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Geometry of tetrahedrally coordinated Fe in silicate glasses

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The geometry of tetrahedrally coordinated Fe in silicate glasses of different compositions (rhyolitic, phonolitic, basaltic, sodium disilicate) has been studied by Fe K-edge EXAFS and XANES spectroscopy. EXAFS determined <Fe^{3+}-O> distances display values similar to 1.85 $\pm$ 0.01 Å, in agreement with $^{[4]}Fe^{3+}$-O distances in tetraferriphlogopite and synthetic kimzeyite (Giuli et al., 2001; 2012). On the other hand, EXAFS derived <Fe-Si> distances show a wider variation due to a wider distribution of <Fe-O-Si> angles. Theoretical XANES spectra have been calculated ab initio by means of the MXAN package starting from an initial structural model consisting of tetrahedrally coordinated Fe sharing oxygens with 4 SiO_4 tetrahedra. Fit of the experimental XANES spectra have been performed providing Fe-O distances in excellent agreement with those derived by EXAFS. Taking into consideration of the SiO_4 units linked to the FeO_4 tetrahedron in the structural model is essential to successfully reproduce all the features of the XANES spectra. This proves to be a useful probe to effectively determine when low coordinated Fe is linked to a tetrahedral network and can be effectively considered as a network former. Comparison of the experimental XANES spectra with a suite of theoretical spectra calculated to simulate different degrees of distortion of the tetrahedron allows to affirm that the $Fe^{3+}O_4$ unit is a regular tetrahedron in the glasses studied.

Accurate data on the geometry of the Fe coordination polyhedra in silicate glasses are important for a better understanding of the thermodynamic of the Fe oxidation reaction in silicate melts. Moreover, these data add to the paucity of structural data on tetrahedrally coordinated Fe^{3+} in minerals.