



RESEARCH LETTER

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Key Points:

- Almost one half of sulfur from Bezymianny volcano is emitted as sulfuric acid
- Catalytic oxidation of SO₂ occurs inside the volcanic dome
- High primary sulfate results in underestimation of the total sulfur flux from a volcano

Supporting Information:

- Text S1, Figures S1–S5, and Tables S1–S4

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High emission rate of sulfuric acid from Bezymianny volcano, Kamchatka

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Abstract High concentrations of primary sulfuric acid (H₂SO₄) in fumarolic gases and high emission rate of sulfuric acid aerosol in the plume were measured at Bezymianny volcano, an active dome-growing andesitic volcano in central Kamchatka. Using direct sampling, filter pack sampling, and differential optical absorption spectroscopy measurements, we estimated an average emission of H₂SO₄ at 243 ± 75 t/d in addition to an average SO₂ emission of 212 ± 65 t/d. The fumarolic gases of Bezymianny correspond to arc gases released by several magma bodies at different stages of degassing and contain 25–92% of entrained air. H₂SO₄ accounts for 6–87 mol% of the total sulfur content, 42.8 mol% on average, and SO₂ is the rest. The high H₂SO₄ in Bezymianny fumaroles can be explained by catalytic oxidation of SO₂ inside the volcanic dome. Because sulfate aerosol is impossible to measure remotely, the total sulfur content in a plume containing significant H₂SO₄ may be seriously underestimated.

1. Introduction

Sulfur dioxide SO₂ is the second or third most abundant component and is the major sulfur component in high-temperature volcanic gases. A distinctive absorption spectrum between 280 and 320 nm and low background concentrations in the atmosphere enable remote ground-based and satellite spectroscopic measurements of SO₂ fluxes from volcanoes [Stoiber *et al.*, 1983; Manatt and Lane, 1993; Galle *et al.*, 2003; McGonigle and Oppenheimer, 2003]. Such continuous and discrete measurements are now routinely performed worldwide to monitor volcanic activity and to assess the geochemical and environmental impact of volcanic degassing [e.g., Galle *et al.*, 2010]. Fluxes of H₂O, CO₂, HCl, and some other components can be estimated remotely using open-path Fourier transform infrared (FTIR) spectrometers or via a combination of SO₂ flux data obtained by differential optical absorption spectroscopy (DOAS) with data on the gas composition measured by multigas sensors, direct sampling, or filter pack sampling [e.g., Fischer *et al.*, 1998; Lopez *et al.*, 2013].

In addition to SO₂, volcanic gas can contain sulfur in all possible oxidation states from –2 to +6, depending on temperature, pressure, magma redox conditions, gas-rock interaction, and possible incorporation of atmospheric air. Primary gases exsolved from magma have low oxygen fugacity close to Ni-NiO buffer [Symonds *et al.*, 1994]; i.e., they are reduced. The SO₂/H₂S ratio of the gas released from magma or lava decreases upon cooling under quasi-closed conditions and increases due to depressurization of the gas during degassing [e.g., Aiuppa *et al.*, 2005, and references therein; de Moor *et al.*, 2013]. When there is no direct air entrainment, mixing with meteoric vapor, even in 1:1 proportion with magmatic vapor, does not change SO₂/H₂S significantly, because the redox capacity of the volcanic vapor with 2–3 mol% of sulfur species is sufficient to consume O₂ with a concentration in meteoric vapor of ~ 5 · 10^{–4} mol%. At >500°C, the equilibrium concentrations of species other than SO₂ and H₂S are low [e.g., Symonds and Reed, 1993] and do not change significantly with increased meteoric vapor. However, when pure air is added to the volcanic gas, the redox conditions drastically change; oxygen becomes the main oxidant, and the equilibrium composition of sulfur species changes: SO₃ and H₂SO₄ vapor become the major sulfur components (see section 4.3).

A significant amount of air is entrained to volcanic gases through fractured rocks. Air oxygen oxidizes S(IV) to S(VI), but real speciation of sulfur for air-rich fumarolic gases is poorly constrained because of the difficulties of the sampling procedure. Giggenbach bottles [Giggenbach, 1975] cannot be used for direct sampling of air-rich gases. Multigas sensors allow to measure SO₂ in diluted gas-air mixtures but do not respond to the SO₃/H₂SO₄ vapors and aerosol. Two useful methods are bubbler traps with alkaline solution

[e.g., Taran *et al.*, 2001] and filter packs [e.g., Aiuppa *et al.*, 2002] and a combination of a filter with tube diffusive samplers [Aiuppa *et al.*, 2004; Ferm and Rodhe, 1997]. These methods do not allow precise measurements of sulfur speciation in the gas due to possible oxidation of HS^- and SO_3^{2-} ions in solution or on a filter in the presence of air [Möller, 1980; Huie, 1986; Saxena and Seigneur, 1987]. However, filter packs separate particulate (mostly sulfates) and gaseous (mostly SO_2) forms of sulfur [Allen *et al.*, 2000, 2002; de Moor *et al.*, 2013]. A significant excess fraction of SO_4^{2-} ions was reported in alkaline traps from Colima volcano [Taran *et al.*, 2001]. Although this can be connected with the presence of H_2SO_4 in Colima gases, oxidation of the sulfite ion SO_3^{2-} in the alkaline solution obviously occurred, obscuring the real concentrations of sulfuric acid in the gas. The sulfite ion can readily undergo oxidation in an alkaline solution [e.g., Linek and Mayrhoferova, 1970; Sivaji and Murty, 1982, and references therein], especially in the presence of transition metal ions [Huie, 1986; Shaikh and Zaidi, 1998]. Such transition metals (Fe, Co, and Cu) are available directly from fumarolic gases on degassing domes [Allen *et al.*, 2000; Taran *et al.*, 2001], including Bezymianny (supporting information Table S4).

