# Halogens role in volcanic sulphur oxidation: photochemical modelling and isotopic constraints

**Abstract:** The photochemical box-model CiTTyCAT is used to simulate volcanic sulphur oxidation and the resulting volcanic sulphate oxygen isotopic composition within the core of volcanic plumes. The focus is on volcanic halogens role in volcanic sulphur chemistry during small volcanic eruptions or passive degassing. The model accounts for SO<sub>2</sub> oxidation by OH in the gas phase, and by  $H_2O_2$ ,  $O_3$ ,  $O_2$  catalysed by transition metal ions (TMI), and HOX (HOX = HOBr + HOCI) in the liquid phase of either volcanic water droplets (referred here as condensing plume), or sulphate aerosols (referred here as non-condensing plume). It also describes transfer of oxygen mass-independent anomalies (O-MIF) from atmospheric oxidants to sulphate.

For condensing plumes (liquid water), the first finding is that ozone depletion events (ODEs) triggered by halogens heterogeneous chemistry may also occur in plumes cores in presence of water droplets. The second finding is that, halogens presence does not affect the hierarchy of oxidation pathways. The O<sub>2</sub> /TMI sulphur oxidation pathway remains dominant even for relatively low TMI aqueous concentrations, generating volcanic sulphates with low O-MIF ( $\approx 0$  %), this result is comparable to isotopic measurements on sulphates collected from volcanic ash-deposits. For noncondensing plumes (only sulphate aerosols), the first finding is that ODEs can occur even at very low halogen loadings ( $\approx$ 50 ppbv). The rate of sulphur oxidation is much lower than for condensing plumes, and sulphur oxidation is dominated by  $H_2O_2$  on sulphate aerosols and by OH in the gas phase. The second finding is that, the relative contributions of H<sub>2</sub>O<sub>2</sub> and OH is determined by halogens loading, and that the higher the halogens concentration is, the higher is the  $H_2O_2$  contribution to sulphate production. The third finding for non-condensing plumes is that halogens presence does not impact significantly the final sulphate O-MIF, which remains between the range of 0.8 - 1.4 %. The latter result is in contrast with the lack of O-MIF measured in sulphates collected from volcanic ash, suggesting different hierarchy of oxidation pathways might be active for different plume environments. The condensing and non-condensing simulations results suggest that the sulphate found on volcanic ash-deposits is likely to be formed via SO<sub>2</sub> oxidation in water-rich phases and not in the gas phase or on sulphate aerosols during passive degassing.

# 1 Introduction

Volcanoes release vast amounts of particles and reactive gases into the atmosphere and they are a significant natural source of atmospheric pollutants, notably sulphur (Textor et al., 2004; Ayris and Delmelle, 2012; Mather, 2015). Tropospheric volcanic emissions are mostly limited to local and regional scales (Robock, 2000), but they can have significant environmental impacts, such as: acid rain formation, crop destruction, or severe air traffic perturbation (Delmelle et al., 2001; Delmelle, 2003; Schumann et al., 2011; Schmidt et al., 2014). Exposure to high concentrations of sulphate particles and sulphur bearing gasses has also detrimental effects on human health (Durand and Grattan, 2001; Longo et al., 2008; Longo, 2013). Volcanic sulphur, indeed, can lead to "vog" (volcanic smog) and SO<sub>2</sub> pollution events formation in neighbouring urban areas, as frequently observed in Mexico City or on the island of Hawai'i (Raga et al., 1999; de Foy et al., 2009). Nonetheless, volcanic emissions have also a significant influence on the chemistry of the atmosphere and therefore on climate (Stocker et al., 2013). In the atmosphere volcanic sulphur is easily converted into sulphate aerosols, which can cool the Earth's surface via scattering and absorption of solar and terrestrial radiation (LeGrande et al., 2010; Robock, 2013; Stoffel et al., 2015; Zanchettin et al., 2016). Notably, observations and climate models have demonstrated that stratospheric volcanic eruptions have caused major changes in atmospheric composition and climate of both present-day and past geological eras (Stocker et al., 2013). In more details, stratospheric sulphur aerosols can impact global climate for several years typically, as observed after the stratospheric eruption of Mount Pinatubo in June 1991 (Minnis et al., 1993; McCormick et al., 1995; Robock, 2002).

