



HAL
open science

Volcanic sulfate aerosol formation in the troposphere

Erwan Martin, Slimane Bekki, Charlotte Ninin, Ilya Bindeman

► **To cite this version:**

Erwan Martin, Slimane Bekki, Charlotte Ninin, Ilya Bindeman. Volcanic sulfate aerosol formation in the troposphere. *Journal of Geophysical Research: Atmospheres*, 2014, 119 (22), pp.12,660-12,673. 10.1002/2014JD021915 . hal-01103142

HAL Id: hal-01103142

<https://hal.sorbonne-universite.fr/hal-01103142>

Submitted on 14 Jan 2015

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

RESEARCH ARTICLE

10.1002/2014JD021915

Key Points:

- Topospheric volcanic sulfates are mainly isotopically mass dependent
- In the troposphere, volcanic SO₂ is oxidized by OH and/or TMI-catalyzed O₂
- The study of volcanic sulfate allow to "probe" the atmospheric chemistry

Correspondence to:

E. Martin,
erwan.martin@upmc.fr

Citation:

Martin, E., S. Bekki, C. Ninin, and I. Bindeman (2014), Volcanic sulfate aerosol formation in the troposphere, *J. Geophys. Res. Atmos.*, 119, doi:10.1002/2014JD021915.

Received 29 APR 2014

Accepted 10 OCT 2014

Accepted article online 16 OCT 2014

Volcanic sulfate aerosol formation in the troposphere

Erwan Martin^{1,2}, Slimane Bekki³, Charlotte Ninin^{1,2}, and Ilya Bindeman⁴¹Sorbonne Universités, UPMC Université Paris 06, UMR 7193, ITeP, Paris, France, ²CNRS, UMR 7193, ITeP, Paris, France,³Sorbonne Universités, UPMC Université Paris 06; Université Versailles St.-Quentin, CNRS/INSU, LATMOS-IPSL, Paris, France,⁴Department of Geological Sciences, University of Oregon, Eugene, Oregon, USA

Abstract The isotopic composition of volcanic sulfate provides insights into the atmospheric chemical processing of volcanic plumes. First, mass-independent isotopic anomalies quantified by $\Delta^{17}\text{O}$ and to a lesser extent $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ in sulfate depend on the relative importance of different oxidation mechanisms that generate sulfate aerosols. Second, the isotopic composition of sulfate ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$) could be an indicator of fractionation (distillation/condensation) processes occurring in volcanic plumes. Here we present analyses of O- and S isotopic compositions of volcanic sulfate absorbed on very fresh volcanic ash from nine moderate historical eruptions in the Northern Hemisphere. Most of our volcanic sulfate samples, which are thought to have been generated in the troposphere or in the tropopause region, do not exhibit any significant mass-independent fractionation (MIF) isotopic anomalies, apart from those from an eruption of a Mexican volcano. Coupled to simple chemistry model calculations representative of the background atmosphere, our data set suggests that although H₂O₂ (a MIF-carrying oxidant) is thought to be by far the most efficient sulfur oxidant in the background atmosphere, it is probably quickly consumed in large dense tropospheric volcanic plumes. We estimate that in the troposphere, at least, more than 90% of volcanic secondary sulfate is not generated by MIF processes. Volcanic S-bearing gases, mostly SO₂, appear to be oxidized through channels that do not generate significant isotopically mass-independent sulfate, possibly via OH in the gas phase and/or transition metal ion catalysis in the aqueous phase. It is also likely that some of the sulfates sampled were not entirely produced by atmospheric oxidation processes but came out directly from volcanoes without any MIF anomalies.

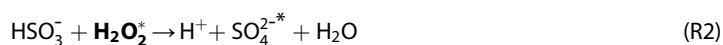
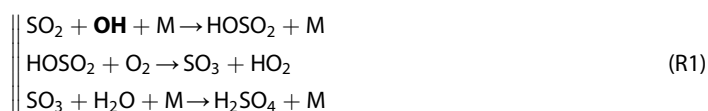
1. Introduction

Volcanic eruptions release large but variable amounts of gas (such as H₂O, CO₂, SO₂, and halogens) into the atmosphere. Sulfur-bearing gases (mainly SO₂, H₂S, and COS) have a direct impact on the atmosphere and climate, as their oxidation in the atmosphere to SO₃ and H₂SO₄ forms sulfate aerosols that disturb the radiative balance of the atmosphere [Forster and Ramaswamy, 2007; Rap et al., 2013]. Furthermore, sulfate particles also act as cloud condensation nuclei, affecting clouds and climate indirectly [Intergovernmental Panel on Climate Change, 2007; Schmidt et al., 2012a, 2012b]. Therefore, a detailed understanding of the sulfur cycle and the role played by volcanic eruptions is critical for accurate estimation of the impact of sulfur emissions on sulfate aerosol distribution and hence on climate [e.g., Robock, 2004; Schmidt et al., 2012a, 2012b]. Large pyroclastic eruptions having a volcanic explosivity index (VEI) ≥ 4 are the most studied in terms of climate impact because they release huge amounts of sulfur (e.g., 20 Mt for the Mount Pinatubo eruption in 1991) into the stratosphere, where they stay for about a year typically [e.g., Robock, 2000], instead of a week in the troposphere, where the hydrologic cycle washes them down. As a result, they tend to be dispersed on a hemispheric scale or even globally if injected into the tropics. It has also been shown that moderate volcanic eruptions (VEI < 4) can also have an impact on the stratospheric aerosol background [Vernier et al., 2011]. When the eruptive column does not reach the stratosphere or even the tropopause region, volcanic eruptions still affect the atmospheric radiation balance but on more regional scales (e.g., the Laki lava eruption in 1783–1784). Moderate eruptions are by far the most frequent, and this makes them one of the greatest natural sources of atmospheric S-bearing gas [Bates et al., 1992; Andres and Kasgnoc, 1998]. On average, tropospheric eruptions (i.e., the injection of volcanic material mainly into the troposphere) release about 10–20 Mt of SO₂ per year, which is 2 orders of magnitude higher than stratospheric eruptions that result in the release of very large amounts of SO₂ into the stratosphere but are much less frequent (<0.2 Mt of SO₂ per year) [e.g., Bluth et al., 1992; Andres and Kasgnoc, 1998; Wallace, 2001].

To characterize the atmospheric cycle of sulfur, one needs to determine its burden and the different components of its budget: fluxes (that is, source and sink rates). Sources/sinks are associated with processes

such as emissions, chemical reactions (resulting in the production or destruction of the compound), transport, and deposition. Conventional methods for inferring chemical reaction terms rely mostly on models that are evaluated and constrained with atmospheric concentration measurements, because there is no direct means of measuring chemical fluxes associated with specific oxidation channels [e.g., *Morin et al.*, 2007].

The most abundant volcanic sulfur gas is generally SO_2 . Once emitted into the atmosphere, SO_2 can be removed via deposition at the surface level or undergo oxidation through several dominant channels according to the following reactions [e.g., *Seinfeld and Pandis*, 2006]:



(*: mass-independent O isotopes signature in the troposphere, expressed as $\Delta^{17}\text{O} > 0$; TMI: transition metal ion; for (R4), S(IV) is in aqueous phase and can be present as $\text{SO}_2 \cdot \text{H}_2\text{O}$, HSO_3^- , or SO_3^{2-} and S(VI) corresponds to sulfate SO_4^{2-})

The main SO_2 oxidants are O_3 , OH , H_2O_2 , and O_2 catalyzed by TMI (TMI: transition metal ion; Figure 1) [e.g., *Seinfeld and Pandis*, 2006, and references therein]. The oxidation by OH (R1) takes place in the gas phase only. Sulfuric acid produced via (R1) can either condense on preexisting particles or form new acid sulfuric particles by homogeneous nucleation. Its oxidation by O_3 , H_2O_2 , and O_2 ((R2), (R3), and (R4), respectively) is heterogeneous, resulting in sulfate production in liquid phases such as cloud droplets. Ultimately, the fate of this sulfate is determined by the fate of the liquid phases themselves, for instance, precipitation or evaporation. It is also worth pointing out that studying the fate of volcanic sulfur can also help to better constrain the atmospheric consequences of anthropogenic SO_2 emissions that are 5–10 times higher than volcanic emissions on average (110 Mt per year) [e.g., *Smith et al.*, 2011]. All of these four dominant oxidation channels occur in a background atmosphere and lead to the production of secondary sulfate production. On top of the sulfate generated via the oxidation of sulfur-bearing gases (mostly SO_2), there is also some sulfate emitted directly by volcanoes [e.g., *Mather et al.*, 2003, 2006]. These sulfates are called “primary” in opposition to sulfates chemically produced in the atmosphere which are called “secondary.” The sulfate samples analyzed in this study are probably a mix of these two sulfate sources.

Other oxidation channels have been proposed, some occurring in the vent of the volcanoes. For example, a sulfate such as anhydrite can be formed in the magma itself, in the magma chamber, or possibly during the magma ascent [e.g., *Rye et al.*, 1984]. S-bearing gases can be oxidized very quickly after being exsolved from the magma at high temperatures by the fragmented magma or possibly by magmatic and/or atmospheric oxidant compounds [e.g., *Mather et al.*, 2006]. As these sulfates are produced within volcanic vents, they are seen as primary sulfates. They can also be released during future eruptions by remobilizing the hydrothermal deposits from the conduit’s walls [e.g., *Rye et al.*, 1984]. Further on in the volcanic plume, S-bearing gases can be converted to sulfate by chemical and photochemical reactions on mineral and dust surfaces [e.g., *Cwierny et al.*, 2008]. Among others, processes such as SO_2 gas-tephra reactions at relatively high temperatures by Ca^{2+} diffusion-driven mechanisms [*Ayris et al.*, 2013] or SO_2 oxidation by OH produced by UV irradiation of dust particles [*Dupart et al.*, 2012] could be responsible for sulfate formation in dense volcanic plume conditions. Oxidation by halogen species in the aqueous phase has also been invoked in modeling studies [*von Glasow et al.*, 2002]. However, some of the rate constants are still unknown [e.g., *Alexander et al.*, 2012]. Overall, several of the processes are still very poorly characterized or even speculative.

