

The Effects of Temperature and Composition on Fe and S Redox Equilibrium in Silicate Melts

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Previous experimental studies suggest Fe and S redox states follow the equilibrium, $8\text{Fe}^{3+} + \text{S}^{2-} = 8\text{Fe}^{2+} + \text{S}^{6+}$, which is shifted to the left at lower temperatures [1, 2]. Application of these results to natural glasses, for which $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{S}^{6+}/\text{S}^{2-}$ have been measured [3], yields equilibrium temperatures well below the temperature at which the glasses would have been liquids, suggesting that electron exchange between Fe^{2+} and S^{6+} may occur due to the lower quench rates of natural glasses. Despite the potential importance of sulfur in the redox evolution of magmatic systems there exists a dearth of information on the interaction of Fe and S redox pairs in silicate melts.

We have synthesized a series of silicate glasses under controlled $f\text{O}_2$ and $f\text{S}_2$ conditions at 1 bar over temperatures ranging from 1300 to 1500°C to evaluate the Fe – S redox equilibria in natural magmas. Both the $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{S}^{6+}/\text{S}^{2-}$ ratios of our run products were determined using synchrotron-based X-ray Absorption Near-Edge Structure (XANES) spectroscopy. Our results show the effect of temperature on the Fe – S redox equilibrium is in general agreement with estimates based on tabulated thermodynamic data.

These results support hypothesis that measured $\text{Fe}^{3+}/\text{Fe}^{2+}$ of natural glasses may be modified through electron exchange with sulfur and suggest that accurate measurement of magmatic redox state requires measurement of S in addition to Fe. Furthermore, cooling of magmas and the destabilization of S^{6+} in silicate melt is an efficient mechanism to drive sulfide saturation.

- [1] Nash et al. (2019) *Earth Planet. Sci. Lett.* 507, 187-198.
[2] Jugo et al. (2010) *Geochim. Cosmochim. Acta* 74, 5926-5938. [3] Brounce et al. (2017) *Proc. Natl. Acad. Sci.* 114, 8997-9002.