

STRUCTURE, ELEMENTAL COMPOSITION AND ISOTOPIC COMPOSITION OF PRESOLAR SILICATES IN MET 00426. R. M. Stroud¹, C. Floss², and F. J. Stadermann², ¹Code 6360 Naval Research Laboratory, 4555 Overlook Ave. SW, Washington, DC 20375, ²Laboratory for Space Sciences and Physics Dept., Washington University, 1 Brookings Dr., St. Louis, MO 63130.

Introduction: Other than nanodiamonds, silicates are the most abundant circumstellar condensate grains found in meteorites and interplanetary dust particles [1]. Laboratory analyses of these grains can provide complementary information to telescope-based IR-spectroscopy studies of grains in circumstellar disks, as well as inform our understanding of the circumstellar condensation process. The 10-micron region of the IR spectra of most circumstellar disks appears devoid of sharp features, which is consistent with a predominance of amorphous grains [2]. However, crystalline fractions above 50% have been estimated for some disks [3]. Previous transmission electron microscopy studies of circumstellar silicates are limited to ~ 18 grains in total, of which 4 were olivine [4-7], 1 a metastable grain with a perovskite-like structure and pyroxene composition [8], and the remainder amorphous to finely nanocrystalline [6, 9-12]. The laboratory analysis and astronomical observations appear to be in general agreement over the predominance of amorphous grains. However, further work is needed to understand whether the laboratory data are biased by choice of host meteorite, targeting of larger grains, or other effects, and to look for signatures of post-condensation processes, such as radiation or grain-grain collisions effects. By performing coordinated analysis of in situ silicates in primitive meteorites using secondary ion mass spectrometry for isotopic identification, Auger electron spectroscopy for high-spatial resolution surface composition measurements, and transmission electron microscopy (TEM) for structure and cross-section composition measurements, we aim to address the range of circumstellar dust primary microstructures and elemental compositions, and any correlation with the type of progenitor star. Here we report TEM analysis of two grains from the MET 00426 CR3 chondrite, previously characterized by NanoSIMS and Auger spectroscopy [13].

Experimental: We targeted three grains identified as isotopically anomalous for focused ion beam lift-out and subsequent TEM study. The isotopic compositions of the grains were measured using the Cameca NanoSIMS at Washington University. Elemental spectra of the surface of these grains were obtained with the Washington University Auger Nanoprobe, and quantified based on sensitivity factors for olivine and pyroxene standards.

We used the FEI Nova 600 FIB-SEM at the Naval Research Laboratory (NRL) to relocate and extract electron transparent sections of the grains. To overcome the difficulty of extracting very small grains (<350 nm) and relocating one silicate in a matrix of other silicates, we deposited a Pt fiducial marker directly on top of each grain, prior to carrying-out the standard lift-out procedure. Two of the three grains were successfully extracted. The third detached during milling and was lost due to an underlying crack in the thin section.

Structural and elemental composition studies were performed using the JEOL 2200FS scanning transmission electron microscope at NRL. Full elemental spectral images were obtained in STEM mode with a Noran System Six energy dispersive spectrometer, using a nominal probe size of 1 nm. Compositional analysis was performed using default k-factors. Selected area electron diffraction and conventional dark-field imaging were used to assess the crystallinity of the grains.

After TEM characterization, the extracted section of grain 4c_3 was returned to the Auger and NanoSIMS instruments to confirm that presolar material was successfully extracted, to search for additional presolar grains, and to obtain further compositional data. These measurements are also planned for grain 2b_8.

Discussion: The oxygen isotopic measurements of grain 4c_3 made in situ in the thin section ($^{17}\text{O}/^{16}\text{O} = 5.31 \pm 0.3 \times 10^{-4}$ and $^{18}\text{O}/^{16}\text{O} = 1.75 \pm 0.05 \times 10^{-3}$) and on the extracted FIB section ($^{17}\text{O}/^{16}\text{O} = 5.47 \pm 0.78 \times 10^{-4}$ and $^{18}\text{O}/^{16}\text{O} = 2.34 \pm 0.17 \times 10^{-3}$) are in good agreement, and confirm that a portion of the original presolar grain is present in the extracted slice. The agreement of the ^{18}O values is outside the 1σ error bars, but these error estimates do not fully account for instrumental effects associated with the FIB section geometry. No additional isotopically anomalous grains were found in the section.

Results from STEM-based studies of the extracted section show grain 4c_3 to be distinctly enriched in Mg compared to the surrounding matrix material, qualitatively consistent with previous Auger analysis of 4c_3 in situ in the thin section, which indicated an elemental composition consistent with Mg-rich olivine: $\text{Mg}_{25}\text{Fe}_4\text{Si}_{14}\text{O}_{57}$. The higher spatial resolution of the STEM measurements, in this case ~ 5 nm com-

pared to 20 to 30 nm, reveals that the grain is compositionally heterogeneous at a ~ 10 nm scale. This heterogeneity is easily observed with conventional elemental mapping or principle component analysis (Figure 2b). The EDS-determined composition is non-stoichiometric and varies across the grain from $(\text{Mg} + \text{Fe})/\text{Si}$ of 0.7 to 1.5. Variation between the Auger Nanoprobe results obtained from the top and bottom surfaces of the extracted grain further confirms the heterogeneity. Minor amounts (< 3 at. %) of Al and S are observed by EDS in some regions of the grain. Despite the compositional heterogeneity, NanoSIMS measurements on the extracted section show the entire grain to be isotopically anomalous.

