

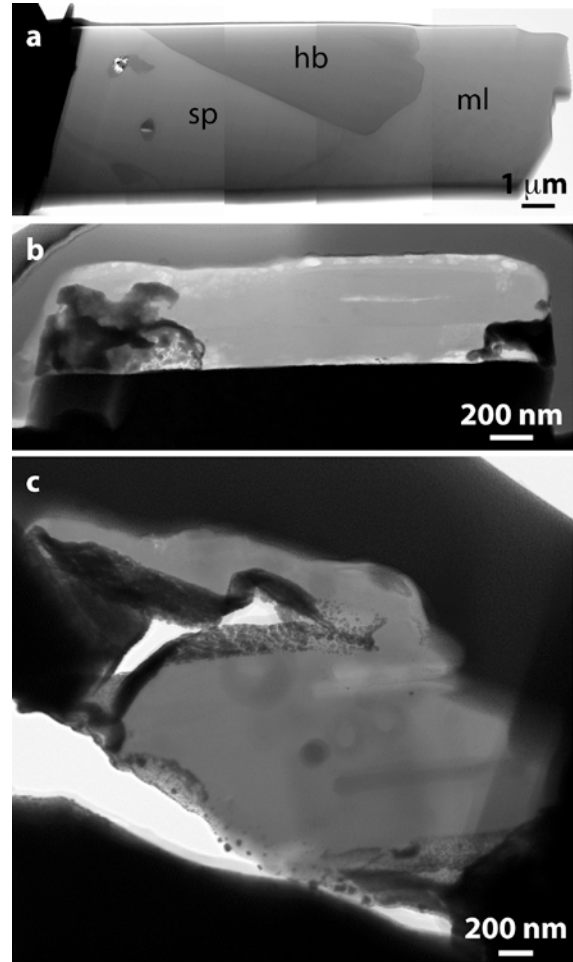
**Ti-XANES OF SOLAR AND PRESOLAR HIBONITE.** T. J. Zega<sup>1</sup>, L. R. Nittler<sup>2</sup>, R. M. Stroud<sup>1</sup>, C. M. O'D. Alexander<sup>2</sup>, and A.L.D. Kilcoyne<sup>3</sup>, <sup>1</sup>Code 6366, Materials Science and Technology Division, Naval Research Laboratory, 4555 Overlook Ave. SW, Washington, DC 20375. <sup>2</sup>Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd. NW, Washington, DC 20015. <sup>3</sup>Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720. (tzega@nrl.navy.mil).

**Introduction:** Hibonite is the first phase after corundum that is thermodynamically predicted to condense from a gas of solar composition [1]. It has been identified as an important constituent of calcium-aluminum-rich inclusions (CAIs) [2] and as a bona fide presolar grain [3]. Knowledge of the structure and composition of hibonite can therefore provide information on the physical and chemical conditions of the early solar system and that of ancient stars.

In pure form, hibonite has a composition of  $\text{CaAl}_{12}\text{O}_{19}$ . However, [4-6] have shown that solar and presolar hibonite grains can contain variable amounts of minor elements, including Mg, Ti, Fe, V, and Si. Ti is particularly interesting because it can occur in reduced ( $\text{Ti}^{3+}$ ) and oxidized states ( $\text{Ti}^{4+}$ ) [4], reflecting the redox conditions under which the host grain formed or last equilibrated. We have initiated an investigation into the oxidation state of Ti in hibonite using X-ray absorption near-edge structure (XANES) spectroscopy. Here we report our first measurements from solar and presolar hibonite grains.

**Samples and Analytical Methods:** We measured one solar and two presolar hibonite grains (Fig. 1): (1) a lath-shaped hibonite grain, sandwiched between spinel and melilite grains within a petrographic thin section of a Wark-Lovering rim (WLR) surrounding a CAI in the Allende CV3 chondrite (TS25, U. Chicago) previously identified in a petrographic study by [7]; (2) a Group 2 presolar grain (KH15) identified in an acid-resistant residue of the Krymka LL3.1 ordinary chondrite; and (3) a Group 4 presolar grain (UOC-H1) identified in a mixed acid-resistant residue of unequilibrated ordinary chondrites (UOC) Queen Alexandra Range 97008, Mount Wisting 95300, and Meteorite Hills 00452. We attempted to measure a third presolar grain (KH2), but its Ti abundance was too low to produce spectra with good signal-to-noise ratios. The presolar grains were previously identified based on their O-isotopic compositions; grain KH15 is believed to have formed in a low-mass star, evolved through the asymptotic giant branch (AGB), whereas UOC-H1 formed in a Type II supernova [3].

