Fe$^{3+}$ and Fe$^{2+}$ iron in feldspar: Calibration and interpretation of XANES spectra

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ABSTRACT

Feldspars are a key rock-forming mineral group in a majority of parageneses, yet their total iron and Fe$^{3+}/\Sigma$Fe contents are poorly understood, largely because of low Fe concentrations and difficulties in discriminating between Fe in feldspar and Fe in inclusions. The technique of synchrotron micro-XANES (X-ray-absorption near-edge spectroscopy) was used to obtain polarized pre-edge and main-edge XANES spectra of feldspars. Samples were selected based upon availability of independent determinations (by Mössbauer, optical, EPR spectroscopy) of their Fe$^{3+}/\Sigma$Fe contents and coverage of a compositional range from 0-100% Fe$^{3+}$. Micro-XANES was used to analyze Fe$^{3+}/\Sigma$Fe in feldspars on thin sections with a beam size of 10x20 μm, and in single crystals with a beam size of 20x30 μm. Spectra acquired over a range of crystallographic orientations are contrasted with spectra for which the beam was polarized parallel to the X, Y, and Z optical directions, and used to assess the errors introduced into the measurements by orientation effects. A feldspar-specific calibration line based on three feldspars with known Fe$^{3+}/\Sigma$Fe was developed to relate the centroid energy of the Fe pre-edge envelope to Fe$^{3+}/\Sigma$Fe in feldspars. It can be used to measure Fe$^{3+}$ and Fe$^{2+}$ contents of unknown feldspars with an uncertainty of roughly ±6% in individual grains and <±2% in traverses within single grains; possible sources of these errors are identified and discussed here. This technique offers great promise for studies of Fe$^{2+}$ and Fe$^{3+}$ in feldspars.
INTRODUCTION

Although feldspars are the most commonly-occurring mineral group in the Earth’s crust, their use as a petrogenetic indicator of oxygen fugacity has not been explored until recently (e.g., Sugawara 2001), as evolving analytical techniques have refined characterizations of the amount, valence state, and site occupancy of Fe in the feldspar structure. Understanding of Fe valence and site occupancy in feldspar is of particular importance in igneous petrology because it can be used to infer redox conditions, and therefore oxygen fugacity, during crystallization. Through use of Fe-Ti oxides (e.g. Spencer and Lindsley 1981; Anderson and Lindsley 1988) in mafic magmas for which pressure and temperature can be constrained, it is known that oxygen fugacity exercises a strong control over phase assemblages during the crystallization of magmas (Rutherford and Devine 1990; Martel et al. 1998). However, many felsic magma systems lack such key oxides, and thus the evolution of oxygen fugacity in felsic magmas is poorly understood. Development of methodology for analysis of this constituent of felsic magmas has the potential to greatly expand our knowledge of how such systems evolve during crystallization.

In this study, results of the technique of synchrotron micro-XANES spectroscopy for microscale measurement of Fe$^{3+}/\Sigma$Fe in feldspar on thin sections and single crystals with a 10x15 $\mu$m or 20x30 $\mu$m beam (respectively) are presented. The goals of this paper are four-fold: 1) review the literature on measurements of Fe$^{3+}$ in feldspar; 2) discuss appropriate models for interpretation of the XANES pre-edge for Fe in feldspar, 3) describe a calibration line to be used in evaluating Fe$^{3+}/\Sigma$Fe in feldspars, and 4) evaluate the effects of crystal orientation on the feldspar XANES spectra. This paper provides the methodology for future, more applied petrologic studies of Fe in feldspar using this technique.

BACKGROUND

Previous Studies of Fe in Feldspar

Over the last 50 years, many workers have analyzed the Fe contents of feldspar with varying degrees of success. Four methods have been employed: 1) wet chemistry, 2) Mössbauer spectroscopy, 3) electron paramagnetic resonance (EPR), and 4) optical spectroscopy. Of these, wet chemistry (e.g., titration, oxidation, and colorimetry) generally gave good results but did have some inherent weaknesses. Because wet chemical procedures all involve some type of titration for Fe$^{2+}$ followed by a determination for total Fe, Fe$^{3+}$ is never determined directly, but
always by difference. Such measurements are difficult when the feldspars being analyzed are close to 0.5 wt% FeO, which is typical in rock-forming parageneses. Furthermore, with such low Fe concentrations, problems with contamination of blanks used in the measurements often contributed to significant errors. Finally, and most importantly, wet chemistry cannot distinguish between Fe in feldspar and Fe in micro-inclusions in feldspar (this eventually became the major advantage of the electron microprobe over wet chemistry). In spite of these difficulties, several analyses do exist for feldspar from pre-1970 studies, including Coombs (1954), Stewart et al. (1966), and other references listed in Deer et al. (1963).

Spectroscopic studies of Fe in feldspar are scattered throughout the literature and rarely directly referenced; for this reason, a fairly thorough review will be presented here. Relatively few Mössbauer studies of feldspar appear in the literature because the detection limit for Mössbauer is around 0.5 wt% FeO - above the concentration of most typical compositions; a brief review is given by Lehmann (1984). Early work on orthoclase by Brown and Pritchard (1969) reported Fe\(^{3+}\) in sites for which the Mössbauer doublets had an isomer shift of about 0.46 mm/s (commonly assigned to Fe\(^{3+}\) in octahedral sites). There may be a problem associated with how this parameter was reported in that paper; it seems likely that the value was given relative to sodium nitroprusside (a common practice in early Mössbauer studies), in which case the actual isomer shift may be 0.20 mm/s, a value more typical of tetrahedral Fe\(^{3+}\). A later study by Annersten (1976) reported isomer shifts (\(\delta\)) of 0.21 mm/s and 0.22 mm/s (and quadrupole splittings of 0.48-0.65 mm/s) for Fe\(^{3+}\) in potassium feldspar, though a later worker (Marfunin 1979) attributed at least one of these doublets to an impurity. Bychkov et al. (1995) synthesized feldspars of various compositions to examine the changes in Mössbauer parameters with composition. They observed exclusively tetrahedral Fe\(^{3+}\), with parameters varying from \(\delta=0.21-0.23\) mm/s and primary quadrupole splitting (\(\Delta\)) values of 0.28-0.33 mm/s; they also noted that isomer shift increases with Fe, Si ordering in their ferrisilicates.

The availability of lunar samples in the early 1970's spurred interest in Mössbauer spectra of plagioclase. Hafner et al. (1971) observed two dominant Fe\(^{2+}\) doublets and assigned them to tetrahedral and octahedral coordination; they also estimated the presence of up to 10% of the total Fe atoms as Fe\(^{3+}\) (based on differences in peak areas). Similar site assignments were reached by Appleman et al. (1971) though they did not detect any Fe\(^{3+}\); they also documented the
presence of an ilmenite impurity in their samples. Schürmann and Hafner (1972) also detected a small amount of Fe$^{3+}$ in dominantly Fe$^{2+}$ lunar plagioclase.

