

**EVIDENCE FOR DIVALENT VANADIUM IN ALLENDE CAI FASSAITE AND IMPLICATIONS FOR FORMATION CONDITIONS.** S.R. Sutton<sup>1,2</sup>, S. Simon<sup>1</sup>, L. Grossman<sup>1</sup>, J.S. Delaney<sup>3</sup>, J. Beckett<sup>4</sup>, M. Newville<sup>2</sup>, P. Eng<sup>2</sup>, and M. Rivers<sup>1,2</sup>. <sup>1</sup>Department of Geophysical Sciences and <sup>2</sup>Consortium for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637 (sutton@cars.uchicago.edu); <sup>3</sup>Geology Department, Rutgers University, New Brunswick, NJ; <sup>4</sup>Division of Geological & Planetary Sciences, Caltech, Pasadena, CA 91125

**Introduction:** Fassaite, a Ti-, Al-rich clinopyroxene, is a major mineral in Type B refractory inclusions in carbonaceous chondrites. Stoichiometric treatment of electron microprobe data reveals that  $\text{Ti}^{3+}/\text{Ti}^{4+} \sim 1$  [1] in the fassaite, and experimental work shows that this implies crystallization at  $f\text{O}_2 \sim 10^{-19}$  at 1200°C [2], very close to the  $f\text{O}_2$  of a gas of solar composition. Many fassaite grains are strongly zoned in Ti, whose abundance decreases from core to rim [3], probably due to the compatibility of  $\text{Ti}^{3+}$  in fassaite during crystallization of the molten CAI. Superimposed on these profiles are zones where Ti and V contents spike upward together, within which the  $\text{Ti}^{3+}/\text{Ti}^{4+}$  ratio also increases significantly. As  $\text{Ti}^{3+}$  is more compatible than  $\text{Ti}^{4+}$ , the spikes are thought to be due to variable  $f\text{O}_2$  during crystallization. Thermodynamic calculations show that VO and  $\text{V}_2\text{O}_3$  are in equilibrium at approximately the same T- $f\text{O}_2$  conditions as  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$ , but whether variable  $f\text{O}_2$  can be responsible for the V spikes is unclear, as  $\text{V}^{2+}$  would not be expected to be more compatible than  $\text{V}^{3+}$  in clinopyroxene.

We report here on our initial results using x-ray absorption near edge structure (XANES) spectroscopy for determining the oxidation state of vanadium [4,5,6] in the zoned Allende fassaite and synthetic pyroxene. The ultimate goal is to place constraints on the oxygen fugacity history of the nebular environment during the crystallization of individual fassaite grains by also determining the pyroxene/liquid partitioning behavior of V as a function of oxidation state.

**Methods:** The Allende fassaite studied here was grain ZF2 in thin section TS34, a Type B1 inclusion [3]. In addition, spectra were obtained on synthetic pyroxene and melilite crystallized at the C-CO buffer (CMAS @  $T_{\text{max}}=1280^\circ\text{C}$ ;  $\log(f\text{O}_2) \sim -17$ ) and cooled at 50K/hr to 1000°C before quench.

The microXANES analyses were performed with the GeoSoilEnviroCARS x-ray microprobe at the Advanced Photon Source (APS, Argonne National Laboratory, IL). The apparatus consisted of an APS undulator x-ray source, silicon (111) cryogenic monochromator, Kirkpatrick-Baez microfocusing mirrors and a germanium solid state x-ray fluorescence detector. The x-ray beam size was 5  $\mu\text{m}$ . XANES spectra were typically measured over the V K absorption edge (5465 eV) from 5450 to 5500 in 0.2 eV steps ( $\sim 10$  sec dwell) with additional measurements made well below (5400 eV) and well above (5700 eV) the absorption edge for

