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Introduction: Spinel can be a significant host phase for V which has multiple oxidation states $V^{2+}, V^{3+}, V^{4+}$ or $V^{5+}$ at oxygen fugacities relevant to natural systems. The magnitude of $D(V)$ spinel/melt is known to be a function of composition, temperature and $fO_2$, but the uncertainty of the oxidation state under the range of natural conditions has made elusive a thorough understanding of $D(V)$ spinel/melt. For example, $V^{3+}$ is likely to be stable in spinels, based on exchange with Al in experiments in the CaO-MgO-Al$_2$O$_3$-SiO$_2$ system [1]. On the other hand, it has been argued that $V^{4+}$ will be stable across the range of natural oxygen fugacities in nature [2,3]. In order to build on our previous work in more oxidized systems [4], we have carried out experiments at relatively reducing conditions from the FMQ buffer to 2 log $fO_2$ units below the IW buffer. These spinel-melt pairs, where V is present in the spinel at natural levels ($\sim$300 ppm V), were analyzed using an electron microprobe at NASA-JSC and micro-XANES at the Advanced Photon Source at Argonne National Laboratory. The new results will be used together with previous results to understand the valence of V in spinel-melt systems across 12 orders of magnitude of oxygen fugacity, and with application to natural systems.

Experimental: Previous studies have highlighted the potential effects of Ti and V content on the magnitude of $D(V)$ spinel/melt. In order to isolate this effect, a series of compositions were prepared that would yield variable spinel compositions, by doping with Ti and V. Five compositions – undoped natural Hawaiian ankaramite, +1% $V_2O_3$, +5% $V_2O_5$, +5% TiO$_2$ and +10% TiO$_2$ – were equilibrated at both the IW and FMQ buffers in order to investigate these potential effects; all compositions were doped with 1% Cr$_2$O$_3$ to promote spinel growth. A Hawaiian ankaramite was studied because it is primitive (11 wt% MgO) and has a composition that is relevant to many natural systems such as OIB, MORB, arc, and planetary basalts. These compositions were placed on either Re or Fe pressaturated Pt loops in Deltech furnaces, with $fO_2$ controlled by mixing of CO and CO$_2$ at 1300 °C. The samples were held in the furnace hotspot for 2 to 5 days, and then quenched by rapid removal. All runs contain spinel and glass (Fig. 1), and several also contain olivine.

Several additional runs were undertaken to produce V-bearing spinels as standards to compare to glass calibrations produced by [5]. These were synthesized at 1300 °C, from mixtures of MgO, $V_2O_3$ and VO$_2$, at oxygen fugacities equivalent to air, FMQ and IW buffers, with the intent to produce Mg$_2$VO$_4$ at the first two conditions, and Mg$_3$V$_2$O$_4$ at the latter.

Analytical: Electron microprobe analyses were made using a Cameca SX100 at the NASA Johnson Space Center. Measurements of the valence of V were made using synchrotron micro-XANES (X-ray Absorption Near-Edge Structure) spectroscopy (SmX), at the Advanced Photon Source (APS), Argonne National Laboratory (beamline 13-ID, the Consortium for Advanced Radiation Sources or CARS). SmX measurements are made by focusing a monochromatic (cryogenic, Si (111) double crystal monochromator) X-ray beam (5x5 μm) from the synchrotron onto a spot on the sample and measuring the fluorescent X-ray yield from that spot as a function of incident X-ray energy. Synchrotron XANES spectroscopy can resolve small energy differences since the energy of the incident X-ray beam used to excite K-absorption edges can be controlled with resolution of $\sim$0.1eV. Changes of fluorescent X-ray intensity and energy of features in the XANES spectrum (notably the pre-edge peak) depend on oxidation state and coordination (e.g., [6]). The oxidation states of V have been inferred using this technique on a range of planetary materials [7,8].

Results: Measurements on spinels of known V oxidation state are required to calibrate these spinel spectra
in terms of oxidation state. The pre-edge peak intensity obtained on the reduced synthesized spinels is similar to that for glasses containing V$^{3+}$, as might be expected if

![Figure 2: Variation of D(V) Cr-spinel melt with oxygen fugacity (relative to the iron-wustite IW buffer, 1300°C).](image)

the spinel is MgV$_2$O$_4$. We are continuing characterization of the end member spinels to confirm the similarity of glass and spinel spectra for the various valences. In the meantime, the glass calibration of [5] is considered to be appropriate for spinels since V in spinel and glass have similar coordination - octahedral under reducing conditions, and lower under oxidized conditions [9].

Spinel compositions are chromian-rich in contrast to more Fe$^{3+}$ rich spinels synthesized in previous work. V contents of spinels in the more reduced V-doped runs are as high as 41 wt% (similar to levels reported by [1]). TiO$_2$ contents of spinels in the Ti-doped runs are as high as 10 wt%. Values of D(V) spinel/melt are 5 to 8 at FMQ and 10 to 30 at IW. When combined with previous work at higher oxygen fugacities on the same compositions, it is clear that D(V) is strongly dependent upon fO$_2$ (Fig. 2). In addition, the effect of Ti and V content on D(V) can be evaluated with these new results. The value of D(V) increases with V contents, but is unaffected with addition of Ti. This information, combined with previous work at different temperatures will allow the effect of T, fO$_2$ and spinel composition on D(V) to be evaluated more completely.

Micro-XANES spectra, including well defined pre-edge peaks, were obtained on experimental spinels and glasses containing between 50 ppm and 40 wt% V, and in areas as small as 5x5 $\mu$m$^2$. Spinels of variable composition grown at oxygen fugacities of FMQ all have similar pre-edge intensities consistent with V$^{3+}$, and spinels grown at IW+2, and IW have a similar or slightly lower intensity (or valence) (Fig. 3).

Also, glasses in all cases have higher pre-edge intensities (and valence) than the spinel (Fig. 3). Application of the glass calibration results of [5] to the glass pre-edge intensities indicates that the FMQ fO$_2$ glasses are dominated by V$^{4+}$, while the lowest fO$_2$ glass (HM) contains mixed valence of 4+ and 3+.

**Conclusions:** These new data demonstrate a strong dependence of D(V) spinel/melt upon oxygen fugacity, and confirm that V in spinel is likely to be 3+ at most redox conditions, but 4+ at more oxidized conditions. In addition, V is always more reduced in the spinel than coexisting melt (preferential incorporation of V$^{3+}$ in spinel). Combination of these new data with previous results will allow D(V) spinel/melt to be predicted as a function of T, fO$_2$, and spinel composition.

![Figure 3: V valence vs. logfO$_2$ for spinel-glass pairs from this study and [4]. All runs were done at 1300 ºC.](image)