

In situ microanalysis of Fe³⁺/ΣFe in amphibole by x-ray absorption near edge structure (XANES) spectroscopy

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Abstract—Determination of Fe³⁺/ΣFe in micrometer scale volumes on individual mineral grains has long been a goal of petrologists and crystallographers. Such measurements can be made using Synchrotron microXANES (SmX) spectroscopy. Comparison of microXANES determinations of the Fe³⁺/ΣFe in 50 × 30 μm areas on polished amphibole samples, with Mössbauer and wet chemical analyses of the bulk material on which the SmX analyses were made, shows generally good matches. Results presented indicate that the Fe³⁺/ΣFe of amphiboles can be calibrated against data from simple oxides and silicates despite the known influence of the crystal structure on the position and intensity of the measured features of XANES spectra. The measurement technique used successfully minimizes crystal chemical influences and permits direct assessment of iron oxidation state. Measurements of the Fe³⁺/ΣFe in complex silicate minerals such as amphibole can be made, therefore, with comparable spatial resolution to the microanalysis techniques used for major element abundance. Zoning of Fe³⁺/ΣFe in amphibole crystals has been detected and can be quantified.

INTRODUCTION

ELEMENTS FREQUENTLY occur in multiple oxidation states in geological and extraterrestrial materials. Fe, Cr, Ti, Mn, V, Eu, Ce and U are all elements whose existence in different oxidation states reflects the conditions under which the host phase crystallized. Of these, the most commonly studied is iron. The variability of Fe³⁺/ΣFe [Fe³⁺/(Fe³⁺ + Fe²⁺)] in minerals has been recognized almost since the beginning of geochemical research, and its significance as an indicator of oxygen fugacity is widely recognized. However, modern reliance on instrumental microanalytical techniques that are incapable of measuring oxidation state in addition to element abundance has resulted in this fundamental parameter often being ignored.

The influence of oxygen fugacity is fundamental in both phase equilibria and geochemical kinetics involving iron (FROST, 1991). Unfortunately, the oxygen fugacity under which a natural rock or assemblage formed is difficult to measure. One possible approach for estimating oxygen fugacity is to establish the oxidation states of multivalent elements such as iron in diagnostic mineral assemblages and compare these results with calibrations of the influence of f_{O_2} on those oxidation states. The coexistence of minerals containing an element in different oxidation states strongly constrains the environment in which equilibration occurred.

Measurements of the Fe³⁺/ΣFe in minerals have been made using bulk analytical techniques, as no microanalytical technique was available. The mea-

surement of Fe³⁺/ΣFe at spatial resolutions comparable with those of modern microanalytical techniques (sampling nanogram instead of milligram masses) is a fundamental technological challenge to geochemists. The use of x-ray spectroscopic techniques that have become possible with the availability of intense synchrotron x-ray sources now permits this challenge to be addressed (CALAS *et al.*, 1984; CHEN *et al.*, 1984; BROWN *et al.*, 1988; WAYCHUNAS, 1988). Synchrotron based spectroscopy can be carried out on the K and L absorption edges of iron with sufficient energy resolution to distinguish between ferrous iron and ferric iron (BAJT *et al.*, 1994; CRESSEY *et al.*, 1993). A synchrotron x-ray beam can be focussed and collimated to produce a true microbeam (1–100 micrometers in diameter) permitting the use of petrographic constraints in the selection of the areas to be analyzed.

Other techniques for analysis of Fe³⁺/ΣFe in micrometer scale volumes are beginning to be explored by HÖFER *et al.* (1994) and ILTON *et al.* (1993). HÖFER *et al.* (1994) have developed a refined version of the ALBEE and CHODOS (1970) electron microprobe technique of monitoring Fe L α /L β x-ray line ratios as an indicator of iron oxidation state. The technique appears to have provided consistent Fe³⁺/ΣFe for a limited suite of samples but is probably limited by the energy resolution (8–20 eV) of wavelength dispersive spectrometers available on current electron microprobes. Uncertainties about changes in soft x-ray

line shapes as a function of site coordination have not been addressed in that study (BASTIN and HEILIGERS, 1991). Similarly, ILTON *et al.* (1993) use x-ray photoelectron spectroscopy to determine $\text{Fe}^{3+}/\Sigma\text{Fe}$ in the near surface region (~ 5 nm thick) of biotite samples in a 2×0.1 mm spot. This technique has potential although the areas analyzed are much larger than those associated with true microbeam techniques. In addition, the strong surface sensitivity of XPS may limit its usefulness in petrographically constrained studies.

