

Interactive comment on “Halogen activation in the plume of Masaya volcano: field observations and box model investigations” by Julian Rüdiger et al.

Christoph Kern (Referee)

ckern@usgs.gov

Received and published: 15 July 2020

In this manuscript, Rüdiger et al. present new measurements and model results that provide insights into a system of complex chemical reactions involving halogens in aging volcanic plumes. Using alkaline traps, the authors were able to measure total halogen amounts as well as selectively quantify reactive halogens. By mounting these traps onto a UAS and flying them into the plume as well as placing them at various distances from the actively degassing vent of Masaya volcano, information on the progression of halogen chemistry as a function of time and distance was obtained. In addition, electrochemical sensors measured the SO₂ concentration, which is thought to be a good proxy for plume dilution. Finally, a scanning DOAS instrument was located downwind of the vent and used to measure the SO₂ emission rate as well as the

C1

ratio of BrO to SO₂. This ratio has been studied at numerous volcanoes around the world and changes in the ratio are thought to possibly be early indicators of changes in volcanic activity. The authors then conducted an impressive modeling study using the CAABA/MECCA atmospheric box model and attempted to explain various aspects of the measurement results, highlighting the need for efficient entrainment of ozone into the plume and the availability of HxOy and/or NOx to explain the progressing chemistry.

This study represents a valuable contribution to the field. The measurements are highly innovative and difficult to perform. The modeling work is complex, and given the fact that previous modeling studies by other groups used models other than the CAABA/MECCA model, this study provides a semi-independent validation / comparison. The results are relevant and important to both the atmospheric sciences and volcanology communities. I do feel that the presentation of the results could be improved somewhat. The modelling section in particular is somewhat convoluted and difficult to follow. I also feel like the conclusions section is missing clear statements on (1) what are the novel results of this study that have not been previously reported elsewhere, (2) which results are not new but consistent with those obtained by others in the past, and (3, 4) what are the implications of the results for atmospheric chemistry and volcanology? I have provided more detail on these questions and a few other concerns in the list below and am also attaching a marked-up PDF which contains numerous suggestions for minor corrections and edits. Once these have been addressed, I recommend the manuscript be published in Atmospheric Chemistry and Physics.

Specific issues:

Conclusions Section: As mentioned before, the manuscript would really benefit from an expanded conclusions section in which four things are clearly identified:

(1) Which of the results obtained in this study are truly novel? What information does this study add to our current understanding of halogen chemistry in volcanic plumes? Which results have not been previously reported by others, or only hinted at but not

C2

conclusively measured? Which observations (if any) go against our previous understanding of how halogen chemistry in volcanic plumes works?

(2) Which results are not new, but consistent with observations reported in the past? These observations are important just the same, as they may help solidify our understanding of certain processes that were perhaps somewhat speculative previously.

(3) What are the implications of the results (especially the new ones) for atmospheric chemistry? Some questions to address could be: What is the local, regional or even global impact of passive halogen degassing on tropospheric atmospheric chemistry? Do global volcanic chlorine emissions play a significant role in destroying methane in the background atmosphere? I'd also be very interested in whether or not you think that bromine and chlorine activation will typically be limited by in-mixing of ozone and other atmospheric oxidants, or whether the mixing 'threshold' for efficient halogen activation is typically exceeded and the process is therefore not limited by availability of oxidants (or maybe your study can't answer this in such general terms?).

(4) What are the implications of the results (especially the new ones) for volcanology? My main question here is whether you think that BrO/SO₂ ratios can be used to study volcanic activity. I noted with some alarm that the BrO/SO₂ ratios measured in this study seemed to be fairly consistent with those we measured in 2008 (Kern et al 2009) despite there being a factor of 2 increase in Br output between 2009 and 2016 (page 13 line 33). It's understood that the LP-DOAS measurements weren't made at the same time as the Br measurements made by Martin et al (2010), yet on first order this result would seem to indicate that the BrO/SO₂ ratio may not be a good indicator of HBr emissions. Is this true? Or am I missing something? Do you think that the BrO/SO₂ ratio could still be useful for volcanology, perhaps because it indicates some other process is ongoing? Also, do you think DOAS measurements of OCIO are useful at all for volcanology? I have suggested in the past that they may help interpret the BrO measurements. What do you think? I think a discussion along these lines would greatly increase the value of this study for the scientific community.

C3

Once the above issues are addressed, I recommend editing the abstract to better reflect these conclusions.

Other substantive comments:

Page 9 Line 3 - Why use an average wind speed of 5 m/s for the in-situ sampling if more detailed information is available? Is this average really representative for the entire measurement period? It appears that a variable wind speed was used in interpreting the DOAS measurements – so why not for the others as well?

Equation 1 – What is the rationale for describing the ratio of reactive halogens to total halogens with this equation? Most curves presented in Figure 6 do not appear to have this shape. Why not just use a rejection sampling scheme that eliminates model runs that are not consistent with all the measurements (within their error ranges)? And the best model runs could be determined by a least-squares minimization between measurement and model values, without the need for prescribing a formula for the progression of the ratios over time.

Section 5.3 Nighttime sample anomaly: It is my understanding that the DB samples were collected for somewhere between 18 and 30 hours at a time. Wouldn't that mean that these samples reflect some combination of daytime and nighttime chemistry? Given the anomaly that you recorded in your nighttime sample, do you think the DB samples might be skewed when compared to the DOAS measurements (which are recorded during the day)?

Page 22 Line 1 – It seems unlikely to me that the measured BrX/S ratio could be significantly underestimated because only SO₂ is measured. You mentioned that H₂S emissions are negligible. You also mentioned that conversion of SO₂ to sulfate is much slower than the timescales which we are considering here (6 minutes). I'm also not sure that the electrochemical sensor missing SO₂ in the diluted plume is responsible. What is the detection limit of the sensor? From this you could calculate how much S you might be missing during the course of a measurement and determine if this is enough

C4

to make the measurements consistent with the models.

Section 5.4.1 and Figure 6- I found this section very hard to follow, mainly because so many different cases are considered and discussed. If I understand correctly, a number of model runs are presented and discussed that fit certain measurements but aren't actually consistent with measurements of other parameters. Can't these be omitted from discussion on the grounds that they aren't consistent with all the measurements? Also, I would suggest eliminating the separate discussion of r-Br and BrX. It's understood that there is some uncertainty with regards to which is actually measured, but by presenting both of these cases throughout doubles the number of scenarios to consider and really makes it hard to follow the discussion. In the end, the results are fairly similar, regardless of which of these is chosen. A sentence or two describing the effect of using r-Br vs BrX in the comparison is probably sufficient here.

Further corrections and comments are included in the attached marked-up manuscript. In addition to these, the manuscript would benefit from some careful English language proof-reading.

Thank you for the opportunity to review this work. Please do not hesitate to contact me if any questions arise with regards to this review.

Christoph Kern

Please also note the supplement to this comment:
<https://www.atmos-chem-phys-discuss.net/acp-2020-284/acp-2020-284-RC1-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2020-284>, 2020.