A significant limitation of both wet chemistry and Mössbauer analyses of feldspars is the fact that they are bulk techniques and they assume homogeneity of Fe$^{2+}$ and Fe$^{3+}$. Given the variability and known zoning of other major elements in feldspar, especially Ca and Na, the assumption of homogeneity with respect to Fe seems unfounded.

Both EPR and optical spectroscopy have been successful in differentiating the small amounts of Fe$^{3+}$ and Fe$^{2+}$ present in different feldspar species, though there has been controversy over the appropriate number of sites in the spectra, which may be poorly resolved. EPR is best suited to study the magnetically dipole Fe$^{3+}$ in feldspar. Höchli (1963), Marfunin et al. (1967), and Niebuhr et al. (1973) observed only $[4]$Fe$^{3+}$ in a range of feldspar compositions, with Fe$^{3+}$ in a single site in microcline and two tetrahedral sites in orthoclase (Gaite and Michoulier 1970). Weeks (1973) and Scala et al. (1978) also suggested the existence of Fe$^{3+}$ in octahedral or defect sites. This interpretation was clarified by the work of Hofmeister and Rossman (1984), who noted the presence of some axially-coordinated Fe$^{3+}$ in microclines, but concluded that all the Fe$^{3+}$ in the K feldspar polymorph structures is tetrahedral. Petrov and Hafner (1988) showed that Fe$^{3+}$ is disordered over the T1 and T2 positions, with some preference for T1.

Optical spectra of feldspar were measured on samples from Itrongay, Madagascar by Faye (1969), who observed only $[4]$Fe$^{3+}$, and Manning (1970), who assigned transitions to the bands observed at 417 and 442 nm. Work by Bell and Mao (1972) used optical spectra to study labradorite from Lake County, Oregon, and detected bands from both $[4]$Fe$^{2+}$ and $[M]$Fe$^{3+}$ (where M represents the 5- to 10-fold, highly distorted sites in the structure); they later confirmed their peak assignments through study of lunar plagioclase (Bell and Mao 1973). Luna 24 plagioclases were studied by Telfer and Walker (1975) and Telfer and Fielder (1980), who used optical excitation spectroscopy to show the presence of Fe$^{3+}$ in the plagioclase. Hofmeister and Rossman (1984) observed the same four Fe$^{2+}$ bands as Bell and Mao (1972), and interpreted them to represent a “continuum of microenvironments” between two specific, distorted Ca-like M sites. Hofmeister and Rossman (1984) successfully integrated their EPR results with optical spectra of Fe$^{3+}$ to determine Fe$^{3+}$ and Fe$^{2+}$ concentrations for a suite of feldspars with a range of Fe$^{3+}$/Fe$^{2+}$ contents. In plagioclase, they concluded that Fe$^{3+}$/ΣFe increases with increasing An content.
because the number of favorable sites for Fe\textsuperscript{2+} increases as Ca and Al are incorporated into the structure. The number of cations of Fe\textsuperscript{3+} (apfu) also increases with increasing Al substitution into the structure.

The work of Hofmeister and Rossman (1984), in particular, confirmed that the best approach for analyzing Fe\textsuperscript{3+}/Fe\textsuperscript{2+} contents on feldspars was a combination of EPR and optical spectra. Unfortunately, such work on oriented single crystals is too difficult for routine analysis of Fe in large numbers of feldspars of unknown compositions. Thus, despite the ubiquitous presence of feldspar in a wide variety of rock types, little is known about Fe valence in most rock-forming feldspars. To our knowledge, the only previous microanalysis of Fe\textsuperscript{3+}/ΣFe was the semi-quantitative study of Delaney et al. (1992). They measured XANES spectra of feldspars in three lunar, two Martian, two achondrite, a mesosiderite, and one terrestrial (Stillwater) sample. They concluded that the oxidation state of the Fe in the feldspar matched the expected fugacity of the mineral assemblages in each rock (although samples from the lunar highlands showed anomalously high Fe\textsuperscript{3+} contents). The work of Delaney et al. (1992) was severely limited by 1) low X-ray intensity that precluded quantitative interpretation of the pre-edge features, and 2) large beam sizes (>100 μm) that prevented them from systematically avoiding inclusions in the feldspar. Calibration was based on hematite and Fe metal main-edge shifts, which was a simplistic approach (though it yielded consistent answers). This work provided the early impetus for the current study.

The papers just summarized represent the body of literature on quantitative spectroscopic measurements of Fe\textsuperscript{3+} in feldspar; wet chemical data are largely viewed as suspect due to the effects of contamination by microscopic or submicroscopic inclusions in their bulk separates. The data presented in this paper will show that synchrotron micro-XANES can produce reliable measurements of Fe\textsuperscript{3+}/ΣFe in feldspar, at scales less than 10x15 μm on thin sections. It is hoped that this advance will open the door for future studies of this critically-important mineral group.

**Methods for Interpretation of XANES Pre-Edge Spectra**

XANES spectroscopy is a technique for defining features near the X-ray absorption edge of the element of interest. Variations of the bonding environment of an element produce features with energies clustered around the absorption edge energy (which for is Fe K\textsubscript{abs}=7112 eV) when fluoresced by tuned monochromatic incident energy comparable to the natural X-ray line width.
Synchrotron micro-XANES spectroscopy is able to produce systematic, quantitative in situ measurements of Fe\(^{3+}/\Sigma\)Fe in micrometer scale areas (currently better than 10x15 \(\mu\)m for thin sections with <30 \(\mu\)m sampling depth) that match or are close to the spatial resolution of modern microbeam analytical techniques. This advance was made possible by the availability of intense synchrotron X-ray sources (Sparks 1980; Chen et al. 1984). The positions of features associated with the X-ray K-absorption edge of Fe have been shown to be sensitive and at least qualitative indicators of Fe\(^{3+}/\Sigma\)Fe in the phase being studied (Sutton et al. 1993; Bajt et al. 1994; Delaney et al. 1992, 1996). The major disadvantage of the synchrotron microXANES spectroscopic technique is currently the limited number of facilities (major synchrotron storage rings) at which such measurements can be made.

