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Scanning Transmission X-Ray Microscopy on Calcium Aluminate From the Early Solar System And Ancient Stars

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Introduction: $CaAl_{12}O_{19}$ (hibonite) is a refractory oxide that occurs naturally in primitive meteorites. Some hibonite grains formed within our solar system ('solar') from the cooling nebular gas that gave rise to our Sun and planets, whereas others condensed within the gaseous envelopes that surrounded ancient stars ('presolar') [1,2]. Hibonite can contain substitutional Ti in reduced (Ti^{3+}) and oxidized (Ti^{4+}) states [3], reflecting the redox conditions under which the host grain formed or last equilibrated. We are investigating the oxidation state of Ti in hibonite using X-ray absorption near-edge structure spectroscopy to gain insight into the physical and chemical conditions of the early solar system and primordial circumstellar environments.

Samples and Analytical Methods: We measured one solar and two presolar hibonite grains (Fig. 1) previously identified via electron microprobe and secondary ion mass spectrometry [2,4]. All grains were extracted and thinned, *in situ*, to electron and X-ray transparency using previously described focused-ion-beam (FIB) methods [5]. Grain structure and composition were investigated with transmission electron microscopy [6]. We used the scanning transmission X-ray microscope on beamline 5.3.2 at the Advanced Light Source to measure the near-edge structure of the Ti $L_{2,3}$ edge in the FIB sections. We performed high-resolution (0.1 eV) scans of the Ti $L_{2,3}$ edge and 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 hibonite grains are shown in Figure 2 together with TiO_2 and Ti_2O_3 from [7] for reference to Ti^{4+} and Ti^{3+}, respectively. The signal-to-noise ratio varies somewhat, due to the Ti abundances within the grains, i.e., 1.5 at% for the solar grain, 1.3 at% for presolar grain KH15, <1 at% for presolar grain UOC-H1. Nonetheless, the overall near-edge structures (NES) of the spectra from the 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_3 and L_2 edges, which are due to electronic transitions from 2*p* to 3*d* states [8,9]. We will discuss each at the meeting, but here we note that the most significant difference among the spectra is the splitting of the high-energy peak of the L_3 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 solar grain (Allende CAI), peak d is approximately 25% of peak e. Spectra from crystalline materials containing ^{VI}Ti exhibit this characteristic splitting, whereas those containing ^{IV}Ti and ^{V}Ti lack such splitting [7]. Thus, comparison of the hibonite spectra suggests a gradual increase in octahedrally coordinated Ti from the solar grain to presolar grain KH15 to supernova grain UOC-H1. Further, the overall NES of the spectra from the solar and KH15 hibonites more closely resemble that from rutile, suggesting an abundant Ti^{4+} component, whereas that from the supernova grain is more similar to that of Ti_2O_3, suggesting an abundant Ti^{3+} 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^{4+}/Ti^{3+} ratio (underway) should reveal the range of oxygen fugacity conditions under which the grains formed and verify whether this trend holds.

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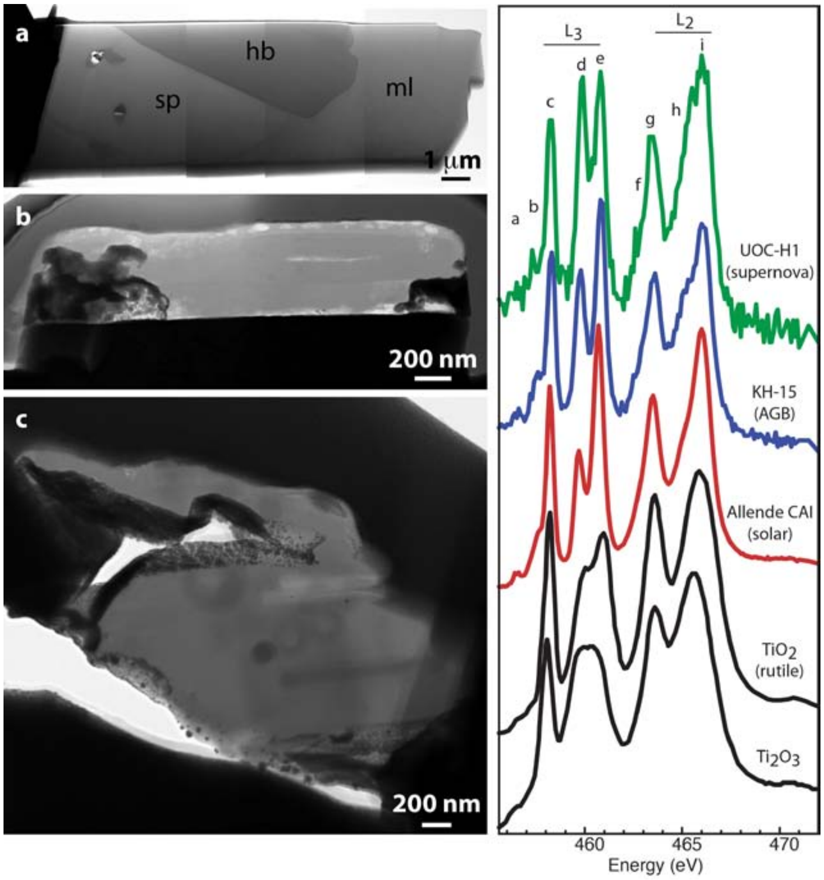

FIG. 1. Left: Bright-field scanning TEM images of FIB sections of (a) solar hibonite (hb) between spinel (sp) and melilite (ml) from a calcium-aluminum-rich inclusion (CAI) of the Allende meteorite, (b) presolar supernova grain UOC-H1, and (c) presolar grain KH-15 from a star evolved through the asymptotic giant branch (AGB). Right: X-ray absorption spectra of the Ti $L_{2,3}$ edge for the various grains as indicated, together with oxides from [7].