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Oxidation state and coordination structure of Fe in silicate glasses and melts

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In both magmatic and industrial systems, Fe is the most abundant transition element. Due to its heterovalent nature and the different crystal- chemical behavior of the reduced and oxidized species, Fe affects a wide number of physical and chemical properties of magmas or final glass products, such as density, viscosity, stability of phases, and nucleation during crystallization. Particularly, the viscosity of Fe-bearing silicate melts decreases with decreasing Fe^{3+} content of the melt, which provides clear but indirect evidence for differences in the structural role of Fe^{3+} and Fe^{2+} . Many studies have addressed the structural role of Fe in melts using glasses as structural analog (Calas and Petiau, 1983). In most cases, Fe^{3+} in silicate melts was assigned to tetrahedral site geometry, although evidence for higher coordination was also found. On the other hand Fe^{2+} was found distributed over sixfold-, fivefold- and fourfold-coordinated sites in melts, with the last two dominating (Rossano et al., 2000).

In the work presented here, in-situ X-ray absorption spectroscopy at the Fe K-edge was used to characterize the local structural environment of Fe^{3+} and Fe^{2+} in alumino-boro-silicate melts at high temperature (up to 2000K) in comparison to their quenched glassy analog at room temperature. Changes in the structural environment of Fe were evaluated by analyzing the pre-edge feature of the EXAFS spectra. The most useful characteristics of the Fe-K pre-edge for determining Fe oxidation state and coordination number are the position of its centroid and its integrated intensity. To plot these pre-edge parameters in the variogram after Wilke et al. (2001) allow determining the oxidation state and the coordination of iron. In an effort to complete this variogram, a series of Fe-bearing minerals, with Fe^{3+} and Fe^{2+} coordination ranging from 4 to 6 O atoms, has also been analysed by X-ray diffraction and Fe K-edge EXAFS techniques. The coordination structure of Fe and Fe-O distances in minerals were thus determined. The characteristics of the pre-edge features of the EXAFS spectra are now related with oxidation state, local coordination environment of Fe atoms but also with Fe-O distances.

In this study, new information about incorporation of Fe^{3+} and Fe^{2+} into a variety of alumino-boro-silicate glasses and melts will be presented. These results on the coordination structure of iron in silicate glasses and melts will be also discussed in regards to the kinetics of iron redox reactions in silicate melts (Magnien et al., 2008; Cochain et al., 2010).

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