

## ***Interactive comment on “Photochemical box-modelling of volcanic SO<sub>2</sub> 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 Reviewer suggestions and comments:**

#### **1.1 1st Comment**

The only significant comment I have is that I think the paper should put more into a discussion of the implications of the lack of reactive halogen chemistry. Even in a

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volcanic eruption with zero halogens (is this possible?), entrainment of background air would supply some halogens. Could this be important? Perhaps it wouldn't take much from background to have halogen recycling in this acidic environment. What are the implications for sulfate O-MIF formed in volcanic plumes?

#### **Reply**

Halogen composition of volcanic emissions vary widely between different volcanic systems. Hotspot (such as Kīlauea) and rifting-plate volcanoes (such as Erta'ale in Ethiopia and Icelandic volcanoes) are characterised by low halogen contents (i.e. compared to the extent of sulphur emissions) whereas arc-volcanoes in subduction areas are characterised by emissions with relatively high halogen content (Aiuppa, 2009; Oppenheimer, 2013). Among volcanic eruptions with low halogen loading (compared to sulphur), one can cite the Bárðarbunga eruption in 2012-2014 (Ilyinskaya, 2017; Stefánsson, 2017) or the Kīlauea eruption in 2008 (Mather, 2012). Volcanic emissions from Kīlauea were characterised by HCl/SO<sub>2</sub> ratios (i.e. HCl most abundant halogen species) of the order of 10<sup>-2</sup> (HCl concentrations 10-50 ppbv). Keep in mind that only volcanic plumes with liquid water (cloudy conditions) are considered. It is important for the chemistry of halogens.

Liquid water is assumed here to be present on ash surfaces or as water droplets. The question is about the fate of emitted halogens in water-rich plumes. Most of the halogens are emitted in the form of HCl and HBr which are very soluble species. In our model, pH values range between 1 and 2. These pH values are not low enough to limit significantly halogens dissolution in water (i.e. limited effect on halogens effective Henry's law coefficient). HCl and HBr should have relatively short lifetimes with respect to dissolution in cloudy conditions. The only way these soluble species can impact very significantly the plume chemistry is via rapid conversion into radical species, a process called halogen activation.

Halogen activation in the gas phase should be slow and would be inhibited by

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HCl/HBr fast dissolution and deposition processes when liquid water is present (Roberts, 2009; von Glasow, 2010). The other pathway for halogen activation is heterogeneous. Experimental measurements show that halogens reactive uptakes on water are typically much slower than on sulphate aerosols (about 10 to 100 times slower) (Sander, 2006; Davidovits, 2009; Ammann, 2013). For example:

Reaction	$\gamma_r(\text{sulphate})$	$\gamma_r(\text{water})$
$\text{BrONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOBr}_{(\text{aq.})} + \text{HNO}_3_{(\text{aq.})}$	0.8	$3 \cdot 10^{-2}$
$\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl}_{(\text{aq.})} + \text{HNO}_3_{(\text{aq.})}$	n.a	$2.5 \cdot 10^{-2}$

The second column reports reactive uptakes on sulphate aerosols  $\gamma_r(\text{sulphate})$ , while the third column reports reactive uptakes on water  $\gamma_r(\text{water})$ .

A similar trend can be assumed for other halogens reactions when reactive uptakes on water and sulphuric acid are compared. Halogen activation on water is expected to be much slower on a per molecule basis compared to activation on sulphate aerosols. Therefore, for our cloudy conditions, halogen activation should be relatively slow. Nonetheless, if very large amounts of halogens were emitted, the small fraction of halogen activation could be important for the chemistry. However, we are only considering low halogen emissions. Therefore, we have simply assumed that most of the volcanic HCl and HBr would be washed out from plumes. We accept that neglecting halogens might be an oversimplification for many volcanic plumes, especially for halogen-rich plumes. Only a full study about the role of volcanic halogens for halogen-rich plumes could answer this question. We are now more cautious in the text and stressing in the conclusions that the potential role of halogens should be explored.

