Vanadium K-Edge MicroXANES of Glasses and Minerals: Valence State Calibration by Optical Spectroscopy

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Vanadium K-edge x-ray absorption near-edge structure (XANES) spectra exhibit a pronounced pre-edge feature whose energy and intensity are sensitive to valence state.[1] Both energy and intensity increase with increasing oxidation (Fig. 1). Quantitative calibration of these systematic shifts in terms of valence state has been obtained using XANES measurements on experimental glasses and minerals for which independent determinations of V valence are available from optical spectroscopy, electron paramagnetic resonance (EPR) spectroscopy, or stoichiometry.[2] The XANES measurements were performed using the x-ray microprobe at beamline 13-ID-C, sector 13, Advanced Photon Source, Argonne National Laboratory.[3,4]

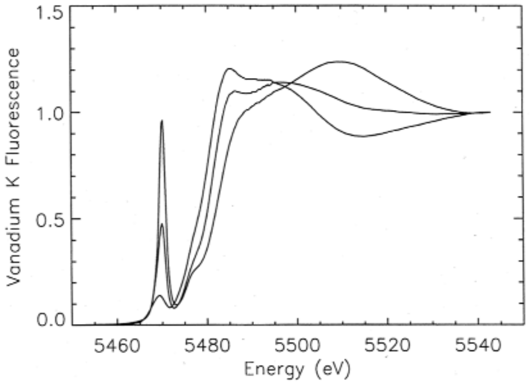

FIG. 1. Synchrotron microXANES spectra of V for glasses produced at different fO_2 (0, -6.8, -9; log units). The systematic increase in energy and intensity of the feature near 5470 eV is the basis of the valence state determination.

The calibration experimental glasses (basaltic composition with minor V added) were kindly supplied by H. Schreiber (Virginia Military Institute) and provide independent calibration of the valence state of the V at relatively high logfO_2 (0 to –9).[5] These glasses (1500ºC; FAD composition) cover the valence range from V^{5+} to V^{3+}. In addition, two V^{4+}-bearing minerals were measured, vanadium apophyllite and cavansite, both kindly supplied by G. Rossman (Caltech).

A plot of vanadium pre-edge peak intensity versus "known" valence state shows a well-defined trend (Fig. 2). Based on the fact that glasses, minerals, and model compounds (oxides) fall on the same trend, matrix effects appear to be minor. Also, the two mineral V^{4+} crystals are reasonably consistent, suggesting crystal orientation effects may be minor, although admittedly the dataset is small at this point.

MicroXANES measurements have also been obtained on two additional experimental basaltic suites: isothermal (FAD, 1315ºC; B. Hanson and J. Jones[6]) and isobaric (FAD, logfO_2=–8; J. Beckett). The isobaric suite provides information on the effect of temperature on pre-edge peak intensity. We expect the log of the pre-edge peak intensity to depend on the inverse of temperature,[7,8] where the negative slope indicates that higher temperatures lead to more reduced systems. Converting the peak intensities to valence state will allow us to obtain the enthalpy change from the slope. These data indicate that the pre-edge peak intensity is 30% lower at 1500ºC than at 1275ºC (0.36 versus 0.50, respectively). Roughly speaking, this is a 30% difference in vanadium valence state (Fig. 2). The data for Beckett's samples extrapolated to 1500ºC (0.36) yield a higher intensity than the data for Schreiber's samples at the same T, fO_2 (0.23). This intensity difference corresponds to a valence difference of about 0.3 of an electron, i.e., a charge state of 4.0 versus 3.7, respectively. The Hanson and Jones data at logfO_2=–8, 0.28 after extrapolation to 1500ºC, are reasonably consistent with the Schreiber data.

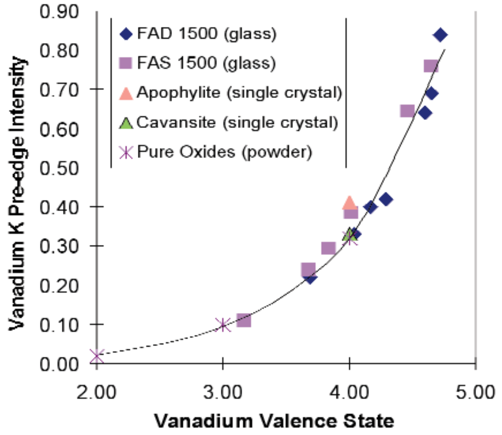

FIG. 2. Variation in pre-edge peak intensity as a function of "known" valence state.

We conclude that using the current data for calibration purposes, valence state determinations on unknowns have an effective uncertainty of about 0.3 charge states.

Acknowledgments

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