IN SITU MEASUREMENTS OF FE^{3+} IN PYROXENE USING X-RAY ABSORPTION SPECTROSCOPY: USING AN ORIENTED CRYSTAL CALIBRATION TO REFINE GEOTHERMOBAROMETRIC CALCULATIONS. M. C. McCanta[1], M. D. Dyar[2], C. Steven[3], M. Gunter[3], and A. Lanzirotti[4], [1]Dept. of Earth & Planetary Sciences, University of Tennessee, 1621 Cumberland Ave, Knoxville TN 37996 (mmccanta@utk.edu), [2]Dept. of Astronomy, Mt. Holyoke College, South Hadley MA 01075, [3]Dept. of Geological Sciences, University of Idaho, Moscow, ID 83844, [4]Center for Advanced Radiation Sources (CARS), The University of Chicago, Chicago, IL 60637.

Introduction: Of all the major elements, Fe is the only one that commonly exists in multiple valence states in silicate melts. Thus, accurate knowledge of the Fe^{2+}/Fe^{3+} ratio provides the best proxy for the amount of oxygen that was present when the minerals crystallized, and allows estimation of magmatic oxygen fugacity (f_{O2}). To decipher the origin of an igneous rock, it is essential to first understand the compositional differences, phase changes, and crystallization sequence variations that can be caused by magmatic processes in a closed system at a given initial f_{O2}. Subsequently, the redox state of a magma can be determined to be primary or to have been changed by one of the above processes. For these reasons, development of oxybarometers to assess f_{O2} is important to a wide array of petrologic problems.

Mafic minerals have $Fe^{3+}/\Sigma Fe$ ratios that are a function of two factors: (1) crystal chemistry and (2) crystallization f_{O2}. Olivine and orthopyroxene have steric constraints on the extent to which Fe^{3+} can be incorporated in their structures, and may not record changes in magmatic f_{O2} that can be measured easily [1,2]. The composition of clinopyroxene (cpx), however, allows for extensive incorporation of Fe^{3+}, making it a potentially useful oxybarometer [3-5]. To date, there have been few systematic experimental studies of the variation of the $Fe^{3+}/\Sigma Fe$ ratio as a function of f_{O2} in mafic silicates. If a systematic variation of mineral $Fe^{3+}/\Sigma Fe$ with f_{O2} is identified, this finding could provide a valuable way of measuring f_{O2} in rocks that lack residual glass or where other oxybarometers are unusable.

Geothermobarometry: In addition to the Fe^{2+}/Fe^{3+} ratio providing a record of f_{O2}, many geothermometers and barometers are based on Mg-Fe partitioning within and among mineral phases. Here, knowledge of the Fe^{2+}/Fe^{3+} ratio is imperative because the substitution mechanisms in question rely on Mg-Fe^{2+} variation. Many studies either assume all measured Fe is Fe^{2+} or rely on pyroxene stoichiometric measurements from microprobe data, a difficult proposition [e.g., 6-8]. There are many ways of calculating Fe^{2+}/Fe^{3+} ratios stoichiometrically [e.g., 9,10]. All methods rely on some simplifying assumptions, such as iron being the only element with variable valence and oxygen being the only anion; these can result in significant analytical discrepancies. For example, the assumption that Fe is the only multivalent cation is particularly problematic in natural samples. Both Cr and Ti, important pyroxene components, can exist in more than one valence state (Cr^{2+}, Cr^{3+}; Ti^{3+}, Ti^{4+}), which would affect charge balance calculations.

Since original wet chemical analyses were first reported [e.g., 11] it has been widely known that most pyroxenes, especially cpx, contain Fe^{3+}. Models to calculate Fe^{3+} using electron microprobe data and chemical stoichiometry are generally incorrect for pyroxenes [12]. For example, a decrease of 1% in the SiO_2 content of a pyroxene, equivalent to a decrease of ~0.01 formula units of Si per six oxygens, can result in a tenfold increase in calculated Fe^{3+} [13]. Therefore, the use of the commonly reported total Fe ($Fe^{2+}+Fe^{3+}$) is not accurate and can lead to errors in calculated temperature or pressure. To circumvent these issues, previous studies have used Mössbauer analyses to directly measure Fe^{3+} content. However, this is a bulk measurement that destroys the sample and provides no spatial information, so zoning behavior of iron in pyroxene is virtually unknown. For all these reasons, the ability to measure $Fe^{3+}/\Sigma Fe$ *in situ* in geologically relevant phases is important in assessing temperature and pressure estimates from many igneous and metamorphic assemblages.

Analytical Methods: Measurement of iron oxidation states at microscopic scales has historically represented a formidable task. At present, microfocused X-ray Absorption Spectroscopy (XAS) is one of the most promising technologies for making these measurements on standard thin sections in small areas ($<1\times1$ µm at the Advanced Photon Source (APS), Argonne National Lab). The issue with *in situ* measurements is that synchrotron x-rays are plane-polarized within the ring, and thus they interact with anisotropic minerals in a fashion analogous to the phenomena that arise on a plane-polarized visible light microscope. X-ray "pleochroism" is caused when the x-rays interact with different atomic densities at different orientations within a crystal structure. In order to analyze *in situ* grains in random orientations, a calibration derived from crystals in known orientations must first be developed.

