

Crustal sequestration of magmatic sulfur dioxide

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ABSTRACT

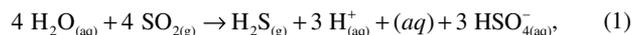
Volcanism is responsible for copious discharge of sulfur-bearing magmatic gases. A dominant sulfur-bearing species is SO₂, yet sulfite (S⁴⁺) minerals are rare in geological settings, testifying to the reactivity of SO₂. Disproportionation of SO₂ to reduced (sulfide), neutral (elemental sulfur), and oxidized (sulfate) species is one expression of this reactivity. Previous studies of SO₂ disproportionation reactions have focused on low-pressure, low-temperature conditions involving SO₂ gas and liquid water, such as those close to volcanic vents or in water-free gas systems. However, release of magmatic volatiles in volcanic systems can occur at depth where hot magmatic gas meets crustal rocks ± pore fluids. We investigate the viability of such high-pressure reactions with experiments in which SO₂ gas is reacted with a mixture of calcite and a metal-bearing saline fluid at 1.0–1.5 kbar pressure and 400–800 °C. At all temperatures, the calcite-bearing experiments produced anhydrite and sulfide. In the experiment where calcite was replaced by quartz, no sulfide was produced, establishing that Ca is a crucial component of this reaction. We show that extensive production of anhydrite and sulfide through calcite-mediated SO₂ disproportionation takes place on time scales of just a few hours. This could occur where hot magmatic SO₂ gas encounters magmatic brines in igneous rocks, basinal brines within sedimentary rocks, or calcium-bearing saline groundwaters.

INTRODUCTION

Magmas generated in a wide variety of tectonic settings contain dissolved volatile sulfur species that are released during crustal differentiation and eruptions. Of particular note are arc magmas generated above subduction zones that not only play a role in global gas emissions (Wallace, 2005), but also in continental crust formation (Kelemen and Behn, 2016), eruption-related climate change (Mather et al., 2013), and the formation of hydrothermal ore deposits (Hedenquist and Lowenstern, 1994). Arc magmas are distinguished from those formed in other tectonic settings by their relatively high oxidation state (Evans et al., 2012) and their elevated contents of dissolved volatiles, including H₂O, CO₂, and sulfur species (SO₂, H₂S). During magma ascent and crystallization this volatile load is progressively released due to the pressure dependence of volatile solubility; the chemistry of the exsolved volatile phase is sensitive to the pressure (depth) at which degassing occurs (Lesne et al., 2011). (We use the term degassing to denote the exsolution and separation of a magmatic volatile phase from magma; e.g., Shinohara, 2008.) Depending on initial magmatic volatile contents degassing may begin at several kilometers depth below the volcano and continue as magmas ascend to the surface (e.g., Christopher et al., 2015). Thus, magmatic gas may be released syneruptively or passively, as magmas within the crust degas without eruption. As magmatic gas is released it will, inevitably, pass through and interact with crustal rocks (igneous, metamorphic, and sedimentary) and their pore fluids. The nature of these interactions can play an important role in modifying volcanic gas chemistry (Symonds et al., 2001) and in forming ore deposits (Giggenbach, 1992). Thus, the flux of volatiles out of magmas and their fate within continental crust at depths of several kilometers up to the surface is worthy of examination.

Here we present a novel methodology to explore experimentally the high-temperature reactivity of SO₂ gas in the presence of fluid-bearing crustal rocks at pressures equivalent to a few kilometers depth.

