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# The oxidation state of sulfur in magmatic fluids

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ABSTRACT

Sulfur compounds in volcanic gases are responsible for the global cooling after explosive eruptions and they probably controlled the early evolution of the Earth's atmosphere. We have therefore studied the oxidation state of sulfur in aqueous fluids under the pressure and temperature conditions and oxygen fugacities typical for magma chambers (0.5–3 kbar, 650–950 °C, Ni–NiO to Re–$ReO_2$ buffer conditions). Sulfur speciation was determined by Raman spectroscopy of quenched fluids trapped as inclusions in quartz. Our results show that sulfur in hydrothermal fluids and volcanic gases is much more oxidized than previously thought and in particular, some explosive eruptions may release a significant fraction of sulfur as $SO_3$ or its hydrated forms. In the pressure range from 500 to 2000 bar, the equilibrium constant $K_1$ of the reaction $2H_2S + 3O_2 = 2SO_2 + 2H_2O$ in aqueous fluids can be described by $\ln K_1 = -(57.1 \pm 7.1) + (173{,}480 \pm 7592)T^{-1}$, where T is temperature in Kelvin. The equilibrium constant $K_2$ for the reaction $SO_2 + ½O_2 = SO_3$ in aqueous fluids, where $SO_3$ may include hydrated forms, such as $H_2SO_4$, was found to be strongly pressure dependent, with $\ln K_2 = -(5.2 \pm 5.7) + (19{,}243 \pm 5993)T^{-1}$ at 1500 bar; $\ln K_2 = -(11.1 \pm 1.3) + (25{,}383 \pm 1371)T^{-1}$ at 2000 bar and $\ln K_2 = -(22.1 \pm 2.2) + (37{,}082 \pm 2248)T^{-1}$ at 2500 bar. Our data imply that volcanoes may directly inject hexavalent sulfur in the form of $H_2SO_4$ into the atmosphere, not only on Earth, but possibly also on Venus and on Mars, when it was still tectonically active. Remote measurements from satellites may have underestimated the sulfur yield of some recent eruptions. Moreover, the mechanisms of the interaction of volcanic gases with the stratosphere need to be reconsidered.

## 1. Introduction

The 1991 eruption of Mount Pinatubo has reduced average surface temperatures by about 0.5 °C and therefore compensated the effect of anthropogenic warming for several years (McCormick et al., 1995; Robock, 2000). Similar or even larger cooling events occurred after many large explosive volcanic eruptions (Briffa et al., 1998). The 1815 eruption of Tambora is believed to be responsible for the "year without summer" of 1816 (Briffa et al., 1998; Robock, 2000). The Russian famine of 1601–1603 was probably caused by the eruption of Huaynaputina in Peru (Briffa et al., 1998; de Silva and Zielinski, 1998). Even more catastrophic events may have occurred in the recent geologic history. The Toba eruption in Sumatra about 74,000 yr ago probably reduced global surface temperatures by 8–17 K and produced a decade-long volcanic winter (Robock et al., 2009) that may have brought the human population to the edge of extinction (Ambrose, 1998).

The cooling after volcanic eruptions is caused by the injection of sulfur compounds into the stratosphere. These sulfur compounds are then photochemically oxidized to sulfate aerosols that backscatter sunlight and therefore cool the surface of the Earth (McCormick et al., 1995; Robock, 2000). Both for remote sensing the sulfur yield of eruptions and for predicting the chemical reactions occurring in the stratosphere, it is essential to know the speciation of sulfur in volcanic gases. It is generally believed that volcanoes release sulfur primarily in the form of $SO_2$ and perhaps as $H_2S$, in agreement with predictions from thermodynamic calculations (Scaillet and Pichavant, 2003). However, this does not agree with observations of the direct emission of sulfate aerosols from active volcanoes (Allen et al., 2002; Mather et al., 2006). Moreover, there appears to be a discrepancy between the predicted and observed oxidation state of sulfur in volcanic gases (Burgisser and Scaillet, 2007). The fluids released during explosive volcanic eruptions consist mostly of water and they typically contain a few wt.% of sulfur compounds. We therefore experimentally studied the oxidation state of sulfur dissolved in aqueous fluids under the conditions that are expected to prevail in the magma chambers below explosive volcanoes. Sulfur speciation was studied by trapping fluids at 0.5–3 kbar and 650–950 °C as synthetic fluid inclusions in quartz and by analyzing the fluid inclusions after quenching to room temperature by Raman spectroscopy.