Current regional and global models used to assess volcanic emissions impacts are limited in their chemistry description (Schmidt et al., 2014, 2015). Most models, indeed, do not include the full chemical complexity of volcanic emissions, potentially underestimating their overall environmental impacts. Volcanic emissions are a rich chemical cocktail composed by a mix of very reactive gases. The most abundant volcanic gas is water vapour, followed by CO<sub>2</sub>, sulphur (i.e. SO<sub>2</sub> and H<sub>2</sub>S), and halogens (i.e. chlorine, bromine, iodine) respectively. Volcanic sulphur and halogen gases are the most reactive species released within the plume, where they react in the gas and in the liquid phase of water droplets and sulphate aerosols. The chemistry of a plume is driven, indeed, by the rich multiphase reactions of sulphur and halogens gases.

Most of last decades investigations have focused predominantly on the atmospheric and climatic impacts of volcanic sulphur. Volcanic halogens, indeed, are initially released at the magma surface mostly as hydrogen halides (i.e. HX = HCI + HBr mostly), which are rather unreactive species in the gas phase. As a result, volcanic halogens impacts on the atmosphere have been neglected for long times, mostly because it was assumed that hydrogen halides were very efficiently washed out from plumes by particles, water droplets, and ash. Nowadays, however, there is growing evidence that large concentrations of highly reactive halogen compounds are present in tropospheric volcanic plumes from passive degassing. Multiple observations report, indeed, very large amounts of bromine radicals (BrO) within tropospheric plumes of various volcanoes. These measurements also represent the highest BrO concentrations ever observed in the atmosphere so far (Bobrowski et al., 2003; Bobrowski and Platt, 2007; Bobrowski et al., 2007).

Volcanic HX can be converted into reactive halogen radicals either via high temperature chemistry in volcanic vents (Gerlach, 2004; Martin et al., 2006; Roberts et al., 2009), or via multi-phase chemistry within young volcanic plumes, the latter being a process called "halogens activation" (Oppenheimer et al., 2006, 2010; von Glasow, 2010). Since halogen radicals are generally less soluble than

HX in both water and sulphate aerosols (Sander et al., 2006; Sander, 2015), HX conversion into halogen radicals prevents their washing-out from volcanic plumes and the atmosphere. It follows that radicals formation within volcanic plumes can extend halogens atmospheric residence time, therefore affecting also the temporal and spatial extension of their atmospheric impacts, including possibly the transport to the stratosphere (Zuev et al., 2015).

Halogen radicals are very reactive species, destroying atmospheric ozone via auto-catalytic chemical cycles (von Glasow, 2010). Ozone depletion events (ODEs), indeed, are a relatively common feature of halogen-rich environments, and they are frequently observed over sea-salt lakes, in the polar and marine boundary layer, and recently also in tropospheric volcanic plumes (Saiz-Lopez, 2004; Stutz, 2002; Hönninger, 2004; Millard et al., 2006; Vance et al., 2010; Kelly et al., 2013). Within volcanic plumes very high BrO concentrations are frequently coupled to massive ODEs (Millard et al., 2006; Vance et al., 2010; Boichu et al., 2011; Kelly et al., 2013), suggesting that volcanic halogens can influence the oxidative state of the plume. Atmospheric ozone, indeed, is a major source of hydroxyl radical (OH), the dominant atmospheric oxidant (von Glasow and Crutzen, 2013). In particular, recent investigations suggest that halogens activation could influence volcanic sulphur processing within plumes, notably with regards to volcanic SO<sub>2</sub> oxidation (Jourdain et al., 2016). Moreover, halogens mobilization from the condensed phase requires the production of HOX (i.e. hypohalous acids, HOX = HOBr + HOCI) (von Glasow, 2010), which is also a major SO<sub>2</sub> oxidant in the liquid phase. It has been suggested that HOX concentrations as low as 0.1 pptv could drive SO<sub>2</sub> oxidation in the marine atmosphere (Chen et al., 2016). Notably, isotopic investigations on marine atmosphere sulphates and their oxygen isotopes compositions have highlighted that up to 30% of sulphate can be produced via SO<sub>2</sub> oxidation by HOX in the marine boundary layer (MBL) (Vogt et al., 1996; Von Glasow et al., 2002a,b; Chen et al., 2016).