To demonstrate the significance of this effect, single crystals of selected pyroxenes of varying composition (including Mössbauer-determined Fe^{3+}/Fe^{2+}) from terrestrial rocks and meteorites were oriented morphologi-
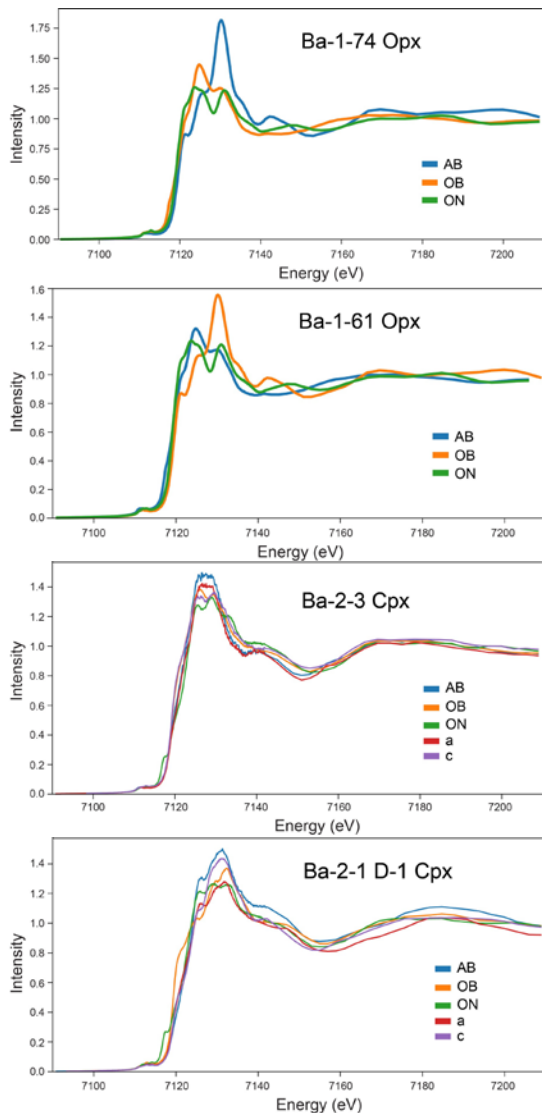
Figure 1. Comparison of XAS spectra from different optical and crystallographic orientations.

cally and with the aid of EXCALIBR [14] using a spindle stage equipped polarizing light microscope. The 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 and (for monoclinic cpx) crystallographic orientations relative to the vibration direction of the synchrotron beam: for biaxial+ minerals, AB=γ, ON=β, and OB=α; for biaxial- samples, AB=α, ON=β, and OB=γ.

Results: Preliminary results are shown in Figure 1, where it is clear that orientation has a significant effect on the XAS spectra of pyroxene. Moreover, this variation is apparently composition-dependent. For example, the two cpx grains have very different main edge spectra despite having similar crystal structures.

Earlier studies have used only the pre-edge features to $Fe^{3+}/\Sigma Fe$, but these features, too, are orientation-dependent (Fig. 2). Previous work in our group demonstrated this effect u[15,16], and found that this crystallographically-controlled variation resulted in large errors of ±20% in predictions of $Fe^{3+}/\Sigma Fe$.
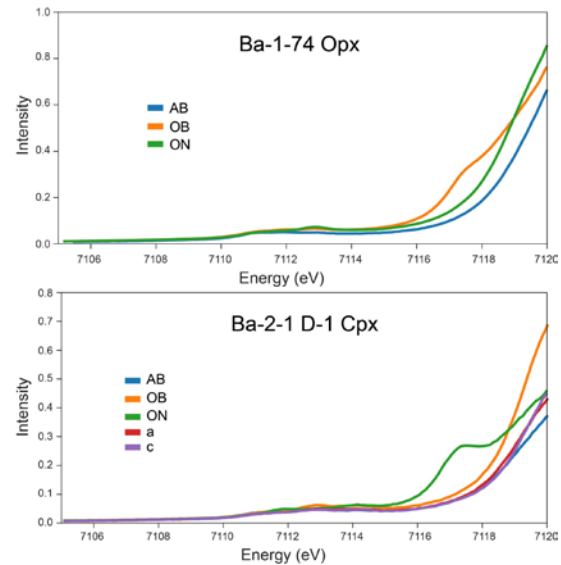

Figure 2. Close-up of two of the spectra at left showing variations in pre-edge spectra with orientation.

Discussion: Because of the unique capabilities of XAS in predicting valence state, many workers aspire to use this method to measure Fe^{3+} contents at microscales. This work shows that caution is needed to avoid over-interpreting pre-edge (and main-edge) spectra when analyzing anisotropic minerals. Multivariate analyses techniques have been shown to be useful in quantifying Fe^{3+} in amphibole [17] for which oriented single crystal spectra of all crystallographic orientations in a set of Fe^{3+} standards are available. A similar approach is needed to develop a pyroxene calibration, though more standards will be needed given the dramatic differences between ortho- and clinopyroxenes.

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