Isotopic ratio measurements can provide insights into the nature and magnitude of fluxes associated with oxidation processes, thus providing unique information regarding processes that are often difficult to quantify from concentration measurements alone. Stable isotope variations in atmospheric compounds can often act as source markers for compounds and provide both qualitative and quantitative constraints on the chemical and

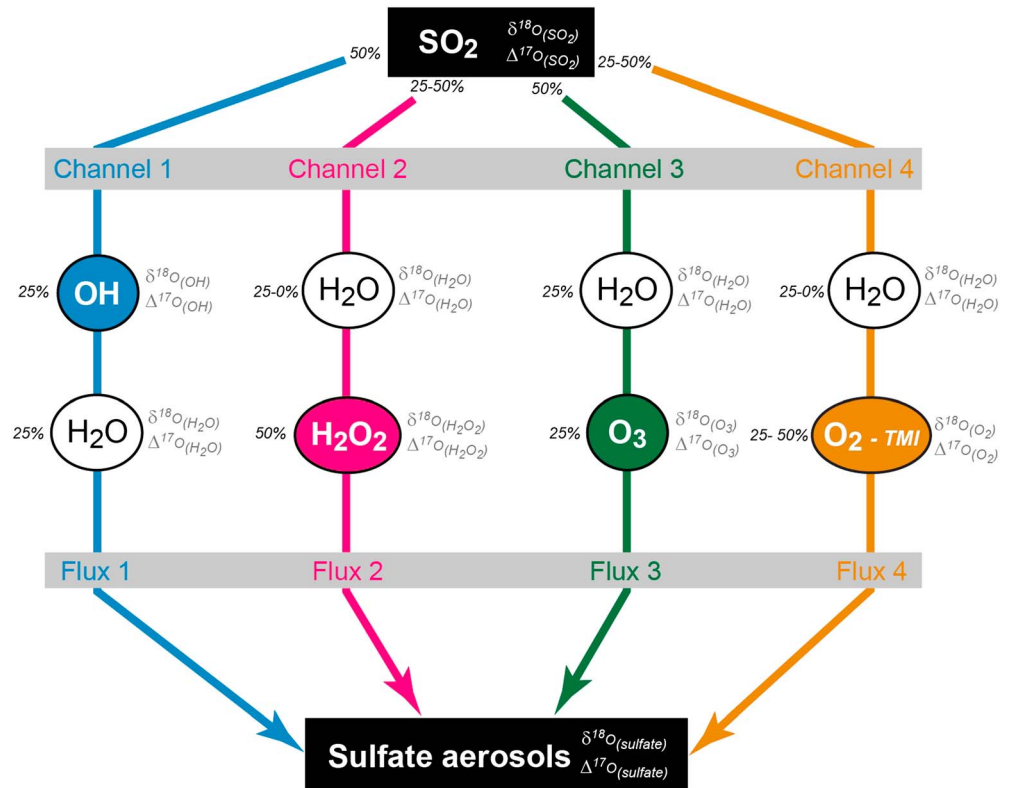


Figure 1. Simplified diagram showing the 4 dominant oxidation channels through which volcanic SO₂ is converted to sulfate aerosols in the atmosphere. Although chemical fluxes 1, 2, 3, and 4 cannot be measured directly, oxygen isotopic composition of sulfate provides constraints in their estimations according to the following mass balance (the same equation is used for Δ¹⁷O):

$$\begin{aligned} \delta^{18}\text{O}_{(\text{sulfate})} = & \text{flux1} \cdot [0.5 \cdot \delta^{18}\text{O}_{(\text{SO}_2)} + 0.25 \cdot \delta^{18}\text{O}_{(\text{OH})} + 0.25 \cdot \delta^{18}\text{O}_{(\text{H}_2\text{O})}] \\ & + \text{flux2} \cdot [(0.25 \text{ or } 0.5) \cdot \delta^{18}\text{O}_{(\text{SO}_2)} + 0.5 \cdot \delta^{18}\text{O}_{(\text{H}_2\text{O}_2)} + (0 \text{ or } 0.25) \cdot \delta^{18}\text{O}_{(\text{H}_2\text{O})}] \\ & + \text{flux3} \cdot [0.5 \cdot \delta^{18}\text{O}_{(\text{SO}_2)} + 0.25 \cdot \delta^{18}\text{O}_{(\text{O}_3)} + 0.25 \cdot \delta^{18}\text{O}_{(\text{H}_2\text{O})}] \\ & + \text{flux4} \cdot [(0.25 \text{ or } 0.5) \cdot \delta^{18}\text{O}_{(\text{SO}_2)} + (0.25 \text{ or } 0.5) \cdot \delta^{18}\text{O}_{(\text{O}_2)} \\ & + (0 \text{ or } 0.25) \cdot \delta^{18}\text{O}_{(\text{H}_2\text{O})}] \end{aligned}$$

Percentages correspond to the proportion in sulfate of oxygen originating from the different compounds during each oxidation chain (mainly from Savarino *et al.* [2000], more details are in the main text). The most likely ranges for δ¹⁸O and Δ¹⁷O of each compound are provided in Table 2. The resulting O isotope compositions of sulfate aerosols are the following: Channel 1 δ¹⁸O = −5 to 1‰ and Δ¹⁷O = 0‰ / Channel 2 δ¹⁸O = 14 to 27‰ and Δ¹⁷O = 8‰ / Channel 3 δ¹⁸O = 13 to 25‰ and Δ¹⁷O = 1‰ / Channel 4 δ¹⁸O = 4 to 15‰ and Δ¹⁷O = −0.17 to −0.08‰.

physical pathways that determine their fate [Johnson *et al.*, 2002; Brenninkmeijer *et al.*, 2003; Thiemens, 2006; Morin *et al.*, 2008]. Stable isotope analysis has been particularly useful in constraining global trace gas budgets [Quay *et al.*, 1999; Yoshida and Toyoda, 2000; Brenninkmeijer *et al.*, 2003; Harris *et al.*, 2012, 2013]. Kinetic isotope effects associated with sinks can also be used to identify and evaluate chemical reactions occurring in the atmosphere.

Most processes lead to isotopic fractionation according to mass differences in the isotopes. However, some processes, called mass-independent fractionation (MIF), do not follow this general rule of fractionation and generate isotope ratios that do not scale with isotope masses [e.g., Thiemens, 1999]. The most common example is the large and distinctive oxygen-MIF anomaly in the atmospheric ozone that is produced during its formation [Mauersberger *et al.*, 2003; Vicars *et al.*, 2012]. For oxygen, the MIF is quantified from the triple-oxygen isotope ratios with the quantity Δ¹⁷O that reflects the difference between measured δ¹⁷O and δ¹⁸O and those expected from mass-dependent fractionating processes: Δ¹⁷O = δ¹⁷O − 1000[(1 + δ¹⁸O/1000)^{0.52} − 1]. The O-MIF signature

in the ozone is propagated to other oxygen-bearing compounds, in particular oxidants and oxidation products, through chemical reactions [e.g., Lyons, 2001] and can be used to study the atmospheric chemistry.

Emitted volcanic S-bearing gases and atmospheric oxidants have different oxygen isotopic composition. Therefore, the oxygen isotopic composition of sulfate, the end product of sulfur-bearing compounds oxidation, should reflect not only emission sources but also the relative contributions of the different oxidation channels with their respective fractionations, both mass-dependent and mass-independent (Figure 1).

Measurements of sulfate isotopic composition have already been used successfully in identifying key sources and sinks in the cycle of sulfur in the atmosphere [Alexander et al., 2002, 2005; McCabe et al., 2006; Hill-Falkenthal et al., 2012; Harris et al., 2012, 2013] including volcanic sulfur. For instance, oxygen and sulfur mass-independent signatures have been measured in sulfate from large stratospheric volcanic eruptions in ice cores [e.g., Savarino et al., 2003a, 2003b; Baroni et al., 2007, 2008] or volcanic deposits [e.g., Bao and Reheis, 2003; Bindeman et al., 2007; Martin and Bindeman, 2009]. S-MIFs measured in these volcanic sulfates confirm the existence of MIF channels in stratospheric sulfur oxidation, possibly photooxidation of SO₂ while O-MIF measurements tend to indicate that OH radicals contribute very substantially to stratospheric sulfur oxidation. During volcanic eruptions, especially tropospheric eruptions, a large part of the generated sulfate is integrated into the volcanic ash during or after its deposition by different mechanisms (uptake on solid surfaces, condensation, dissolution in liquid layers around particles, etc.). The isotopic composition of this volcanic sulfate should provide constraints on the relative importance of different tropospheric oxidants assuming that the isotopic composition of the volcanic sulfur injected is known.

This paper presents new measurements of the isotopic composition of sulfate found in volcanic ash deposits from worldwide eruptions that are mainly tropospheric. Measured isotopic compositions are then compared to sulfate isotopic compositions derived from oxidant fields provided by a global 3-D atmospheric chemistry model. The consistency between measurements and model calculations is discussed along with the limitations of such a comparison. These comparisons allow us to attempt to test our understanding of volcanic sulfur oxidation in the atmosphere. Previously, high mass-independent signatures in oxygen isotopes have been measured in volcanic sulfate from large eruptions, stimulating the study of such volcanic events on a global scale. Here the focus is on volcanic sulfate produced in the troposphere or the tropopause region. One of the objectives is to explore to what extent isotopic measurements can constrain the fate of the volcanic sulfur in the troposphere.

2. Samples and Methods

2.1. Samples

Ash samples were supplied by several researchers (Table 1) who, along with their colleagues, collected freshly deposited ash during a few days or less after the eruptions, at different distances from the volcanic vents, from 5 km to 400 km and without being washed out by rain (Figure 2). These conditions are optimum for sulfate conservation in the volcanic product. The ash samples considered here were collected during tropospheric eruptions of the Popocatepetl (2008, Mexico), Gjalp (1998, Iceland), Mayon (1968, Philippines), Parícutin (1948, Mexico), Negro Cerro (1947, Nicaragua), and to some degree stratospheric eruptions of Mount Spurr (1992, Alaska), Mount St. Helens (1980, USA), Volcán de Fuego (1974, Guatemala), and Tungurahua (2008, Ecuador); Figure 2. For the latest eruptions, volcanic plumes could have reached almost 20 km (Table 1) but the majority of particles (such as ash and sulfate aerosols) traveled hundreds of kilometers in the upper troposphere or the tropopause region.