The energy of the pre-edge peak (1s–3d transition) associated with the Fe-K x-ray absorption edge in amphibole minerals is correlated with the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the amphibole. The pre-edge energy can be determined with good energy resolution (~ 1 – 1.5 eV) by using synchrotron microXANES spectroscopy (XANES = x-ray absorption near-edge structure.) Early studies on relatively simple minerals show that the energy of the main K-absorption edge shifts 2–3 eV per valence charge, but high resolution spectra show also that the shape and position, of the main absorption edge, is sensitive to the coordination geometry (WAYCHUNAS *et al.*, 1983; SUTTON *et al.*, 1993a). In contrast, pre-edge peak energies appear to be sensitive mainly to element oxidation states (WAYCHUNAS *et al.*, 1983; MANCEAU *et al.*, 1992 a,b) although its intensity is dependent on coordination. The coordination geometry affects the pre-edge energy much less than the main absorption edge. The 3d final states represented by these peaks are more tightly bound and therefore less sensitive to coordination changes in the local environment and solid state effects than the higher energy states associated with the main edges. In the amphibole minerals the potential for complex variation of both composition and structure requires that the features of the absorption edge be studied in great detail to distinguish between oxidation state and coordination related energy shifts. The presence of several crystallographic sites hosting ferric and ferrous iron implies that the interactions that are characteristic of the XANES region will be very complex. *This preliminary study will not attempt to provide that level of coverage.* The original calibration of the pre-edge energy shifts generated using oxide minerals (BAJT *et al.*, 1994) will be compared here with an independent “calibration” based on the available bulk analyses of these amphiboles by wet chemistry and Mössbauer spectroscopy.

WHY MEASURE $\text{Fe}^{3+}/\Sigma\text{Fe}$ IN AMPHIBOLE?

ROBINSON *et al.* (1982) describe amphibole as “a mineralogical shark in a sea of unsuspecting ele-

ments.” The amphibole minerals are among the most compositionally complex of the silicate mineral groups and have a variety of sites (M1–M4, A) that can accommodate many different cations. Amphibole is one of the few mineral groups in which there is sufficient ‘flexibility’ in the structure that it can accommodate ferric and ferrous iron in response to both the crystallization environment *and* the crystal chemical constraints. Fe^{2+} is generally located in the M1–M3 sites with Fe^{3+} often in M2 (HAWTHORNE, 1981) although in oxyamphibole Fe^{3+} shows a preference for M1 and M3 (PHILLIPS *et al.*, 1988). The responsiveness of amphibole $\text{Fe}^{3+}/\Sigma\text{Fe}$ to external conditions, makes them potentially valuable indicators of system oxygen fugacity.

The substitution of Fe^{3+} and Fe^{2+} into amphibole may be diagnostic of oxygen and hydrogen fugacities at the time of equilibration. Two major mechanisms for the substitution of Fe^{3+} into amphibole have been discussed in recent work: (i) Charge balance of the excess charge of Fe^{3+} by oxidation/dehydrogenation of amphibole. The end member substitution of ferric iron corresponds to the formation of an oxyamphibole component (by dehydrogenation) (POPP *et al.*, 1990, 1995; DYAR *et al.*, 1993). (ii) Substitution of Fe^{3+} for Al^{3+} (POPP *et al.*, 1990). The strong anti-correlation of Fe^{3+} with H^+ in a variety of kaersutitic amphibole samples is, however, very suggestive that oxidation/dehydrogenation is the dominant mechanism for stabilizing these Fe^{3+} bearing amphiboles (DYAR *et al.*, 1993; POPP *et al.*, 1990, 1995). The sensitivity of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in amphibole to f_{H_2} and f_{O_2} , in turn, suggests that the $\text{Fe}^{3+}/\Sigma\text{Fe}$ be dependent on water fugacity of the source region. Thus study of amphibole $\text{Fe}^{3+}/\Sigma\text{Fe}$ *in situ* provides information on the volatile components extant during crystal growth and/or recrystallization.

