# Iron Redox Analysis of Silicate-based Minerals and Glasses Using Synchrotron X-ray Absorption and Laboratory X-ray Emission Spectroscopy

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## Abstract

There is considerable need for robust, accessible, and non-destructive Fe redox analysis methods for silicate-based minerals and glasses. A popular method assigns the distribution of Fe2+ and Fe3+ atoms using pre-edge features in the Fe K-edge X-ray absorption near edge structure (XANES). We expand on this work in two ways. First, we use XANES to assign the Fe redox distribution in four silicate materials: two geological reference materials and two industrial glasses. This example highlights the effect of the Fe atomic environment on pre-edge features’ intensities and stresses the need for specifically developed calibration curves. We then investigate Fe Kβ X-ray emission spectroscopy as an independent complement for redox assignments. Here, the silicates do not show a systematic dependence on oxidation state. This is explored with electronic structure calculations, which support previous claims that the lack of sensitivity is due to charge transfers following creation of the 1s core hole.

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## Introduction

Information on the oxidation state distribution of Fe in glasses and minerals is desirable for several industrial and fundamental research applications. Two examples will be briefly discussed, namely: characterizing geological phenomena and rational manufacturing of glass products. First, in geophysical research, Fe redox is routinely used to estimate oxygen fugacity in silicate-based[1] and mantle-derived basaltic melts[2] as well as crystal-rich rocks.[3, 4] These measurements probe oxidation conditions inside the earth and provide key insights into the evolution of magmas and mining ore deposits.[5, 6] Second, in glass manufacturing applications, the redox state of Fe can significantly impact the structural, thermal, and optical properties of the glass melt.[7, 8] For example, the redox state of Fe can affect radiative heat transfer in a glass melt and, therefore, slight variations can substantially vary the energy consumption of the furnace and quality of the final product.[9] These are just two cases, and many other examples exist which illustrate the importance of understanding Fe redox in glass and mineral systems.

The demands for Fe redox information have catalyzed the development of several characterization procedures based on well-known techniques, however many of these procedures possess notable deficiencies and/or experimental challenges. One of the most common and oldest analysis methods is to perform redox titrations using wet-chemical extraction followed by colorimetric measurements.[10-13] However, this method is destructive, requires the use of hazardous acids, and inconsistent results can be produced by the presence of interfering species and oxidation of the sample during analysis.[10, 12-14] Another method is Raman spectroscopy,[15] which, while non-destructive, can be difficult to perform robustly as analyses rely on complex fitting algorithms and is sensitive to unrelated compositional changes.[16] Recent advances in this method have included utilizing machine-learning approaches in interpreting Raman results.[17] A third measurement method is 57Fe Mössbauer spectroscopy.[18-21] A challenge of this analysis method is that may require large quantities of material, long acquisition times, and may require the use of cryogenics.[2] Glass spectra are also substantially broadened relative to their crystalline counterparts and are difficult to deconvolve.[22] Some researchers have reported Mössbauer results are prone to systematically overestimate the Fe3+ component in glasses unless corrections are made, such as, for variable recoil free fractions of ferrous and ferric iron.[23, 24]

In contrast, X-ray absorption near edge structure (XANES) measurements of the Fe K-edge pre-edge features requires relatively little sample, is quick (few seconds to an hour), is amenable to a wide range of concentrations and morphologies, and, as with many spectroscopies, can be adapted for spatially-resolved studies.[2, 14, 25-27] Recent work has mitigated challenges related to XANES data analysis and interpretation through the use of full spectral range data as the input to modern statistical learning algorithms. For example, the least absolute shrinkage and selection operator (lasso) regression technique has enabled improved predictions for silicate glasses which yield uncertainties in the %Fe3+/FeTot results of ±3.6 %.[28] Despite these advances, the wide utilization of XANES for the measurement of Fe redox has been limited as the technique is usually performed at synchrotron light sources. These are shared user facilities that necessarily operate under a restrictive access model often precluding routine characterizations which, while they do not push the forefront of science, are critical for many industrial applications and the development of robust spectroscopic databases. This constraint can be alleviated by laboratory-based X-ray emission and X-ray absorption spectrometers.[29-36]