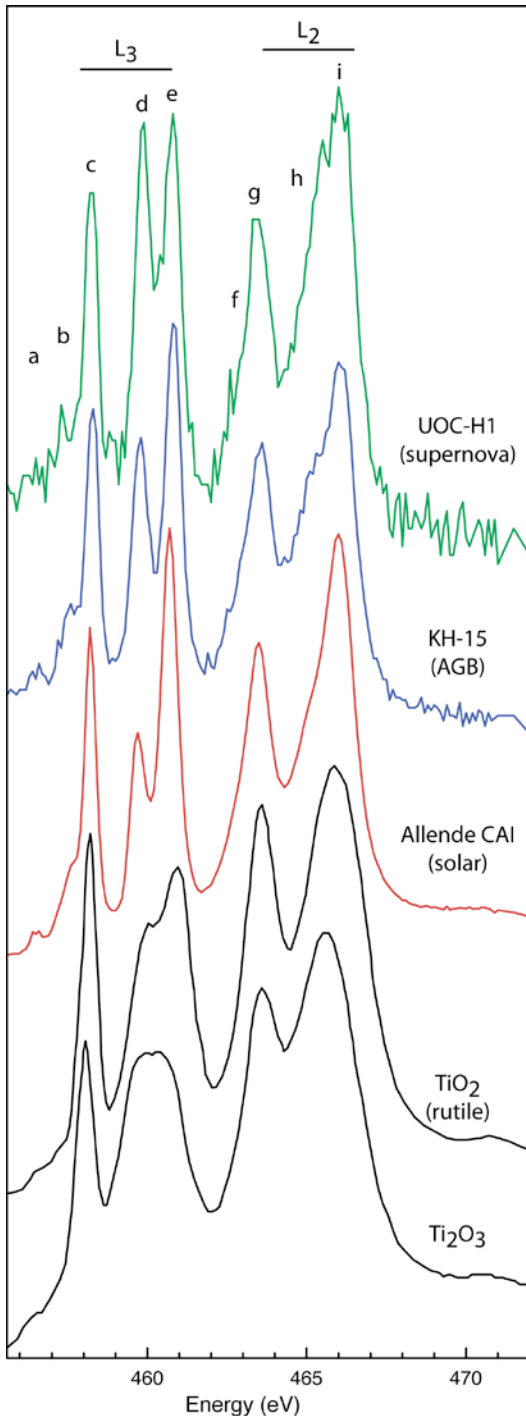
All hibonite grains were extracted and thinned, *in situ*, to electron and X-ray transparency with an FEI Nova 600 focused-ion-beam scanning-electron microscope using previously described methods [8]. Grain microstructure and chemistry were investigated with transmission electron microscopy (TEM) [6,8]. The



**Fig. 1.** Bright-field TEM images of hibonite grains. (a) from a WLR surrounding a CAI in Allende TS25 sandwiched between spinel (sp) and melilite (ml), (b) presolar supernova grain UOC-H1, (c) presolar AGB grain KH15.

FIB sections were taken to the Advanced Light Source (LBNL) where we used the scanning transmission X-ray microscope (STXM) on beamline 5.3.2 to measure the near-edge structure of the Ti  $L_{2,3}$  edge. X-ray absorption images were acquired over energy ranges of 330 to 485 eV and 440 to 471.5 eV with an energy step between images  $\leq 0.5$  eV. Both ranges included high-resolution scans (0.1 eV) at the Ti  $L_{2,3}$  edge, but the larger energy range included scans of the Ca  $L_{2,3}$  edge as well. We used pixel size and dwell times that respectively ranged from 25 to 50 nm and 3 to 6 ms.

