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 \(<Fe-O>\) 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 \(Fe^{3+}/\Sigma Fe\) ratios in rock-forming minerals, specifically resolving intracrystalline variations in these ratios, is important in estimating geologically important variables (T, P, fO₂ and fH₂). For glasses, \textit{in situ} measurements of the \(Fe^{3+}/\Sigma Fe\) 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 \textit{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 \(Fe^{3+}/\Sigma Fe\) ratios. We have thus proposed a method for determining \(Fe^{3+}/\Sigma Fe\) 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 (\(Fe^{3+} + e^- \rightarrow Fe^{2+}\)). 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⁺ 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.