Primary sulfate aerosol emitted directly from the volcanic vent has been reported for several volcanoes. At Masaya (Nicaragua), the in-plume gas phase/aerosol mass ratio for sulfur was 458 on average, with low absolute concentrations of particulate sulfate at a level of $\sim 0.1 \text{ mg/m}^3$ [Allen *et al.*, 2002]. Approximately the same low contents of particulate sulfate were measured in the Etna plume [Andres *et al.*, 1993; Aiuppa *et al.*, 2003]. Hobbs *et al.* [1991] reported that less than 0.1% SO_2 was oxidized to sulfate in a plume from the 1990 eruptions of Mount Redoubt. Mather *et al.* [2004b] reported that the sulfate aerosol fraction in the Lascar and Villarrica (Chile) plumes accounted for 1–2% of the total sulfur content or $0.08\text{--}0.5 \text{ mg/m}^3$. Similar amounts of sulfate aerosol ($0.006\text{--}0.2 \text{ mg/m}^3$) were measured by Mather *et al.* [2004a] in near-source emissions from Vulcano and Stromboli in Italy. To our knowledge, the only paper to report a relatively high content of primary sulfate aerosol in fumarolic gases or an early plume of Soufriere Hills volcano, Lesser Antilles, was Allen *et al.* [2000]. They measured in emissions from Castle Peak very low gas phase/aerosol mass ratio of 1.39 simultaneously with a high absolute content of particulate sulfuric acid of $\sim 2.3 \text{ mg/m}^3$. Both Colima and Soufriere Hills, like Bezymianny, are volcanoes with active extrusive domes.

SO_2 in the plume gradually oxidizes in the gaseous phase, in water droplets and adsorbed on solid particles [Sander and Seinfeld, 1976; Möller, 1980; Saxena and Seigneur, 1987; Eatough *et al.*, 1994]. Homogeneous oxidation in the gaseous phase occurs primarily by hydroxyl radical OH, but this mechanism is relatively slow and removes 1–10% of SO_2 per hour, depending on temperature and relative humidity [Möller, 1980; Eatough *et al.*, 1994; McGonigle *et al.*, 2004]. Homogeneous oxidation of SO_2 in the aqueous phase is more efficient [e.g., Eatough *et al.*, 1994; Feichter *et al.*, 1996, and references therein] and can remove up to 100% of SO_2 within an hour [Eatough *et al.*, 1994] if SO_2 is emitted into an atmospheric cloud. The SO_2 -to-particle reaction can be fast (removes up to $\sim 30\%$ of SO_2 per hour) [Möller, 1980] but is limited by a low free surface of available particles. McGonigle *et al.* [2004] concluded that the observed depletion rate of SO_2 in a plume in the absence of clouds has little influence on the accuracy of SO_2 remote measurements. All oxidation mechanisms of SO_2 eventually result either in droplets of diluted sulfuric acid or in solid particulate sulfates.

Sulfuric acid has a high boiling point (338°C). If fumarolic gas contains sulfuric acid vapor, it condenses upon cooling into fine aerosol. Similarly to any small particles, sulfate aerosol in a plume absorbs and scatters light depending on the particle size and regardless of the composition. This means that the concentration of sulfuric acid cannot be measured remotely using spectroscopic methods. It was considered until now that primary sulfate aerosol occurs in volcanic plumes in some rare cases and in small amounts. Here we report new data on a high emission rate of primary sulfate aerosol (sulfuric acid) from Bezymianny volcano, Kamchatka. We show that the fumarolic gases of Bezymianny contain a significant or even prevailing fraction of hexavalent sulfur, in the form of either molecular sulfuric acid H_2SO_4 or sulfur trioxide SO_3 ; the latter also forms sulfuric acid aerosol because of the fast reaction with water. All sulfur emitted as sulfuric acid remains unaccounted for during remote measurements of SO_2 . The high fraction of S(VI) in the gas can thus result in underestimation of the total sulfur emission from a volcano.

2. Bezymianny Volcano

Bezymianny ($55^\circ 59' \text{N}$, $160^\circ 36' \text{E}$, 2890 m above sea level) is an active andesitic stratovolcano near the northernmost termination of the Kurile-Kamchatka volcanic arc (Figures 1a and 1b). Bezymianny is renowned for

