

**MICROANALYSIS OF IRON OXIDATION STATES USING X-RAY ABSORPTION SPECTROSCOPY** S. R. Sutton<sup>1</sup>, S. Bajt<sup>1</sup>, and J. S. Delaney<sup>2</sup>. <sup>1</sup>Dept. Geophys. Sci. and CARS, The Univ. of Chicago, Chicago, IL 60637; Dept. Applied Science, Brookhaven National Laboratory, Upton, NY 11973; <sup>2</sup>Dept. Geol. Sci., Rutgers Univ., New Brunswick, NJ 08903.

**Abstract:** Initial results are reported on a new microanalytic technique for determining  $\text{Fe}^{3+}/\Sigma\text{Fe}$  in iron oxides and Fe-bearing silicates in conventional thin sections. The technique is based on the monotonic energy shift of a pre-edge peak in x-ray absorption near edge spectra obtained using the synchrotron x-ray microprobe. Reasonable results were obtained for pallasitic olivine, altered magnetites and synthetic wüstite.

**Introduction:** Oxygen fugacity is one of the most important parameters in determining the cosmochemical and geochemical evolution of a system. Petrogenetic models generally assume particular oxygen fugacities based on indirect evidence. Independent methods for the determination of oxygen fugacity have been unavailable. The oxidation states of minor and trace elements in specific phases can be used to directly probe oxygen fugacity, however, no microanalytical technique currently is available with this capability. We report here progress on development of synchrotron-based techniques to determine the oxidation states of 3d transition metals in individual mineral grains in conventional thin sections based on X-ray Near Edge Absorption Spectroscopy (XANES). This report focuses on the determination of  $\text{Fe}^{3+}/\Sigma\text{Fe}$  in iron oxides and Fe-bearing silicates. The oxidation state of iron is of fundamental interest. Iron's ubiquity in rock-forming minerals means that it is frequently possible to study the chemical state of iron in a variety of co-existing minerals. Equally significant, iron-dominated phase relations are important chemical controls under the reducing conditions that exist in cosmochemical systems.

**XANES Determination of Oxidation State:** The basis of XANES is the mapping of the x-ray absorption cross section of the element of interest with high energy resolution. The precise energy of the main absorption edge and associated structural features provide information on the oxidation state(s) and bonding environment of that element [1-3]. A pre-edge peak in transition metal K-edge spectra is typically due to  $1s \rightarrow 3d$ , bound-state, electronic transitions. Previously, we have used the intensity of the pre-edge peak to infer  $\text{Cr}^{6+}/\Sigma\text{Cr}$  in waste encapsulation media [4]. The present work is the first attempt to use the pre-edge peak energy to quantify the proportions of various oxidation states in mixed-valence samples. The basis of this technique is the derivation of an oxidation state versus pre-edge peak energy calibration curve using fayalite ( $\text{Fe}_2\text{SiO}_4$ ;  $\text{Fe}^{3+}/\Sigma\text{Fe}=0$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ;  $\text{Fe}^{3+}/\Sigma\text{Fe}=0.67$ ), and hematite ( $\text{Fe}_2\text{O}_3$ ;  $\text{Fe}^{3+}/\Sigma\text{Fe}=1.0$ ). The main complication in this approach is decoupling energy shifts due to oxidation state from those due to coordination geometry. The expectation is that pre-edge peak energies will be determined largely by the former because the resonances involve bound state transitions and therefore molecular effects are minimized. However, one of the main purposes of this initial work on relatively well characterized specimens is to determine experimentally the magnitude of *matrix effects*.

**Analytical Technique:** The synchrotron x-ray fluorescence microprobe on beamline X26A at the National Synchrotron Light Source (NSLS) was used in its normal configuration (see e.g., [5]) including a Si (111) channel-cut monochromator (energy bandwidth  $\Delta E/E=10^{-4}$ ) and x-ray focusing mirror (ellipsoidal 8:1). A focused monochromatic x-ray beam size of  $100 \mu\text{m} \times 150 \mu\text{m}$  was used in the present work. An ion chamber was located down stream of the slit assembly for incident beam intensity normalization. The detector was a Si(Li) energy dispersive instrument with an area of  $30 \text{mm}^2$  mounted at  $90^\circ$  to the incident beam (i.e., incident and takeoff angle at  $45^\circ$ ).

