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Fe K-EDGE X-RAY ABSORPTION SPECTROSCOPY OF SILICATE MINERALS AND GLASSES

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Abstract Structural parameters determined for crystalline iron, fayalite and aegirine agree closely with X-ray crystallographic data. A glass of $\text{NaFeSi}_2\text{O}_6$ composition has Fe predominantly present as Fe^{3+} in tetrahedral coordination i.e. as a network former. CaFeSiO_4 and $\text{CaFeSi}_2\text{O}_6$ glasses have about $\frac{1}{3}$ of the total Fe in octahedral coordination i.e. as a network modifier.

Introduction An understanding of the structural role of iron in silicate melts is important not only in explaining rheological and diffusion properties and phase relations, but also because of the significance of redox ratios as oxygen fugacity indicators. As part of an ongoing study of the application of synchrotron techniques to geological problems we have, therefore, investigated silicate minerals and glasses by Fe K-edge X-ray absorption spectroscopy. Spectra were recorded in transmission at the SRS using a harmonic rejecting double crystal monochromator (Si 220).

Crystalline body-centred metallic iron, fayalite (Fe_2SiO_4) and aegirine ($\text{NaFeSi}_2\text{O}_6$) were used as model compounds for Fe as Fe^0 , Fe^{2+} and Fe^{3+} , respectively. Background subtracted, k^3 weighted spectra were analysed using the Daresbury Library Program EXCURVE which utilises spherical wave theory and least squares routines [1]. Glasses having the compositions of aegirine, hedenbergite ($\text{CaFeSi}_2\text{O}_6$) and kirschsteinite (CaFeSiO_4) were prepared by quenching melts produced under atmospheric conditions at 1300°C . Microprobe analyses showed these to be homogeneous and on-composition while chemical analyses gave $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of 0.9, 0.8 and 0.9 (± 0.03), respectively.

Results The absorbance spectra for the samples studied are figured in an earlier progress report [2]. The derivative of the absorbance is shown here (figure 1) allowing the energies of the absorption edge and associated features to be deduced to an accuracy of ± 0.5 eV. As expected, the model compounds show an increase in the edge energy with increasing oxidation state of Fe, from 7115 eV (iron Fe^0 , fig. 1a) through 7123 eV (fayalite, Fe^{2+} , b) to 7128 eV (aegirine, Fe^{3+} , c). Weak pre-edge features occur in both fayalite and aegirine due to $1s \rightarrow 3d$ transitions enhanced by hybridization of iron 3d with oxygen 2p orbitals [4]. This feature should increase in intensity in the order: regular octahedral-distorted octahedral-tetrahedral coordination. The pre-edge feature occurs at 7114 eV in fayalite and 7116 eV in aegirine confirming the 2 eV shift previously reported for Fe^{2+} and Fe^{3+} [3].

Figure 2 shows background subtracted EXAFS (as measured), Fourier filtered spectra, and the Fourier transform of the spectra. Dotted lines refer to the best curved wave fit to experiment: comparison is made with respect to Fourier filtered spectra for clarity. All the model compounds show excellent agreement between the EXAFS and crystallographic data ($\pm 0.02\text{\AA}$ for first shell distances). Mean Fe-O

distances of 2.22 Å and 2.03 Å for fayalite and aegirine are consistent with the presence of octahedrally coordinated Fe^{2+} and Fe^{3+} , respectively. The EXAFS data also reproduce the distorted nature of the oxygen ligands in both minerals. The asymmetry of the Fe sites is also responsible for the small pre-edge feature around 7115 eV.

