

## Comparison of quantitative Synchrotron microXANES (SMX) $\text{Fe}^{\text{III}}/(\text{Fe}^{\text{II}}+\text{Fe}^{\text{III}})$ results for amphibole and silicate glass with independent measurements.

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**ABSTRACT** *In situ* measurements of the oxidation states of elements such as Fe, Cr, V, Mn, Ti, Ce, Eu, Re, U can be made using synchrotron microXANES (SmX) techniques. Iron oxidation state measurements are of fundamental importance in most terrestrial systems and are useful in meteoritic and planetary materials. Oxidation state measurements of other transition metals have great implications for extraterrestrial samples that equilibrated at oxygen fugacities lower than typical terrestrial systems. The development of microbeam techniques using synchrotron x-ray sources, permits oxidation state measurements in microvolumes of sample comparable to the compositional microprobe analysis volumes. Comparison of Fe oxidation state ratios by SmX with independent data for amphibole samples and other minerals shows a good correlation between the microanalytical and bulk techniques. The spatial resolution of SmX permits zoning of oxidation states to be documented and also allows inclusions in minerals to be avoided. Analyses of Fe oxidation states can be made quantitatively in microvolumes comparable with those analyzed for composition by other microanalytical techniques. The consistence of the SmX results and conventional techniques implies that the simple calibration scheme used for SmX can be used for quantitative analyses of a broad range of terrestrial and extraterrestrial materials.

The SmX technique [1] exploits changes in energy of features in the x-ray absorption spectrum as a function of both the oxidation state and the coordination of the element of interest. This study focuses on the Fe K-absorption edge, but similar measurements can be made for other elements and for other absorption edges. Because the SmX technique should be sensitive to both oxidation state and site coordination effects, it is essential that it be calibrated against materials for which the different effects of oxidation state and coordination may be assessed. Proof-of-concept studies for oxidation state measurements of Fe and Cr have been provided by [1] and [2] respectively. The technique used for Fe monitors the energy of the Fe pre-edge peak, as it is relatively insensitive to coordination effects [1]. Calibration of the Fe oxidation state uses a linear best fit to data for pure fayalite (0%  $\text{Fe}^{\text{III}}$ ); magnetite (67%  $\text{Fe}^{\text{III}}$ ) and hematite (100%  $\text{Fe}^{\text{III}}$ ). These standards have slight variations in the coordination of iron but not as much as may be seen in geophysically important minerals. We have initiated a program of systematic measurements of geophysically important minerals and glasses for which independent analyses of the ratio  $\text{Fe}^{\text{III}}/(\text{Fe}^{\text{II}}+\text{Fe}^{\text{III}})$  are available, either from wet chemical analyses or from Mössbauer spectroscopy. Minerals that have significantly different site geometries from the standards, but a comparable range of  $\text{Fe}^{\text{III}}/(\text{Fe}^{\text{II}}+\text{Fe}^{\text{III}})$  ratios are used to test the sensitivity to coordination effects relative to oxidation state.

**$\text{Fe}^{\text{III}}/(\text{Fe}^{\text{II}}+\text{Fe}^{\text{III}})$  ratios in Amphibole:** A suite of 20 kersutitic amphiboles with very similar bulk compositions but  $\text{Fe}^{\text{III}}/(\text{Fe}^{\text{II}}+\text{Fe}^{\text{III}})$  ratios (0.2 to 1) [3] were analyzed by SmX. All grains were mounted and polished in epoxy butts for electron microprobe analysis and analyzed to confirm that their compositions were identical to those quoted [3,4]. The same polished surfaces used for electron probe analysis were analyzed by SmX using a 20x50  $\mu\text{m}$  beam spot. A good correlation between the bulk Mössbauer analyses and the SmX results is obtained (Figure 1). Two phenomena cause several points to deviate significantly from the 1:1 line: (a) Two individual grains show repeatable differences in their SmX  $\text{Fe}^{\text{III}}/(\text{Fe}^{\text{II}}+\text{Fe}^{\text{III}})$  ratios between analyses separated by about 300  $\mu\text{m}$  that appear to reflect ZONING of oxidation states. (b) several grains contain linear arrays of micrometer sized oxide inclusions that would be impossible to remove from the aliquots used for Mössbauer. These grains with inclusions have systematically higher  $\text{Fe}^{\text{III}}/(\text{Fe}^{\text{II}}+\text{Fe}^{\text{III}})$  from Mössbauer than from SmX as expected for contamination of the Mössbauer result by Fe-oxide

minerals. A suite of 8 amphiboles analyzed by wet chemical techniques [5] and SmX show equally good results. Of particular importance, is the strong correlation between the SmX predictions of the  $Fe^{III}/(Fe^{II}+Fe^{III})$  ratios based on simple standards, and the ratios of the complex amphiboles measured independently by bulk techniques. The differences between the crystal structures of the amphiboles and the simpler standard minerals has NOT influenced the results. Oxidation state measurements calibrated against the fayalite-magnetite-hematite standard set can be used reliably for a range of mineral groups with octahedral Fe. Further systematic studies of other mineral groups should confirm this result.

