Raman and infrared studies of gas-solid reactions between SO_2 and basaltic glasses

T.P. MERNAGH[1]*, A.B. PALM[1], C.J. RENGGLI[1], AND P.L. KING[1]

[1] Research School of Earth Sciences, Australian National University, Canberra ACT 2601 Australia

Sulfur dioxide gas ($SO_{2(g)}$) is the most abundant of the corrosive gases in volcanoes and it has also been detected on a number of other planetary bodies. 'Chemisorption' reactions between silicate materials and $SO_{2(g)}$ are shown to occur rapidly, causing sulfur to disproportionate into sulfate (SO_4^{2-}) and sulfide (S^{2-}) along with the formation of oxide minerals [1,2]. Raman and Fourier Transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM), were used to investigate the mineralogy of surface coatings on basaltic glasses formed by reaction with $SO_{2(g)}$.

Raman spectroscopy and SEM have identified a wide range of sulfates in the surface coatings. These include anhydrite ($CaSO_4$), glauberite ($Na_2Ca(SO_4)_2$), thenardite (Na_2SO_4), and three hydrated magnesium sulfate phases including $MgSO_4 \cdot H_2O$ (kieserite), $MgSO_4 \cdot 2H_2O$ (sanderite) and $MgSO_4 \cdot 3H_2O$ (trihydrate). The coatings also commonly contain oxide phases such as hematite (Fe_2O_3), magnetite (Fe_3O_4) and anatase (TiO_2). Raman mapping has shown that hematite and magnetite commonly co-exist within the same crystal, with interior hematite surrounded by an outer-zone of magnetite; this assemblage helps constrain S-O gas fugacities.

Attenuated total reflectance FTIR and SEM obtained from surface coatings revealed the presence of an anhydrous Ca-Na-rich sulfate phase, likely glauberite ($Na_2Ca(SO_4)_2$) on one of the basaltic glasses. Glauberite is distinct from anhydrite, thenardite and blödite ($Na_2Mg(SO_4)_2.4H_2O$) based on the absence or presence of other bands [3]. This technique enabled an increased penetration depth and the sampling of both the sulfate coating and a mineral phase(s), most likely pyroxene, within the modified basaltic glass. The increased penetration depth tends to minimize the signal from the <10 µm glauberite coating.

Our experiments revealed a diversity in the mineral phases formed in reactions between $SO_{2(g)}$ and basaltic glasses, consistent with thermodynamic models. This is in contrast to past experimental studies with a prevalence of $CaSO_4$ as the sole or dominant reaction product.

[1] Henley *et al.* (2015) *Nat. Geosci.* **8**, 210-215. [2] Renggli and King (2018) Rev. Mineral. Geochem. 84, in press, [3] Lane (2007) *Am. Mineral*. **92**, 1-8.