## 2. Experimental methods

### 2.1. Preparation of sample capsules

Between 3 and 21 mg of 2.5 m aqueous solution of $H_2SO_4$ were welded together with some natural quartz crystals and quartz powder

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into gold capsules (25 mm long, 2.5 mm outer diameter, and 0.2 mm wall thickness). The quartz crystals contained numerous cracks that were produced by heating them to 500 °C in a furnace and quenching them with cold water. For experiments under Re–$ReO_2$-buffer conditions (Pownceby and O'Neill, 1994), these capsules were welded together with distilled water, Re and $ReO_2$ powder into outer gold capsules of 5 mm outer diameter and 0.2 mm wall thickness.

### 2.2. High-pressure experiments

Experiments were carried out in vertical rapid-quench autoclaves using water as pressure medium. The autoclaves were made from a Ni–Cr super alloy (IN 713 LC). For experiments under Re–$ReO_2$ buffer conditions, the double capsules described above were used. For experiments with the Ni–NiO buffer (Huebner and Sato, 1970), a 1:1 mixture of Ni and NiO powder was placed in an open gold capsule immediately below the sample capsule, since the reaction of the autoclave alloy with water already produces an oxygen fugacity close to the Ni–NiO buffer. Additional experiments were carried out in a specially designed vertical rapid-quench autoclave using a Shaw membrane (Shaw, 1963) in a design similar to Scaillet et al. (1992). The Shaw membrane was introduced from the upper end of the autoclave into the hot zone immediately adjacent to the sample capsule. Hydrogen partial pressures were imposed through the Shaw membrane and measured by an Ashcroft Type 1082 gauge with an accuracy of ±0.25%. The time required for reaching osmotic equilibrium for hydrogen between the interior of the sample capsules and the external buffer or the Shaw membrane was calculated from the hydrogen permeability data given by Chou (1986). The actual run durations were always several times longer than the time required for reaching osmotic equilibrium. Temperatures were measured by an external Ni–NiCr (Type K) thermocouple in an external borehole of the autoclave close to the sample location. Pressure was measured by a sensor that was regularly calibrated against a Heise CM Bourdon tube gauge with an accuracy of 0.1%. Pressures and temperatures are believed to be accurate to ±7 °C and ±20 bars, respectively. At the end of an experiment, the capsules were isobarically quenched to room temperature within a few seconds by dropping them into a water-cooled zone inside the autoclave.

### 2.3. Investigation of run products

All capsules were checked for leaks after the experiments and if solid buffers were used, the buffering assemblage was checked by X-ray diffraction. Runs where either the capsule had leaked or the buffer was exhausted were discarded. The quartz crystals were then embedded into Crystalbond 509 resin and ground and polished on the surface. After polishing, the embedding medium was completely removed by dissolution in acetone. Fluid inclusions produced in the quartz crystals by healing of cracks during the experiment were then investigated by a Raman microspectrometer (Dilor Labram 2, 1800 $mm^{-1}$ grating, 488 nm Ar laser, 11 mW at sample, 30 s accumulation time). The concentrations of $SO_2$, $H_2S$, $SO_4^{2-}$ and $HSO_4^-$ in the quenched liquid phase were obtained by measuring the integral ratio of the main Raman peaks of these species relative to the peak of the bending vibration of water at 1640 $cm^{-1}$. This ratio was calibrated by measuring aqueous solutions of $SO_2$, $H_2S$, $SO_4^{2-}$ and $HSO_4^-$ of known concentration using the same experimental parameters as for measuring the fluid inclusions. $H_2S$ concentrations in the gas phase in the fluid inclusions were calculated from the concentrations in the coexisting liquid (Suleimenov and Krupp, 1994). For calculating bulk sulfur concentrations, it was assumed that the volume ratio of liquid to fluid in the fluid inclusions was the same as for inclusions of pure water produced under the same conditions. Bulk sulfur concentrations obtained in this way were usually within analytical error of the sulfur concentrations loaded into the capsule.