2.2. Sulfate Extraction, Oxygen, and Sulfur Isotopes Measurements

The nature of sulfates in our samples has not been characterized. Sulfates might consist of various alkali-bearing sulfates mainly precipitated from aerosol liquid droplets (B. Grobety, personal communication, 2014). All soluble sulfates were extracted from each sample by leaching in diluted HCl (<0.1 M) solution. All sulfates in solution were integrally precipitated into barite and purified by double dissolution-reprecipitation in a chelating diethylene triamine penta acetic acid (DTPA) agent [Bao, 2006; Martin and Bindeman, 2009]. For practical reasons, more than 95% of the precipitated barite was collected, leading to a slight underestimation of the SO₄²⁻ concentration in the ash samples. The O₂ was extracted and purified from 4 to 6 mg of purified barite on a laser fluorination line, and its isotopic composition was measured on a MAT 253 at the Stable

Table 1. Oxygen and Sulfur Isotopic Composition of Volcanic Sulfate Extracted From Ash Collected Soon After Tropospheric Eruptions

| Volcano and Date of Eruption | Sample Name ^a | Distance From Vent (km) | Maximum Plume's Height (km) | Latitude (°N) | Longitude (°W) | SO ₄ ²⁻ (ppm) | Δ ¹⁷ O (‰) | δ ¹⁸ O (‰) | δ ³⁴ S (‰) |
|-----------------------------------|-----------------------------|-------------------------|-----------------------------|---------------|----------------|-------------------------------------|-----------------------|-----------------------|-----------------------|
| Popocatepetl (15 February 2008) | Popo 15/2/2008 ^b | 25 | 8.4 | 19.0 | 98.6 | 7517 | 0.35 | 9.83 | 9.1 |
| Spurr (18 August 1992) | Spurr 42 ^c | 360 | 16 | 61.3 | 152.3 | 4084 | -0.09 | 2.92 | 9.4 |
| Spurr (18 August 1992) | Spurr 57 ^c | 265 | 16 | 61.3 | 152.3 | 3914 | -0.14 | 4.26 | 9.2 |
| Volcán de Fuego (14 October 1974) | VF 74-200 ^c | 78 | 15 | 14.5 | 90.9 | 3015 | -0.03 | 7.32 | 6.8 |
| Volcán de Fuego (14 October 1974) | VF 74-45 ^c | 57 | 15 | 14.5 | 90.9 | 1215 | -0.04 | 9.15 | 10.5 |
| Negro Cerro (9 July 1947) | 116286-10 ^d | 44 | 8 | 17.1 | 93.0 | 574 | -0.03 | 7.18 | 6.6 |
| Negro Cerro (9 July 1947) | 116286-11B ^d | 45 | 8 | 17.1 | 93.0 | 2645 | -0.08 | 7.91 | 7.4 |
| Negro Cerro (9 July 1947) | 116286-9 ^d | 12 | 8 | 17.1 | 93.0 | 665 | -0.06 | 7.01 | 7.7 |
| Mayon (1-9 May 1968) | 111170 ^d | | 10 | 13.3 | 236.31 | 410 | -0.04 | 7.63 | 7.5 |
| Parícutin (June 1948) | 16300-42 ^d | 5 | 8 | 19.5 | 102.3 | 442 | 0.13 | 8.12 | 6.8 |
| Mt St Helens (18 May 1980) | 115315 ^d | 400 | 19 | 46.2 | 122.2 | 1062 | 0.02 | 4.67 | 9.0 |
| Mt St Helens (18 May 1980) | 14 Davis ^e | 400 | 19 | 46.2 | 122.2 | - | -0.04 | 0.21 | 7.6 |
| Tungurahua (February 2008) | Tung 04 ^f | <30 | 14 | 1.5 | 78.4 | 318 | -0.02 | 5.15 | 3.9 |
| Tungurahua (February 2008) | Tung 27 ^f | <30 | 14 | 1.5 | 78.4 | 351 | -0.06 | 6.61 | 4.1 |
| Gjálp (December 1998) | Gjálp ^g | <30 | 10 | 64.4 | 16.8 | - | -0.07 | 13.24 | - |

^aThe samples from the same eruption have been collected at different location.

^bRoberge J. (IPN, Mexico).

^cRose B. (Michigan Tech, USA).

^dThe rock collection at the Smithsonian Institution of Washington DC.

^eSarna-Wojcicki A.M. (USGS).

^fHidalgo S. (IGEPE, Ecuador).

^gSigmarsson O. (LMV, France/University of Iceland).

Isotope Laboratory at the University of Oregon. Because BaSO₄ fluorination has a 35–45% yield, we used NBS127 and IBO4-13 standards [Bindeman *et al.*, 2007] to correct the measured raw δ¹⁸O values (8.6‰ correction was required). This correction has no effect on the Δ¹⁷O value as fractionation processes during measurements are mass dependent. The reader is referred to Martin and Bindeman [2009] for further details on analytical method. Based on duplicates, analytical error (in 2σ) on oxygen isotopes is 0.05‰, 0.16‰, and 0.3‰ for Δ¹⁷O, δ¹⁷O, and δ¹⁸O, respectively. The error (in 2σ) of this whole method (sulfate extraction + analysis) is about 0.1‰, 0.5‰, and 1.0‰ for Δ¹⁷O, δ¹⁷O, and δ¹⁸O, respectively. Note that in this study all duplicates have been analyzed in only five very reproducible sessions in a short period of time (2 weeks).

Sulfur isotopes were analyzed via an elemental analyzer at the New Mexico Tech Stable Isotope Lab. Multiple analyses of international standard NBS127 give δ³⁴S = 15.94‰ ± 0.09 (in 2σ, n = 4), δ³⁴S = 12.28‰ ± 0.02 (in 2σ, n = 2) for NBS123, and δ³⁴S = -8.98‰ ± 0.06 (in 2σ, n = 2) for an in-house standard Cpy-4.6. Considering the certified values of 21‰, 17‰, and -4.6‰ for NBS127, NBS123, and Cyp-4.6, respectively, the samples measured during the analytical session were corrected using a factor that is between 4.3 and 4.9‰.

2.3. Modeling

As illustrated in Figure 1, the O isotopic composition of the collected sulfate depends on the relative contributions of different oxidants to sulfur oxidation as well as the isotopic composition of the SO₂ source. In order to see whether our measurements of sulfate O isotopic composition are consistent with expected levels of oxidant, we extracted concentration fields of oxidants from a present-day multiyear global 3-D chemistry transport model simulation. The model is the Model for Ozone and Related Chemical Tracers (MOZART) [Horowitz *et al.*, 2003; Emmons *et al.*, 2010a], run at 1.9° latitude and 2.5° longitude and forced with NASA GEOS 5 analyses from 1 January 2007 to 31 December 2011. The simulation uses anthropogenic emissions based on David Streets' inventory for Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (<http://www.cgrrer.uiowa.edu/arctas/emission.html>) and fire emissions from FINN-v1 [Wiedinmyer *et al.*, 2011]. MOZART model calculations have been extensively evaluated against a range of atmospheric chemical measurements [Horowitz *et al.*, 2003; Pfister *et al.*, 2006, 2008; Emmons *et al.*, 2010b]. Like almost all global models, MOZART does not account for the oxidation of sulfur catalyzed by TMI in condensed phases. Therefore, TMI concentrations have to be specified. It has to be stressed that our model calculations are only valid for very diluted and mixed volcanic plumes. Some of the sulfates are produced in

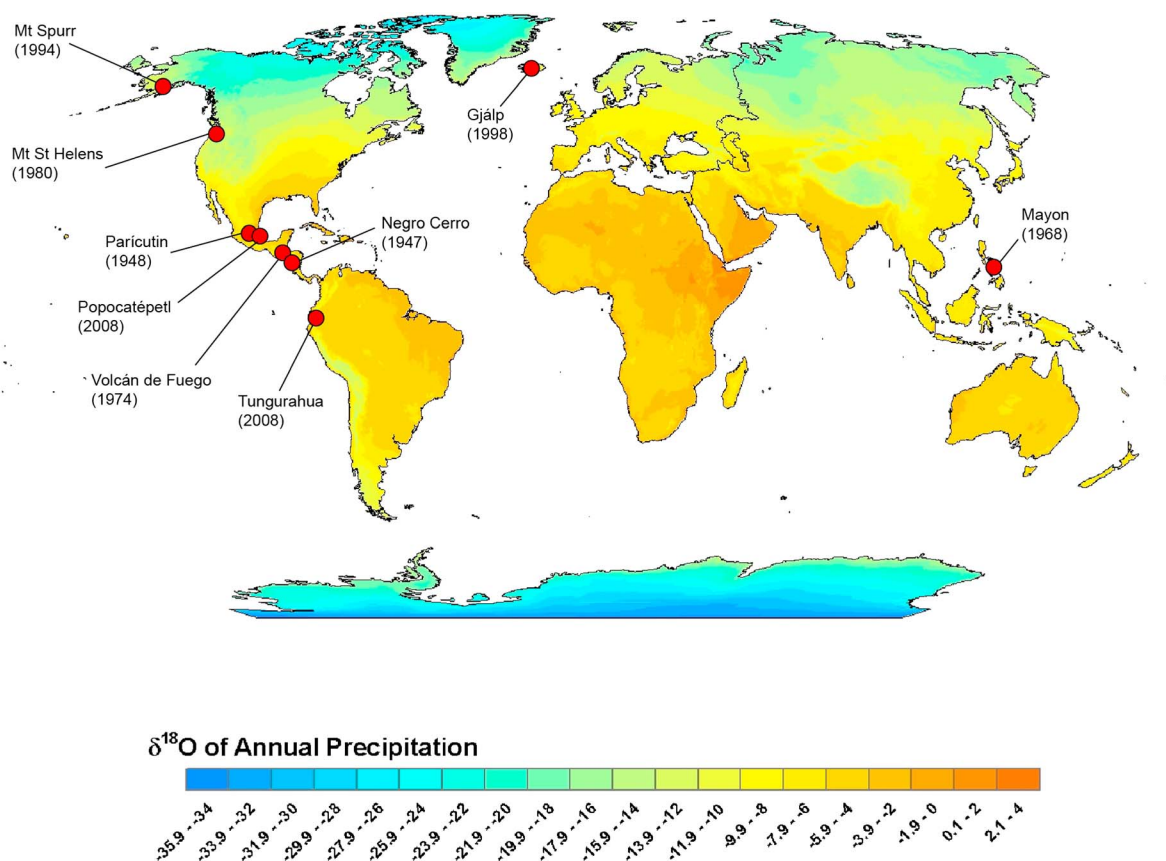


Figure 2. Location of the studied historical tropospheric eruptions (red dots) and the O isotope composition of annual worldwide precipitation (<http://www.water-isotopes.org>). The water isotopic composition in the atmosphere close to each volcano is between -5 and -15 ‰ as reported in Table 2.

dense volcanic plumes where complex multiphase processes are important. This type of model calculation is difficult to constrain because some kinetic data and rate constants are poorly characterized or even missing.

