

Geometric constraints of *in situ* synchrotron micro-XANES determinations of oxidation state

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Many different microanalytical techniques are being applied to the study of multivalent cations: optical, IR, XANES, SEM/TEM, EELS, ELNES, auger, EPMS, micro-Mössbauer, etc. A fundamental constraint on interpretation of such spectra is the fact that minerals studied in thin section are generally randomly oriented. The pleochroism that is well-known in minerals at optical wavelengths also occurs throughout the EM spectrum. In X-ray spectra, the intensities of closely-spaced peaks in the pre-edge and main-edge regions vary with crystal orientation, producing a “color” change that is characteristic of all types of polarized energy spectroscopy.

Systematic orientation studies in thin section and on oriented single grains reveal a range of uncertainty in oxidation state measurements that may be directly related to lattice geometry. Thus, oriented samples must be used to obtain truly quantitative spectroscopic results, whether in thin section or grain mount. Failure to consider orientation effects leads to false optimism about the relative precision of relevant techniques.

A marriage of traditional universal stage techniques (or electron backscatter selected area diffraction, its modern equivalent) with X-ray microanalytical tools provide solutions to orientation-related problems. Such combined studies are essential to full characterization of micrometer-sized extraterrestrial returned samples.

Transmission and fluorescence mode microXAS analysis of oriented mineral grains

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Using a 20x30 μm beam size, transmission and fluorescence mode Fe $K\alpha$ X-ray absorption spectra were acquired on identical spots on each of a suite of optically biaxial mineral grains oriented with their optical directions (i.e, X, Y, and Z) in the plane of the beam polarization. Mineral samples were selected to represent varying Fe contents, bulk compositions, grain sizes, and crystal systems. This method allows comparison of the relative effects of 1) differential x-ray absorption as a function of orientation (“x-ray pleochroism”), 2) self-absorption phenomena relating to Fe abundance, and 3) sample thickness. Results show significant variation in peak intensities as a function of orientation, suggesting that interpretations of valence state or coordination number based upon XAS of grains in thin sections or as single crystals require knowledge of the lattice orientation of each mineral for optimal results.

Fluorescence mode spectroscopy is more flexible in terms of sample preparation, but transmission mode spectra can be acquired more quickly, making them optimal for studies where high count rates are needed. Transmission mode spectra can only be acquired on thin samples for which the 1/e sampling depth allows the beam to pass, but the optimal thickness for most minerals is comparable to the standard 30 μm thickness already widely in use, so this constraint does not pose a significant problem. Fluorescence mode measurements have the advantage of being able to work on any sample bigger than the focussed X-ray beam and thick enough to fluoresce Fe atoms (even in very low Fe samples), making them more conducive to the study of minerals in thin section. Both methods require control of grain orientation for optimum results. Accordingly, novel procedures for orienting mineral grains and preparing them for analysis are being developed.