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COMMENTARY

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On the Budget and Atmospheric Fate of Sulfur Emissions From Large Volcanic Eruptions

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Key Points:

- The impact of volcanic activity on climate remains difficult to quantify for eruptions prior to the instrumental era
- The petrological and glaciochemical methods each provide answers, but are still fraught with large uncertainties
- We need to further our understanding of the physicochemical processes occurring both within magma reservoirs and volcanic plumes

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Abstract Today, volcanic sulfur emissions into the atmosphere are measured spectroscopically from the ground, air and space. For eruptions prior to the satellite era, two main sulfur proxies are used, the rock and ice core records, as illustrated by Peccia et al. (2023, <https://doi.org/10.1029/2023gl103334>). The first approach is based on calculations of the sulfur content of the magma, while the second uses traces of sulfur deposited in ice. Both approaches have their limitations. For glaciochemistry, the volcano responsible for a sulfur anomaly is often unknown and the atmospheric pathway by which the sulfur reached the ice uncertain. The petrologic method relies, too, on uncertain estimates of eruption size and a number of geochemical assumptions that are hard to verify. A deeper knowledge of processes occurring both within magma bodies prior to eruption, and within volcanic plumes in the atmosphere is needed to further our understanding of the impacts of volcanism on climate.

Plain Language Summary Volcanic emissions of sulfur gases during large eruptions can change the global climate. Today, advanced spectroscopic tools allow us to measure sulfur from the ground, air and space. But to understand the impacts of volcanic activity on climate back through history we need to estimate volcanic sulfur releases in other ways. Clues can be found in the pumice deposits found around a volcano and, perhaps more surprisingly, in the ice caps of the polar regions, which receive the eventual fallout from large eruptions. Both approaches have limitations that are addressed in a recent work by Peccia et al. (2023, <https://doi.org/10.1029/2023gl103334>) and that are at the focus of our commentary.

1. Introduction

Volcanic outgassing established the Earth's secondary atmosphere, and all volcanic gaseous emissions contain sulfur, variously speciated (including S, SO₂ and H₂S; Oppenheimer et al., 2011, 2014). Native sulfur deposits often encrust fumarole vents at degassing volcanoes but sulfur may also exist in more (sulfates) and less (sulfides) oxidized forms. In the atmosphere, both H₂S and SO₂ oxidize (Figure 1), forming sulfate aerosol, the key protagonist in the climate forcing associated with volcanism (Marshall et al., 2019, 2022). Interest in the climatic effects of eruptions can be traced back to the late 18th Century but it accelerated since the 1960 s thanks to airborne sampling and satellite remote sensing of volcanic plumes, along with advances in historical climatology. In particular, the eruption of Pinatubo in 1991 fueled our understanding of the generation of stratospheric sulfate aerosol via oxidation of volcanically emitted sulfur, and the consequences of the resulting “dust veil” encircling the Earth for atmospheric chemistry and radiation (e.g., Brasseur & Granier, 1992; McCormick et al., 1995; Minnis et al., 1993).

As the most relevant parameter, the yield of sulfur from an eruption needs to be calculated in order to model and evaluate climatic variation. While SO₂ emissions can be measured from space with increasing sensitivity (e.g., Carn et al., 2017; Theys et al., 2013), other sulfur species (notably H₂S and sulfate aerosol, which may represent a significant fraction of total emitted sulfur) are more challenging to quantify from satellite observations. Accurate measurements can also be hindered by the presence of volcanic ash (leading to underestimated SO₂ amounts), and emitted SO₂ can be efficiently scavenged by hydrometeors. Thus, estimates of the total sulfur yield can be subject to considerable uncertainties, even for “well-observed” eruptions.

For eruptions that occurred before the instrumental era (i.e., before around 1960), there are two main approaches to evaluating sulfur yield: the petrologic method based on studies of the rock record, and the ice core method that draws on measurements of the sulfur that is eventually deposited over the polar regions from airborne aerosol

