

Ionizing irradiation effects on the redox state of alkali silicate glasses.

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In silicate melt different iron species can be present, which implies variations in $\langle\text{Fe-O}\rangle$ distances and affects melt polymerization and, among other things, Fe oxidation state. Moreover, alkalis also modify the Fe structural role in melts [1]. Accurately measuring the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in rock-forming minerals, specifically resolving intracrystalline variations in these ratios, is important in estimating geologically important variables (T, P, $f\text{O}_2$ and $f\text{H}_2$). For glasses, *in situ* measurements of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios are essential to elucidate, for instance, the oxidation mechanisms related to diffusion of chemical species [2]-[3]. The electron microprobe (EMP), a standard analytical tool for the chemical characterization of minerals, allows *in situ* analyses of minerals in thin section with a spatial resolution on the order of a few micrometers. Nevertheless, conventional EPMA is not typically suited for determining the oxidation state of iron through measurements of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios. We have thus proposed a method for determining $\text{Fe}^{3+}/\Sigma\text{Fe}$ in minerals and glasses using this instrument, commonly denoted as 'the peak shift method' [4].

In this study we investigate changes in the oxidation state of iron that occur as the result of the Alk^+ electromigration in glasses upon electron irradiation with the EMP. We propose mechanisms for explaining the charge trapping processes under ionizing radiation as a function of iron content in the glasses. The Fe^{3+} reduction to Fe^{2+} classically occurs by electron transfer ($\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$). This occurs by 3d-orbital electron transfers from Fe^{2+} ions to Fe^{3+} ion for Fe^{3+} -rich glasses. The inward diffusion (to the bulk) of Alk^+ s is correlated with the outward diffusion (to the surface) of electrons transferred from a Fe^{2+} site to a neighbouring Fe^{3+} site. This reduction process is somewhat different when iron is found at low amounts in glasses. In the latter case, Fe^{3+} is an efficient electron trap and its reduction to Fe^{2+} occurs by direct capture of a free electron. The Fe^{2+} oxidation is induced by the formation and the outward diffusion of O^{2-} interstitial ions produced at the sites of paired non bridging oxygens after the departure of the charge compensating Alk^+ s. The accumulation of free oxygens beneath the surface makes Fe^{3+} -rich oxide phases to precipitate as separate nanometer sized particles. Outgassing of atomic oxygens as bubbles is also observed.

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