SAMPLES STUDIED

Two suites of amphibole samples were used for this study. Both suites were used previously for comprehensive studies of the significance of $\text{Fe}^{3+}/\Sigma\text{Fe}$ in amphibole crystal chemistry (COSCA *et al.*, 1991; DYAR *et al.*, 1993) and both were previously analyzed by bulk analytical techniques. These samples provide a test of the ability of synchrotron microXANES spectroscopy to reproduce “conventional” measurements of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of amphibole. Eight hornblendes (Table 1) from amphibolites and granulites of the Grenville Orogen, were described by COSCA *et al.* (1991), have a range of $\text{Fe}^{3+}/\Sigma\text{Fe}$ between 0.18 and 0.35 and were analyzed by wet chemistry. These Grenville amphiboles have a range of major element compositions and therefore provide a test of the sensitivity of the SmX technique to crystal chemical variables as well as $\text{Fe}^{3+}/\Sigma\text{Fe}$. Fourteen samples described by DYAR *et al.* (1993) were studied by Mössbauer spectroscopy and have $\text{Fe}^{3+}/\Sigma\text{Fe}$ between 0.23 to 1.00 (Table 1). These samples

Table 1. Analytical Results

Sample	Fe ³⁺ /ΣFe %	XANES Pre-Edge (eV)	Notes
FA86-1	18	-1.54	a
HL8611	31	-0.86	a
HL862C	35	-0.78	a
MIN864	33	-1.16	a,d
MR865A	22	-1.21	a
SSA-5	29	-1.12	a
SSA-10	23	-1.20	a
SSA-13	35	-0.52	a
AK-M1	28.2	-1.31	b
AK-M2	25	-1.18	b
AK-M3	27.7	-0.24	b,c,d
AK-M4	28.8	-0.85	b
AK-M5	36.1	-0.76	b
BA-5	36.6	-0.89	b
DL-9	98.7	0.95	b
FR-11	72.2	-0.74	b,c,d
FR-12	100	0.78	b,d
84-BR	44.4	-0.5	b,c
H366A	34	-0.56; -1.00	b,d,e
H366-92	92.3	0.64	b
Kakanui	28.3	-0.79	b
TM	77	-0.11	b,d

Notes: (a) Wet chemical analysis from COSCA *et al.*, 1991. (b) Mössbauer analysis from DYAR *et al.*, 1993. (c) Published FeO and microprobe analyses of grains studied show slight mismatch (10-15% difference). (d) Fe-oxide inclusions present in the analyzed grains. (e) Heterogeneity of Fe³⁺/ΣFe detected.

are kaersutite rich mantle megacrysts that grew in an oxidized metasomatic fluid (DYAR *et al.*, 1993). This suite of mantle megacrysts has a narrow range of major element compositions and varies mainly in the Fe³⁺/ΣFe. The similarity of compositions indicates that crystal chemical differences between the mantle amphiboles are small and that these grains are particularly suitable to test the SmX technique as a measure of Fe³⁺/ΣFe.

Chips (diam. 0.5–2.0 μm) of all the amphiboles were mounted on pure SiO₂ glass disks with an epoxy resin adhesive known to be Fe-free and the samples polished to 1 μm relief as for electron microprobe investigation. The samples were analyzed with a JEOL JXA-8600 electron microprobe at the Rutgers University Microanalysis facility (at 15 kV and 15 nA beam current with analyses corrected using standard BENCE and ALBEE type procedures) to confirm that they were the same amphiboles analyzed by COSCA *et al.* (1991) and DYAR *et al.* (1993). Several grains that had major element compositions significantly different from the published analyses of DYAR *et al.* (1993) were rejected at this point. The polished samples were photographed and used for synchrotron microXANES analysis. The thickness of the samples was not controlled rigorously but was typically ~100 μm.