In recent years, laboratory-based X-ray emission and X-ray absorption spectrometers have contributed substantial scientific findings to several materials research fields.[37-52] These instruments are frequently discussed as enabling technologies to broaden the applicability and quicken the feedback provided by X-ray spectroscopies.[34, 53, 54] It has recently been reported that commercially available laboratory-based X-ray spectrometers are able to reliably measure the pre-edge XANES features at the Fe K-edge for rapid and routine speciation studies with projected minimal concentrations as low as a few molar percent.[55] A key feature of this instrumentation is the implementation of X-ray tube sources. Such sources are well-suited to X-ray emission spectroscopy (XES) studies due to an efficient utilization of their broadband flux.[29, 33] This has enabled a number of XES studies aimed at redox characterizations of various materials. These include, a novel procedure for quick, non-destructive Cr(VI) fractionation determinations in manufactured plastics,[42] sulfur speciation in biochars for ecology research,[45] and probing phosphate defects in InP quantum dots used for photoluminescence applications.[38] The instrumentation can also be adapted for Fe speciation research through Fe core-to-core XES (CTC-XES).

Fe CTC-XES has gained substantial popularity as a tool for characterizing the local spin state and, indirectly, the redox state of the Fe atoms in a system for a variety of applications.[56, 57] For inorganic systems, this approach has proven useful in studying pressure-induced spin transitions in Fe-based high temperature superconductors[58] and similarly in minerals found in the Earth’s interior.[59, 60] There are also several notable examples in biological systems, such as research on metalloenzymes[61] and heme proteins.[62, 63] A clear target at the convergence of these approaches is the study of silicate-based minerals and glasses given the rapid growth in the use of laboratory-based X-ray spectroscopy instrumentation and the utility of Fe CTC-XES measurements for a variety of dilute systems. However, a careful evaluation of the sensitivity of Fe CTC-XES for assessing Fe redox in these materials is needed. This is especially true as the Fe-oxide series is known to demonstrate diminished sensitivity due to a charge transfer event in the photoexcited state.[64]

To date, no reports have systematically characterized the corresponding silicates. Here, we report measurement of both the Fe K-edge XANES and also Fe Kβ XES for Fe reference oxides, several Fe-bearing silicate minerals, and four Fe-bearing silicate reference glasses chosen to represent geological and industrial materials. With the XANES, we see good agreement with prior work, when it exists, and useful fits to extract the Fe3+ fraction for the new materials studied here. The Fe Kb XES is unfortunately less informative. Our results on the reference oxides agree with prior work. The measurements on the silicate minerals and glasses, however, show especially strong consequences of charge transfer in the photoexcited state. All spectra, even for samples that have a nominal Fe2+ oxidation state, have Kβ mainline features that are close to that of a Fe3+ reference oxide, and furthermore the mainline features do not show a systematic trend with respect to the Fe3+ fractions known from the Fe K-edge XANES analysis or redox titration methods. Hence, while there is significant demand for an accessible and high-throughput method (lab-based XES) to study the Fe oxidation state, and while the present results show the necessary spectra can be collected despite the low Fe concentrations and strong absorption from the silicate matrices, the underlying spectroscopy itself does not permit oxidation state determinations.

## Methods

### Compounds

The following minerals were measured to serve as empirical standards: wüstite (beamline provided Fe sample set), olivine (peridot quality, San Carlos Reservation, Arizona, USA), staurolite (Madagascar), hematite (beamline provided Fe sample set and Lake Superior District, Minnesota, USA), aegirine (Zomba, Malawi), and epidote (Dalnegorsk, Russia). The following reference glasses and minerals were measured in this work to assess the effectiveness of Fe Kβ XES for characterizing non-crystalline silicates: BIR-1a (Basalt, Iceland) from the United States Geological Survey (USGS), BCR-2 (Columbia River Basalt, USA) from the USGS,[65] a material developed by the American Society for Testing and Materials (ASTM) which is referred to as ASTM 0.5% in this work, and a similar material from ASTM referred to here as ASTM 1.5%. Table S1 provides compositional information for ASTM 0.5% and ASTM 1.5%.