Vertical profiles of oxidant concentrations (from the surface to 10 km) at the location (latitude, longitude) of each volcanic eruption were extracted by simple linear interpolation of the global 3-D MOZART fields. We only consider the 3 days of profiles following the date of each eruption. As the considered volcanic eruptions mostly occurred prior to the period covered by the simulation (from 1 January 2007 to 31 December 2011), model-calculated oxidant vertical profiles are averaged temporally over the 5 years of simulation in order to produce climatological atmospheric oxidant levels corresponding to the present-day conditions over each volcano. For the aqueous oxidation of SO_2 by O_3 and H_2O_2 , aqueous concentrations of SO_2 , O_3 , and H_2O_2 are calculated from Henry's law constants exploring a range of pH values (from 1 to 9) and liquid water content (from 0.005 to 3 g of water \cdot m^{-3} of air) [Seinfeld and Pandis, 2006]. The calculation of the SO_2 aqueous concentrations also takes into account the fact that some of the dissolved SO_2 dissociates twice to form HSO_3^- and SO_3^{2-} . This dissociation is a reversible reaction that reaches equilibrium rapidly, resulting in an effective solubility of SO_2 in aqueous phases strongly dependent on the pH [Seinfeld and Pandis, 2006]. The rate constant for the gas phase reaction between SO_2 and OH, the rate constants for the aqueous reactions of SO_2 with O_3 and H_2O_2 , the Henry's law coefficients for SO_2 by O_3 and H_2O_2 , and the equilibrium constants between SO_2 and HSO_3^- and between HSO_3^- and SO_3^{2-} are taken from recommended chemical kinetic and photochemical data [Sander et al., 2006]. The TMI concentrations in the liquid phase that are specified in the model are based on recent field measurements in bulk cloud water where TMIs are derived from mineral dust [Harris et al., 2013]. We focus on Fe^{3+} and Mn^{2+} , the most widely studied system. Both ions oxidize sulfur, S(IV), but they also have a very strong positive synergistic effect on the oxidation rate [Seinfeld and Pandis, 2006]. As done in Alexander et al. [2009], reaction rates for sulfur oxidation by Fe^{3+} and Mn^{2+} are taken from Martin and Good [1991].

Finally, the overall oxidation rate of volcanic SO_2 for each oxidant is calculated by vertically integrating the profiles of instantaneous oxidation rates assuming that volcanic SO_2 plumes are distributed homogeneously from the surface to 10 km. We tested spreading volcanic plumes over different altitude ranges, a couple of kilometers from the surface. However, in terms of the relative contributions of the different oxidation channels (the determining factor for the oxygen isotopic composition of the sulfate), the results remain unchanged.

There are important caveats that have to be kept in mind when analyzing the results of the comparisons. First, as the atmospheric composition has changed substantially over the last century, the comparison is not entirely fair for some isotopic measurements that correspond to eruptions occurring half a century earlier (for instance, Negro Cerro in 1947). Second, the comparison assumes that oxidant levels are not affected by the eruptions themselves; this is only valid for very diluted volcanic plumes. As a result, model-calculated profiles can only be viewed as rough indicators of oxidant levels prevailing in the background atmosphere during the volcanic eruptions.

3. Results

3.1. Oxygen and Sulfur Isotopes

Overall, the SO_4^{2-} concentration in ash samples varies from 350 to 7500 ppm (Table 1 and Figures 3c–3e). Note that these units of mass mixing ratio (ppm) refer to the mass of extracted BaSO_4 compared to the mass of ash leached. The $\delta^{18}\text{O}$ of the extracted sulfate covers a wide range from 0.2‰ to 13.2‰ as well as the $\delta^{34}\text{S}$ that varies from 3.9 to 10.5‰. However, the $\Delta^{17}\text{O}$ ranges from -0.14 ‰ to 0.35‰ with 80% of the samples between -0.1 and 0.1‰, which is relatively homogeneous. In the $\Delta^{17}\text{O}$ versus $\delta^{18}\text{O}$ diagram (Figure 3a), with the exception of Mexican samples, the data set describes a horizontal trend that indicates no correlation between $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$. The same observation holds between $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ as the data set looks scattered in the $\delta^{34}\text{S}$ versus $\delta^{18}\text{O}$ diagram (Figure 3b). In detail, as shown in Figure 3, samples from the same eruption but collected at different locations have a significantly similar composition. Only the Mount St. Helens samples show a significant difference in $\delta^{18}\text{O}$ but it is still in the same range, among the lowest values. However, differences in the sulfate concentration (up to 2100 ppm) can possibly be observed in samples from the same eruption. It is noteworthy that in our data set there is no apparent correlation between the sulfate concentration and the isotopic composition (Figure 3). This confirms that at least in our samples, processes affecting the sulfate concentration (e.g., volcanic SO_2 emission and natural ash leaching by rain before sampling) are clearly distinct from and do not interfere with processes determining the isotopic composition (e.g., oxidant composition and fractionation processes). Finally, an apparent correlation between $\delta^{18}\text{O}$ and the distance from the vents is observed (Figure 3f). The same correlation is observed between $\delta^{18}\text{O}$ and the maximum height of the volcanic plumes, but it might not be relevant as the larger the eruption is, the farther from the vent volcanic material can be deposited and hence collected.

The main result of this geochemical study is the compositional difference between the initial volcanic SO_2 and the sulfates extracted from volcanic ash (Figure 3). Indeed, differences of up to 6‰ in $\delta^{18}\text{O}$ and up to 0.25‰ in $\Delta^{17}\text{O}$ are observed, which is significantly higher than the analytical uncertainties (error bars in Figure 3). However, the variations measured in sulfate $\delta^{34}\text{S}$ are comparable to what can be expected for the volcanic SO_2 worldwide (Figure 3).

3.2. Atmospheric Modeling

Model-calculated respective percentage contributions of O_3 , H_2O_2 , OH, and $\text{O}_2\text{-TMI}$ to the total volcanic SO_2 oxidation (expressed as percent of the total) are presented in Figure 4 as a function of the pH of the liquid phase. The colored areas in Figure 4 represent the range of values obtained for all the different volcanic eruptions for varying liquid water content (from 0.005 to 3 g of water $\cdot \text{m}^{-3}$ of air). Our model results are consistent with previous modeling results [Seinfeld and Pandis, 2006; Harris et al., 2012, 2013]. As expected, at $\text{pH} < 6$, H_2O_2 is by far the most effective oxidant. At higher pH ($> 6\text{--}7$), O_3 becomes the most important oxidant. However, because of the SO_2 oxidation, volcanic liquid phases are expected to be rather acidic. Therefore, according to the equilibrium calculations, H_2O_2 should be the overwhelmingly dominant oxidant for volcanic SO_2 . In addition, as long as there are significant amounts of liquid phases

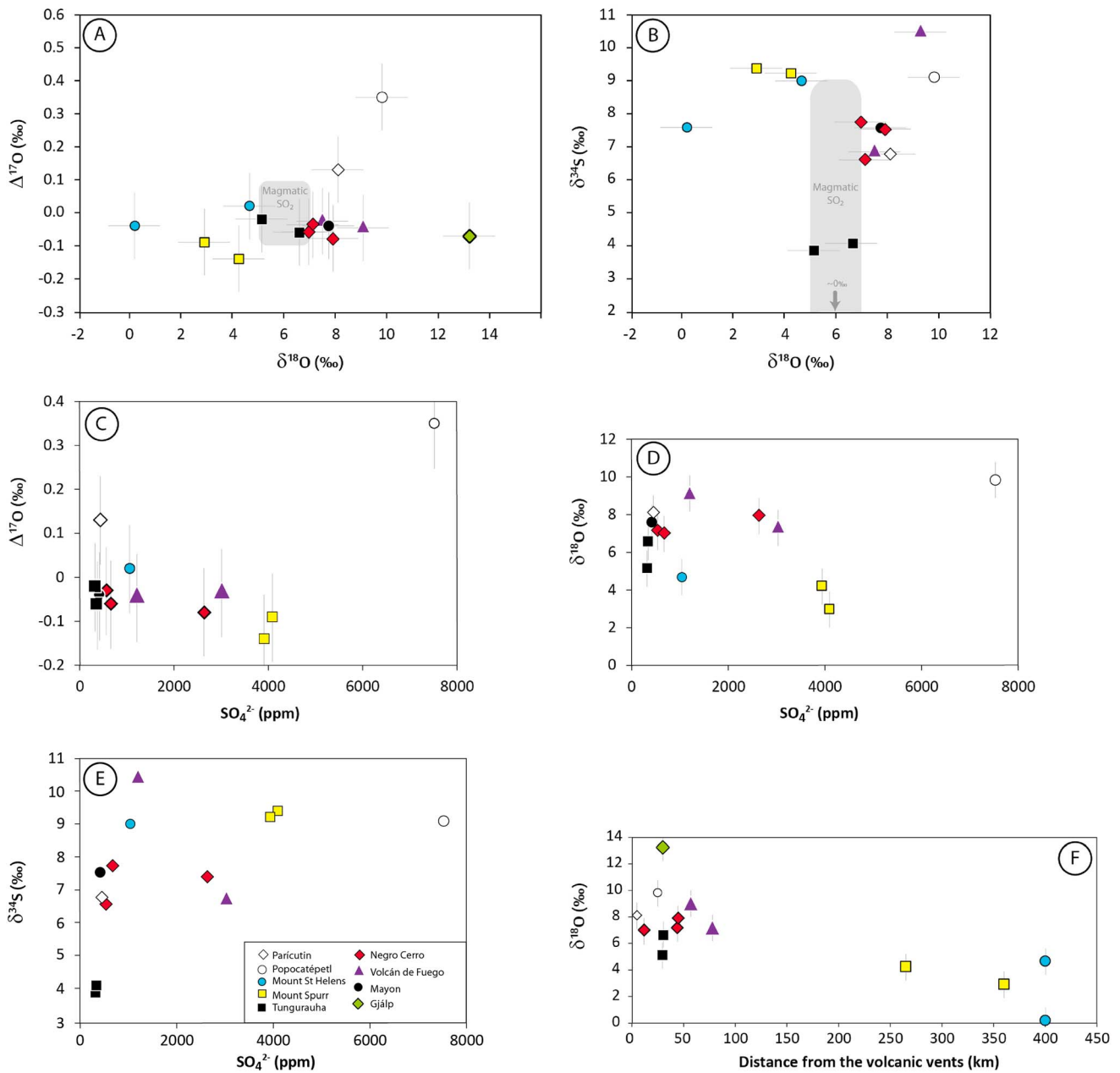


Figure 3. Oxygen and sulfur isotope composition and sulfate concentration of the samples. The grey area is the initial magmatic SO_2 composition which is very close to the magmatic value for O isotopes [e.g., Eiler, 2001] and potentially up to 2‰ higher than mantle value for S isotopes [e.g., Maarten de Moor et al., 2010]. However, the S isotope composition of magmatic SO_2 is highly variable because it strongly depends on (a) the mantle source composition that can differ from the mantle value ($\delta^{34}\text{S} = -0.91 \pm 0.50\text{‰}$) [Labidi et al., 2012, 2013] by interactions with subduction fluids, (b) the magma degassing processes, and (c) the oxidation state of magmatic sulfur [e.g., Rye et al., 1984; Alt et al., 1993; Mather et al., 2006; Maarten de Moor et al., 2010].

in the volcanic plumes (amounts equivalent to cloudy conditions in the atmosphere), the oxidation of SO_2 in the gas phase (by OH) is almost negligible. The results vary little with the location and time of the year of the volcanic eruptions considered here.

