VANADIUM VALENCE IN SPINEL FROM A Y98 COMPOSITION MELT AS DETERMINED BY X-RAY ABSORPTION NEAR EDGE STRUCTURE (XANES). P. V. Burger1, J. J. Papike1, A. S. Bell, and C. K. Shearer1. 1Institute of Meteoritics, Department of Earth and Planetary Science, University of New Mexico, Albuquerque, New Mexico 87131 (pvburger@unm.edu)

Introduction: Papike et al. [1,2] demonstrated the dependency of vanadium partitioning into spinel in a Yamato 980459 (Y98)-composition melt on oxygen fugacity. They determined that partitioning of V into spinel (as V^{3+} in the octahedral site as in magnesiocoulsonite, see Fig. 1a) decreases markedly in melts buffered at IW-1 through FMQ. Papike et al. [1,2] suggested that this \( f_{O2} \) dependency was the result of changing V valence in the melt, with V^{3+} overwhelmingly preferred to V^{4+} in the spinel structure. As \( f_{O2} \) is increased from IW-1 to FMQ, the amount of V^{3+}/V^{Total} drops from 0.90 to ~0.05, resulting in a drop in \( D_{V}\text{spinel/melt} \) from 45.2 to 6.2. At \( f_{O2} \) > FMQ, however, there is a slight increase in the partition coefficient, from 6.2 to 7.6, between FMQ and FMQ+1. Papike et al. [2] speculated that this increase was real, and was determined by changing crystal chemical characteristics of spinels over this range in \( f_{O2} \). The region in \( f_{O2} \) space between FMQ and FMQ+1 is characterized by a drastic increase in the magnetite component, a change that results in an increase in the proportion of inverse domains in the spinel. This reorientation of the structure seems to make the incorporation of V^{4+} more permissible (Fig. 1c).

In order to build on the study of Papike et al. [1,2], we’ve made direct measurements on spinels of the same composition, and a protracted crystallization history (to maximize grain size), using X-Ray Absorption Near Edge Structure (XANES) to determine the valence ratio of V^{3+}/V^{4+}.

Experimental Approach: To investigate the effects of \( f_{O2} \) on the valence of V in spinel, we conducted a 1-bar gas mixing experiment. This experiment was designed for the purpose of growing a spinel of sufficient size to be analyzed using XANES (i.e., >10 \( \mu \)m). Spinel was grown from a melt under controlled redox conditions, specifically IW+2.2 (Fig. 2). The starting material consisted of a glass powder with a composition patterned after the whole rock composition of Yamato 980459 (Y98). The experiment was carried out in the one-bar gas mixing laboratory at the University of New Mexico. The experiment was run at superliquidus conditions before being cooled to a final temperature of 1200°C, at a cooling rate of 0.5 °C/min.

XANES Data Acquisition: Vanadium K-edge XANES data were acquired with the x-ray microprobe of GSECARS beamline 13-ID-E at the Advanced Photon Source (APS), Argonne National Laboratory, Illinois. The x-ray source at APS beamline 13-ID-E was a 72-pole, 33 mm period undulator. The beam was focused to final spot size of approximately 5\( \mu \)m by 5\( \mu \)m with dynamically configured Kirkpatrick-Baez focusing mirrors.

All spectra were acquired in fluorescence mode utilizing a cryogenically cooled Si(311) monochromator and a silicon-drift solid state detector offset at a 45° angle from the sample.

Results & Discussion: We have calculated the mean valence of V in the experimental spinels using the pre-edge feature in the V K-edge XANES spectra (Fig. 3a,b) and the calibration of [3]. The calculated mean V valence values range from ~2.6-2.7. Taken at face value, these low values suggest that the spinels V content is comprised of approximately 70% V^{3+} and 30% V^{2+}, which is certainly incorrect. These low values are quite inconsistent with V partitioning data and
V valence modeling for Y98 melts [2]. Previous studies of V valence in basaltic melts suggest that the mean V valence in the melt is defined by binary mixtures of V$^{3+}$ and V$^{4+}$ at oxygen fugacities between IW and FMQ. Based on these results, there is little evidence supporting a significant presence of V$^{2+}$ in the melt, therefore, the low V valence values in the spinels cannot have been inherited from the melt. Alternatively, the low intensity of the pre-edge feature used to calculate the V-valence may result from structural factors in the spinel. It has been noted in previous studies [4] that the pre-edge feature in the V XANES spectra is not only related to its formal valence state, but is also influenced by its coordination symmetry. Additionally, the probability of the 1s-3d electron transition responsible for the pre-edge absorption feature is nearly zero for the case of perfect regular octahedral symmetry [4]. Therefore, the low intensity of the pre-edge feature suggests that V$^{3+}$ resides in highly symmetrical octahedral sites in spinel.

Despite the fact that V valence modeling suggests that the melt contains ~82% V$^{4+}$ at $f_O$ conditions of IW+2.2 [2], the total magnetite (i.e., inverse) component is what is controlling the partitioning of V into the spinel. At this $f_O$, the magnetite mole fraction, relative to chromite and spinel is 9%. This sets an upper limit on the amount of V$^{4+}$ which might be accommodated in the spinel, and is not strongly displaced from the error of the XANES measurements, which is likely 5-6%. Based on our observations, the valence ratio of V in spinel is not a useful oxybarometer at $f_O$ <FMQ, though it may prove more valuable at higher $f_O$, where there is a more substantial inverse component, and consequently, potentially a mixture of V$^{4+}$ and V$^{2+}$. At $f_O$ lower than this, the slight variations in $V^{3+}/V^{Total}$ in the spinels are un-resolvable with the XANES technique. Conveniently, [1,2] demonstrated that over this same range (i.e., at $f_O$ from IW-1 to FMQ), V spinel-melt partitioning can be used for the same purpose. These measurements also provide an important insight into the site occupancy of V$^{3+}$ in spinel. The observation that the mean V valence is <3 is likely the result of the highly symmetric nature of the crystallographic site it occupies in the spinel structure.


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