### X-ray Absorption Fine Structure (XAFS): Experiment and Analysis

The excitation mechanism of XAFS is depicted in Fig. 1 a,c. The Fe K-edge XAFS results were acquired on beamline 6-BM at the National Synchrotron Light Source II (NSLS-II). X-rays were delivered by a 3-pole wiggler source, were unfocused, and were analyzed by a Si(111) monochromator with an energy resolution of approximately 0.9 eV at the Fe K-edge. High-order harmonics were rejected via a Si stripe on a harmonic rejection mirror at a deflection angle of 7 millirad. Mineral and glass materials except for NSLS-II sourced samples were ground to a fine powder in a low moisture (≈ 0 ppm, where 1 ppm is 1 mg of the gas of interest per kg of total gas), low oxygen (< 1.0 ppm), inert environment with an agate mortar and pestle on a cold pad. Coarse particles were rejected via the sedimentation method, which was repeated in triplicate and sizing confirmed by optical microscopy.[66] After sedimentation, the materials were spread onto polyimide tape using a fine brush. Particle sizes and coverage were checked using a 5 MP microscope (AM7515MT8A, Dino-Lite Edge Series). Several layers of the tape enclosed samples were stacked to reduce the possibility of pinholes. Spectra were collected in transmission or fluorescence mode. A reference Fe foil between two downstream ionization chambers was used to align all spectra to a universal scale according to the first derivative peak reported at 7110.75 eV by Kraft et al.[67]

Data processing and normalization was performed according to standard methods available in the Demeter package.[68] Next, the LMFIT package and its built-in mathematical functions were used to fit the features and backgrounds in the pre-edge region of each XANES spectrum.[69] Note that proper selection of a background model is crucial to achieving an accurate and manageable analysis. This is completed with two Gaussian functions in accordance with established procedures.[22] The first function represents 1s-4d electronic transitions above the pre-edge and the other models the edge jump.[70, 71] Likewise, two Gaussian functions were selected to represent the pre-edge features except for wüstite and hematite, which each contained three such functions. For the latter, this was needed to represent non-local excitations which are known to occur in hematite,[72] though it should be noted that reported model fits to either material’s pre-edge require more than two features.[27] In all fits, the width of the two Gaussian functions representing the pre-edge features were constrained to be equal and their remaining parameters were used to calculate a pre-edge centroid and total integrated intensity. While these quantities have a rich history of revealing the redox state of Fe in minerals and glasses,[27, 73] they are also strongly dependent on the local atomic structure found at the Fe sites. For that reason, it is vital that the analysis employs empirical standards that closely represent the bonding environment of Fe in the materials of interest.[74, 75] For the present systems, %Fe3+/FeTot values for the samples were calculated using two calibration curves that rely on the energy of the pre-edge centroid. The first was reported by Wilke et al. in a study of basaltic glasses[22] and the second was developed by Knipping et al. for alkali silicate glasses.[76] The end points of the calibration curve were set to be equal to the mean centroid position of this work’s Fe2+ and Fe3+ mineral standards to ensure that the spectra in this work and the literature spectra used to form the calibration curves were on the same energy scale. Finally, uncertainties were calculated for each calibration curve by propagating the uncertainties in the mineral centroid positions along with the uncertainties in the pre-edge feature fitting parameters after fixing the backgrounds. All uncertainties are reported to one standard deviation.

### XES: Experiment and Analysis

The excitation mechanism of XES is depicted in Fig. 1 a,c. Data were collected using a laboratory-based spectrometer developed at the University of Washington[33] and based on an earlier design by Seidler et al.[29] An X-ray tube source (Varex, VF80 - W anode) operating at 35 kV and 100 W total tube power was used to directly illuminate a sample that was affixed as a powder and aligned behind an entrance slit. The incorporation of this entrance slit, which was approximately 0.8 mm in width and was located on a 1-m Rowland circle, allows high energy-resolution to be achieved and the sample-alignment procedure has been shown to maintain an energy scale with better than 20 meV sample-to-sample reproducibility.[42, 77, 78] X-rays emitted by the sample were monochromatized by a spherically bent crystal analyzer (XRS Tech LLC. - Ge(620)) which was aligned in the tilt-free implementation described by Mortensen and Seidler.[79] The analyzer refocused X-rays toward a silicon drift detector positioned on the Rowland circle (Amptek, X-123SDD). Spectra were collected via step-scanning in 0.25 eV increments from 7005 to 7080 eV.

