

VALENCE OF Ti AND V IN FASSAITE: A RECORDER OF OXYGEN FUGACITY DURING CRYSTALLIZATION OF COARSE-GRAINED REFRACTORY INCLUSIONS. S. B. Simon¹, S. R. Sutton^{1,2}, and L. Grossman^{1,3}. ¹Dept. Geophysical Sci., 5734 S. Ellis Ave.; ²Consortium for Advanced Radiation Sources; ³Enrico Fermi Institute, 5640 S. Ellis Ave., The University of Chicago, Chicago, IL 60637, USA (sbs8@midway.uchicago.edu).

Introduction. Fassaite (Ti-, Al-rich clinopyroxene [1]) is a major phase in Type B (pyroxene-rich), coarse-grained refractory inclusions, which are found in CV3 carbonaceous chondrites. Both Ti and V are compatible in this phase during fractional crystallization of inclusion melts, and both have two valence states that are stable at the oxygen fugacity of the solar nebula, ~ 7 log units below the iron-wüstite buffer. This makes fassaite a potential recorder of f_{O_2} that can tell us whether inclusions crystallized in a solar gas. The Ti^{3+}/Ti^{4+} ratio of fassaite can be calculated from electron probe (EMP) analyses assuming stoichiometry [2] and it can be measured directly by X-ray absorption near edge structure (XANES) spectroscopy. Measurement of V^{2+}/V^{3+} ratios in fassaite requires XANES.

Typically V_2O_3 , Sc_2O_3 and total Ti oxides ($TiO_2 + Ti_2O_3$) decrease from core to rim in Type B fassaite [3]. The Ti^{3+}/Ti^{4+} ratio commonly decreases from core to rim in fassaite in Type B1 (having a melilite-rich mantle) inclusions but not in fassaite in Type B2 (no mantle) inclusions. Also, Type B1 fassaites commonly exhibit sharp increases, or “spikes”, in their Ti and V contents and their Ti^{3+}/Ti^{4+} ratios but not in Sc or rare earth element contents [4], which seems to rule out a simple change in crystallization assemblage, such as incoming of anorthite, as the cause of the spikes. As the only affected elements are the two with multiple valence states, a redox change is suggested. To investigate this feature we have measured the Ti^{3+}/Ti^{4+} and V^{2+}/V^{3+} ratios in fassaite in a Type B1 and a Type B2 inclusion from Allende.

Methods. Major element zoning and Ti oxidation state were documented by EMP, and abundances and valence states of Ti and V were determined by XANES. As in [5], with a 5 μm X-ray beam, XANES spectra were measured over the V K pre-edge peak (~ 5468 eV) from 5450 to 5500, with additional normalization measurements at 5600 eV. Analogous measurements were made over the Ti K pre-edge peak, at 4969 eV. By comparing the spectra to those for pure oxidation state standards, we determined oxidation states for each analysis spot, reported as values between 3 and 4 for Ti and between 2 and 3 for V.

Results. EMP and XANES traverses were conducted across two spikes in TS34 (B1) and across

two grains in TS21 (B2). XANES results agree with EMP data, which show sharp increases in Ti (e. g., in one grain in TS34, from 3.57 to 5.10 wt%) and V (0.03 to 0.12 wt%) oxide contents and in Ti^{3+}/Ti^{4+} at the spike. In that grain, the Ti oxidation state drops from a pre-spike value of 3.54 ± 0.05 (i.e., $Ti^{3+} \approx Ti^{4+}$) to 3.14 ± 0.11 ($Ti^{3+} \gg Ti^{4+}$). Surprisingly, across the same spike, we did not detect a change in V valence, with measurements of 2.51 ± 0.03 pre-spike and 2.49 ± 0.08 at the spike. In Type B2 inclusions, fassaite Ti^{3+}/Ti^{4+} ratios are within the range of those of Type B1 fassaites, and the V valence in two B2 fassaite crystals we analyzed averages 2.40 ± 0.09 and 2.52 ± 0.09 , within error of the results for the two B1 grains, 2.39 ± 0.08 and 2.42 ± 0.10 . These results are clear evidence for the presence of V^{2+} in both Type B1s and B2s, with $V^{2+} \approx V^{3+}$.

Discussion. The measured Ti^{3+}/Ti^{4+} and V^{2+}/V^{3+} ratios are consistent with crystallization from a liquid in equilibrium with a gas of solar composition. Fassaite favors Ti^{3+} over Ti^{4+} [2] so fractional crystallization can cause the Ti^{3+}/Ti^{4+} ratio to decrease from core to rim in a crystal, but only if the residual liquid is isolated from the nebular gas and prevented from reequilibrating. This seems to have occurred in the B1s but not in the B2s. Many late B1 liquids had low Ti^{3+}/Ti^{4+} but were exposed to the nebular gas before completion of crystallization, causing reequilibration and sharp increases in Ti^{3+}/Ti^{4+} of crystallizing pyroxene. The V^{2+}/V^{3+} ratio of the residual liquid should have behaved similarly, in which case the spikes in V contents would imply that V^{2+} is more compatible in fassaite than V^{3+} . This scenario is feasible, as V^{2+} can enter the pyroxene M1 or M2 site and does not require a coupled substitution for charge balance, but experiments are needed for confirmation. If $D_{V^{2+}} > D_{V^{3+}}$, it is unclear why a change in the V oxidation state at the concentration spike was not detected. One possibility is that the V valence in the fassaite reequilibrated by subsolidus charge transfer with relatively abundant Ti.

References: [1] Dowty E. and Clark J. (1973) *Am. Min.* 58, 230-242. [2] Beckett J. (1986) Ph. D. dissert. U. Chicago. [3] Simon S. et al. (1991) *GCA* 55, 2635-2655. [4] Simon S. et al. (1992) *Meteoritics* 27, 289-290. [5] Sutton S. et al. (2002) *LPS XXXIII*, Abstract #1907.