**Features in the Pre-edge.** Proper interpretation of pre-edge features and their relationship to Fe\(^{3+}/\Sigma\)Fe requires an understanding of their causes. In order to curve fit the pre-edge of each spectrum, a model must be selected to determine how many components are present. The model used here is often referred to as the “Z+1” model. Fundamentally, Fe K edge absorptions result from 1\(s\) \(\rightarrow\) 3\(d\) transitions enhanced by 4\(p\) mixing into the 3\(d\) orbitals. The number of transitions present (i.e., the strong field many-electron states) can be modeled for the \(d^{n+1}\) excited state, assuming that the dominant effect of the 1\(s\) core hole is an increase in potential because it is spherically symmetrical (Westre et al. 1997). This 1\(s\) hole is so close to the nucleus that the outer orbitals see a configuration equivalent to that of the next highest ion on the periodic chart, with a fully occupied 1\(s\) shell. So, the final state of the ion, rather than having an atomic number of \(Z\) with a 1\(s\) hole, is instead best approximated by that of a different nucleus with atomic number \(Z+1\) (Shulman et al. 1976; Calas and Petiau 1983). Thus, XANES spectra will show the energy levels predicted by the optical spectra for these \(Z+1\) states.

For example, the unexcited energy levels of a Fe\(^{2+}\) cation normally assume a 3\(d^6\) configuration, but in a XANES experiment, the additional electron added to the 3\(d\) orbitals gives the ion a 3\(d^7\) configuration. So the XANES spectrum of Fe\(^{2+}\) is best approximated by the optical spectrum of Co\(^{2+}\), which also has a 3\(d^7\) configuration. Similarly, Fe XANES spectra of excited Fe\(^{3+}\) (3\(d^6\)) are best understood by analogy with Co\(^{3+}\) (3\(d^6\)) optical spectra. The easiest Fe XANES pre-edge spectra to predict are therefore those for which Co optical spectra already exist and are well understood. For those minerals (e.g., periclase, hematite, magnetite, olivine,
pyroxene) direct calculation of Fe XANES pre-edge peak energies can be made using the appropriate Tanabe-Sugano diagram for each site in each mineral. In each case, experimentally-derived values for crystal field splitting ($\Delta$ in crystal field theory and $10Dq$ in ligand field theory) and for the Racah $B$ parameter can be used to predict the energies of each state, though in practice correspondence between them is not always perfect. Ideally these can in turn be used to understand which peaks in the optical spectra of Co (or the XANES pre-edge spectra of the analogous valence state of Fe) correspond to which transitions. Note that care must be taken to ensure proper assignment of the correlative optical orientations.

Unfortunately, spectroscopy of Co in minerals has not been thoroughly studied by any means, probably reflecting the lack of natural occurrence of Co in typical geologic provenances. For many important mineral groups, such as feldspar, amphibole, and mica, Co spectra are not available. Therefore, it is necessary to employ a slightly more convoluted set of arguments to find a set of optical measurements with which to compare our Fe XANES data directly. As noted by Burns (1993), direct comparisons can be made between cations with similar electronic configurations in similar sites if done with caution. He cites the example of cyanide complexes $[\text{Fe}^{2+}(\text{CN})_6]^{4-}$ and $[\text{Co}^{3+}(\text{CN})_6]^{3-}$, which have $10Dq$ values of 32,500 cm$^{-1}$ and 34,500 cm$^{-1}$ and $B$ values of 377 cm$^{-1}$ and 412 cm$^{-1}$, respectively (data from Lever 1984). On a Tanabe-Sugano diagram, the energy levels in these two complexes will be very similar. Therefore, in cases where Co optical spectra are not available for comparison with Fe XANES data, other approximations can be made. Fe$^{2+}$ optical spectra ($3d^6$) can be related to Fe$^{3+}$ XANES spectra ($3d^6$) when the cations occupy the same sites, as is the case of some micas, pyroxenes, and amphiboles. Similarly, optical spectra of Ni$^{3+}$ ($3d^7$), though extremely rare, can be related to Fe$^{2+}$ XANES spectra ($3d^7$). Unfortunately, neither of these indirect methods will work for feldspar, because Fe$^{2+}$ and Fe$^{3+}$ do not occupy the same site (Fe$^{3+}$ substitutes dominantly into tetrahedral sites and Fe$^{2+}$ into the metal site normally occupied by K, Ca, or Na) and because Ni spectra of feldspar are not available.

Accordingly, a simple model must be used for fitting feldspar spectra at present. For Fe$^{3+}$ in the tetrahedral site, an Orgel diagram or Tanabe-Sugano diagram for tetrahedral Co$^{3+}$ ($3d^6$) can be used to determine that two states should be observed: a lower energy $^5E$ state and a higher energy $^5T_2$ state. However, the crystal field splitting of Co$^{3+}$ in tetrahedral sites should be
relatively small (Burns 1993) and these states may not be resolved. Fe K-edge studies by Westre et al. (1997) of (Et₄N)[FeCl₄], a high-spin \(^{4}\text{Fe}^{3+}\) complex with \(T_d\) site geometry, showed a single very intense pre-edge that could be modeled by superposition of the two states with an energy splitting of 0.6 eV (which is not resolvable by current instrumentation). Thus, the \(\text{Fe}^{3+}\) site in feldspar, which is presumed to be tetrahedral based on the previous optical and EPR studies cited above, can be fit with a single peak.

For the M cations, prediction of the XANES spectra is presently intractable because of the range of 5- to 10-fold coordination polyhedra observed in feldspars. Co\(^{2+}\) in feldspar has not been studied, and the closest analog, \(^{8}\text{Co}^{2+}\) in cubic zirconia, shows five transitions in the visible region (Burns 1993). Optical spectra of Fe in plagioclase may show up to four components, which have been interpreted to reflect a continuum of site occupancies between two similar types of M sites (Stewart et al. 1966; Hoffmeister and Rossman 1984; Bell and Mao 1972), so it might be expected that the peak envelope of an Fe XANES spectrum might be very broad. However, without stronger theoretical or experimental constraints on models of the Fe K-edge of \(^{1[M]}\text{Fe}^{2+}\), the most pragmatic strategy is the simplest one. Therefore, a singlet envelope is used to fit the pre-edge of the \(\text{Fe}^{2+}\) endmember anorthite.

