

Micro-XANES measurements on experimental spinels and the oxidation state of vanadium in coexisting spinel and silicate melt.

K. Righter¹, S.R. Sutton^{2,3}, M. Newville³, L. Le⁴, and C.S. Schwandt⁴
¹Mail Code KT, NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058, kevin.righter-1@nasa.gov; ²Dept. of the Geophysical Sciences, ³GSECARS, University of Chicago, 5734 S. Ellis Ave., Chicago, IL 60637 and ⁴Lockheed-Martin Engineering and Science, Houston, TX 77058.

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-Al₂O₃-SiO₂ 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 (~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% V₂O₃, +5% V₂O₃, +5% TiO₂ and +10% TiO₂ – were equilibrated at both the IW and FMQ buffers in order to investigate these potential effects; all compositions were doped with 1% Cr₂O₃ 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 pre-saturated Pt loops in Deltech furnaces, with fO_2 controlled by mixing of CO and CO₂ 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

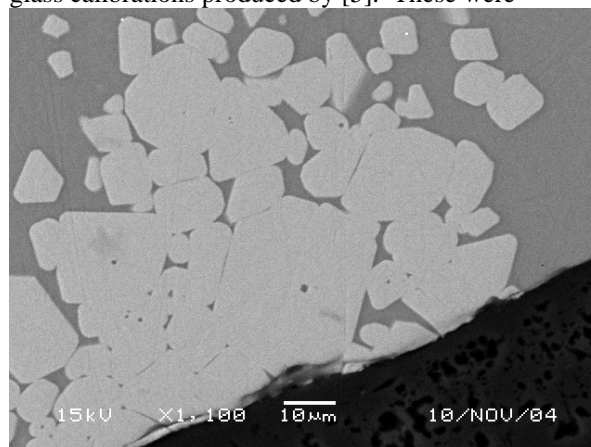


Figure 1: Chromian spinels grown from ankaramite composition at 1300 °C, log $fO_2 = -10.58$ (IW buffer), for 5 days. Light gray = spinel, darker gray = glass, black = epoxy.

synthesized at 1300 °C, from mixtures of MgO, V₂O₃ and VO₂, at oxygen fugacities equivalent to air, FMQ and IW buffers, with the intent to produce Mg₂VO₄ at the first two conditions, and MgV₂O₄ 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 ~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

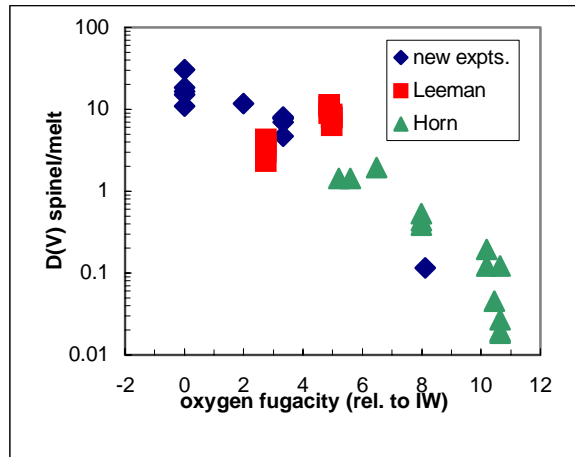


Figure 2: Variation of D(V) Cr-spinel melt with oxygen fugacity (relative to the iron-wustite IW buffer, 1300°C).

the spinel is MgV_2O_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 $5 \times 5 \mu m^2$. Spinel 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.

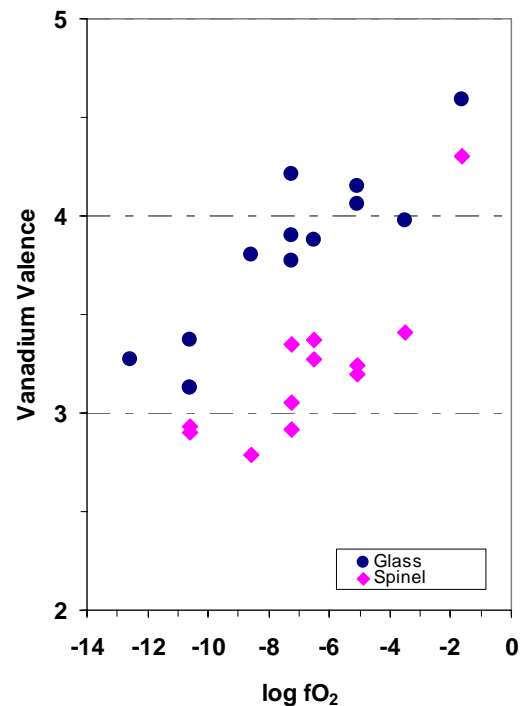


Figure 3: V valence vs. $\log fO_2$ for spinel-glass pairs from this study and [4]. All runs were done at 1300 °C.

References: [1] Canil, D. (1999) GCA 63, 557-572; [2] Toplis, M.J. and Corgne, A. (2002) CMP 144, 22-37; [3] Borisov, A. et al. (1987) Geokhimiya 7, 915-920; [4] Righter, K. et al. (2004) OTP meeting abstract; [5] Karner, J.M. et al. (2004) LPSC XXXV, #1269; [6] Wong, J. et al. (1984) Phys Rev B 30, 5596-5610; [7] Sutton, S.R. et al. (2002) LPSC XXXIII, #1907; [8] Karner, J.M. et al., (2003) LPSC XXXIV, #1998; [9] Sutton, S.R. et al. (2005) GCA, in press.