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EMAS 2018

13th EMAS Regional Workshop

MICROBEAM ANALYSIS IN THE EARTH SCIENCES

4 - 7 September 2018
University of Bristol, Wills Hall, Bristol, Great Britain

Organised in collaboration with:
Mineralogical Society of Great Britain and Ireland
and
University of Bristol

DETERMINING THE REDOX STATE OF IRON IN SILICATE GLASSES USING XANES

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ABSTRACT

Over the last ~10 years a combination of Fe K-edge X-ray absorption near-edge spectroscopy (XANES) and Mössbauer spectroscopy has allowed us to make precise, in-situ, micrometre-scale (~10 to 100 μm) measurements of the ferric-ferrous contents of basaltic glasses. Here, we briefly discuss the theory behind a XANES measurement, and some of the benefits, and drawbacks, of using XANES to measure ferric/ferrous ratios compared to other techniques. Then, we follow a sample through a typical workflow, from preparation of the sample, acquisition of spectra (including beam damage), reducing/ fitting spectra, and converting a XANES measurement to a ferric/ferrous ratio.

1. *INTRODUCTION*

Iron is the most abundant naturally-occurring element that has multiple oxidation states and the relative concentrations of Fe^{3+} and Fe^{2+} in minerals and melts provide important information about the oxygen fugacities (fO_2s) under which they were formed. Given the extent to which oxidation state controls many geological processes (e.g., planetary core formation and magma degassing; [1, 2]), there have been many efforts made measure the Fe^{3+} and Fe^{2+} concentrations of natural samples. These enable estimates of the fO_2 inside the Earth and the other terrestrial planets (e.g., [3, 4]). Traditionally, the oxidation states of glasses have been measured either by wet chemistry (e.g. [5]) or by Mössbauer spectroscopy (e.g., [6]). Perhaps the most significant drawback of these two widely-used approaches is that they usually require tens to hundreds of milligrams of powdered sample (e.g., [7] use ~ 500 mg of powdered basalt for their wet-chemical measurements), meaning that they are only applicable to relatively large, homogeneous samples. Recently, X-ray absorption near-edge spectroscopy (XANES) has been applied to the measurement of the redox state of iron in geologically-relevant glasses (e.g., [8-10]). The principal benefit of Fe-XANES is its ability to analyze samples at the micron scale: incident X-ray beams can be focused to relatively small diameters (~ 5 - 10 μm, equivalent to other commonly-used micro-analytical techniques, e.g., EPMA and SIMS), making it possible to analyze small features (such as melt inclusions), and natural samples that exhibit heterogeneities at longer (i.e., hundreds of micrometres) length scales. There are two other, widely-used, analytical methods that are able to measure the ferric/ferrous ratios of samples over the same length scale as micro-XANES, the flank method (EPMA) and micro-Mössbauer. Hughes *et al.* (this volume) provide a detailed description of the flank method and how it can be applied to measure the ferric/ferrous ratios of melt inclusions. Although it will not be discussed at any length here, users should be aware of synchrotron-based micro-Mössbauer. Although relatively new [11], this technique uses synchrotron X-rays and an iron borate crystal to generate Mössbauer radiation. The principal benefit to this analytical method is the high-brilliance, which allows spectra to be acquired quickly (timescales of hours, compared to days for a typical radioactive source), and small spot size (beamline ID18 at ESRF can focus down to a spot of ~ 5 x 10 μm [12]). As we detail below, the XANES method relies on standards with known ferric/ferrous ratios, which are usually measured by Mössbauer spectroscopy. Therefore, using synchrotron-based micro-Mössbauer to measure the ferric/ferrous ratios directly may be a viable alternative.