It is difficult to investigate chemical processing within volcanic plumes, due to the very optically dense environment and highly reactive nature of volcanic emissions. Among post-processing investigations, isotopic studies are a very powerful tool to the interpretation of chemical budgets. During the last decades an increasing number of studies have used oxygen isotopes of atmospheric compounds to constrain chemical oxidation fluxes (Michalski et al., 2003; Alexander et al., 2005; Morin et al., 2008; Gromov et al., 2010; Michalski and Xu, 2010). Notably, several chemical reactions generate specific isotopic distributions also defined as isotopic fractions. Most chemical processes maintain the elemental isotopic relative mass abundances during reactions. For instance, oxygen mass dependent fractions are characterised by a change in the <sup>17</sup>O/<sup>16</sup>O ratio which is half the magnitude of the respective change in the <sup>18</sup>O/<sup>16</sup>O ratio. Nonetheless, some processes can generate non-mass dependent anomalous isotopic distributions, also defined as mass-independent fractions (MIFs). The oxygen

mass-independent fractionation (O-MIF =  $\Delta^{17}$  O) is defined with respect to a mass-dependent reference line, and for its linear approximation is expressed as:

$$\Delta^{17}\mathcal{O} = \delta^{17}\mathcal{O} - 0.52 \times \delta^{18}\mathcal{O} \tag{1}$$

Where  $\delta^{17}$  O and  $\delta^{18}$  O are the deviations from the isotopic ratios of a standard of reference ( $R_{std}$ ):

$$R_x = \frac{{}^x \mathrm{O}}{{}^{16} \mathrm{O}} \qquad \qquad x = 17 - 18 \tag{2}$$

And:

$$\delta^x \mathcal{O} = \frac{R_x}{R_{std}} - 1 \tag{3}$$

Oxygen mass-independent fractionations are particularly useful to investigate atmospheric oxidation mechanisms, since most atmospheric oxidants are characterised by peculiar O-MIFs. In particular, these anomalous isotopic fractionations are directly or indirectly inherited from ozone, the atmospheric molecule with the largest intrinsically generated O-MIF (Thiemens, 2006). During oxidation reactions, O-MIFs can be further transmitted from oxidants to their reaction products, typically in relation to the number of oxygen atoms transferred during the reaction. For instance, when SO<sub>2</sub> is oxidised via a specific oxidation pathway, a fraction of the oxidant-specific  $\Delta^{17}$  O is found into the product molecule. It results that the overall sulphate oxygen isotopic composition is the linear combination of the oxidant-specific isotopic signatures, weighted by their respective contributions to total sulphate production. Therefore, oxygen isotopic investigations are very useful to track the formation of secondary sulphates, (i.e. formed by SO<sub>2</sub> processing in the atmosphere). Obviously, the specific  $\Delta^{17}$  O signatures transmitted to sulphate by the different oxidants have all to be known if different oxidation pathways are to be constrained simply, and even inferred in some cases.

Generally, a combination of several reactions is involved during secondary sulphate production in the background troposphere: radical OH in the gas phase, H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, O<sub>2</sub> catalysed by Transition Metal Ions (TMI), and HOX in the liquid phase (Vogt et al., 1996; Seinfeld and Pandis, 2016). In addition within fogs and polluted air masses, SO<sub>2</sub> can be oxidised also by NO<sub>2</sub> (He et al., 2014). However, because of the high acidity of volcanic water droplets and sulphate aerosols, the NO<sub>2</sub> contribution to volcanic sulphate production should be negligible (Seinfeld and Pandis, 2016). During SO<sub>2</sub> oxidation, the transfer of isotopic anomalies from ozone and H<sub>2</sub>O<sub>2</sub> produces sulphates with very significant O-MIF ( $\Delta^{17}O \neq 0 \pm 0.1\%$ ), whereas SO<sub>2</sub> oxidation by OH in the gas phase, and by O<sub>2</sub>/TMI and HOX in the liquid phase, are thought to produce sulphate without significant O-MIF ( $\Delta^{17}O = 0 \pm 0.1\%$ ) (Savarino and Thiemens, 1999b,a; Savarino et al., 2000; Martin et al., 2014; Chen et al., 2016).

