

AMORPHOUS MATERIALS: PROPERTIES, STRUCTURE, AND DURABILITY†

Effect of alkalis on the Fe oxidation state and local environment in peralkaline rhyolitic glasses

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ABSTRACT

Iron oxidation state and coordination geometry have been determined by Fe *K*-edge X-ray absorption near edge spectroscopy (XANES) for three sets of silicate glasses of peralkaline rhyolitic composition with different peralkalinity values. These compositions were chosen to investigate the effect of alkali content (and oxygen fugacity) on the Fe oxidation state. The samples were produced by means of hydrothermal vessels at 800 °C with oxygen fugacity conditions ranging from NNO-1.61 to NNO+2.96 log units.

Comparison of the pre-edge peak data with those of Fe model compounds of known oxidation state and coordination number allowed determination of the Fe oxidation state and coordination number in all glasses analyzed. Within each group of samples, Fe tends to oxidize with increasing oxygen fugacity as expected. However, alkali content is shown to have a strong effect on the Fe³⁺/(Fe³⁺+Fe²⁺) ratio at constant oxygen fugacity: this ratio varies from 0.25 to 0.55 (±0.05) for the least peralkaline series, and from 0.45 to 0.80 (±0.05) for the most peralkaline series. Moreover, pre-edge peak data clearly indicate that Fe³⁺ is in fourfold coordination in the most peralkaline glasses. Extrapolation of pre-edge peak data suggests the presence of both fourfold and fivefold coordination for trivalent Fe in the other two series. Divalent Fe is suggested to be mainly in fivefold coordination in all the three glass series. The presence of minor amounts of sixfold- and fourfold-coordinated Fe cannot be ruled out by XANES data alone. XANES data suggest that the amount of alkalis also affects the Fe³⁺ coordination environment resulting in a decrease in the average coordination numbers.

Extended X-ray absorption fine structure (EXAFS) data of the most oxidized and peralkaline sample indicate that Fe³⁺ is in tetrahedral coordination with <Fe-O> = 1.85 Å (±0.02). This value compares well with literature data for ⁵⁷Fe³⁺ in crystalline phases (e.g., in tetra-ferriphlogopite or rodolicoite) or in silicate glasses (e.g., phonolite glasses) supporting the XANES-determined coordination number obtained for the most peralkaline glasses.

Calculated NBO/T ratios decrease slightly with Fe oxidation because of the higher fraction of network forming Fe, thus increasing the polymerization of the tetrahedral network.

Keywords: Iron local environment, rhyolitic glasses, EXAFS, XANES, alkalis