

Oxybarometry Based on Valence State Proxies: Progress and Challenges

STEPHEN SUTTON^{1,2}, ANTONIO LANZIROTTI¹, MATTHEW NEWVILLE¹, M. DARBY DYAR², JEREMY DELANEY³

¹Center for Advanced Radiation Sources and ²Department of the Geophysical Sciences, The University of Chicago, Chicago, IL; sutton@cars.uchicago.edu

²Planetary Science Institute, Tucson, AZ

³Rutgers University, New Brunswick, NJ

X-ray absorption fine structure (XAFS) spectroscopy has proven to be a valuable tool in defining valence states of multivalent elements in minerals and glasses that can then be used as oxybarometry proxies. First row transition multivalent elements are common targets (Ti, V, Cr, and Fe). MicroXAFS provides wide coverage of oxygen fugacity on all minerals and glasses, with high spatial resolution, trace level sensitivity, and no stoichiometry constraints.

These methods have been applied to an extensive array of Solar System materials including achondrites, lunar rocks and glasses, Martian meteorites, chondrules and refractory inclusions in chondrites, as well as terrestrial basalts and metamorphic rocks and minerals. Valence states alone can be insightful indicators of oxidation, such as the presence or absence of Ti³⁺ and the effects of metamorphism on asteroidal parent bodies [1]. Importantly, the methods can be extended to infer oxygen fugacity of parent melts by calibration using XAFS on laboratory experiment products under controlled conditions [e.g., 2]. When valence measurements on minerals are used, oxygen fugacity determinations require careful calibration of oriented samples along with knowledge of valence-specific partition coefficients to infer the valence [3]. XAFS offers the ability to apply multiple oxybarometers (e.g., Ti, Cr, and V valence proxies) to individual, potentially zoned, mineral grains [4].

Challenges include corrections for orientation effects, definitive interpretation/assignment of XAFS features, x-ray beam induced modifications, and the sparsity of valence-specific partition coefficient measurements. New spectral analysis methods are being developed, such as partial least-squares (PLS) analysis and least absolute shrinkage and selection operator (Lasso) regressions, to circumvent some of these complicating factors [5].

References: [1] Simon *et al.* (2015) *LPSC* **46**, 2141. [2] Hanson & Jones (1998) *Am. Min.* **83**, 669–684. [3] Kamber *et al.* (2007) *Am. Min.* **92**, 1238-1241. [4] Sutton *et al.* (2017) *GCA* **204**, 313-330. [5] Dyar *et al.* (2016) *Am. Min.* **101**, 1171-1189.