

MICRO-XANES MEASUREMENTS ON EXPERIMENTAL SPINELS AND THE OXIDATION STATE OF VANADIUM IN SPINEL-MELT PAIRS. K. Righter¹, S.R. Sutton^{2,3}, and M. Newville³ ¹Mail Code ST, NASA Johnson Space Center, 2101 NASA Parkway, Houston, TX 77058, kevin.righter-1@nasa.gov; ²Dept. of the Geophysical Sciences and ³GSECARS, University of Chicago, 5734 S. Ellis Ave., Chicago, IL 60637.

Introduction: Spinel can be a significant host phase for V as well as other transition metals such as Ni and Co. However, vanadium has multiple oxidation states V^{2+} , V^{3+} , V^{4+} or V^{5+} at oxygen fugacities relevant to natural systems. We do know that D(V) spinel/melt is correlated with V and TiO_2 content 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 $CaO-MgO-Al_2O_3-SiO_2$ 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 gain a better understanding of D(V) spinel/melt we have equilibrated spinel-melt pairs at controlled oxygen fugacities, between HM to NNO, where V is present in the spinel at natural levels (~300 ppm V). These spinel-melt pairs were analyzed using micro-XANES at the Advanced Photon Source at Argonne National Laboratory. The new results will be used together with spinel compositional data (Ti, V content) and oxygen fugacity, to unravel the effects of these variables on D(V) spinel/melt.

Experimental: A Hawaiian ankaramite was doped with 1% each of Cr, Ni and Ru or Cr, Rh and Os. These compositions were placed in 3 mm AuPd capsules and crimped (but not welded) at the top. These capsules were then welded, together with a buffer mixture in a separate alumina crucible, into an evacuated silica tube. Buffers used were hematite-magnetite (HM), $MnO-Mn_3O_4$ (MNO), $Re-ReO_2$ (RRO), and $Ni-NiO$ (NNO), covering ~5.5 $\log fO_2$ units at 1300 °C. The silica tubes were held in the hotspot of vertical 1 atm furnaces for 48 hrs., and then quenched by rapid removal from the furnace. All runs contain spinel, glass, and Ru or RhOs metal; full details of these experiments were reported by [4].

Synchrotron Micro-XANES spectroscopy (SmX): Measurements of the valence of V were made using synchrotron micro-XANES (X-ray Absorption Near-Edge Structure) spectroscopy, 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 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 as the energy of the monochromatic incident beam is increased across an absorption edge are a function of oxidation state and coordination (e.g., [5]).

The oxidation states of V have been inferred using this technique on a range of planetary materials [6,7].

Results: Micro-XANES spectra, including well defined pre-edge peaks, were obtained on experimental spinels and glasses containing between 70 ppm and 2 wt% V, and in areas as small as $5 \times 5 \text{ } \mu\text{m}^2$. Spinel grown at oxygen fugacities between NNO and MNO (three lowest fO_2 s of this study) all have similar pre-edge intensities, but spinel grown at HM has a much higher intensity (Fig. 1). Glasses in all cases have higher pre-edge intensities than the spinel. Application of the glass calibration results of [8] to the glass pre-edge intensities indicates that the three lowest fO_2 glasses are dominated by V^{4+} , while the highest fO_2 glass (HM) contains mixed valence of 4+ and 5+. Although measurements on spinels of known V oxidation state are required to calibrate these spinel spectra in terms of oxidation state, the glass calibration of [8] provides some preliminary insight (particularly appropriate if V in spinel resides in octahedral sites). In this case, the results suggest V^{3+} dominance except for the most oxidized system (HM) which is inferred to be dominated by V^{4+} . However, the similar spectra for glass and spinel in the HM runs must be confirmed with additional measurements. These results show that V oxidation states can be determined using micro-XANES. Future plans include characterization of spinels with known V oxidation state, as well as experimental spinel-melt pairs at lower fO_2 's.

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) GCA 68, 867-880; [5] Wong, J. et al. (1984) Phys Rev B 30, 5596-5610; [6] Sutton, S.R. et al. (2002) LPSC XXXIII, #1907; [7] Karner, J.M. et al., (2003) LPSC XXXIV, #1998; [8] Karner, J.M. et al. (2004) LPSC XXXV, #1269.