2. SAMPLE PREPARATION AND SPECTRA ACQUISITION

Natural basaltic glasses are usually not homogeneous over cm-scale lengths (e.g., Fig. 1). Thus, the primary concern when preparing samples for analysis by XANES is ensuring that that the X-rays sample only the intended phase. Practically, this is done by doubly polishing the samples, until they are optically clear (e.g., [13]), and choosing regions for analysis that are free from crystals, microphenocrysts, bubbles, cracks and/or alteration products. Thus, the thickness of each sample will depend on the amount of non-glass phases in the sample (i.e., a sample with a high density of microphenocrysts will have to be polished thinner to obtain an optically-clear path than one that is almost pure glas), and the composition of the glass itself. Although not a problem with doubly-polished samples, if only a single polish is required (i.e., you are working with experimentally-produced glasses), ensure that iron-free epoxy or mounting media is used.

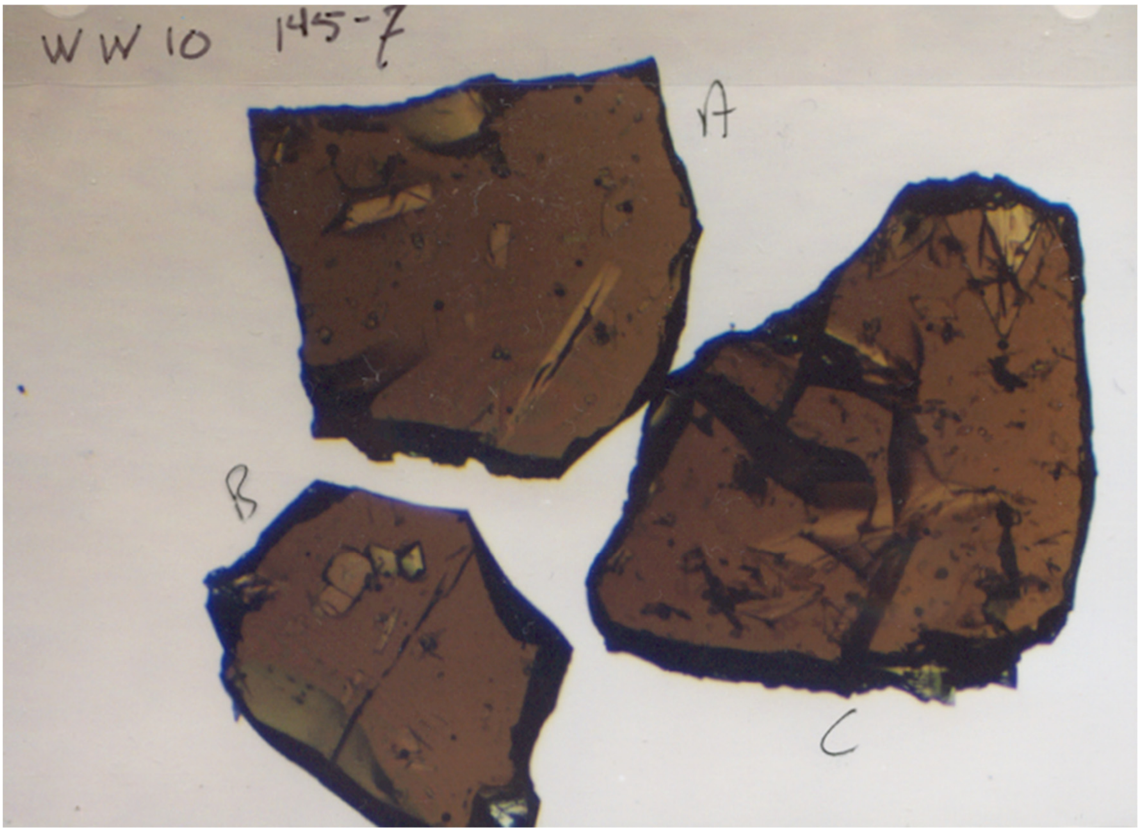

Figure 1. Transmitted-light image of doubly-polished mid-ocean ridge basalt chips from the Gakkel Ridge. Each chip is approximately 2 mm across.

