

SYNCHROTRON MICRO-XANES ANALYSIS OF Fe^{3+} IN ORIENTED AMPHIBOLES. E. A. Speicher¹, M. D. Dyar¹, M. E. Gunter², A. Lanzirotti³, J. M. Tucker⁴, S. E. Peel¹, E. B. Brown¹, and J. S. Delaney⁵. ¹Dept. of Astronomy, Mount Holyoke College, 50 College St., South Hadley, MA 01075, espeiche@mtholyoke.edu, ²Dept. of Geol. Sciences, Univ. of Idaho, Moscow, ID 83844, ³GSECARS and Dept. of Geophysics, University of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637, ⁴Dept. of Earth Planet. Sci., Harvard Univ., 20 Oxford Street, Cambridge, MA 02138, ⁵Dept. of Geol. Sciences, Rutgers University, Piscataway, NJ 08854.

Introduction: Development of techniques for microanalysis of $\text{Fe}^{3+}/\text{Fe}^{2+}$ remains a high priority for analyses of microscopic returned samples from extra-terrestrial sources as well as meteorite studies. Several methods for microscale characterization of Fe^{3+} and Fe^{2+} in minerals have been developed with varying degrees of success, but the synchrotron-based method of X-ray Absorption Near-Edge Spectroscopy (XANES) is perhaps the most promising for making Fe^{3+} and Fe^{2+} measurements *on standard thin sections* on a wide range of minerals. This technique utilizes the energy of the Fe K α absorption edge as well as the pre-edge feature found ~15-20 eV below it; both are very sensitive to the oxidation state of Fe.

Routine application of micro-XANES was initially hampered by X-ray pleochroism (differential interactions of the plane-polarized X-ray beam with anisotropic crystals) that resulted in $\pm 15\text{-}20\%$ error for $\text{Fe}^{3+}/\Sigma\text{Fe}$ measurements on randomly-oriented crystals [1,2]. Moreover, different mineral groups were found to require separate calibration lines (Fig. 1). Limitations in energy resolution of Si(111) monochromators also made it difficult to resolve fundamental absorptions in the pre-edge. Ongoing upgrades at hard X-ray microprobe beamline x26a at the National Synchrotron Light Source (both in terms of beam intensity and improved energy resolution available from a higher order Si(311) monochromator) have remedied the latter problem.

In this work, we address the orientation issue by

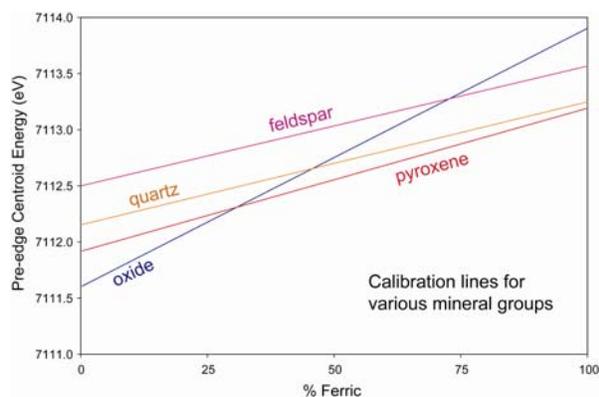


Fig. 1. Calibration lines for different mineral groups based on area-normalized pre-edge centroid positions. Differences among these lines show why mineral group specific standards for analysis of Fe^{2+} and Fe^{3+} using XANES pre-edge spectra must be developed and characterized.

studying oriented amphibole crystals with the X-ray beam polarized along the X, Y, and Z optical directions. Results provide calibration curves useful for data acquisition on carefully-selected oriented amphibole grains in thin sections, and pave the way for studies of other mineral groups.

Methods: Single crystals were oriented optically using a polarizing light microscope with a spindle stage. Each crystal was mounted with the Z optical orientation parallel to the rotation axis of a spindle stage, permitting acquisition of polarized XANES spectra perpendicular to the double chains (the *a* crystallographic axis) or within them (*b* and *c*). XANES measurements used a beam geometry described in [1].

