Goldschmidt 2026 Abstract
https://doi.org/10.46427/gold2026.37299

Vanadium Kα-edge X-ray absorption spectroscopy in silicate glasses as a function of oxygen fugacity, composition and pressure

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The oxygen fugacity (fO_2) of silicate melts influences magmatic phase assemblages, element partitioning relationships and the speciation of dissolved volatiles in melts. While fO_2 cannot be measured directly in natural melts, the speciation of multivalent elements, like vanadium, in glasses can act as a proxy for fO_2 if all factors influencing element valence are known. Sutton et al. (2005) developed a V-XANES calibration for silicate melts that related the intensity of the V pre-edge peak to effective V valence in the glass using 1 atm experiments equilibrated at known temperatures and fO_2s. However, the glasses in the calibration covered a somewhat limited compositional space and did not include hydrous and/or high-pressure glasses. Here we present new V-XANES spectra for experimental glasses with diverse compositions equilibrated at T=1100-1500 °C, P=0.0001- 3 GPa, log fO_2= 2 log units below the quartz-fayalite-magnetite (QFM) to 6 log units above (ΔQFM-2 to ΔQFM+6). We evaluate the effect of radiation-induced beam damage in V-XANES spectra in multiple ways for hydrous Fe-bearing and Fe-free glasses. Glasses containing dissolved H_2O exhibit signs of radiation induced beam damage to lower photon flux densities than measured in anhydrous glasses by Lanzirotti et al. (2022). We observe a systematic increase in V pre-edge intensities and centroids with increasing fO_2 at constant P, T and X, consistent with the results of Sutton et al. (2005). As equilibration pressure increases at constant T, fO_2 and X, the intensity of V-XANES pre-edges decreases. Glasses equilibrated at 1450 °C, 1 atm and fO_2= QFM have pre-edge intensities that are negatively correlated with TiO_2 content. Iron-bearing glasses yield lower pre-edge intensities compared to iron-free glasses formed at similar conditions and are less susceptible to beam-induced radiation damage. Our new results suggest that V pre-edge intensities cannot be directly linked to fO_2 without a parameterization that accounts for all factors that contribute to the electronic and molecular environment of V in glasses.

Sutton, S. R., et al. (2005) *Geochimica et Cosmochimica Acta* 69: 2333-2348

Lanzirotti, A. et al. (2022) *American Mineralogist* 107: 729-738.