

The oxidation state of copper in silicate melts

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Copper is a chalcophile, siderophile and moderately volatile element. Furthermore, Cu is a redox variable element and can occur as either Cu⁺ or Cu²⁺ during geological processes. The oxidation state of an element exerts a first order control on its behaviour, in particular its partitioning between coexisting melts (silicate/sulphide), minerals, and fluids. Hence, to understand the geochemical behaviour of Cu we need to know how its oxidation state varies with properties such as oxygen fugacity (fO_2), melt composition, temperature, and pressure. Previous experimental studies have been hampered by the siderophile and volatile nature of Cu, however, a novel experimental set-up has enabled us to prepare silicate glasses in which the oxidation state of Cu varies systematically.

Glasses of six Fe-free and one Fe-bearing silicate compositions were prepared by quenching melts equilibrated over a range of $\log fO_2$ s (-8 to 0) at 1300 °C (QFM -0.7 to +7.3) using a 1-atm gas mixing furnace. Glasses were also synthesised at 0.5 and 1 GPa using a piston cylinder apparatus and metal/metal-oxide buffers to control the fO_2 . The oxidation state of Cu was determined using *K*-edge X-ray absorption near edge structure (XANES) spectra recorded in fluorescence mode at the XAS beamline of the Australian Synchrotron.

The redox ratio, $Cu^{2+}/(Cu^+ + Cu^{2+})$, was found to vary from 0.05 to 0.95, with the theoretically expected dependence on fO_2 , over the range QFM-4.5 to QFM+5.7, showing that Cu⁺ predominates in all natural basaltic melts with only small proportions of Cu²⁺ present. Melt composition was observed to have a minimal effect on $Cu^{2+}/(Cu^+ + Cu^{2+})$ while higher pressures were found to favour Cu²⁺ relative to Cu⁺. Comparison with the results on the Fe-bearing composition suggests that the electron exchange reaction $Fe^{2+} + Cu^{2+} = Fe^{3+} + Cu^+$ occurred upon quenching.

The results of this study, together with similar results obtained recently for Sb, provide insight into the relationship between oxidation state and coordination environment for not only these elements but Pb, Tl, As and Bi with implications for their partitioning.