On average, most sulphates collected in the troposphere have a  $\Delta^{17}$ O of about 1 % typically (Lee et al., 2001; Lee and Thiemens, 2001), reflecting the



Figure 1: Left panel: Oxygen isotopic composition of tropospheric volcanic sulphates from small tropospheric volcanic eruptions of the present geological era. Right: Oxygen isotopic composition of volcanic sulphates from stratospheric and tropospheric eruptions of present and past geological eras. For a full review see Martin, 2018.

importance of ozone and H<sub>2</sub>O<sub>2</sub> as global sulphur oxidants. In contrast, volcanic sulphates are characterised by peculiar oxygen isotopes compositions. Most tropospheric volcanic sulphates extracted from volcanic ashes of historical and present tropospheric small eruptions have no O-MIF (-0.1  $<\Delta^{17}{\rm O}<$  0.1%) (Bao et al., 2003; Mather et al., 2006; Martin et al., 2014; Martin, 2018) (see: Fig.:1). Remarkably, it is a feature observed for volcanic sulphates in ash-deposits that are also far from the point of emission (5-400 km), where secondary volcanic sulphates are the most abundant (Martin et al., 2014). On the other hand, volcanic sulphates collected from ice cores tend to have very positive O-MIF (see Fig.:1-2) (Bao et al., 2008). Notably, these sulphates are formed and transported within the stratosphere, or have originated from tropospheric super eruptions (Baroni et al., 2008; Gautier et al., 2019). The chemistry of a dense volcanic plume is certainly very different from the chemistry of the surrounding background atmosphere because of the intensity and composition of volcanic emissions. Therefore, volcanic sulphate production is expected to be very different from average tropospheric sulphur oxidation in terms of the mix of oxidants. Isotopic measurements suggest, indeed, that for different eruption stages and styles peculiar oxidation pathways might dominate volcanic SO<sub>2</sub> oxidation in the atmosphere.

The present work is a follow-on of a detailed photochemical modelling study on sulphur oxidation in volcanic plumes and on the implications for oxygen isotopic compositions of tropospheric volcanic sulphate (Galeazzo et al., 2018). A range of conditions and scenarios were previously explored, but the model could not reproduce most volcanic sulphate isotopic composition measurements (i.e. a negligible O-MIF). Potentially important elements were previously neglected, notably the presence of volcanic halogens and heterogeneous chemistry on sulphate particles. The purpose of the present work is to address these limitations. It aims at gauging the role of halogens in sulphur oxidation within volcanic plumes. Some volcanic plumes contain, indeed, very high levels of halogens, which, in some cases, can be as high as sulphur levels (Aiuppa et al., 2009; Cadoux et al., 2015). The implications for the isotopic composition of volcanic secondary sulphate are analysed here, and this is particularly useful for probing eruptions from the distant past, or when no optical measurements are available. Notably, so far halogen chemistry has mostly been ignored when dealing with isotopic investigations on tropospheric volcanic sulphate formation (Savarino et al., 2000; Martin et al., 2014).

The main tool of the present study is a photochemical box-model (CiTTy-CAT) which already describes standard tropospheric chemistry and sulphur chemistry in cloud water droplets (Galeazzo et al., 2018). It also contains a sulphur isotopic scheme tracking O-MIF anomalies during sulphur oxidation. This chemical scheme is here extended to include sulphur heterogeneous chemistry on sulphate aerosols, and halogen heterogeneous chemistry on both sulphate particles and water droplets. Diverse model simulations are carried out for a range of environmental conditions and scenarios. Model results are then used to investigate in details the chemistry of volcanic halogen-rich plumes, and to elucidate the role of halogens in tropospheric plumes chemistry, notably during sulphur oxidation. Model-calculated sulphate O-MIFs are compared to volcanic sulphate isotopic measurements, collected either in proximity of volcanic vents or from volcanic ash-deposits (Bao et al., 2003; Mather et al., 2006; Martin et al., 2014) (see Fig.:1). Note, however, that oxygen isotopic measurement techniques are characterised commonly by a  $\Delta^{17}$  O uncertainty value of at least 0.1 % (Bao et al., 2003; Martin and Bindeman, 2009), and here only values above 0.1 ‰ are therefore considered as O-MIFs. Results enable to assess dominant volcanic sulphur oxidation pathways in presence of varying levels of halogens.