EXPERIMENTAL TECHNIQUES

Synchrotron microXANES spectroscopy of hornblende

Measurements were made at the synchrotron x-ray microprobe (beamline X26A at the National Synchrotron

Light Source, Brookhaven National Laboratory, New York). The basis of XANES is the mapping of the x-ray absorption edge of the element of interest with energy resolution comparable to the natural x-ray line width. The Fe³⁺/ΣFe in 30 × 50 μm areas on polished sections of amphibole grains are derived from measurements of the energy of a pre-edge peak at the Fe K-absorption edge (Fig. 1). Previous *in situ* measurements of the Fe³⁺/ΣFe in minerals were used to establish a calibration line (Fig. 2a) based on the pre-edge peak energies of synthetic fayalite (Fe₂SiO₄), and natural magnetite (Fe₃O₄) and hematite (Fe₂O₃) as a function of their known Fe³⁺/ΣFe (BAJT *et al.*, 1994). Details of the beamline operation are given in BAJT *et al.* (1994) who demonstrated that reproducible Fe³⁺/ΣFe could be determined for a suite of oxide minerals.

XANES spectra were obtained by measuring the Fe Kα fluorescence intensity from the sample as a function of incident beam energy from 65 eV below the main absorption edge energy (7111 eV for Fe) to about 60 eV above the main edge. The incident beam energy was controlled by a Si(III) channel cut monochromator. The incident X-ray energy was incremented by 0.3 eV intervals over the most critical energy range of -10 to +20 eV relative to the main absorption-edge energy. This provides detailed mapping of the relationship between the pre-edge

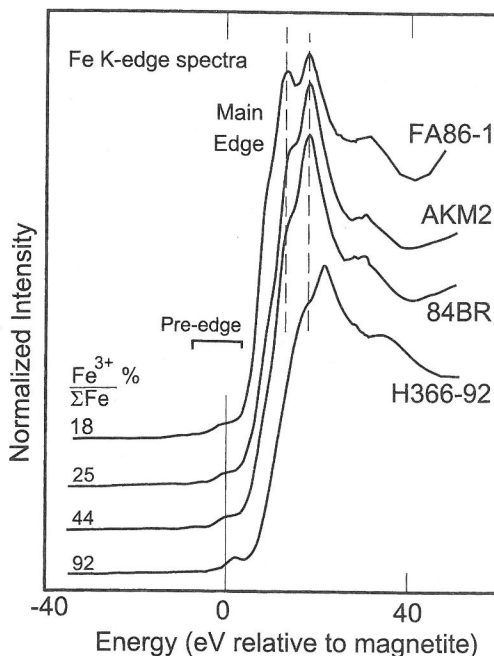


FIG. 1. Synchrotron microXANES spectra of four amphibole samples (FA86-1; AKM2; 84BR and H366-92, with Fe³⁺/ΣFe of 0.18; 0.25; 0.44; 0.92 respectively) with energies expressed relative to the pre-edge peak energy for Minas Gerais magnetite (USNM standard). Spectra are intensity normalized to the maximum intensity of the main Fe K-absorption edge and to the synchrotron ring current. The individual spectra are offset vertically to facilitate comparison of shapes.

peak and the main absorption edge for comparison with a selected magnetite standard for which the pre-edge position is arbitrarily defined as 0.0 eV. Between -65 and -30 eV, and above +30 eV, the x-ray energy was incremented by larger intervals (2 eV) to reduce data collection times. Each energy interval was counted between 10 and 20 live seconds for a total XANES spectrum acquisition time of ~30 minutes. Counting times were adjusted to obtain at least 10^3 counts per energy step at energies above the absorption edge.

