

Microprobe XAFS/Polarized XAFS

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XANES studies of Fe-bearing glasses

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The information about the local environment and valence ratio $\text{Fe}^{3+}/\Sigma\text{Fe}$ ($\Sigma\text{Fe}=\text{Fe}^{3+}+\text{Fe}^{2+}$) of Fe ions in silicate glasses has not yet been completely understood. Here we present the results of the experimental X-ray absorption near edge structure (XANES) at Fe K edge in conjunction with *ab initio* full multiple-scattering (MS) simulations in silicate glasses by using proposed Fe tetrahedral and pentahedral cluster models. Our main results are: (1) the coordination number (CN) of Fe ions is mainly fourfold-coordinated with probably a small part of fivefold structure; (2) the bond length of Fe-O are 1.90 Angstrom for ^{57}Fe (II)-rich glass and 2.01 Angstrom for ^{57}Fe (II)-rich glass, respectively, similar or slightly larger than that of tetrahedrally coordinated Fe states in crystalline materials.

Keywords: XANES; Fe-bearing glass; valence ratio; Full Multiple Scattering calculation.

One of the few element-selected methods which is sensitive to short- and medium-range environment and can provide information on chemical bonding and oxidation states is X-ray absorption spectroscopy. Synchrotron based micro-XANES is able to produce systematic and quantitative measurements of Fe valence ratio $\text{Fe}^{3+}/\Sigma\text{Fe}$ ($\Sigma\text{Fe}=\text{Fe}^{3+}+\text{Fe}^{2+}$) (Delaney et al., 1998). In this paper we present briefly the experimental and theoretical investigations for Fe-bearing silicate glasses at Fe K edge.

We choose the sample CH98-DR11, which is a submarine basaltic glass collected during the MAPCO II mission (Mid-Atlantic Ridge), because it contains high quantity of total iron oxides as well as its composition is quite closed to the glasses we interested (e.g. glass/melt inclusions). This glass is rich in Si, Al, Mg, Ca, Na and contains 10.25 wt.% of total iron oxides. The oxidation state is mainly 2+ in the natural glass (DR11a). The trivalent oxidation state has been obtained at high temperature (about 1300°C) in air. Hence, the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in the natural glass is about 0.107, and 0.821 in the oxidized sample (DR11b). The relative proportion of FeO and Fe_2O_3 has been analyzed by wet chemical analysis (CRPG, Nancy). The glasses were double-faced polished with Al_2O_3 to 0.3 μm grain size. They were checked by optical microscopy that they contain no mineral phase or bubble.

XANES experiments at the Fe K edge were performed at the synchrotron X-ray microprobe (beamline X26A at the National Synchrotron Light Source, Brookhaven National Laboratory, New York) by measuring the Fe $K\alpha$ fluorescence intensity, with a resolution of about 0.8 eV.

XANES spectra were simulated by full multiple-scattering approach which has been widely and successfully used to interpret the X-ray absorption spectra in different systems (Lee & Pendry, 1975; Natoli et al., 1980, 1986, 1990; Durham et al.,

(1982); Lee & Beni, 1977; Bianconi, 1988; Durham, 1988; Rehr et al. 1992; Wu et al. 1992, 1996a, 1996b, 1997). We have used the Mattheiss prescription (Mattheiss, 1964) to construct the cluster electronic density and the Coulomb part of the potential by superposition of neutral atomic charge densities obtained from the Clementi-Roetti tables (Clementi & Roetti, 1974). For the exchange-correlation part of the potential, we have used the optical energy- and position-dependent Hedin-Lundquist (H-L) potential. The calculated spectra are further convoluted with a lorentzian function with a full width $\Gamma=2.0$ eV to account for the core hole lifetime and experimental resolution.

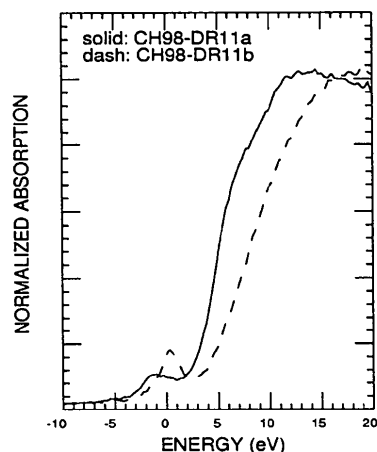


Figure 1
Experimental Fe K-edge XANES spectra in Fe^{2+} -rich (CH98-DR11a) and Fe^{3+} -rich (CH98-DR11b) glasses.

