American Mineralogist, Volume 97, pages 1348–1353, 2012

In-situ Raman spectroscopic study of sulfur speciation in oxidized magmatic-hydrothermal fluids

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ABSTRACT

The sulfur compounds released by volcanic eruptions, generally believed to be in the form of SO_2 and H_2S, may cause global cooling of the atmosphere. However, several recent field and experimental studies suggested that under moderately oxidized conditions hexavalent sulfur species may coexist with SO_2 in magmatic fluids and may later be directly emitted at volcanic vents, which contradicts some thermodynamic predictions. We have investigated sulfur speciation in magmatic-hydrothermal fluids by loading different amounts of dilute sulfuric acid into a hydrothermal diamond-anvil cell and performing in situ Raman spectroscopy at temperatures up to 700 °C. Upon heating SO_4^{2-} disappeared beyond 100 °C, and SO_2 formed at >250 °C probably due to reduction by the rhenium or iridium gasket. With high-fluid densities (such as >0.9 g/mL), the initial acid and air bubble homogenized into the liquid phase and most sulfur was present in the form of either HSO_4^- or H_2SO_4 (the rest being SO_2) within investigated T–P conditions (with pressures up to 10 kb). With low-fluid densities (such as <0.2 g/mL), the system homogenized into the vapor phase and molecular H_2SO_4 appeared to dominate (with pressures less than 1 kb). These observations strongly suggest that hexavalent sulfur is stabilized by hydration in magmatic fluids.

Keywords: Sulfur speciation, magmatic fluid, hydrothermal fluid, volcanic gas