The following second section of this work describes halogens gas phase and heterogeneous chemistry operating in volcanic plumes. Successively, the third section presents the modelling methodology adopted for simulating the in-plume halogens and sulphur chemistry. This section also covers the extension of the chemistry scheme (i.e. heterogeneous chemistry on sulphate aerosols), and of the isotopic balance equations implemented in CiTTyCAT to cover the SO<sub>2</sub> oxidation by halogens. The fourth section presents and discusses model results for typical plume conditions (here called standard), when only specific processes are considered (i.e. sulphate particles or cloud droplets, with or without halogens). Here the focus is on the role of heterogeneous chemistry and halogens during sulphur oxidation, and the resulting implications for sulphate O-MIF. The fifth section is devoted to sensitivity studies where a range of plume cases are considered. Notably, they are conducted to investigate how sensitive sulphate O-MIF is to different in-plume parameters. Here, dominant SO<sub>2</sub> oxidation pathways are identified for the two main liquid phase model scenarios (i.e. cloud droplets, sulphate aerosols). The model ability to reproduce observed isotopic compositions from volcanic sulphate ash-deposits and from volcanic sulphate aerosols is also further discussed. Finally, the main findings from the study are recalled in the conclusive section. More in-depth descriptions on model set-up and on model sensitivity to different initial parameters are reported in the Supplementary material section.

# 2 Volcanic halogens and sulphur chemistry

The most abundant volcanic halogen species are chlorine, fluorine and bromine, emitted at the vent as HCl, HF, and HBr respectively (Aiuppa et al., 2009; Oppenheimer et al., 2013). Fluorine is not significantly involved in tropospheric chemistry because of its very low reactivity. Small amounts of iodine are also present among volcanic emissions (Aiuppa et al., 2005), but as the effects of volcanic iodine chemistry are still poorly characterised its chemistry is mostly neglected. In conclusion, bromine and chlorine are the most relevant halogen species among volcanic emissions and the ones that can directly interact with volcanic sulphur.

A thorough description of tropospheric volcanic plumes chemistry has been covered by modelling simulations and experimental observations (Bobrowski and Platt, 2007; Roberts et al., 2009; von Glasow and Crutzen, 2013). In more details, these investigations highlight that halogens mobilization from plumes particles liquid phase to the gas phase (i.e. halogens activation), and volcanic bromine radical chain reactions in the gas phase (i.e. bromine explosion) are fundamental in-plume chemical mechanisms. In addition, modelling simulations suggest that during the first stages of young plumes development the interaction of halogens radicals emitted from the vent and  $HO_x$  species from the background atmosphere results in the formation of sulphur oxidizing species: hypohalous acids (HOX), in particular HOBr.

### 2.0.1 Oxidation of SO<sub>2</sub> by hypohalous acids (HOX)

Recently, significant attention has been devoted to HOX and their role during sulphate production in the MBL. HOX are produced via reactions R?? and R?? during the first stages of young plume development, and potentially they can lead to secondary sulphate production via oxidation of both  $SO_3^{2-}$  and  $HSO_3^{-}$  in the plume liquid phase (Fogelman et al., 1989; Troy and Margerum, 1991; Vogt et al., 1996; Von Glasow et al., 2002a,b):

$$SO_3^{2-} + HOX \rightarrow XSO_3^{-} + OH^{-}$$
 (4)

$$HSO_3^- + HOX \to XSO_3^- + H_2O$$
(5)

$$XSO_3^- + H_2O \to SO_4^{2-} + X^- + 2H^+$$
 (6)

Notably, it has been observed that HOX can drive  $SO_2$  oxidation in the gas phase even at very low concentrations ( $\approx 0.01-0.1$  pptv) (Chen et al., 2016, 2017). Remarkably, so far current regional models have not explored HOX influence on volcanic sulphate production.