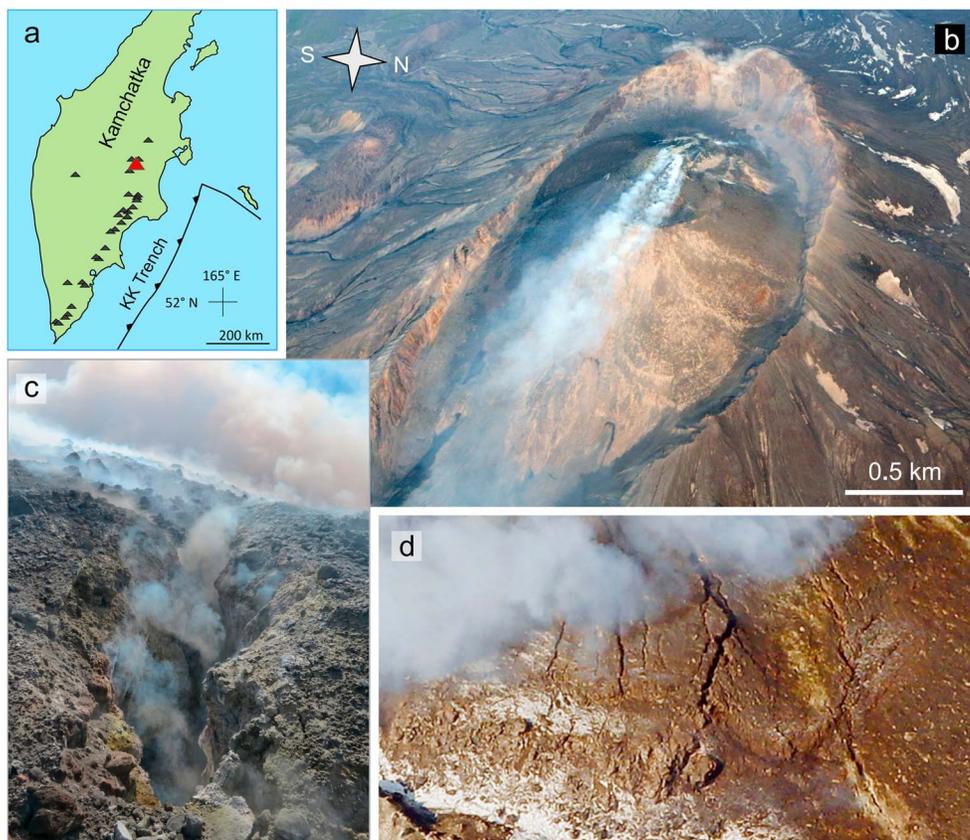


Figure 1. (a) Location of Bezymianny volcano (red); (b) an aerial view of the 1956 eruptive crater and the degassing active dome of Bezymianny; (c) a wide open degassing fracture with thick fume of sulfuric acid aerosol in the background; (d) fractured lava carapace of the Bezymianny dome near its summit. Depending on droplet size, sulfuric acid aerosol changes its color from intense blue (the smallest droplets) to gray (the largest ones). A bluish tint and fuzzy edges (Figure 1b) are two distinct features of a plume containing large amounts of sulfuric acid; steam clouds are typically neutral white or gray and have sharp edges. Figures 1b and 1d courtesy of Alexey Nagaev.

its awakening in October 1955 after a >1000 year period of dormancy followed by the catastrophic eruption on 30 March 1956. Since 1956, Bezymianny has been in the state of persistent degassing (Figure 1 and supporting information Figures S1 and S2). The degassing periods alternate with short explosive eruptions occurring approximately 1–2 times per year, accompanied by pyroclastic flows and effusion of viscous lava [e.g., *Girina*, 2013, and references therein]. The edifice of Bezymianny is a truncated cone with a 1.3 km wide horseshoe explosive crater and a ~ 1 km high active dome inside the crater (Figure 1b). The eruptive products of Bezymianny range from andesite to basaltic andesite (~ 56.8 – 60.4 wt % SiO_2) [Turner *et al.*, 2013]. In 2012, a moderate Pelean eruption (VEI 2, plume height 8 km) took place on 9 March, 4.5 months prior to our field work. At the time of the field work, from 21 July to 18 August 2012, Bezymianny emitted gas with temperatures from ~ 140 to 760°C from numerous fumaroles and fractures located on the dome summit and on its slopes (Figures 1b and 1c). Simultaneously, a viscous flow of andesitic lava was ejected and creeping down the slope at a rate of several centimeters per hour. On 2 September 2012, 2 weeks after our last visit to the dome, a strong Pelean eruption (VEI 3, plume height 12 km) destroyed the majority of the fumarolic fields and formed a new crater 200×300 m on the dome summit (supporting information Figure S2).

3. Measurements

Emission of SO_2 was determined using two ground-based scanning mini-DOAS instruments such as used in Network for Observation of Volcanic and atmospheric Change [Galle *et al.*, 2010]. Because the measurements require information about plume height, plume direction, and plume speed, measurements of these parameters

Table 1. Temperatures, Fractions of Air, Magmatic Gas and S(VI) (mol% in the Total Discharge), and Chemical Composition (mmol/mol in the Gas Without Air) in Fumarolic Gases From the Dome of Bezymianny

	T (°C)	% Air	% Gas Without Air	H ₂ O (mmol/mol)	CO ₂ (mmol/mol)	S Total (mmol/mol)	HCl (mmol/mol)	% S(VI)
Minimum	140	25.4	8	969	1.8	0.6	0.9	5.9
Maximum	760	92	74.6	997	17.7	15.0	15.9	87.1
Average	474	52.8	47.2	984	7.2	6.2	4.8	42.8

were also conducted using optical remote sensing methods. An improved concept for plume speed measurements was tested using a cylindrical lens yielding a rectangular elongated field of view. The method was further extended to provide flux measurements with high time resolution (1 s). In addition, the emission was quantified by traversing under the plume using a mobile DOAS instrument. For the first 4 days of field work, the weather conditions were good, whereas after 25 July, the conditions worsened, with rain, fog, and even snow. Nevertheless, the results from 22 to 30 July 2012 indicate a relatively stable SO₂ degassing of approximately 212 ± 65 t/d (2.45 ± 0.75 kg/s), which is consistent with previous measurements. Earlier, Lopez *et al.* [2013] measured the SO₂ flux from Bezymianny in 2007–2009 at 140–280 t/d, 200 t/d on average.

Four gas samples from Bezymianny fumaroles were collected in September 2010, and 17 gas samples with 7 filter pack samples were collected simultaneously in August 2012. Standard Giggenbach bottles were used in 2010 to collect fumarolic gases that were only slightly contaminated with air. In 2012, all accessible fumaroles contained significant air, thus making Giggenbach bottles useless. For this reason, we pumped gas through two consecutive traps partially filled with different absorbing solutions. Each fumarole was examined using three methods: (1) traps with alkaline 4 N NaOH solution to collect acid species, (2) traps with 5% BaCl₂-10% HCl-20% glycerol solution to collect solely sulfuric acid, and (3) empty traps for condensate collection. Gas was pumped through the traps at a flow rate of ~5 L/min air (measured by a rotameter after the traps and the pump) until the volume gain of the condensed solution reached 15–20 mL. The sampling procedure in each of the methods lasted 5–40 min, depending on the air/gas ratio. Seventeen fumaroles were sampled in this manner. The solution of BaCl₂ in diluted HCl with glycerol absorbs sulfuric acid but does not react with SO₂ (see supporting information for details). The comparison with the total sulfur content in the alkaline solution provides fractions of hexavalent and tetravalent sulfur in the gas.

