

BROAD SPECTRUM CHARACTERIZATION OF RETURNED SAMPLES: ORIENTATION CONSTRAINTS OF SMALL SAMPLES ON X-RAY AND OTHER SPECTROSCOPIES. J.S. Delaney¹, M.D. Dyar², M.E. Gunter³, S.R. Sutton⁴, and A. Lanzarotti⁴. ¹Dept. Geol. Sci., Rutgers University, Piscataway, NJ 08854, jsd@rci.rutgers.edu; ²Mount Holyoke College, Dept. Earth and Environment, Mount Holyoke College, South Hadley, MA, 01075; ³Dept. Geological Sciences, Univ. of Idaho, Moscow, ID 83844; ⁴GSECARS and Dept. of Geophysics, Univ. of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637.

Introduction: Microanalysis of minute (<1 μm) returned samples, such as those from the Genesis, Stardust, and putative Mars and asteroid missions, will present significant analytical challenges. In most cases, micrometer and smaller grain sizes prevent use of the routine techniques that represent the “gold standard” methods of today. These include studies of elemental and isotopic abundance, morphology, and chemical state. There is a need for microanalytical methods because of the importance of obtaining analyses in petrographic context.

Currently there are many different microanalytical techniques being applied to the study of multivalent cations: optical, IR, XANES, SEM/TEM, EELS, ELNES, auger, EPMS, micro-Mössbauer, etc. These techniques use forms of input excitation but all monitor the changes in output energy, in most cases relative to known standards. A fundamental constraint on interpretation of the results is the fact that minerals studied in thin section are generally randomly oriented.

Only for the case of optical spectroscopy have the systematics of orientation been rigorously modeled [1]. Here, we present an initial framework for interpretation of micro-XANES spectroscopy for the study of oxidation state variations (e.g., $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{V}^{2+}/\text{V}^{3+}/\text{V}^{4+}/\text{V}^{5+}$, $\text{Cr}^{2+}/\text{Cr}^{3+}/\text{Cr}^{6+}$, $\text{Ti}^{3+}/\text{Ti}^{4+}$, etc.), and draw inferences from this work that will also apply to the other kinds of spectroscopy.

Although dealing with well-documented optical pleochroism is intuitive for most geologists, pleochroism at other wavelengths is not usually considered. The ability of minerals to transmit or absorb energy of different wavelengths in different directions is universal. For example, indices of refraction of a mineral are controlled by absorption bands in the UV. More broadly, anisotropy in biaxial materials would be possible and expected at longer wavelengths in the infrared etc. as well as shorter wavelengths (UV, X-ray, and gamma ray). Pleochroism/anisotropy at these wavelengths needs to be characterized.

Background: The ultimate goal for returned samples analysis is to provide *complete* mineral analysis, inclusive of *all* elements, isotopes, and crystal structure, at resolutions approaching the single-atom limit. Such analyses need to be done within a petrological

context, a constraint that remains fundamental to extraterrestrial samples and prevents the use of powders.

To accomplish this goal, it is critical to understand the interrelationships among the crystal lattice, the bonds, and the wavelength of energy being employed. It is easy to be fooled by reproducibility of analyses when precision cannot be constrained by independent measurements.

Past work by our group has had a consistent problem with precision, which was the result of our use of thin sections rather than powders. Initially, the low signal to noise ratios in our data prevented discrimination of fine spectral details from noise, making it difficult to assess precision. Even persistent repetition of analyses on identical spots did not improve the situation. Early attempts to quantify sample geometric effects were inconclusive because of poor precision and the inability to constrain crystallographic orientation on thin sections in that geometry. Both the early data and more modern data collected with higher signal to noise displayed excellent reproducibility on individual spots using the same geometry. Quantification of those spectra still led to large variations in derived $\text{Fe}^{3+}/\Sigma\text{Fe}$ results. The implication was that a significant orientation effect existed, which led us to design of experiments to quantify it in multiple mineral groups.

Orientation Experiments on Single Crystals:

As reported in [2], data were collected at the synchrotron X-ray microprobe (beamline X26A at the National Synchrotron Light Source of Brookhaven National Laboratory, NY). A special beam geometry was required. On the beamline, a spindle stage was mounted with the plane of rotation perpendicular to the path of the beam. This geometry is similar to that used in normal spindle stage measurements when the spindle stage is mounted on to a microscope stage [3]. This geometry allowed spectra to be acquired with the beam polarized directly parallel to the X, Y, and Z optical directions, or any other direction of choice.

The intensity of both pre-edge and main edge peaks is greatly variable as a function of orientation. As expected, structural similarities among these mineral groups result in similarities among their XANES spectra. Spectra acquired along the length of the chains (*c* for px, *c* for amph, and *a* for sheet silicates)

are similar, with corresponding changes in the optical directions, such that $Y_{\text{musc}} \approx Z_{\text{bt}} \approx Z_{\text{amph}} \approx Z_{\text{opx}} \approx X_{\text{aegirine}}$ (cpx is intermediate). Spectra taken along the b crystallographic axes (along the octahedral layer, across the I-beam) are similar for all groups ($Z_{\text{musc}} \approx Y_{\text{bt}} \approx Y_{\text{amph}} \approx X_{\text{opx}} \approx Y_{\text{cpx}}$), and more similar for the amphiboles and micas. Lastly, spectra acquired along the stacking direction, which is the a crystallographic direction for pyroxene and amphiboles the c crystallographic direction in sheet silicates, are analogous. Based on these results, the error in $\text{Fe}^{3+}/\Sigma\text{Fe}$ is roughly $\pm 20\%$ for pyroxene and amphibole and probably $\pm 10\text{--}15\%$ for micas if peak centroid fits are used.