**Fe\(^{3+}/\Sigma\text{Fe}\) Determinations.** Approaches to calibration of Fe XANES spectra have varied. Of these, the most straightforward is the method of Bajt et al. (1994), which uses a calibration line based on Gaussian line shape fits to single peaks for each pre-edge. The resultant pre-edge peak energies from synthetic fayalite (Fe\(_2\)SiO\(_4\)), natural magnetite (Fe\(_3\)O\(_4\)), and hematite (Fe\(_2\)O\(_3\)) are used to derive a calibration line for determining Fe\(^{3+}\) content from pre-edge energy. Pre-edge peak position for the spectrum of each unknown mineral is referenced to the pre-edge peak position (Posn) of the magnetite spectra run before and after it:

\[
\text{Posn}_{\text{unknown}} = \text{Posn}_{\text{measured}}^{\text{unknown}} - \text{Posn}_{\text{measured}}^{\text{magnetite}}.
\]

Because the position of the magnetite centroid is known to be at 7113.25 eV (Petit et al. 2001; Wilke et al., 2001), spectra can then be converted to absolute eV. The regression (calibration) line is fit to the Fe\(^{3+}\) contents vs. pre-edge peak positions of fayalite, magnetite, and hematite in each session (and is therefore variable). A typical linear regression is of the form:

\[
\%\text{Fe}^{3+} = \text{Const}_1 + \text{Const}_2 \text{Posn}_{\text{unknown}}^{\text{unknown}}
\]
This method has permitted measurements of Fe$^{3+}$/ΣFe in garnet, olivine, pyroxene, amphibole, micas, tourmaline, and other minerals and glasses in an array of terrestrial materials (Delaney et al. 1998). However, it yields results with large errors (±10-25%) for many minerals because their pre-edges are actually composed of multiple, superimposed peaks with variable positions depending on the Fe valence state and the nature of the Fe atom’s coordination polyhedra. Furthermore, when multiple chips of the same standards are used in the calibration, orientation effects introduce significant errors into the pre-edge peak positions. A smaller part of the error is also attributable to heating and cooling of the monochromator during each session; this problem is now being solved through use of water-cooled crystals used in the monochromator.

Recent work by Galoisy and Calas (1999) and Galoisy et al. (2001) employs reference spectra for Fe in different sites, utilizing pseudo-Voigt line shapes to fit the pre-edge spectra into 2-4 peaks each as follows: andradite spectra are used for [6]Fe$^{3+}$, augite glass for [4,5]Fe$^{2+}$, berlinite for [4]Fe$^{3+}$, staurolite for [4]Fe$^{2+}$, and siderite for [6]Fe$^{2+}$. Spectra of unknowns are fit to linear combinations of the pure reference spectra. Errors on resultant Fe$^{3+}$/ΣFe are reported to be ±5-10%, and discrepancies are attributed to the method for numerically extracting the pre-edge from the main edge, and to differences in site geometry between their references and the unknown minerals. This method uses powdered samples, so at present its results are more accurate than those based on thin sections because errors from orientation effects are not present. However, a limitation of this method is the use of a universal calibration line and a small number of reference spectra that are based on variably distorted coordination polyhedra. This method also requires large sample amounts and introduces the possibilities of contaminants in the samples and precludes application on a petrologically relevant scale.

Within the chemistry literature, Fe XANES pre-edge spectra have been modeled based on molecular orbital calculations; for simple compounds, normalized pre-edge positions and intensities can successfully be predicted. For example, Randall et al. (1995) quantified the coordination number and symmetry of Fe$^{2+}$ atoms in synthetic high-spin Fe$^{2+}$ complexes, and Westre et al. (1997) used ligand field theory to describe systematic relationships between spin state, oxidation state, and site geometry and the energy (i.e., position), splitting, and intensity distribution in a large variety of ferrous and ferric model compounds. These workers have shown that the Fe K pre-edge is extremely sensitive to the electronic structure of the Fe cation.
In particular, the latter study makes it clear than distortions from ideal octahedral symmetries to tetrahedral and square pyramidal geometries (as are found in most mineral spectra) allow for $3d \rightarrow 4p$ mixing, and affect both the intensity and energy distribution in the pre-edge region. In general, pre-edge intensities are greater in Fe$^{3+}$-bearing minerals because of the additional hole that is present in their ground state. The work of Westre et al. (1997) implies that mineral and site specific considerations should be used in interpretation of Fe K pre-edge XANES spectra in minerals. Accordingly, in this paper we establish a calibration line specific to feldspars.

In addition, the effects of orientation that are introduced when studying mineral grains in thin section must also be considered. Perhaps the only paper to previously address the issue of the multipole character of the pre-edge in minerals was Dräger et al. (1988). They used thin plates cut from oriented single crystals. They confirmed that isotropic samples show identical spectra when the polarization direction is either parallel or perpendicular to an oriented crystal. They also demonstrated that a conspicuous angular dependence of pre-edge absorption was found in the optically anisotropic (hexagonal) minerals hematite and siderite. In hematite, for example, the intensity of a pre-edge peak at 7114 eV is twice as intense with E parallel to (001) than it is with E perpendicular to (001). Thus, some orientation dependence is expected in feldspars because they are either monoclinic or triclinic, and thus should exhibit anisotropic behavior. Magic angle experiments are also possible and may provide a method to minimize orientation effects (Mottana et al. 2001, Dyar et al. 2001).

**METHODS**

**Samples Studied**

Samples for this study were obtained from the collections of one of the authors (GRR) and are listed in Table 1. Samples used for the calibration line were analyzed by Hofmeister and Rossman (1984), while the samples used for polarization studies came from studies of the dielectric constant in feldspar (Shannon et al. 1992a, b). For a pure Fe$^{2+}$ endmember of the calibration line, we used anorthite from the Serra de Mage meteorite, obtained from the American Museum of Natural History (sample 3782-6; analysis 5 in Table 1). A sample with intermediate Fe$^{3+}/\Sigma$Fe contents came from Lake County, Oregon (GRR #13761; analyses 1-4 in Table 1). For the Fe$^{3+}$ endmember, we used yellow orthoclase from Itrongay, Madagascar (GRR...
#13762, analyses 8 and 9 in Table 1), the same locality studied by earlier workers (Faye 1969; Manning 1970).

For the orientation studies, two different samples with contrasting compositions were chosen: a clear, pale straw colored anorthite from Great Sitka Island, Aleutian Islands, AK (USNM 137041; RDS 56163-6; analysis 6 in Table 1) and a colorless orthoclase crystal from Madagascar (RDS 62047-48, analysis 7 in Table 1). For the first set of experiments, these samples were oriented with the use of polarized light and by back-reflection Laue photographs. Rectangular slabs were then cut perpendicular to the reciprocal axes $a^*$, $b^*$, and $c^*$ with a low-speed diamond saw. Finally, these slabs were doubly polished (Shannon et al. 1992a,b). For the orientation studies, XANES spectra were taken every 30º over a 180º range by rotating the crystals between spectra.

In a second set of orientation experiments, single crystals of the Great Sitka Island anorthite and the Madagascar orthoclase were oriented using two methods. The anorthite was oriented using a polarized light microscope equipped with a spindle stage and the computer program EXCALIBR (Gunter and Twamley 2001). The orthoclase was oriented morphologically on the spindle stage; this was possible because $b = Z$ for this monoclinic crystal and the crystal has perfect (010) cleavage. The other two optical directions (i.e., X and Y) in the orthoclase were found based upon their extinction positions.

