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$_2$S, 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$_2$ disappeared beyond 100 °C, and SO$_3$ 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$_2$SO$_4$ (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$_2$SO$_4$ 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

INTRODUCTION

Contrary to the global warming effect caused by anthropogenic carbon dioxide, sulfur compounds released by human activities and more importantly by explosive volcanic eruptions can result in large-scale cooling (Robock 2000; Self 2005; Self and Blake 2008; Kaufmann et al. 2011). Although it is the H$_2$SO$_4$ aerosol in the stratosphere that absorbs and backscatters solar radiation to cause this cooling effect, this H$_2$SO$_4$ aerosol is generally believed to be the oxidation product of primary SO$_2$ (plus some H$_2$S) in volcanic gases, according to in situ sampling and remote sensing (e.g., Gerlach 1993; Stremme et al. 2011). However, there is recent field evidence from persistently degassing volcanoes that sulfate is directly emitted from volcanic vents (Allen et al. 2002; Mather et al. 2004, 2006). Binder and Keppler (2011) built on these field studies to investigate what sulfur speciation might be in the fluid phase in relatively oxidized magma chambers. They found that hexavalent sulfur may coexist with SO$_2$ in magmatic fluids at 650–850 °C and 1.5–3 kb under Re-ReO$_2$ buffer conditions. To reconcile with the thermodynamic estimation of negligible SO$_2$ under such conditions, Binder and Keppler (2011) suggested that hexavalent sulfur must be present in some hydrated form (i.e., H$_2$SO$_3$, HSO$_4^-$, and SO$_2^-$) in the fluids. Their explanation is yet to be fully verified because the measurements were made on quenched fluid inclusions. Even if it had existed at high temperatures, SO$_2$ would have been hydrated during cooling. This inadequacy of previous work motivated us to perform in situ Raman analyses of sulfur species in oxidized magmatic-hydrothermal fluids at conditions up to 700 °C and 10 kb in a hydrothermal diamond-anvil cell, broadly covering the conditions investigated by Binder and Keppler (2011) or those of a typical felsic magma chamber before an explosive eruption (650–850 °C and 1–3 kb; Whitney 1988; Bachmann and Bergantz 2008).

EXPERIMENTS

Sulfuric acid has been used as the starting material for studying sulfur-bearing magmatic fluids in previous studies (e.g., Keppler 2010; Binder and Keppler 2011). A dilute sulfuric acid (5 N H$_2$SO$_4$, prepared from certified standard solution) was loaded into a Bassett-type hydrothermal diamond-anvil cell (see Bassett et al. 1993 for more details) with two type Ila diamonds (600 µm culet diameter). Three kinds of 250 µm thick (before compression) gaskets were used, including gold-lined rhenium, gold-lined iridium, and plain iridium. The Ir gaskets had a pinhole of 500 µm diameter. For the gold-lined Re and Ir gaskets, a pinhole of 250 µm diameter was drilled into a gold inlet of 500 µm diameter by spark erosion. In some runs we further coated a ~40 nm thick gold layer on both surfaces of the gold-lined Re gasket. Different fluid densities were examined; one extreme with no air bubble loaded and the other with homogenization into the vapor phase upon heating (starting from either a large air bubble or a tiny acid drop).

To avoid complicating the system, we chose not to load a pressure sensor, but to infer pressure from the estimated fluid density. Bassett et al. (1993) showed that after the first heating cycle, a hydrothermal diamond-anvil cell behaves nearly isochorically with further temperature variation, therefore for a dilute aqueous solution at a given temperature, the pressure inside the cell can be approximately calculated from fluid density and from the equation of state of H$_2$O. Fluid density can again be inferred from the homogenization temperature of the system if the system initially contains both a liquid phase and a vapor phase. For example, if the vapor phase dissolves into the liquid phase at 133 °C, based on the equation of state of H$_2$O in Saul and Wagner (1989), the bulk density of the cell is estimated to be ~0.93 g/mL, and one can infer the pressure inside the cell to be 3.0 kb at 300 °C and to be 10.2 kb when further heated to 700 °C. Considering the uncertainties in fluid density estimation, temperature measurement, cell-volume variation, and the equation of state of fluid, the overall uncertainty of the inferred pressure is estimated to be ~20% relative.

External heating, up to 700 °C, was provided by two Mo wire heaters, with the temperature monitored by two chromel-alumel thermocouples in direct contact with diamonds. The cell was flushed with a 98% Ar + 2% H$_2$ gas mixture to...