

RELATIONSHIPS BETWEEN GRAPHITE AND ORGANIC MATTER IN THE ABEE ENSTATITE CHONDRITE; A TEM AND NANOSIMS STUDY. L. Remusat¹, C. LeGuillou^{2,3}, A. Thomen¹, J.-N. Rouzaud³, Y. Guan⁴ and J. Eiler⁴, ¹Museum National d'Histoire Naturelle - CNRS, Paris, France (remusat@mnhn.fr), ²Dep of Earth and Planetary Sciences, Univ. of New Mexico, Albuquerque, USA, ³Lab. de Géologie, ENS-CNRS, Paris, France, ⁴GPS division, Caltech, Pasadena, USA.

Introduction: Abee EH4 chondrite is an impact-melt breccia [1]. It has experienced a high temperature (up to 800°C for some parts, and 500°C for dark inclusions) resulting in partial melting of the parent body. These high temperatures resulted in a complex structure with centimetric clasts embedded into a reduced matrix (including enstatite, metal and sulfides).

The step-heating carbon release patterns of EH4 chondrites, including Abee, indicates that carbon occurs as minor organic matter and more abundant graphite, along with some diamonds [2, 3]. Yang and Epstein [4] have reported very low D/H ratios for the acid residue of Abee (D/H = -450‰), the lowest D/H ratio reported so far for chondritic carbonaceous matter. As organic matter is the main H reservoir in the acid residue, it means that this thermally processed organic matter is anomalously depleted in D compared to other non-hydrated chondrites (enstatites or ordinary, [4]). We recovered Abee acid residue studied by Yang and Epstein from the Caltech sample collections to re-examine their isotopic compositions using micro-analytical techniques. A surprising pattern in ¹²C images lead us to focus also on the relationships between graphite and disordered carbonaceous matter, (hereafter called 'organic matter').

Experimental: An HF/HCl residue of Abee was extracted by conventional procedures [5]. The sample was pressed on clean indium foil and gold coated for preliminary NanoSIMS measurements. Afterwards, SEM and Raman microspectrometry were used to better characterize the carbonaceous phases in the sample. A TEM grid preparation was also made, to characterize the morphology of the carbonaceous phases. To this end, an IOM grain was powdered and suspended in pure ethanol and a droplet of the suspension was transferred onto the carbon lacey of a Cu TEM support grid. Some grains studied by TEM were imaged by NanoSIMS during a second session.

High Resolution TEM images were acquired on a Jeol 2011 (LaB6 filament, 200 kV) installed at University Paris VI Jussieu, equipped with a Gatan Orius camera (pixel size: 0.014 nm).

Raman microspectrometry confirms the occurrence of graphite in the indium mounts. We used a Renishaw INVIA spectrometer equipped with an Ar laser source (wavelength 514.5 nm) and installed at the Ecole Normale Supérieure, in Paris. The spot size is about 1 μm² and the penetration depth about 0.1 μm. Very low inci-

dent power (1-5 mW) was used to avoid heating effects. Each spectrum represents a stack of three measurements.

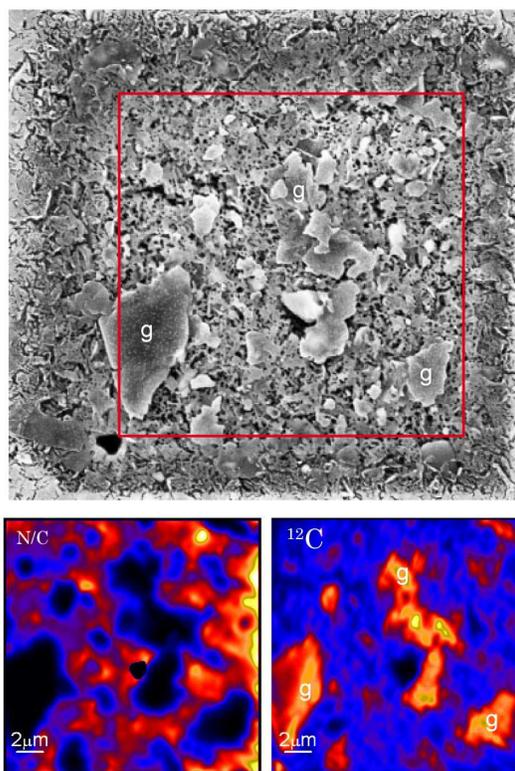


Figure 1: SEM image (top) of Abee acid residue pressed in indium. The red square represents the area sputtered by NanoSIMS (bottom images). Note that the sputtering induces more damage to organic matter than to graphite (g).

NanoSIMS images were acquired on the NanoSIMS 50L installed at the Caltech center for microanalysis and on the NanoSIMS 50 at MNHN. At Caltech, H⁻, D⁻, ¹²C⁻, ¹³C⁻, ¹⁶O⁻, ²⁶CN⁻, ²⁷CN⁻, ²⁸Si⁻ secondary ions were collected to look for isotopic anomalies. A Cs⁺ primary beam of 3 pA was rastered on a surface of 20×20 μm² with a resolution of 256×256 pixels, and a counting time of 3ms/pixel. A standard charcoal, with known D/H, ¹³C/¹²C and ¹⁵N/¹⁴N isotopic ratios, was used to correct for instrumental fractionation. For more precise characterization of the ¹³C/¹²C ratio of carbonaceous phases, ¹²C⁻, ¹³C⁻, ²⁶CN⁻ and ²⁸Si⁻ secondary ions were imaged during a second session on the MNHN NanoSIMS. The primary Cs⁺ beam was set to 1.3 pA, and images were acquired at

the same resolution as previously described (1 pixel=78 nm). For this session, a graphite and a type 3 kerogen standards were used to correct for instrumental fractionation on the $^{13}\text{C}/^{12}\text{C}$ ratio. Raw data were corrected for the QSA effect [6] on $^{13}\text{C}/^{12}\text{C}$ ratios. During each session, a presputtering with a high primary current was used to remove surface contamination and coating and to reach sputtering equilibrium.

