

In situ study of redox reactions between Fe and Cu in silicate melts

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The oxidation state of an element in a glass may not be the same as the oxidation state in the melt from which it quenched. Electron exchange reactions that are dependent on temperature can occur between two redox variable elements, such as Fe and Cu, resulting in changes in the oxidation states of both elements. Given the abundances of Fe and Cu in natural melts, where Fe is a major element and Cu a trace element, a large change in the oxidation state of Cu is expected to be accompanied by only a small change in the oxidation state of Fe. Cu is an economically important element and variations in its oxidation state could provide insights into the formation of ore deposits. However, before we can assume that the oxidation state of Cu in a glass is representative of that in a melt we need to investigate the possibility of an electron exchange reaction with Fe.

The oxidation states of Fe and Cu were determined in (i) a CaO-MgO-Al₂O₃-SiO₂ composition doped with varying amounts of Fe and Cu (5 to 0.2 wt. %) and varying Fe/Cu ratios (2 to 0.2), (ii) a synthetic mid-ocean ridge basalt (MORB) doped with 2000 ppm Cu, and (iii) a 'Cu-MORB', a novel composition, with Cu as a major element (10 wt. %) and Fe as a trace element (2000 ppm). The melts were equilibrated at temperatures from 1200 to 1500 °C and oxygen fugacities (fO_2) from QFM-2.4 to QFM+8.4 (where QFM is the fO_2 in log units relative to the quartz-fayalite-magnetite buffer). The melts were analysed in situ using a 1 atm gas mixing furnace that was designed and manufactured at the Australian National University for use at synchrotron beamlines. The oxidation states of Fe and Cu were also determined for a series of glasses that were quenched at different rates to investigate the kinetics of the reaction. *K*-edge X-ray absorption near edge structure (XANES) spectra were recorded in fluorescence mode at the XAS beamline of the Australian Synchrotron. The electron exchange reaction $Cu^{2+} + Fe^{2+} = Cu^+ + Fe^{3+}$ was found to occur upon quenching. The dependence of the reaction on the proportion of reactive species was determined. The results show that the oxidation state of Cu in natural glasses will be more reduced than in the melts from which they formed.