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Bruno Scaillet, Clive Oppenheimer. On the Budget and Atmospheric Fate of Sulfur Emissions From Large Volcanic Eruptions. *Geophysical Research Letters*, 2024, 51, 10.1029/2023GL107180 . insu-04647672

HAL Id: insu-04647672

<https://insu.hal.science/insu-04647672>

Submitted on 15 Jul 2024

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Geophysical Research Letters®



COMMENTARY

10.1029/2023GL107180

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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Citation:

Scaillet, B., & Oppenheimer, C. (2024). On the budget and atmospheric fate of sulfur emissions from large volcanic eruptions. *Geophysical Research Letters*, 51, e2023GL107180. <https://doi.org/10.1029/2023GL107180>

Received 15 FEB 2024

Accepted 12 JUN 2024

Author Contributions:

Writing – original draft: Bruno Scaillet

Writing – review & editing:

Clive Oppenheimer

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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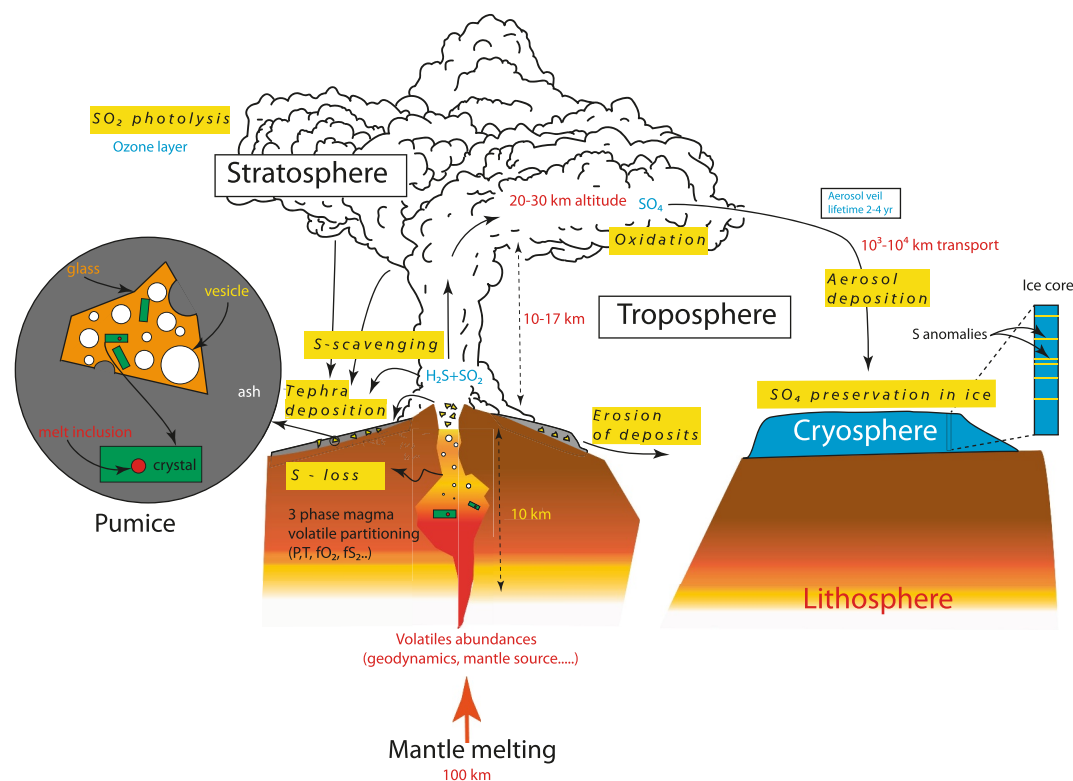


Figure 1. Diagram representing key pathways and speciation of sulfur below ground, and the chemistry and transport of sulfur in the atmosphere and deposition back to the surface. Inset on left depicts pumice clast and melt inclusion within a crystal. Note that some processes may result in fractionation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