4. Discussion

4.1. Oxygen and Sulfur Isotopes

The range of oxygen isotope compositions of the initial volcanic SO_2 is relatively small and strongly depends on the magmatic isotope composition which commonly varies between 5 and 7‰ [e.g., Eiler, 2001] (Figure 3).

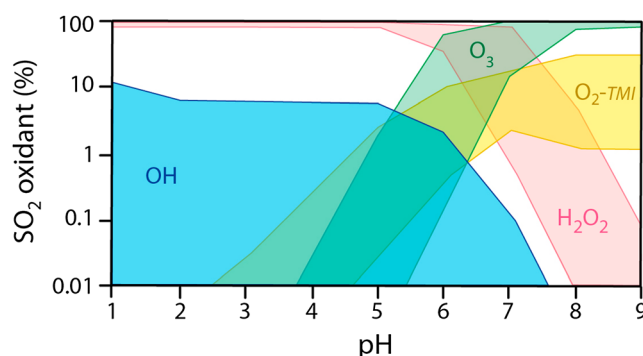


Figure 4. Model-calculated contributions (in %) of OH, O₃, H₂O₂, and O₂-TMI to SO₂ oxidation as a function of pH of the liquid phases (note the logarithmic scale). The colored areas represent the range of values obtained for all the different volcanic eruptions for varying liquid water content (from 0.005 to 3 g of water · m⁻³ of air). Gas phase concentrations of OH, O₃, and H₂O₂ are taken from 3-D chemistry transport model calculations (see text for more details). The only TMIs considered here are Fe³⁺ and Mn²⁺. Based on recent field measurements in bulk cloud water, [Fe³⁺] = 1 μM and [Mn²⁺] = 0.1 μM.

Sulfur isotope compositions of magmatic SO₂ show a much wider range because of its strong dependence on the mantle source composition that can differ from the “mantle value” [Labidi *et al.*, 2012, 2013] by interactions with high δ³⁴S subduction fluids but also by magma degassing processes and by different oxidation states of magmatic sulfur (δ³⁴S_{SO₂} ≈ 0–9‰; Figure 3) [e.g., Rye *et al.*, 1984; Alt *et al.*, 1993; Mather *et al.*, 2006; Maarten de Moor *et al.*, 2010].

After the oxidation and transport of volcanic SO₂ within the atmosphere, the resulting products (sulfate aerosols) are expected to differ in terms of δ³⁴S and δ¹⁸O from the initial magmatic SO₂. Our data set clearly confirms this for oxygen isotopes (Figure 3). However, it is less

clear for sulfur isotopes because the variations in isotopic composition among initial SO₂ are as large as the variations from the resulting sulfates (Figure 3). In addition, all the samples whose S isotopic compositions have been determined are from subduction zones where the mantle source can be more or less metasomatized by relatively high δ³⁴S fluids.

The high δ³⁴S variability of initial magmatic SO₂ more or less covers the composition range observed in sulfate compositions. Therefore, it is difficult to quantitatively discuss processes that can generate this type of isotopic fractionation during SO₂ oxidation. Indeed, isotopic fractionation can occur in the volcanic plume itself by distillation/condensation processes as described by the Rayleigh distillation equation [e.g., Castleman *et al.*, 1974] and also during homogeneous and heterogeneous oxidation reactions [Harris *et al.*, 2012]. The only way to discuss such processes in detail would be to know exactly what the initial magmatic SO₂ isotopic composition is for each of the studied eruptions, which is not the case here. It is worth pointing out that even for a specific volcano, the sulfates extracted from ash deposits have isotopic compositions (δ¹⁸O and δ³⁴S) that can vary from one eruption to another as observed, for instance, at the Popocatepetl [Armienta *et al.*, 2010].

The 13‰ variation observed in δ¹⁸O can also be at least partially explained by processes such as distillation/condensation processes in the volcanic plume as described by the Rayleigh distillation equation. However, the contributions of oxidants with contrasted δ¹⁸O compositions (Table 2) can significantly affect the sulfate composition too. Through the oxidation channel (R1), 50% of the sulfate oxygen atoms come from SO₂, 25% from OH, and 25% from H₂O [Savarino *et al.*, 2000] (Figure 1), leading to sulfate having δ¹⁸O between –5 and 1‰. Considering now the oxidation channel (R2), Savarino *et al.* [2000] experimentally demonstrated that 50% of the sulfate oxygen comes from H₂O₂, but the other 50% can be derived from SO₂ only or 25% SO₂ and 25% H₂O (Figure 1). In both cases, the resulting δ¹⁸O of the sulfate is similar, between 25 and 13‰ (Table 2). Considering now the SO₂ oxidation via O₃ (R3), 50%, 25%, and 25% of the sulfate oxygen comes from SO₂, O₃, and H₂O respectively [Savarino *et al.*, 2000] (Figure 1), leading to sulfate δ¹⁸O of about 14–27‰ (Table 2). Finally, the O₂-TMI channel (R4), is expected to generate sulfate having δ¹⁸O between 4 and 15‰ (Table 2) as 25–50% of the sulfate’s oxygen atoms are thought to come from the initial SO₂, 0–25% from H₂O, and 25–50% from O₂ (Figure 1).

As a consequence, the O isotope compositions of secondary sulfate are the result of the mixing between the isotopic signatures of the initial volcanic SO₂ and the atmospheric oxidants. Therefore, if we consider a low primary sulfate contribution, the lowest δ¹⁸O measured in our volcanic sulfate could be explained mainly by OH oxidation (R1) and most of our samples δ¹⁸O could be derived from the O₂-TMI channel (R4). Furthermore, there are isotopic fractionation processes (e.g., distillation/condensation) operating in the initial volcanic plume and during the atmospheric transport of S-bearing volcanic gas and aerosols that can

Table 2. (Top) Most Likely Isotopic Composition of Volcanic SO₂ and Its Oxidant in the Troposphere [Krankowsky et al., 1995; Johnston and Thiemens, 1997; Savarino and Thiemens, 1999; Mather et al., 2006] (www.waterisotope.org; Figure 2)^a

| | $\Delta^{17}\text{O}$ | Min $\delta^{18}\text{O}$ | Max $\delta^{18}\text{O}$ |
|---|-----------------------|------------------------------|------------------------------|
| <i>Volcanic Gas</i> | | | |
| SO ₂ | 0 | 5 | 7 |
| <i>Tropospheric Oxidants</i> | | | |
| OH | 0 | -15 | -5 |
| H ₂ O ₂ | 2 | 45 | 25 |
| H ₂ O | 0 | -15 | -5 |
| O ₃ | 32 | 60 | 100 |
| O ₂ -TMI | -0.33 | 23 | 23 |
| <i>Secondary Volcanic Sulfate Composition</i> | | | |
| (R1) (OH) | 0 | -5 | 1 |
| (R2) (O ₃) | 8 | 14 | 27 |
| (R3) (H ₂ O ₂) | 1 | 25 | 13 |
| (R4) (O ₂ -TMI) | -0.17 to -0.08 | 4 | 15 |

^aThe $\Delta^{17}\text{O}$ value for O₂ is the one established during our measurements at the University of Oregon and is consistent with what Young et al. [2014] measured. (bottom) Expected isotopic composition of sulfate produced by the different oxidation channels (see the text for further explanations).

primary sulfate, which is unlikely at least for samples collected hundreds of kilometers from the volcanic vents or (2) secondary sulfates formed by SO₂ oxidation via atmospheric oxidants that are overwhelmingly MD. In the troposphere, H₂O₂ and O₃ exhibit consistent oxygen-MIF signatures with $\Delta^{17}\text{O}$ ~2‰ and ~32‰, respectively (Table 2). Regarding the oxidation channels (R2) (H₂O₂) and (R3) (O₃), 50% and 25% respectively of the sulfate oxygen atoms are from the MIF oxidant (H₂O₂ and O₃). Consequently, we should expect volcanic sulfate generated through (R2) and (R3) to have $\Delta^{17}\text{O}$ of ~1‰ and ~8‰, respectively (Table 2 and Figure 1). OH radicals that derived from the photodissociation of O₃ should inherit some MIF signature. This is the case in the stratosphere where the water content is very low (few ppmv), several orders of magnitude lower than in the troposphere. However, in the humid troposphere, OH very quickly loses its MIF signature through isotopic exchanges with MD water vapor. Therefore, tropospheric OH radicals can be assumed to have a $\Delta^{17}\text{O}$ = 0‰ resulting in secondary volcanic sulfates (R1) that are MD (Figure 1 and Table 2). Tropospheric O₂ has a slightly negative $\Delta^{17}\text{O}$ (-0.33‰) resulting in secondary volcanic sulfates (R4) that can be very slightly mass independent with a negative $\Delta^{17}\text{O}$ between -0.17 and -0.08‰, which is barely detectable in our measurements. From our data set, it can be inferred that in the troposphere, volcanic sulfates that are MD must be overwhelmingly generated by the oxidation of S-bearing gas via OH radicals and/or O₂-TMI ((R1) or (R4); Table 2) and certainly not H₂O₂ (R2) and O₃ (R3).

4.2. Atmospheric Modeling

The modeling results illustrated in Figure 4 show that in the expected acidic volcanic plume conditions [e.g., Symonds et al., 1990; Giggerbach et al., 2001, and references therein], H₂O₂ is by far (>>90%) the main SO₂ oxidant in the troposphere (R2) and the oxygen isotopic composition of volcanic sulfate should reflect that. However, as shown in section 4.1, this is not consistent with the isotopic measurements which indicate that non-MIF channels (gaseous OH channel (R1) and/or aqueous O₂-TMI channel (R4)) are the dominant pathways in the formation of volcanic sulfate in the troposphere. This contradiction can be explained by the fact that we assume in our model that oxidant levels are not affected by the oxidation of volcanic SO₂. This hypothesis necessarily implies that H₂O₂ concentrations are well in excess of the SO₂ available for oxidation [Kreidenweis et al., 2003]. However, SO₂ levels in volcanic plumes are extremely high compared to the tropospheric background, which is typically < 0.2 Dobson unit (DU; where 1 DU = 2.69 × 10¹⁶ molecules/cm⁻²). Satellite SO₂ vertical column measurements during minor volcanic eruptions [Yang et al., 2007; Lee et al., 2009; Yang et al., 2009] (see also <http://so2.gsfc.nasa.gov/>) can exceed tens of Dobson unit with peaks at 1000 DU, even during effusive eruptions [Yang et al., 2009]. Once converted into local concentrations, such amount of SO₂ is equivalent to approximately tens of ppbv of SO₂ throughout the tropospheric column. In situ measurements

contribute to $\delta^{18}\text{O}$ variations in the analyzed volcanic sulfate. Finally, one should keep in mind that the contribution of potential primary sulfate as well as their isotopic composition is very difficult to assess.