The three glasses have spectra with less XANES structure above the edge compared with the crystalline silicates; this is consistent with decreased long-range order in the glasses. For each of the three glasses the absorption edge threshold occurs at 7127 eV consistent with the bulk of the Fe existing as Fe^{3+} . In addition, all the glasses have more-pronounced pre-edge features than those shown for the crystalline materials (fig. 1). This is particularly true for aegirine glass ($\text{NaFeSi}_2\text{O}_6$) which exhibits the strongest pre-edge feature pointing to tetrahedrally coordinated Fe sites. Analysis of the EXAFS spectra for the glasses (fig. 2e, f, g) generates first shell Fe-O distances of 1.86 Å for $\text{NaFeSi}_2\text{O}_6$ and 1.92 Å for $\text{CaFeSi}_2\text{O}_6$ and CaFeSiO_4 compositions composed to 2.03 Å for crystalline $\text{NaFeSi}_2\text{O}_6$. The shorter average Fe-O distance for $\text{NaFeSi}_2\text{O}_6$ glass compared to crystalline aegirine (together with the narrower, more intense Fourier transform peak for the glass, fig. 2c, d) confirms that Fe^{3+} is almost certainly tetrahedrally coordinated

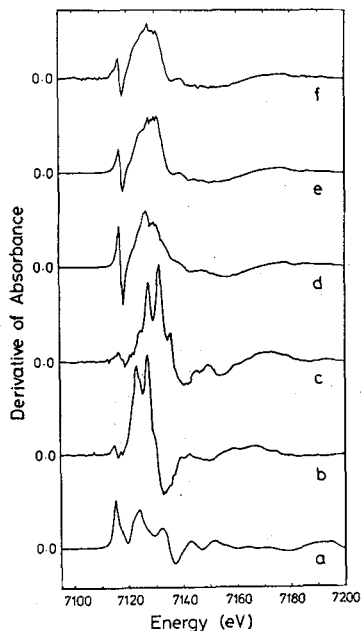


Figure 1. Derivative of absorbance for Fe EXAFS spectra. a = Fe metal; b = fayalite crystal; c = aegirine crystal; d = $\text{NaFeSi}_2\text{O}_6$ glass; e = CaFeSiO_4 glass; f = $\text{CaFeSi}_2\text{O}_6$ glass.

P. Henderson et al. [9] found a regular relationship between diffusion coefficients measured for a series of rock melts and conventionally-calculated NBO/T (i.e. Fe^{3+} as modifier). However data for a pantellerite melt (alkali-rich granite) fell off these trends. The pantellerite melt is relatively poor in Al and rich in Fe^{3+} ($\text{Fe}^{3+}/\Sigma\text{Fe}$ 0.82) and it seems likely that much of the Fe^{3+} would be acting as a tetrahedral network former. Recalculation of NBO/T on this basis brings the pantellerite melt into line with the others for Ba, Eu and Fe diffusion.

in the glass. In contrast, the slightly longer Fe-O distances in the Ca-bearing glasses suggest that up to $\frac{1}{3}$ of the of the Fe is present in octahedral coordination. These results confirm the observations of Mysen and his colleagues [e.g. 5,6] that, for samples prepared under oxidizing conditions, Ca-bearing glasses contain substantial amounts of Fe^{2+} while equivalent Na-bearing glasses contain >95% Fe^{3+} . Moreover in both systems the Fe^{3+} present occurs predominantly in tetrahedral coordination.

Discussion The presence of Fe^{3+} in tetrahedral coordination in glasses quenched from silicate melts prepared under oxidizing conditions indicates that it acts as a network-former in both Na- and Ca-bearing systems. In contrast, Fe^{2+} occurs in octahedral coordination i.e. as a network modifier. It has been suggested that tetrahedrally coordinated Fe^{3+} may not be randomly mixed with Si in framework units but instead may exist as discrete Fe-rich clusters [6,7]. If this is the case we might expect to resolve Fe-Fe interactions in the EXAFS spectra but we find no evidence of this phenomenon with glasses studied here.

Models for calculating viscosities and structural parameters such as the ratio non-bridging O/tetrahedral cations (NBO/T; [8]), depend on the correct assignment of Fe^{3+} to network-forming or -modifying roles.