References

- Aubry, T. J., Toohey, M., Marshall, L., Schmidt, A., & Jellinek, A. M. (2020). A new volcanic stratospheric sulfate aerosol forcing emulator (EVA_H): Comparison with interactive stratospheric aerosol models. *Journal of Geophysical Research: Atmospheres*, 125(3), e2019JD031303. <https://doi.org/10.1029/2019jd031303>
- Bengtsson, L., & Hodges, K. I. (2019). Can an ensemble climate simulation be used to separate climate change signals from internal unforced variability? *Climate Dynamics*, 52(5–6), 3553–3573. <https://doi.org/10.1007/s00382-018-4343-8>
- Binder, B., Wenzel, T., & Keppler, H. (2018). The partitioning of sulfur between multicomponent aqueous fluids and felsic melts. *Contributions to Mineralogy and Petrology*, 173(2), 1–14. <https://doi.org/10.1007/s00410-018-1445-6>
- Black, B. A., Lamarque, J. F., Marsh, D. R., Schmidt, A., & Bardeen, C. G. (2021). Global climate disruption and regional climate shelters after the Toba supereruption. *Proceedings of the National Academy of Sciences*, 118(29), e2013046118. <https://doi.org/10.1073/pnas.2013046118>
- Boulliung, J., & Wood, B. J. (2022). SO₂ solubility and degassing behavior in silicate melts. *Geochimica et Cosmochimica Acta*, 336, 150–164. <https://doi.org/10.1016/j.gca.2022.08.032>
- Brasseur, G., & Granier, C. (1992). Mount Pinatubo aerosols, chlorofluorocarbons, and ozone depletion. *Science*, 257(5074), 1239–1242. <https://doi.org/10.1126/science.257.5074.1239>
- Brenna, H., Kutterolf, S., Mills, M. J., & Krüger, K. (2020). The potential impacts of a sulfur-and halogen-rich supereruption such as Los Chocoyos on the atmosphere and climate. *Atmospheric Chemistry and Physics*, 20(11), 6521–6539. <https://doi.org/10.5194/acp-20-6521-2020>
- Bureau, H., Keppler, H., & Métrich, N. (2000). Volcanic degassing of bromine and iodine: Experimental fluid/melt partitioning data and applications to stratospheric chemistry. *Earth and Planetary Science Letters*, 183(1), 51–60. [https://doi.org/10.1016/s0012-821x\(00\)00258-2](https://doi.org/10.1016/s0012-821x(00)00258-2)
- Burgisser, A., & Scaillet, B. (2007). Redox evolution of a degassing magma rising to the surface. *Nature*, 445(7124), 194–197. <https://doi.org/10.1038/nature05509>
- Cadoux, A., Scaillet, B., Bekki, S., Oppenheimer, C., & Druitt, T. H. (2015). Stratospheric ozone destruction by the Bronze-Age Minoan eruption (Santorini volcano, Greece). *Scientific Reports*, 5(1), 12243. <https://doi.org/10.1038/srep12243>

Acknowledgments

The authors gratefully acknowledge Steve Self and two anonymous reviewers for their help in improving the manuscript, as well as the editorial support of Christian Huber. We acknowledge support from both LabEx VOLTAIRE (ANR-10-LABX-100-01) and EquipEx PLANEX (ANR-11-EQPX-0036) projects.