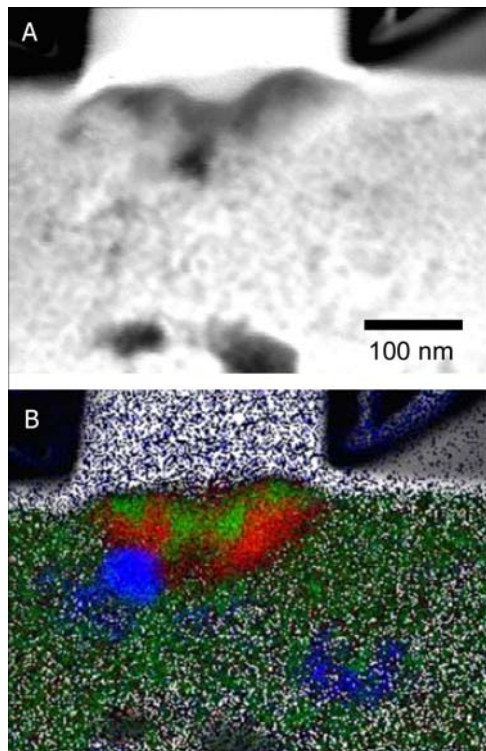


Figure 1. (a) HAADF image of the FIB slice of grain 4c_3. (b) Principal component EDS map. (red) Mg-O (blue) FeS; (green) Si-O.

In bright-field TEM imaging (Fig. 2) grain 4c_3 is distinct from the adjacent matrix material, which consists of a porous aggregate of Fe-rich olivine and Fe-sulfide nanoparticles. The SAED pattern of the grain (not shown) contains broad rings with a few distinct spots, consistent with an amorphous + nanocrystalline microstructure. The rings index to forsteritic olivine. Individual crystallites are revealed using dark-field imaging (Figure 2 inset).

Results from grain 2b_8 also show qualitative, but not quantitative agreement for major elements between Auger measurements of the grain surface composition and STEM-EDS of the grain cross-section. The micro-

structure of this grain is similarly finely-nanocrystalline, although the composition appears more homogenous.

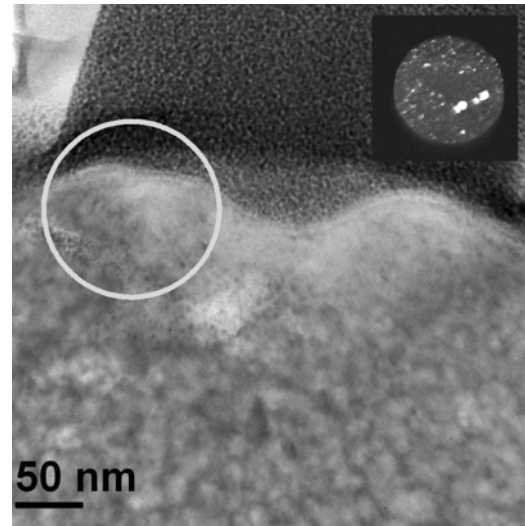


Figure 2. Bright-field TEM and dark-field (inset) images of grain 4c_3. The white circle indicates the SAED aperture position for the dark-field image.

In summary, we investigated the composition and microstructure of two Group 1 presolar silicates (low-mass AGB condensates) from MET 00426. The lack of parent body processing signatures in surrounding matrix materials, the finely nanocrystalline microstructures and the non-stoichiometric compositions together indicate that these grains condensed under complex, non-equilibrium conditions. Optical constants for modeling of the IR absorption of these grains are not available, however it is reasonable to assume, based on the poor crystallinity and heterogeneous compositions, that these grains would exhibit broad, featureless spectra indistinguishable from fully amorphous grains. This suggests that circumstellar disks could contain a larger fraction of crystalline material than previously estimated, in the form of fine-grained, compositionally heterogeneous, nanoscale aggregates.

References: [1] Nguyen A. N., et al. (2007) *ApJ*, 656, 1223-1240. [2] Zhang K. and Jiang B. W. (2008) *Sci. China Ser. G-Phys. Mech. Astron.*, 51, 1187-1199. [3] Molster F. and Kemper C. (2005) *Space Sci. Rev.*, 119, 3-28. [4] Messenger S., et al. (2005) *Science*, 309, 737-741. [5] Messenger S., et al. (2003) *Science*, 300, 105-108. [6] Keller L. P. and Messenger S. (2008) *LPSC 39*, #2347. [7] Busemann H., et al. (2008) *Meteor. & Planet. Sci. Suppl.*, 43, A30. [8] Vollmer C., et al. (2007) *ApJ*, 666, L49-L52. [9] Vollmer C., et al. (2007) *LPSC 38*, #1262. [10] Vollmer C., et al. (2006) *Meteor. & Planet. Sci.*, 41, 5194. [11] Nguyen A. N., et al. (2007) *ApJ*, 656, 1223-1240. [12] Stroud R. M., et al. (2008) *Meteor. & Planet. Sci. Suppl.*, 43, A148. [13] Floss C. and Stadermann F. J. (2009) *GCA*, in press.