

Analysis of Redox Changes in Silicate Glasses Using EPMA and Raman Spectroscopy

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In earth sciences, oxygen fugacity (f_{O_2}) is an important parameter to quantify in natural and experimental processes. The iron oxidation state of silicate melts can be used to calculate f_{O_2} , consequently silicate glasses quenched from these melts are commonly analysed for their Fe^{2+}/Fe_T [1]. The areas of glass are often small (10s – 100s μm in diameter), therefore a variety of micro-analytical techniques have been developed for these analyses, such as the Fe L lines using EPMA and the Fe K-edge using $\mu XANES$ [2,3]. Unfortunately, it has been found that glasses analysed using these techniques can change oxidation state during analysis, leading to spurious results [4,5]. Here, we investigate redox changes caused by electron beam irradiation using EPMA and Raman Spectroscopy.

In EPMA the Fe L lines involve transitions from outer shell 3d orbitals, therefore their peak position and intensity are dependent upon Fe concentration, coordination and oxidation state, which means they can be used to quantify Fe oxidation state [2]. These peaks have low intensity and therefore require high beam currents and/or count times to analyse them. This is problematic when analysing glasses which are typically unstable under these conditions and previous studies have observed both oxidation and reduction of Fe during electron beam irradiation [4]. As glasses are insulators they trap electrons during electron beam irradiation, which build up an area of negative charge [6]. Alkalis migrate towards this region of negative charge, leaving behind O which combines with FeO to produce Fe_2O_3 , thus oxidising [7,8]. Conversely, electrons can move between O and Fe^{3+} causing reduction [9].

The compositional controls on these changes have not been investigated, therefore we analysed silicate glasses covering a wide range of compositions using a time-dependent intensity modified Flank Method. This measures the ratio of the intensity of the high wavelength flank of the $L\beta$ peak to the low wavelength flank of the $L\alpha$ peak ($Fe\ L\beta_f/L\alpha_f$), which is sensitive to changes in Fe^{2+}/Fe_T , over time. Additionally, changes in Fe and K concentrations were measured. Samples were analysed at a range of analytical conditions (accelerating voltage of 15 – 30 kV, beam currents of 50 – 500 nA and a defocussed beam of 4 – 20 μm diameter). The rate of change of $Fe\ L\beta_f/L\alpha_f$ at time zero (I'_0) was calculated, which indicates the direction and rate of redox change. Raman spectra were collected on fresh and electron beam irradiated glass to identify changes in structure and H_2O caused by analysis.

Glass composition controlled the direction of redox change and, with analytical conditions, the rate of redox change. We define the compositional parameter Total Mobile Cations (TMC), molar sum of H_2O , Na_2O and K_2O ($g \cdot mol^{-1}$), which gives an indication of the number of oxygens made available during migration caused by sub-surface charging. At $TMC > 0.1\ g \cdot mol^{-1}$ glasses oxidise (mostly hydrous glasses), whereas for $TMC < 0.1\ g \cdot mol^{-1}$ glasses reduce (anhydrous glasses) (Figure 1a,b). The rate of reduction is controlled by initial Fe oxidation state, whereas the rate of oxidation is controlled by H_2O , silica content and total Fe concentration. For a specific glass composition, increasing the H_2O content increases the rate of oxidation. High-silica glasses oxidise much faster than low-silica glasses because the rate of H_2O and alkali migration during electron beam irradiation is much faster in high-silica glasses. Glasses with low total iron cannot oxidise because FeO groups must be close together for oxidation to occur [10]. The presence of Fe-bearing nanolites prevented oxidation.

Raman spectra showed that during oxidation, Fe-bearing nanolites precipitated (Figure 1c). Also, the H_2O peak decreased in size showing H_2O , as well as Na and K, migrated during electron beam irradiation, which cannot be measured using EPMA. The Raman spectra were also used to identify

when oxidation had occurred when it had been too fast to observe using EPMA. Combining Raman spectroscopy and EPMA allowed the changes in composition (including H₂O), oxidation state and glass structure during electron beam irradiation to be investigated, showing that both hydrous and anhydrous glasses suffer from beam damage [11].