# 3 Modelling approach

The chosen model to pursue the investigation is the Cambridge Tropospheric Trajectory model of Chemistry and Transport (CiTTyCAT). The model describes standard tropospheric gas-phase photochemistry (bimolecular, termolecular, and photodissociation reactions), emissions and deposition fluxes (Evans et al., 2000; Real et al., 2007; Arnold et al., 2007). The reaction rate constants and photolysis cross-sections are taken from JPL's datasheets (Sander et al., 2006), and photolysis rates are evaluated via the Fast-J code (Wild et al., 2000). The chemistry scheme has been recently extended with aqueous sulphur chemistry, a parametrization of cloud water droplets acidity, and oxygen isotopes transfers occurring during sulphate production (Galeazzo et al., 2018). Hereby, the scheme is further extended through the parametrization of SO<sub>2</sub> oxidation by O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, HOX and O<sub>2</sub>/TMI on sulphate aerosols, and via the addition of SO<sub>2</sub> oxidation by HOX in cloud water droplets. Moreover, new reactions have been implemented to account also for halogens heterogeneous chemistry in both sulphate aerosols and cloud water droplets.

Volcanic plumes from passive degassing can take multiple forms, and two main plume subcategories can be defined by the nature of plumes particles liquid phase: non-condensing plumes (i.e. primary sulphate aerosols) and condensing plumes (i.e. cloud water droplets). If the relative humidity of the background atmosphere is low and water saturation is not reached, sulphate aerosols constitute the bulk of in-plume liquid phase. Meanwhile, when large amounts of water vapour are emitted and relative humidity is high, volcanic water can condense into cloud droplets, either on the surface of primary sulphate aerosols, or on ash particles surfaces when some solid emissions are also present.

Reaction rates are strongly influenced by chemical activity of water and sulphuric acid, and therefore, heterogeneous chemistry is implemented through different modules for the two plume scenarios (i.e. condensing vs. non-condensing plume). Notably, large uncertainties are still pertaining to chemistry within sulphate aerosols, since the elementary aqueous reactions that drive halogens heterogeneous chemistry are not well characterized experimentally. As a result, in this study halogens heterogeneous chemistry, and all heterogeneous reactions on sulphate aerosols (i.e. also SO<sub>2</sub> heterogeneous oxidation) are implemented via reactive uptake coefficients. In contrast, sulphur aqueous reactions occurring within cloud droplets are explicitly modelled, accounting for all the elementary reactions occurring in the liquid phase. The non-condensing plume chemical scheme is schematically represented and summarised in **Fig.: 2**.



Figure 2: A diagram representing the new chemistry scheme implemented in CiTTyCAT for sulphate aerosols, including: SO<sub>2</sub> oxidation, and halogens heterogeneous reactions within sulphate aerosols.

# 3.1 General continuity equations

CiTTyCAT resolves coupled differential mass balance equations (continuity equations) describing the time evolution of atmospheric species concentrations (Evans et al., 2000; Real et al., 2007; Pugh et al., 2012). For given concentrations and environmental conditions (e.g. pressure, temperature), continuity equations are solved considering chemical production and loss terms, and deposition and mixing fluxes with background air:

$$\frac{d[C_i]}{dt} = \sum_k P_k - \sum_j L_j - D_i - M_i \tag{7}$$

where  $C_i$  is species *i* concentration in the plume,  $P_k$  the sum of gas phase and heterogeneous chemical production channels for species *i*,  $L_j$  is the sum of gas phase and heterogeneous chemical loss rates for species *i*, and finally  $D_i$ and  $M_i$  represent respectively species *i* deposition and mixing fluxes. Note that, heterogeneous chemistry production and loss terms include also mass-transfer between the gas and liquid phases.

