

Universal Fe³⁺/Fe²⁺ Calibration and Prediction of Oxygen Fugacity from XAS of Silicate Glasses

M. D. DYAR^{1,2}, M.C. McCANTA³, AND A. LANZIROTTI⁴

¹Planetary Science Institute, 1700 E. Fort Lowell, Tucson, AZ 85719, USA (*correspondence: mdyar@psi.edu)

²Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075, USA

³Dept. of Earth and Planetary Sciences, Univ. of Tennessee, Knoxville, TN 37996, USA

⁴Center for Advanced Radiation Sources (CARS), The University of Chicago, Chicago, IL 60637, USA

Fe k-edge x-ray absorption spectra (XAS) have the potential to determine not only the valence state of Fe (and many other elements) but also Fe site ordering and equilibration conditions such as oxygen fugacity (f_{O_2}) [1]. To develop a universal calibration for predicting these variables in silicate glasses, we have synthesized, characterized (using Mössbauer spectroscopy and electron microprobe), and analyzed >400 silicate glasses with compositions from basalt to rhyolite, covering a range of $\log f_{O_2}$ from -13 to 0. Spectra show obvious variation (Fig. 1) across the entire range from the pre-edge to the EXAFS region.

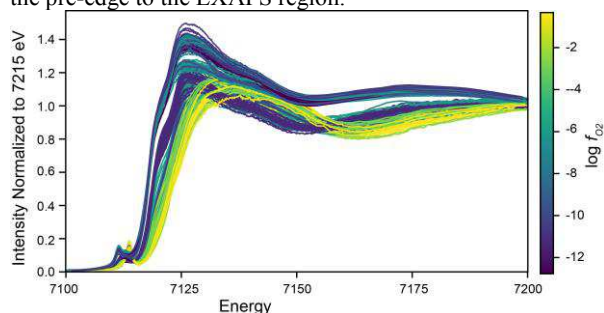


Figure 1: Fe XAS spectra of 429 silicate glasses covering a broad range of f_{O_2} and bulk composition, showing the dependence of XAS spectral shape on f_{O_2} .

Fe XAS spectra are affected by the general shape of the site occupied by the Fe cation. This is affected by valence state, site distortion, bond length, and bond type. Degree of polymerization of the melt also affects spectra shape as next nearest neighbors vary from ionically-bonded cations like Fe and Mg (e.g., in basaltic glasses) to Si⁴⁺ (rhyolitic glass) which is a strong network-former. The net effect is that large calibration data sets, such as the one described here, are needed to develop prediction models to measure %Fe³⁺ and f_{O_2} in glasses and minerals [2].

[1] Lanzirotti *et al.* (in review) *Amer. Mineral.* [2] Dyar *et al.* (2016) *Amer. Mineral.* **101**, 744-748, 1171-1189.