- Carn, S. A., Fioletov, V. E., McLinden, C. A., Li, C., & Krotkov, N. A. (2017). A decade of global volcanic SO₂ emissions measured from space. *Scientific Reports*, 7(1), 44095. <https://doi.org/10.1038/srep44095>
- Chesner, C. A., & Luhr, J. F. (2010). A melt inclusion study of the Toba Tuffs, Sumatra, Indonesia. *Journal of Volcanology and Geothermal Research*, 197(1–4), 259–278. <https://doi.org/10.1016/j.jvolgeores.2010.06.001>
- Cisneros de León, A., Schindlbeck-Belo, J. C., Kutterolf, S., Danišić, M., Schmitt, A. K., Freundt, A., et al. (2021). A history of violence: Magma incubation, timing and tephra distribution of the Los Chocoyos supereruption (Atitlán Caldera, Guatemala). *Journal of Quaternary Science*, 36(2), 169–179. <https://doi.org/10.1002/jqs.3265>
- Clemente, B., Scaillet, B., & Pichavant, M. (2004). The solubility of sulphur in hydrous rhyolitic melts. *Journal of Petrology*, 45(11), 2171–2196. <https://doi.org/10.1093/petrology/egh052>
- Costa, A., Smith, V. C., Macedonio, G., & Matthews, N. E. (2014). The magnitude and impact of the Youngest Toba Tuff super-eruption. *Frontiers in Earth Science*, 2, 16. <https://doi.org/10.3389/feart.2014.00016>
- Crick, L., Burke, A., Hutchison, W., Kohno, M., Moore, K. A., Savarino, J., et al. (2021). New insights into the ~74 ka Toba eruption from sulfur isotopes of polar ice cores. *Climate of the Past*, 17(5), 2119–2137. <https://doi.org/10.5194/cp-17-2119-2021>
- DallaSanta, K., & Polvani, L. M. (2022). Volcanic stratospheric injections up to 160 Tg (S) yield a Eurasian winter warming indistinguishable from internal variability. *Atmospheric Chemistry and Physics*, 22(13), 8843–8862. <https://doi.org/10.5194/acp-22-8843-2022>
- Devine, J. D., Sigurdsson, H., Davis, A. N., & Self, S. (1984). Estimates of sulfur and chlorine yield to the atmosphere from volcanic eruptions and potential climatic effects. *Journal of Geophysical Research*, 89(B7), 6309–6325. <https://doi.org/10.1029/jb089ib07p06309>
- Ding, S., Plank, T., Wallace, P. J., & Rasmussen, D. J. (2023). Sulfur_X: A model of sulfur degassing during magma ascent. *Geochemistry, Geophysics, Geosystems*, 24(4), e2022GC010552. <https://doi.org/10.1029/2022gc010552>
- Guillet, S., Corona, C., Oppenheimer, C., Lavigne, F., Khodri, M., Ludlow, F., et al. (2023). Lunar eclipses illuminate timing and climate impact of medieval volcanism. *Nature*, 616(7955), 90–95. <https://doi.org/10.1038/s41586-023-05751-z>
- Hammer, C. U., Clausen, H. B., & Dansgaard, W. (1980). Greenland ice sheet evidence of post-glacial volcanism and its climatic impact. *Nature*, 288(5788), 230–235. <https://doi.org/10.1038/288230a0>
- Holasek, R. E., Self, S., & Woods, A. W. (1996). Satellite observations and interpretation of the 1991 Mount Pinatubo eruption plumes. *Journal of Geophysical Research*, 101(B12), 27635–27655. <https://doi.org/10.1029/96jb011179>
- Iacovino, K., Ju-Song, K., Sisson, T., Lowenstern, J., Kuk-Hun, R., Jong-Nam, J., et al. (2016). Quantifying gas emissions from the “Millennium eruption” of Paektu volcano, democratic People’s Republic of Korea/China. *Science Advances*, 2(11), e1600913. <https://doi.org/10.1126/sciadv.1600913>
- Keppeler, H. (1999). Experimental evidence for the source of excess sulfur in explosive volcanic eruptions. *Science*, 284(5420), 1652–1654. <https://doi.org/10.1126/science.284.5420.1652>
- Keppeler, H. (2010). The distribution of sulfur between haplogranitic melts and aqueous fluids. *Geochimica et Cosmochimica Acta*, 74(2), 645–660. <https://doi.org/10.1016/j.gca.2009.10.010>
- Kutterolf, S., Hansteen, T. H., Appel, K., Freundt, A., Krüger, K., Perez, W., & Wehrmann, H. (2013). Combined bromine and chlorine release from large explosive volcanic eruptions: A threat to stratospheric ozone? *Geology*, 41(6), 707–710. <https://doi.org/10.1130/g34044.1>
- Liu, Y., Anderson, A. T., Wilson, C. J., Davis, A. M., & Steele, I. M. (2006). Mixing and differentiation in the Oruanui rhyolitic magma, Taupo, New Zealand: Evidence from volatiles and trace elements in melt inclusions. *Contributions to Mineralogy and Petrology*, 151(1), 71–87. <https://doi.org/10.1007/s00410-005-0046-3>
