**PRELIMINARY RESULTS OF QUANTIFYING OXYGEN FUGACITY IN SOLAR SYSTEM MATERIALS WITH X-RAY ABSORPTION SPECTROSCOPY OF PYROXENES.**

C. J. Steven[1], M. D. Dyar[1,2], and M. C. McCanta[3], [1]Planetary Science Institute, Tucson, AZ 85719-2395, U.S.A., csteven@psi.edu; [2]Department of Astronomy, Mount Holyoke College, South Hadley, MA 01075, U.S.A.; [3]Department of Earth and Planetary Sciences, University of Tennessee, Knoxville, TN 37996, U.S.A.

Introduction: Oxygen fugacity (fO_2) is of extreme importance in geology in part due to the sensitivity of stable mineral assemblages on oxidation potential. The fO_2 of natural systems has long been established from experimental petrology, where controlling oxidation potential of metal-oxide starting material influences the reaction end-products. Thus, the oxidation environment of a system can be bracketed using composition of the stable mineral assemblage in a rock. Specific values of fO_2 are typically related to the ratios of Fe^{2+} and Fe^{3+} of Fe-bearing components in a system as Fe is the most common multivalent rock-forming element. Magmatic systems on Earth range to highly oxidizing value, while extraterrestrial bodies like the Moon, Mars, and asteroids display different, more reduced, oxidation states (**Figure 1**). For these more reducing conditions, analytical methods that can evaluate valence states of transition metals other than Fe are needed to provide the best understanding of fO_2 in natural systems [1].
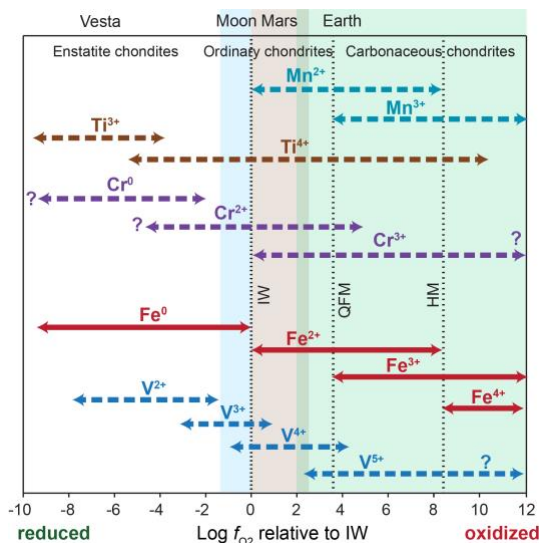
Figure 1. Oxygen fugacity of magmatic systems represented relative to the iron-wüstite (IW) buffer for Earth, the Moon, and Mars with a selection of redox states of several multivalent elements.

X-ray absorption spectroscopy (XAS) is a promising recent microanalysis method that uses the energy range near the K-edge lines to evaluate valence state. Although XAS spectra are orientation-dependent for anisotropic crystals and calibrations are specific to individual mineral groups, XAS can determine accurate ratios of individual redox components in minerals and
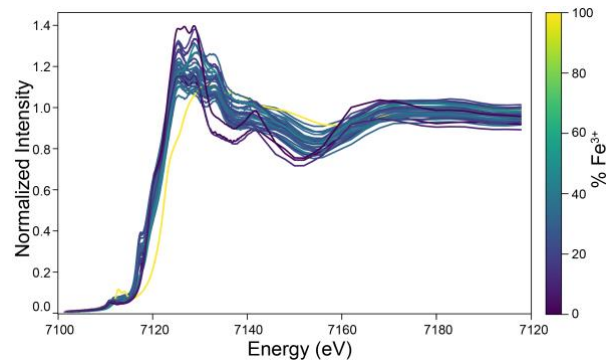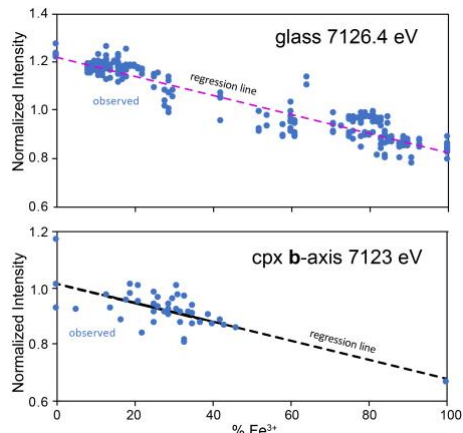

Figure 2. XAS spectra of a single orientation of several clinopyroxenes color-coded by $Fe^{3+}/\Sigma Fe$ measured from Mössbauer spectroscopy.

glasses and even be used for microscale redox mapping [2, 3, 4]. This study focuses on the nature of anisotropy of XAS spectra in clinopyroxene for Fe, and places the results in the context of yet-to-be-calibrated Mn, Ti, and Cr XAS data. These results show the potential for using XAS to determine redox ratios of those elements in pyroxene (and eventually, other) mineral groups.

Background: Minerals in igneous rocks often display multiple growth phases, and sometimes encapsulate glass that represents an earlier melt composition. Studies on fO_2 histories of such melts have been limited by analytical restrictions for determining the redox state of elements in minerals and glass. Absolute redox ratios for point analyses can be determined given knowledge of orientation, anisotropy, and a comparative database of standard spectra for a given mineral group. Maps require only a few energies that are sensitive to redox ratio, such as those near the absorption edge (**Figure 2**), and can be selected using multivariate analysis (MVA) methods.

