**MEASUREMENT OF THE OXIDATION STATE OF Ti IN SOLAR AND PRESOLAR HIBONITE.** T. J. Zega[1] L. R. Nittler[2], R. M. Stroud[3], C. M. O'D. Alexander[2], and A.L.D. Kilcoyne[4], [1]Lunar and Planetary Laboratory, University of Arizona, 1629 E. University Blvd., Tucson AZ 85721. [2]Department of Terrestrial Magnetism, Carnegie Institution of Washington, 5241 Broad Branch Rd. NW, Washington, DC 20015. [3]Code 6366, Materials Science and Technology Division, Naval Research Laboratory, 4555 Overlook Ave. SW, Washington, DC 20375. [4]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720. (tzega@lpl.arizona.edu).

**Introduction:** Hibonite is a refractory oxide (nominally $CaAl_{12}O_{19}$) believed to be among the first solids to have condensed in the early solar system [1]. It has been reported to contain Fe, V, Ti, Mg, and Si in solid solution [2,3]. Beckett *et al.* [4] showed that hibonite within Ca-Al-rich inclusions (CAIs) contains both $Ti^{3+}$ and $Ti^{4+}$ and that the ratio of these cations reflect the oxygen fugacity ($fO_2$) under which the grains condensed in the early solar nebula. In a previous effort, we reported on intial measurements of Ti in both solar (CAI) and presolar hibonite grains using X-ray absorption near-edge structure (XANES) spectroscopy [5]. We have expanded that effort and here report on measurements of additional hibonites and quantification of the Ti-valence ratio.

**Samples and Analytical Methods:** We measured a combination of natural and synthetic hibonites: (1) a lath-shaped hibonite grain (E8-10) contained within the core melilite of a CAI in the Allende CV3 chondrite (TS25, U. Chicago), and (2) synthetic hibonites prepared by [4] under controlled $fO_2$ conditions. These measurements complement those we made previously on a hibonite grain extracted from a Wark-Lovering rim (WLR) and two presolar hibonites (supernova grain UOC-H1 and AGB grain KH15) [5].

The solar and presolar grains (PSGs) were extracted and thinned to electron and X-ray transparency with FEI Nova 200 and Nova 600 focused-ion-beam scanning-electron-microscopes (FIB-SEM) respectively at Arizona State University and the Naval Research Laboratory, according to procedures previously described by [6]. The synthetic hibonites were embedded in epoxy and mechanically sliced with an ultramicrotome for analysis and comparison with their natural counterparts. The FIB and microtome sections were taken to the Advanced Light Source at Lawrence Berkeley National Laboratory (LBNL) where we used the scanning transmission X-ray microscope on beamline 5.3.2 to measure the Ti $L_{2,3}$ near-edge structure (see [5] for analytical details).

**Results:** Selected spectra of natural and synthetic hibonite are shown in Figure 1, together with rutile ($TiO_2$) and $Ti_2O_3$, for reference to $Ti^{4+}$ and $Ti^{3+}$, respectively. The near-edge structure (NES) of rutile and $Ti_2O_3$ has been previously characterized by four main peaks, labeled a, b, c, and d (Fig. 1), also referred to as white lines [e.g., 7]. The four main peaks are part of two doublets comprising the $L_3$ (a&b) and $L_2$ (c&d) edges, which are due to electronic transitions from $2p$ to $3d$ states. In both rutile and $Ti_2O_3$, the Ti is coordinated to six O atoms (and each O to three Ti atoms). Previous work has shown that the octahedrally coordinated Ti is largely responsible for the splitting of the $L_3$ and $L_2$ edges into the doublets (a&b and c&d) [7,8], but the fine structure also depends on site symmetry and valence state.

In comparison, the NES of the hibonite spectra are more similar to that acquired from rutile than $Ti_2O_3$, qualitatively suggesting that they contain an abundant, octahedrally coordinated $Ti^{4+}$ component, consistent with the hibonite structure and crystal chemistry [9]. However, previous measurements by [4] indicated that meteoritic hibonite can also contain $Ti^{3+}$ substituting for $Al^{3+}$ in five-fold sites. Comparison of the hibonite spectra (Fig. 1) with that of $Ti_2O_3$ reveals broad overlap of the former's pre-peak (a') with the latter's first white-line (a), qualitatively suggesting a minor amount of $Ti^{3+}$ in the meteoritic hibonite. In order to quantify the $Ti^{3+}/Ti^{4+}$ ratio, we employed a modified form of the white-line ratio method that [10] reported for quantification of Ti-valence ratios in Ti oxides based on TEM-EELS measurements.

