

Oxybarometry of reduced silicate glasses: Using multivariate methods to constrain Cr oxidation states with application to lunar glasses

MOLLY C. McCANTA^{1,*}, M. DARBY DYAR^{2,3}, STEPHEN R. SUTTON^{4,5,†}, SARAH E. ROBERTS⁶, AND CAI R. YTSMA^{7,8}

¹Department of Earth, Environment, and Planetary Sciences, University of Tennessee, 1621 Cumberland Avenue, Knoxville, Tennessee 37996, U.S.A.

²Planetary Science Institute, 1700 East Fort Lowell, Suite 106, Tucson, Arizona 85719, U.S.A.

³Department of Astronomy, Mount Holyoke College, 50 College Street, South Hadley, Massachusetts 01075, U.S.A.

⁴Center for Advanced Radiation Sources, University of Chicago, Chicago, Illinois 60637, U.S.A.

⁵Department of the Geophysical Sciences, University of Chicago, Chicago, Illinois 60637, U.S.A.

⁶Corning Glass, Corning, New York 14830, U.S.A.

⁷Cai Consulting, Glasgow, Scotland, U.K.

⁸Institute of Health Informatics, University College London, Gower Street, London WC1E 6BT, U.K.

ABSTRACT

Iron redox works well for constraining oxygen fugacity (f_{O_2}) in terrestrial igneous materials due to the relatively high f_{O_2} of the Earth's atmosphere, crust, and upper mantle [$f_{\text{O}_2} \geq$ quartz-fayalite-magnetite (QFM)], where there are large changes in $\text{Fe}^{2+}/\text{Fe}^{3+}$ with relatively small changes in f_{O_2} . At f_{O_2} values <QFM, Fe redox becomes less sensitive, and analytical uncertainties may make it difficult to determine f_{O_2} differences between samples. The valence change between Cr^{2+} and Cr^{3+} occurs at lower f_{O_2} values than for iron, potentially making it a more sensitive oxybarometer for materials equilibrated under reducing conditions. The current approach to measuring f_{O_2} from X-ray absorption (XAS) measurements derives Cr valence first from the $1s \rightarrow 4s$ transition and then uses that redox couple to estimate f_{O_2} as a function of temperature and composition. Here, that method is compared to an alternate approach of predicting f_{O_2} directly from the spectra of experimentally homogenized glasses of geological relevance without an intermediate step of attempting to discern $\text{Cr}^{2+}/\text{Cr}^{3+}$. In this study, partial least-squares (PLS) multivariate (MVA) regression models were trained on the whole XAS energy spectral range, and accuracy was quantified using root mean square error (RMSE). MVA results showed significantly higher accuracy (RMSE-C of ± 0.75 log units) for predicting f_{O_2} Δ IW relative to known experimental conditions relative to the two-step method, which yielded RMSE-C of ± 2.75 to ± 7.65 log units for our data set vs. those of Berry and O'Neill (2004) and Berry et al. (2006), respectively. The MVA results calibrate a new Cr oxybarometer for use in low- f_{O_2} glasses with a cross-validated (RMSE-CV) accuracy of ± 0.84 log units f_{O_2} relative to a standard oxygen buffer. Finally, the new Cr oxybarometer was applied to lunar glasses, both volcanic and impact metamorphosed, to assess the range in oxidation conditions the materials experienced during formation. Lunar volcanic glasses cluster $\sim \text{IW} \pm 1$, close to that of previous studies while agglutinates and lunar impact melts record a wide range of f_{O_2} values using Cr oxybarometry.

Keywords: Oxidation, XANES, chromium, lunar glasses