Using mutually-orthogonal Kirkpatrick-Baez mirrors, the beam was focused to a $7\times 9\text{-}\mu\text{m}$ area. Incident beam energy was controlled by a Si(311) channel cut monochromator. The structure of the Fe K α absorption edge was scanned in the near-edge region. Incident beam energies were scanned from 7020-7220 eV. XANES spectra were collected in fluorescence mode using a 9-element high purity Ge solid state detector array. Spectra were edge-step normalized and corrected for self-absorption using the IFEFFIT Athena software package written by Ravel and Newville, which corrects XANES data measured with the fluorescence technique for self-absorption effects. Energies were calibrated to the magnetite centroid at 7113.25 eV (cf. [4]).

Each spectrum was cropped to only the pre-edge region. The main edge was removed by fitting with a segment of a DHO and a linear offset. The remaining pre-edge signal was fit using the Peak Analysis (PAN) processing package written by R. M. Dimeo. Each pre-edge was fit with two or three Lorentzian peaks, depending on the spectrum (Fig. 2). Fits were repeated with slight variations in starting parameters until a consistent set of peak positions was obtained for the data set as a whole. X, Y, and Z spectra for each sample were fit individually, and then an area-normalized centroid energy was calculated for each spectrum by multiplying each peak relative area by its centroid energy.

Results: Pre-edge peaks occurred consistently near 7114.3, 7112.9, and 7111.4 eV. Peaks are consistent in position, though intensities vary slightly with orientation. In Fe^{3+} -rich samples, total peak areas are greater for the X and Y orientations for all but the aegirine.

Discussion: The intensity of the ~ 7114.3 eV Fe^{3+} peak in the X orientation is often increased, corresponding to the direction perpendicular to the chains in the amphibole structure; this may result from higher distortion in that direction. Previous work [4] suggests that distortions from ideal octahedral symmetries allow for $3d \rightarrow 4p$ mixing, and affect both the intensity and energy distribution in the pre-edge region. The X direction is not collinear with any of the Fe-O bonds surrounding the Fe cation in the amphibole structure; rather, it bisects a triangle formed by O(1), O(2), and O(3) anions and is collinear with the H-O(1) bonds. We thus speculate that the enhanced intensity of the ~ 7114.3 eV peak is related to charge distribution and distortion associated with the H-O(1) bond.

Peak assignments for pre-edge transitions can be made using our data and previous work [5,6]. For $^{60}\text{Fe}^{3+}$, two electronic transitions are expected. For $^{60}\text{Fe}^{3+}$, the $^5T_2g(^5D)$ state is lower in energy than the $^5E_g(^5D)$ state by approximately 1.1-1.5 eV [5]. These can both be seen in completely oxidized samples at ~ 7114.3 and ~ 7112.9 eV. $^{60}\text{Fe}^{2+}$ pre-edges should be composed of (at least) three peaks corresponding, from lowest to highest energies, to the $T_1g(4F)$, $T_2g(4F)$, and $T_1g(4P)$ states respectively; a fourth predicted transition, A_2g , is not visible because it is a two electron transition with low probability. In samples studied here, only one (ca. 7111.4 eV, tentatively the $T_1g(4F)$ state) of these three peaks can be positively identified; the other $T_2g(4F)$, and $T_1g(4P)$ peaks may well overlap with the Fe^{3+} peak at ~ 7112.9 eV. Thus, the mid-