XANES data analysis

The energy of the pre-edge peak that was used as an indicator of Fe oxidation state, was defined to be the centroid of a Gaussian fit to the peak after background subtraction. The centroid of the pre-edge peak for a magnetite standard (USNM114887) from Minas Gerais, Brazil (JAROSEWICH *et al.*, 1980) was used as the reference x-ray energy (zero relative energy) and all pre-edge energies were computed relative to that energy. The peak fitting procedure consisted of a least-squares fit of a second-order polynomial to the background (including the low energy part of the main absorption-edge) followed by a Gaussian curve fit to the pre-edge peak. The Gaussian function was determined empirically to be a better approximation to the shape of the peak than a Lorentzian function (BAJT *et al.*, 1994). The magnetite standard was typically measured between every two or three unknown samples during each experimental session in order to correct for long-term monochromator drifts (about 0.5 eV) caused by crystal heating and/or small vertical drifts in the synchrotron source position. Using the magnetite as a reference, relative energies for all other pre-edge peak measurements could be determined with a reproducibility of about ± 0.1 eV. This reproducibility reflects comparison of multiple (usually >5) Gaussian fits to each standard and unknown pre-edge peak and has been tested by comparison of repeated samples from multiple analytical sessions. These repeated fits used data points that differed from fit to fit to assess the sensitivity of the peak position to background subtraction. In the present study, the apparent centroid position derived from these procedures appears to be fairly insensitive to the details of these fitting procedures, but this is a potential problem when dealing with very weak pre-edges that may be typical of minerals with undistorted octahedral sites. The pre-edge energies of all 'unknowns' are reported relative to that of the pre-edge centroid in a magnetite spectrum acquired within two hours of the unknown.

The siting of iron in amphiboles is exclusively in octahedral M-sites, so the pre-edge peak being measured in these studies will contain only octahedral site contributions. It is certain that the pre-edge studied is a composite peak with Fe^{3+} and Fe^{2+} components (CALAS and PETIAU, 1983). The resolution of the monochromator system used in this study is not, however, sufficient at present to permit recognition of these subpeaks. Future studies using higher energy resolution may well resolve pre-edge features that are presently obscured.

The pre-edge peaks in amphiboles are quite weak, as would be expected for octahedrally coordinated Fe, (WAYCHUNAS *et al.*, 1983) and are similar in this respect to the oxides studied by BAJT *et al.* (1994). A potential spectral interference from Mn $K\beta$ has been identified in Mn rich samples. However, tests of the magnitude of this interference suggest that it is trivial for these amphiboles

which mostly contain less than 0.5% MnO. Well defined differences in the shape of the main absorption edge features between oxide standards (BAJT *et al.* 1994) and between different amphiboles (Fig. 1) can be recognized but are not being used for interpretation of oxidation state, or structural information at present. There is a clear sequence of shape changes in the main edge with increasing $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Fig. 1), but the relative influences of oxidation state and site coordination on the absorption edge shape are unknown. The mantle kaersutites documented by DYAR *et al.* (1993) all have similar compositions and their spectral shapes are similar, despite differences in their $\text{Fe}^{3+}/\Sigma\text{Fe}$ (Fig. 1). The spectrum of the COSCA *et al.* (1991) sample (FA86-1), which is compositionally distinct, shows a well developed extra peak at the top of the main edge but this feature may be also represented in the Dyar samples by a much weaker peak. The differences between the spectra illustrated do not reflect the differences of their $\text{Fe}^{3+}/\Sigma\text{Fe}$ in a manner that can be readily quantified at present but may relate instead to the abundance and distribution of iron in the M-sites relative to other cations. The COSCA *et al.* (1991) amphiboles appear to have more Fe^{2+} substituting for Ti and Al in their M-sites, than the DYAR *et al.* (1993) samples. There is clearly great potential for study of these main edge features in the future.

RESULTS

The relative pre-edge energies of 23 amphibole samples with $\text{Fe}^{3+}/\Sigma\text{Fe}$ between 0.18 and 1.0 have been obtained during three separate analytical sessions. The $\text{Fe}^{3+}/\Sigma\text{Fe}$ determined by wet chemical techniques (COSCA *et al.*, 1991); and by Mössbauer spectroscopy (DYAR *et al.*, 1993) have been used as the nominal $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the analyzed grains (Fig. 2a). Most amphiboles fall in a linear array correlating pre-edge position with the $\text{Fe}^{3+}/\Sigma\text{Fe}$. Fig. 2 also contains the linear fit of the oxide mineral data that were acquired during the last amphibole run and were used to monitor fluctuations in the operating conditions for comparison with the original SmX calibration of BAJT *et al.* (1994). The oxide data provide both a "calibration" of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the amphibole and a test of the stability of the beamline and the x-ray microprobe during measurements. Experimental changes in the configuration of the synchrotron during the period of these measurements (50% changes in maximum ring current available) resulted in changes in the thermal regime at the beamline. The combined data sets show greater apparent scatter than would be seen within a single session. For this reason, although each analytical session produced similar relationships among the samples, only data for the last of the three analytical sessions are shown in Fig. 2.

