

Interactive comment on “Photochemical box-modelling of volcanic SO₂ oxidation: isotopic constraints” by Tommaso Galeazzo et al.

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We would like to thank the two anonymous reviewers for their helpful comments on this work.

1 Answers to 2nd reviewer suggestions and comments:

1.1 Description of Isotopes data:

My main comment is to improve the description of the sulfate isotopes data used in the model comparison. The model development to include isotopes is well described,
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as are the sensitivity tests whose results are compared to reported sulfate isotope data leading to conclusions on oxidation pathways. The use of isotopes to study atmospheric pathways is also well described. However, fewer details are given about the existing/reported isotope samples themselves or about variability in the isotopic data used for the mode comparison. Even though these are existing reported data it would be useful to mention some more information, so the reader has a better idea of the data the model is being compared to. e.g. are these measured in-situ the plume or measured by sampling sulfate preserved in ash-deposits? From what kinds of eruptions to the troposphere, how many different volcanic emissions have been sampled, how far back in the past? A short description or visualization of the reported isotopes data and their variability given early in the manuscript (e.g. when introduced in page 4) would then enable the reader to better place the model results in context (e.g. when discussed later page 15 line 1-3, page 15 line 28, page 17 line 17).

Reply

We fully agree. A new table has now been added to enable to compare our results with oxygen isotopic measurements on tropospheric volcanic sulphate (**see attached figure**).

The text has also been amended. The first change in page 4 (line 22) specifies the origins of most of volcanic sulphates from isotopic experimental measurements:

“[...] Tropospheric volcanic sulphates of the present era distinguish themselves from other tropospheric sulphates by having a $\Delta^{17}\text{O}$ often close to zero (within the measurement error of about 0.1). This feature is found all over the world in sulphates collected from volcanic ashes of small and medium-size tropospheric explosive eruptions, independently from location, or geology of ash-deposits (Bao et al., 2003; Bindeman et al., 2007; Martin et al., 2014; see Table: 1). This is also the case for volcanic sulphate extracted from ash-deposits which are found very far from volcanoes, where secondary sulphate is expected to dominate.

[. ..]”

A second change is introduced in page 15 (lines 27-30), in order to recall the origins of experimental measurements. In this case, the values observed in sulphate aerosols collected at volcanic vents are also reported in the new table (Mather, 2006):

“[. . .] **The resulting model $\Delta^{17}\text{O}(\text{S}(\text{VI}))$ (i.e. from standard and sensitivity simulations) are compared to sulphate O-MIF found in tropospheric volcanic sulphates extracted from ash-deposits of small and medium-size tropospheric explosive eruptions of the present geological era (Bindeman et al., 2007; Martin et al., 2014; Bao, 2015), or in sulphate aerosols collected at volcanic vents, most certainly primary sulphate (Mather et al., 2006). [. . .]**”

1.2 Modelling Detail:

Page 12 line 16: Season and time of the simulations is given but details of the Pressure/Altitude, Temperature and Humidity for the model simulations should also be stated. These can affect the photolysis and reaction rates. For example: the reaction $\text{SO}_2 + \text{OH} + \text{M}$ is slower at lower pressures, higher altitudes. Species abundances are reported as mixing ratios (e.g. $\text{SO}_2 = 1$ ppmv) in the model set-up but the concentration in the model hence reaction rates will also depend on atmospheric density, as well as temperature. Would the findings of the study be similar or very different for model simulations assuming a different injection altitude in the troposphere?

Reply

The pressure/altitude and temperatures of simulations are now given in Page 12.

“[. . .] Since most of volcanoes are situated in remote areas with their peaks close to the free troposphere, or, at least, with volcanic plumes often ending up in the free

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troposphere, **the environmental conditions are chosen to be representative of the lower free troposphere with temperature set at 283.15 K, and pressure fixed at 640 mbar (about 3 km altitude). Since we consider cloudy conditions, the relative humidity is set to 100%.**

Furthermore, concentrations of reactive species are also set to typical levels found in the tropical lower free troposphere: $\text{O}_3 = 45$ ppbv and $\text{H}_2\text{O}_2 = 0.1$ ppbv. [. . .]”

It is difficult to claim that our conclusions are valid for the entire troposphere. For example, the competition on the OH budget between the isotopic exchange with H_2O and the reaction with SO_2 (crucial for OH isotopic signature) would change according to the water vapour concentration and hence the altitude. If lower (higher) altitudes were considered, the water vapour concentration is expected to be much higher (lower) and therefore higher (lower) SO_2 levels would compete with the isotopic exchange with water. In the same way, O_3 levels would also vary depending on the altitude and region. The purpose of the paper is to identify and explore the key processes for sulphate production and isotopic composition in a volcanic plume. It is, indeed, a process study not meant to cover the full range of possible tropospheric conditions. Ideally, this kind of investigation should be done through a global 3-D model.

1.3 Always cloudy conditions?

Page 12 Line 27: You state that due to the large amounts of water injected during eruptions relatively high LWC can be expected i.e. cloudy conditions. This is true, but the abundance of volcanic H_2O relative to background humidity will depend on how dilute the plume is. The relative abundances can be calculated for the chosen starting mixing ratio for SO_2 (1 ppmv standard case, varying from 0.1 to 10 ppmv in sensitivity simulations) and assuming an example composition of a volcano plume as can be found in the literature (e.g. 80-90% H_2O and up to a few % SO_2). Would high LWC be expected for all of the SO_2 dilution scenarios tested – or only if background conditions

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are also already at high RH/cloudy?