Filter pack samples were collected at different points of the dome summit to obtain in-plume H₂SO₄/SO₂ ratios. The filter pack assembly contained 25 mm Nuclepore 0.45 μm filter followed by two acetate cellulose filters impregnated with NaOH. Gas was pumped through the filters at a flow rate of ~5 L/min for 1–4 min. The short duration of sampling was enough due to the high concentrations of aerosol and acid gases in the plume. The majority of H₂SO₄ droplets were stopped by the Nuclepore filter, whereas acid gaseous species (SO₂ and HCl) were absorbed by NaOH. A full description of the sampling procedure is given in the supporting information.

4. Results and Discussion

4.1. Bezymianny Gas Composition

Bezymianny fumarolic gases (Table 1 and supporting information Tables S1 and S2) contained a variable amount of air. The lowest air content of < 1 mmol/mol O₂ and high H₂S were measured in the 2010 gas samples; H₂S accounted for 6–8 mol% of the total sulfur content. The 2012 samples contained 25.4–92.0 mol% air, 52.8 mol% on average, and no H₂S was detected. Without air, Bezymianny gases in 2012 had variable concentrations of water and acid species (Figure 2a). Such variations can be accounted for by simultaneous degassing of several magma bodies at different stages of degassing, possibly located at different depths [Taran *et al.*, 2001; Lopez *et al.*, 2013]. Gases with the highest temperatures (>600°C) corresponded to diluted “mean arc gas” [Shinohara, 2013; Taran and Zelenski, 2014] with 968–975 mmol/mol H₂O and CO₂:S:Cl ratios close to 2:1:0.2. The δD-δ¹⁸O plot for Bezymianny (Figure 2b) demonstrates a minor role of mixing with meteoric water but the visible trend of degassing.

4.2. High Sulfuric Acid Levels in Bezymianny Gas

High concentrations of H₂SO₄ were measured in 2012 in the fumarolic gases and within the plume over the Bezymianny dome (Tables 1 and S2). The concentrations of H₂SO₄ in the fumarolic gases

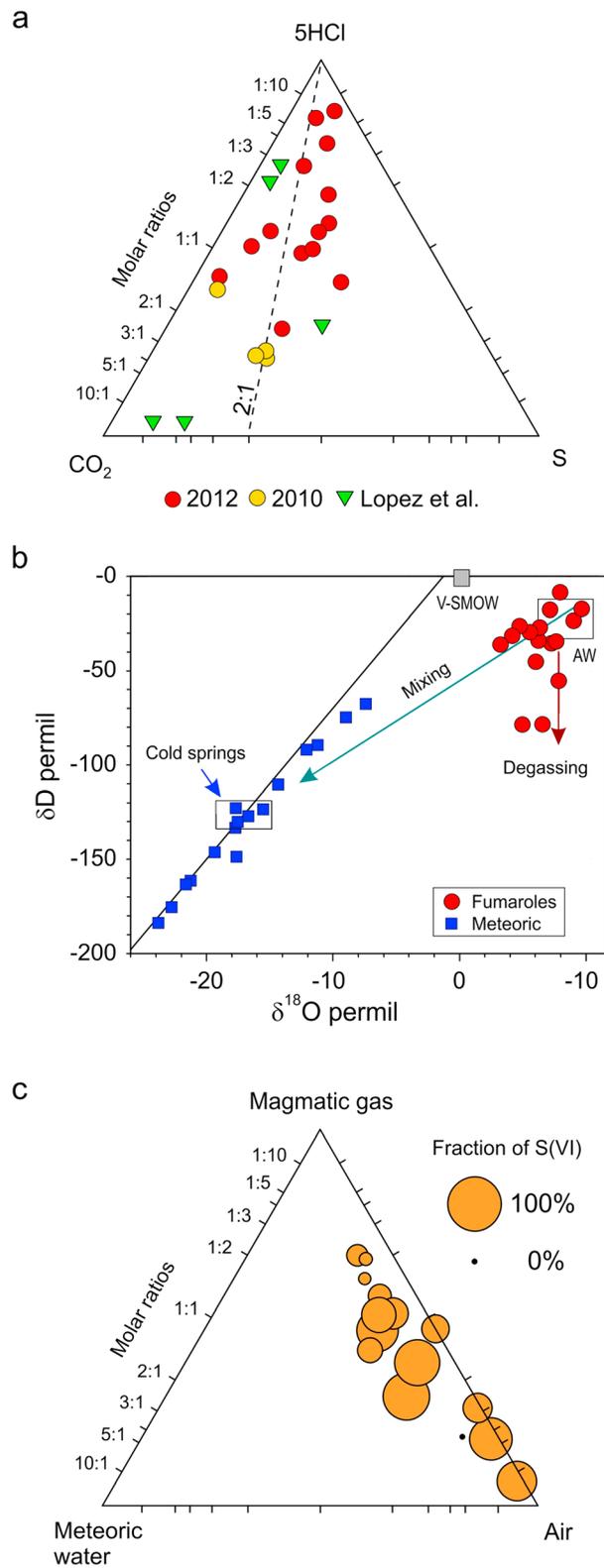


Figure 2. Bezymianny volcanic gases. (a) CO₂-HCl-S diagram; (b) δD versus δ¹⁸O diagram for volcanic gases and meteoric water; (c) meteoric water-magmatic gas-air, the circle area corresponds to the fraction of S(VI) in the gas. Figures 2a and 2c are on mmol/mol basis, and Figure 2b is on per mil basis.