 Acquired data was processed in several steps. First, a region-of-interest was selected, and a substantial portion of the background signal was rejected from all spectra. Second, the spectra were dead time corrected. Note that, in general, this step did not change the spectra considerably as typical total count rates were a few hundred per second for the glasses to several thousand per second for the empirical standards. Thus, typical live times did not differ from the real times by more than a fraction of a percent. Third, a constant background was subtracted from the spectra according to the average of the first 5 eV of each spectrum. Fourth, the results were integral normalized over the range 7020 eV to 7070 eV. This fourth step involved calculating the summation of the count rates over this range and then reporting each point as a percentage of this total. Finally, each sample was analyzed for radiation damage. Data for this analysis was collected by iteratively acquiring scans with an acquisition time of about 7.5 min per scan. From this data the first moment position of the diagram line was calculated, and the samples were partitioned into two groups: those which were concentrated and provided intense signals, and those which were dilute and produced weaker signals. For intense signals, the set of scans was truncated when, if at any point, a scan’s first moment position shifted by more than 15 meV from the first scan. As this is less than the sample-to-sample reproducibility, any effects from irradiation would not contribute to a chemically meaningful change. For especially dilute compounds, the spectra could become sufficiently noisy to make this approach impractical. In such cases, the scans were truncated if, at any point, the first moment position deviated by more than 1.5 standard deviations from the first scan. This conservative approach ensured that any effects from irradiation were excluded.

### Electronic Structure Calculations: Spin Analysis

The number of unpaired 3d electrons serves a significant role in determining the spectral shape of CTC-XES features (Fig. 1b). For Kα XES the width of the features is governed largely by (2p,3d) exchange (Fig. 1a). For the spectral region studied here, the number of unpaired 3d electrons determines the intensity of the Kβ’ feature and the chemical shifts are largely governed by (3p,3d) exchange (Fig. 1a).[56] However, it should be noted that, as a secondary process, it is the number of unpaired 3d electrons in the excited state possessing a core hole which is reflected in the measured spectrum.

In an article by Kawai et al., it was argued that the chemical insensitivity in Fe Kα XES of high-spin oxides was due to a charge transfer event in the photoexcited state.[64] Specifically, calculations on a minimal, oxygen-bearing Fe cluster showed that this process leads to a similar density of unpaired 3d electrons on both the divalent and trivalent system. Motivated by that work, this manuscript reports electronic structure calculations on four silicate minerals as well as the two clusters reported by Kawai et al. Experimental cif files[80-83] were reduced to minimal charged clusters consisting of the central atom and its first coordination shell. All calculations were performed using NWChem.[84, 85] Ground state calculations were performed using the fragment approach, where the appropriate spin state was achieved by first simulating just the Fe(II) or Fe(III) ion in a fully paramagnetic configuration. The resulting molecular orbital vectors served as inputs for the ground state calculations of the full charged cluster. Next, two core hole calculations were performed. In one, a spin-up core (Fe 1s) electron was removed from the system and a spin-down core (Fe 1s) electron was removed in the other. In both cases, variational collapse of the core hole was prevented with the maximum overlap method as implemented in NWChem.[86, 87] Determination of the number of unpaired 3d electrons was achieved with a Mulliken population analysis of the spin density and tallying the value reported in each d-orbital of the central Fe atom. All calculations were performed at the Hartree-Fock level of theory. The def2-TZVP basis set was used for all atoms.[88] Example input files can be found in the supporting information.