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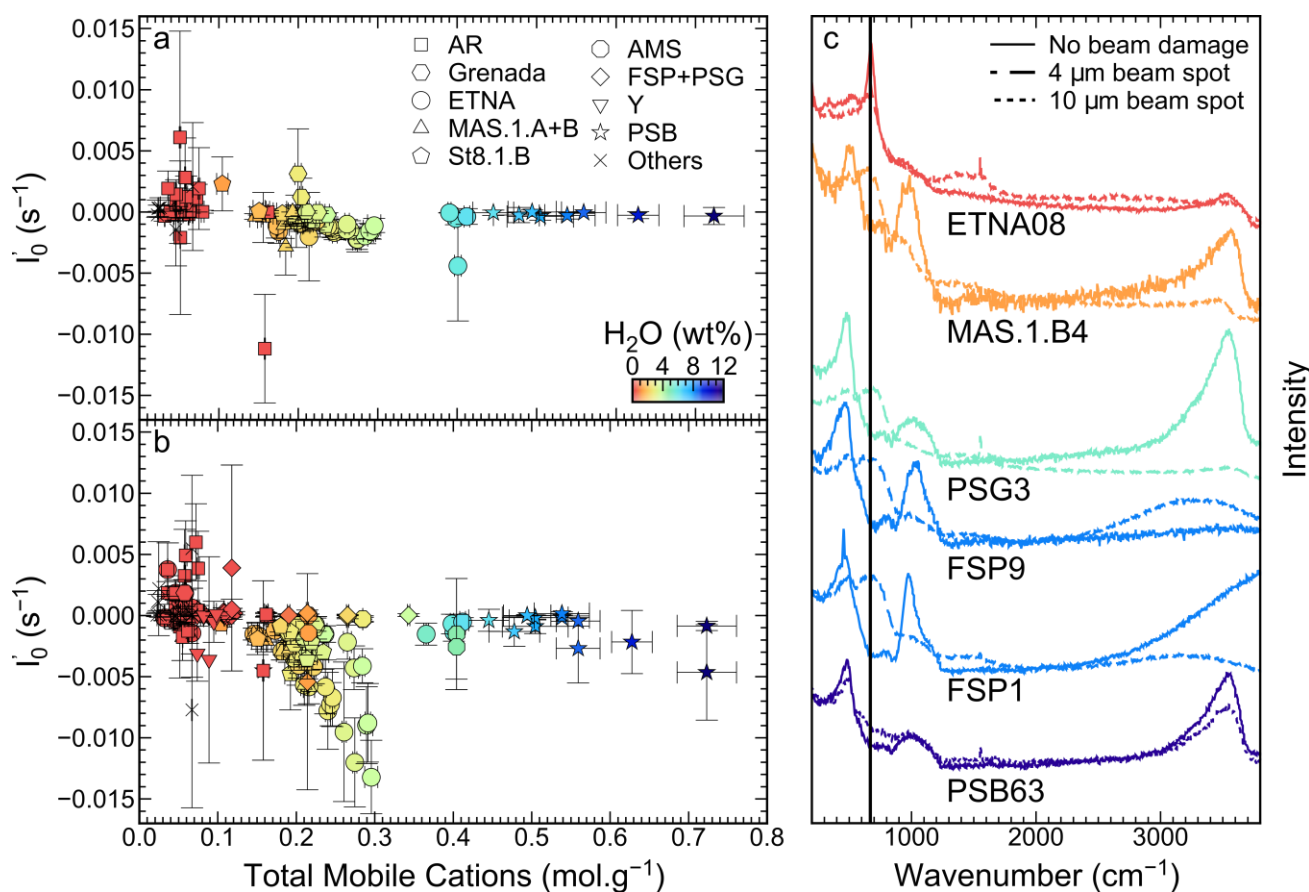


Figure 1. Rate of change of $L\beta_F/L\alpha_F$ at time zero (I'_0) against TMC collected using a defocused beam of 10 (a) and 4 (b) μm diameter. Symbol shape indicates glass composition and colour indicates H₂O content. Raman spectra (c) for fresh and damaged glasses. The intensity is arbitrary and samples are offset for clarity. The black horizontal line is the wavelength of Fe-bearing nanolites.