**Results and Discussion:** The spectra for the three hibonite grains are shown in Figure 2 together with



**Fig. 2.** XANES spectra from the three hibonite grains shown together with oxides from [9].

TiO<sub>2</sub> and Ti<sub>2</sub>O<sub>3</sub> from [9] for reference to Ti<sup>4+</sup> and Ti<sup>3+</sup>, respectively. The signal-to-noise ratio varies somewhat for the spectra, due to the Ti abundances within the grains, i.e., 1.5 at% for the Allende CAI, 1.3 at% for AGB grain KH15, <1 at% for supernova grain UOC-H1. Nonetheless, the overall near-edge structure (NES)

of the spectra from solar and presolar hibonite grains are similar to one another and to those of the oxides.

The hibonite spectra contain two primary sets of peaks, corresponding to the L<sub>3</sub> and L<sub>2</sub> edges, which are due to electronic transitions from 2*p* to 3*d* states [10,11]. The L<sub>3</sub> edge occurs at lower energy and is split into three main peaks (c,d,&e). The L<sub>2</sub> edge, at slightly higher energy contains two main peaks (g&i) with shoulders (f&h). Two pre-peaks (a&b) also occur, possibly due to core-hole interactions [12]. The high-energy splitting of L<sub>3</sub> edge (peaks d&e) has been attributed to distortion of the coordination environment; the absence of such splitting in the L<sub>2</sub> edge was attributed to lifetime broadening effects [10].

The most significant difference among the three hibonite spectra is the splitting of the high-energy peak of the L<sub>3</sub> edge. Specifically, the relative intensities of peaks d and e vary: they are approximately equal in the spectrum from UOC-H1; peak d is approximately 50% of peak e in KH15; and in the Allende CAI, peak d is approximately 25% of peak e. Spectra from crystalline materials containing <sup>48</sup>Ti exhibit this characteristic splitting, whereas those containing <sup>46</sup>Ti and <sup>47</sup>Ti lack such splitting [9]. Thus, comparison of the hibonite spectra suggests a gradual increase in octahedrally coordinated Ti from the solar grain (Allende CAI) to the AGB grain (KH15) to the supernova grain (UOC-H1). Further, the overall NES of the spectra from the solar and AGB hibonites more closely resemble that from rutile, suggesting an abundant Ti<sup>4+</sup> component, whereas that from the supernova grain is more similar to that of Ti<sub>2</sub>O<sub>3</sub>, suggesting an abundant Ti<sup>3+</sup> component. These data qualitatively suggest that the redox state of the circumstellar environment in which the supernova grain formed was possibly more reducing than the AGB and solar grains. Measurements on additional grains and quantification of the Ti<sup>4+</sup>/Ti<sup>3+</sup> ratio, which we plan to do, should reveal the range of temperature and *f*O<sub>2</sub> conditions under which the grains formed and verify whether this trend holds.

**References:** [1] Ebel D. S. 2006 *MESS II*, 253-277. [2] MacPherson G. J. (2005) *Treatise on Geochemistry*, 201-246. [3] Nittler L. R. et al. (2008) *ApJ.*, 682, 1450-1478. [4] Beckett J. R. (1988) *Geochim. Cosmochim. Acta*, 52, 1479-1495. [5] Simon S. B. et al. (2006) *Amer. Min.*, 91, 1675-1687. [6] Zega T. J. et al. (2010) *ApJ. Submitted*. [7] Cosarinsky M. et al. (2006) *LPS XXXVII*, Abstract #2357. [8] Zega T. J. et al. (2007) *Meteoritics & Planet. Sci.*, 42, 1373-1386. [9] Henderson G. S. et al. (2002) *Phys. Chem. Minerals*, 29, 32-42. [10] de Groot F. M. F. et al. (1990) *Phys. Rev. B*, 41, 928-937. [11] Brydson R. (1989) *J. Phys. Condens. Matter*, 1, 797-812. [12] Crocombette J. P. (1994) *J. Phys. Condens. Matter* 6, 10811-10821.