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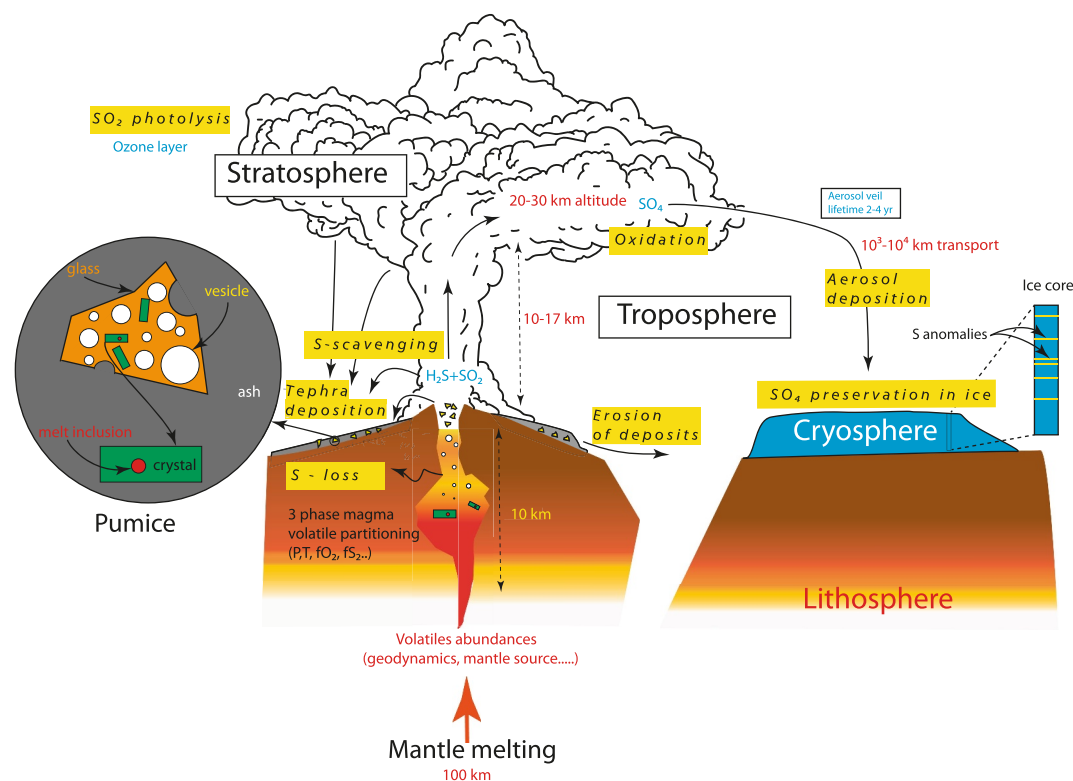


Figure 1. Diagram representing key pathways and speciation of sulfur below ground, and the chemistry and transport of sulfur in the atmosphere and deposition back to the surface. Inset on left depicts pumice clast and melt inclusion within a crystal. Note that some processes may result in fractionation of sulfur isotopes. Scales shown are indicative only.

veils (Figure 1) (Hammer et al., 1980). The extent to which these two approaches can give different results is highlighted in a new study by Peccia et al. (2023), who show how petrologic estimates of eruptive sulfur yield can be a poor guide to the climatically-effective amount of sulfur that reaches the stratosphere. In particular their analysis shows that a significant component of emitted sulfur does not cross the tropopause and thus experiences a much reduced atmospheric lifetime and transport.

The petrologic method relies on sedimentological and stratigraphic fieldwork aimed at determining the erupted mass (magnitude), as well as evaluation of the proportions of reactive volatiles released to the atmosphere from the melt (e.g., Schmidt & Black, 2022). The latter demands robust constraints on the volatile budgets of erupting magmas, which are usually based on analyses of volatile abundances (including sulfur) in melt inclusions (MI), small aliquots of melt trapped in crystals (Figure 1). The volatile amounts in the MIs are assumed to represent the pre-eruptive magma chemistry (Devine et al., 1984). Such calculations of volatile yield are then particularly sensitive to assumptions made for element partitioning (e.g., Liu et al., 2006; Papale, 2005; Wallace et al., 1995, 1999; Wallace & Gerlach, 1994) and conservation (e.g., Iacovino et al., 2016; Vidal et al., 2016), in addition to issues concerning MI occurrence and integrity (e.g., volatile leakage).

Since Luhr et al. (1984), in an investigation of the 1982 El Chichón eruption, showed that the large sulfur release to the atmosphere was sourced primarily from a separate fluid phase present in the magma reservoir prior to eruption (vesicles in Figure 1), much effort has gone into quantifying gas/melt partitioning of sulfur in silicate melts (D_S), in particular for felsic compositions (e.g., Binder et al., 2018; Keppler, 1999, 2010; Masotta et al., 2016; Scaillet & Macdonald, 2006; Scaillet et al., 1998; Zajacz & Tsay, 2019; Zajacz et al., 2012). These and other studies have revealed the high sensitivity of D_S to the oxygen fugacity (fO_2) and composition of the melt.

