientific LabRAM 300 with a 632nm He:Ne exciting laser. A 10x objective was used and the spot size of the laser was $\sim 140\mu\text{m}$ with a power of $\sim 70\text{mW}$. Spectra were collected in the spectral range 800–1800 cm^{-1} in order to measure the D (“disordered”) and G (“graphite”) bands at $\sim 1355\text{cm}^{-1}$ and 1581 cm^{-1} respectively. For calibration a graphite grain and well characterized IOM were also analyzed.

TEM. Foils for transmission electron microscopy (TEM) were prepared from three carbonaceous grains, two of which were milled to a thickness of $\sim 100\text{nm}$, the other $\sim 200\text{nm}$, using a FIB-SEM. Diffraction-contrast images and selected area electron diffraction (SAED) patterns were obtained from the foils using an FEI Tecnai T20 TEM with a 200kV electron source.

Results: Isotopes. The C, N and O isotopic compositions of nearly all the carbonaceous grains were solar within 1σ errors. Grain B4a-W-1 had a $\delta^{15}\text{N}$ ratio of $+1640 \pm 430\%$. All grains were typically enriched in D relative to SMOW, with δD values between $+134$ to $+333\%$, and 1σ errors on average $\sim 110\%$.

Raman. Figure 2 shows typical Raman spectra obtained from graphite and IOM (used as standards, [2]), and from two carbonaceous grains. Most grains (e.g. B4a-W-1, but also a grain not sputtered by SIMS) had very broad D and G band peak widths (Γ_{D} and Γ_{G}) consistent with the presence of highly disordered carbon. In many cases the D and G bands overlapped, a common feature of amorphous carbon. Figure 3 shows Γ_{G} as a function of peak position (ω_{G}) in the grains. The Γ_{G} values of the carbonaceous grains were often higher, and ω_{G} lower, than those reported in IOM [2], IDPs [8] and cometary dust [4]. This suggests that they consist of carbon of a higher degree of disorder than previously observed in extra-terrestrial samples. Three grains had D and G band characteristics comparable to those measured in other primitive samples.

TEM. Figure 1 includes a bright-field TEM image of B4a-X-1. It is featureless, without any diffraction contrast or internal structure. The SAED pattern contained only very weak rings, with a major d-spacing of $\sim 0.11\text{nm}$. Images and patterns for the other two foils were similar, confirming the amorphous nature of the grains. We also note that all three grains had angles of $\sim 135^\circ$ between outer surfaces suggesting that they had crystalline structures prior to amorphization.

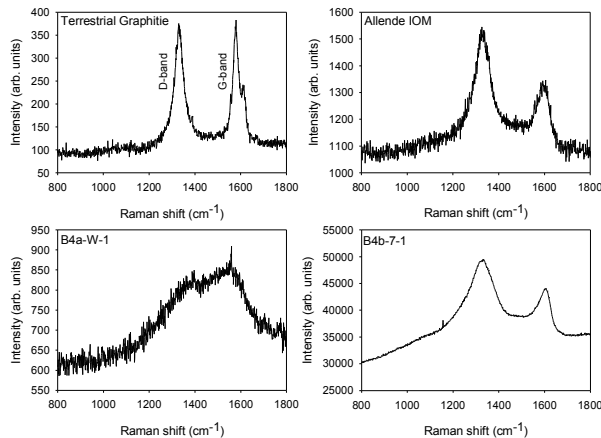


Figure 2. Raman spectra from graphite, Allende IOM, amorphous grain B4a-W-1, and the more ordered B4b-7-1. Amorphous carbon produces overlapping D and G bands.

Discussion: SIMS effects. Sputtering by high energy ion beams could have led to amorphization of the outer tens of nanometers of the grains. However, Raman spectra of a grain not analyzed by SIMS, were consistent with amorphous carbon. TEM results also indicated that the SIMS measurements did not cause the amorphization as grain cores, not just outer layers, were found to be amorphous (see Figure 1).

Origins. The isotopically normal C, N and O compositions of the carbonaceous grains cannot prove circumstellar environments as their source. Organic particles or mantles on grains in the ISM or proto-solar nebula can contain large (>10,000‰) D and ^{15}N enrichments from ion-molecule reactions and mass fractionation processes [e.g. 9]. With the exception of B4a-W-1 extreme D and ^{15}N enrichments were not detected in the amorphous carbonaceous grains. The grains' slight D enrichments are comparable to those measured in some IDPs [e.g. 10], indicating that they may have formed in similar environments.