The Fe K-edge XANES spectra in Fe^{3+} -rich and Fe^{2+} -rich glasses are shown in Fig. 1. The features observed in the spectra such as pre-edge and main edge shape are similar to those in ^{57}Fe contained compounds. In several aluminosilicate glasses, XAS data have also shown that Fe occurs in four and five coordination. It is clearly seen that the pre-edge peak and main edge slope shift to higher energy as the oxidation number increases.

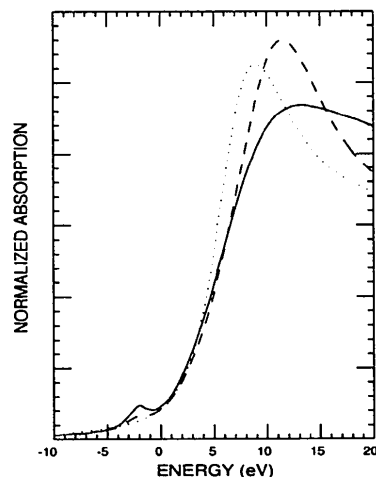


Figure 2
Simplified MS calculations at Fe K edge using different cluster models: tetrahedron with bond distance 2.0 Angstrom (solid line), pentahedron with bond distance 2.05 Angstrom (dash line), and octahedron with bond distance 2.14 Angstrom (dot line).

It is a very known fact that 3d final states are more tightly bound and MS effects is less important in glassy systems. The spectral features are mostly characteristic of the cluster composed of the first coordinated shell, especially for the lower-lying pre-edge structures. In Fig. 2 we present several simplified cluster model calculations, tetrahedron, pentahedron and octahedron with typical values of 2.0, 2.05 and 2.14 Angstrom, respectively. The structures of pre-edge region and the shape of main absorption slope in the later two cases do not match well the experimental data and seem not to favor these atomic environments.

The gross features in Fe K-edge XANES spectra are roughly reproduced by using of a tetrahedral MO_4 (M =transition metal) (Bianconi et al. 1985; Garcia et al. 1986). The pre-edge peak in these systems with acentric tetrahedral symmetry is clearly pronounced. It is the result of a transition from $1s$ to d part of final states T_2 (irreducible representation of T_d point group) which includes not only the p but also the d_{xy} , d_{xz} , d_{yz} bases of orbital. It is a dipolar transition partially allowed due to the mixing of them. In Fig. 3 we show the MS calculations as a function of bonding distance (1.96, 2.00, and 2.04 Angstrom, respectively) in tetrahedral coordination. We have found theoretically that the pre-peak position is not shifted significantly, but its intensity and the shape of main edge are varying, as observed in the previous experimental works (Waychunas et al. 1983).

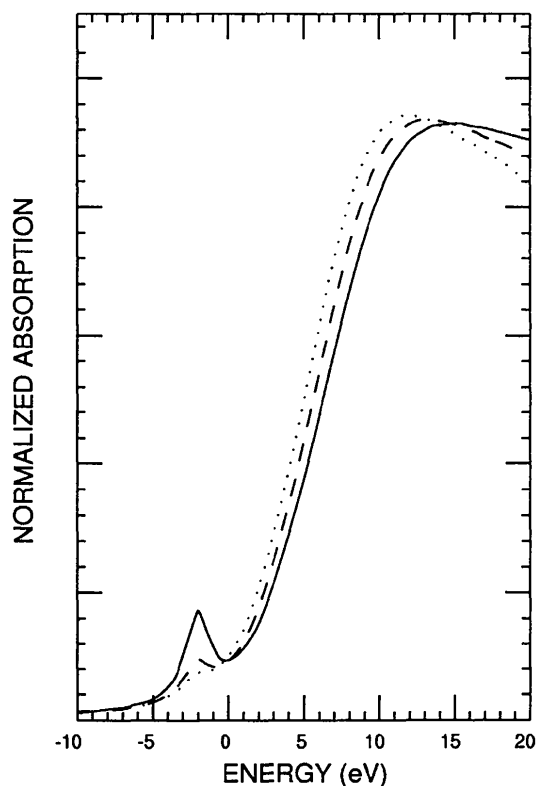


Figure 3
MS calculations at Fe K edge in tetrahedral coordination state as a function of bond distances.

