TI-XANES AND EELS OF PRESOLAR TIC SUBGRAINS WITHIN LOW-DENSITY SUPERNOVA GRAPHITE GRAINS.

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Introduction: Presolar graphite grains from supernovae often contain 10-100 nm diameter subgrains that are predominantly TiC but also include some TiO_2. Here, we use X-ray absorption near-edge structure (XANES) [1] and electron energy loss spectroscopy (EELS) to probe the structure of the Ti atomic bonds in presolar TiC subgrains. Since atomic bonds are influenced by sample chemistry (e.g. composition, atom coordination, valance) and lattice defects (affecting atom coordination, bond distances, etc.), the bond structure can provide insight into the formation conditions in the grains' parent stellar outflows.

Samples and Methods: We measured TiC subgrains in 4 presolar supernova graphite grains from the Orgueil meteorite [2], in addition to terrestrial TiC and TiN standards. The presolar graphite grains and standards were embedded in resin and microtomed into 70-nm-thick sections, which were deposited on SiO-coated TEM grids. The sections were taken to the scanning transmission X-ray microscope at Beamline 5.3.2.2 of the Advanced Light Source, Lawrence Berkeley National Laboratory, where we measured the Ti $L_{3,2}$ near-edge structure. These data were compared with previous XANES [3] and EELS [4] measurements of Ti-oxide standards. Following [5], the fine structure of $L_{3,2}$ edges was parameterized by measuring the L_3/L_2 integrated intensity ratio and the position of the L_3 peak; these were correlated to Ti valance. For spectra with apparently split L_3 peaks we used the most dominant L_3 peak in our analysis, although for future work we will expand this parameterization to include minor peak positions and heights.

Results: The L_3 peak position and L_3/L_2 integrated ratio allows us to distinguish between the valence states of our standards which contain minimal peak splitting: TiC, TiN, and TiO. However, the results for the Ti_xO_y (x,y>1) samples overlap considerably and are complicated by significant peak splitting. The L_3 peak position for most of our presolar TiC subgrains match that of our TiC standard, although their L_3/L_2 integrated ratios exhibit a larger spread. One particularly large TiC subgrain (~300nm) has an L_3/L_2 integrated ratio that matches well with that of the TiC standard, but its L_3 peak position is shifted to a lower energy than any of the standards.

Discussion: By studying presolar TiC subgrains with both XANES and EELS we will be able to utilize the benefits of both techniques, notably the higher energy resolution (~0.1eV) of XANES and the higher spatial resolution (~10nm) and signal-to-noise ratio of EELS. Future EELS measurements of these samples will allow us to quantify the effects of the different energy calibration procedures for each technique and to confirm the L_3 energy shift observed in the large TiC subgrain. C, N, and O-XANES data acquired on the presolar grains will be addressed in future work.

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References: [1] Nittler, L. et al. 2011. *Meteoritics & Planetary Science*, 46:A178 #5361 [2] Groopman, E. et al. 2011. *Meteoritics & Planetary Science*, 46:A82 #5031. [3] Zega, T. J. et al. 2011. 42nd Lunar & Planetary Science Conference. Abstract #1465. [4] Dhumal, S. Y. et al. 2009. *Applied Catalysis B* 86:145-151 [5] Daulton, T. L. and Brenda, J. L. 2006. *Ultramicroscopy* 106:561