In this paper, we refer to X, Y, and Z, which are the three mutually perpendicular vectors that describe the biaxial indicatrix. X and Z always correspond to the directions $\alpha$ and $\gamma$, respectively. Then $\beta$ corresponds not only to the Y direction, which is perpendicular to X and Z, but also to an infinite number of vectors of the same length located in the two circular sections of the biaxial indicatrix (c.f. Figure 3.8, Bloss 1981). In the analogous optical spectroscopy literature, $\alpha$, $\beta$, and $\gamma$ are often used to refer to X, Y, and Z.

**Mössbauer Analysis**

Only the Lake County sample had sufficient mass available for Mössbauer analysis. That sample was prepared by grinding in a mortar and pestle under acetone to avoid oxidation. Approximately 200 mg of the sample (close to the thin absorber thickness as calculated by the method of Long et al. (1983) were then mixed with sugar and acetone and placed in the sample
holder for the spectrometer, which is a Plexiglass ring 3/8" in diameter. The sample+sugar mixture was held in place by cellophane tape.

Spectra were acquired using the WEB Research Co. Mössbauer spectrometer in the Mineral Spectroscopy Laboratory at Mount Holyoke College, using a 50 mCi $^{57}$Co in Rh source. Data were fit with the software package WMOSS by WEB Research Co., which has the ability to use Lorentzian or Voigt doublets or quadrupole splitting distributions as described above. The sample was run for seven days in order to obtain the best possible spectrum for this low-Fe sample (~3500 ppm). Because the data were of poor quality, we used a simple Lorentzian quadrupole pair model to fit the spectrum. Parameters are calculated relative to the center of an Fe foil spectrum.

**XANES Measurements**

XANES (X-Ray Absorption Near Edge Structure) measurements were made at the synchrotron X-ray microprobe (beamline X26A at the National Synchrotron Light Source of Brookhaven National Laboratory, NY). The structure of the Fe K absorption edge was scanned in the near edge region. Incident beam energies from 50 eV below the main absorption edge energy (7111 eV for Fe) to about 60 eV above the main edge were used. The beam was positioned to strike an oriented razor blade edge to that the beam position could be constrained to within <5-15 $\mu$m. Using mutually orthogonal Kirkpatrick-Baez mirrors, the beam was focused to a 10 x 15 $\mu$m size for the thin sections and a 20 x 30 $\mu$m size for the single crystals. The X-ray sampling depth is large but >90% of the signal comes from the top 10 $\mu$m of the sample. Polished grains of the samples were mounted in epoxy on 25 mm lucite disks (standard electron microprobe mounts). The incident beam energy was controlled by a Si(111) 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 energy. This provides detailed mapping of the relationship between the pre-edge peak and the main absorption edge for comparison with the magnetite standard (see below) for which the pre-edge position is arbitrarily defined as 0.0 eV. Between -50 and -10 eV and above +20 eV, the X-ray energy was incremented by larger intervals to reduce data collection times. Each energy interval was counted between 5 and 20 live seconds (depending on the intensity of the main edge signal) for a total XANES spectrum acquisition time of about 20-30 minutes. Counting times were adjusted
to obtain at least $10^4$ counts per energy step at energies greater than the absorption edge. For additional details, see Delaney et al. (1996).

Two different beam geometries were used in this study (Figure 1). The standard beam geometry at X26A does not allow rotations in a plane perpendicular to the beam because the sample surface (in this case, the surface of the slab) is oriented at a 45° angle from both the beam and the detector, as is the microscope used for sample selection and focusing. Thus, the rotations noted in the measurements on slabs refer to rotations in the plane perpendicular to the microscope, and the feldspar slabs are 45° from the beam.

For the single crystal measurements, a special beam geometry was used. On the beamline, a spindle stage was mounted with the plane of rotation perpendicular to the path of the beam. This geometry is similar to that used in normal spindle stage measurements when the spindle stage is mounted on to a microscope stage (Bloss 1981; Gunter and Twamley 2001). This geometry allowed spectra to be acquired with the beam polarized directly parallel to the X, Y, and Z optical directions in the feldspars, or any other direction of choice.

Peak energies are reported in this paper in two different ways. For the oriented slabs, results are reported in eV relative to the center of the Fe pre-edge in magnetite. This method of reporting results avoids any assumptions regarding the absolute pre-edge position of magnetite. For the single crystal spectra, results are given in absolute eV, which was determined by adding the energy of the magnetite pre-edge (7113.25 eV) to the relative eV.

RESULTS

Mössbauer Spectrum

The Mössbauer spectrum of the Lake County sample (Figure 2) was fit with three Lorentzian doublets having the parameters given in Table 2. The Fe$^{3+}$ doublet contains only 38% of the total peak area. It is very likely that this value needs to be adjusted to compensate for the effects of differential recoilless emission of Fe$^{2+}$ and Fe$^{3+}$ in the different sites, but the temperature dependence of the hyperfine parameters in feldspar is not known. Based on comparison with other mineral groups, the magnitude of this differential recoil-free fraction ($f$) correction could be significant. For example, in diopside, for $^{[M1]}$Fe$^{2+}$ at room temperature, $f = 0.700, 0.747, \text{ and } 0.708$ while for $^{[4]}$Fe$^{3+}, f = 0.906$ and 0.862 (DeGrave and Van Alboom 1991). Because we have no way of knowing the appropriate correction factors for feldspar, and
determining them is beyond the scope of the present paper, we simply assign rough error bars of ±15% to our measurements, with a caveat that the actual error could be very different.

The spectral parameters given in Table 2 are assigned to only tetrahedral coordination. However, these parameters must be viewed with some reservation given the poor quality of the data. Note that the peak widths are so large that they had to be constrained at 0.50 mm/s; this suggests that there is considerable variation in site geometries around all the Fe atoms in the structure. Based on these data, we cannot rule out the presence of some small amount (<10% of the total Fe) as M-site Fe$^{2+}$, though it is clear that the majority of the Fe is in tetrahedral coordination.

**Main Edge Spectra**

XANES spectra for the feldspar samples are shown in Figures 3, 4, and 5. Until very recently, XANES spectra in this region, which begins 2-3 eV above the pre-edge and continues to about 50 eV above it, were impossible to interpret quantitatively. Features in this region represent superimposed contributions from both the multiple scattering interactions of the photoelectron and reflect both long-range and short-range ordering. Thus, the features are difficult to discriminate and assess quantitatively.