Once at the synchrotron there are seven main parameters that the user/analyst can control: the order of the reflection of the monochromator, the spot size of the analysis, the energy range the spectra will be acquired over, the step size of the monochromator, the counting time at each step, if the incident beam will be attenuated at all, and the location of the detector relative to the sample. It has been found that a higher order (311 or 333) reflection from the Si monochromator gives better spectral resolution (e.g., [10]), and these should be used whenever possible. The spot size of the analysis should be chosen with the lengthscales of sample heterogeneities, and the size of analyzable spots in mind as well as the reproducibility of the stage. Deciding the scan parameters (energy range, step size, and dwell time at each point), is a difficult task for a new user. These parameters will ultimately control the precision of your analyses yet, likely because of the low-availability of beamtime, and the desire for data from one session to be self-consistent, end users tend to spend little time optimizing them. Longer scans (longer energy ranges, smaller step sizes, and longer dwell times) hold the promise of better data. However, the quest for the highest-quality data is often moderated by the length of time available and the number of samples (or duplicates) to be analyzed. Figure 2 shows a typical XANES spectra of a basaltic glass.

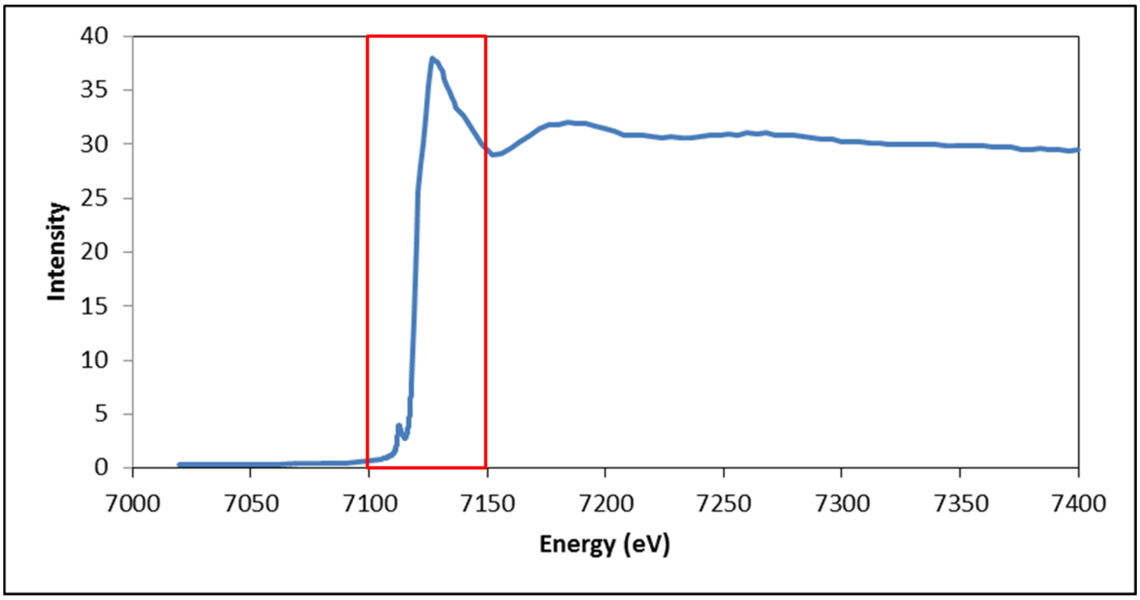

Figure 2. XANES spectra of a typical mid-ocean ridge basalt. The edge region is highlighted by a red box.

The principal feature in this spectra is the Fe-K edge at ~7,120 eV (intensity goes from ~ 5 to 35). The pre edge features can be seen as a little bump before the edge from ~7,110 - 7,115 eV. The part of the spectra before ~7,110 is called the pre-edge, and, correspondingly, the spectra after ~7,150 is termed the post-edge. The details of the pre- and post-edge are not critical for XANES analyses, in fact they are often only used for normalizing the spectra (discussed below), and this often results in one choosing large step sizes and short dwell times in these regions. Small step sizes and long dwell times are critical over the pre-edge, as this is the feature used in the analysis. See Table 1 for suggested initial scan parameters.