Using standards with known Fe redox from Mössbauer spectroscopy, absorption intensities from XAS can be related to redox ratios (**Figure 3**). If the anisotropy of XAS is well-constrained for standards, as for pyroxenes (**Figure 4**), then spectra from a randomly oriented crystal with unknown Fe^{3+} content can be matched to the database and Fe^{3+} can be measured with quantified accuracy. Our group is actively pursuing this approach and initial results are promising. Related work has also shown that fO_2 can be predicted directly from well-calibrated standards in glasses [5] using MVA.

Samples studied: This project examined pyroxenes from Apollo 12 sample 12021,629 and the

Figure 3. Main edge relationship to $Fe^{3+}/\Sigma Fe$ determined from Mössbauer spectroscopy for glass (top) and a single orientation of clinopyroxene (bottom).

GRA95209,276 lodranite. Results were compared against pyroxenes from a variety of terrestrial igneous parageneses and localities including Cima and Dish Hill, CA, Kilbourne Hole, NM; Harrat al Kishb and Harrat Hutaymah in Saudi Arabia, New South Wales, Australia, and Goose Creek, VA.

Methods: All samples were analyzed by electron microprobe and Mössbauer spectroscopy to determine crystal chemistry. Individual crystals from each sample were then selected and oriented for XAS using single crystal X-ray diffraction along with spindle stage methods and the spreadsheet EXCELIBR [6]. XAS were acquired on each crystal data (2 μm beam size) at the GSECARS 13-ID-E beamline at the Advanced Photon Source using a special beam geometry [7] and appropriate energy ranges for each element of interest (Fe, Cr, Mn, Ti, and V (**Figure 5**).

The absorption indicatrix for each sample was modeled using the orientation and magnitude of characteristic absorption vectors at each energy; macroscopic models to describe the resultant absorption indicatrices are described in [8].
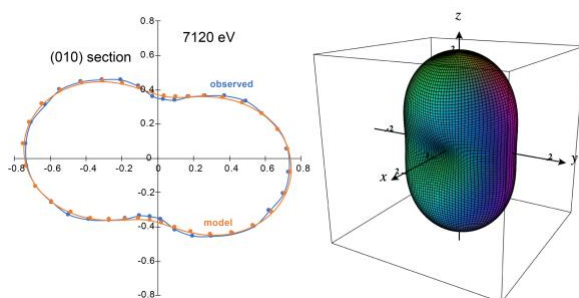
Figure 4. Observed and modeled absorption magnitude viewing the (010) section of a 0.33 $Fe^{3+}/\Sigma Fe$ pyroxene. Anisotropic absorption magnitude is represented as a 2D geometric object (left) plotted radially and its 3D counterpart, the absorption indicatrix (right).

Results: The absorption indicatrix models the anisotropy of the rising edge energies well, with an average 2.7% discrepancy between the modeled and observed absorption (**Figure 4**). The lunar sample is pure Fe^{2+} though its Ti and Mn spectra overlap with terrestrial samples (**Figure 5**). The lodranite sample has a reduced Cr spectrum but a Mn spectrum with oxidized characteristics.
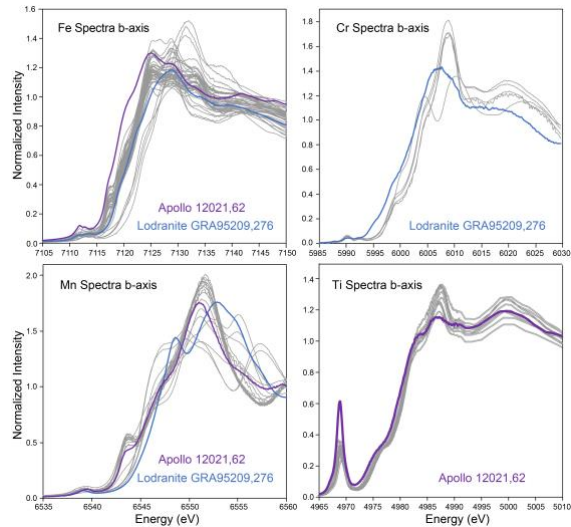
Figure 5. Terrestrial pyroxenes (grey) compared to extraterrestrial samples 12021,62 and GRA95209,276 with measurable Fe, Cr, Mn, and/or Ti. Reduced samples have peak intensities and edge features at lower energies, and correspond to the environments from **Figure 1**, with the exception of the apparently oxidized Mn of GRA95209,276.

Future work: Fe redox maps will be constructed using main-edge energies (~7119 to 7123 eV), and normalized to an intensity at 7354 eV, where absorption is nearly isotropic. Main-edge absorption magnitudes will greatly benefit from improved resolution, due to the large change in intensity/energy in the main edge energy range. Low-detection elements such as Mn, V, Cr, Ti, and Eu will be collected at longer count times, leveraging the capabilities of high energy resolution detectors (HERFD) as they become available. Other anisotropy tests will also be performed to examine the pre-edge more closely.

References: [1] Papike, J. J. et al. (2016) *Amer. Mineral.*, 101, 907-918. [2] Muñoz, M. et al. (2006) *Geochem., Geophys., Geosys.* 7, 1525-2027. [3] Sutton, S. R. et al. (1995) *Revs. Sci. Instrum.*, 66, 1464-1467. [4] McCanta, M. C., et al. (2019) *Amer. Mineral.*, *104*, 453-458. [5] Lanzarotti, A. et al., (2018) *Amer. Mineral.*, 103, 1282-1297. [6] Steven and Gunter (2017) *The Micro.*, 65, 147-152. [7] Dyar et al., 2002 *Amer. Mineral.*, 87, 1500-1504. [8] Steven et al. (In Review) *Amer. Mineral.*