## Results and Discussion

This section will begin with a discussion of the absorption spectra. In Fig. 2(a), the Fe K-edge XANES spectrum of each mineral standard is shown. Here, several trends become apparent and merit comment. First, the divalent and trivalent Fe compounds congregate in two separate groups. The nominal edge positions of these two groups are split by roughly 4 eV. Fig. 2(b) shows the corresponding XANES spectra of the glasses studied in this work in between a Fe2+ and Fe3+ mineral for reference. The USGS glasses include Fe atoms that favor the divalent oxidation state, while the ASTM glasses are closer to the trivalent minerals. This dataset showcases why this metric is unable to provide quantitative redox distribution information as many of the spectra exhibit large, sloping white line features, multiple shoulder features, and extended pre-edge peaks. This is especially clear in the divalent compounds at incident energies around 7120 eV. Here, wüstite and olivine exhibit significant shoulders and the first of several large peaks in staurolite’s spectrum can be found. These features complicate the shape of the edge and preclude the usual linear regression of edge position to evaluate oxidation state information. This difficulty is well known and has been previously noted.[89, 90]

The pre-edge region of each mineral compound can be seen in Fig. 3(a-d). To facilitate comparisons within and between oxidation states, the centroid position and integrated intensities of the pre-edge features can be found in Table 1. The centroids of the divalent and trivalent iron compounds are separated by about 1.5 eV as expected. Similarly, the intensity of the 6-fold coordinated trivalent compounds is slightly elevated relative to their divalent analogs. The centroid positions of the minerals were largely consistent within an oxidation state. The 4-fold coordinated divalent compound was observed to have a substantially larger intensity than its 6-fold coordinated counterparts. This is consistent with previous findings and an increase in 3d-4p hybridization. These observed trends are in agreement with the existing literature which has established methods for Fe redox determinations based on the relationships between the oxidation state distribution of the present Fe atoms and the centroid position of the Fe K-edge pre-edge features.[22, 25, 27, 55, 74] Note that the pre-edge region of the oxides can be found in Fig. S1 for comparison.

The above results validate the fitting process used to analyze each pre-edge region. The same procedure was applied to each glass compound and the results are plotted in Fig. 3(e-h) and quantified in Table 2. In each case, the spectrum produced by the fit matched exceedingly well with the measured spectrum. Starting with the USGS materials, both calibration curves predicted that most of the Fe atoms were divalent, as expected from Fig. 2. The estimate calculated following the method of Wilke et al. [22] is slightly lower than that from the method of Knipping et al.[76] The results provided by Wilke et al.’s method are of a similar chemistry to these samples and, therefore, are likely more representative of their Fe redox states. Here, calculated results are slightly elevated relative to the values produced by wet chemical redox methods. This is not surprising as the titration methods are noted for often producing lower than expected results if not conducted with care.[13] For the ASTM glasses, results from both XANES calibration curves predict that most Fe atoms are in the trivalent state, as expected from Fig. 2(b). Interestingly, the integrated intensity of the pre-edge region is substantially larger for the ASTM glasses and suggests that those Fe atoms may be 4-fold coordinated. The results provided by the calibration curve of Knipping et al. may be more relevant to these glasses as their curve was developed using alkali silicate glasses. In summary, the pre-edge features in Fe K-edge XANES demonstrate several notable sensitivities to the redox state of the compound measured and the oxidation state distribution can be deduced using established methods. This information will now be used to assess whether the XES results exhibit similar behavior.

Fe Kβ CTC-XES results for several oxides and minerals are shown in Fig. 4. In order, Fig. 4(a) shows the XES results for the divalent and trivalent oxides. Here, the most significant differences are seen in the Kβ1,3 feature, which becomes sharper and moves to higher energies upon oxidation. This trend suggests an increase in nominal spin state, which is consistent with the current system.[91] The difference in peak positions is roughly 0.5 eV; this sensitivity is significantly less than the XES lines observed from comparable elements as the differences are muted due to a charge transfer event in the excited state.[64] Nonetheless, the difference is meaningful as it is 25x larger than the upper limit of values typically reported for sample-to-sample reproducibility in the present type of instrumentation.[42, 77, 78] This observation suggests that Fe Kβ XES bears some merit for ascertaining the redox state of a compound of interest if the instrumentation possesses sufficient energy resolution and stability. However, this utility is not borne out as this behavior is not universal to other high-spin Fe compounds. Specifically, it can be seen from Fig. 4(b) and 4(c) that the spectra corresponding to silicate minerals are both higher in energy than those of oxides in the same oxidation state. Fig. 5(a) reveals that there is no clear relationship between the oxidation state of Fe in the silicate-based minerals and the energy of the Kβ1,3 feature. This is evidenced by the fact that staurolite and epidote roughly agree in position despite differing oxidation states, yet olivine and aegirine are found together at slightly higher fluorescence energies despite, again, comprising a divalent and trivalent Fe system, respectively. Another way to visualize this behavior is provided in Fig. S2. Here, each silicate is compared to the oxides and a residual is shown of the silicate’s spectrum subtracted from the trivalent oxide. From this figure, it can again be seen that the spectra of aegirine and olivine are very similar despite their differing oxidation states. Yet, these spectra are slightly shifted from that of epidote and staurolite which, again, are similar to each other despite their differing oxidation states. This reinforces the claim that the effect of oxidation state on the Fe Kβ CTC-XES lines of silicates is small and not systematic.

