

No detectable redox exchange between sulfur and iron during cooling of basalts

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The valence states of iron and sulfur in mantle-derived melts influence and respond to the evolution of melts as they crystallize and degas. Characterizing the valence state of iron and sulfur in silicate melts that have quenched to form glasses is therefore critical to understanding fluid and volatile behavior in magmatic systems. Glasses quenched from silicate melts offer the opportunity to precisely measure sulfur and iron valence states, but whether the transition from melt to glass affects the valence state of sulfur and iron is uncertain. Here, we use the glassy margins of two pillow basalts, one from a mid-ocean ridge and one from a back-arc basin to test the effect of quench rate on sulfur and iron valence state. We report micro-X-ray Absorption Near Edge Structure (XANES) measurements of $S^{6+}/\Sigma S$ ($S^{6+}/[S^{6+}+S^{2-}]$) and $Fe^{3+}/\Sigma Fe$ ($Fe^{3+}/[Fe^{2+}+Fe^{3+}]$) along transects from the rapidly quenched rim of the pillows down into the slowly-quenched crystal-rich interiors. The range of average quench rates estimated for our selected analysis areas span those experienced by natural and experimental glasses. This means that we can use each transect as a natural experiment to vary quench rate in a volatile-bearing basalt of constant composition. The average and standard deviation of measured values in the mid-ocean ridge sample is $S^{6+}/\Sigma S = 0.09 \pm 0.01$ and $Fe^{3+}/\Sigma Fe = 0.147 \pm 0.002$. In the back-arc sample, these values are $S^{6+}/\Sigma S = 0.21 \pm 0.01$ and $Fe^{3+}/\Sigma Fe = 0.153 \pm 0.004$ [1]. We find that the $S^{6+}/\Sigma S$ and $Fe^{3+}/\Sigma Fe$ values along transects in each sample are within error of each other and show no systematic changes with depth. This observation is consistent with either sluggish reaction kinetics between sulfur and iron, or an insignificant temperature effect on sulfur-iron redox exchange equilibria. These observations demonstrate that sulfur and iron valence state in glasses with varying quench rate can be directly compared, and that changes in sulfur and iron valence experiencing quench rates typical of basaltic volcanism and laboratory experiments are below the limits of detection with XANES.

[1] Zhang et al. (2018) *Chemical Geology* 279, 166-175.