Interpretation of the main edge spectra of feldspars is especially challenging. As seen in Figures 3, 4, and 5, the main edge region is composed of many superimposed peaks. Because these samples may contain [M]$^{2+}$, [M]$^{3+}$, and [4]$^{3+}$, there are potentially three sets of scattering events represented here. In other mineral groups, some progress in recognition and numerical characterization of key features has been made through careful studies of suites of minerals with contrasting compositions. For example, work by Mottana et al. (1997) on Al K edges showed that features corresponding to octahedral and tetrahedral Al could be distinguished in the XANES spectra of synthetic micas with compositions ranging from fluor-phlogopite to polylithionite. Next nearest neighbor effects were also characterized. Such studies led the way to the recent development of curve-fitting software that can process data from this region (Benfatto et al., 2001); this software has great potential for elucidating the electronic properties of micas. Unfortunately, such numerical analysis of feldspar spectra is beyond the scope of the current work, though we hope to undertake it in the near future.
Figures 3 and 4 demonstrate that crystallographic orientation has an effect on the intensities of the peaks in the main-edge region, and this effect will complicate interpretation of those features. Orientation has been shown to have a strong effect on peak intensity in other Fe-rich silicates such as the micas (Manceau et al. 2000; Mottana et al., 2001). Based upon the similarity of the $\alpha$, $\beta$, and $\gamma$ refractive indices, as well as the correspondence of the $\alpha$, $\beta$, and $\gamma$ optical spectra of feldspar (c.f. Hoffmeister and Rossman 1984), we expected little difference in the XANES spectra among the different orientations.

Figures 3 and 4 show systematic differences in peak intensities in the main-edge as a function of orientation. In order to compare these spectra, it is necessary to note the following correspondences that result from the different positions of the optical directions relative to the crystallographic directions in alkali feldspar vs. plagioclase: $X(\text{Or}) \approx Y(\text{An})$, and both are slightly inclined from the $a$ axis; $Y(\text{Or}) \approx Z(\text{An})$, with $Y(\text{Or})$ inclined $\sim20^\circ$ from the $c$ axis and $Z(\text{An})$ inclined $\sim45^\circ$ from $c$; and $Z(\text{Or})$ is directly equivalent to $b$ while in An, $b$ is inclined to $Z$ at a large angle.

Accordingly, we would expect the $X$ main-edge in Or to most closely resemble the $Y$ main-edge spectrum in An, and this is, in fact, observed. These spectra have three prominent peaks at 16.75, 22.75, and 28.75 relative eV (in absolute energy, at 7130, 7136 and 7142 eV), with the latter two roughly equal in intensity. The $Y$ spectrum of Or is also similar to the $Z$ main-edge in An, although there is slightly more structure visible in the An spectrum. The $Z(\text{Or})$ spectrum bears little resemblance to the $X(\text{An})$ spectrum, but probably results from their dramatically different orientations with respect to the $b$ axis.

Finally, it is important to note that in these measurements, the intensities of spectra cannot be compared among samples because the height of the main edge may not be proportional to Fe concentration because of self-absorption effects. A simple relationship between Fe K-edge fluorescent intensity and the abundance of Fe in the sample cannot be assumed. This is an artifact of the fluorescent mode of XAS (used in these microprobe analyses) that has less effect on absorption mode measurements. For this reason, Figures 3, 4, and 5 are shown with “Normalized Intensity” on the $y$ axis, because the intensity is (arbitrarily) normalized at about 40-60 eV above the main edge.

**Pre-edge Spectra**
Close-ups of the extracted pre-edge spectra for the two oriented feldspar samples are shown in Figures 6 and 7. In each set of data, the slight anisotropy of the feldspar spectra is apparent. There is no suggestion of underlying structure in these pre-edges, as might be expected from superimposed contributions of $^{[4]}\text{Fe}^{3+}$, $^{[6]}\text{Fe}^{3+}$, and $^{[6]}\text{Fe}^{2+}$ as described above, and the data do not justify undertaking deconvolutions of them.

The pre-edge peak shapes of the oriented slabs are similar, despite the fact that their compositions are so variable, suggesting that Fe is in similar coordination polyhedra in each set of spectra. These contrast with the spectra from the set of calibration data, for which Fe$^{3+}$ and Fe$^{2+}$ contents and site occupancies are known (Figure 8). In the standards, as noted above, coordination has a significant influence on the energy and intensity of peaks in the pre-edge region. The least intense spectrum is that from the Serra de Mage sample, which has been shown to contain only Fe$^{2+}$ in the M site. This Fe$^{2+}$ is in a roughly symmetric site that has been suggested to be a composite of up to four microenvironments attributed to two principal sites (c.f. Stewart et al. 1966; Hofmeister and Rossman 1984; Bell and Mao 1972). The Serra de Mage pre-edge spectrum, which is relatively noisy due to the low Fe contents in the sample, does indeed suggest the presence of at least two components.

In contrast, the high intensity spectrum in Figure 8 is taken from the Itrongay sample, which contains Fe$^{3+}$ only in the tetrahedral site. Previous workers such as Galoisy et al. (2001) have suggested that pre-edge intensity should vary inversely with coordination number for noncentrosymmetric environments, such that $I_{\text{oct}} < I_{5\text{-fold}} < I_{\text{tet}}$, and this is observed here when the Itrongay spectrum is compared with that from Serra de Mage.

Calibration

One goal of this paper is to establish the procedure for use of a calibration line to measure Fe$^{3+}$ contents in unknown feldspars. Figure 8 shows the pre-edges of the two standard endmembers; centroid positions for all three standards from a recent data collection session are shown in Figure 9. The positions of each of the three standards form a linear trend. However, centroid positions vary slightly from beam session to beam session (for reasons that are poorly understood), so calibrations must be run contiguously along with the unknowns for best results.

DISCUSSION
The usefulness of the calibration method developed here depends upon the reproducibility of the peak positions of the standards. Based upon Tables 3 and 4, the net reproducibility of measurements at assorted orientations is no better than ±6% absolute for values of the percentage of the total Fe that is present as Fe$^{3+}$. Many factors contribute to this total error.

First, there is numerical error associated with multiple fits to each pre-edge. At least five fits to each spectrum are made, and the results are averaged to produce the centroid used in the calibration. Standard deviations on the centroid positions are typically less than 0.05 eV for most feldspar spectra, which are easy to fit when the samples contain $^{4}$Fe because the peaks are so intense. In general, the centroid of the peak is reproducible within <1% absolute if the peak of interest is the highest peak in the chosen part of the spectrum.

Second, there is error introduced by the assumptions inherent in extracting the pre-edge from the shoulder of the main edge. Ideally, we would be able to explicitly identify the absorption step associated with the ionization potential of the Fe absorption edge and any other resonances on the main-edge in the near-edge region. This would allow us to make rigorous fits to the main edge, and thus realistically obtain a “true” pre-edge from the residuals of the main-edge fits. However, because there is at present no good model for the main-edge peaks, we must resort to a spline fit to the low energy tail of the main-edge structure, which is essentially an empirical fit of the data around the pre-edge. This empirical procedure avoids the errors inherent in choosing specific models for main-edge peak shapes. Thus, the spline method probably contributes little error to the pre-edge centroid determinations.