A strong correlation exists between the nominal $\text{Fe}^{3+}/\Sigma\text{Fe}$ of the samples and those estimated from the linear fits to the oxide data of BAJT *et al.* (1994)

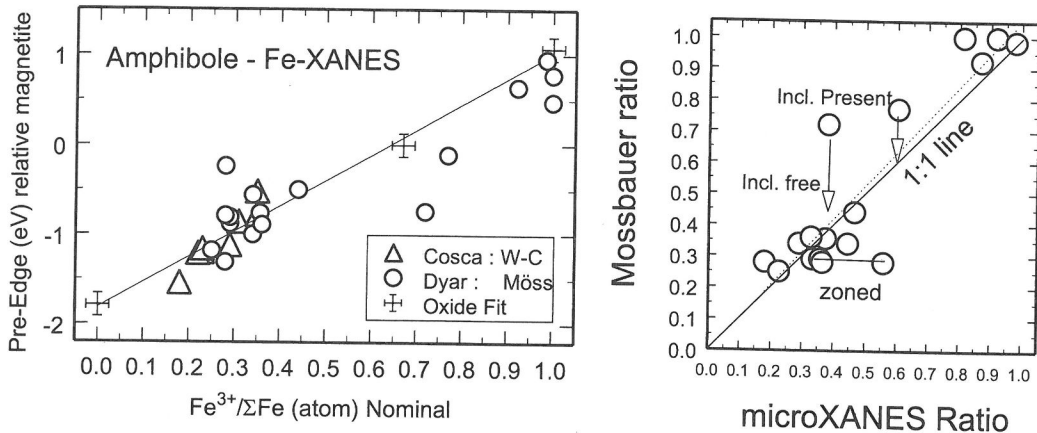


FIG. 2(A) *Left*. Changes of pre-edge energy (relative to the energy of Minas Gerais magnetite) of the Fe K-absorption edge for the amphibole samples, as a function of nominal Fe³⁺/ΣFe determined by Mössbauer spectroscopy and wet chemical techniques. Calibration curve (solid line) for Fe³⁺/ΣFe of simple oxides and silicates as a function of pre-edge energy from BAJT *et al.* (1994) is also shown. FIG. 2(B) *Right*. Comparison of Fe³⁺/ΣFe for amphibole grains determined by Mössbauer spectroscopy and using the microXANES technique of BAJT *et al.* (1994). The dotted line is the linear best fit for the amphibole data using the microXANES calibration, and includes three grains known to have iron oxide inclusions that may have modified the bulk ratios of these samples. Removal of these data results in superposition of the linear best fit on the 1 : 1 line.

within each of the three analytical sessions. Most of the samples have Fe³⁺/ΣFe between 0.2 and 0.4, and within this region the fit of the microXANES data to the “classical” measurements are very good. Greatest scatter is seen in comparison of the ferric rich amphiboles with the Mössbauer data tabulated by DYAR *et al.* (1993). At least one grain of amphibole H366A has provided reproducibly different spectra from areas separated by about 150 μm (Table 1), indicating the presence of zoning of Fe³⁺/ΣFe. Measurement of Fe³⁺/ΣFe zoning in amphibole crystals may, therefore, be made quantitatively. Three amphibole grains (TM, FR-11, and one analysis of FR-12) have pre-edge energies suggesting that they are significantly enriched in ferrous iron relative to the wet chemical and Mössbauer analyses. Micrometer sized inclusions of iron oxide minerals were identified in each of these samples. (Linear arrays of tiny inclusions with ~300 μm spacing between the arrays were observed in two of the three samples). Closely spaced inclusions could skew the results from bulk analytical techniques toward ferric iron as a result of incomplete phase separation. This effect may be seen in the comparison of the nominal Fe³⁺/ΣFe data and the SmX results for these samples. Only one grain (AKM3) appears to be ferric iron enriched relative to the Mössbauer data, but this grain has a slightly different electron microprobe composition (11.6% “FeO” instead of 12%; 2.9% Na₂O instead

