In situ microXANES determination of ferrous/ferric ratio in terrestrial and extraterrestrial plagioclase: first reconnaissance

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INTRODUCTION: Microanalytical determination of the oxidation state of transition metals in silicates and other geological materials has proven to be impractical using most instrumental techniques. Classical gravimetric techniques and Mössbauer spectroscopy are currently the methods of choice for bulk samples, but even these methods retain high levels of uncertainty when applied to high ferrous/ferric ratios [1,2]. Measurements of the Fe Ka absorption edges in Fe bearing minerals [3-5] using synchrotron-based x-ray absorption near edge spectroscopy (XANES) suggest that the position of this edge can vary systematically with ferrous/ferric ratio although variable coordination of the Fe site causes complications [5].

Samples of the Earth, the Moon, the basaltic achondrite parent body and possibly Mars have been documented. Plagioclase data for some of these samples (An95-An98), measured using synchrotron based XANES, suggest that this technique has promise as a microanalytical procedure for the determination of the ferrous/ferric ratio within particular mineral groups. Spectra of the x-ray fluorescence yield across the Fe Ka absorption edge (taken as 7111 eV in silicates and other geological materials) has proven to be impractical using most instrumental techniques.

The quoted energy of each edge is the assumed energy. A silicon [220] channel-cut two surface monochromator was rotated about the energy of the Fe Ka absorption edge to select the incident x-ray energy. Typically rotation of 0.3 to 0.4° corresponding to 7111 eV ±60 eV was sufficient to define the Fe edge and related spectral features. The energy resolution of the monochromator's rotator is 0.2 eV, although the bandpass is about 0.5 eV. Visual inspection of the resultant spectra reveals that most are dominated by steep discontinuities at the absorption edge. However, pre-edge and above edge features appear in several spectra. These features reflect details of the crystallographic sites of the Fe atoms. To calibrate the absolute variation of the Fe Ka absorption edge position with oxidation state of iron, spectra were taken for an NBS Fe-Ni alloy standard and for pure hematite, corresponding to pure Fe²⁺ and Fe³⁺ respectively (Figure 1). The hematite spectrum has a simple absorption edge, but the Fe alloy spectrum is more complex and has a slope break in the edge related to the geometry of the Fe site. To minimize the complexities associated with these fine details, the region of MAXIMUM POSITIVE SLOPE, on each spectrum studied, was selected to represent the absorption edge for that sample. The steepest region was selected by visual inspection of the intensity-normalized spectrum. A linear regression was generated for the normalized data from this region. This visual procedure appears adequate for samples with intense edges (i.e. high Fe contents) that have long straight portions, but for spectra with weak edges (low Fe content) this procedure is imprecise. All the plagioclase spectra yielded linear regressions with similar slopes and vary mainly in their position relative to the Fe edge (Figure 1).

The maximum slope criteria appears to provide a reasonable basis for comparison, the regression lines are characterized by their energy variation relative to the edge from the NBS Fe standard (which has the lowest energy observed). For example, the Fe²⁺ edge in hematite standard lies +5.2±0.2 eV above the Fe²⁺ edge. Thus the energy shift per charge state is about 3 eV. The quoted energy of each edge is determined from the average energy displacement of its regression line from the Fe²⁺ line (Figure 1). Quoted errors reflect deviations from parallelism of the plotted slopes.