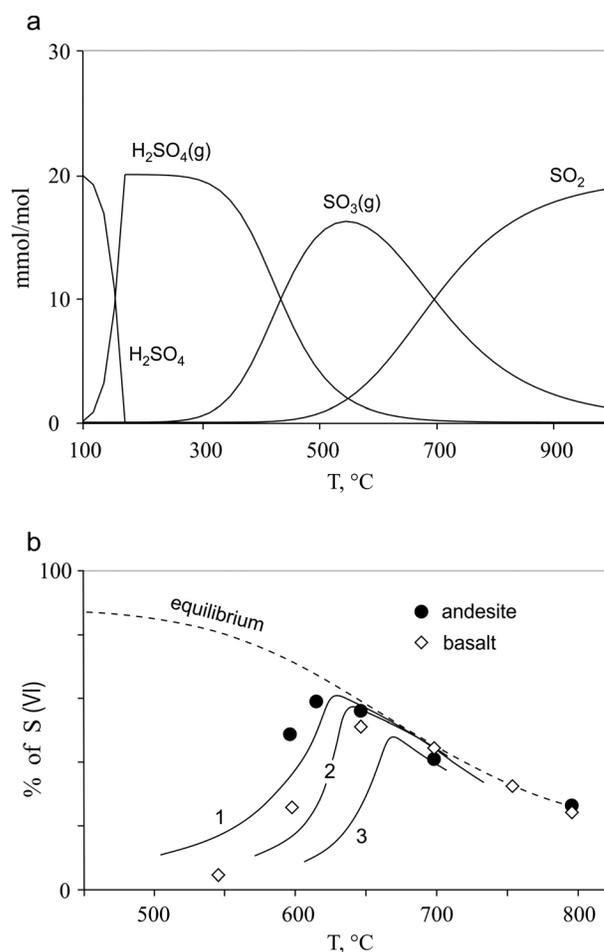


Figure 3. (a) Calculated equilibrium concentrations of sulfur species in a 50:50 mixture of magmatic gas and air, similar to the gas of Bezymianny. Hexavalent sulfur in the forms of gaseous SO_3 and gaseous and liquid H_2SO_4 dominates below 700°C . (b) Catalytic activity of natural andesite and basalt in the oxidation of SO_2 by air oxygen occurs above 600°C . Below this temperature, the catalytic activity of silicate rocks decreases and becomes almost zero below 500°C . Industrial Fe_2O_3 -based catalysts (curves 1–3) show similar behavior [Boreskov, 1954].

in terms of equilibrium thermodynamics and kinetics. The equilibrium compositions were computed using the Outokumpu HSC 6.1 Chemistry code [Roine, 2007]. Gibbs energy minimization was performed for the H-O-S-C-N system from 100 to 1000°C with a model consisting of 120 species. The used system represents a 50:50 mixture of “magmatic gas” and air that is close to the average composition of the fumarolic gas of Bezymianny. The modeling shows that SO_2 dominates at the highest temperature (Figure 3a). At approximately 700°C , the equilibrium amounts of SO_2 and SO_3 become equal. Gaseous H_2SO_4 appears with a further decrease of temperature and prevails below 440°C . Liquid (aerosol) H_2SO_4 and $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ are the main sulfur compounds below 260°C . Homogeneous oxidation of SO_2 to SO_3 (without a catalyst) occurs according to the following reaction:



The reaction has a very slow rate even at high temperatures of several hundred degrees Celsius [Boreskov, 1954; Sander *et al.*, 1984]. Papers on the behavior of sulfur dioxide in the atmosphere [e.g., Sander and Seinfeld, 1976; Möller, 1980] merely do not consider the direct interaction of SO_2 and O_2 . On the contrary, the catalytic oxidation of SO_2 by oxygen is widely used in industry. Among other industrial catalysts, iron

(which included magmatic gases and incorporated air) ranged from 1.5 to 20 g/kg, 8.3 g/kg on average. Hexavalent sulfur accounted for 5.9–87.1 mol% of the total sulfur content, 42.8 mol% on average. After mixing with air and cooling, such gas forms a thick fume (Figures 1b–1d and S1). The moderately diluted plume measured on the dome summit contained $4\text{--}18\text{ mg/m}^3$ H_2SO_4 , 13 mg/m^3 on average, which corresponds to a dilution ratio of approximately 1:1000. The highest concentration of sulfate aerosol of $\sim 120\text{ mg/m}^3$ was measured in the plume in a close proximity of a powerful 540°C fumarole. In comparison to direct sampling, filter packs showed slightly higher proportions of S(VI) in the plume that ranged from 15.0 to 74.6 mol%, 54.2 mol% on average. In-plume measurements validate our measurements in fumaroles because of the weight-averaging of fumarolic emissions with different outputs and species ratios. However, the absolute and relative concentrations of H_2SO_4 were different, even in the plume (supporting information Table S3). The measured concentrations of primary sulfate aerosol in the Bezymianny plume are 2–60 times higher than the highest concentrations reported for the Soufriere Hills volcano [Allen *et al.*, 2000]. The fraction of hexavalent sulfur lacks correlations with any other gas species and displays a weak negative correlation with temperature.

4.3. Catalytic Oxidation of SO_2 as a Source of SO_3 and H_2SO_4

The occurrence of sulfuric acid in fumarolic gases with entrained air can be described

(III) oxide (Fe_2O_3) was used earlier in sulfuric acid production. Because iron oxides are important components of volcanic rocks, the rock itself can play the role of the catalyst. Several attempts are known to use magnetite Fe_3O_4 or even silicate rocks as the industrial catalysts for SO_2 oxidation [Boreskov, 1954].

According to our laboratory experiments [Zelenski *et al.*, 2014], oxidation of SO_2 inside the Bezymianny dome can occur on a thin layer composed of Fe_2O_3 , $\text{Fe}_2(\text{SO}_4)_3$, and Na-K-Mg-Ca-Al sulfates, which covers the fracture walls within the dome (see supporting information Text S1 (Implementation of Experiments) and Figures S3–S5). The catalyst appears within several hours on a surface of rock fragments under the influence of the reaction mixture containing air, H_2O , SO_2 , and HCl. The role of HCl is unclear, but the catalyst does not form (or forms extremely slowly) in its absence. Altered andesite has better catalytic activity at lower temperatures in comparison to basalt (Figure 3b). Oxidation of SO_2 by air oxygen in the presence of crushed andesite is highly efficient. The reaction mixture at 600–700°C reaches equilibrium within seconds. Fast kinetics in the presence of the catalyst suggests that the reaction rate inside the volcano is controlled by convective transport of the reaction mixture toward the fracture walls. Widely opened fractures or high ascending rates of the gas decrease the efficiency of the catalysis.