- Mann, M. E., Steinman, B. A., Brouillette, D. J., Fernandez, A., & Miller, S. K. (2022). On the estimation of internal climate variability during the preindustrial past millennium. *Geophysical Research Letters*, 49(2), e2021GL096596. <https://doi.org/10.1029/2021gl096596>
- Marshall, L., Johnson, J. S., Mann, G. W., Lee, L., Dhomse, S. S., Regayre, L., et al. (2019). Exploring how eruption source parameters affect volcanic radiative forcing using statistical emulation. *Journal of Geophysical Research: Atmospheres*, 124(2), 964–985. <https://doi.org/10.1029/2018jd028675>
- Marshall, L. R., Maters, E. C., Schmidt, A., Timmreck, C., Robock, A., & Toohey, M. (2022). Volcanic effects on climate: Recent advances and future avenues. *Bulletin of Volcanology*, 84(5), 54. <https://doi.org/10.1007/s00445-022-01559-3>
- Masotta, M., Keppeler, H., & Chaudhari, A. (2016). Fluid-melt partitioning of sulfur in differentiated arc magmas and the sulfur yield of explosive volcanic eruptions. *Geochimica et Cosmochimica Acta*, 176, 26–43. <https://doi.org/10.1016/j.gca.2015.12.014>
- McCormick, M. P., Thomason, L. W., & Trepte, C. R. (1995). Atmospheric effects of the Mt Pinatubo eruption. *Nature*, 373(6513), 399–404. <https://doi.org/10.1038/373399a0>
- McGraw, Z., DallaSanta, K., Polvani, L. M., Tsigaridis, K., Orbe, C., & Bauer, S. E. (2024). Severe global cooling after volcanic super-eruptions? The answer hinges on unknown aerosol size. *Journal of Climate*, 37(4), 1449–1464. <https://doi.org/10.1175/jcli-d-23-01116.1>
- Minnis, P., Harrison, E. F., Stowe, L. L., Gibson, G. G., Denn, F. M., Doelling, D. R., & Smith Jr, W. L. (1993). Radiative climate forcing by the Mount Pinatubo eruption. *Science*, 259(5100), 1411–1415. <https://doi.org/10.1126/science.259.5100.1411>
- Mittal, T., & Richards, M. A. (2019). Volatile degassing from magma chambers as a control on volcanic eruptions. *Journal of Geophysical Research: Solid Earth*, 124(8), 7869–7901. <https://doi.org/10.1029/2018jb016983>
- Moretti, R., Papale, P., & Ottonello, G. (2003). A model for the saturation of C-O-H-S fluids in silicate melts. In C. Oppenheimer, D. M. Pyle, & J. Barclay (Eds.), *Volcanic degassing*. Geological Society of London. <https://doi.org/10.1144/GSL.SP.2003.213.01.06>
- Naen, G. N. R. B., Toramaru, A., Juhri, S., Yonezu, K., Wibowo, H. E., Gunawan, R. M. P. P., & Disando, T. (2023). Distinct pumice populations in the 74 ka Youngest Toba Tuff: Evidence for eruptions from multiple magma chambers. *Journal of Volcanology and Geothermal Research*, 437, 107804. <https://doi.org/10.1016/j.jvolgeores.2023.107804>
- O’Neill, H. S. C. (2021). The thermodynamic controls on sulfide saturation in silicate melts with application to ocean floor basalts. *Magma Redox Geochemistry*, 177–213. <https://doi.org/10.1002/9781119473206.ch10>
- Oppenheimer, C. (2002). Limited global change due to the largest known Quaternary eruption, Toba ≈ 74 kyr BP? *Quaternary Science Reviews*, 21(14–15), 1593–1609. [https://doi.org/10.1016/s0277-3791\(01\)00154-8](https://doi.org/10.1016/s0277-3791(01)00154-8)
- Oppenheimer, C., Fischer, T. P., & Scaillet, B. (2014). Volcanic degassing: Process and impact. *Treatise on Geochemistry (Second Edition)*, 4, 111–179. <https://doi.org/10.1016/b978-0-08-095975-7.00304-1>
- Oppenheimer, C., Scaillet, B., & Martin, R. S. (2011). Sulfur degassing from volcanoes: Source conditions, surveillance, plume chemistry and earth system impacts. *Reviews in Mineralogy and Geochemistry*, 73(1), 363–421. <https://doi.org/10.2138/rmg.2011.73.13>
- Osipov, S., Stenichikov, G., Tsigaridis, K., LeGrande, A. N., Bauer, S. E., Fnaiss, M., & Lelieveld, J. (2021). The Toba supervolcano eruption caused severe tropical stratospheric ozone depletion. *Communications Earth & Environment*, 2(1), 71. <https://doi.org/10.1038/s43247-021-00141-7>
- Papale, P. (2005). Determination of total H₂O and CO₂ budgets in evolving magmas from melt inclusion data. *Journal of Geophysical Research*, 110(B3), B03208. <https://doi.org/10.1029/2004jb003033>