In hydrous magmatic gases the ratio of SO₂ to H₂S varies with redox state, pressure, temperature, and sulfur fugacity (Burgisser and Scaillet, 2007; Moretti and Papale, 2004; Burgisser et al., 2015). For typical basaltic arc magmas the gas released has molar H₂S/SO₂ < 1.5 (Burgisser et al., 2015), the ratio decreasing with decreasing pressure. These gases are, however, predominantly steam with 30–90 mol% H₂O. Upon cooling below ~400 °C in the presence of H₂O, SO₂ gas undergoes disproportionation via the reaction:



(where aq is aqueous and g is gas). This reaction is considered important in generating low-temperature hydrolytic alteration associated with many hydrothermal ore deposits and in modifying the chemistry of discharged volcanic gases (e.g., Holland, 1965; Hemley and Jones, 1964; Burnham, 1979; Giggenbach, 1988; Reed, 1997). Reaction 1 is often referred to as volcanic gas scrubbing, due to its ability to reduce the SO₂ content of volcanic gases discharged at the surface (Doukas and Gerlach, 1995). Volcanic gas scrubbing has been explored at low pressures (≤50 bar) for interactions between hot (≤915 °C) SO₂ gas (Fegley and Prinn, 1989; Ayris et al., 2013; Henley et al., 2015) and at low temperatures in the context of removal of SO₂ from magmatic gases via reaction with liquid H₂O in the shallow subsurface (Symonds et al., 2001).

Symonds et al. (2001) explored the involvement of rock in their scrubbing calculations, showing that a range of product minerals arises, including anhydrite and sulfides. Similarly, Fegley and Prinn (1989) and Henley et al. (2015) showed that dry SO₂ reacts with Ca-rich phases to produce anhydrite at high temperatures (600–800 °C). Ayris et al. (2013) reacted SO₂ with volcanic glass at 25–800 °C (at 1 atm) to form anhydrite at high temperatures (>600 °C). These are important results because reduced sulfur in the source is no longer required to generate sulfide, a ubiquitous ore mineral. In the context of hydrothermal ore formation, Blundy et al. (2015) showed that sulfur from a mafic source reacts with sulfur-free, saline aqueous fluids (brines) to form copper sulfides. However, the experiments of Blundy et al. (2015) contained a mixture of reduced and oxidized sulfur. In our work, only SO₂ is introduced to the brine, such that the anhydrite-forming reaction alone is responsible for production of reduced sulfur to form sulfides.

Evidently, there is more than one way to scrub a gas. In all of the examples cited here, the focus was on the near-surface volcanic vent environment, where SO₂-rich volcanic gas encounters Ca-bearing materials with or without aqueous solutions. However, for relatively deep degassing, especially when passive (e.g., Edmonds et al., 2001; Edmonds, 2008; Nadeau et al., 2013; Christopher et al., 2015), reactions of SO₂ can occur at pressures as high as 3 kbar, with SO₂ the dominant S species below 1–1.5 kbar. Reactions involving SO₂ and hot crustal rocks at these pressures have not previously been studied. Given the high porosity and permeability of volcanic edifices as imaged sesimically (e.g., Farquharson et al., 2015), it is likely that magmatic gases encounter rocks and pore fluids during ascent. Electrical conductivity surveys of shallow crust beneath volcanic edifices testify to the ubiquity of conductive, variously saline, fluids at depths of a few kilometers or less (e.g., Aizawa et al., 2005; Comeau et al., 2015).

As a first step toward exploring high-pressure crustal scrubbing of volcanic gas, we chose the mineral calcite (CaCO_3) and saline pore fluids composed of $\text{NaCl-KCl-H}_2\text{O}$ solutions with dissolved base metals (Cu and Fe). We chose calcite because of its structural simplicity and its ubiquity in limestone. However, many other calcium-bearing minerals can be found in igneous or sedimentary crustal rocks; the salty pore fluids could represent groundwater (e.g., Toner and Sletten, 2013), deep basinal brines, seawater, or condensed magmatic fluids. Our choice of calcite and metaliferous saline fluid is simply a first step in exploring the large number of potential scrubbing reactions that may occur where sulfur-bearing magmas are emplaced into the crust at a few kilometers depth.