Deposition only applies to liquid phase species dissolved in cloud water droplets or in sulphate aerosols. It is implemented as a first order loss process, where rate coefficients ( $k_{dep}$ ) are assumed to be proportional to the mean lifetime of cloud droplets and sulphate aerosols in the free troposphere (Stevenson et al., 2003b). Deposition fluxes are defined as:

$$D_i = -k_{dep} \cdot [C]_i \tag{8}$$

Exchange of species between volcanic plumes and background air due to atmospheric mixing is also accounted for. Mixing is parametrised via a simple linear relaxation scheme, inducing an exponential decay of plume concentrations towards background concentrations (Methven et al., 2006; Real et al., 2007; Arnold et al., 2007):

$$M_{(i)} = K_{mix} \cdot ([C]_i - [C]_{(i,bck)})$$
(9)

where  $K_{mix}$  is a first-order mixing rate coefficient quantifying volcanic air mixing with the background atmosphere, and  $[C_{(i,bck)}]$  is the concentration of species *i* in the background air.  $K_{mix}$  is set to 0.4 day<sup>-1</sup>, a value more representative of mixing in the lower atmosphere and equivalent to a 2.5 days dilution timescale.

Mass-transfer fluxes between gas phase and condensed phase are modelled considering trace gases non-reactive and reactive uptake to cloud water droplets and sulphate aerosols respectively. The general uptake rate on a particle is defined by the following kinetic regime expression (Hanson et al., 1994):

$$-\frac{d[C_i]}{dt} = \gamma_i \cdot \frac{\overline{\nu}_i}{4} \cdot SA \cdot [C_i]$$
(10)

where  $\gamma_i$  is species *i* uptake coefficient onto the condensed phase,  $\overline{\nu}_i$  represents the average molecular speed of *i* in the gas phase, and *SA* is the surface area density of the considered condensed phase (the condensed phase surface area per unit volume of air). Molecular uptake coefficient is not constant for most atmospheric gases, and it varies with time depending on the chemical composition of condensed phase and air. The uptake into a liquid particle, indeed, encompasses into a single variable multiple physical and chemical processes (Davidovits et al., 2006; Ammann et al., 2013).

The uptake coefficient can encompass in a single variable the physical uptake and reactions of molecules, notably for those reactions whose individual reaction mechanisms are not well constrained. In this case the molecular uptake becomes effectively a reactive uptake coefficient ( $\gamma_r$ ). Its formulation is based on a resistor model, where the different processes driving the heterogeneous reaction are expressed as separate resistances in series (Hanson et al., 1994; Davidovits et al., 2006) (see the Supplementary Material section for more information). Notably, halogens reactions in sulphate aerosols are extremely fast and mostly parametrised via experimental measurement of species reactive uptakes. Therefore, in the new version of CiTTyCAT halogens reactions are modelled using reactive uptake values from IUPAC datasheets. On the other hand, there are very few studies covering the reactive uptake of halogens on water droplets. Therefore, two different scenarios are investigated to explore halogens reactions in condensing plumes. The first one assumes no significant halogens reactivity in water (i.e.  $\gamma_r = 0$ ), while the second one considers very slow reactivity in water droplets (i.e.  $\gamma_r = 10^{-5}$ ). The latter value is at the lower bound of known reactive uptake values (Ammann et al., 2013). The values of  $\gamma_r$  for halogens heterogeneous reactions in condensing and non-condensing volcanic plumes are illustrated in Table:1.

Table 1: Values of  $\gamma_r$  used for halogens heterogeneous reactions in condensing plumes (WD) and non-condensing plumes (SA) (Sander et al., 2006).

Reaction	$\gamma_i$ (SA)	$\gamma_i$ (WD)
$HOCI + Br^{-}_{(aq.)} + H^{+} \longrightarrow BrCI_{(aq.)} + H_{2}O$	0.002	0 - 10 <sup>-5</sup>
$HOBr + Cl^{(aq.)} + H^+ \longrightarrow BrCl_{(aq.)} + H_2O$	$0.2 \cdot rac{[\operatorname{BrCl}]_{aq.}}{[\operatorname{BrCl}]_{aq.} + [\operatorname{Br}_2]_{aq.}}$	0 - 10 <sup>-5</sup>
$HOBr + Br^{(aq.)} + H^+ \longrightarrow Br_{2(aq.)} + H_2O$	$0.2 \cdot \frac{[\operatorname{Br}_2]_{aq.}}{[\operatorname{BrCl}]_{aq.} + [\operatorname{Br}_2]_{aq.}}$	0 - 10 <sup>-5</sup>
$BrONO_2 + H_2O \longrightarrow HOBr_{(aq.)} + HNO_{3(aq.)}$	0.8	3· 10 <sup>−2</sup>
$\text{CIONO}_2 + \text{H}_2 O \longrightarrow \text{HOCI}_{(\text{aq.})} + \text{HNO}_{3(\text{aq.})}$	-	<b>2.5</b> ⋅ <b>10</b> <sup>-2</sup>
$N_2O_5 + H_2O \longrightarrow 2HNO_{3(aq.)}$	0.03	0 - 10 <sup>-5</sup>