Using STXM, we measured samples of hibonites synthetically produced by [4] over a range of $fO_2$ conditions. From these measurements, we developed a calibration curve to quantify the $Ti^{4+}$ to total Ti ($Ti^{4+}/\Sigma Ti$) ratios, and hence, the $fO_2$ under which the unknown hibonites formed or last equilibrated. From these measurements, we quantify $Ti^{4+}/\Sigma Ti$ ratios of 0.85 and 0.86 ($\pm 0.01$), respectively, for presolar supernova grain UOC-H1 and AGB grain KH15; these ratios translate into log $fO_2$ of -19.2 ($\pm 1.1$) and -16.6 ($\pm 1.3$) respectively. In comparison, we quantify $Ti^{4+}/\Sigma Ti$ ratio of 0.89 ($\pm 0.01$) and 0.95 ($\pm 0.02$) for the solar grains respectively extracted from the melilite inclusion and WLR of an Allende CAI; these ratios respectively translate into log $fO_2$ of -13.9 ($\pm 1.9$) and -4.5 ($\pm 3.0$).

**Discussion:** In general, we find that the relationship between the white-line ratio and the Ti-oxidation state is strongly dependent on the signal-to-noise ratio. We are still exploring the sources of error in our measurements, but taken at face value, the data suggest that

these hibonite grains could have recorded a wide range of $fO_2$ conditions. Supernova grain UOC-H1 recorded reducing conditions comparable to those inferred by [11] for Type A and B CAIs in CV3 chondrites (average log $fO_2$ = -19.9), whereas AGB grain KH15 recorded more oxidizing conditions. In comparison, the $fO_2$ conditions recorded by the solar hibonite grains (Allende) are highly oxidizing relative to those recorded by the PSGs, and for those inferred previously for CAIs.

Understanding whether or not the inferred conditions represent those that prevailed during condensation or at some point later is important for determining what they can tell us about the histories of these grains. Of the samples reported here, grain KH15 and EH-10 were isolated from meteorite falls, and are likely to be the most pristine. In comparison, UOC-H1 was identified in a residue of three unequilibrated ordinary chondrites [12] that were recovered from Antarctica with varied weathering grades. While it is possible that terrestrial alteration could have affected the crystal chemistry of UOC-H1, it seems unlikely given that its nuclesynthetic history has been preserved, and the $fO_2$ conditions recorded by it are comparable to those reported previously for solar hibonites. The inferred conditions should therefore represent those that prevailed in the circumstellar envelopes from which the PSGs condensed.

In comparison, the $fO_2$ values recorded by the solar grains are high relative to those inferred for other CAIs. Interestingly, the inferred $fO_2$ for the WLR is higher than that of the inclusion. Prior isotopic measurements on WLRs suggest that some could have formed as much as 130,000 years after the core melilite [13] and could have done so under conditions that were much more oxidizing than that of the inclusion [14]. However, the $fO_2$ inferred for the solar grains are ≥5 orders of magnitude higher than canonical nebular values.

Models indicate that the $fO_2$ could have been locally enhanced in the early solar nebula via shock-induced vaporization of solids and water vapor in an icy region, but such enhancement is not expected to have exceeded five orders-of-magnitude above canonical values [15]. We have not observed evidence of such effects in this WLR assemblage from the Allende chondrite. An alternative explanation and working hypothesis is that secondary processing on the Allende parent body could have affected the crystal chemistry of the Allende hibonites measured here. We note that Allende is part of the oxidized subgroup of CV3 chondrites, and thermal processing of it up to 600°C was previously reported [16,17]. Continued measurements

of the kind we describe here will reveal whether such a disparity holds true for additional grains.

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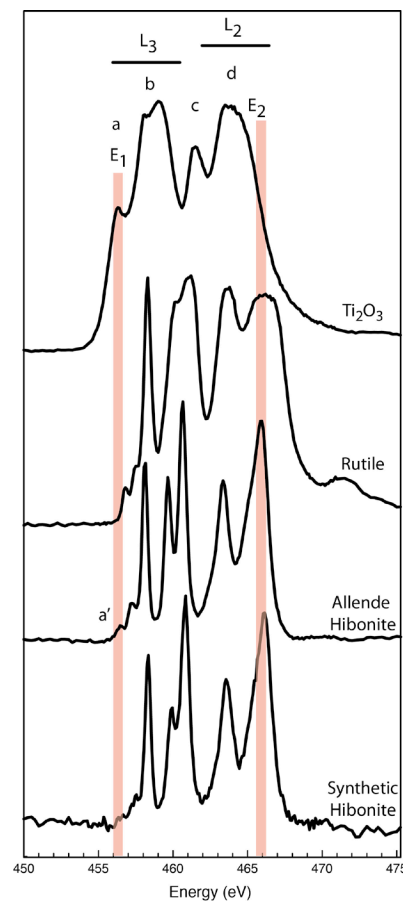


**Fig. 1.** Ti $L_{2,3}$ XANES spectra from reference oxides and hibonites. Energy windows ($E_1$ & $E_2$) used for quantification of the $Ti^{4+}/\Sigma Ti$ ratio shown (red). Synthetic hibonite (All 2-1) was equilibrated at log $fO_2$ = -7.5; $Ti^{4+}/\Sigma Ti$ = 0.96 [4].