

**THE NEED FOR EXPERIMENTS IN THE INTERPRETATION OF MEASUREMENTS FROM NATURAL SAMPLES: SOME EXAMPLES.** S. B. Simon<sup>1</sup> and L. Grossman<sup>1,2</sup>, <sup>1</sup>Dept. of the Geophysical Sci., 5734 S. Ellis Ave., Univ. of Chicago, Chicago, IL 60637 (sbs8@uchicago.edu) <sup>2</sup>The Enrico Fermi Institute, 5640 S. Ellis Ave., Univ. of Chicago, Chicago, IL 60637.

**Introduction:** Experiments are necessary for calibration of measurements on natural samples. They can provide important constraints that help us understand and draw conclusions about our observations. Described below are several of our investigations for which successful experiments could lead to major breakthroughs in data interpretation.

**Coexistence of  $Ti^{3+}$  and  $Fe^{2+}$  in chondrule olivine:** The  $Ti_2O_3/TiO_2$  buffer curve is ~5 log units below (more reducing than) that for  $Fe/FeO$  (IW). A system of solar composition, at ~IW-7, is so reducing that  $Ti^{3+}$  and  $Ti^{4+}$  can coexist, making the valence of Ti in an assemblage a valuable indicator of whether or not it equilibrated at solar nebular  $f_{O_2}$  conditions. In an effort to determine if the precursors of type I (forsteritic, FeO-poor) chondrules were more reduced than those of type II (relatively FeO-rich) chondrules, we used XANES (X-ray absorption near-edge spectroscopy) to determine the oxidation state of Ti in both chondrule types in Semarkona [1]. We found  $Ti^{3+}$  in both chondrule types and that Ti valence is not correlated with fayalite content. In type I olivine, the  $Ti^{3+}/Ti^{4+}$  ratio decreases from cores to rims of olivine crystals while the fayalite content is constant. In type II olivine, the Ti valence is uniform while fayalite content increases from crystal cores to rims. Under conditions where  $Ti^{3+}$  is stable, however, the proportion of iron that is oxidized would be vanishingly small, so  $Ti^{3+}$  should not be found in a phase with measurable amounts of FeO. At this point our best explanation for the coexistence of  $Ti^{3+}$  and  $Fe^{2+}$  is that both chondrule types started with reduced precursors, were exposed to relatively oxidizing conditions, and the Fe oxidation state equilibrated more rapidly than that of Ti. This inference should be tested by experiments in which the relative rates of redox equilibration of Ti and Fe in chondrule compositions are measured.

**Calibration of  $Ti^{3+}/Ti^{4+}$  ratios in hibonite, spinel and olivine against oxygen fugacity:** The Ti-rich pyroxene in refractory inclusions, termed fassaite [2], is well-known to contain  $Ti^{3+}$ . From exchange reactions between fassaite components and coexisting melilite and spinel, the  $Ti^{3+}/Ti^{4+}$  ratios in this phase have been shown to be quantitatively consistent with equilibration with a gas that was at least as reducing as a solar gas [3]. Another phase known to contain  $Ti^{3+}$  is hibonite, from electron spin resonance analysis of a

Murchison inclusion [4]. Using XANES, we [5] found that spinel, pyroxene and hibonite in a suite of Murchison inclusions also contain  $Ti^{3+}$  and, like typical chondrule olivine [1], can have  $Ti^{3+}/Ti^{4+}$  ratios within the range observed for fassaite. These phases do not occur in assemblages for which the redox equilibria have been calibrated and we cannot assume that a given  $Ti^{3+}/Ti^{4+}$  ratio in any of these phases reflects equilibration at the same  $f_{O_2}$  as it would for fassaite. Fassaite remains the only calibrated  $f_{O_2}$  indicator that shows that anything in chondrites formed in a system that was anywhere close to solar in composition. Experiments are needed to calibrate  $Ti^{3+}/Ti^{4+}$  ratios of hibonite, spinel and olivine occurring in representative assemblages as a function of their equilibrium  $f_{O_2}$ 's of formation.

**Partitioning of  $V^{2+}$  between liquid and pyroxene:** Electron probe traverses across fassaite in Type B1 inclusions have shown that, near their edges, some grains exhibit sharp increases in Ti and V contents and in  $Ti^{3+}/Ti^{4+}$  but, XANES shows, not in  $V^{2+}/V^{3+}$  [6]. From the preference of fassaite for  $Ti^{3+}$  over  $Ti^{4+}$  [7] and the change in Ti valence at the spikes, it appears that these grains recorded late reduction events in the crystallization histories of these inclusions, but we do not know if this explanation is consistent with the behavior of V. The ionic radius of  $V^{3+}$  gives it a better fit in the pyroxene M1 site than that of  $V^{2+}$  [8], but the latter cation does not require a coupled substitution for charge balance, so  $V^{2+}$  and  $V^{3+}$  may be equally compatible in fassaite. To better understand the measurements, partitioning data for  $V^{2+}$  between fassaite and CAI liquids are needed.

**Conclusion:** Although experiments at near-solar  $f_{O_2}$ 's are quite challenging to perform, they can lead to improvements in our fundamental understanding of early solar system history and processes related to the formation of refractory inclusions and chondrules.

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