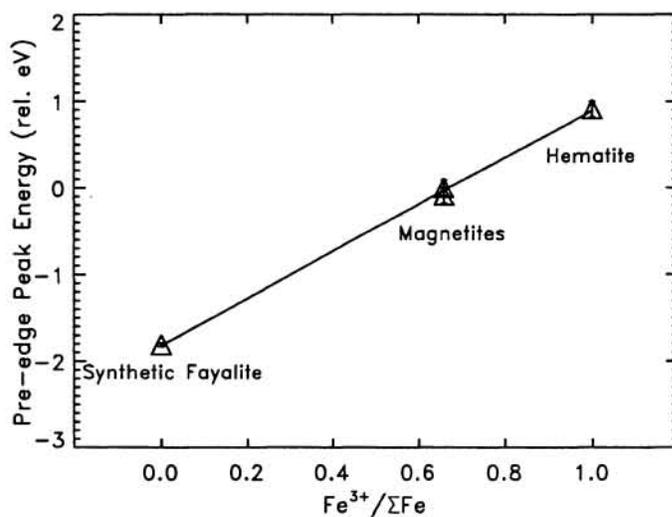
XANES spectra were obtained by recording the Fe  $K_\alpha$  fluorescence intensity as the incident monochromatic beam energy was scanned in 0.2 eV intervals over the range approximately -30 to +40 eV relative to the main absorption edge energy. Each energy interval

was counted between 3 and 5 live seconds for a total XANES spectrum acquisition time of  $\leq 30$  minutes. Counting times were adjusted to obtain at least  $10^4$  counts per pixel above the absorption edge. This resulted in about  $10^3$  counts at the maximum of the pre-edge peak (about  $10^4$  counts integrated peak area). Under these conditions, the minimum Fe concentration for which a useable Fe K XANES spectrum could be obtained was about 400 ppm. The energy of the pre-edge peak was defined to be the centroid of a Gaussian fit to the peak after background subtraction. All XANES energies were computed relative to the centroid of the pre-edge peak for a pure magnetite which had been characterized by the Mössbauer method.

**Results:** Four samples with well-defined Fe oxidation states by other methods (e.g., Mössbauer spectroscopy) were used to generate a calibration curve of "pre-edge peak energy" versus " $\text{Fe}^{3+}/\Sigma\text{Fe}$ ". These standards were: a pure hematite ( $\text{Fe}^{3+}/\Sigma\text{Fe}=1.0$ ), two pure magnetites ( $\text{Fe}^{3+}/\Sigma\text{Fe}=0.67$ ) and a synthetic fayalite ( $\text{Fe}^{3+}/\Sigma\text{Fe}=0.0$ ). The resulting calibration curve (Figure 1) yielded a linear regression line with a correlation coefficient of 0.99 indicating that the pre-edge peak energy shift was monotonic. Several "unknowns" were also analyzed. Six altered magnetites gave reasonable results for  $\text{Fe}^{3+}/\Sigma\text{Fe}$  based on the calibration curve: Mineville ( $0.75 \pm 0.09$ ), Snarum ( $0.78 \pm 0.07$ ), Sterling ( $0.83 \pm 0.09$ ), Elba ( $0.86 \pm 0.09$ ), Warwick ( $0.91 \pm 0.07$ ) and Monroe ( $0.95 \pm 0.07$ ). A fine-grained, synthetic pigment yielded a  $\text{Fe}^{3+}/\Sigma\text{Fe}$  value of  $0.68 \pm 0.09$ , in exact agreement with the Mössbauer spectroscopy result. A pallasitic olivine gave  $\text{Fe}^{3+}/\Sigma\text{Fe}=0.02 \pm 0.06$ . A synthetic wüstite sample ( $\text{Fe}_{(1-x)}\text{O}$ ) yielded  $\text{Fe}^{3+}/\Sigma\text{Fe}=0.18 \pm 0.10$  suggesting a reasonable value of  $x = 0.06$ . These initial results are encouraging particularly in terms of the apparent insensitivity of the pre-edge peak energy to bonding environment.

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**References:** [1] Manceau A., et al. (1992) *Amer. Mineral.* 77: 1133-1143. [2] Sutton S. R., et al. (1993) *Geochim. Cosmochim. Acta* 57: 461-468. [3] Waychunas G. A., et al. (1983) *Phys. Chem. Minerals* 10: 1-9. [4] Bajt, S., et al. (1993) *Anal. Chem.* 65, 1800-1804. [5] Sutton, S. R., et al. (1993) *Nucl. Instrum. Methods B* 75, 553-558.



**Figure 1:** Plot of "pre-edge peak energy" vs " $\text{Fe}^{3+}/\Sigma\text{Fe}$ " for well-characterized standards: a pure hematite ( $\text{Fe}^{3+}/\Sigma\text{Fe}=1.0$ ), two pure magnetites ( $\text{Fe}^{3+}/\Sigma\text{Fe}=0.67$ ) and a synthetic fayalite ( $\text{Fe}^{3+}/\Sigma\text{Fe}=0.0$ ). The trend is linear with a correlation coefficient of 0.99.