To simulate the supply of volcanic SO_2 we used a source that undergoes SO_2 release upon thermal decomposition; sodium metabisulfite (MBS, $\text{Na}_2\text{S}_2\text{O}_5$) was placed in a small, unwelded, gold inner capsule to flux the fluid + calcite mixture in the outer capsule with SO_2 at experimental run conditions. Note that in these experiments MBS provides only SO_2 , without any H_2S , Cl, or metals. In nature magmatic gas will not be pure SO_2 , but will also carry H_2S , H_2O , and other volatile species, such as CO_2 . The chemistry of the fluid phase mixed with calcite was designed to mimic that of magmatic brines reported from the Bingham Canyon (Utah, USA) copper deposit (Seo et al., 2012). However, the experimental design enables a range of other reactant fluid chemistries to be explored and our results are not contingent on the exact fluid composition employed. The proportion of saline fluid added to the calcite was 20% by mass, in order to enhance the number of reactant pathways. This is somewhat higher than the likely porosity of an igneous or sedimentary fluid reservoir, but enables the reaction to proceed more efficiently. The mass proportion of brine does not have any bearing on our results; we are looking simply at chemical reactions of the form $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$; the relative proportions of A and B are irrelevant. However, as we argue here, elevated fluid solute levels and SO_2 -rich gas will tend to drive precipitation at the site of reaction, whereas in nature, where solutions and gases are more dilute, precipitation may only occur at shallower levels following cooling.

METHODS

Experiments utilized double capsules (Fig. 1) in which reactant calcite and fluid were isolated initially from the SO_2 source ($\text{Na}_2\text{S}_2\text{O}_5$). Salt mix (NaCl , KCl , CuCl_2 , and FeCl_2 in the ratios of Table 1), water, and calcite were added to the outer (3.5-mm-diameter Au) capsule and MBS ($\text{Na}_2\text{S}_2\text{O}_5$) was added to the inner, crimped (2-mm-diameter Au) capsule. At experimental conditions SO_2 produced by thermal decomposition exits the inner capsule and reacts with the saline fluid phase plus calcite in the outer capsule. As a control, in one experiment (M44) quartz was substituted for calcite to test if Ca is crucial in these controlling reactions. Welded outer capsules were placed into cold-seal autoclaves at the University of Bristol and held at pressure and temperature for 2 h and quenched rapidly, in 2–3 s. Run times were intentionally kept short to simulate the transient nature of likely scrubbing reactions as gas passes through rock. A few test runs were made to determine how long these reactions might take. After 10 min sulfide had formed, and reactions were complete well before 2 h. Thus, copper loss to the capsule walls was not considered an issue. In addition, post-run scanning electron microscope (SEM) analyses of gold capsules showed no copper.

The oxygen fugacity (f_{O_2}) of the experiments was not externally buffered, but through experience it is known to remain just above the nickel-nickel oxide (NNO+2) buffer in cold-seal autoclaves (Riker et al., 2014). These conditions are consistent with the presence of sulfide and sulfate in the run products. It has been shown experimentally that, at low pressure, sulfide and sulfate can coexist over a region of oxygen fugacity space from NNO-1 to NNO+2 (Matjuskin et al., 2016); thus, the reactions described here would be confined to this range of redox conditions.

After removal from the autoclave, capsules were pierced and dried prior to vacuum impregnation with epoxy resin. Samples were dry-polished

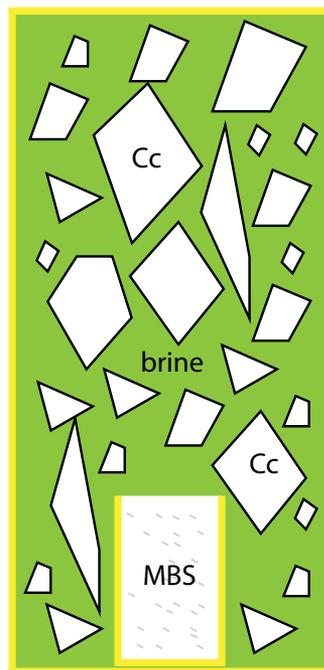


Figure 1. Schematic of the experimental design: a sealed gold capsule (3.5 mm diameter) containing calcite (Cc; or in one case, quartz) chips (white) and Fe, Cu, Na, K brine (green) and an inner, unwelded, SO_2 -producing gold capsule containing sodium metabisulfite (MBS, gray). The compositions of the starting materials are given in Table 1.