The lack of chemical sensitivity shown by the silicate and oxide spectra can be attributed to charge transfer events in the photoexcited state. Table 3 shows the results of calculations for the ground and core hole excited configurations. There is an observable difference in the number of unpaired electrons in the ground states when comparing the divalent and trivalent Fe compounds. However, this difference is minimized in the excited states. This general trend is consistent with the findings of Kawai et al.[64] Nonetheless, the densities reported here are slightly different than those reported by Kawai et al. which are reiterated in Table 3. Considering the ground states, the densities reported in this manuscript are in better agreement with the nominal spin density of four electrons for the divalent case and five electrons for the trivalent case. These small disagreements can be attributed to differences in the computational approaches, including the choice of functional. Here, pure Hartree-Fock exchange was chosen to achieve a localized solution consistent with expectation.

Fig. 5(b-c) provides evidence that the position of the Fe Kβ1,3 is also not a robust indicator of oxidation state in amorphous systems of Fe-based silicates. In this figure, the spectra generated from measurements of wüstite and aegirine are shown with a variety of Fe-based silicate glasses. It should be noted that wüstite and aegirine were selected as standards as they were the most dissimilar of the oxides and minerals measured. Here, nearly all the glasses produced spectra in rough agreement with aegirine, which is a mineral bearing trivalent Fe atoms. This is in stark contrast to the above results based on XANES analysis which revealed quantifiable sensitivities to the local atomic and electronic structure of Fe atoms in the minerals and glasses.

## Conclusions

Established analyses of the Fe K-edge XANES results permitted quantification of the redox distribution of Fe atoms in both the silicate-based minerals and glasses. This study demonstrates a satisfactory application of traditional peak fitting procedures to the pre-edge region of a variety of silicate-based minerals and glasses despite complex local atomic environments. This procedure provided Fe redox estimates for four glasses which serve as community reference materials for geological and industrial applications. It is apparent that combining this approach with the rapidly growing capabilities of laboratory-based X-ray spectrometers is a promising direction for future studies in need of accessible X-ray analyses. As lab-based emission spectroscopy is amenable to lower Fe concentrations than lab-based absorption spectroscopies, Fe Kβ XES has been assessed as a potential complement to Fe K-edge XANES measurements for characterizing Fe redox distributions in silicate-based materials. The usual chemical sensitivity of CTC-XES was found to be dampened for the materials studied in this work. This prevents the immediate application of Fe Kβ XES to routine Fe redox analyses. On the basis of the calculations in this work, the lack of sensitivity can be attributed to charge transfer events in the photoexcited state that lead to a similar number of unpaired 3d electrons on the absorbing Fe atoms in the divalent and trivalent silicate compounds.

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Fig. 1: XES and XAFS excitation/relaxation mechanisms. (a) Simplified energy band diagram for XES (red, blue, black) and XAFS (green). (b) 3d spin orbital diagrams for Fe2+ and Fe3+. (c) Diagrams of XES (left) and XAS (right) spectrum. Color notation are conserved from (a).



Fig. 2: Measurements of the Fe K-edge XANES. Subpanel (a) shows six minerals with hematite and wüstite being oxides while the rest are silicates. Subpanel (b) compares the spectra collected from the glass reference materials to a divalent and a trivalent Fe-based silicate mineral.



Fig. 3: The measured pre-edge region of each silicate-based glass or mineral’s Fe K-edge XANES spectrum (Experiment) is shown along with the corresponding components of the fit and their sum (total). These components include two functions representing the pre-edge features and two representing the edge (designated by arrows in subpanel e). The minerals are in the left column (a-d). Glass compounds are in the right column (e-h).



