

## **XAS determination of the Fe local environment and oxidation state in phonolite glasses**

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### **ABSTRACT**

The Fe oxidation state, coordination geometry, and  $\langle\text{Fe-O}\rangle$  distances have been determined by Fe *K*-edge XANES and EXAFS for a set of silicate glasses of phonolite composition produced at different oxygen fugacity conditions with the aim of determining the effect of iron oxidation state and local structural environment on the viscosity of the corresponding melts. Comparison of the pre-edge peak data with those of Fe model compounds with known oxidation state and coordination number allowed for determination of the Fe oxidation state and coordination number for all the glasses analyzed. The  $\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Fe}^{2+})$  ratio varies from 0.44 to 0.93 ( $\pm 0.05$ ) in the glasses studied. The determined values are in excellent agreement (within 0.03 difference) with those independently measured by the titration method. Moreover, pre-edge peak data clearly indicate that  $\text{Fe}^{3+}$  is in fourfold coordination, whereas  $\text{Fe}^{2+}$  exists both in fourfold and fivefold coordination for this phonolitic composition, although the presence of minor amounts of sixfold-coordinated Fe cannot be ruled out by XANES data alone. EXAFS data of the most oxidized sample indicate that  $\text{Fe}^{3+}$  is in tetrahedral coordination with  $\langle\text{Fe-O}\rangle = 1.85 \text{ \AA}$  ( $\pm 0.01$ ). This value compares well with literature data for  $^{54}\text{Fe}^{3+}$  (e.g., in tetra-ferriphlogopite or rodolicoite). Calculated NBO/T ratios decrease with Fe oxidation (from 0.23 to 0.19).

For phonolitic glasses of this study, going from reducing to oxidizing conditions results in a higher fraction of network-forming Fe, thus increasing the polymerization of the tetrahedral network and producing shorter (and stronger)  $\langle\text{Fe-O}\rangle$  bond distances. Both the polymerization increase and the structural variations in the Fe local environment can qualitatively explain the strong increase in melt viscosity observed at higher oxygen fugacity.

**Keywords:** Iron local environment, silicate glasses, EXAFS, XANES