Table 1. Suggested initial XANES scan parameters.

Energy range (eV)	Step size (eV)	Dwell time (s)
7,020 - 7,105	10	1
7,105 - 7,118	0.1	5
7,118 - 7,126	0.5	2
7,127 - 7,140	1.0	2
7,144 - 7,400	4.0	2

Recently it has been shown that hydrous silicate glasses can be oxidised by exposure to high-intensity X-ray beams [14]. Thus, it is essential to check for time-dependent changes in the pre-edge features of your samples. Attenuating the incoming beam, below some threshold, seems to prevent, or avoid, beam damage. All else being equal, attenuating the incident beam reduces the counts received at the detector, and thus has potential consequences for the ultimate precision of the analyses. One way to increase the counts at the detector is to move it as close as possible to the sample. One must take care, however, as moving the detector close to the sample may make it difficult to change samples and it may oversaturate the detector. If analysing high-iron, anhydrous samples a filter (usually Al) between the sample and the detector may be used to ensure that the count rate of the detector remains in its linear range.

3. DATA PROCESSING

The first step in data processing is normalising the spectra: different iron concentrations, detector positions, and presence or absence of filters can affect the count rates at the detector. Thus, to accurately compare spectra, we must first normalise the spectra. A spectra is normalised by first fitting a function to both the pre- and post-edge features. Typically the pre-edge is fit by a line and the post-edge by either a line or a 2^{nd} order polynomial. Fig. 3a shows a typical XANES spectra (in blue), along with the pre-and post-edge fits (a green and orange lines, respectively).

