Concerning the use of standards for identifying coordination environments in glasses

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Abstract. It is an established methodology to use crystallographically well-defined standard materials for understanding site geometries in glasses. Here we discuss the benefits and the limitations of this approach for the investigation by Mössbauer and EXAFS of Fe\textsuperscript{2+} and Fe\textsuperscript{3+} in aluminosilicate glasses. As a case study we specifically consider [5]Fe\textsuperscript{2+} and [5]Fe\textsuperscript{3+} sites and whether these exist in our glasses; and if so, whether they have defined site geometries or occur simply as a consequence of the site distortions and Fe-O bond length distributions. Results are consistent with the existence of [5]Fe\textsuperscript{2+} and [5]Fe\textsuperscript{3+} but do not prove this because site distortion and a mixture of 4- and 6-coordinated sites can produce comparable results. This exemplifies the need for caution when interpreting glass data based on standards.

1. Introduction
Understanding the relationships between oxidation state and structural environment of Fe in glasses is important because they affect processing and performance, as discussed in our recent studies of vitrified sewage sludge ashes (SSA) [1, 2]. \textsuperscript{57}Fe Mössbauer spectroscopy and Fe K-edge X-ray absorption spectroscopy (XAS) have been widely used in similar studies and both rely, to an extent, on data for crystallographically well-defined materials in which the oxidation state and local environment of Fe is known. For Mössbauer data this involves comparing fitted centre shift (CS), quadrupole splitting (QS), linewidth (LW) and area ratio between samples and standards and thereby determining Fe environments and the Fe\textsuperscript{2+}/Fe\textsuperscript{3+} ratio. Further information may be obtained from XAS, with the pre-edge peak and XANES providing a measure of coordination and redox ratio whilst the EXAFS region provides Fe-O bond lengths and (average) Fe coordination. Some authors [3, 4] have suggested the existence of \textsuperscript{57}Fe in oxide glasses. As a case study on the benefits and limitations of using standards to identify coordination in glasses we present research into the possible existence of \textsuperscript{5}Fe\textsuperscript{2+} and/or \textsuperscript{5}Fe\textsuperscript{3+} in aluminosilicate silicate glasses using Mössbauer spectroscopy and Fe K-edge EXAFS.

2. Experimental procedures
Six mineral standards were analysed. Staurolite (Fe\textsuperscript{2+},Mg,Zn)\textsubscript{1.5-2}Al\textsubscript{9}O\textsubscript{6}(OH,O)\textsubscript{2}(SiO\textsubscript{4})\textsubscript{4}, grandidierite (Mg,Fe\textsuperscript{2+})Al\textsubscript{5}(BO\textsubscript{3})(SiO\textsubscript{4})O and siderite Fe\textsuperscript{2+}CO\textsubscript{3} represent Fe\textsuperscript{2+} in 4-, 5- and 6-fold
symmetries and Fe-Berlinite Fe$^{3+}$PO$_4$, yoderite Mg$_2$(Al,Fe$^{3+}$)$_5$Si$_2$O$_{18}$(OH)$_2$ and aegerine NaFe$^{3+}$(Si$_2$O$_6$) represent Fe$^{3+}$ in 4-, 5- and 6-fold symmetries. Several mixed-redox glasses modelling vitrified SSA were studied (see [1, 2] for compositional details); some (Table 1) were melted under conditions ensuring that > 95% of Fe was present in one oxidation state, i.e. redox-pure. Glasses were reduced by melting in a H$_2$/N$_2$ atmosphere for 48h or were oxidized by adding CeO$_2$ at a Ce:Fe ratio of 3:2.

Table 1. Nominal and (a) analysed compositions of redox-pure glasses in mol %

| Sample  | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | P$_2$O$_5$ | SO$_3$ | MgO | Na$_2$O | K$_2$O |
|---------|---------|-------------|-------------|-----|-----------|-------|-----|---------|-------|
| SSA+Ca$^+$ | 48.7    | 12.2        | 5.4         | 14.3| 8.1       | 0.0   | 5.9 | 1.8     | 1.8   |
| DoE 39  | 44.4    | 13.1        | 8.3         | 19.0| 1.4       | 5.0   | 5.8 | 1.1     | 1.9   |

$^{57}$Fe Mössbauer spectroscopy was performed at room temperature using a Wissel spectrometer in transmission with a $^{57}$Co/Rh source and calibrated relative to $^{57}$Fe. Extended Voigt-based fitting (xVBF) was performed using RECOIL software [5]. It has been proven useful to adjust the hyperfine parameters of glasses by Voigt profiles. A sigma value of 1 describes a large distribution width and 0 represents a pure Lorentzian line with no distribution of parameters. Two sites were fitted to represent Fe$^{3+}$ and one for Fe$^{2+}$ except in the redox pure glasses, in which one site for each oxidation state gave the best fit, consistent with previous results [1, 2]. Fe K-edge EXAFS was performed in air at room temperature in transmission at Station 16.5 SRS, KMC-2 BESSY II and BM29 ESRF. Energy calibrations used Fe foil. Spectra were fitted using FEFF software packages [6].

