Experimental use of olivine-hosted melt inclusions to explore the thermodynamics and kinetics of Fe and S redox equilibria in silicate melts

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Natural silicate melts contain sulfur (dissolved as S^{2-} and S^{6+}), an important participant in redox chemistry. However, low-pressure experiments used to calibrate Fe oxybarometers, which relate melt Fe^{3+}/Fe^{2+} to oxygen fugacity (fO_2), are based on sulfur-free compositions and this leads to uncertainties in calculating the fO_2 of S-bearing glasses based on their measured Fe^{3+}/Fe^{2+}[1]. Furthermore, if electron exchange between dissolved S and Fe is temperature-dependent, then liquid S^{6+}/S^{2-} and Fe^{3+}/Fe^{2+} ratios will change during cooling. Olivine-hosted melt inclusions (MIs) equilibrate rapidly with the fH_2 and fH_2O in 1-atm furnaces[2] while retaining their sulfur. This offers a way to explore electron exchange between S and Fe in silicate melts as a function of T and fO_2, and to assess whether melts equilibrated at the same T and fO_2 but cooled at different rates and quenched at different temperatures record the same S and Fe speciation.

Olivine-hosted MIs were held at 1225°C for 24–48 hours at nine fO_2s (ΔFMQ–3 to ΔFMQ+3) and then drop-quenched (>700°C/s)[3] or cooled at rates as low as ~30°C/s and drop-quenched at lower T. A subset of the glasses was analyzed using S and Fe μ-XANES. Based on furnace fO_2s, the measured Fe^{3+}/Fe^{2+} in the glasses are low relative to estimates from published Fe oxybarometers[1]. The S^{6+}/S^{2-} of the MI glasses in the 1225°C experiments follow the sigmoidal dependence on fO_2 determined for hydrous basalts[4]. At the same fO_2, the cooling-rate experiments have systematically lower S^{6+} than MIs quenched from 1225°C. Two unheated MIs from Mauna Loa with cooling rates[3] of ~1°C/s and ~130°C/s follow the same sigmoidal relationship between ΔFMQ and S^{6+}/S^{2+} as the experimental inclusions. The ~1°C/s natural MI retained ~90% of S as S^{6+} as it cooled to $T < 900$°C[3], consistent with a relatively weak T-dependence for S-Fe redox equilibria in Hawaiian tholeiitic melts. However, the kinetics of S-Fe electron exchange are sufficiently rapid to modify S speciation in melts cooled at rates lower than ~30°C/s.

[1] Graz *et al.* (2006) *AGU*, V43B-01;[2] Gaetani *et al.* (2012) *Geology* 40, 915;[3] Saper & Stolper (2020) G^3 21, e2019GC008772;[4] Jugo *et al.* (2010) *GCA* 74, 5926