Comparison of Reflectance and Transmission Mode Measurements: More recently, an additional set of experiments [in prep] sought to compare the relative effects of 1) differential x-ray absorption as a function of orientation, 2) self-absorption phenomena relating to Fe abundance, and 3) sample thickness. Results again show significant variation in peak intensities as a function of orientation. By analogy with optical spectra, it is likely that peak energies do not change as a function of orientation, though individual features may only be present at some crystallographic directions. However, peak intensities clearly change with orientation in both XAS and optical spectra. Although the effects of sample thickness in both transmission and fluorescence are notable, it is also clear that the effects of lattice orientation are clearly the most dominant feature in affecting the shape of the spectra in the XANES region.

X-ray Pleochroism in SNC Meteorites: A set of spectra from Shergotty pyroxene were acquired to graphically demonstrate this effect, which is characteristic of all anisotropic crystalline phases. Fig. 1 shows a typical plot of apparent $\text{Fe}^{3+}/\Sigma\text{Fe}$ vs. orientation, using measurements acquired on a single $8 \times 15 \mu\text{m}$ spot on a single pyroxene crystal on a rotating thin section. The resultant plot is exactly as predicted by [1] for an anisotropic material studied at any wavelength; similar results would be obtained by any spectroscopic technique that exploits interactions of electromagnetic radiation with a crystal lattice.

The spread of $\text{Fe}^{3+}/\Sigma\text{Fe}$ values shown here goes a long way toward explaining the anomalous results on Shergotty pyroxenes that were observed by [4] using the same beamline and techniques. Apparent zoning of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in QUE94201 may also be an artifact of space group changes as pyroxene composition changes from pigeonite to augite [5].

Discussion: Truly quantitative spectroscopic results cannot be obtained from randomly-oriented samples, because knowledge of the geometric relationship between the beam and the crystal lattice is required for

maximum information return. Failure to consider orientation effects leads to false optimism about the relative precision of relevant techniques.

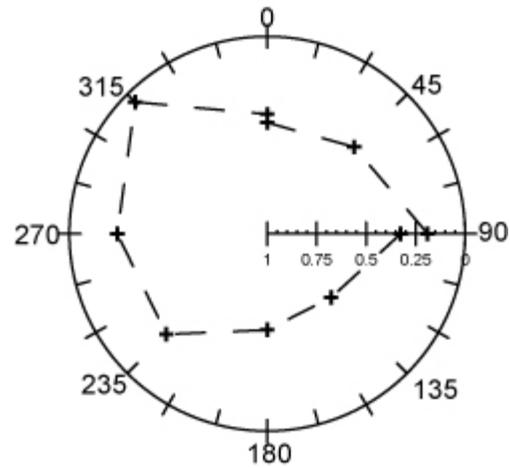


Figure 1. $\text{Fe}^{3+}/\Sigma\text{Fe}$ vs. orientation, using measurements acquired on a single $8 \times 15 \mu\text{m}$ spot on a randomly-oriented pyroxene grain.

Spectroscopic techniques are still useful to study unoriented samples, but results must be used with caution and awareness of orientation effects (and their inherent variability). Advances in technology will inevitably lead to 1) the capability to manipulate small targets relative to illumination in order to obtain desired orientations, and 2) tricks to exploit the limitations of analyses of randomly-oriented grains. Classic techniques already exist for finding grain orientations and manipulating thin sections to obtain data parallel to crystallographic orientations. A marriage of traditional universal stage techniques (or electron backscatter selected area diffraction, its modern equivalent) with state of the art microanalytical tools may well provide solutions to orientation-related problems.

Finally, we note that even spectroscopic studies of glasses may be affected by orientation effects, as natural glasses are seldom completely amorphous, and possess medium-range order. Transitions from glassy $^{55}\text{Fe}^{2+}$ to $^{66}\text{Fe}^{2+}$ in crystals have been observed in experimental charges of "glass."

References: [1] Libowitzky E. and Rossman G.R. (1996) *Phys. Chem. Mins.*, 23, 319-327. [2] Dyar M.D. et al. (2002) *Canad. Mineral.* 40, 1347-1365. [3] Bloss, D. (1981) *An introduction to the methods of optical crystallography*, Holt, Rinehart, and Winston, 294 p.; Gunter M.E. and Twamley B. (2001) *Canad. Mineral.* 39, 1701-1711. [4] Hale V.P.S. et al. (1999) *GCA*, 63, 1459-1470. [5] Delaney J.S. et al. (1999) *LPSC*, 30, #1861.