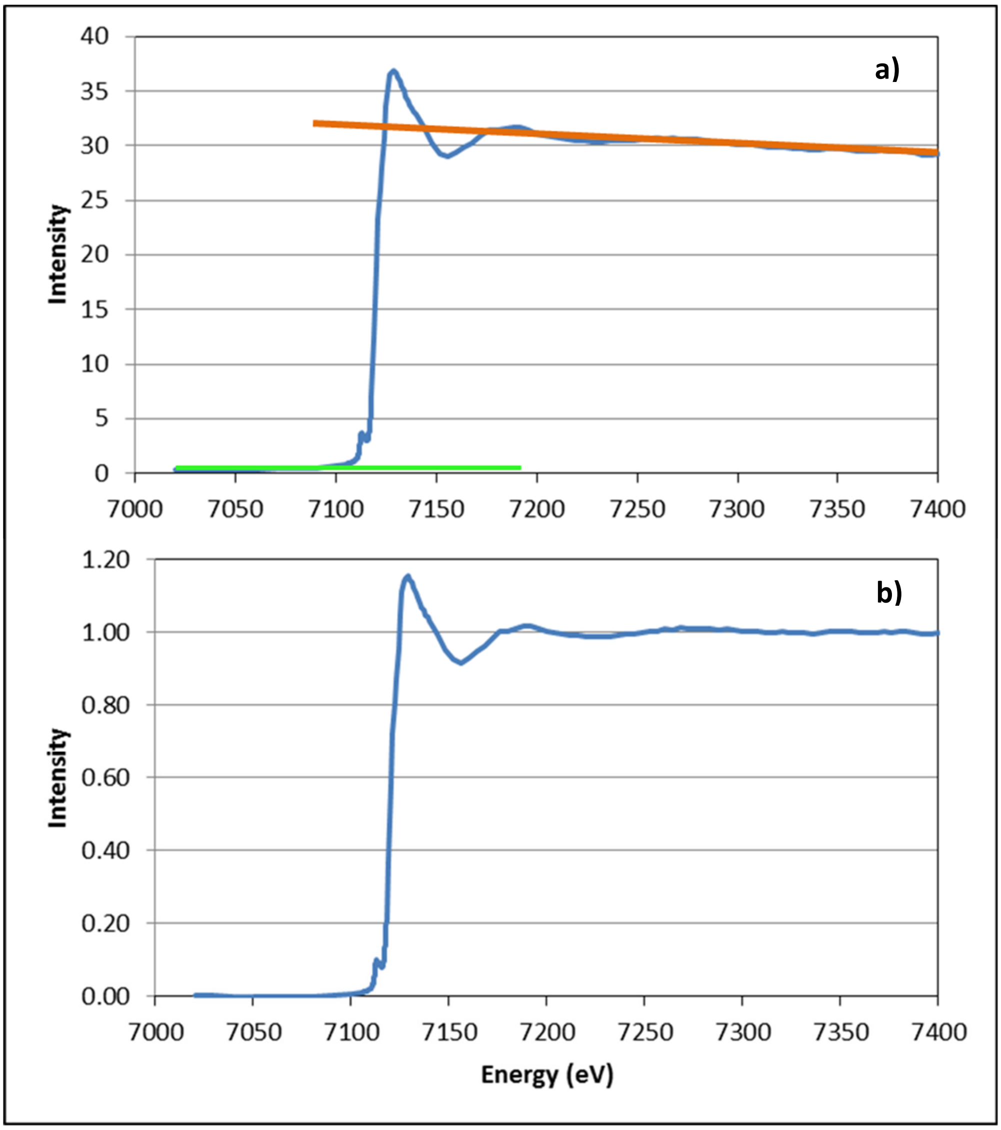

Figure 3. a) Un-normalised XANES spectra showing fits to the pre-edge (green line), and post-edge regions (orange line). b) Normalised XANES spectra.

The pre-edge region of this spectra is fairly flat already, but the post-edge is characterised by a gradual decrease in average intensity with increasing energy. The spectra are then transformed such that pre- and post-edge regions are flat, with intensities of zero and one, respectively (see [15] for more about normalising spectra. Figure 3b shows a normalized spectra, note that the post-edge region is now horizontal, with a value of ~ 1.

With normalized spectra we can now focus on quantifying the pre-edge features. Figure 4 shows part of the pre-edge region of a suite of experimentally-produced glasses. These glasses all have the same nominal composition and were equilibrated at $\log_{10}f\mathrm{O}_2$s of -10 to -0.68, and as a result they have a wide range of ferric/ferrous ratios. These pre-edge features are dominated by two peaks, the first located at ~7,111 eV and the second at ~ 7,113 eV; these peaks can be thought of as corresponding to the abundance of ferrous and ferric iron, respectively (samples from low *f*O2s, that are dominated by Fe^{2+}, have a higher peak at ~7,111, and samples from high *f*O2s, that have more Fe^{3+}, have a higher peak at ~7,113). There are many ways in which one could quantify the spectra but the way that most widely-used in the literature ueses the centroid, or the area-weighted average of the pre-edge. To quantify the area of the pre-edge features we must separate them out from that of the rest of the spectra. The first step in this process is usually only working with a portion of the normalized spectra (7,106 to 7,118 eV in the example shown below), as fitting the whole spectra would be too difficult (and unlikely to yield better insights into the pre-edge features). Next, a series of functions are chosen: e.g., Gaussians for the ferric and ferrous peaks at 7,113 and 7,111 eV, and a background that is a combination of a line and a damped-harmonic oscillator (e.g., [10]). Next, a routine is run that minimizes the difference between the observed and the modeled spectra, by changing all of the fit parameters (e.g., the locations and intensities of the Gaussians).