The suggested model of the catalytic oxidation of SO_2 by entrained air inside a volcanic dome requires a permeable (fractured) dome structure that allows air to penetrate deep inside. The appropriate structures can occur inside a dome with endogenous inflation, where viscous lava is injected into a dome interior causing expanding and fracturing of a brittle outer carapace [Calder *et al.*, 2015]. Parts of the carapace break apart, forming surrounding loose talus [Hale, 2008], which is also permeable to air. The present-day Bezymianny dome grows over an old dome, partially broken by the 1985 explosion. As of 2012, the summit area of Bezymianny was a fractured lava carapace (Figure 1d) partially overlapped by several short lava flows of less viscous basaltic andesite composition. Similar deep fractures are visible at the dome bottom where talus is absent. Air is heated inside the dome and rises due to free convection to escape from the summit area. During this movement, air mixes with gases released from magma. If the gas-rock interaction is long enough, then the surfaces of the fractures within a hot zone are covered by a layer of iron oxide + sulfates that catalyzes the reaction (1). Degassing conditions on a dome can change after an eruption or block movements. For example, many fumaroles in 2010 emitted almost pure magmatic gas, whereas all fumaroles in 2012 contained at least 25 mol% of air. Similar processes can occur on other volcanoes, especially andesitic domes with fractured internal structure. In particular, Soufriere Hills and Colima volcanoes, where lava is constantly extruding [Hale *et al.*, 2009; Lavallée *et al.*, 2012] and high concentrations of primary sulfate aerosol [Allen *et al.*, 2000] or elevated sulfate content in the gas [Taran *et al.*, 2001] were actually measured, are two possible candidates.

4.4. Implications of High H_2SO_4 Content in a Plume

Two evident implications of high primary H_2SO_4 are underestimation of the total sulfur emission from a volcano and anomalous concentrations of sulfate aerosol in the troposphere downwind from the volcano. Fumarolic gas with a high content of sulfuric acid vapor produces thick and very stable fumes of sulfate aerosol (Figures 1b, 1c, and S1). Sulfate fume is clearly visible and has bluish or gray color, depending on the average droplet size. However, aerosol cannot be measured either by DOAS or FTIR spectrometry. This results in significant underestimation of the total sulfur flux from a volcano in the presence of sulfate aerosol, if the sulfur flux was calculated solely from remote SO_2 measurements. For example, Bezymianny in July 2012 emitted 212 t/d SO_2 , which corresponds to 106 t/d of sulfur. In addition, ~243 t/d of primary H_2SO_4 was emitted, which totals 79 t/d of sulfur that was emitted but was not measured remotely. Therefore, the measured sulfur flux from Bezymianny should be multiplied by a factor of 1.75. If emissions of other gas components (H_2O , CO_2 , and HCl) are evaluated on the basis of direct sampling coupled with remote measurements of the SO_2 flux (using component/total sulfur ratios), this can also result in corresponding underestimation of the related components. Abundant primary sulfuric acid affects further chemical evolution of gaseous species and particulate matter in the volcanic plume and environment in the volcano vicinities.

5. Conclusions

The chemical composition of Bezymianny fumarolic gases is determined not only by chemical and physical properties of the degassing magma but also, and to a large extent, by the entraining of ambient air and intense gas-rock interaction. The latter occurs as a catalytic effect of the direct oxidation of SO_2 by oxygen,

a very slow reaction in the absence of catalysis. As a result, Bezymianny gases contain up to half of the sulfur in the hexavalent form (sulfur trioxide and sulfuric acid). The high emission rate of primary H_2SO_4 can result in serious underestimation of the total sulfur flux from a volcano, if the estimate of the sulfur flux was made using remote measurements. High sulfuric acid in volcanic emissions can occur more frequently than was formerly recognized, especially on persistently degassing fractured domes. The role of primary sulfate aerosol in volcanic plumes is insufficiently studied because of difficulties in its detection.