With the exception of one sample from Mexico that shows significant oxygen-MIF signature ($\Delta^{17}\text{O}$ > 0.1‰), all the other samples are mass-dependent (MD) within 2 σ error of our method ($\Delta^{17}\text{O}$ = 0 ± 0.1‰). As the initially emitted volcanic SO₂ is not expected to contain any significant MIF isotopic signature and that fractionation processes such as the distillation/condensation occurring in the volcanic plume are MD, the formation of MD sulfates with a significant isotopic composition range has two possible sources: (1) mostly

of SO₂ in volcanic plumes from moderate eruptions indicate concentrations ranging from a few tens of ppbv [e.g., Carn *et al.*, 2011; Rix *et al.*, 2012] to about a ppmv [e.g., Hunton *et al.*, 2005; Rose *et al.*, 2006]. In contrast, atmospheric H₂O₂ concentrations do not typically exceed the ppbv level [e.g., Bey *et al.*, 2001]. Overall, SO₂ levels are expected to exceed H₂O₂ levels by several orders of magnitude in plumes from large volcanic eruptions. Therefore, our equilibrium calculations that assume H₂O₂ is constant (well in excess of SO₂) do not appear to be applicable to SO₂ oxidation even after moderate volcanic eruptions. H₂O₂ is probably consumed very early in volcanic plumes, and hence, only a small fraction of volcanic SO₂ can be oxidized by H₂O₂.

As the volcanic liquid phases are expected to be rather acidic [e.g., Symonds *et al.*, 1990; Giggerbach *et al.*, 2001, and references therein], the SO₂ oxidation by O₃ cannot be significant (Figure 4). Therefore, most of the volcanic sulfate should be produced via gas phase oxidation by OH and/or via O₂-TMI aqueous oxidation. This is consistent with the lack of significant isotopic MIF anomalies in our measurements. The most likely fate of volcanic SO₂ during a large tropospheric eruption would be first to react quickly in liquid phases with H₂O₂, the most effective oxidant (Figure 4), leading to rapid H₂O₂ depletion. Since volcanic SO₂ concentrations would vastly exceed H₂O₂ concentrations, only a very small fraction of SO₂ could be oxidized by H₂O₂. Once H₂O₂ is depleted within the volcanic plume, the second most effective oxidant, the OH radical, can take over the S-bearing gas oxidation (Figure 4). Furthermore, OH concentrations are not expected to be as affected by SO₂ oxidation as H₂O₂, because OH radicals are regenerated on a time scale of the order of a second [Brasseur and Solomon, 1986], whereas H₂O₂ is typically regenerated on a time scale of a day [von Kuhlmann *et al.*, 2003]. It is also possible that O₂-TMI oxidation could play a significant role in this phase of volcanic SO₂ oxidation but only if the pH does not drop below 3. No data about the amount of TMI present in volcanic plumes are considered here. However, recent field measurements demonstrated that O₂-TMI oxidation could be one of the dominant pathways for in-cloud sulfur oxidation [e.g., Harris *et al.*, 2013]. In terms of isotopic signature, it would lower the sulfate $\Delta^{17}\text{O}$ to slightly negative values (Table 2), which could partly explain some sample compositions with small negative $\Delta^{17}\text{O}\text{‰}$ (down to -0.14‰ ; Table 1 and Figure 3).

Considering the quick tropospheric H₂O₂ depletion in volcanic plumes, it can be estimated that the formation of MD volcanic secondary sulfates ($-0.1\text{‰} < \Delta^{17}\text{O} < 0.1\text{‰}$) requires the participation of H₂O₂ for less than 10% and consequently OH radicals and/or O₂-TMI for more than 90%. This estimation is in agreement with our isotopic data set indicating that volcanic sulfates generated in the troposphere are massively mass dependent. The only exception would be one Mexican sample for which the H₂O₂ oxidation channel could have been responsible for up to 35% of the total sulfate formation. Without further data, notably on the isotopic composition of volcanic SO₂ and possibly of the fraction of primary versus secondary sulfates in the sampled volcanic ash, it is not possible to conclude unambiguously on the importance of the H₂O₂ channel for this specific volcanic eruption.

In the troposphere, volcanic sulfates produced by the oxidation channels (R1) (OH) and (R4) (O₂-TMI) are expected to have $\delta^{18}\text{O}$ between -5‰ and 1‰ and between 4 and 15‰ , respectively (Table 2). Sulfate produced by channel (R2) (H₂O₂) should have $\delta^{18}\text{O}$ between 13‰ and 25‰ . From our data sets, we have inferred that $>90\%$ of the volcanic sulfates in the troposphere are generated via (R1) and/or (R4) and $<10\%$ via (R2). Consequently, the mass balance calculation based on Table 2 indicates that volcanic sulfate should have $\delta^{18}\text{O}$ between -5‰ and 14‰ , which is similar to the composition range observed in our data set (Figure 3). However, as discussed before, fractionation processes such as distillation/condensation could be also responsible for at least some of the $\delta^{18}\text{O}$ variations observed in our samples. Indeed, during the release of S-bearing volcanic gases, the first sulfate aerosols formed quickly fall to the ground and relatively close to the volcanic vent. The not yet oxidized S-bearing gases are oxidized later on after traveling, depending on the wind, in the troposphere or in the tropopause region. The sulfate aerosols generated from these volcanic gases fall to the ground farther away from the volcanic vent than the first sulfate generation. According to the Rayleigh distillation equation, the first and latest generation of aerosol sulfate should be isotopically the heaviest and the lightest, respectively. Therefore, if distillation/condensation processes play an important role, we should expect sulfate having the highest $\delta^{18}\text{O}$ to be found in the volcanic deposits closest to the vent.

As discussed above, the $\delta^{34}\text{S}$ values from this study cannot be interpreted in terms of distillation/condensation processes as that would require a precise knowledge of the initial magmatic SO₂ isotopic composition

for each eruption. In order to better constrain the formation of sulfate and its isotopic composition, it is also necessary to have more precise fractionation factors than those experimentally determined by *Harris et al.* [2012] during SO₂ oxidation in the atmosphere. Then the discrimination between distillation/condensation processes and fractionation during SO₂ oxidation reactions would allow us to link the sulfate $\delta^{34}\text{S}$ with the distillation/condensation processes which should be somewhat a function of the distance to the studied volcano. As a consequence, the fractionation factors of the O and S isotopes during such processes that occur in complex environments such as volcanic plumes could be explored, as initiated by *Harris et al.* [2013]. This could certainly increase our knowledge of volcanic plume conditions and behavior in the troposphere. For instance, it could lead to the estimation of the distance from the source and potentially the altitude that a volcanic plume reached during a specific eruption based on the isotopic composition of the sulfate found in a volcanic deposit. This could obviously have major implications in tephra stratigraphy where the location and magnitude of eruptions are investigated from the study of different volcanic ash deposits.

5. Summary and Conclusions

In this paper, we illustrate how sulfate extracted from volcanic ash deposits could be useful to understand the oxidation of S-bearing gases in the atmosphere. Indeed, combining the S and O isotope compositions of these volcanic sulfates and model calculations may help to constrain the relative importance of some of the oxidation channels through which sulfate aerosols are generated in the atmosphere. While volcanic sulfates generated in the stratosphere during large eruptions show that most of the time, MIF oxidation channels dominate, volcanic sulfate formation in the troposphere is poorly constrained. In this study, we extracted sulfate from ash deposits of moderate eruptions, in order to assess volcanic sulfates that had been most likely generated in the troposphere and the tropopause region. Our isotopic measurements and modeling indicate that if H₂O₂—a MIF anomaly carrier—is by far the most important SO₂ oxidant in the background atmosphere, it must be quickly consumed by the volcanic SO₂ in the initial phase of the eruption. Oxidation of volcanic sulfur in the troposphere appears to be dominated by significantly non-MIF oxidation channels, notably oxidation via tropospheric OH radicals in the gas phase and by O₂ catalyzed by transition metal ions in the aqueous phase. Other more speculative non-MIF channels could be involved.

It has to be emphasized that the volcanic sulfate sampled was certainly a mix of primary sulfate (i.e., directly emitted by the volcanoes) and secondary sulfate (i.e., produced in the atmosphere). The MIF anomaly of primary sulfate is expected to be negligible. Nonetheless, in order to conclude unambiguously on the isotopic anomaly resulting from atmospheric processes, the isotopic composition of primary sulfate should be characterized for each eruption. This study shows that the individual variations in $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ for specific eruptions could also help to better constrain volcanic sulfur oxidation processes. However, in order to do so, the isotopic composition of initial volcanic SO₂ for specific eruptions needs to be known. Better constraints on volcanic sulfur oxidation processes would have important implications for our understanding of volcanic sulfate aerosol formation and hence the impact of volcanic eruptions on climate. Finally, the study of the isotopic composition of sulfate deposits from volcanoes that are found everywhere and have been present on Earth from its early stages could provide a window onto the atmospheric chemistry of the past.

Acknowledgments

We would like to thank S. Hidalgo, J. Roberge, B. Rose, A.M. Sarna-Wojcicki, O. Sigmarsson, and the rock collection at the Smithsonian Institution of Washington DC for providing volcanic ash samples as well as V. Atudorei for sulfur isotope analyses at the University of New Mexico. Constructive reviews from T. Mather and anonymous reviewers improved the manuscript. Finally, we are grateful to L. Whiteley for proofreading this manuscript. The city of Paris and the Agence Nationale de la Recherche (ANR) via contract 14-CE33-0009-02-FOFAMIFS are acknowledged for the financial support. Data can be requested from Erwan Martin (erwan.martin@upmc.fr).