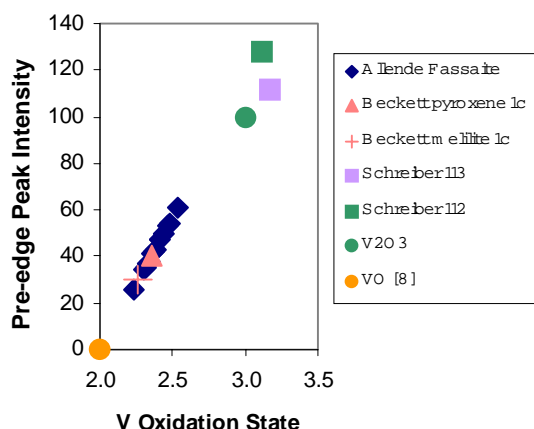
normalization purposes (absorption step defined to be 1000). The pre-edge peak (near 5470 eV) was characterized by the energy and normalized intensity at the maximum. Previous work has shown these parameters to be useful for V oxidation state determinations [4,5,6]. Energy calibration was accomplished using a V metal foil spectrum and assigning the first inflection point to be 5465 eV. Standardization in terms of pre-edge peak energy and intensity versus oxidation state was accomplished using glasses characterized by optical spectrometry (H. Schreiber suite) [7] and oxides ( $\text{VO}$ ,  $\text{V}_2\text{O}_3$ ,  $\text{V}_2\text{O}_4$ , and  $\text{V}_2\text{O}_5$ ) [8].

**Results:** A scan of V concentration versus position was performed (2  $\mu\text{m}$  step) across the V spike in a TS34 fassaite grain previously studied by electron microprobe. This scan showed the presence of the narrow ( $< \sim 10 \mu\text{m}$ ), high-vanadium zone. The concentration “step” of about 10:1 was comparable to that observed in the electron microprobe data. Vanadium oxide concentrations in the spots analyzed varied from 100 to 3300 ppm.

XANES spectra were obtained as spot analyses at pre-selected positions near those chosen for electron microprobe analysis. Qualitatively, the fassaite spectra were similar to one another, exhibiting very small pre-edge peaks indicative of a highly reduced oxidation state. The pre-edge peak intensities fall between those of  $\text{V}^{3+}$ -dominated oxides (e.g., Schreiber 112 and 113) and  $\text{V}^{2+}$  oxides (Figure 1). The latter are expected to show no pre-edge intensity (as in VO) due to the expected high symmetry of the octahedral site. Thus, the presence of a pre-edge peak indicates vanadium in the fassaite is not totally divalent.

XANES spectra can also be sensitive to crystallographic orientation relative to the polarization direction of the synchrotron radiation, but this effect is less important as site symmetry increases. To check for this effect, two spot analyses repeated with the thin section rotated 90 degrees produced identical spectra, suggesting negligible orientation effect.

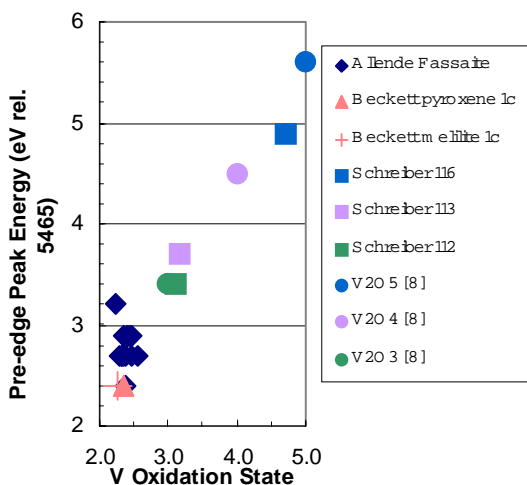
Quantitative oxidation states were computed from the pre-edge peak intensities using a linear interpolation between the intensity measured for Schreiber glass 112 (oxidation state determined by optical spectrometry of 3.12) and zero ( $\text{V}^{2+}$ ). The results are shown graphically in Figure 1. The mean V oxidation state for the fassaite measurements is 2.4 with a standard deviation of 0.1. The fairly tight range of intensity



**Figure 1:** Pre-edge peak intensity versus V oxidation state showing  $V^{2+}$ - $V^{3+}$  region only. Oxidation states for the unknowns are shown on a tie line between the  $V^{+2}$  oxide (VO) and the Schreiber 112 glass (oxidation state = 3.1).

values is comparable to the typical measurement precision. The pre-edge peak energies are also consistent with the “intensity-based” oxidation states, being lower in energy (more reduced) than the peaks for the  $V^{3+}$ -dominant standards, Schreiber glasses 112 and 113 and  $V_2O_3$  (Figure 2). The V oxidation state variation within the Allende fassaite grain is uncorrelated with vanadium content (correlation coefficient = 0.07).