- Pearce, N. J., Westgate, J. A., Gualda, G. A., Gatti, E., & Muhammad, R. F. (2020). Tephra glass chemistry provides storage and discharge details of five magma reservoirs which fed the 75 ka Youngest Toba Tuff eruption, northern Sumatra. *Journal of Quaternary Science*, 35(1–2), 256–271.
- Pearson, C., Sigl, M., Burke, A., Davies, S., Kurbatov, A., Severi, M., et al. (2022). Geochemical ice-core constraints on the timing and climatic impact of Aniakhak II (1628 BCE) and Thera (Minoan) volcanic eruptions. *PNAS nexus*, 1(2), pgac048. <https://doi.org/10.1093/pnasnexus/pgac048>
- Peccia, A., Moussallam, Y., Plank, T., DallaSanta, K., Polvani, L., Burgisser, A., et al. (2023). A new Multi-method assessment of stratospheric sulfur load from the Okmok II Caldera-forming eruption of 43 BCE. *Geophysical Research Letters*, 50(21), e2023GL103334. <https://doi.org/10.1029/2023gl103334>
- Pinto, J. P., Turco, R. P., & Toon, O. B. (1989). Self-limiting physical and chemical effects in volcanic eruption clouds. *Journal of Geophysical Research*, 94(D8), 11165–11174. <https://doi.org/10.1029/jd094id08p11165>
- Rampino, M. R., & Self, S. (1984). Sulphur-rich volcanic eruptions and stratospheric aerosols. *Nature*, 310(5979), 677–679. <https://doi.org/10.1038/310677a0>
- Robock, A., Ammann, C. M., Oman, L., Shindell, D., Levis, S., & Stenchikov, G. (2009). Did the Toba volcanic eruption of ~ 74 ka BP produce widespread glaciation? *Journal of Geophysical Research*, 114(D10), D10107. <https://doi.org/10.1029/2008jd011652>
- Scaillet, B., Clemente, B., Evans, B. W., & Pichavant, M. (1998). Redox control of sulfur degassing in silicic magmas. *Journal of Geophysical Research*, 103(B10), 23937–23949. <https://doi.org/10.1029/98jb02301>
- Scaillet, B., & Macdonald, R. (2006). Experimental and thermodynamic constraints on the sulphur yield of peralkaline and metaluminous silicic flood eruptions. *Journal of Petrology*, 47(7), 1413–1437.
- Scaillet, B., & Oppenheimer, C. (2023). Reassessment of the sulfur and halogen emissions from the millennium eruption of Changbaishan (Paektu) volcano. *Journal of Volcanology and Geothermal Research*, 442, 107909. <https://doi.org/10.1016/j.jvolgeores.2023.107909>
- Schmidt, A., & Black, B. A. (2022). Reckoning with the rocky relationship between eruption size and climate response: Toward a volcano-climate index. *Annual Review of Earth and Planetary Sciences*, 50(1), 627–661. <https://doi.org/10.1146/annurev-earth-080921-052816>
- Sigl, M., Toohey, M., McConnell, J. R., Cole-Dai, J., & Severi, M. (2022). Volcanic stratospheric sulfur injections and aerosol optical depth during the Holocene (past 11 500 years) from a bipolar ice-core array. *Earth System Science Data*, 14(7), 3167–3196. <https://doi.org/10.5194/essd-14-3167-2022>
- Sigmarrsson, O., Haddadi, B., Carn, S., Moune, S., Gudnason, J., Yang, K., & Clarisse, L. (2013). The sulfur budget of the 2011 Grímsvötn eruption, Iceland. *Geophysical Research Letters*, 40(23), 6095–6100. <https://doi.org/10.1002/2013gl057760>
- Su, Y., Huber, C., Bachmann, O., Zajacz, Z., Wright, H., & Vazquez, J. (2016). The role of crystallization-driven exsolution on the sulfur mass balance in volcanic arc magmas. *Journal of Geophysical Research: Solid Earth*, 121(8), 5624–5640. <https://doi.org/10.1002/2016jb013184>