Third, there might be errors associated with the peak shape used to fit the pre-edge. Our experience has shown that the choice of peak shape is critical in curve-fitting of individual peak contributions to the peak shape. However, in this study we are only interested in the peak centroid for calibration purposes. Thus, we employ a Gaussian fit to the entire pre-edge envelope. The effect of peak shape on the location of the peak centroid is probably minimal, because the differences in the various peak shapes are most dramatic at the limbs, not at the center of mass, of each peak. This was tested by Bajt et al. (1994), who found that a fit of a Lorenztian function did not give as good a result as that of the Gaussian function. Details of the iterative fitting process and its effect on peak centroid positions are given in Bajt et al. 1994).
Fourth, long-term calibration drift (about 0.5-1 eV) appears to result from heating of the monochromator crystal by the very intense incident X-ray beam and/or small drifts in the synchrotron source position. We correct for this problem by normalizing all our data to the centroid of a magnetite standard that is run as every third or fourth spectrum. However, the position of the magnetite centroid does vary considerably during a beam session, and thus this may contribute up to 0.05 eV uncertainty to the centroid positions of our unknowns.

Fifth, XANES spectra of Fe in feldspar must be affected by count rates because the amount of Fe is so small (especially in the anorthite). In our current geometry, all the beam current is passed through the sample, but long count times (sometimes up to one hour) are still necessary to get satisfactory signal to noise ratios. In turn, the longer the count rates, the more significant the effects of electronic instabilities throughout the setup will become. It is evident in Figure 8 that the spectrum of Serra de Mage is of lower quality than that of the Lake County and Itrongay plagioclases. However, because we are interested in the centroid of the peak rather than its precise shape, the signal to noise problems contribute little error to our calibration.

Sixth, orientation effects are effectively documented in Tables 3 and 4 and Figures 3-7, which show the variation in peak position at assorted angles to the beam. The standard error on the anorthite measurements (4.3% of the total Fe) is comparable to that of the orthoclase data (5.8%). Taken together, these data suggest that the cumulative error on the peak locations in feldspar spectra is roughly ±0.1 eV, while the summed error on %Fe$^{3+}$ as predicted by related calibrations is ±6%. Note that these error estimates encompass all the previously mentioned sources of error.

How much of this error is the result of variable orientation? Traverses across single grains of unzoned feldspar from the Atascosa lookout Lava Flow (Cartwright et al., 2000; Cartwright, 2001) give consistent peak positions and %Fe$^{3+}$ results within ±2% absolute. Traverse across megacrystals of hornblende grains have shown <1% variability in Fe$^{3+}$ contents (unpublished data by the authors). Based upon comparison with these data, we believe that the majority of the error shown in Tables 3 and 4 is the result of variations in grain orientation.

Seventh, contamination of feldspar spectra by fluorescence from adjoining, Fe-richer phases is a known problem when measurements are made in thin sections. Recent experiments show that grains as far as 200 μm from the focused position of the beam can “contaminate” the
spectra. Usually this problem can be diagnosed easily because the shape of the main-edge is
diagnostic of each mineral species. Scattered fluorescence can be avoided by putting aluminum
apertures over the feldspar grains of interest when other Fe-rich phases are in the beam path. In
the data reported here, single crystals were used, so the spectra do not have contributions from
other phases. Note that Fe in the glass slides underlying the thin sections may also lead to
contamination; this problem can be solved by using high-purity glass.

Eighth, the effect of Fe coordination on the shape of the feldspar pre-edge is still
unknown. Both Fe$^{2+}$ and Fe$^{3+}$ in tetrahedral coordination polyhedra have intense pre-edges due
to their noncentrosymmetry. If either valence state of Fe occupies the M sites in the structure
(which can have coordination numbers of 5 up to 10; c.f. Smyth and Bish, 1988), additional
components would be introduced to the pre-edge envelope. If the M site happens to be very
symmetrical, then the peaks contributed by those Fe atoms would be less intense than those from
tetrahedral Fe (as is the case with the Serra de Mage spectra presented here). In such a case, the
signal from the lower intensity M-site peaks might be swamped by the very-intense tetrahedral
peaks, such that the envelope fit to their sum would not fully reflect the contribution from the
octahedral Fe peaks. Because so few well-characterized feldspars exist, this effect has not yet
been quantified or even tested, so its contribution to overall error in our Fe$^{3+}/\Sigma$Fe measurements
cannot even be approximated. Great care must be taken with interpretation of pre-edge features
in such mixed site minerals as feldspar. Future work should focus on this problem.

Finally, the error on determinations of Fe$^{3+}$ in unknowns is also dependent upon the
errors inherent in the Fe$^{3+}$ contents of the standards as determined by the other techniques.
Hofmeister and Rossman (1984) give errors of up to ±15% on their integrated peak intensities
resulting from the areas of Fe$^{2+}$ and Fe$^{3+}$ Gaussian components. Note that in Table 1, %Fe$^{3+}$
measurements for the Lake County samples range from 55% (Stewart et al. 1996), 76%
(Emmons et al. 1953) to 67% (Hofmeister and Rossman 1984). Our Mössbauer value of
38±15% Fe$^{3+}$ falls closest to the value given by Stewart. Either the sample is inherently
heterogeneous (this is likely!) or there is variability in these determinations. Our choice of using
the Hofmeister and Rossman values was purely arbitrary. Better characterization of the
standards would greatly improve the calibration line. Additional high sensitivity Mössbauer
measurements of these and other potential feldspar standards are planned, and it is hoped that future refinements of the feldspar calibration line will be made.

The current calibration line, consisting of Serra de Mage anorthite, Lake County labradorite, and Itrongay orthoclase, can be used to measure Fe$^{3+}$ and Fe$^{2+}$ contents of unknown feldspars with an error of roughly ±6% for individual grains and probably <±2% for traverses across single grains. Within this constraint, the synchrotron micro-XANES technique presents a unique opportunity for analyses of feldspars in thin sections at resolution comparable to that of the electron microprobe. Numerous studies are now ongoing to exploit this method for the study of feldspar in petrologic contexts.