**$Fe^{III}/(Fe^{II}+Fe^{III})$  ratios in silicate glasses.** Synthetic glasses equilibrated at various oxygen fugacities have also been measured by SmX. Comparison of the  $Fe^{III}/(Fe^{II}+Fe^{III})$  ratios predicted by SmX and those from an initial group of wet chemical analyses show some systematic differences with the SmX ratios appearing more oxidized at low  $Fe^{III}$  (Figure 2). The amphibole results suggest that the differences in coordination of the Fe in the glasses may not be a factor, but further comparisons of glass samples analyzed by SmX and other bulk techniques are essential to assess the potential effect of tetrahedral Fe in the glass. Despite this ambiguity, SmX results for glass generally confirm the relationships expected between  $Fe^{III}/(Fe^{II}+Fe^{III})$  ratios of the glass and the oxygen fugacity at equilibration. In one experimental glass, failure to equilibrate resulted in a visible color gradient from green to brown over ~1 mm.  $Fe^{III}/(Fe^{II}+Fe^{III})$  ratio changes of 35% were measured across this charge by SmX (Figure 2). Significant differences are also seen between  $Fe^{III}/(Fe^{II}+Fe^{III})$  ratios in glasses that coexist with olivine (liquidus glass) and superliquidus glasses as a function of oxygen fugacity. The superliquidus and liquidus glasses have different  $Fe^{III}/(Fe^{II}+Fe^{III})$  - oxygen fugacity slopes as a result of the reduced variance of the 2 phase liquidus systems. In superliquidus glasses changes of fugacity cause direct changes in Fe/O ratios but in olivine-glass systems the  $Fe^{III}/Fe^{II}$  ratio reflects the projection of oxygen isobars from the liquidus surface. Measurements of more glass ratios are in progress and further comparison with independent bulk analyses is needed to identify the cause of the differences between the amphibole systematics and the glass systematics. Differences between  $Fe^{III}/(Fe^{II}+Fe^{III})$  ratios in liquidus and superliquidus glasses at similar oxygen fugacities result from fundamental phase equilibrium constraints and must be treated carefully.

**References:** (1) Bajt et al. (1994) GCA, 58, 5209; (2) Sutton et al. (1993) GCA 57, 461; (3) Dyar et al., (1993) Am. Min. 78, 969; (4) Delaney et al. (1996) Burns Mem. Volume, submitted (5) Cosca et al. (1991) CMP, 108, 472. Acknowledgments: NAG9-304; NAGW-3469; EAR95-08128; NAGW-3651

Figure 1: Comparison of Smx with Mössbauer for amphibole.

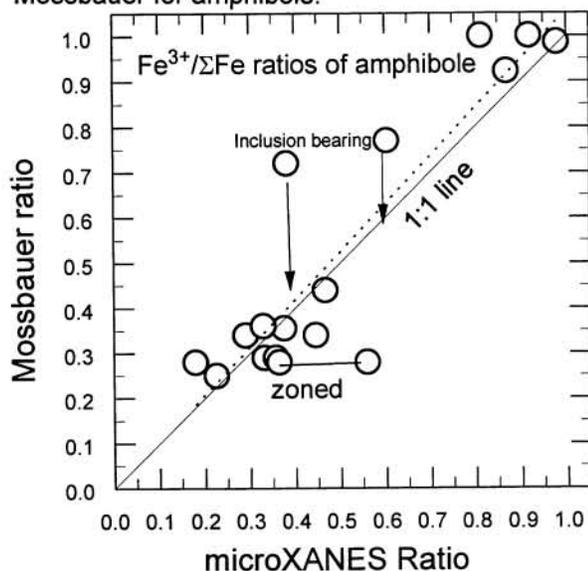


Figure 2: Comparison of SmX and wet chemical analyses of expt. glass.