- Szymanowski, D., Forni, F., Phua, M., Jicha, B., Lee, D. W., Hsu, Y. J., et al. (2023). A shifty Toba magma reservoir: Improved eruption chronology and petrochronological evidence for lateral growth of a giant magma body. *Earth and Planetary Science Letters*, 622, 118408. <https://doi.org/10.1016/j.epsl.2023.118408>
- Textor, C., Graf, H. F., Herzog, M., & Oberhuber, J. M. (2003). Injection of gases into the stratosphere by explosive volcanic eruptions. *Journal of Geophysical Research*, 108(D19), 4606. <https://doi.org/10.1029/2002jd002987>
- Theys, N., Campion, R., Clarisse, L., Brenot, H., Van Gent, J., Dils, B., et al. (2013). Volcanic SO₂ fluxes derived from satellite data: A survey using OMI, GOME-2, IASI and MODIS. *Atmospheric Chemistry and Physics*, 13(12), 5945–5968. <https://doi.org/10.5194/acp-13-5945-2013>
- Tilmes, S., Mills, M. J., Zhu, Y., Bardeen, C. G., Vitt, F., Yu, P., et al. (2023). Description and performance of a sectional aerosol microphysical model in the Community Earth System Model (CESM2). *Geoscientific Model Development*, 16(21), 6087–6125. <https://doi.org/10.5194/gmd-16-6087-2023>
- Timmreck, C., Graf, H. F., Zanchettin, D., Hagemann, S., Kleinen, T., & Krüger, K. (2012). Climate response to the Toba super-eruption: Regional changes. *Quaternary International*, 258, 30–44. <https://doi.org/10.1016/j.quaint.2011.10.008>
- Toohey, M., & Sigl, M. (2017). Volcanic stratospheric sulfur injections and aerosol optical depth from 500 BCE to 1900 CE. *Earth System Science Data*, 9(2), 809–831. <https://doi.org/10.5194/essd-9-809-2017>
- Vidal, C. M., Métrich, N., Komorowski, J. C., Pratomo, I., Michel, A., Kartadinata, N., et al. (2016). The 1257 samalas eruption (Lombok, Indonesia): The single greatest stratospheric gas release of the common era. *Scientific Reports*, 6(1), 1–13. <https://doi.org/10.1038/srep34868>
- Wallace, P. J., Anderson Jr, A. T., & Davis, A. M. (1995). Quantification of pre-eruptive exsolved gas contents in silicic magmas. *Nature*, 377(6550), 612–616. <https://doi.org/10.1038/377612a0>
- Wallace, P. J., Anderson Jr, A. T., & Davis, A. M. (1999). Gradients in H₂O, CO₂, and exsolved gas in a large-volume silicic magma system: Interpreting the record preserved in melt inclusions from the Bishop Tuff. *Journal of Geophysical Research*, 104(B9), 20097–20122. <https://doi.org/10.1029/1999jb900207>
- Wallace, P. J., & Gerlach, T. M. (1994). Magmatic vapor source for sulfur dioxide released during volcanic eruptions: Evidence from mount Pinatubo. *Science*, 265(5171), 497–499. <https://doi.org/10.1126/science.265.5171.497>
- Wilson, C. J., Cooper, G. F., Chamberlain, K. J., Barker, S. J., Myers, M. L., Hilsley-Kemp, F., & Farrell, J. (2021). No single model for supersized eruptions and their magma bodies. *Nature Reviews Earth & Environment*, 2(9), 610–627. <https://doi.org/10.1038/s43017-021-00191-7>
- Zajacz, Z., Candela, P. A., Piccoli, P. M., & Sanchez-Valle, C. (2012). The partitioning of sulfur and chlorine between andesite melts and magmatic volatiles and the exchange coefficients of major cations. *Geochimica et Cosmochimica Acta*, 89, 81–101. <https://doi.org/10.1016/j.gca.2012.04.039>
- Zajacz, Z., & Tsay, A. (2019). An accurate model to predict sulfur concentration at anhydrite saturation in silicate melts. *Geochimica et Cosmochimica Acta*, 261, 288–304. <https://doi.org/10.1016/j.gca.2019.07.007>