Fig. 4: Fe Kβ XES results as measured for oxides of different redox states (a), three Fe2+ compounds (b), and three Fe3+ compounds (c).



Fig. 5: A narrow view of the Fe Kβ XES region focusing on the Kβ1,3 line. (a) The compounds shown here are four Fe-based silicate minerals. Two of the compounds possess Fe2+ ­atoms while another two possess Fe3+ atoms as denoted in the legend. (b) Olivine and aegirine are shown as examples of a Fe2+ and Fe3+ samples, respectively. Also shown are BIR-1a and BCR-2, two basaltic glasses from the USGS. (c) Olivine and aegirine are again shown as examples of a Fe2+ and Fe3+ samples, respectively. Also shown are ASTM 0.5% and ASTM 1.5%, two alkali silicate glasses from the ASTM.

Table 1: The coordination and oxidation state of Fe is listed for each mineral compound. Also given are the centroid positions and integrated pre-edge intensities calculated in the fitting procedure along with their corresponding uncertainties.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Reference Mineral | Redox State | Coordination Number | Centroid Position (eV) | Integrated Pre-Edge Intensity |
| Wüstite | 2+ | 6 | 7111.708 ± 0.014 | 0.0584 ± 0.0008 |
| Olivine | 2+ | 6 | 7111.53 ± 0.03 | 0.0449 ± 0.0010 |
| Staurolite | 2+ | 4 | 7111.57 ± 0.04 | 0.158 ± 0.006 |
| Hematite | 3+ | 6 | 7112.994 ± 0.015 | 0.0620 ± 0.0010 |
| Epidote | 3+ | 6 | 7113.1 ± 0.4 | 0.09 ± 0.04 |
| Aegirine | 3+ | 6 | 7113.223 ± 0.019 | 0.0607 ± 0.0012 |

Table 2: The centroid positions and integrated pre-edge intensities as calculated by the fitting procedure is given for each glass compound. Quantification of Fe3+/∑Fe was performed according to the calibration curves provided by Wilke et al.[22] and Knipping et al.[76] These are compared to values from wet chemical redox titrations provided in correspondence with the issuing institution.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Sample | Centroid Position (eV) | Integrated Pre-Edge Intensity | Fe3+/∑Fe (%) [Wilke et al.][22] | Fe3+/∑Fe (%) [Knipping et al.][76] | Fe3+/∑Fe (%) Redox Titration |
| BCR2 | 7112.23 ± 0.02 | 0.0830 ± 0.0016 | 25 ± 4\* | 34 ± 6 | 15.2 |
| BIR1a | 7112.304 ± 0.017 | 0.0864 ± 0.0011 | 29 ± 4\* | 39 ± 6 | 19.3 |
| ASTM 0.5% | 7112.793 ± 0.016 | 0.1782 ± 0.0019 | 58 ± 7 | 74 ± 7\* | - |
| ASTM 1.5% | 7112.757 ± 0.018 | 0.182 ± 0.002 | 56 ± 7 | 72 ± 7\* | - |

\*These XAFS results can be expected to be the most accurate as the calibration curves were developed for a glass system most closely related to the sample’s chemistry.

Table 3: The number of unpaired 3d electrons estimated by a Mulliken spin density analysis for a variety of systems. The clusters with the designation (Kawai) are taken from a calculation performed by Kawai et al.[64] and is described in the methods section above.

|  |  |
| --- | --- |
|  | Unpaired 3d Electrons |
| System | **Ground** | **1s↑ - hole** | **1s↓ - hole** |
| Olivine (+2) | 3.92 | 3.69 | 3.69 |
| Staurolite (+2) | 3.85 | 3.60 | 3.61 |
| Fe(II) Cluster | 3.90 | 3.68 | 3.69 |
| Fe(II) Cluster - Kawai | 3.8 | 3.22 | 3.22 |
| Aegirine (+3) | 4.72 | 3.79 | 3.80 |
| Epidote (+3) | 4.72 | 3.83 | 3.87 |
| Fe(III) Cluster | 4.76 | 3.74 | 3.74 |
| Fe(III) Cluster – Kawai | 4.38 | 3.33 | 3.33 |