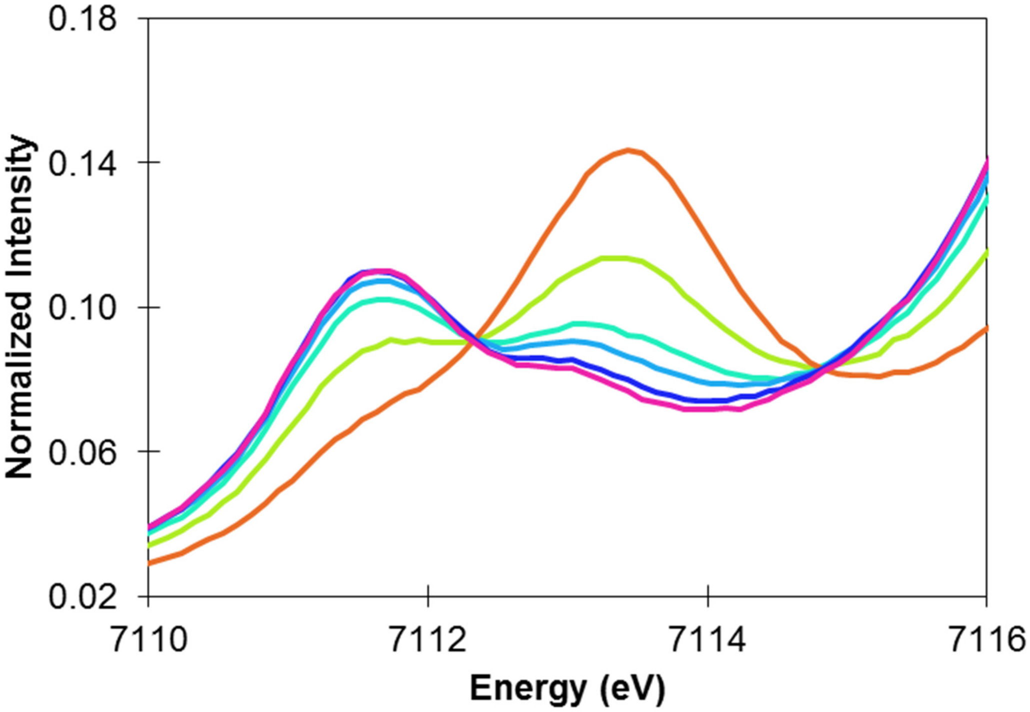

Figure 4. Normalised XANES spectra showing only the pre-edge region. These spectra are from a suite of experimentally produced glasses equilibrated under a wide range of oxygen fugacaties. With increasing oxygen fugacity the peak at ~7,111 eV decreases wheras the peak at ~7,113 eV increases, reflecting the increasing proportion of Fe^{3+} in the melt.

In the example shown in Fig. 5, there are 12 fit parameters. As can be seen in Fig. 5, the data acquired at the synchrotron (black dots) is well fit by this combination of functions used to construct the synthetic spectra (magenta line). With a spectra that is well described by a series of function, it is then trivial to calculate the centroid energy.

