Behaviour of sulfur during volcanic degassing: insights using a thermodynamic model. 2022 Young Scientists Award

ERY C HUGHES[1], LEE SAPER[2], PHILIPPA LIGGINS[3] AND EDWARD STOLPER[4]

[1]GNS Science - Te Pū Ao
[2]University of Edinburgh
[3]University of Cambridge
[4]California Institute of Technology
Presenting Author: e.hughes@gns.cri.nz

Sulfur has multiple valence states in silicate melts (i.e., sulfide: S^{2-} and sulfate: SO_4^{2-}), causing complex behaviour during degassing, which is intrinsically linked to the evolution of oxygen fugacity (f_{O2}). Quantitative interpretation of volcanic volatile data depends on magmatic degassing models that explicitly and rigorously deal with f_{O2} and multiple C-O-H-S species in the melt and vapor. We developed a thermodynamic model to calculate the equilibrium concentrations, speciation, and isotopic compositions of C-O-H-S bearing components in coexisting basaltic melt and vapor. Our approach builds on the concepts of sulfide and sulfate capacity [1,2], which relate dissolved S^{2-} and SO_4^{2-} concentrations in the melt to f_{O2} and f_{S2}.

Applying our model to a representative Hawaiian tholeiitic melt, we predict a sulfur solubility minimum at δFMQ+1.3, and that this feature can exert important controls on degassing. For example, the pressure at which sulfur begins to degas can depend significantly on the initial f_{O2} of the melt and the onset of degassing occurs at maximum pressure at the sulfur solubility minimum. Likewise, whether the Fe^{3+}/Fe^{2+} of the melt increases or decreases during degassing also depends on the initial f_{O2} of the system relative to the sulfur solubility minimum, as this controls the dominant sulfur species in the melt. As a result during ascent from the pressure of vapor-saturation to 1 bar, at conditions more reducing than the sulfur solubility minimum, the f_{O2} of the coexisting melt and vapor are predicted to decrease (e.g., from δFMQ+0.7 to -0.5); whereas at more oxidising conditions, the f_{O2} increases (e.g., δFMQ+1.8 to +3.0). Our model also predicts that the H_2O content of the melt can have an important influence on degassing, with water-rich magmas degassing sulfur at greater depths than water-poor magmas. This has implications for using volatile contents as a barometer; inferring magma depths from CO_2/S ratios of volcanic gases; using S^{2-}/S^{6+} and Fe^{3+}/Fe^{2+} in silicate glasses to infer the f_{O2} levels relevant to magmatic processes; and deep degassing of S from water-rich, oxidized magmas as they ascend.

[1] Fincham & Richardson (1954) *Proc. R. Soc. Lond.* 223, 40–62; [2] O'Neill (2021) *Magma Redox Geochemistry*.