Proposed change: “[...]”**The focus here is on volcanic clouds that are rich in sulphur but poor in halogens, such in the case of intra-plate and rifting plate volcanoes (e.g. Nyarogongo in Congo, Erta’ale in Ethiopia, Kīlauea in Hawai’i) (Aiuppa et al., 2009; Oppenheimer et al., 2013). Volcanic eruptions with remarkable low**

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**halogens to sulphur emissions are the Holuhraun (Bárðarbunga) eruption of 2012-2014 in Iceland (Ilyinskaya et al., 2017; Stefánsson et al., 2017), and the Kīlauea eruption of 2008 in Hawai’i (Mather et al., 2012). In particular, HCl/SO<sub>2</sub> ratios of the order of 10<sup>-2</sup> have been observed for the Kīlauea eruption of 2008 (i.e. HCl ≈ 10-50 ppbv). [...]”**

At the end of the conclusion section: “[...]”**Overall, the present simulations might only be representative of degassing or eruptions with extremely low halogen emissions, typically originating from intraplate and rift volcanic activity. It is certainly worth exploring the potential impact of halogens in the case of halogen-rich eruptions, notably for volcanic plumes where water does not condense and hence only sulphate aerosols are present. Since the heterogeneous conversion of halogen halides into radicals is known to be fast on sulphate aerosols (references), halogens might impact significantly the plume chemistry and the isotopic composition of secondary sulphate under those conditions. [...]”**

## 1.2 2nd Comment

One general comment: I think it would be good to helpful to highlight the observations of sulfate O-MIF, including the types of volcanos measured, in the paper. I suggest adding a Table describing the observations with appropriate references. As currently written it’s hard for readers to compare model results with observations.

### Reply

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

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The text has also been amended:

**“[...] 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 et al., 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). [...].”**

### 1.3 3rd Comment

Page 2 line 22: How much is “most”? The current thinking is that globally, DMS oxidation is the largest natural source of  $\text{SO}_2$  to the troposphere.

#### Reply

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DMS is the largest natural source of  $\text{SO}_2$ , which however is a by-product of DMS oxidation (Chin, 1996,200). The largest direct source of natural  $\text{SO}_2$  is volcanic activity, which roughly releases 10.4-13 Tg/year of  $\text{SO}_2$  (Andres and Kasgnoc, 1998) mostly via quiescent degassing. We have rephrased this part:

Proposed change:

**“[...]Nowadays, anthropogenic  $\text{SO}_2$  emissions outweigh those from natural sources (Smith et al., 2011). Volcanic emissions release about 10-13 Tg  $\cdot$  y<sup>-1</sup> of  $\text{SO}_2$  to the atmosphere (Bates et al., 1992; Graf et al., 1998, Andres and Kasgnoc, 1998) and contribute to up to 10% to total sulphur emissions to the atmosphere (Stevenson et al., 2003a). [...].”**

### 1.4 4th Comment

Page 5 line 1: How common are these types of volcanoes that are halogen-poor? Are the observations of sulfate O-17 excess from these types of volcanoes?

#### Reply

Rift and hotspot volcanoes are usually characterised by halogen-poor emissions, because of the absence of subduction fluids in melts. In addition, volcanic emissions composition can widely change for a same volcano in relation to its erupting phases. Even for arc-volcanoes, it is possible to observe emissions with low halogen-to-sulphur ratios, notably for emissions from fumaroles (Aiuppa, 2009; Oppenheimer, 2013). Overall, we expect halogens-poor plumes to originate from both hotspot and intraplate eruptions. Unfortunately, most oxygen isotopic measurements are from arc-volcanoes (Bindeman et al., 2007; Martin et al., 2014; Martin, E. 2018). Some measurements are also from rifting volcanoes, notably from Icelandic eruptions (e.g. Gjalp eruption 1996).

Proposed change: Some examples of volcanic systems and recent volcanic eruptions

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with low halogens/sulphur emissions are already provided in the first comment. (See 1st comment)

#### 1.5 5th comment

Page 7 R1: There is no other ion that can influence acidity? Ion balance equations are not the best way to calculate pH. In the future, perhaps it would be better to explicitly calculate the droplet pH in the model. This would certainly be necessary if these calculations were for ambient air, and not an SO<sub>2</sub> rich volcanic plume.