TABLE 1. CHEMISTRY OF EXPERIMENTAL SOLUTION AND FLUID INCLUSIONS FROM BINGHAM CANYON PORPHYRY COPPER DEPOSIT (UTAH, USA)

%*	Experiment (S-free brine)	Experiment†	Brine§	Intermediate density**
S		10.3	0.6 ± 0.3	1.0 ± 0.5
Na	10.1	6.3	11.9 ± 1.6	2.3 ± 0.3
Fe	4.1	2.6	5.7 ± 2.5	0.6 ± 0.2
Cu	1.4	0.87	0.5 ± 0.4	0.5 ± 0.2
K	6.0	3.7	9.3 ± 3.5	1.5 ± 0.4
$\text{NaCl}_{\text{eq}}^{\dagger\dagger}$	25.8	23.7	41.7 ± 6.1	8.9 ± 1.2

*All concentrations are given as weight percent of the element.

†Bulk solution added to experimental capsule. Sulfur is derived exclusively from $\text{Na}_2\text{S}_2\text{O}_5$ thermal decomposition. It is assumed that sodium sulfite residual to decomposition does not participate in reactions in the outer capsule. All Na quoted in the starting mixture is derived from added NaCl.

§Average (and standard deviation) of 27 quartz-hosted brine inclusions from Seo et al. (2012).

**Average (and standard deviation) of 13 quartz-hosted intermediate density fluid inclusion from Seo et al. (2012).

††NaCl equivalent.

with abrasive paper prior to final polishing on diamond laps with oil to avoid dissolution of water-soluble run products. Polished, carbon-coated run products were mapped by an FEI Quanta QEMSCAN (quantitative evaluation of minerals by scanning electron microscopy; www.fei.com) system operating at 15 kV, 10 nA at a step resolution of 2 μm and 2000 counts per pixel) and by FE-SEM (field emission scanning electron microscope; Hitachi 4300 SE/N, 15 kV) at the Australia National University (ANU) Centre for Advanced Microscopy. Mineral compositions were determined by electron microprobe analysis (Cameca SX100, 15 kV) at the Research School of Earth Sciences (RSES, ANU). After completion of the quartz-bearing experiment (M44), the Au capsule was opened and the entire contents removed, ground, and placed on a glass slide for X-ray diffraction (XRD) analysis (RSES, ANU).

RESULTS

The experiments (Table 2) produced abundant copper-iron sulfides (chalcopyrite, cp, or intermediate solid solution, ISS), iron sulfides (pyrrhotite, po, at 800 °C and pyrite, py, at lower temperature), anhydrite, sodium sulfite (SS), and salt (NaCl). XRD analysis of quartz-bearing experiment M44 indicates a total absence of sulfide (Table 2). Images

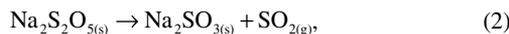
TABLE 2. EXPERIMENTAL CONDITIONS AND RUN PRODUCTS

Experiment	Starting mix	T (°C)	P (kbar)	Sulfides	Sulfate	Other
M28	Cc + MBS + CuFeNaCl + H ₂ O	600	1.5	ISS	CaSO ₄	NaCl + Cc
M42	Cc + MBS + CuFeNaCl + H ₂ O	800	1.5	FeS + ISS	CaSO ₄	NaCl + Cc
M43	Cc + MBS + CuFeNaCl + H ₂ O	500	1.0	FeS ₂ + ISS	CaSO ₄	NaCl + Cc
M44	Qtz + MBS + CuFeNaCl + H ₂ O	700	1.0	none	Na ₂ SO ₄	NaCl + Qtz
M45	Cc + MBS + CuFeNaCl + H ₂ O	700	1.0	FeS ₂ + ISS	CaSO ₄	NaCl + Cc
M49	Cc + MBS + CuFeNaCl + H ₂ O	400	1.0	FeS ₂ + ISS	CaSO ₄	NaCl + Cc

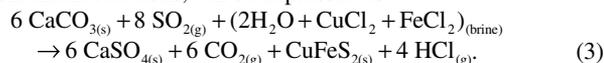
Abbreviations: T—temperature; P—pressure; Cc—calcite; MBS—sodium metabisulfite; Qtz—quartz; ISS—intermediate solid solution.

of the entire sectioned experimental capsule, including X-ray maps of selected areas, are provided in Figure 2.

