

Sulfur speciation in low to high temperature silicate melts

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The oxygen fugacities recorded by volcanic liquids and their source rocks are crucial to Earth's history, as they influence and reflect the composition of C-O-H-S gases released into the atmosphere and control the distribution of economically valuable metals (e.g., Cu, Sn, Te, Pt) between the mantle and crust. Sulfur plays a key role in magmatic redox states due to its ability to exist in both oxidized and reduced forms in melts (e.g., SO_4^{2-} and S^{2-}) and vapours (e.g., SO_2 and H_2S). Understanding these processes requires precise knowledge of sulfide and sulfate solubility as a function of oxygen fugacity ($f\text{O}_2$), temperature, and melt composition.

Previous studies have characterized sulfate and sulfide solubilities (C_{SO_4} and $C_{\text{S}^{2-}}$) in silicate melts at 1 atm between 1500 and 1200 °C. Boulliang and Wood (2023) recently suggested that sulfate concentrations may increase non-linearly at lower reciprocal temperatures. To investigate this, we experimentally determined sulfate and sulfide solubilities in silicate melts between 1250 and 1050 °C. Natural and synthetic melts were equilibrated over 1–5 days using gas mixtures of air, SO_2 , CO, and CO_2 to control $f\text{O}_2$ and $f\text{S}_2$ at ambient pressure. The resulting sulfate and sulfide capacities were modelled using reciprocal solution theory, showing excellent agreement with previous 1-atm experiments in the overlapping temperature range.

By combining these models, we can determine sulfur speciation ($\text{S}^{6+}/\text{S}^{2-}$) as a function of $f\text{O}_2$, melt composition, and temperature. Our results indicate that sulfate solubility decreases non-linearly with decreasing reciprocal temperature, shifting the sulfide-sulfate transition ($\text{S}^{6+}/\Sigma\text{S} = 0.5$) from QFM +1 at 1200 °C to QFM +2 at 1050 °C. Additionally, our findings allow us to simulate C-O-H-S degassing pathways under conditions relevant to subduction zones, demonstrating that sulfur degassing under hydrous conditions can drive significant oxidation, potentially explaining the elevated oxidation states of subduction zone magmas compared to those at mid-ocean ridges.