3. Results and Discussion

Fitted Mössbauer parameters are shown in Table 2 and spectra in Figure 1. Spectral quality varies due to relative abundances of Fe and distributions of lattice sites. Some minerals also contain multiple sites, especially Staurolite and Grandidierite. Dyar et al. [7] associated “zones” with Fe oxidation state and coordination in a plot of CS vs. QS. Our glass CS and QS (Figure 2a) correspond with these zones and are consistent with our standards and Dyar’s [7]. Two Fe$^{3+}$ sites occur in all mixed-redox glasses [1, 2] but in redox-pure glasses only one Fe$^{3+}$ site consistent with distorted $^{[4]}$Fe$^{3+}$ or distorted $^{[5]}$Fe$^{3+}$ occurs. CS and QS values for mixed-redox glasses suggest distorted $^{[4]}$Fe$^{3+}$ or $^{[5]}$Fe$^{3+}$ with distorted $^{[6]}$Fe$^{3+}$ (since site distortion increases QS) [7]. The Fe$^{2+}$ CS and QS exhibit two distinct groupings consistent with $^{[4]}$Fe$^{2+}$ and $^{[5]}$Fe$^{2+}$. Only one doublet was fitted to Fe$^{2+}$ components (two doublets produced unsatisfactory results) so it is equally possible that (CS, QS) values suggesting $^{[5]}$Fe$^{2+}$ are produced by a combination of $^{[4]}$Fe$^{2+}$ and $^{[6]}$Fe$^{2+}$; a point noted by others [4]. Linewidths indicated by σ are broader for the glasses than most standards owing to the range of site distortions typical of glasses.

We have studied (not shown here) the integrated pre-edge peak area as a function of centroid position for samples and standards [8] using Fe K-edge XANES. Average CN of ~5 (Fe$^{3+}$) and ~4.5 (Fe$^{2+}$) are obtained for the samples. As with the Mössbauer results, no distinction can be made between $^{[5]}$Fe sites and a distribution of distorted $^{[4]}$Fe and $^{[6]}$Fe sites [9]. EXAFS (Figure 3) provides average CN of ~4.5 (Fe$^{3+}$) and ~4.2 (Fe$^{2+}$) for the redox-pure glasses. Whilst there is broad agreement between the Mössbauer and EXAFS results, they do not fully agree. However, all results are consistent with the existence of $^{[5]}$Fe$^{2+}$ and $^{[5]}$Fe$^{3+}$. The main difficulty in definitively answering the $^{[5]}$Fe question is that CS and QS for $^{[5]}$Fe lie between those for $^{[4]}$Fe and $^{[6]}$Fe and both XANES and EXAFS provide only average CN and Fe-O distances. Therefore any data points found to lie between $^{[4]}$Fe and $^{[6]}$Fe can be attributed to $^{[5]}$Fe sites or, equally justifiably, to a mixture of distorted $^{[4]}$Fe and $^{[6]}$Fe sites.

The differences between CS, QS and fitted EXAFS data for the glasses and for the standards are consistent with a distribution of site geometries and distortions found in glasses but they also lead us to question the use of conventional site geometries to describe local environments in glasses. Based on the results of this study a limited “continuum of sites” may be a more suitable description. This allows for the existence of exotic site geometries as a consequence of the range of site distortions and Fe-O bond lengths occurring in glasses.
Table 2: Fitted hyperfine Mössbauer parameters for the mineral standards and the redox-pure glasses

| Material     | Fe Valence | Nominal CN | CS ±0.02 / mm s⁻¹ | σ (CS) / mm s⁻¹ | QS ±0.02 / mm s⁻¹ | σ (CS) / mm s⁻¹ |
|--------------|------------|------------|-------------------|----------------|------------------|----------------|
| Staurolite   | II         | 4          | 0.90              | 0.12           | 2.35             | 0.00           |
| Granddierite | II         | 5          | 1.10              | 0.07           | 1.77             | 0.20           |
| Siderite     | II         | 6          | 1.24              | 0.08           | 1.80             | 0.12           |
| Fe-Berlinite | III        | 4          | 0.29              | 0.13           | 0.62             | 0.01           |
| Yoderite     | III        | 5          | 0.30              | 0.22           | 1.07             | 0.42           |
| Aegerine     | III        | 6          | 0.40              | 0.01           | 0.34             | 0.16           |
| SSA + Ca (Red.) | II     | ~4         | 0.99              | 0.29           | 1.84             | 0.48           |
| DoE 39 (Red.) | II       | ~4         | 1.00              | 0.33           | 1.82             | 0.47           |
| SSA + Ca (Oxi.) | III   | ~4         | 0.27              | 0.18           | 1.33             | 0.42           |
| DoE 39 (Oxi.) | III      | ~4         | 0.29              | 0.23           | 1.29             | 0.35           |

Figure 1. Fitted Mössbauer spectra for mineral standards (left) and sample glasses (right).

Figure 2. Mössbauer CS vs. QS for standards, redox-pure glasses and mixed redox glasses from [1, 2].
Table 3. Glass samples with fitted parameters.

| Glass Sample | CN  | d(Fe-O) / Å | $\Delta\sigma^2$ |
|--------------|-----|-------------|------------------|
| SSA+Ca (Oxi.) | 4.2 | 1.89        | 0.0081           |
| SSA+Ca (Red.) | 4.5 | 1.98        | 0.0121           |
| DoE 39 (Oxi.) | 4.2 | 1.88        | 0.0086           |
| DoE 39 (Red.) | 4.5 | 1.98        | 0.0143           |

Figure 3. Fourier transforms of Fe K-edge EXAFS for oxidised and reduced glass samples.

Conclusions
Measurable differences have been observed between the fitted parameters of the glass spectra and those of the mineral standards for the Mössbauer and XAS techniques employed. This confirms that comparisons between glasses and crystalline standards by either technique should be made with caution. The apparent identification of “exotic” coordination geometries such as pentahedral may indeed be correct, but it may also be due to the presence of a combination of distorted tetrahedral and octahedral sites. Neither our study nor others have provided conclusive evidence either for or against the presence of distinct $^{56}$Fe sites in glasses and this serves to highlight the limitations of crystalline analogues for modelling vitreous coordination sites. Structural differences in terms of Fe-O bond lengths and site distortions make direct comparisons between glasses and crystalline materials difficult and crystalline standards are best used to ascertain qualitative trends in coordination states.

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