References

- Alexander, B., J. Savarino, N. I. Barkov, R. J. Delmas, and M. H. Thiemens (2002), Climate driven changes in the oxidation pathways of atmospheric sulfur, *Geophys. Res. Lett.*, 29(14), 1685, doi:10.1029/2002GL014879.
- Alexander, B., R. J. Park, D. J. Jacob, Q. B. Li, R. M. Yantosca, J. Savarino, C. C. W. Lee and M. H. Thiemens (2005), Sulfate formation in sea-salt aerosols: Constraints from oxygen isotopes, *J. Geophys. Res.*, 110, D10307, doi:10.1029/2004JD005659.
- Alexander, B., R. J. Park, D. J. Jacob, and S. L. Gong (2009), Transition metal-catalyzed oxidation of atmospheric sulfur: Global implications for the sulfur budget, *J. Geophys. Res.*, 114, D02309, doi:10.1029/2008JD010486.
- Alexander, B., D. J. Allman, H. M. Amos, T. D. Fairlie, J. Dachs, D. A. Hegg, and R. S. Sletten (2012), Isotopic constraints on the formation pathways of sulfate aerosol in the marine boundary layer of the subtropical northeast Atlantic Ocean, *J. Geophys. Res.*, 117, D06304, doi:10.1029/2011JD016773.
- Alt, J. C., W. C. Shanks Iii, and M. C. Jackson (1993), Cycling of sulfur in subduction zones: The geochemistry of sulfur in the Mariana Island Arc and back-arc trough, *Earth Planet. Sci. Lett.*, 119(4), 477–494.
- Andres, R. J., and A. D. Kasgnoc (1998), A time-averaged inventory of subaerial volcanic sulfur emissions, *J. Geophys. Res.*, 103(D19), 25,251–25,261, doi:10.1029/98JD02091.
- Armienta, M. A., S. De la Cruz-Reyna, A. Soler, O. Cruz, N. Cenicerros, and A. Aguayo (2010), Chemistry of ash-leachates to monitor volcanic activity: An application to Popocatepetl volcano, central Mexico, *Appl. Geochem.*, 25(8), 1198–1205.

- Ayris, P. M., A. F. Lee, K. Wilson, U. Kueppers, D. B. Dingwell, and P. Delmelle (2013), SO₂ sequestration in large volcanic eruptions: High-temperature scavenging by tephra, *Geochim. Cosmochim. Acta*, *110*(0), 58–69.
- Bao, H. (2006), Purifying barite for oxygen isotope measurement by dissolution and reprecipitation in a chelating solution, *Anal. Chem.*, *78*, 304–309.
- Bao, H., and M. C. Reheis (2003), Multiple oxygen and sulfur isotopic analyses on water-soluble sulfate in bulk atmospheric deposition from the southwestern United States, *J. Geophys. Res.*, *108*(D14), 4430, doi:10.1029/2002JD003022.
- Baroni, M., M. H. Thiemens, R. J. Delmas, and J. Savarino (2007), Mass-independent sulfur isotopic compositions in stratospheric volcanic eruptions, *Science*, *315*, 84–87.
- Baroni, M., J. Savarino, J. H. Cole-Dai, V. K. Rai, and M. H. Thiemens (2008), Anomalous sulfur isotope compositions of volcanic sulfate over the last millennium in Antarctic ice cores, *J. Geophys. Res.*, *113*, D20112, doi:10.1029/2008JD010185.
- Bates, T. S., B. K. Lamb, A. Guenther, J. Dignon, and R. E. Stoiber (1992), Sulfur emissions to the atmosphere from natural sources, *J. Atmos. Chem.*, *14*(1–4), 315–337.
- Bey, I., D. J. Jacob, R. M. Yantosca, J. A. Logan, B. D. Field, A. M. Fiore, Q. Li, H. Y. Liu, L. J. Mickley, and M. G. Schultz (2001), Global modeling of tropospheric chemistry with assimilated meteorology: Model description and evaluation, *J. Geophys. Res.*, *106*(D19), 23,073–23,095, doi:10.1029/2001JD000807.
- Bindeman, I. N., J. M. Eiler, B. A. Wing, and J. Farquhar (2007), Rare sulfur and triple oxygen isotope geochemistry of volcanogenic sulfate aerosols, *Geochim. Cosmochim. Acta*, *71*, 2326–2343.
- Bluth, G. J. S., S. D. Doiron, C. C. Schnetzler, A. J. Krueger, and L. S. Walter (1992), Global tracking of the SO₂ clouds from the June, 1991 Mount Pinatubo eruptions, *Geophys. Res. Lett.*, *19*(2), 151–154, doi:10.1029/91GL02792.
- Brasseur, G. P., and S. Solomon (1986), *Aeronomy of the Middle Atmosphere: Chemistry and Physics of the Stratosphere and Mesosphere*, Springer, Dordrecht, Netherlands.
- Brenninkmeijer, C. A. M., C. Janssen, J. Kaiser, T. Röckmann, T. S. Rhee, and S. S. Assonov (2003), Isotope effects in the chemistry of atmospheric trace compounds, *Chem. Rev.*, *103*(12), 5125–5162.
- Carn, S. A., et al. (2011), In situ measurements of tropospheric volcanic plumes in Ecuador and Colombia during TC4, *J. Geophys. Res.*, *116*, D00J24, doi:10.1029/2010JD014718.
- Castleman, A. W., H. R. Munkelwitz, and B. Manowitz (1974), Isotopic studies of the sulfur component of the stratospheric aerosol layer^{1,2}, *Tellus*, *26*(1–2), 222–234.
- Cwiertny, D. M., M. A. Young, and V. H. Grassian (2008), Chemistry and photochemistry of mineral dust aerosol, *Annu. Rev. Phys. Chem.*, *59*(1), 27–51.
- Dupart, Y., et al. (2012), Mineral dust photochemistry induces nucleation events in the presence of SO₂, *Proc. Natl. Acad. Sci. U.S.A.*, *109*(51), 20,842–20,847.
- Eiler, J. (2001), Oxygen isotope variations of basaltic lavas and upper mantle rocks, in *Reviews in Mineralogy and Geochemistry*, edited by J. W. Walley and D. R. Cole, pp. 319–364, The Mineralogical Society of America, Washington.
- Emmons, L. K., et al. (2010a), Description and evaluation of the model for ozone and related chemical tracers, version 4 (MOZART-4), *Geosci. Model Dev.*, *3*(1), 43–67.
- Emmons, L. K., et al. (2010b), Impact of Mexico City emissions on regional air quality from MOZART-4 simulations, *Atmos. Chem. Phys.*, *10*(13), 6195–6212.
- Forster, P., and V. Ramaswamy (2007), Changes in atmospheric constituents and in radiative forcing, in *Climate Change 2007: The Physical Science Basis*, edited by S. Solomon et al., pp. 129–234, Cambridge Univ. Press, Cambridge, U. K., and New York.
- Giggenbach, W. F., et al. (2001), Evaluation of results from the fourth and fifth IAVCEI field workshops on volcanic gases, Vulcano island, Italy and Java, Indonesia, *J. Volcanol. Geotherm. Res.*, *108*(1–4), 157–172.
- Harris, E., B. Sinha, P. Hoppe, J. N. Crowley, S. Ono, and S. Foley (2012), Sulfur isotope fractionation during oxidation of sulfur dioxide: Gas-phase oxidation by OH radicals and aqueous oxidation by H₂O₂, O₃ and iron catalysis, *Atmos. Chem. Phys.*, *12*(1), 407–423.
- Harris, E., et al. (2013), Enhanced role of transition metal ion catalysis during in-cloud oxidation of SO₂, *Science*, *340*(6133), 727–730.
- Hill-Falkenthal, J., A. Priyadarshi, and M. Thiemens (2012), Differentiating sulfate aerosol oxidation pathways for varying source altitudes using ³⁵S and Δ^{17} O tracers, *J. Geophys. Res.*, *117*, D18302, doi:10.1029/2012JD018242.
- Horowitz, L. W., S. Walters, D. L. Mauzerall, L. K. Emmons, P. J. Rasch, C. Granier, X. Tie, J. Lamarque, M. Schultz, and G. P. Brasseur (2003), A global simulation of tropospheric ozone and related tracers: Description and evaluation of MOZART, version 2, *J. Geophys. Res.*, *108*(D24), 4784, doi:10.1029/2002JD002853.
- Hunton, D. E., et al. (2005), In-situ aircraft observations of the 2000 Mt. Hekla volcanic cloud: Composition and chemical evolution in the Arctic lower stratosphere, *J. Volcanol. Geotherm. Res.*, *145*(1–2), 23–34.
- Intergovernmental Panel on Climate Change (2007), *Climate Change 2007: The Scientific Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Rep.*, 996 pp, Cambridge.
- Johnson, M. S., K. L. Feilberg, P. V. Hessberg, and O. J. Nielsen (2002), Isotopic processes in atmospheric chemistry, *Chem. Soc. Rev.*, *31*(6), 313–323.
- Johnston, J. C., and M. H. Thiemens (1997), The isotopic composition of tropospheric ozone in three environments, *J. Geophys. Res.*, *102*(D21), 25,395–25,404, doi:10.1029/97JD02075.
- Krakovsky, D., F. Bartheck, G. G. Klees, K. Mauersberger, K. Schellenbach, and J. Stehr (1995), Measurement of heavy isotope enrichment in tropospheric ozone, *Geophys. Res. Lett.*, *22*(13), 1713–1716, doi:10.1029/95GL01436.
- Kreidenweis, S. M., C. J. Walcek, G. Feingold, W. Gong, M. Z. Jacobson, C.-H. Kim, X. Liu, J. E. Penner, A. Nenes, and J. H. Seinfeld (2003), Modification of aerosol mass and size distribution due to aqueous-phase SO₂ oxidation in clouds: Comparisons of several models, *J. Geophys. Res.*, *108*(D7), 4213, doi:10.1029/2002JD002697.
- Labidi, J., P. Cartigny, and M. Moreira (2013), Non-chondritic sulphur isotope composition of the terrestrial mantle, *Nature*, *501*(7466), 208–211.
- Labidi, J., P. Cartigny, J. L. Birck, N. Assayag, and J. J. Bourrand (2012), Determination of multiple sulfur isotopes in glasses: A reappraisal of the MORB $\delta^{34}\text{S}$, *Chem. Geol.*, *334*(0), 189–198.
- Lee, C., R. V. Martin, A. van Donkelaar, G. O'Byrne, N. Krotkov, A. Richter, L. G. Huey, and J. S. Holloway (2009), Retrieval of vertical columns of sulfur dioxide from SCIAMACHY and OMI: Air mass factor algorithm development, validation, and error analysis, *J. Geophys. Res.*, *114*, D22303, doi:10.1029/2009JD012123.
- Lyons, J. R. (2001), Mass-independent fractionation of oxygen-containing radicals in the atmosphere, *Geophys. Res. Lett.*, *28*(17), 3231–3234, doi:10.1029/2000GL012791.
- Maarten de Moor, J., T. P. Fischer, Z. D. Sharp, E. H. Hauri, D. R. Hilton, and V. Atudorei (2010), Sulfur isotope fractionation during the May 2003 eruption of Anatahan volcano, Mariana Islands: Implications for sulfur sources and plume processes, *Geochim. Cosmochim. Acta*, *74*(18), 5382–5397.

