TOWARD QUANTIFYING OXYGEN FUGACITY IN SOLAR SYSTEM MATERIALS: IN SITU MULTIVALENT ELEMENT ANALYSES IN PYROXENE.

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Introduction: One of the most important science questions relating to planetary materials is the role played by oxygen fugacity (f_{O2}), which constrains the evolution of planetary interiors as well as post-crystallization processes. Common methods for constraining f_{O2} measure the valence state of redox sensitive elements in in melts (glasses) and minerals. The redox states of Fe, measured using Mössbauer or x-ray absorption spectroscopies (XAS), have been exensively utilized for this purpose. However, as seen in **Figure 1**, Fe valence states tend to be insensitive to changing redox conditions (< iron wustite, IW0) found in the extremely reduced environments that are prevalent in numerous places in our solar system. Examples include the Moon and many meteorite types (e.g., cumulate eucrites, lodranites, diogenites, aubrites). However, other multivalent elements (especially Ti and V) have the potential to change valence states at these low f_{O2}'s, and may be more discerning and useful for solar system materials if well calibrated. Pyroxene in particular shows great promise as a recorder of f_{O2} values because it typically
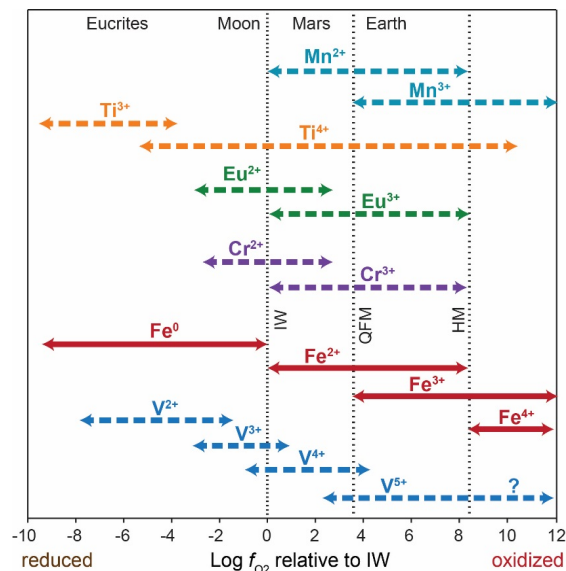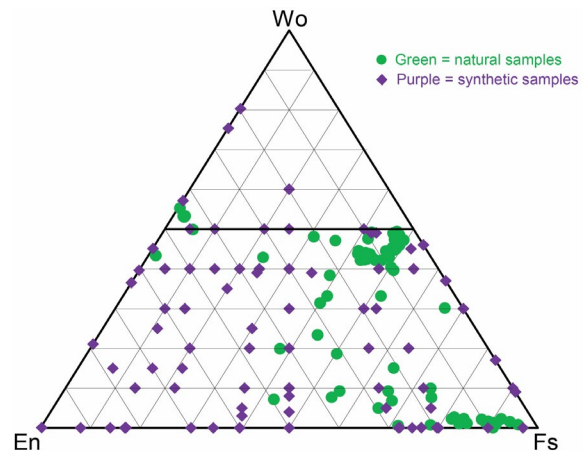

Figure 2. Compositions of 330 samples in our study suite, which includes both natural and synthetic pyroxenes.

contains all these elements and is ubiquitous on the surfaces of terrestrial bodies. The ability to explore the relationship between pyroxene multivalent element composition and f_{O2} hinges on being able to measure multivalent elements *in situ*. Microfocused XAS presents one of the most promising technologies for measuring valence states of phases in standard thin sections. Here, we report on efforts to develop oxygen fugacity calibrations based on XAS data from oriented pyroxenes.

Samples studied: Samples for this study are a subset of a large suite of synthetic and natural pyroxenes from Dyar's collections, as seen in Figure 2. $Fe^{3+}/\Sigma Fe$ ratios have been measured in all samples by Mössbauer spectroscopy. Electron microprobe analyses from previous studies [1-3] were combined with new data collected at Brown University by Joseph Boesenberg.

Experimental Methods: Single crystals were oriented morphologically and with the aid of EXCALIBR [4] using a spindle stage equipped polarizing light microscope. Optical orientations of all the samples were either checked morphologically or determined. Goniometer head settings were recorded to allow each crystal to be oriented along optical orientations: for biaxial+ minerals, AB=γ, ON=β, and OB=α while for biaxial- samples, AB=α, ON=β, and OB=γ. The μXANES data (2 μm beam size) were acquired at the GSECARS 13-ID-E beamline at the Advanced Photon Source using a special beam geometry. On the beamline, a spindle stage was mounted with the plane of rotation perpendicular to the path of the beam. The structure of each K
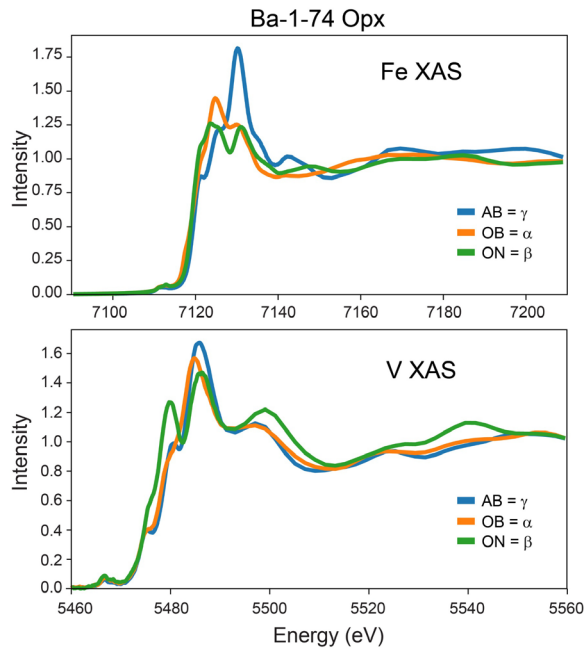

