Sulfur content controls the apparent fO_2 of basaltic glasses

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We have measured the concentration and redox state of sulfur in a series of synthetic silicate melts ranging in composition from Fe-rich basalt to dacite in order to constrain the relative proportions of S^{6+} and S^{2-} present in natural magmas. Experiments were done under controlled fO_2 and fS_2 conditions at 1300°C and 1 bar. The S^{6+}/S^{2-} ratios of our run products were determined by S *K*-edge X-ray Absorption Near-Edge Structure (XANES) spectroscopy in combination with Secondary Ion Mass Spectrometry (SIMS).

Over the fO_2 range under which our experiments were equilibrated (-1.67 to +1.60 log units relative to the Fayalite-Magnetite-Quartz, FMQ, buffer) the S redox state undergoes an abrupt transition from S^{2-} to S^{6+} with increasing fO_2 in all investigated compositions. The S^{6+}/S^{2-} of our samples shows a linear relationship with calculated Fe^{3+}/Fe^{2+} [1], following the equilibrium $FeS + 8FeO_{1.5} = 8FeO + FeSO_4$, indicating that the redox couples for Fe and S can be directly related. Using existing thermodynamic data to model the effect of temperature on Fe-S equilibrium yields excellent agreement between our results and those from previous experimental studies performed at lower temperatures [2].

We used our results to assess the effects of electron transfer between Fe and S on quenching of natural glasses. Considering glasses from Mauna Kea, Hawaii [3] we estimate an increase in Fe^{3+}/Fe_{Total} of approximately 0.05 during quenching from the liquidus. This results in a calculated fO_2 (from Fe XANES) of ~0.8 log units higher than the true value. Our results demonstrate that a reassessment of previous Fe^{2+}/Fe^{3+} measurements of basaltic glasses, taking into account the concentration and redox state of sulfur is now required.

[1] Kress and Carmicheal (1991) Contrib. Mineral. Pertol. 108, 82-92. [2] Jugo et al. (2010) Geochim. Cosmochim. Acta 74, 5926-5938. [3] Brounce et al. (2017) Proc. Natl. Acad. Sci. 114, 8997-9002.