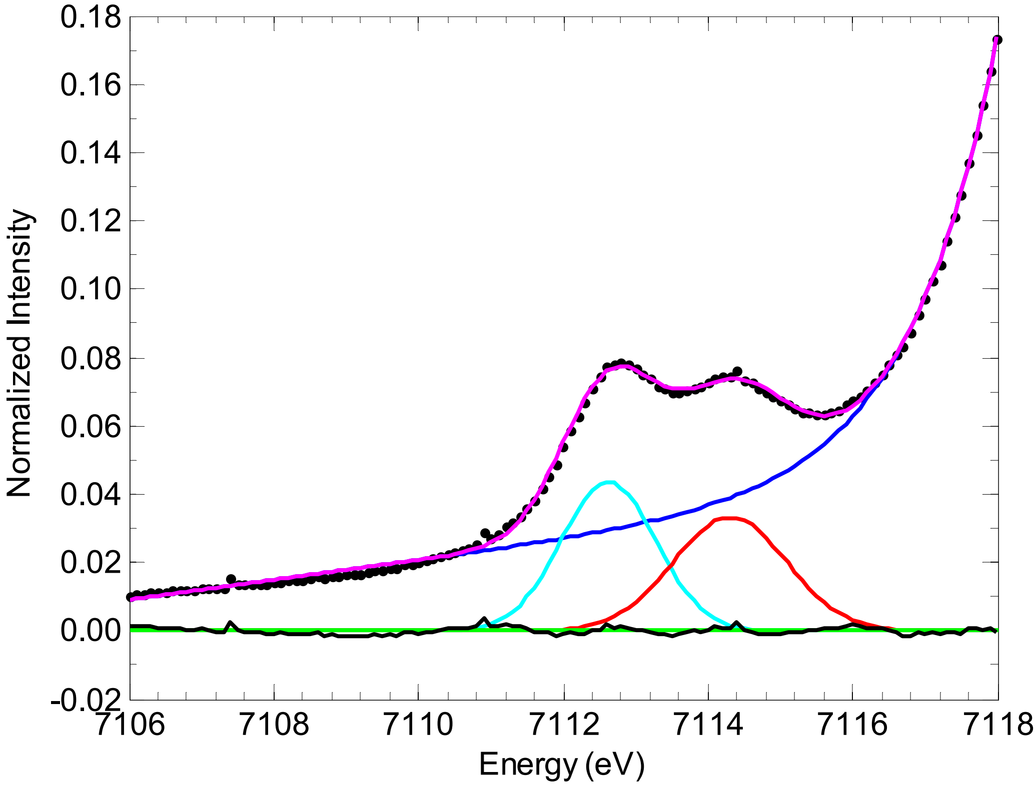

Figure 5. Normalised pre-edge spectra showing the spectra as acquired (black points), and the individual functions (background, blue line; Gaussians, red and cyan lines) that make up the synthetic spectra (magenta line). The misfit between the observed spectra and they synthetic or modeled spectra is shon by the black line that oscilates around zero (green line).

The fitting process described above seems somewhat arbitrary, that is because it is. Any combination of functions can be used to describe the observed spectra (e.g., Voigt profiles instead of Gaussians, or a polynomial instead of a damped harmonic oscillator). The functions above were used simply because the are the ones that others have used most often. Furthermore, there are alternate approaches available; Shorttle *et al.* [16] used principal component analysis to process the pre-edge region of their spectra. As emphasized by Berry *et al.* [8] the functions chosen to fit the spectra are of secondary importance; what matters most is fitting the spectra, including those of the standards, in a self-consistent manner.

As mentioned earlier, converting a centroid energy into a ferric/ferrous ratio requires a set of well-characterized standards. Cottrell *et al.* [10] used Mössbauer spectroscopy to determine the ferric/ferrous ratios of a suite of experimentally produced glasses. Fortunately, they have made their standard block freely available through the Smithsonian for other researchers to use. These samples are in high demand; thus, if you are interested in using them as standards for your study you should try to arrange a loan as soon as your beamtime is scheduled. Figure 6 is the relationship between centroid energy and ferric/ferrous concentration from by Cottrell *et al.* [10], their Fig. 8. 8. With a suitable calibration, it is then straightforward to turn a XANES measurement into a ferric/ferrous measurement, and using an empirical relationship between ferric/ferrous ratio and temperature and composition (e.g., [17]), approximate the fO_2. Note that the difference in centroid energy for the large majority of geologic samples (~QFM-1 to QFM +2) is small, about 0.5 eV. This is why it is imperative to choose a small scanning step over the pre-edge region. Lastly, the K-absorption edge corresponds to the binding energy of a 1s electron. In Fe this occurs at 7.1 keV. The pre-edge features in a Fe-XANES spectrum are results of the 1s→3d transitions, i.e., the excitation of core 1s electrons to outer, bound, states. The energies of these transitions naturally depend on the number of 3d electrons and hence on the oxidation state of the Fe atom.

