

MICROANALYSIS OF IRON OXIDATION STATE IN IRON OXIDES USING X-RAY ABSORPTION NEAR EDGE STRUCTURE (XANES)

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An exploratory application of x-ray absorption near edge structure (XANES) analysis using the synchrotron x-ray microprobe was undertaken to obtain Fe XANES spectra on individual sub-millimeter grains in conventional polished sections. The experiments concentrated on determinations of Fe valence in a suite of iron oxide minerals for which independent estimates of the iron speciation could be made by electron microprobe analysis and x-ray diffraction.

Introduction: The valence states of transition metals are of fundamental importance in many cosmo- and geochemical systems. In particular, a vast body of literature exists relating the ratio of ferric to ferrous iron to the geological environment. Iron may occur in both ferrous and ferric states in important rock-forming minerals (e.g. pyroxene, amphiboles, micas, feldspars, and oxide minerals). Minerals that can simultaneously accept both Fe²⁺ and Fe³⁺ are particularly valuable as these minerals directly provide constraints on the oxygen fugacity of the environment in which they equilibrated. The limited availability of extraterrestrial samples suitable for conventional techniques for ferrous/ferric ratio determination (such as Mössbauer and wet chemistry) has inhibited the study of valence states. Models of lunar and achondrite petrogenesis generally assume particular oxygen fugacities based on indirect evidence. Since many of these assumptions involve low oxidation states that can stabilize reduced species of Ti and Cr (Ti³⁺ and Cr²⁺) as well as Fe⁰ and Fe²⁺, a technique that can directly measure these valences could provide valuable constraints on these models. We report here an exploratory application of x-ray absorption near edge structure (XANES) analysis [1] using the synchrotron x-ray microprobe to obtain Fe XANES spectra on individual sub-millimeter grains in conventional polished sections. Previous microXANES studies have included Cr in lunar olivine [2], Cr in diamond inclusions [3], and Fe in plagioclase [4]. The experiments reported here concentrated on Fe valence in a suite of iron oxide minerals for which independent estimates of the iron speciation could be made by electron microprobe analysis and x-ray diffraction.

Samples: Magnetite crystals consisted of Rutgers University Geological Museum specimens, commercial samples and the NMNH magnetite microprobe standard. The Fe³⁺ standard was a hematite (Fe₂O₃) powder pressed into a pellet with boric acid as a binder. The magnetites provide a particularly useful test of the ability of microXANES to determine ferrous/ferric ratios. Although, magnetite is theoretically Fe₃O₄ with Fe²⁺/Fe³⁺=0.5, natural samples can deviate significantly from this ideal ratio either by substitution of other spinel end-members or by alteration. Of the seven magnetites studied here the maximum observed substitution was about 10% (mol.) ulvöspinel (Fe₂TiO₄). Only two samples were essentially unaltered (NMNH standard from Minas Gerais, Brazil; and the Mineville, NY magnetite) and these were used as pure magnetite standards. All other magnetites and the commercial "Fe₃O₄" analytical grade reagent were significantly altered (as determined by XRD) containing predominantly either hematite (Fe₂O₃) or an iron oxyhydride phase. The Fe²⁺/Fe³⁺ ratio of these magnetites was therefore significantly higher than that of an ideal magnetite.

Analytical Techniques: The synchrotron x-ray fluorescence microprobe on beamline X26 at the National Synchrotron Light Source (Brookhaven National Laboratory, NY) was used in its normal configuration [see e.g., 5-7] with the addition of a silicon (111) channel-cut monochromator on the incident radiation. A beam size of about 50 μm was used. XANES spectra were obtained by scanning the incident beam energy from just below to just above the Fe K absorption edge and recording the Fe K_α count rate at each incident energy. The detector was a Si(Li) energy dispersive instrument with an area of 30 mm² mounted at 90° to the incident beam (i.e., incident and takeoff angles = 45°). Fe K_α count rates were reduced to sufficiently low levels (~5000-7000 cps) by increasing the sample to detector distance to about 25 cm and adding a 3 mm detector aperture. A total energy scan of about 100 eV was made in 300 steps (0.3 eV/step) with each step counted for between 1 and 5 live seconds. Energies were defined relative to the energy of the half-height of the Fe metal absorption edge.

Results: The hematite and unaltered magnetite XANES spectra are shown in figure 1. The general form of these spectra are consistent with those reported by Waychunas et al. [8]. Derivatives of the XANES spectra were used to determine the energies and relative intensities of the XANES spectral features. Four peaks were present in the derivative spectra at relative energies of -7, 1, 4, and 7 eV (figure 2). The unaltered magnetite spectra were dominated by the pre-edge peak at -7 eV and a peak at 1 eV. The hematite spectrum also contained the pre-edge peak but was dominated by peaks at 4 and 7 eV instead of the 1 eV peak seen in the magnetite spectra. Also shown in figure 2 is a representative derivative spectrum for the altered magnetities. As expected, the intensities of the peaks in the altered magnetite spectrum are intermediate to those of the two standards. Qualitatively, the XANES spectra suggest that the altered magnetites are roughly equal mixtures of magnetite and hematite. Work is in progress to quantify the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in these crystals.

Conclusions: MicroXANES has great potential for tackling lunar, meteoritic and terrestrial petrogenesis. It may, for example, eventually be possible to determine f_{O_2} from $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios after careful studies of crystals grown under controlled conditions. In principle, such determinations should be possible on zones of individual crystals. The chemical states of other elements such as Ti, V, Mn, and Ni should also be measurable using microXANES.

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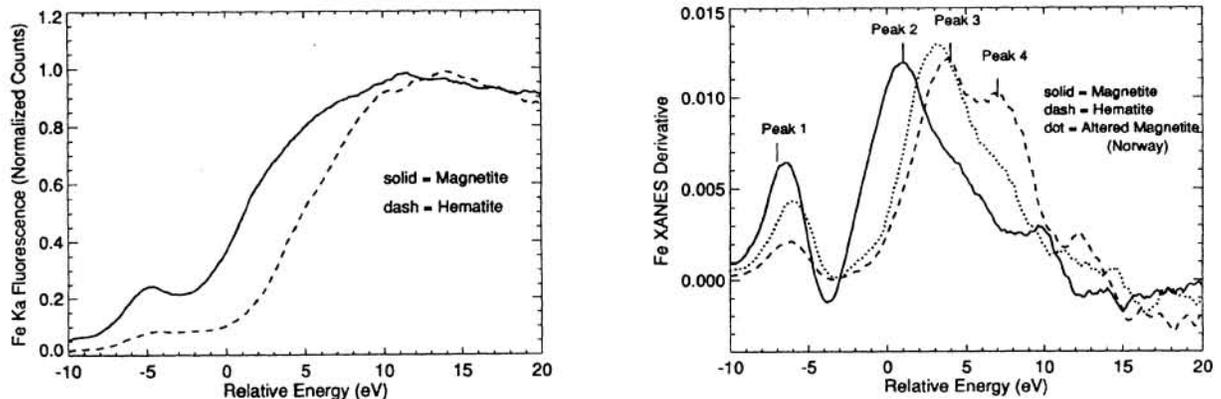


Figure 1: Fe K XANES spectra for unaltered magnetite ($\text{Fe}^{2+}/\text{Fe}^{3+} = 0.5$; solid line) and hematite ($\text{Fe}^{2+}/\text{Fe}^{3+} = 0$; dashed line). The shift in edge energy is due to the difference in oxidation state.

Figure 2: Derivatives of the spectra in figure 1 plus that of an altered magnetite (dotted line). The derivative spectra consist of 4 peaks which vary in intensity.