In order to simulate the experimental spectra, we make a simply linear combinations, (i.e. superposition) in terms of valence ration by using some MS calculations based on proposed model cluster with possible variation of Fe-O bond lengths. Fe^{3+} -rich glass was found to be mainly tetrahedrally coordinated by oxygen, but with less than 5% pentahedral contribution, with mean Fe^{3+} -O distance of 1.90 Angstrom. The good agreement, as shown in Fig. 4(a),

between the theoretical MS calculation and experimental data indicates that the medium-range order in this glass is not significant as reported by Calas et al (Calas et al. 1984). The simulation of Fe^{2+} -rich experimental spectrum is more complicated. The cluster of FeO_4 seems not to be enough to match well the experimental spectrum. A medium-range ordered cluster composed of central Fe tetrahedron linked through its corners to other AlO_4/SiO_4 tetrahedral network (21-atom cluster model) should be taken into account. The best simulation, presented in Fig. 4(b), consists also almost ^{49}Fe coordination state with mean Fe^{2+} -O distance of 2.01 Angstrom, connected through its four corner oxygens to SiO_3 (tetrahedral) units with bond length Si-O=1.61 Angstrom and Fe-O-Si angle 150° . A complete discussion will be published in a forthcoming paper.

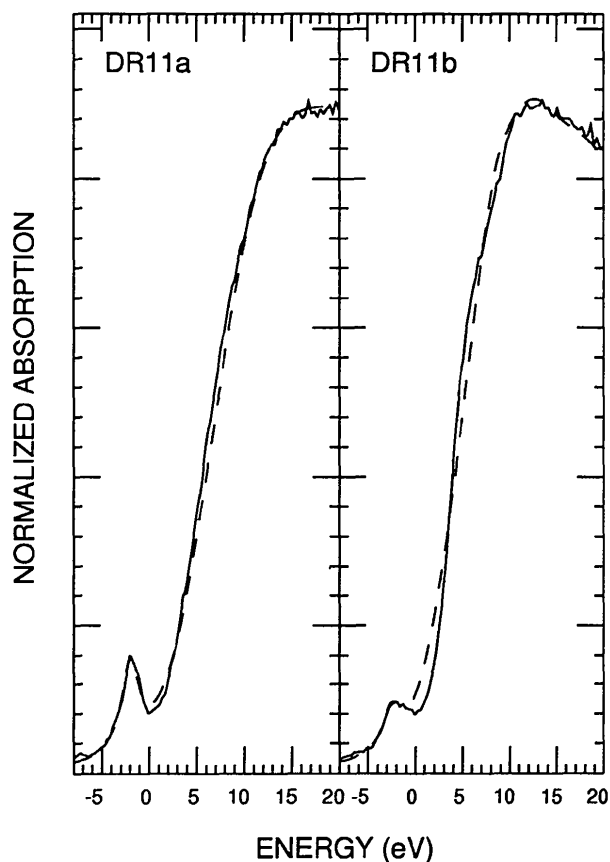


Figure 4
Linear combinations of some MS calculations at Fe K edge along with experimental data of DR11a and DR11b glasses.

Our result and finding in the structural studies is in agreement with many other studies on Fe-bearing glasses/melts (Waychunas et al., 1988; Jackson et al., 1993; Brown et al., 1995). There is no indication of significant amounts of ^{61}Fe in our silicate glasses. In conclusion, we have presented the experimental XANES and MS theoretical simulations to determine Fe short- and medium-range structures. Iron seems to occur as a network-former in both glasses and has a well defined first coordination state. In terms of the proportion of different valence contribution in the MS simulation, we find that the $Fe^{3+}/\Sigma Fe$ ratio is comparable to other bulk analyses in these glasses. Our present work has possible application in the study of other amorphous systems.

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