

Accurate predictions of microscale oxygen barometry in basaltic glasses using V *K*-edge X-ray absorption spectroscopy: A multivariate approach

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ABSTRACT

Because magmatic oxygen fugacity (f_{O_2}) exerts a primary control on the discrete vanadium (V) valence states that will exist in quenched melts, V valence proxies for f_{O_2} , measured using X-ray absorption near-edge spectroscopy (XANES), can provide highly sensitive measurements of the redox conditions in basaltic melts. However, published calibrations for basaltic glasses primarily relate measured intensities of specific spectral features to V valence or oxygen fugacity. These models have not exploited information contained within the entire XANES spectrum, which also provide a measure of changes in V chemical state as a function of f_{O_2} . Multivariate analysis (MVA) holds significant promise for the development of calibration models that employ the full XANES spectral range. In this study, new calibration models are developed using MVA partial least-squares (PLS) regression and least absolute shrinkage and selection operator (Lasso) regression to predict the f_{O_2} of equilibration in glasses of basaltic composition directly. The models are then tested on a suite of natural glasses from mid-ocean ridge basalts and from Kilauea. The models relate the measured XANES spectral features directly to buffer-relative f_{O_2} as the predicted variable, avoiding the need for an external measure of the V valence in the experimental glasses used to train the models. It is also shown that by predicting buffer-relative f_{O_2} directly, these models also minimize temperature-relative uncertainties in the calibration. The calibration developed using the Lasso regression model, using a Lasso hyperparameter value of $\alpha = 0.0008$, yields nickel-nickel oxide (NNO) relative f_{O_2} predictions with a root-mean-square-error of ± 0.33 log units. When applied to natural basaltic glasses, the V MVA calibration model generally yields predicted NNO-relative f_{O_2} values that are within the analytical uncertainty of what is calculated using Fe XANES to predict $Fe^{3+}/\Sigma Fe$. When applied to samples of natural basaltic glass collected in 2014 from an active lava flow at Kilauea, a mean f_{O_2} of NNO-1.15 \pm 0.19 (1 σ) is calculated, which is generally consistent with other published f_{O_2} estimates for subaerial Kilauea lavas. When applied to a sample of pillow-rim basaltic glass dredged from the East Pacific Rise, calculated f_{O_2} varies from NNO-2.67 (± 0.33) to NNO-3.72 (± 0.33) with distance from the quenched pillow rim. Fe oxybarometry in this sample provides an f_{O_2} of NNO-2.54 \pm 0.19 (1 σ), which is in good agreement with that provided by the V oxybarometry within the uncertainties of the modeling. However, the data may indicate that V XANES oxybarometry has greater sensitivity to small changes in f_{O_2} at these more reduced redox conditions than can be detected using Fe XANES.

Keywords: XANES, vanadium, valence, oxygen fugacity, basalts, multivariate analysis