#### Reply

We agree. In our case, sulphur is in excess and drives the pH of water. The effect of other ions is overwhelmed by the presence of very high S(VI) concentrations in water.

#### 1.6 6th comment

Page 7: Why consider sulfate loss via deposition but not SO<sub>2</sub>? Globally, dry deposition of SO<sub>2</sub> represents about half of tropospheric SO<sub>2</sub> loss.

#### Reply

There is a misunderstanding. The text was not clear about this point. We are only considering the fate of SO<sub>2</sub> in the core of a volcanic plume. Dry deposition as such is not expected to be important in the plume compared to wet deposition. Therefore, only wet deposition is accounted for in the model. Under those conditions, the wet deposition rate is determined by the scavenging of soluble species (including SO<sub>2</sub>) by liquid water phases (followed either or not by oxidation). The model includes deposition of S(IV) and S(VI) species dissolved (including dissolved SO<sub>2</sub>). More details are now

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provided to clarify this point.

Proposed change:

**“[...] where  $k_j$  the rate constant of the aqueous reaction between oxidant  $C_j$  and relevant [S(IV)] species (see the list of aqueous oxidation reaction in Table: 2), and  $k_d$  is the deposition coefficient of dissolved sulphur species. Dry deposition as such is not expected to be important in the plume itself compared to wet deposition for our cloudy conditions. Since only wet deposition is considered, only species dissolved in water phases such as aqueous S(IV) ( $\text{SO}_{2(\text{aq})} + \text{HSO}_3^- + \text{SO}_3^{2-}$ ) and S(VI) ( $\text{HSO}_4^- + \text{SO}_4^{2-}$ ) species are deposited in the model. The deposition is treated as a first order loss with  $k_d = 2 \cdot 10^{-6} \text{ s}^{-1}$ , equivalent to a characteristic time scale of 5.7 days (Stevenson et al., 2003a) [...].”**

#### 1.7 7th comment

Page 17 line 6: Does the O-17 excess of OH decrease as SO<sub>2</sub> decreases? I think you should state why this is happening.

#### Reply

Proposed change:

**“[...] The final O-MIF in deposited sulphate is 1.1 permil, originating mostly from OH oxidation. Recall that, when OH is generated via its main production channel, it carries an isotopic anomaly. Under common (non-volcanic) conditions, the OH anomaly is so rapidly erased by isotopic exchange with H<sub>2</sub>O that, when OH reacts, it carries no anomaly. However, when SO<sub>2</sub> levels are very high, OH might react very quickly with SO<sub>2</sub> without having lost its anomaly by isotopic exchange.**

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**In this situation, the value of  $\Delta^{17}\text{O}(\text{OH})$  is determined by the competition between the  $\text{SO}_2 + \text{OH}$  reaction and the OH isotopic exchange with  $\text{H}_2\text{O}$ . As  $\text{SO}_2$  concentration decays with time,  $\Delta^{17}\text{O}(\text{OH})$  decreases because the  $\text{SO}_2 + \text{OH}$  reaction slows down and becomes less competitive with respect to the isotopic exchange [...]**

#### 1.8 8th comment

In the figures, I don't understand why  $\text{SO}_2$  concentrations do not decrease over time. Sulfate increases, so mass balance suggests that  $\text{SO}_2$  should decrease, unless there is a continuous supply of  $\text{SO}_2$ .

#### Reply

During S1 and S2 simulations  $\text{SO}_2$  concentrations drop from an initial value of 1.5 ppmv, to roughly 1.2 ppmv with 7 days from injection; in S3  $\text{SO}_2$  concentration drops from 1.5 to 1 ppmv. Unfortunately, the small drop in concentration is not very noticeable with a logarithmic scale covering from pptv to ppmv concentrations. Therefore, for each figure showing the concentration evolution of key trace species, we have now reported in the figure captions the initial and final value of  $\text{SO}_2$  concentration.

#### 1.9 References:

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