Acknowledgments

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References

- Aiuppa, A., C. Federico, A. Paonita, G. Pecoraino, and M. Valenza (2002), S, Cl and F degassing as an indicator of volcanic dynamics: The 2001 eruption of Mount Etna, *Geophys. Res. Lett.*, *29*(11), 1–4, doi:10.1029/2002GL015032.
- Aiuppa, A., G. Dongarra, M. Valenza, C. Federico, and G. Pecoraino (2003), Degassing of trace volatile metals during the 2001 eruption of Etna, in *Volcanism and the Earth's Atmosphere*, *Geophys. Monogr. Ser.*, vol. 139, edited by A. Robock and C. Oppenheimer, pp. 41–54, AGU, Washington, D. C., doi:10.1029/139GM03.
- Aiuppa, A., S. Bellomo, W. D'Alessandro, C. Federico, M. Ferm, and M. Valenza (2004), Volcanic plume monitoring at Mount Etna by diffusive (passive) sampling, *J. Geophys. Res.*, *109*, D21308, doi:10.1029/2003JD004481.
- Aiuppa, A., S. Inguaggiato, A. J. S. McGonigle, M. O'Dwyer, C. Oppenheimer, M. J. Padgett, D. Rouwet, and M. Valenza (2005), H_2S fluxes from Mt. Etna, Stromboli, and Vulcano (Italy) and implications for the sulfur budget at volcanoes, *Geochim. Cosmochim. Acta*, *69*, 1861–1871, doi:10.1016/j.gca.2004.09.018.
- Allen, A. G., P. Baxter, and C. Ottley (2000), Gas and particle emissions from Soufrière Hills Volcano, Montserrat, West Indies: Characterization and health hazard assessment, *Bull. Volcanol.*, *2*, 8–19, doi:10.1007/s004450050287.
- Allen, A. G., C. Oppenheimer, M. Ferm, P. J. Baxter, L. A. Horrocks, B. Galle, A. J. S. McGonigle, and H. J. Duffell (2002), Primary sulfate aerosol and associated emissions from Masaya Volcano, Nicaragua, *J. Geophys. Res.*, *107*(D23), 1–8, doi:10.1029/2002JD002120.
- Andres, R. J., P. R. Kyle, and R. L. Chuan (1993), Sulphur dioxide, particle and elemental emissions from Mount Etna, Italy during July 1987, *Geol. Rundsch.*, *82*, 687–695, doi:10.1007/BF00191496.
- Boreskov, G. K. (1954), *Catalysis in Sulfuric Acid Production* [in Russian], Goskhimizdat, Moscow-Leningrad.
- Calder, E. S., Y. Lavalleye, J. E. Kendrick, M. Bernstein (2015), Lava dome eruptions, in *The Encyclopedia of Volcanoes*, 2nd ed., edited by H. Sigurdsson et al., pp. 343–362, Academic Press, Elsevier, San Diego, Calif., doi:10.1016/B978-0-12-385938-9.00018-3.
- de Moor, J. M., et al. (2013), Sulfur degassing at Erta Ale (Ethiopia) and Masaya (Nicaragua) volcanoes: Implications for degassing processes and oxygen fugacities of basaltic systems, *Geochem. Geophys. Geosyst.*, *14*, 4076–4108, doi:10.1002/ggge.20255.
- Eatough, D. J., F. M. Caka, and R. J. Farber (1994), The conversion of SO_2 to sulfate in the atmosphere, *Isr. J. Chem.*, *34*, 301–304, doi:10.1002/ijch.199400034.
- Feichter, J., E. Kjellström, H. Rodhe, F. Dentener, J. Lelieveld, and G.-J. Roelofs (1996), Simulation of the tropospheric sulfur cycle in a global climate model, *Atmos. Environ.*, *30*, 1693–1707, doi:10.1016/1352-2310(95)00394-0.
- Ferm, M., and H. Rodhe (1997), Measurements of air concentrations of SO_2 , NO_2 and NH_3 at rural and remote sites in Asia, *J. Atmos. Chem.*, *27*, 17–29, doi:10.1023/A:1005816621522.
- Fischer, T. P., W. F. Giggenbach, Y. Sano, and S. N. Williams (1998), Fluxes and sources of volatiles discharged from Kudryavy, Kurile Islands, *Earth Planet. Sci. Lett.*, *160*, 81–96, doi:10.1016/S0012-821X(98)00086-7.
- Galle, B., C. Oppenheimer, A. Geyer, A. J. S. McGonigle, M. Edmonds, and L. A. Horrocks (2003), A miniaturised UV spectrometer for remote sensing of SO_2 fluxes: A new tool for volcano surveillance, *J. Volcanol. Geotherm. Res.*, *119*, 241–254, doi:10.1016/S0377-0273(02)00356-6.
- Galle, B., M. Johansson, C. Rivera, Y. Zhang, M. Kihlman, C. Kern, T. Lehmann, U. Platt, S. Arellano, and S. Hidalgo (2010), NOVAC—A global network for volcanic gas monitoring, network layout and instrument description, *J. Geophys. Res.*, *115*, D05304, doi:10.1029/2009JD011823.
- Giggenbach, W. F. (1975), A simple method for the collection and analysis of volcanic gas samples, *Bull. Volcanol.*, *39*, 132–145, doi:10.1007/BF02596953.
- Girina, O. (2013), Chronology of Bezymianny Volcano activity, 1956–2010, *J. Volcanol. Geotherm. Res.*, *263*, 21–40, doi:10.1016/j.jvolgeores.2013.05.002.
- Hale, A. J. (2008), Lava dome growth and evolution with an independently deformable talus, *Geophys. J. Int.*, *174*, 391–417, doi:10.1111/j.1365-246X.2008.03806.x.
- Hale, A. J., E. S. Calder, S. C. Loughlin, G. Wadge, and G. A. Ryan (2009), Modelling the lava dome extruded at Soufrière Hills Volcano, Montserrat, August 2005–May 2006. Part I: Dome shape and internal structure, *J. Volcanol. Geotherm. Res.*, *187*, 53–68, doi:10.1016/j.jvolgeores.2009.08.014.
- Hobbs, P. V., L. F. Radke, J. H. Lyons, R. J. Ferek, D. J. Coffman, and T. J. Casadevall (1991), Airborne measurements of particle and gas emissions from the 1990 volcanic eruptions of Mount Redoubt, *J. Geophys. Res.*, *96*, 18,735–18,752, doi:10.1029/91JD01635.
- Huie, R. (1986), Chemical kinetics of intermediates in the autoxidation of SO_2 , in *Fossil Fuels Utilization, Ser.*, vol. 319, edited by R. Markuszewski and B. D. Blaustein, pp. 284–292, Am. Chem. Soc., Washington, D. C., doi:10.1021/bk-1986-0319.ch023.
- Lavallée, Y., N. R. Varley, M. A. Alatorre-Ibargüenito, K. U. Hess, U. Kueppers, S. Mueller, D. Richard, B. Scheu, O. Spieler, and D. B. Dingwell (2012), Magmatic architecture of dome-building eruptions at Volcán de Colima, Mexico, *Bull. Volcanol.*, *74*, 249–260, doi:10.1007/s00445-011-0518-4.
- Linek, V., and J. Mayrhoferova (1970), The kinetics of oxidation of aqueous sodium sulphite solution, *Chem. Eng. Sci.*, *25*, 787–780, doi:10.1016/0009-2509(70)85114-4.
- Lopez, T., S. Ushakov, P. Izbekov, F. Tassi, C. Cahill, O. Neill, and C. Werner (2013), Constraints on magma processes, subsurface conditions, and total volatile flux at Bezymianny Volcano in 2007–2010 from direct and remote volcanic gas measurements, *J. Volcanol. Geotherm. Res.*, *263*, 92–107, doi:10.1016/j.jvolgeores.2012.10.015.
- Manatt, S. L., and A. L. Lane (1993), A compilation of the absorption cross-section of SO_2 from 106 to 403 nm, *J. Quant. Spectrosc. Radiat. Transfer*, *17*, 267–276, doi:10.1016/0022-4073(93)90077-U.
- Mather, T. A., C. Oppenheimer, A. G. Allen, and A. J. S. McGonigle (2004a), Aerosol chemistry of emissions from three contrasting volcanoes in Italy, *Atmos. Environ.*, *38*, 5637–5649, doi:10.1016/j.atmosenv.2004.06.017.
- Mather, T. A., V. I. Tsanev, D. M. Pyle, A. J. S. McGonigle, C. Oppenheimer, and A. G. Allen (2004b), Characterization and evolution of tropospheric plumes from Lascar and Villarrica volcanoes, Chile, *J. Geophys. Res.*, *109*, D21303, doi:10.1029/2004JD004934.