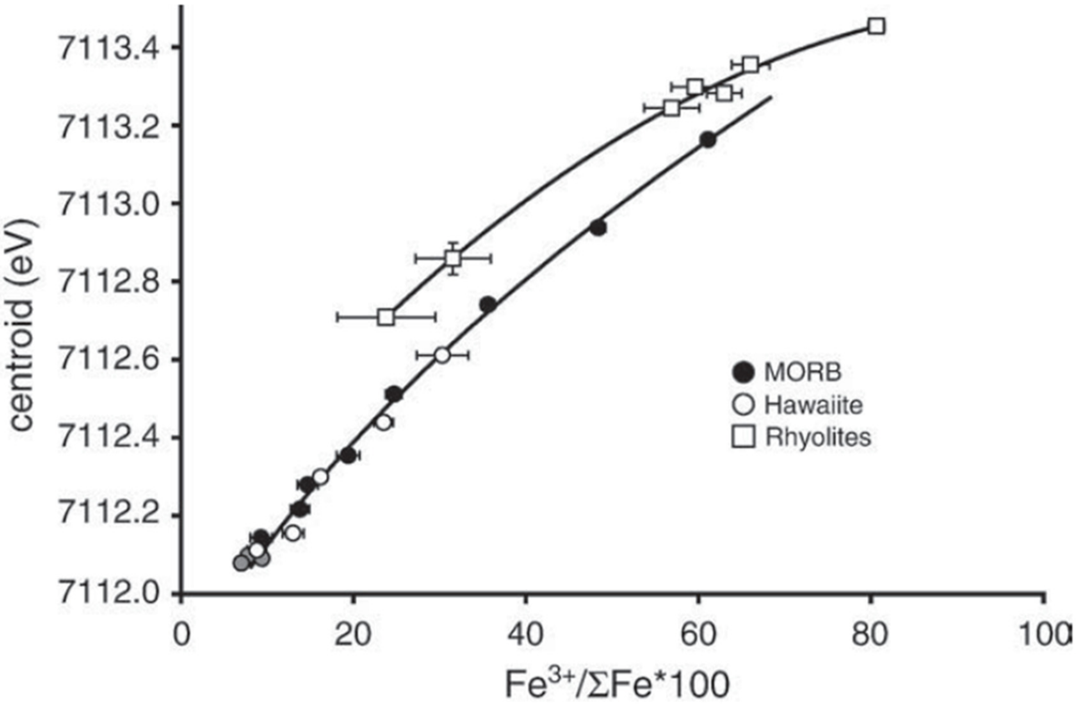

Figure 6. Centroid energy ve $Fe^{3+}/\sum Fe$. Figure from Cottrell *et al.* [10].

Thus, the pre-edge spectrum contains information about oxidation state. Additionally, the pre-edge spectrum must depend on the structural environment, or coordination (e.g., [18]) of the atom of interest. Unlike in crystals, the coordination environment of Fe atoms in glasses is ill-defined and possibly highly variable: it is likely that Fe atoms in silicate glasses occupy many distinct sites [19] or a continuum of coordinations [20]. Therefore, the application of Fe-XANES to glasses represents a distinct challenge: the intensities and shapes of the pre-edge features may change as a function of the local bonding environments of the atoms as well as the relative proportions of Fe^{3+} and Fe^{2+} (e.g., [16]). This effect is shown well in Fig. 6., Cottrell *et al.* [10] collected XANES and Mössbauer spectra from glasses equilibrated at one-atmosphere at known temperatures and fO_2s using 4 starting compositions, two basalts and two rhyolites. The two trends evident on Fig. 6 suggest that, at some level, the Fe-XANES spectra, and therefore the calculated redox state of glasses, is sensitive to composition. Therefore, care must be used when selecting standards.

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