Reply

It is a good point. The conditions prevailing for some of the volcanic plumes might not be favourable for cloud formation, which would depend on the amount of water vapour injected, the local temperature and plume dilution. First, since we consider plumes within the lower free troposphere where temperatures are relatively low (about 15K below than surface temperatures), water condensation is more likely. Second, the mixing between the plume and background is assumed to be weak (timescale of 10 days). Therefore, the plume tends to remain relatively dense during the 7 days simulations, which favours maintaining cloudy conditions. Nonetheless, water clouds do not form in all the volcanic plumes, notably plumes from degassing. Therefore, we have added a comment in the conclusions to point out that our model results so far are only applicable to cloudy volcanic plumes:

“[...] We stress that oxidation by O_2 /TMI is poorly constrained in model simulations because of the lack of measurements of TMI aqueous concentrations in volcanic plumes. **It is worth pointing out that our model results are only applicable to cloudy volcanic plumes. Nonetheless, water clouds do not always form in volcanic plumes, notably during passive degassing. It would be interesting to also consider cloud-free plumes where the condensed phase is concentrated sulphuric acid within sulphate aerosols. In particular, these particles have a chemical reactivity radically different from water droplets.** [...]”

1.4 Conclusions

One possible additional limitation of the study is that upon dispersion and dilution into a low RH atmosphere the volcanic plume may become more of an aerosol plume than a high LWC cloud as mentioned above. Under these conditions the particle phase would

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likely become a very acidic (sulfate-rich) volcanic aerosol instead of cloud droplets. Could this affect the results and how? I would imagine that the highly acid conditions in the sulfate/sulphuric acid aerosol could act to limit extent of SO_2 dissolution hence aqueous-phase pathways for oxidation of SO_2 . But the aerosols might also become more concentrated in Fe/Mn ions (particularly if the volcano emits significant Fe/Mn or ash) and thereby promote aqueous-phase oxidation of SO_2 by TMI/ O_2 .

Reply

We agree with this comment and the possible implications for the plume chemistry. At this stage, it is difficult to speculate in the paper without having carried out this type of simulations. As stated above, few lines have been now added in the conclusion to highlight this limitation and suggest exploring cloud-free plumes.

“[...] We stress that oxidation by O_2 /TMI is poorly constrained in model simulations because of the lack of measurements of TMI aqueous concentrations in volcanic plumes. **It is worth pointing out that our model results are only applicable to cloudy volcanic plumes. Nonetheless, water clouds do not always form in volcanic plumes, notably during passive degassing. It would be interesting to also consider cloud-free plumes where the condensed phase is concentrated sulphuric acid within sulphate aerosols. In particular, these particles have a chemical reactivity radically different from water droplets.** [...]”

1.5 References:

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Volcano & Date of Eruption	Sample distance (km)	Source	$\Delta^{17}\text{O}$ (‰)	Reference
Popocatepetl (Mexico), 2008	25	ash	0.35	(Martin et al., 2014)
Spurr (Alaska, USA), 1992	265	ash	-0.14	(Martin et al., 2014)
Fuego (Guatemala), 1974	57	ash	-0.04	(Martin et al., 2014)
Negro Cerro (Nicaragua), 1947	12	ash	-0.06	(Martin et al., 2014)
Parícutin (Mexico), 1948	5	ash	0.13	(Martin et al., 2014)
Mt. St. Helens (USA), 1980	400	ash	0.02	(Martin et al., 2014)
Gjálp (Iceland), 1998	< 30	ash	-0.07	(Martin et al., 2014)
Pinatubo (Philippines), 1991	< 50	ash	-0.04	(Bindeman et al., 2007)
Pinatubo (Philippines), 1991	< 50	ash	0.19	(Bindeman et al., 2007)
Spurr (USA), 1953	n.a.	ash	0.06	(Bindeman et al., 2007)
Vesuvius (Italy), 1872	n.a.	ash	-0.07	(Bao et al., 2003)
Popocatepetl (Mexico), 1997	n.a.	ash	-0.08	(Bao et al., 2003)
Spurr (USA), 1992	n.a.	ash	0.06	(Bao et al., 2003)
Fuego (Guatemala), 1974	55	ash	-0.03	(Bao et al., 2003)
Pinatubo (Philippines), 1991	n.a.	anhydrite from pumice	-0.01	(Bao et al., 2003)
Santorini (Greece), Minoan age	n.a.	pumice + ash	0.09	(Bao et al., 2003)
Masaya (Nicaragua), 2003	0	aerosols	0.1	(Mather et al., 2006)
Masaya (Nicaragua), 2003	0	aerosols	0.2	(Mather et al., 2006)

* Refer to (Martin, 2018) for a more extensive description regarding oxygen isotopic anomalies measured in tropospheric volcanic sulphate of present and past geological eras.

Fig. 1. Oxygen isotopic composition of volcanic sulphates from different tropospheric eruptions of the present geological era.

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