- McGonigle, A. J. S., and C. Oppenheimer (2003), Optical sensing of volcanic gas and aerosol emissions, in *Volcanic Degassing*, edited by C. Oppenheimer et al., *Geol. Soc. London Spec. Publ.*, 213, 149–168, doi:10.1144/GSL.SP.2003.213.01.09.
- McGonigle, A., P. Delmelle, C. Oppenheimer, V. I. Tsanev, T. Delfosse, H. Horton, G. Williams-Jones, and T. A. Mather (2004), SO₂ depletion in tropospheric volcanic plumes, *Geophys. Res. Lett.*, 31, L13201, doi:10.1029/2004GL019990.
- Möller, D. (1980), Kinetic model of atmospheric SO₂ oxidation based on published data, *Atmos. Environ. Part A Gen. Top.*, 14, 1067–1076, doi:10.1016/0004-6981(80)90037-2.
- Roine, A. (2007), HSC chemistry 6.1, Tech. Rep., Outotec Research Oy, Pori, Finland.
- Sander, S. P., and J. H. Seinfeld (1976), Chemical kinetics of homogeneous atmospheric oxidation of sulfur dioxide, *Environ. Sci. Technol.*, 10, 1114–1123, doi:10.1007/0-306-48390-4_2.
- Sander, U. H. F., H. Fischer, U. Rothe, and R. Kola (1984), *Sulphur, Sulphur Dioxide and Sulphuric Acid*, 1st ed., The British Sulphur Corporation Limited, London.
- Saxena, P., and C. Seigneur (1987), On the oxidation of SO₂ to sulfate in atmospheric aerosols, *Atmos. Environ.*, 21, 807–812, doi:10.1016/0004-6981(87)90077-1.
- Shaikh, A. A., and S. M. J. Zaidi (1998), Kinetics of catalytic oxidation of aqueous sodium sulfite, *React. Kinet. Catal. Lett.*, 64, 343–349, doi:10.1007/BF02475355.
- Shinohara, H. (2013), Volatile flux from subduction zone volcanoes: Insights from a detailed evaluation of the fluxes from volcanoes in Japan, *J. Volcanol. Geotherm. Res.*, 268, 46–63, doi:10.1016/j.jvolgeores.2013.10.007.
- Sivaji, K., and G. S. R. N. Murty (1982), Kinetics of sulfite oxidation reaction, *Ind. Eng. Chem. Fundam.*, 21, 344–352, doi:10.1021/i100008a005.
- Stoiber, R. E., L. L. Malinconico, and S. N. Williams (1983), Use of the correlation spectrometer at volcanoes, in *Forecasting Volcanic Events*, edited by H. Tazieff and J.-C. Sabroux, pp. 425–444, Elsevier, Amsterdam-New York.
- Symonds, R. B., and M. H. Reed (1993), Calculation of multicomponent chemical equilibria in gas-solid-liquid systems: Calculation methods, thermochemical data, and applications to studies of high-temperature volcanic gases with examples from Mount St. Helens, *Am. J. Sci.*, 293, 758–864, doi:10.2475/ajs.293.8.758.
- Symonds, R. B., W. I. Rose, G. J. S. Bluth, and T. M. Gerlach (1994), Volcanic gas studies: Methods, results, and applications, in *Volatiles in Magmas, Rev. Mineral. Geochem.*, vol. 30, edited by M. R. Carroll and J. R. Holloway, pp. 1–66, Mineral. Soc. of Am., Washington, D. C.
- Taran, Y. A., A. Bernard, J.-C. Gavilanes, E. Lunezheva, A. Cortes, and M. A. Armienta (2001), Chemistry and mineralogy of high-temperature gas discharges from Colima volcano, Mexico. Implications for magmatic gas-atmosphere interaction, *J. Volcanol. Geotherm. Res.*, 108, 245–264, doi:10.1016/S0377-0273(00)00289-4.
- Taran, Y., and M. Zelenski (2014), Systematics of water isotopic composition and chlorine content in arc-volcanic gases, in *The Role of Volatiles in the Genesis, Evolution and Eruption of Arc Magmas*, edited by G. F. Zellmer, M. Edmonds, and S. M. Straub, *Geol. Soc. London Spec. Publ.*, 410, 237–262, doi:10.1144/SP410.5.
- Turner, S. J., P. Izbekov, and C. Langmuir (2013), The magma plumbing system of Bezymianny Volcano: Insights from a 54 year time series of trace element whole-rock geochemistry and amphibole compositions, *J. Volcanol. Geotherm. Res.*, 263, 108–121, doi:10.1016/j.jvolgeores.2012.12.014.
- Zelenski, M., B. Galle, and Y. Taran (2014), Catalytic oxidation of SO₂ inside volcanic domes, paper presented at 12th Field Workshop on Volcanic Gases, AMTC, Atacama, Chile.