ACKNOWLEDGMENTS

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Table 1. Compositions of Feldspars Studied, Based on 16 Oxygens

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Table 2. Mössbauer Parameters for Lake County Feldspar

<table>
<thead>
<tr>
<th>Assignment</th>
<th>$\delta$ (mm/s)</th>
<th>$\Delta$ (mm/s)</th>
<th>% Area</th>
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</thead>
<tbody>
<tr>
<td>$[^4]Fe^{2+}$</td>
<td>0.97</td>
<td>2.51</td>
<td>36</td>
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<tr>
<td>$[^4]Fe^{2+}$</td>
<td>0.99</td>
<td>1.37</td>
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</tr>
<tr>
<td>$[^4]Fe^{3+}$</td>
<td>0.22</td>
<td>0.44</td>
<td>38</td>
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Line width for all peaks was 0.50 mm/s; converged fits could not be obtained with more narrow peaks, suggesting considerable variability in site geometry. Parameters are given relative to the center of an Fe foil calibration spectrum.
Table 3. Pre-Edge Positions for Specific Orientations  
Orthoclase Sample 62047-48

<table>
<thead>
<tr>
<th>Crystal Face&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Session Number</th>
<th>Grain’s Orientation&lt;sup&gt;‡&lt;/sup&gt;</th>
<th>Pre-Edge Position&lt;sup&gt;*&lt;/sup&gt;</th>
<th>Fe&lt;sup&gt;3+&lt;/sup&gt;/ΣFe&lt;sup&gt;†&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>a&lt;sup&gt;*&lt;/sup&gt;</td>
<td>442.082</td>
<td>30</td>
<td>0.315</td>
<td>81</td>
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<tr>
<td></td>
<td>442.083</td>
<td>60</td>
<td>0.391</td>
<td>88</td>
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<tr>
<td></td>
<td>442.077</td>
<td>90</td>
<td>0.201</td>
<td>70</td>
</tr>
<tr>
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<td>442.084</td>
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<td>0.358</td>
<td>85</td>
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<td>446.078</td>
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<td>0.282</td>
<td>79</td>
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<tr>
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<td>446.057</td>
<td>120</td>
<td>0.316</td>
<td>83</td>
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<td>446.059</td>
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<td>446.062</td>
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<td>0.229</td>
<td>73</td>
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<td>446.063</td>
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<td>446.108</td>
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<td><strong>Average</strong></td>
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<td><strong>81.9</strong></td>
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<tr>
<td><strong>σ</strong></td>
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<td><strong>0.057</strong></td>
<td><strong>5.8</strong></td>
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</table>

<sup>1</sup>Cut normal to listed reciprocal axes.  
<sup>‡</sup>Orientations given are rotations in a plane at 45° to the incident beam.  
<sup>*</sup>Peak positions are corrected relative to the position of the magnetite standard, such that position<sub>corrected</sub> = position<sub>raw</sub> - position<sub>magnetite</sub>.  
<sup>†</sup>Calculated using the feldspar calibration line for the appropriate session (see text). Value is given as a percentage.
Table 4. Pre-Edge Positions for Specific Orientations  
Anorthite Sample 56163-6

<table>
<thead>
<tr>
<th>Crystal Face</th>
<th>Session Number</th>
<th>Grain’s Orientation</th>
<th>Pre-Edge Position</th>
<th>Fe$^{3+}$/ΣFe$^+$</th>
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</thead>
<tbody>
<tr>
<td>a*</td>
<td>463.182</td>
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<td>0.009</td>
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<tr>
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<tr>
<td></td>
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<td>-0.096</td>
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<tr>
<td>b*</td>
<td>463.177</td>
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<td>0.219</td>
<td>77</td>
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<td></td>
<td>463.229</td>
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<td>0.003</td>
<td>67</td>
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<tr>
<td>c*</td>
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<tr>
<td></td>
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<td>0.159</td>
<td>74</td>
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<tr>
<td>Average</td>
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<td>σ</td>
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<td><strong>0.091</strong></td>
<td><strong>4.3</strong></td>
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</table>

1Cut normal to listed reciprocal axes.  
‡Orientations given are rotations in a plane at 45° to the incident beam.  
*Peak positions are corrected relative to the position of the magnetite standard, such that position$_{corrected} = position_{raw} - position_{magnetite}$.  
†Calculated using the feldspar calibration line for the appropriate session (see text). Value is given as a percentage.
Figure 1. Beam geometry showing samples (i.e., rotatable thin sections with slabs mounted on them, or single crystals) and sample orientations with respect to the incident polarized x-ray beam. In geometry A, the feldspar slabs are rotated perpendicular to the axis of the microscope/video system view, similar to a microscope stage rotating perpendicular to the direction of light travel. Geometry B (used to study single crystals), is similar to a spindle stage mounted on the rotating stage of a polarized light microscope. There are two axes of rotation, one perpendicular to the incident x-ray beam, and a second axis (which is the spindle stage) rotating within the plane of the rotating stage. This configuration allows all crystal orientations to be presented to the beam. Note: stage translation directions apply to both geometries.
Figure 2. Mössbauer spectrum of Lake County plagioclase run for 7 days with a 50 mCi $^{57}$Co source. Two Fe$^{2+}$ doublets and one Fe$^{3+}$ doublet are present in the spectrum; the area represented by the Fe$^{3+}$ doublet is 38% of the total.
Figure 3. Representative XANES spectra of orthoclase 62047-48 collected with the beam polarized parallel to the X, Y, and Z optical directions in the crystal.
Figure 4. Representative XANES spectra of anorthite 56163-6 collected with the beam polarized parallel to the X, Y, and Z optical directions in the crystal.
Figure 5. Representative XANES spectra of anorthite 56163-6 acquired at different orientations. Rotations noted are within the plane of the focusing camera’s view, which is at 45° to the impinging X-ray beam. In none of these spectra is the beam vibration direction parallel to any of the optical directions X, Y, or Z. Therefore, all of these spectra represent intermediates of the orientations shown in Figure 4.
Figure 6. Variations in pre-edge shape as a function of orientation for orthoclase 62047-48. Centroids of singlet peaks fit to these spectra yield corrected energies of 7113.55, 7113.50, and 7113.52 eV for the X, Y, and Z orientations, respectively.
Figure 7. Pre-edge variation for anorthite 56163-6. Centroids of singlet peaks fit to these spectra yield corrected energies of 7113.38, 7113.36, and 7113.314 eV for the X, Y, and Z orientations, respectively. These energies differ from the larger data set on the set of slabs from this sample, probably because the slabs are optically zoned (and therefore probably zoned with respect to Fe$^{3+}$ contents).
Figure 8. Pre-edge spectra of the feldspar standards from Serra de Mage (0% Fe³⁺) and Itrongay (100% Fe³⁺), corrected for magnetite position and normalized to the position of the magnetite pre-edge at 7113.25 eV. Standard spectra like these are acquired at each beam session, and used to formulate a calibration line for that session.
Figure 9. Typical calibration line from beam session 474 (November 2000). Pre-edge positions for Serra de Mage, Lake County, and Itrongay are plotted against their known Fe$^{3+}$ contents based on the work of Hofmeister and Rossman (1984). The regression line is then used to determine the %Fe$^{3+}$ contents of unknowns.