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Discussions

Interactive comment on "Photochemical box-modelling of volcanic SO_2 oxidation: isotopic constraints" *by* Tommaso Galeazzo et al.

Anonymous Referee #2

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Galeazzo et al. have made developments to the atmospheric chemistry box model CiTTyCAT to investigate sulfate O-isotopes in the oxidation of volcanic SO2 emissions. Volcanic sulfur emissions are converted into sulfate by gas- and aqueous-phase pathways in the troposphere. Through a series of model sensitivity studies, Galeazzo et al. show that the oxidation of volcanic SO2 into sulfate cannot simply be assumed to follow the same dominant pathways as oxidation of SO2 in the background atmosphere. They demonstrate the importance of the TMI/O2 pathway in the model, that is consistent with sulfate isotope data. The study is novel in introducing a new modelling tool that enables a much more quantitative interpretation of volcanic sulfate isotopes in terms of the underlying atmospheric SO2 oxidation processes. It is a solid work that makes a substantial contribution to our understanding of the volcanic plume sulfur

chemistry. I find it very suitable for publication in ACP. Comments are given below.

Main comments:

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, 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 isotopes samples themselves or about variability in the isotopic data used for the model 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).

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 SO2 + OH + M is slower at lower pressures, higher altitudes. Species abundances are reported as mixing ratios (e.g. SO2 = 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?

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 H2O 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 SO2 (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% H2O and up to a few % SO2). Would high LWC be expected for all of the SO2 dilution scenarios tested – or only if background conditions are also already at high RH/cloudy?

4) Conclusions - limitations:

A major result of this study is how important the TMI-O2 pathway is for oxidation of SO2 in volcanic plumes. The authors rightly emphasize on page 20 line 18 that uncertainty in Fe/Mn concentrations/speciation in volcanic plumes affects the oxidation by O2/TMI pathway – volcanic plume SO2 oxidation could be faster by this pathway if Fe/Mn concentrations are elevated.

Page20 Line 20: The absence of halogens is mentioned as a limitation of the model study. Whilst halogen emissions will affect oxidant concentrations, the authors are correct in pointing out that some volcanic emissions are halogen poor. Indeed, it is worth highlighting that two of the most important recent volcanic eruptions that impacted the troposphere on regional scales were actually halogen poor (relative to sulfur): the 2014-2015 Bardarbunga/Holuhraun eruption in Iceland and volcanic emissions from Kilauea, Hawaii such as the ongoing eruption.

One possible additional limitation of te 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 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 SO2 dissolution hence aqueous-phase pathways for oxidation of SO2. 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 SO2 by TMI/O2.

5) Previous studies of SO2 oxidation:

Finally, it would be useful to discuss the findings from this isotopic modelling study in the context of some existing (non-isotopic) studies. For example, how do the simulations of SO2 oxidation compare to the SO2 oxidation rate observed by Kroll et al. Env. Sci. Tech. 2015 at Kilauea, Hawaii (in plume with quite high SO2 concentrations)? Also, it seems that this study's findings show some similarities but some differences to a recent review paper: Pattantyus et al. Review of sulfur dioxide to sulfate aerosol chemistry at KÄńlauea Volcano, Hawai'i, Atmospheric Environment, 2018. This could be because Pattantyus et al. considers a more dilute plume and assumes background atmospheric concentrations whereas Galeazzo et al. evaluates in more detail the SO2 oxidation chemistry in the concentrated plume by actively modelling the feedbacks on oxidant concentrations.

Some minor comments/language suggestions:

Page 2 line 13: "Once injected into the troposphere, volcanic SO2 is converted in a few days typically to H2SO4 by a range of gas-phase and liquid-phase reactions taking place in volcanic plumes and clouds (Chin and Jacob, 1996; Stevenson et al., 2003a)." This sentence appears to contradict the rest of the paper. The lifetime of a few days for SO2 is probably true for background atmospheric conditions but the lifetime of SO2 in volcanic plumes can be significantly longer due to the depletion of oxidants. Indeed that is one of the conclusions reached by the authors in the modelling of oxidation pathways according to the figures where SO2 persists over the week-long simulations.

Page 5. Line 7. Perhaps say our standard volcanic plume conditions (as not standard background)

Page 5 line 14. Are species other than sulfate deposited in the model? If so, specify.

Page 6 Line 29, Page 7 line 16: Check labelling of Table 1/2.

Page 7 Line 1: “rate of SO2 dissolution”. If I understood correctly should this rather be “extent of SO2 dissolution” is controlled by pH (as it is determined by equilibrium constants rather than rate constants)?

Page 9 Line 24: Perhaps clarify in the text that after reaction with ozone the remaining O and 2H are provided by reaction with water, - this is not explicitly clear in Table 2.

Page 10. The text of this section starts with the assumption that you already know the origins of OH. This might not be the case for all interdisciplinary readers. It would be better to explain at the beginning of this section the origins of OH eg. That OH is formed in the troposphere from photolysis of Ozone followed by reaction with H2O.

Page 10 Eq(19): Define k*OH+H2O in the text.

Page 13 Line 18: Do you mean: passive/quiescent degassing conditions?

Page 13 line 24: “It is widely recognised that SO2 is the compound emitted by volcanic activity that causes the widest climate impacts” Perhaps add: through its conversion into sulfate aerosols (as it is not SO2 itself that causes climate impacts)

Page 18 Line 26: I think it would be clearer to say -> mostly lie close to zero within measurements uncertainties. Also: Page 19 Line 22

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