



An experimental investigation of reactions between SO₂ and Anorthite-Diopside glasses

Christian Renggli and Penelope L. King

The Australian National University, Research School of Earth Sciences, Australia (christian.renggli@anu.edu.au)

Sulfur dioxide is the most abundant sulfur-bearing volcanic gas species on Earth, with approximately 10 Mt SO₂ emitted on average globally each year. From its largely magmatic source at depths of 3 to 6 km below the surface, SO₂ expands through the subvolcanic environment where it interacts with volcanic rocks from the sub-surface to the eruption plume at high temperatures. The reaction between SO₂ and silicate rocks, forming oxidized sulfate and reduced sulfide, is a key process in the formation of porphyry copper and gold deposits (Henley, King & Wykes et al., 2015). In explosive volcanic eruption plumes SO₂ reacts with volcanic ash and is scavenged onto ash particles (Ayrís et al., 2013).

We present results from an experimental study on reactions between SO₂ and simple aluminosilicate glasses in the anorthite-diopside (An-Di) system. The aim of the study is to identify how SO₂ + glass reactions occur at volcanoes and what properties of the glasses promote and limit these reactions. This information is needed to understand how SO₂ is removed from volcanic gases and how volcanic rocks are altered. Experiments were performed at temperatures (T_{exp}) of 600-800 °C and 1 bar for 10 minutes to 72 hours. Results from electron microscopy, Raman spectroscopy, solution ICP-MS, X-ray micro-CT and nanoSIMS suggest that structural properties of the silicate glass substrate control the diffusive transport of Ca and Mg to the glass surface, which in turn controls the overall reaction rate and the formation of sulfates on the surface.

We observe a diverse range of sulfate textures coating the reacted glass surfaces. Grain sizes formed after reacting SO₂ with glasses for 1 hour range from 20 nm in coatings formed at 600 °C to more than 5 μm at 800 °C. The polycrystalline sulfate coatings can reach several microns in thickness and the coatings show extensive deformation and volume increase with increasing experimental durations. At 800 °C the reaction forms up to 30 000 μmol sulfate per square-meter, approximately one order of magnitude more than at 600 °C. The reaction rate strongly depends on temperature: below the glass transition temperature (T_g) it is relatively slow, and above T_g it is inversely proportional to the liquidus temperature (T_{liq}). Above T_g, the eutectic An₃₆-Di₆₄ glass reacts most, up to four times more than the end-member anorthite and diopside glasses.

Overall, the sulfates are relatively enriched in Ca compared to the silicate glass composition ($((\text{Ca}/(\text{Ca}+\text{Mg}))_{\text{sulfate}} > (\text{Ca}/(\text{Ca}+\text{Mg}))_{\text{unreactedglass}}$). At 800 °C only CaSO₄ is detected in the coatings, whereas at 600 °C coatings on intermediary An-Di glasses contain some MgSO₄. In conclusion, the rate of sulfate formation is not only a function of the Ca and Mg abundance in the reacting aluminosilicate glasses, but also their mobility during the reaction.