

Microscale Oxygen Barometry in Basaltic Glasses Using Vanadium K-edge X-ray Absorption Spectroscopy

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Magmatic oxygen fugacity (fO_2) exerts a primary control on the discrete vanadium (V) valence states in quenched melts. V valence proxies for fO_2 , measured using X-ray absorption near-edge spectroscopy (XANES), can provide highly sensitive measurements of the redox conditions in melts and glasses. Previous studies have used calibration models that relate fO_2 to effective V valence in basaltic glasses using the measured intensity of the V XANES pre-edge peak [1,2]. We have expanded on these earlier methodologies, developing new multivariate analysis (MVA) calibration models that employ the full XANES spectral range to predict fO_2 of equilibration in glasses of basaltic composition directly. This MVA approach independently identifies which energy ranges in V XANES are most strongly correlated to fO_2 , and minimizes temperature-relative uncertainties in the calibration to provide more robust statistical measures of model accuracy.

Applying these approaches and models to samples of natural basaltic glass, V XANES oxybarometry provides calculated fO_2 's that are consistent within ± 0.6 log units for melt fO_2 's calculated based on S and Fe valence state oxybarometry, in systems where we have collected data on all three elements. For glasses equilibrated at more reduced conditions below NNO-2, V XANES oxybarometer retains good sensitivity to small changes in fO_2 down to NNO-8. However, the presence in some glasses of nanoscale precipitates in which V is highly compatible, such as spinels, can lead to difficulties in accurately measuring V speciation within the glass [3]. Additionally, as with other elements, V may be sensitive to beam-induced changes in redox, especially in hydrous glasses, and this must be carefully monitored.

[1] Sutton *et al.* (2005) *GCA* **69**, 2333–2348. [2] Righter *et al.* (2011) *Am.Min.* **96**, 1278-1290. [3] Head *et al.* (2011) *GCA* **226**, 149-173.