

FIB EXTRACTION AND TEM ANALYSIS OF PRESOLAR GRAINS FROM THE CR3 CHONDRITE MET 00426. C. Le Guillou¹, A. J. Brearley¹, C. E. Brunner¹, C. Floss² and F. J. Stadermann². ¹Department of Earth and Planetary Sciences, University of New Mexico, 87106 Albuquerque, NM, USA (corentin.san@gmail.com), Laboratory for Space Sciences and Physics Dept., Washington University, St. Louis, MO 63130, USA.

Introduction: The CR chondrite, MET 00426 is one of the most unprocessed chondrites currently known [1]. Like other very pristine carbonaceous chondrites (e.g. ALH77307 and Acfer 094) it has a matrix that is dominated by amorphous Fe-rich silicates, with minimal evidence for aqueous alteration or thermal metamorphism, consistent with a petrologic classification of 3.00 [1]. The pristine nature of this meteorite is also supported by in situ NanoSIMS studies of interstellar grains. MET00426 contains a higher concentration of isotopically anomalous carbonaceous grains than any other chondrite and is also characterized by one of the highest concentrations of presolar ferromagnesian silicate grains [3]. These observations indicate that MET 00426 preserves an exceptional record of presolar materials that have survived processing in the solar nebula and the CR parent body.

The nature of organic matter in carbonaceous chondrites and IDPs is known to be heterogeneous, in terms of both elemental and isotopic compositions, and particle morphology (nanoglobules, fluffy material, coating on Fe bearing nanoparticles, etc.) [4]. Anomalous isotopic compositions in D/H, ¹⁴N/¹⁵N and ¹²C/¹³C have been detected in a wide range of pristine meteorites, and are thought to originate from ion-molecule reactions at low temperatures [5]. Nevertheless, the location where the isotopic signatures of organic material were acquired is still a matter of debate; cold molecular clouds or the outer solar system are both plausible environments for cold chemistry [5].

In MET00426, numerous C-rich grains show anomalous C isotopic compositions with $\delta^{13}\text{C}$, ranging from -340‰ to +140‰; these C-rich grains generally contain ¹⁵N excesses [2]. Most of the presolar silicate grains from MET 00426 belong to group 1 in terms of O isotopic composition [3] and probably originated from red giant or asymptotic giant branch (AGB) stars.

Recent studies have made efforts to integrate NanoSIMS measurements of presolar grains with TEM observations of isotopically anomalous grains lifted out by Focused Ion Beam (FIB) techniques. Two presolar silicates from MET 00426 were studied by [6] who showed that they were nanocrystalline aggregates with an olivine-like composition and low amounts of sulfur and aluminum; however, subsequent NanoSIMS analyses of FIB sections confirmed the presolar nature of only one of these grains

Here we report the preliminary results of efforts to extract isotopically anomalous carbonaceous and silicate grains from MET 00426 using FIB-TEM techniques. We emphasize that until NanoSIMS measurements have been made on the extracted FIB section, following our TEM characterization, the identification of these grains as presolar remains uncertain. However, irrespective of this uncertainty, the grains we have studied contain unusual features which have not been described elsewhere and provide additional insights into the variability of C and O-bearing materials in this meteorite.

Experimental: One carbonaceous grain (grain # 4b-20c1; $\delta^{13}\text{C} = -335\text{‰} \pm 40\text{‰}$ [2]; grain # 4b-20c1) and one presolar silicate (grain # 4b-20o1; $^{17}\text{O}/^{16}\text{O} = 8.69 \times 10^{-4} \pm 0.12 \times 10^{-4}$ and $^{18}\text{O}/^{16}\text{O} = 1.04 \times 10^{-3} \pm 0.12 \times 10^{-3}$; group 1 [3]) were found close to each other in a typical matrix area and were extracted together in one FIB section.

We used an FEI Quanta Q3D FIB/FEG-SEM at the University of New Mexico to relocate and extract a FIB section containing both grains. Prior to extraction of the FIB section, the locations of the very small grains (<300 nm) were identified with an electron beam-deposited Pt fiducial mark, before protecting the full section with an ion beam-deposited W layer. Microstructural and compositional studies of the grains were carried out using a JEOL 2010F STEM, equipped with a GATAN GIF system and an Oxford INCA EDS system. The grains were studied using a variety of TEM techniques, including bright field TEM, selected area electron diffraction, HRTEM, dark field STEM and energy filtered TEM. .

Results: *Presolar O anomalous silicate grain.* In our FIB section, the grain we targeted as a presolar silicate (grain 1 in Figure 1) is readily distinguished in Z-contrast STEM images. The grain has a higher Z-contrast than the surrounding matrix and has distinct outline, as seen in the EFTEM Fe map (Figure 2). Based on NanoSIMS measurements, the grain targeted for FIB extraction has a grain size of 200 nm. However, in the FIB section, the grain is larger, with a width of ~ 450 nm wide and 200 nm deep. There appear to be three possibilities for this discrepancy: 1) our FIB section did not crosscut the presolar grain, 2) only part of the grain (the core?) is isotopically anomalous or 3) most of the grain was sputtered away during the NanoSIMS analysis and lost from the sample.