Raman spectra of standard solutions used for calibration are shown in Figure 1. Concentrations of the $SO_2$ and $H_2S$ solutions were determined by iodometric titration. The $H_2SO_4$ solutions were prepared by diluting a standard solution of certified concentration. The ratio of $SO_4^{2-}$ and $HSO_4^-$ in these solutions was calculated from the second dissociation constant of $H_2SO_4$ in water (Pitzer et al., 1977). For all species studied, the ratio of the integral area $I_x$ of the main absorption band over the integral area $I_{H2O}$ of the water band at 1640 $cm^{-1}$ was found to be directly proportional to the molality (mol per kg water) of the respective species. The following calibration curves were established:

– for the symmetric stretching vibration of $HSO_4^-$ at 1050 $cm^{-1}$

$$\frac{I_{HSO_4^-}}{I_{H_2O}} = 1.0453 c_{HSO_4^-} \quad \left(R^2 = 0.99\right).$$

– for the symmetric stretching vibration of $SO_4^{2-}$ at 983 $cm^{-1}$

$$\frac{I_{SO_4^{2-}}}{I_{H_2O}} = 11.324 c_{SO_4^{2-}} \quad \left(R^2 = 0.99\right).$$

– for the symmetric stretching vibration of $SO_2$ at 1151 $cm^{-1}$

$$\frac{I_{SO_2}}{I_{H_2O}} = 0.5411 c_{SO_2} \quad \left(R^2 = 0.98\right).$$

– for the symmetric stretching vibration of $H_2S$ at 2590 $cm^{-1}$

$$\frac{I_{H_2S}}{I_{H_2O}} = 1.0453 c_{H_2S} \quad \left(R^2 = 0.99\right).$$

Further experimental details and plots of the calibration curves are given in Binder (2007).

## 3. Results

### 3.1. Sulfur species in quenched fluids

All experimental data are compiled in Table 1. Figure 2 shows the Raman spectra of quenched fluids produced under Ni–NiO and under Re–$ReO_2$ buffer conditions. While $H_2S$ is the dominant sulfur species under the more reducing conditions of the Ni–NiO buffer, $SO_2$, $HSO_4^-$ and $SO_4^{2-}$ coexist under Re–$ReO_2$ buffer conditions. The occurrence of $HSO_4^-$ and $SO_4^{2-}$, which are hydrated forms of $SO_3$ containing sulfur in the +6 oxidation state, is very surprising. Thermodynamic calculations using 1 bar standard state data (Robie and Hemingway, 1995) for $SO_2$ and $SO_3$ would predict a ratio of the fugacity of the two gases $f_{SO_3}/f_{SO_2}$ in the order of $10^{-6}$ at 800 °C, i.e. these fluids should not contain any measurable amount of hexavalent sulfur.

The presence of hexavalent sulfur in the fluid cannot be a result of incomplete attainment of equilibrium with the oxygen buffer. To demonstrate this, we carried out a reversed experiment at 800 °C and 2 kbar where a fluid was first exposed to Ni–NiO buffer conditions for 10 days so that nearly all sulfur was reduced to $H_2S$. However, after rerunning the experiment at Re–$ReO_2$ buffer conditions for 7 days and after producing new fluid inclusions by in-situ cracking, $SO_4^{2-}$ and $HSO_4^-$ were again detected in the quenched fluid.

Any significant change of sulfur oxidation state during quenching can also be ruled out. Table 2 shows the sulfur speciation predicted from standard state thermodynamic data (Robie and Hemingway, 1995) for 2 kbar, 800 °C and Re–$ReO_2$ buffer conditions, as well as the changes in equilibrium speciation upon isochoric quench of the fluid inclusions from 800 to 400 °C. Accurate calculations below 400 °C are difficult because of the separation into a liquid and a vapor phase;