Another approach to probing sulfur behavior during magma degassing (e.g., Burgisser & Scaillet, 2007) is the application of thermodynamic models (e.g., Boulliang & Wood, 2022; Clemente et al., 2004; Ding et al., 2023; Moretti et al., 2003). However, most of these are calibrated for H_2O and S only, and struggle to account for the complex interplay between different volatiles. In particular, the role of CO_2 or Cl on S behavior during magma

degassing remains underexplored. Similarly, sulfide crystallization (which may sequester a significant part of the S budget), while reasonably well understood for H₂O-poor mafic systems (O'Neill, 2021), remains something of a mystery for H₂O-rich silicic magmas. These approaches further assume equilibrium conditions, which may not be attained due to reaction kinetics. Sulfur diffuses comparatively slowly in silicate melts, such that its partitioning may not reach equilibrium on the timescales of magma ascent and fragmentation, especially during explosive eruptions (Su et al., 2016). Ongoing community efforts involving model benchmarking and intercomparison continue to improve petrological S estimates (<https://eartharxiv.org/repository/view/5298>).

The primary basis for estimating sulfur yields from ice core glaciochemistry is the relationship between sulfur concentration in the ice and the amount and dispersal of sulfur released by the eruption into the atmosphere (e.g., Sigl et al., 2022). While ice cores represent an exceptional archive of information on global volcanism (Figure 1), several issues translate into considerable uncertainties in using ice core-derived estimates of sulfur yield for modeling climatic impacts of eruptions (Aubry et al., 2020; Toohey & Sigl, 2017), and in relating historical evidence to volcanic forcing (e.g., Guillet et al., 2023; Pearson et al., 2022). These arise from uncertainties in ice core dating and in the geographic location (importantly latitude) of the volcano responsible for an anomaly in the core. They also reflect the extreme leveraging from sulfur deposition measured in ppb in the ice to atmospheric yields measured in Tg, and ambiguity in the pathways taken by volcanic sulfate aerosol to the ice (i.e., stratospheric vs. tropospheric, Figure 1). Additionally, halogen emissions may impact atmospheric chemistry and radiation (e.g., Brenna et al., 2020; Bureau et al., 2000; Cadoux et al., 2015; Kutterolf et al., 2013) yet are not readily quantified from polar ice records. These issues are particularly acute for understanding the consequences of larger eruptions, owing to their rarity, the complexities of volatile behavior in their source melts, and in the dynamics of their atmospheric plumes, which may be sourced from both buoyant columns and pyroclastic density currents (Wilson et al., 2021).

An emblematic example of the challenges is the 74 ka Youngest Toba Tuff (YTT) eruption for which estimates of sulfur yield range from zero (no excess gas, and no melt degassing) to 3,000 Tg S (see: Rampino & Self, 1984; Scaillet et al., 1998; Oppenheimer, 2002; Chesner & Luhr, 2010). If the YTT signature is eventually definitively identified in polar ice core records it promises to resolve between these extreme scenarios. The uncertainties in sulfur yield, along with those in microphysical processes relevant to sulfate aerosol formation and size distribution (e.g., McGraw et al., 2024; Tilmes et al., 2023), are reflected in wide-ranging scenarios (from regional effects only to globally catastrophic “volcanic winter”) presented for the environmental and climatic impacts of the super-eruption (e.g., Black et al., 2021; Crick et al., 2021; Osipov et al., 2021; Rampino & Self, 1984; Robock et al., 2009; Timmreck et al., 2012). The climatic significance of the YTT may turn out to be muted compared with that of Los Chocoyos eruption (Guatemala), recently dated to circa 74 ka (Cisneros de Leon et al., 2021). Petrologic estimates suggest it released as much as 500 Tg S (Brenna et al., 2020).

