Evidence for Divalent Vanadium in Allende CAI Fassaite and Implications for Formation Conditions

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Introduction

Fassaite, a Ti-rich, Al-rich clinopyroxene, is a major mineral in Type B refractory inclusions in carbonaceous chondrites. Stoichiometric treatment of electron microprobe data reveals that Ti^{3+}/Ti^{4+} is ~1 [1] in the fassaite, and experimental work shows that this implies crystallization at fO_2 of ~10^{-19} at 1200°C [2], very close to the fO_2 of a gas of solar composition. Many fassaite grains are strongly zoned in Ti, whose abundance decreases from core to rim [3], probably as a result of the compatibility of Ti^{3+} in fassaite during crystallization of the molten Ca-rich, Al-rich inclusions (CAIs). Superimposed on these profiles are zones where Ti and V contents spike upward together, within which the Ti^{3+}/Ti^{4+} ratio also increases significantly. Because Ti^{3+} is more compatible than Ti^{4+}, the spikes are thought to be caused by variable fO_2 during crystallization. Thermodynamic calculations show that VO and V_2O_3 are in equilibrium at approximately the same T-fO_2 conditions as Ti^{3+} and Ti^{4+}, but whether variable fO_2 can be responsible for the V spikes is unclear, since V^{2+} would not be expected to be more compatible than V^{3+} in clinopyroxene.

We report here on our initial results from using x-ray absorption near edge structure (XANES) spectroscopy to determine the oxidation state of V [4-6] 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 and Materials

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 (CaO-MgO-Al_2O_3-SiO_2 [CMAS] at T_{max} = 1280°C, log(fO_2) of about -17) and cooled at 50K/h to 1000°C before quenching.

The microXANES analyses were performed by using the GeoSoilEnviro Consortium for Advanced Radiation Studies (GSECARS) x-ray microprobe at the APS. The apparatus consisted of an APS undulator x-ray source, silicon (111) cryogenic monochromator, Kirkpatrick-Baez microfocusing mirrors, and germanium solid-state x-ray fluorescence detector. The x-ray beam size was 5 μm. XANES spectra were typically measured over the V K absorption edge (5465 eV) from 5450 to 5500 eV in 0.2-eV steps (~10-s 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 that these parameters are useful for V oxidation state determinations [4-6]. Energy calibration was accomplished by 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 vs. oxidation state was accomplished by using glasses characterized by optical spectrometry (Schreiber suite) [7] and oxides (VO, V_2O_3, V_2O_4, and V_2O_5) [8].

Results

A scan of V concentration vs. position was performed (2-μm step) across the V spike in a TS34 fassaite grain previously studied by electron microprobe. This scan showed the presence of a narrow (less than about 10 μm) high-V zone. The concentration "step" of about 10:1 was comparable to that observed in the electron microprobe data. VO concentrations in the spots analyzed varied from 100 to 3300 ppm.

XANES spectra were obtained as spot analyses at preselected 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 fell between those of V^{3+}-dominated oxides (e.g., Schreiber 112 and 113) and V^{2+} oxides (Fig. 1). The latter are expected to show no pre-edge intensity (as in VO) because of the expected high symmetry of the octahedral site. Thus, the presence of a
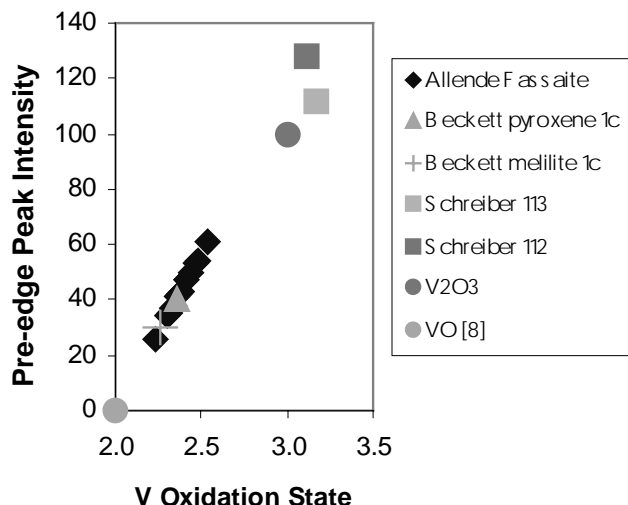
FIG. 1. Pre-edge peak intensity vs. V oxidation state showing V^{2+}-V^{3+} region only. Oxidation states for the unknowns are shown on a tie line between the V^{+2} oxide (VO) and the Schreiber 112 glass (oxidation state = 3.1).

pre-edge peak indicates that V 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° produced identical spectra, suggesting a negligible orientation effect.

Quantitative oxidation states were computed from the pre-edge peak intensities by using a linear interpolation between the intensity measured for Schreiber glass 112 (oxidation state determined by optical spectrometry of 3.12) and zero (V^{2+}). The results are shown graphically in Fig. 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 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 (Fig. 2). The V oxidation state variation within the Allende fassaite grain is uncorrelated with V 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 which the Allende fassaite grain crystallized. They 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 the octahedral coordination of V dominates. VO consists of regular octahedral VO_6 units. Optical spectroscopy on V^{3+} in albite-diopside glass shows V in octahedral sites [9]. In diopside, on the basis of 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 eightfold, 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 by using extended x-ray absorption fine structure (EXAFS) spectroscopy.

No correlation between V concentration and oxidation state was observed in the zoned fassaite at the level of ~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,
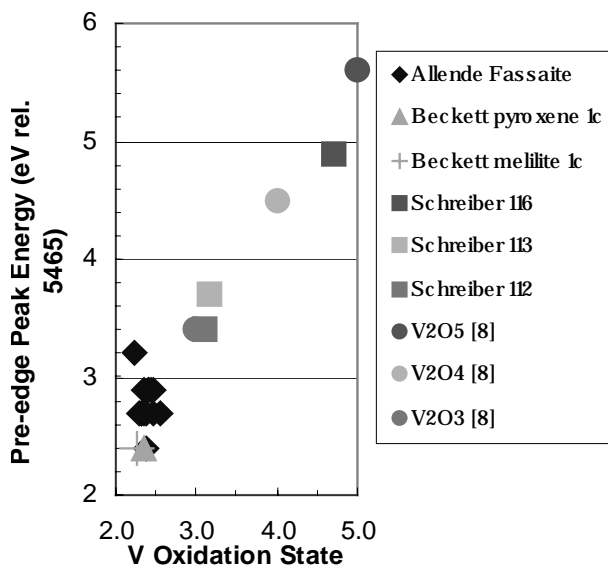

FIG. 2. Peak energies vs. oxidation state. Oxidation states for the Allende and Beckett samples are those determined from using the intensities (Fig. 1).

if it is assumed that fO_2 is the dominant parameter controlling the V oxidation state. In addition, the concordance of the measured oxidation states for the Allende fassaite and synthetic pyroxene supports crystallization under near-solar-gas-oxygen fugacity conditions.

The cause of the apparent difference in redox behavior between V and Ti 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 V. MicroXAFS measurements on Ti in these samples may shed light on this discrepancy.

Acknowledgments

References

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