Results and discussion: SEM and Raman spectrometry confirm that the Abee acid residue is heterogeneous and composed of large graphite chunks embedded in an amorphous organic matter rich in nitrogen (figure 1). These graphite grains are characterized by a high emission in ^{12}C secondary ions, making them easy to identify in ion images. They are also characterized by a very low content in N (as shown by N/C image in figure 1) consistent with carbonaceous phases in shocked objects [1].

We measure a D/H ratio of -330 ± 25 ‰ for the organic component. The H content in the graphite grains is so low that the measured individual ratios are not usefully precise. Nevertheless, integration of data from all measured spots suggests a value near 0 ‰. The isotopic ratio determined by NanoSIMS is consistent with the value reported in [5], taking in account a potential contamination with adsorbed water. We do not detect any enriched anomaly in D or ^{15}N in Abee acid residue.

HRTEM reveals that organic matter and graphite are associated with one another in the acid residue (figure 2), but this association could be a consequence of the demineralization process rather than a petrographic association in the sample prior to pre-treatment; indeed, no association was seen in previous studies [1]. We have measured different $\delta^{13}\text{C}$ values for organic matter and graphite, broadly consistent with stepped pyrolysis studies [3]. Nevertheless, the $\delta^{13}\text{C}$ we determine for organic matter is lower than the value previously reported [3] for this low temperature component (-55 ± 3 vs -30). The values in both sample preparations examined in this study are consistent within error bars. Graphite grains average at -6 ± 3.6 ‰ consistent with stepped pyrolysis experiments. However, a few graphite grains (including the grain in figure 2) have a lower $\delta^{13}\text{C}$, around -22 ± 8 ‰. This may indicate 2 populations in graphite. The most abundant population may have an igneous origin (if we assume these grains correspond to the large graphite laths described in [1]). The least abundant population may be a product of thermal processing of organic matter. Indeed, all the graphite grains observed in both HRTEM (for which we see an intimate association with organic matter) and NanoSIMS are from the later, low $\delta^{13}\text{C}$ population.

Conclusion: Abee acid residue contains 2 different populations of graphite. Some grains may result from the thermal processing of organic matter originally accreted on the parent body. This organic matter appears to be different in origin from organic matter in carbonaceous chondrites, based on its isotopic composition highly depleted in D. It might not have been exposed to the ionized D-rich gas environment that has been hypothesized to give rise to D-rich organics in carbonaceous chondrites [8].

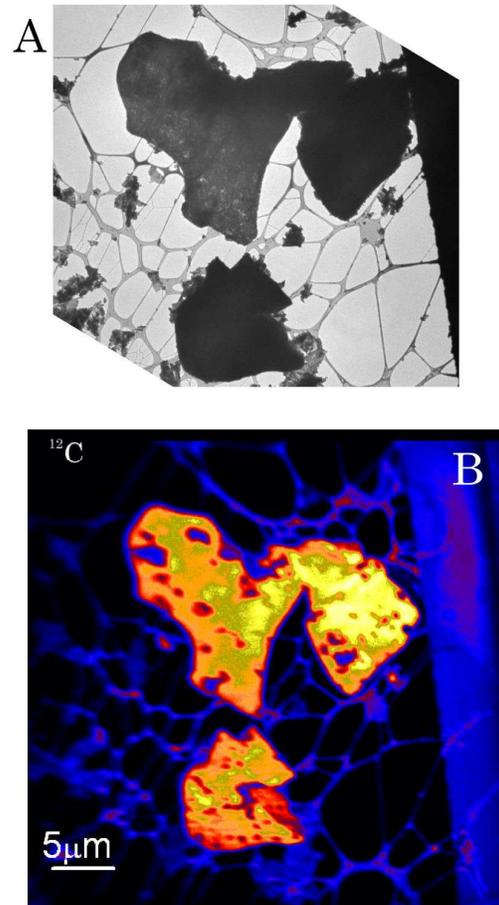


Figure 2: TEM (A) and NanoSIMS (B) images of the same particle on a TEM grid. The carbon lacey grid emission is very low compared to the graphite. Organic matter emission is also low compared to graphite.

References: [1] Rubin A. E. and Scott E. R. D. (1997) *GCA*, 61, 425–435. [2] Grady M. M. et al. (1988) *EPSL*, 87, 293-302. [3] Grady M. M. et al. (1986) *GCA*, 50, 2799-2813. [4] Alexander C. M. O'D. et al. (2007) *GCA*, 71, 4380-4403. [5] Yang J. and Epstein S. (1983) *GCA*, 47, 2199-2216. [6] Slodzian G. et al. (2004) *Appl. Surf. Sc.* 231-232, 874-877. [7] Piani L. et al (2010) *LPS XLI*. [8] Remusat L. et al. (2006) *EPSL*, 243,15-25.