Amorphous carbon has previously been linked to Fischer-Tropsch reactions and precipitation of elemental carbon onto metal grains in the early solar system [11]. We saw no evidence for metal sub-grains during either ESEM analysis or TOFSIMS measurements of several grains detecting positive secondary ions. Amorphous carbon has also been produced through arc-discharge [12], although those grains were tens of nanometers in size, much smaller than the carbonaceous grains reported here.

Irradiation experiments using soot or carbon-ices show that under increasing bombardment with H^+ and He^+ ions these materials are converted to amorphous carbon [13,14]. Figure 3 shows that Raman spectra from soot irradiated with ion fluences of $\sim 10^{15} - 10^{16}$ ions cm^{-2} is very similar to that of the amorphous car-

bonaceous grains and also some IDPs. Such ion doses would have been easily achievable in the early solar system through the solar wind, which may have been up to 1000x stronger than present day conditions [15]. Irradiation of the carbonaceous grains in the solar wind should have implanted H^+ ions causing a dilution in any large D enrichment they initially acquired.

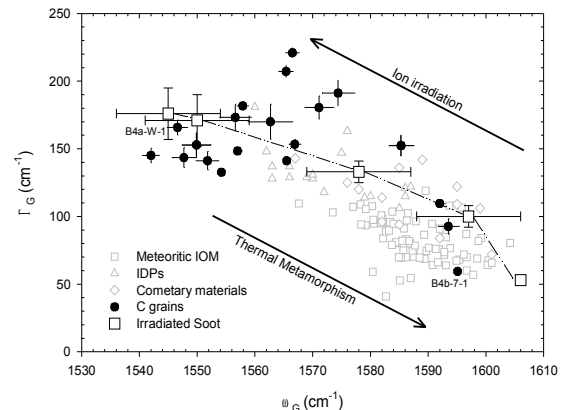


Figure 3. Raman G-band characteristics of carbonaceous grains compared to meteoritic IOM [2], IDPs [8], cometary samples [4] and soots irradiated with H^+ and He^+ ions [14]. The Γ_G and ω_G of the soots evolved as a function of ion fluence, by increasing and decreasing respectively.

References: [1] Tizard J. et al. (2005) *Meteoritics & Planet. Sci.*, **40**, 335–342. [2] Busemann H. et al. (2007) *Meteoritics & Planet. Sci.*, **42**, 1387–1416. [3] Wopenka B. (1988) *Earth & Planet. Sci. Lett.*, **88**, 412–425. [4] Rotundi A. et al. (2008) *Meteoritics & Planet. Sci.*, **43**, 367–397. [5] Garvie L.A.J. and Buseck P.R. (2004) *Earth & Planet. Sci. Lett.*, **224**, 431–439. [6] Nakamura-Messenger K. et al. (2006) *Science*, **314**, 1439–1442. [7] Alexander C.M.O'D. et al. (2007) *Geochim. Et Cosmochim. Acta*, **71**, 4380–4403. [8] Busemann H. et al. (2009) *Earth & Planet. Sci. Lett.*, **288**, 44–57. [9] Millar T.J. et al. (1989) *Astrophys. J.*, **340**, 906–920. [10] Messenger S. (2000) *Nature*, **404**, 968–971. [11] Brearley A.J. (1990) *Geochim. Et Cosmochim. Acta*, **54**, 831–850. [12] Rotundi A. et al. (1998) *Astron. & Astrophys.*, **329**, 1087–1096. [13] Barrata G.A. et al. (2004) *J. Raman Spectrosc.*, **35**, 487–496. [14] Brunetto R. et al. (2009) *Icarus*, **200**, 323–337. [15] Wood B.E. et al. (2002) *Astrophys. J.*, **574**, 412–425.

Acknowledgements: D. Blagburn and B. Clementson for TOFSIMS maintenance, V. Fawcett for the Raman spectrometry, B. Smith and C. How for the FIB and TEM with Prof. A. Craven providing access. The Science and Technology Facilities Council (STFC) is thanked for a studentship (AK), research position (TH), Aurora fellowship (HB), and the UKCAN programme (DR) and (CG).