Based on Auger Nanoprobe analyses [2], the targeted presolar silicate grain should be an Fe-rich silicate with a pyroxene-like composition [2]. Our TEM data show instead that grain 1 is mineralogically quite different from the Auger data, suggesting that possibilities 1 or 3 are most likely. Although grain 1 may not be the targeted presolar grain, it has unusual characteristics compared to typical matrix in MET 00426 [1]. Electron diffraction patterns of the grain show rings with rare discrete diffraction spots, indicating that the grain is composed of a mixture of nanocrystalline and amorphous material. HRTEM studies confirm the presence of abundant nanocrystals, typically ~ 10 nm in size. EDS analysis of the grain shows that it is compositionally heterogeneous, but is dominated by Fe and O, with lesser concentrations of Ni, Si, S, Mg and Ca.

Carbonaceous grain. FEGSEM studies of the C anomalous grain (grain 2), prior to extraction using FIB, showed that the bulk of the isotopic anomaly coincided with a hole in the sample. This suggests that during NanoSIMS analysis a significant part of the grain was lost due to sputtering. In the FIB section, STEM imaging shows that the hole is coated with a layer of electron-beam deposited Pt and infilled with ion-beam deposited W, to a depth of $0.4 \mu\text{m}$. There is no evidence of carbonaceous material at the surface of the sample. Instead, an irregular-shaped grain of low Z material is present below the surface, surrounded by amorphous matrix silicates. EFTEM images, coupled with EDS, SAD and HRTEM analysis show that this grain is highly disordered or amorphous carbonaceous material containing O and S confirming its organic character. This carbonaceous material coats a nanocrystalline Fe-Ni-O rich particle, containing minor amounts of C, Si, S, Ca and Mg.

The NanoSIMS analysis sampled a carbonaceous grain on the upper surface of the sample. We do not know if the material present below the surface exposed in the FIB section is part of the C-anomalous grain that was exposed at the surface of the sample. Texturally, there is some indication that the grain may have extended to the surface. However, NanoSIMS analyses are required to determine whether the subsurface grain is isotopically anomalous or not.

Conclusions: The outcome of our first effort to extract O and C anomalous grains from MET 00426 is equivocal until NanoSIMS analyses of the FIB section are carried out. However, it is apparent that the grains we have sample contain several unusual features that have not been observed before in materials from MET 00426 [1]. Although grain 1 is not similar to the presolar silicate grain that was extracted previously from MET 00426 by [6], it does share the nanocrystalline characteristics of that grain. The carbonaceous grain

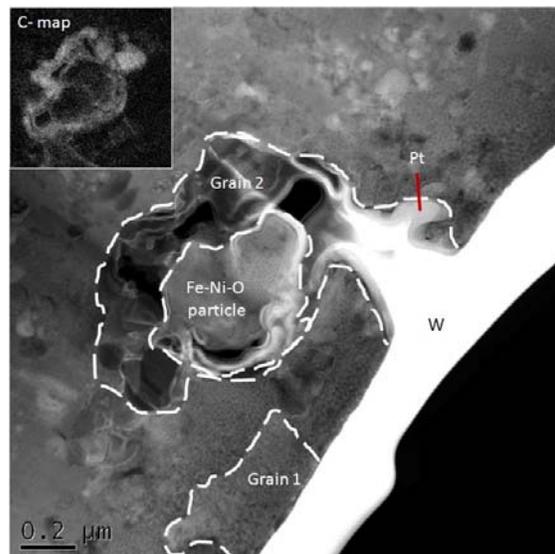


Figure 1. DF STEM image of the FIB section containing the two candidate presolar grains (Grain 1, silicate, Grain 2, carbon-rich). Inset shows EFTEM carbon map.

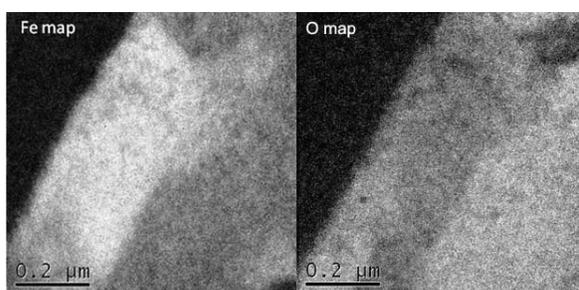


Figure 2. EFTEM maps of Grain 1 showing Fe and O distribution in the grains. The grain has higher Fe and lower O contents, respectively than the adjacent matrix.

extends the range of carbonaceous particle morphology identified in chondrites. For the first time, we have found organic matter associated with an Fe-Ni-O-rich particle in a porous region of a matrix. In contrast with the work of [7], who found 1-10 nm layers of poorly ordered carbon coating nanophase Fe-carbide and sulfides grains, this C coating is more disordered, and much more extensively developed.

References: [1] Abreu N.M. and Brearley A. J. (2009) *GCA*, 73, in press). [2] Floss C. and Stadermann F. J. (2009) *Astr. J.*, 697, 1242-1255. [3] Floss C. and Stadermann F. J. (2009) *GCA* 73, 2415-2440. [4] Remusat L. et al. (2009) *Ap. J.*, 698, 2087-2092. [5] Messenger S. and Walker R. M. (1997) In *Astrophysical Implications of the Laboratory Study of Presolar Materials*, 545-564. [6] Stroud R. et al. (2009) *LPS XXXX*, Abstract #1063. [7] Brearley, A.J. (2004) *LPS XXXV* Abstract #1896. **Acknowledgements:** Funded by NASA Grant NNG06GG37G to A.J. Brearley (PI) and NNX07AI45G and NNX07AI82G to C. Floss (PI).