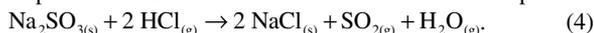
An acrid odor on piercing the capsule suggested that unreacted SO₂ gas was also present at the end of the experiment. Textural evidence (Fig. 2) indicates that the key reactions involve calcite as a source of Ca, with the saline fluid providing Cu and Fe. Sulfur dioxide disproportionation in the presence of calcite and metals is responsible for the production of both sulfide and sulfate. A series of near-simultaneous reactions can be written that describe the formation of the run products. First, MBS in the unwelded inner capsule undergoes thermal decomposition at ~150 °C to produce SO₂ gas and sodium sulfite:



(where s is solid). The SO₂ gas liberated penetrates the outer capsule, where it reacts with calcite and saline fluid to produce sulfide and anhydrite (Fig. 2). As the fluid in the outer capsule starting material was produced from salts of Cu²⁺ and Fe²⁺, these reactant species are written as CuCl₂ and FeCl₂, respectively. The net transfer reaction, a product of several concurrent reactions, can be expressed as:

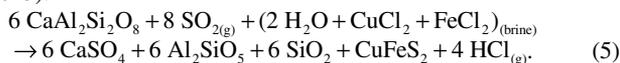


The HCl gas produced then reacts with the sodium sulfite residual from Reaction 2 to produce NaCl both inside and outside the inner capsule:



We have written the reaction with solid NaCl, but at run conditions it was dissolved in H₂O, only precipitating as NaCl crystals upon quench. Thus Reactions 2 and 4 are merely a consequence of the experimental design, and serve only as means to generate SO₂ gas and salt; they are not envisaged to occur in natural situations. In contrast, Reaction 2 simulates the process whereby magmatic SO₂ reacts with calcite in the presence of metal-bearing fluids. Rather than produce H₂S gas, as found by Henley et al. (2015) in their dry, atmospheric pressure experiments, we produce sulfide minerals through reaction with metals dissolved in the aqueous fluid.

Our experiments involved calcite, but SO₂ disproportionation may operate equally well with plagioclase, as shown by Henley et al. (2015), where SO₂ reacts with plagioclase feldspar to produce anhydrite and H₂S. In that case the salient net chemical transfer reaction, by analogy with Reaction 4, would also produce aluminosilicates and quartz (cf. Henley et al., 2015):



IMPLICATIONS

The dominant sulfur species in gas released from oxidized arc magmatic systems is sulfur dioxide (S⁴⁺). However, the predominant sulfur species in silicate melts are S²⁻ and S⁶⁺ (Wilke et al., 2011) and the predominant sulfur-bearing minerals on Earth are sulfides and sulfates, rather than sulfites. Thus, hot, gaseous SO₂ is very reactive in the crust, especially when in contact with Ca-bearing minerals. Our novel experimental set up provides a means to assess this reactivity. The experiments we report here replicate the SO₂-calcite reaction proposed by Fegley and Prinn (1989) and demonstrate further that rock-mediated disproportionation of SO₂