RESULTS: Absorption edges apparently spanning a wide range of oxidation states between Fe⁰ and Fe³⁺ have been obtained. Fe Ka absorption edge energies for the plagioclase samples are: (i) Terrestrial: Stillwater plagioclase: +4.8±0.1 eV; Lake County: +7.3±0.2 eV. (ii) Lunar: 15415: +5.5±0.1 eV; 60035: +4.7±0.1 eV. (iii) Martian: ALHA77005: +4.8±0.2 eV; EET79001: -4.6±0.3 eV and 3.1±0.1 eV. (iv) Achondrites: EET787520: +6.±0.4 eV; Vaca Muerta clast: +3.2±0.4 eV. The edges for several lunar and shergottoid samples and from the terrestrial Stillwater plagioclase lie at 4.7 eV. The common position of these edges is tentatively interpreted to represent the presence of only Fe⁺ in these feldspars. This is reasonable the Fe⁰⁺ edge should lie about 3 eV below the Fe³⁺ edge, i.e. at about 5 eV, although confirmation requires comparison with a Fe²⁺ standard. The Lake County plagioclase spectrum is, in contrast, significantly displaced toward the Fe³⁺ edge. Surprisingly, both 15415 and eucrite EET787520 have Fe absorption edge displaced to high energy side of the assumed Fe³⁺ lines. In addition, three spectra (from 70035, Vaca Muerta and from EET79001) lie between this main cluster and the Fe³⁺ edge, implying the presence of both Fe²⁺ and Fe³⁺. The presence of undetected submicroscopic metal inclusions in the analysed feldspar could produce these edges. The position of these edges is not yet well defined however, as some of the absorption edge...
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spectra have short straight portions making the visual fit method imprecise. [EET79001, the shergottoid, contains maskelynite, instead of plagioclase, that may have incorporated shock melted Fe from its grain boundaries, although no metal is observed in this sample.]

**DISCUSSION:** The variation of the position of Fe Ka absorption edge from metal to hematite and within the analysed suite of minerals suggest that synchrotron-based XANES may eventually be used to measure ferrous/ferric ratios in situ in thin sections of silicate minerals. The position of the edge is independent of the major element composition of the plagioclase. Further calibration of this effect is needed, as neither Fe metal nor pure hematite is likely to be an ideal standard for calibrating measurements of silicates particularly given the complexities discussed by [3-5]. By comparing spectra for a single mineral group, however, the role of site geometry is minimized although plagioclase contains both a tetrahedral and a quasi-octahedral [Ca] site into which Fe may substitute. Comparable data for Cr absorption edges [6] indicates that silicate standards will be essential for accurate measurements. In addition, energy difference of 1.5eV observed between the maskelynite spectra of 2 grains from EET79001 suggests that polarization effects or the effect of submicroscopic inclusions might be significant. The difference in the position of the Fe2+ and Fe3+ absorption edges in plagioclase appears to be about 3.5eV and is significantly larger than the resolution of the technique (which may be less than 0.5eV). The apparent precision of the ferrous/ferric ratios is about ±15-20%. Quantitative estimation of ferrous/ferric ratios in these samples is premature, but if the edge shifts truly reflect variable Fe3+/Fe2+ ratios, microXANES may eventually be an important technique for determining ferrous/ferric ratios. If the variability of terrestrial feldspars is confirmed, then microXANES can provide a powerful technique for comparing the oxidation state of samples from different portions of magmatic systems, in xenoliths from sediments and metasediments, and indeed to assess variation in the oxidation state of mantle samples both as a function of time and location. Measurement of ferrous/ferric ratios in extra-terrestrial samples provides a powerful new constraint on petrogenetic models of these suites.


ACKNOWLEDGEMENTS: This research was supported by the following grants: NASA NAG9-104 (JSD); NAG9-106 (SRS); NSF EAR86-18346 (ML Rivers), Chemical Sciences Division, Office of Basic Energy Sciences, US DOE under Contract No. DE-AC02-76CH00016, Univ. of Chicago CARS Startup Grant, State of Ill. Tech. Challenge Grant. We thank the staff of the NSLS for providing the x-ray beam and Peter Salpas for use of the Stillwater sample.

**FIGURE 1** Linear regression fits (represented by arrays of data points) of the steepest portions of Fe Ka absorption edges for plagioclase. Intensity is normalised between the max. above the edge and the average below the edge. The half height point on the Fe0 edge is the nominal (7111eV) origin for the energy axis.