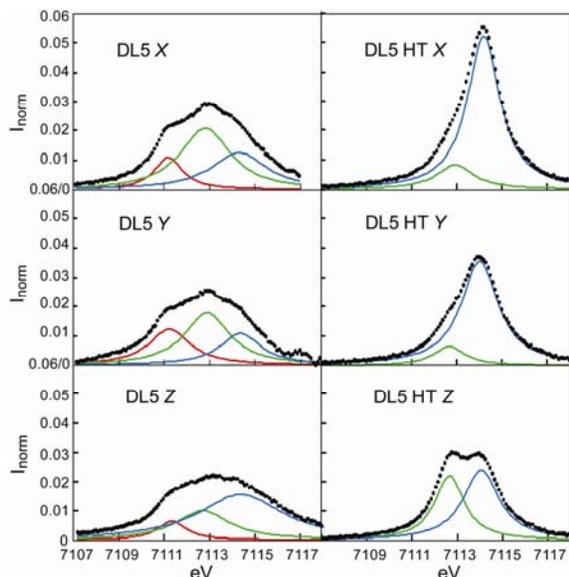


Fig. 2. Pre-edge spectra of amphibole DL-5 before (32% Fe^{3+}) and after (89% Fe^{3+}) oxidizing heat treatment (HT). The oxidized samples have more intense pre-edges because Fe^{3+} in the M sites in amphiboles has lower symmetry than Fe^{2+} . Unpublished data and samples from R. Oberti.

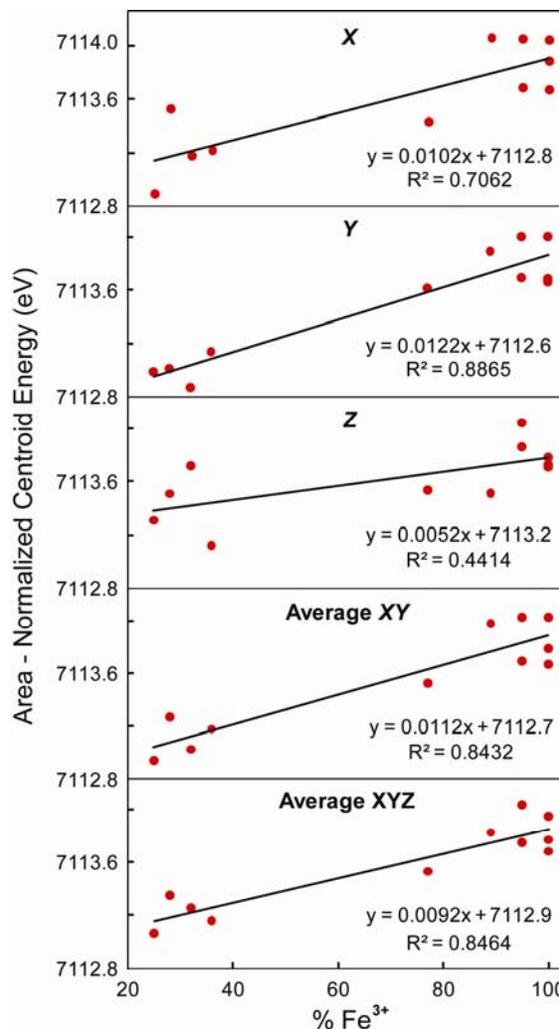


Fig. 3. Results of regressions relating the amount of Fe^{3+} in bulk sample of each amphibole (as measured by Mössbauer spectroscopy) to the area-normalized centroid of each pre-edge at varying orientations.

dle of the three pre-edge peaks in these amphiboles is probably a composite of both Fe^{2+} and Fe^{3+} .

Finally, results shown in Fig. 3 suggest that the most accurate way to measure Fe^{3+} contents of an amphibole single crystal with XANES is to orient the crystal with the beam polarized in the Y orientation. However, using the calibration curve for the average of X and Y would also produce viable results for spectra acquired anywhere in the X-Y plane.

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References: [1] Dyar M. D. et al. (2002) *Amer. Mineral.*, 87, 1500-1507. [2] Dyar M. D. (2002) *Can. Min.*, 40, 1375-1393. [3] Petit P.-E. et al. (2001) *J. Synch. Radiat.*, 8, 952-954. [4] Westre T. E. et al. (1997) *J. Am. Chem. Soc.*, 119, 6297-6313. [5] Calas G. and Petiau J. (1983) *Solid State Comm.*, 48, 625-629. [6] Galoisy L. and Calas G. (2000) *Chem. Geol.*, 174, 307-319.