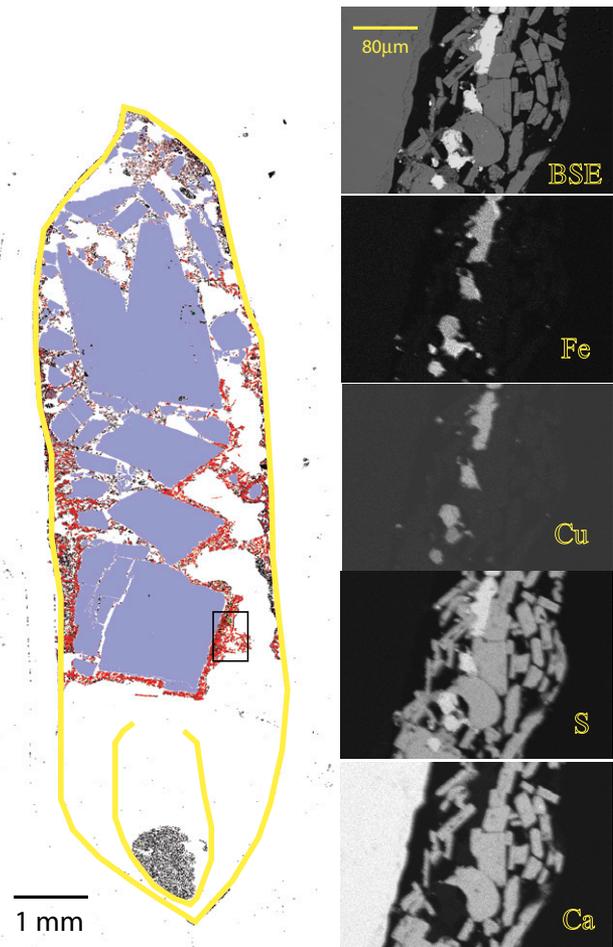


Figure 2. Left: QEMSCAN (www.fei.com; quantitative evaluation of minerals by scanning electron microscopy) map of polished section of the completed experiment (outline shows region of maps on right). Purple denotes calcite, red denotes anhydrite, and black denotes sulfide (ISS [intermediate solid solution] and/or chalcocyprite, FeS or FeS₂, and salt, vacant space or sulfite). Note that the copper iron sulfide imaged is ISS of slightly variable composition due to quench effects. Right: Maps of backscatter electron (BSE) and X-ray intensity of Fe, Cu, S, and Ca. Note the inner open SO₂-producing capsule. The gold capsules are outlined for clarity.

can occur rapidly at high temperatures and pressures when reacted with rock plus fluid. In this respect our experiments also resemble SO₂ gas scrubbing by wet limestone utilized in industry for cleaning gas streams from coal-fired power plants (Córdoba, 2015). In the experiment where we replaced calcite with quartz, no sulfide formed, attesting to the crucial role played by calcium.

CONCLUSIONS

We propose that rock-mediated scrubbing of volcanic SO₂ may be an important process in arc and oceanic crust. Our experiments show that sulfur dioxide scrubbing reactions at high temperatures and pressures in the presence of calcium-bearing minerals and pore fluids can produce simultaneous sulfate and sulfide mineral precipitation. In this context it is noteworthy that Gustafson and Hunt (1975) stated that primary sulfate-sulfide veins were important in the El Salvador (Chile) porphyry copper deposit. If the reactants include metal-bearing fluids, then gas scrubbing may serve as a hydrothermal mineralizing process. Anhydrite-sulfide veins are abundant in the giant Grasberg porphyry as well as the adjacent Ertsberg skarn system (Indonesia; Leys et al., 2012). Deposition in these deposits likely took place via reactions similar to those outlined herein. The products of scrubbing depend on gas pathways, gas temperature, and fluid and rock

chemistry. The case that we have explored here involves saline fluids that have a distinctive magmatic chemistry, i.e., Cu and Fe bearing. We note also that Reaction 3 produces CO₂ gas, resulting in substantial volume increase. Thus where calcite is a reactant, SO₂ gas scrubbing is potentially explosive and would be associated in nature with extensive rock fracturing.

In our experiments, saturation in sulfides and sulfates is achieved in the pore spaces of the calcite host. It is likely that in natural settings, saturation is not achieved at the reaction site. Instead, sulfide and sulfate precipitation could occur at shallower, cooler depths as reaction products move away from the site of reaction and precipitate in fractures. In either case the reactions observed in our experiments on time scales of just 2 h testifies to the efficacy of SO₂ reactions and their potential as ore-forming processes.

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