of 3.3%) than the quoted analysis and the observed differences probably reflect heterogeneity (zoning) within the bulk sample. Comparison of the Fe³⁺/ΣFe determined by Mössbauer spectroscopy (DYAR *et al.*, 1993) and those obtained using the BAJT *et al.* (1994) microXANES calibration technique indicate very good consistence between the two techniques (Fig. 2b). If the samples known to be contaminated by microinclusions were removed from the data set, the best fit of these result would be indistinguishable from the 1 : 1 correlation.

DISCUSSION

The strong correlation between the energy of the Fe-K pre-edge peak for the amphibole samples with the Fe³⁺/ΣFe determined by bulk analytical techniques indicates that synchrotron microXANES spectroscopy can be used for *in situ* determination of the Fe³⁺/ΣFe in complex silicates such as amphibole. This supports the conclusions reached previously from studies of much simpler silicates and oxide minerals with abundant octahedrally coordinated iron (BAJT *et al.*, 1994). The amphibole data fall close to the regression fit for the standard oxide samples determined during the same data collecting sessions and suggest that small differences in the coordination environment of the Fe between simple oxide and complex silicate minerals are *not* influencing the pre-edge mea-

surements made. Consequently the calibration line determined for the oxide mineral study of BAJT *et al.* (1994) can also be applied to the amphibole minerals. Preliminary data for other rock-forming mineral groups suggest that the present calibration can be used for many minerals in which iron occurs at octahedrally coordinated sites. Since that includes many mineral groups, this calibration may be of fairly widespread usefulness. For mineral groups that contain iron in other coordinations the present calibration is not expected to be valid. The present amphibole measurements, although preliminary, suggest that an alternate calibration of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ may also be made using independently analyzed samples although such a protocol does not permit assessment of errors caused by heterogeneity within individual grains of amphibole.

The present results were produced with a relatively large x-ray beam ($30 \times 50 \mu\text{m}$) but smaller beams ($\sim 8 \times 30 \mu\text{m}$) have been used for micro-XANES measurements of Fe-rich minerals and with third generation synchrotron facilities becoming available at the Advanced Photon Source (Argonne National Lab.), beams of a few micrometers diameter should be feasible. The ability to measure $\text{Fe}^{3+}/\Sigma\text{Fe}$ in micrometer scale volumes on thin sections provides a powerful new geochemical technique. Other multivalent elements that occur in natural materials can also be determined by microXANES spectroscopy. Measurements have been made of $\text{Cr}^{2+}/\Sigma\text{Cr}$ in lunar and terrestrial olivine (SUTTON *et al.*, 1993b), U and Mn oxidation states in soils (BERTSCH *et al.*, 1994; SCHULZE *et al.*, 1995), and Zn speciation in individual fluid inclusions (ANDERSON *et al.*, 1995). Many other elements remain to be studied. The ability to make measurements of the OXIDATION STATE of an element as well as its abundance in micrometer scale volumes removes a fundamental limitation of the numerous microbeam analytical techniques that have become the methods of choice in the last three decades.

The ability to investigate the distribution of elements in terms of both their abundance and their physical states holds enormous potential for future mineralogical, petrological and geo/cosmochemical studies of terrestrial and extraterrestrial materials. With the availability of a microanalytical technique for measuring $\text{Fe}^{3+}/\Sigma\text{Fe}$, studies of oxygen, hydrogen or water fugacity and their relationships to mineral zoning as well as studies of differences between crystals of different generations of amphibole become feasible. Systematic measurements of other minerals and glasses containing both ferric and ferrous iron are in progress.

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