Figure 1. Oxygen fugacity (log f_{O2} relative to the IW buffer) of Fe, V, Cr, Eu, Ti, and Mn buffers relevant to planetary science, adapted from Papike et al. (2016). Ranges for Fe oxidation states are well-constrained, but less is known about V. Changes in Cr, Eu, V and Ti valence state at reduced log f_{O2} values are far more diagnostic than Fe, which remains divalent down to extremely reduced conditions.

Figure 3. XAS data for an oriented single crystal of a mantle orthopyroxene for Fe (top) and V (bottom). Each orientation has specific features related to the crystal structure. Spectra of Ti, Mn, and Cr are also being collected on each sample.

absorption edge was scanned from ~50 eV below the main absorption edge energy for each element extending to ~60 eV above the main edge. Details of these techniques can be found in [5,6] for Fe and analogous techniques were used for Mn, Cr, Ti, and V.

Results: Data collected from specific orientations are distinct from those of other orientations, just as in optical spectroscopy. These differences are seen in **Figure 3** for a mantle orthopyroxene from Dish Hill, CA (Ba-1-74). We know from crystal field theory and optical spectroscopy [7] that different cations are affected by interactions with local anion and cation environments that change energies of orbitals and vary with orientation. For example, the ON orientation (β in orthopyroxene) in Figure 3 produces the least intense peak in the Fe spectrum but a comparable-intensity peak in the V data because the energy levels in those cations are different, and thus they interact differently with their coordination polyhedra. For this reason, it is impossible to generalize the orientation dependence of XAS spectra in anisotropic minerals, and thus specific calibrations must be created for each element in each mineral group at each orientation to predict either valence state or f_{O2}. Although this is time-consuming work, the potential benefits of being able to understand and quantify these variables in solar system materials formed at low f_{O2} are critically important, and thus worth the effort.

When orientation is held constant, then subtle variations arising from valence state changes are apparent. **Figure 4** shows spectra cquired with the beam polarized along the AB optical orientation in selected samples in

the data set. The most variation is seen in the V data set, likely because, as seen in Figure 1, when Fe is reduced, there are still multiple possible valence states for V with different signatures. By contrast, Fe, Mn, and Cr do not change much at low oxidation states.

Future Work: This project highlights many issues to be studied using oriented samples: suppression of the pre-edge features, assignment of main-edge peaks to valence states, the potential for understanding cation ordering, and extrapolation to f_{O2}. Coupled equilibration experiments, single crystal refinements, and acquisition of spectra from many more samples are in progress to explore all these issues.

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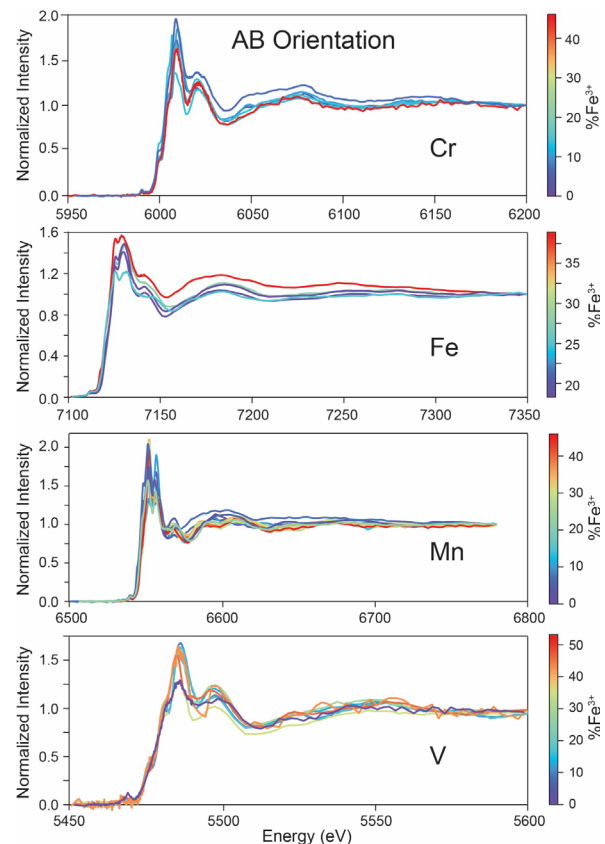

Figure 4. XAS data for single crystals of pyroxene with the beam polarization parallel to the AB optical orientation, color-coded to indicate the %Fe^{3+} in each sample.