In their new study, Peccia et al. (2023) employed the petrologic approach to probe the sulfur budget of a less renowned explosive eruption that of Okmok volcano in Alaska, dated to 43 BCE. Of note, they argued that only around a quarter of the estimated 62 Tg of gaseous sulfur released on eruption crossed the tropopause. This is significant because if all the sulfur been injected into the stratosphere, the climatic impacts would likely have been substantially stronger. By comparing sulfur yields for several other eruptions estimated both from eruption magnitude and petrologic evidence and from ice core glaciochemistry, Peccia et al. (2023) go on to suggest that this sequestration of sulfur in the lower atmosphere (including by adsorption on to tephra) is typical for larger explosive eruptions, whose ash plumes tend to collapse episodically, generating pyroclastic density currents. Another, more recent, example is provided by the 2011 eruption of Grímsvötn in Iceland. Observations for this much smaller eruption suggest that only ~20%–30% of the petrologic sulfur load reached the stratosphere (Sigmarsson et al., 2013). The clear lesson here is that the total sulfur yield of an eruption may not represent a reliable input for climate models, which are predicated on stratospheric sulfur burdens, a conclusion that recapitulates findings of much earlier modeling studies of the chemical and physical processing of gaseous species in volcanic plumes by silicate ash and hydrometeors (e.g., Pinto et al., 1989; Textor et al., 2003). Even with robust measurements of stratospheric sulfur burdens, disambiguating the climatic signatures of external forcing (e.g., volcanism) from internal variability is fraught with difficulties (e.g., Bengtsson & Hodges, 2019; DallaSanta & Polvani, 2022; Mann et al., 2022).

Peccia et al. (2023) relied on maximum concentrations of sulfur recorded in MI to constrain their volatile budget. However, a critical challenge for such petrologic approaches is our still limited knowledge of the pre-eruptive

behavior of volatiles during magma storage in the lithosphere. In this respect, the timescales of reservoir evolution and incubation become important, since longer intervals promote volatile accumulation toward the top of a reservoir while simultaneously favoring volatile escape (Figure 1) (e.g., Mittal & Richards, 2019). The balance of accumulation and loss will determine the quantities of volatiles immediately accessible once an eruption is underway. Estimates of bulk volatile contents based on element conservation (i.e., preservation of a given element during magma evolution from mafic to felsic compositions) will represent upper limits (e.g., Vidal et al., 2016) since they neglect potential pre-eruptive volatile loss. A reassessment of the sulfur budget for the 946 CE Millennium Eruption of Paektu-Changbaishan has suggested that up to half of the volatiles in the reservoir could have escaped the upper crustal reservoir prior to eruption (Scaillet & Oppenheimer, 2023).

Mismatches between petrologic and ice core-based estimates of sulfur yields can arise for other reasons. One is that it may be oversimplistic to regard an eruption being sourced from a single reservoir. For instance, detailed geochemical modeling for the YTT magma suggests that such large eruptions are fed by separate magma bodies in the crust (e.g., Naen et al., 2023; Pearce et al., 2020), adding further complexity to assessments of volatile yields. Furthermore, as noted above, any petrologic calculations of volatile yields depend on estimates of the eruption magnitude, that is, the mass of magma discharged. Sizing an eruption is not straightforward, and disparate estimates for the same deposit often vary significantly. For instance, the YTT “dense rock equivalent” volume was revised from around 3,000 km³ up to 5,000 km³ (Costa et al., 2014), and even estimates for the 1991 Pinatubo eruption have a factor of two uncertainty (Holasek et al., 1996). Tephra deposits are readily eroded and redistributed (Figure 1), and may be hard to quantify owing to lack of basal exposure or sedimentation across wide areas of the deep ocean subject to very limited sampling. A factor of two difference between ice core based and petrologic estimates of sulfur yield can, frankly, be accommodated in most cases by uncertainty in erupted volume.

For very ancient volcanic episodes, erupted volumes may perhaps be best gauged from their exposed plutonic systems. This requires improved understanding of how and on what timescales batholiths develop (e.g., Szymanowski et al., 2023), so that we can better evaluate the tempo of volatile accumulation (and loss) in the upper reaches of magma reservoirs. In addition, computational approaches might consider not only the dynamics of ash plumes, but also the complex chemical and physical interactions of volcanogenic and atmospheric constituents, which remain poorly understood owing in part to the difficulty of in situ observations of the interiors of volcanic plumes. Going forwards, we believe that integration of all these parameters and their feedbacks is required, and this calls for concerted interdisciplinary engagement of petrologists, geochemists, volcanologists, (paleo) climatologists, and atmospheric scientists.

Data Availability Statement

No new data have been used in this paper.

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