- Martin, E., and I. Bindeman (2009), Mass-independent isotopic signatures of volcanic sulfate from three supereruption ash deposits in Lake Tecopa, California, *Earth Planet. Sci. Lett.*, *282*, 102–114.
- Martin, L. R., and T. W. Good (1991), Catalyzed oxidation of sulfur dioxide in solution: The iron-manganese synergism, *Atmos. Environ.*, *25A*, 2395–2399.
- Mather, T. A., A. G. Allen, C. Oppenheimer, D. M. Pyle, and A. J. S. McGonigle (2003), Size-resolved characterisation of soluble ions in the particles in the tropospheric plume of Masaya Volcano, Nicaragua: Origins and plume processing, *J. Atmos. Chem.*, *46*(3), 207–237.
- Mather, T. A., J. R. McCabe, V. K. Rai, M. H. Thieme, D. M. Pyle, T. H. E. Heaton, H. J. Sloane, and G. R. Fern (2006), Oxygen and sulfur isotopic composition of volcanic sulfate aerosol at the point of emission, *J. Geophys. Res.*, *111*, D18205, doi:10.1029/2005JD006584.
- Mauersberger, K., D. Krankowsky, and C. Janssen (2003), Oxygen isotope processes and transfer reactions, *Space Sci. Rev.*, *106*(1–4), 265–279.
- McCabe, J. R., J. Savarino, B. Alexander, S. Gong, and M. H. Thieme (2006), Isotopic constraints on non-photochemical sulfate production in the Arctic winter, *Geophys. Res. Lett.*, *33*, L05810, doi:10.1029/2005GL025164.
- Morin, S., J. Savarino, S. Bekki, S. Gong, and J. W. Bottenheim (2007), Signature of Arctic surface ozone depletion events in the isotope anomaly ($\Delta^{17}\text{O}$) of atmospheric nitrate, *Atmos. Chem. Phys.*, *7*(5), 1451–1469.
- Morin, S., J. Savarino, M. M. Frey, N. Yan, S. Bekki, J. W. Bottenheim, and J. M. F. Martins (2008), Tracing the origin and fate of NO_x in the Arctic atmosphere using stable isotopes in nitrate, *Science*, *322*(5902), 730–732.
- Pfister, G. G., L. K. Emmons, P. G. Hess, J. F. Lamarque, A. M. Thompson, and J. E. Yorks (2008), Analysis of the Summer 2004 ozone budget over the United States using Intercontinental Transport Experiment Ozone-sonde Network Study (IONS) observations and Model of Ozone and Related Tracers (MOZART-4) simulations, *J. Geophys. Res.*, *113*, D23306, doi:10.1029/2008JD010190.
- Pfister, G. G., et al. (2006), Ozone production from the 2004 North American boreal fires, *J. Geophys. Res.*, *111*, D24507, doi:10.1029/2006JD007695.
- Quay, P., J. Stutsman, D. Wilbur, A. Snover, E. Dlugokencky, and T. Brown (1999), The isotopic composition of atmospheric methane, *Global Biogeochem. Cycles*, *13*(2), 445–461, doi:10.1029/1998GB900006.
- Rap, A., C. E. Scott, D. V. Spracklen, N. Bellouin, P. M. Forster, K. S. Carslaw, A. Schmidt, and G. Mann (2013), Natural aerosol direct and indirect radiative effects, *Geophys. Res. Lett.*, *40*, 3297–3301, doi:10.1002/grl.50441.
- Rix, M., P. Valks, N. Hao, D. Loyola, H. Schlager, H. Huntrieser, J. Flemming, U. Koehler, U. Schumann, and A. Inness (2012), Volcanic SO_2 , BrO and plume height estimations using GOME-2 satellite measurements during the eruption of Eyjafjallajökull in May 2010, *J. Geophys. Res.*, *117*, D00U19, doi:10.1029/2011JD016718.
- Robock, A. (2000), Volcanic eruption and climate, *Rev. Geophys.*, *38*, 191–219.
- Robock, A. (2004), Climatic impact of volcanic emissions, in *State of the Planet, Geophys. Monogr. Ser.*, vol. 150, edited by R. S. J. Sparks and C. J. Hawkesworth, pp. 125–134, AGU, Washington D. C.
- Rose, W. I., et al. (2006), Atmospheric chemistry of a 33–34 hour old volcanic cloud from Hekla Volcano (Iceland): Insights from direct sampling and the application of chemical box modeling, *J. Geophys. Res.*, *111*, D20206, doi:10.1029/2005JD006872.
- Rye, R. O., J. F. Luhr, and M. D. Wasserman (1984), Sulfur and oxygen isotopic systematics of the 1982 eruptions of El Chichón Volcano, Chiapas, Mexico, *J. Volcanol. Geotherm. Res.*, *23*(1–2), 109–123.
- Sander, S. P., et al. (2006), Chemical kinetics and photochemical data for use in atmospheric studies: Evaluation number 15Rep.
- Savarino, J., and M. H. Thieme (1999), Analytical procedure to determine both $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ of H_2O_2 in natural water and first measurements, *Atmos. Environ.*, *33*, 3683–3690.
- Savarino, J., C. C. W. Lee, and M. H. Thieme (2000), Laboratory oxygen isotopic study of sulfur (IV) oxidation: Origin of the mass-independent oxygen isotopic anomaly in atmospheric sulfates and sulfate mineral deposits on Earth, *J. Geophys. Res.*, *105*(D23), 29,079–29,088, doi:10.1029/2000JD900456.
- Savarino, J., S. Bekki, J. H. Cole-Dai, and M. H. Thieme (2003a), Evidence from sulfate mass independent oxygen isotopic compositions of dramatic changes in atmospheric oxidation following massive volcanic eruptions, *J. Geophys. Res.*, *108*(D21), 4671, doi:10.1029/2003JD003737.
- Savarino, J., A. Romero, J. H. Cole-Dai, S. Bekki, and M. H. Thieme (2003b), UV induced mass-independent sulfur isotope fractionation in stratospheric volcanic sulfate, *Geophys. Res. Lett.*, *30*(21), 2131, doi:10.1029/2003GL018134.
- Seinfeld, J. H., and S. N. Pandis (2006), *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 2nd ed., John Wiley, New York.
- Smith, S. J., J. van Aardenne, Z. Klimont, R. J. Andres, A. Volke, and S. Delgado Arias (2011), Anthropogenic sulfur dioxide emissions: 1850–2005, *Atmos. Chem. Phys.*, *11*(3), 1101–1116.
- Symonds, R., W. Rose, T. Gerlach, P. Briggs, and R. Harmon (1990), Evaluation of gases, condensates, and SO_2 emissions from Augustine volcano, Alaska: The degassing of a Cl-rich volcanic system, *Bull. Volcanol.*, *52*(5), 355–374.
- Schmidt, A., T. Thordarson, L. D. Oman, A. Robock, and S. Self (2012a), Climatic impact of the long-lasting 1783 Laki eruption: Inapplicability of mass-independent sulfur isotopic composition measurements, *J. Geophys. Res.*, *117*, D23116, doi:10.1029/2012JD018414.
- Schmidt, A., K. S. Carslaw, G. W. Mann, A. Rap, K. J. Pringle, D. V. Spracklen, M. Wilson, and P. M. Forster (2012b), Importance of tropospheric volcanic aerosol for indirect radiative forcing of climate, *Atmos. Chem. Phys.*, *12*(16), 7321–7339.
- Thieme, M. H. (1999), Mass-independent isotope effects in planetary atmospheres and the early solar system, *Science*, *283*, 341–345.
- Thieme, M. H. (2006), History and applications of mass-independent isotope effects, *Annu. Rev. Earth Planet. Sci.*, *34*, 217–262.
- Vernier, J. P., et al. (2011), Major influence of tropical volcanic eruptions on the stratospheric aerosol layer during the last decade, *Geophys. Res. Lett.*, *38*, L12807, doi:10.1029/2011GL047563.
- Vicars, W. C., S. K. Bhattacharya, J. Erbland, and J. Savarino (2012), Measurement of the ^{17}O -excess ($\Delta^{17}\text{O}$) of tropospheric ozone using a nitrite-coated filter, *Rapid Commun. Mass Spectrom.*, *26*(10), 1219–1231.
- von Glasow, R., R. Sander, A. Bott, and P. J. Crutzen (2002), Modeling halogen chemistry in the marine boundary layer 2. Interactions with sulfur and the cloud-covered MBL, *J. Geophys. Res.*, *107*(D17), 4323, doi:10.1029/2001JD000943.
- von Kuhlmann, R., M. G. Lawrence, P. J. Crutzen, and P. J. Rasch (2003), A model for studies of tropospheric ozone and nonmethane hydrocarbons: Model evaluation of ozone-related species, *J. Geophys. Res.*, *108*(D23), 4729, doi:10.1029/2002JD003348.
- Wallace, P. (2001), Volcanic SO_2 emissions and the abundance and distribution of exsolved gas in magma bodies, *J. Volcanol. Geotherm. Res.*, *108*, 85–106.
- Wiedinmyer, C., S. K. Akagi, R. J. Yokelson, L. K. Emmons, J. A. Al-Saadi, J. J. Orlando, and A. J. Soja (2011), The Fire INventory from NCAR (FINN): A high resolution global model to estimate the emissions from open burning, *Geosci. Model Dev.*, *4*(3), 625–641.
- Yang, K., N. A. Krotkov, A. J. Krueger, S. A. Carn, P. K. Bhartia, and P. F. Levelt (2007), Retrieval of large volcanic SO_2 columns from the Aura Ozone Monitoring Instrument: Comparison and limitations, *J. Geophys. Res.*, *112*, D24543, doi:10.1029/2007JD008825.
- Yang, K., N. A. Krotkov, A. J. Krueger, S. A. Carn, P. K. Bhartia, and P. F. Levelt (2009), Improving retrieval of volcanic sulfur dioxide from backscattered UV satellite observations, *Geophys. Res. Lett.*, *36*, L03102, doi:10.1029/2008GL036036.
- Yoshida, N., and S. Toyoda (2000), Constraining the atmospheric N_2O budget from intramolecular site preference in N_2O isotopomers, *Nature*, *405*(6784), 330–334.
- Young, E., Y. Y. Laurence, and E. K. Issaku (2014), On the $\Delta^{17}\text{O}$ budget of atmospheric O_2 , *Geochim. Cosmochim. Acta*, *135*, 102–125.