XANES spectra obtained on synthetic melilite 1c and pyroxene 1c yielded oxidation states consistent with those of the Allende fassaite (2.4). These results suggest that the pyroxene crystallization experiments reproduced fairly closely the redox conditions under



**Figure 2:** Peak energies vs oxidation state. Oxidation states for the Allende and Beckett samples are those determined using the intensities (Figure 1).

which the Allende fassaite grain crystallized, and imply that thermodynamic calculations showing coexistence of pure VO and pure  $V_2O_3$  at solar nebular conditions are applicable to fassaite.

**Discussion:** The oxidation state standards used in this work are the Schreiber 112 and 113 glasses containing predominantly  $V^{3+}$  and a  $V^{2+}$  oxide (VO). An underlying assumption is that the site geometry is the same in the standard and the unknown. This is likely to be a good assumption here because octahedral coordination of V dominates. VO consists of regular octahedral  $VO_6$  units. Optical spectroscopy on  $V^{3+}$  in albite-diopside glass shows vanadium in octahedral sites [9]. In diopside, based on ionic size arguments,  $V^{3+}$  is likely to go into the M1 octahedral site but  $V^{2+}$  is large enough that it may be forced into the M2 site substituting for  $Ca^{2+}$ . The coordination of  $V^{2+}$  in M2 is uncertain. Calcium is 8-fold but divalent cations that substitute for it (e.g.,  $Mn^{2+}$  and  $Fe^{2+}$ ) are octahedral. The coordination geometry of V in these samples needs to be investigated further, perhaps using extended x-ray absorption fine structure spectroscopy.

No correlation between vanadium concentration and oxidation state was observed in the zoned fassaite at the level of  $\sim 0.1$  charge. The difference in oxygen fugacity between  $V^{3+}$ -dominated glass (e.g., Schreiber 112) and the more reduced synthetic pyroxene is about eight orders of magnitude ( $10^{-9}$  vs  $10^{-17}$ ) with a temperature difference of 220K. Thus, the experimental precision of about 0.1 charge corresponds roughly to one order of magnitude in  $fO_2$ . Our results constrain the oxygen fugacity variation during crystallization to be no greater than this magnitude, assuming  $fO_2$  is the dominant parameter controlling V oxidation state. In addition, the concordance of the measured oxidation states for the Allende fassaite and the synthetic pyroxene supports crystallization under near solar gas oxygen fugacity conditions.

The cause of the apparent difference in redox behavior between vanadium and titanium in the fassaite is unclear. The  $Ti^{3+}/Ti^{4+}$  ratio was found to be higher by up to 30% in the high-Ti spike in this fassaite whereas variations of this magnitude were not observed for vanadium. MicroXAFS measurements on titanium in these samples may shed light on this discrepancy.

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**References:** [1] Grossman L. (1975) *GCA* 39, 433. [2] Beckett J.R. (1986) PhD thesis, Univ. Chicago. [3] Simon S.B. et al. (1991) *GCA* 55, 2635. [4] Delaney J. S. et al. (1999) *Meteoritics & Planet. Sci.* 34, A32. [5] Delaney J. S. et al. (2000) *Lunar Planet. Sci.* XXXI, # 1806. [6] Sutton S. R. et al. (1998) *EOS* 79, F954. [7] Schreiber H. et al. (1984) *JGR* 92, 9233. [8] Wong J. et al. (1984) *Phys.Rev.B* 30, 5596. [9] Keppler H. (1992) *Am. Min.* 77, 62-75.