In situ microanalysis of Fe\textsuperscript{3+}/ΣFe in amphibole by x-ray absorption near edge structure (XANES) spectroscopy

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Abstract—Determination of Fe\textsuperscript{3+}/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 Fe\textsuperscript{3+}/ΣFe in 50 × 30 \(\mu\)m 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 Fe\textsuperscript{3+}/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 Fe\textsuperscript{3+}/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 Fe\textsuperscript{3+}/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 Fe\textsuperscript{3+}/ΣFe [Fe\textsuperscript{3+}/(Fe\textsuperscript{3+} + Fe\textsuperscript{2+})] 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 \(f_0\) 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 Fe\textsuperscript{3+}/ΣFe in minerals have been made using bulk analytical techniques, as no microanalytical technique was available. The measurement of Fe\textsuperscript{3+}/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 \textit{et al.}, 1984; Chen \textit{et al.}, 1984; Brown \textit{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 (Bait \textit{et al.}, 1994, Cressey \textit{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 Fe\textsuperscript{3+}/ΣFe in micrometer scale volumes are beginning to be explored by Höfer \textit{et al.} (1994) and Ilton \textit{et al.} (1993). Höfer \textit{et al.} (1994) have developed a refined version of the ALBEE and CHODOS (1970) electron microprobe technique of monitoring Fe La/Lβ x-ray line ratios as an indicator of iron oxidation state. The technique appears to have provided consistent Fe\textsuperscript{3+}/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 HEULIGERS, 1991). Similarly, ILTON et al. (1993) use x-ray photoelectron spectroscopy to determine Fe\(^{3+}/\Sigma\)Fe in the near surface region (~5 nm thick) of biotite samples in a 2 x 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 Fe\(^{3+}/\Sigma\)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 peaks appear to be sensitive mainly to element oxidation states (WAYCHUNAS et al., 1983, MANCEAU et al., 1992a,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 than the main absorption edge. The 3d final states are, 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 Fe\(^{3+}/\Sigma\)Fe in amphibole to \(f_{Hi}\) and \(f_{Ox}\), in turn, suggests that the Fe\(^{3+}/\Sigma\)Fe be dependent on water fugacity of the source region. Thus study of amphibole Fe\(^{3+}/\Sigma\)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 Fe\(^{3+}/\Sigma\)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 Fe\(^{3+}/\Sigma\)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 Fe\(^{3+}/\Sigma\)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 Fe\(^{3+}/\Sigma\)Fe. Fourteen samples described by DYAR et al. (1993) were studied by Mössbauer spectroscopy and have Fe\(^{3+}/\Sigma\)Fe between 0.23 to 1.00 (Table 1). These samples
Table 1. Analytical Results

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

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 Fe\(^{3+}\)/Fe detected.

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 Fe\(^{3+}\)/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 Fe\(^{3+}\)/ΣFe in minerals were used to establish a calibration line (Fig. 2a) based on the pre-edge peak energies of synthetic fayalite (FeSiO\(_4\)), and natural magnetite (Fe\(_3\)O\(_4\)) and hematite (Fe\(_2\)O\(_3\)) as a function of their known Fe\(^{3+}\)/ΣFe (BAJT et al., 1994). Details of the beamline operation are given in BAJT et al. (1994) who demonstrated that reproducible Fe\(^{3+}\)/ΣFe could be determined for a suite of oxide minerals.

XANES spectra were obtained by measuring the Fe Ka 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 Fe\(^{3+}\)/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.](image-url)
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 incre-
mented 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 10^6 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 mag-
etite 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 ap-
proximation to the shape of the peak than a Lorentzian
function (BAIT et al., 1994). The magnetite standard was
typically measured between every two or three unknown
samples during each experimental session in order to cor-
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 compari-
sion of multiple (usually >5) Gaussian fits to each stan-
dard 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 appar-
cent centroid position derived from these procedures ap-
ppears 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 sitting of iron in amphiboles is exclusively in octa-
hedral M-sites, so the pre-edge peak being measured in
these studies will contain only octahedral site contribu-
tions. 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 BAIT et al. (1994). A potential
spectral interference from Mn Kβ 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 fea-
tures between oxide standards (BAIT et al. 1994) and
between different amphibole (Fig. 1) can be recognized
but are not being used for interpretation of oxidation state,
or structural information at present. There is a clear se-
quence of shape changes in the main edge with increasing
Fe^{3+}/ΣFe (Fig. 1), but the relative influences of oxidation
state and site coordination on the absorption edge shape
are unknown. The mantle kaersuits documented by
DYAR et al. (1993) all have similar compositions and their
spectral shapes are similar, despite differences in their
Fe^{3+}/ΣFe (Fig. 1). The spectrum of the COSCA et al.
(1991) sample (FA86–1), which is compositionally dis-
tinct, 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 differ-
ences of their Fe^{3+}/ΣFe in a manner that can be readily
quantified at present but may relate instead to the abun-
dance and distribution of iron in the M-sites relative to
other cations. The COSCA et al. (1991) amphiboles appear
to have more Fe^{3+} 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 Fe^{3+}/ΣFe between 0.18 and 1.0 have
been obtained during three separate analytical ses-
sions. The Fe^{3+}/ΣFe determined by wet chemical
techniques (COSCA et al., 1991); and by Mössbauer
spectroscopy (DYAR et al., 1993) have been used as
the nominal Fe^{3+}/ΣFe of the analyzed grains
(Fig. 2a). Most amphiboles fall in a linear array
correlating pre-edge position with the Fe^{3+}/ΣFe.
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 BAIT et al. (1994). The oxide
data provide both a "calibration" of the Fe^{3+}/ΣFe of the amphibole and a test of the stability
of the beamline and the x-ray microprobe during measurements. Experimental changes in the con-
figuration 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, al-
though each analytical session produced similar rel-
ationships 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 Fe^{3+}/ΣFe of the samples and those estimated from
the linear fits to the oxide data of BAIT et al. (1994)
Fe$^{3+}$/ΣFe in amphibole

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 Fe$^{3+}$/ΣFe determined by Mössbauer spectroscopy and wet chemical techniques. Calibration curve (solid line) for Fe$^{3+}$/ΣFe of simple oxides and silicates as a function of pre-edge energy from BATT et al. (1994) is also shown. FIG. 2(B) Right. Comparison of Fe$^{3+}$/ΣFe for amphibole grains determined by Mössbauer spectroscopy and using the microXANES technique of BATT 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 Fe$^{3+}$/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 Fe$^{3+}$/ΣFe. Measurement of Fe$^{3+}$/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 Fe$^{3+}$/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% Na$_2$O instead of 3.3%) than the quoted analysis and the observed differences probably reflect heterogeneity (zoning) within the bulk sample. Comparison of the Fe$^{3+}$/ΣFe determined by Mössbauer spectroscopy (DYAR et al., 1993) and those obtained using the BATT 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 Fe$^{3+}$/ΣFe determined by bulk analytical techniques indicates that synchrotron microXANES spectroscopy can be used for *in situ* determination of the Fe$^{3+}$/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 (BATT 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-
measurements 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 Fe$^{3+}/\Sigma$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 ($30 \times 50 \mu m$) but smaller beams ($\sim 8 \times 30 \mu m$) 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 Fe$^{3+}/\Sigma$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 micro-XANES spectroscopy. Measurements have been made of Cr$^{3+}/\Sigma$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 \textit{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 Fe$^{3+}/\Sigma$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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