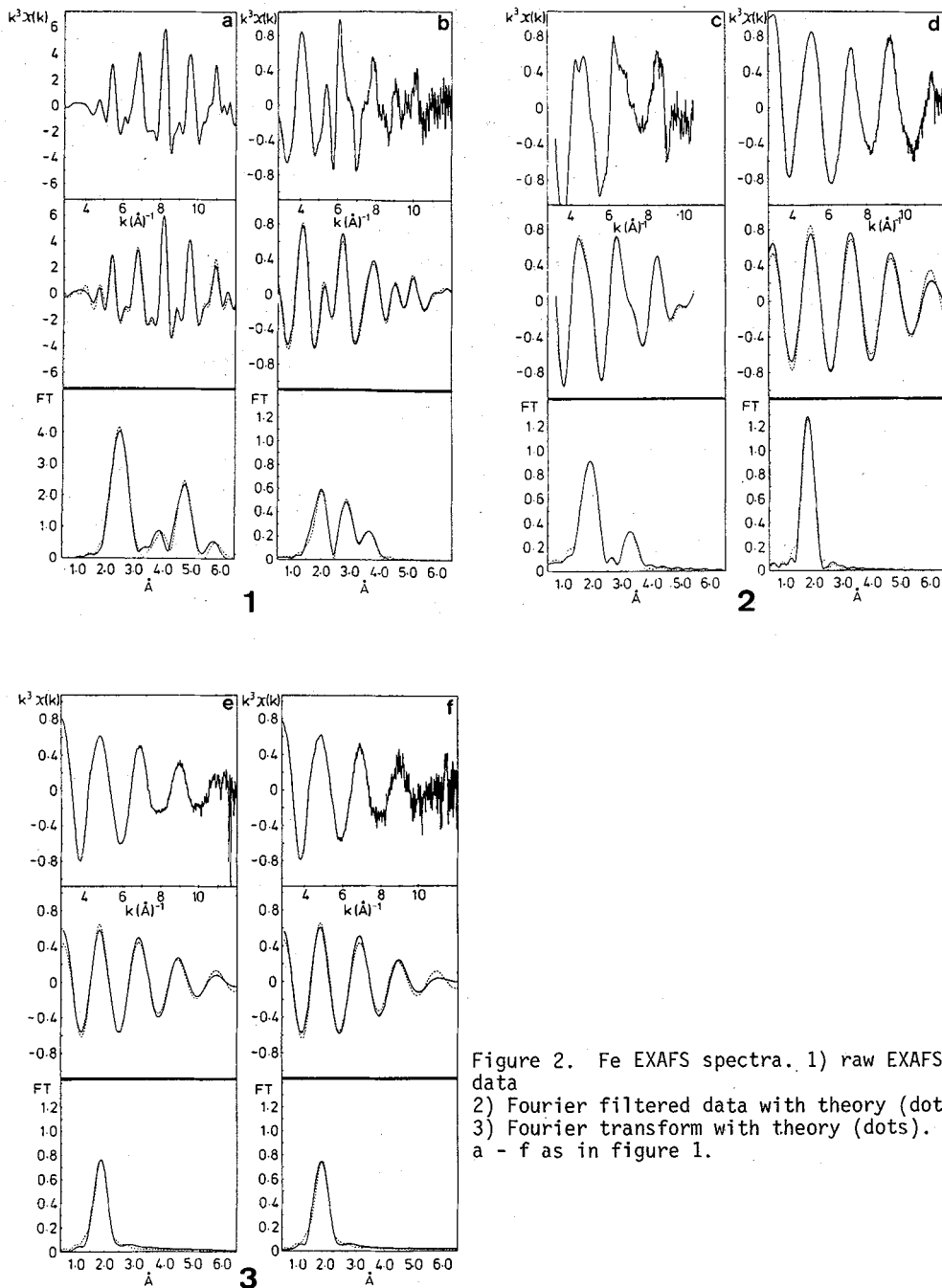


Figure 2. Fe EXAFS spectra. 1) raw EXAFS data
 2) Fourier filtered data with theory (dots)
 3) Fourier transform with theory (dots).
 a - f as in figure 1.

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