# 3.2 Final continuity equations

Based on the physico-chemical framework described above, the mass-balance equation (also defined as continuity equation) for volcanic  $SO_2$  oxidation is expressed differently for the condensing and non-condensing plume scenarios. Retain that, wet deposition of S(IV) species (S(IV) =  $SO_{2(g)} + SO_{2(aq)} + HSO_3^- + SO_3^{2^-}$ ) is ignored in non-condensing plumes, because very little S(IV) species are dissolved in sulphate particles due to the extreme pH of solution. Therefore,  $SO_{2(g)}$  represents all S(IV) family when working in non-condensing plumes. For instance, it is assumed that the mass-balance equation for S(IV) oxidation can be approximated to the one of SO<sub>2</sub>, expressed as:

$$\frac{d[\mathbf{S}(\mathbf{IV})]}{dt} = \frac{d[\mathbf{SO}_2]}{dt} = -k_{\mathrm{OH}+\mathrm{SO}_2} \cdot [\mathbf{SO}_2][\mathrm{OH}] - \left(\sum_j \gamma_j \cdot \frac{\overline{\nu}_{\mathrm{SO}_2}}{4} \cdot SA \cdot [\mathrm{SO}_2]\right) - K_{mix} \cdot \left([\mathrm{SO}_2] - [\mathrm{SO}_2]_{(bck)}\right)$$
(11)

where  $[SO_2]$  and  $[SO_2]_{(bck)}$  are respectively  $SO_2$  concentrations of volcanic plumes and background atmosphere.

Generally, SO<sub>2</sub> chemical reactions within concentrated sulphuric acid solutions are not well constrained in kinetic databases. However, within sulphate aerosols, liquid reactions between SO<sub>2</sub> and O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>/TMI, or HOX can occur in principle, since all species can still partition between gas and sulphuric acid solution. As a result, volcanic SO<sub>2</sub> uptake in non-condensing plume particles ( $\gamma_j$ ) in Eq.:11 are expressed via an effective reactive uptake coefficient. The values are extrapolated via empirical laboratory observations (DeMore et al., 1997; Rattigan et al., 2000) (for more details refer to the Supplementary material section).

The S(IV) continuity equation for condensing volcanic plumes is more complex, and it is expressed as:

$$\frac{d[\mathbf{S}(\mathbf{IV})]}{dt} = -k_{\mathrm{OH}+\mathrm{SO}_2} \cdot [\mathrm{SO}_2][\mathrm{OH}] - \left(\sum_j K_j^{l-g} \cdot [\mathbf{S}(\mathbf{IV})]_{aq.}^{l-g} [\mathbf{C}_j]_{aq.}^{l-g}\right) - k_{dep} \cdot [\mathbf{S}(\mathbf{IV})] - K_{mix} \cdot \left([\mathbf{S}(\mathbf{IV})] - [\mathbf{S}(\mathbf{IV})]_{(bck)}\right)$$
(12)

where [S(IV)] and  $[S(IV)]_{(bck)}$  are respectively S(IV) concentrations in volcanic plumes and in the background atmosphere.

The same approach is used to define continuity equations for sulphate production, in presence of sulphate aerosols (R13), or in presence of water droplets (R14):

$$\frac{d[\mathbf{S}(\mathbf{VI})]}{dt} = k_{\mathbf{OH}+\mathbf{SO}_2} \cdot [\mathbf{SO}_2][\mathbf{OH}] + \left(\sum_j \gamma_j \cdot \frac{\overline{\nu}_{\mathbf{SO}_2}}{4} \cdot SA \cdot [\mathbf{SO}_2]\right) - -k_{dep} \cdot [\mathbf{S}(\mathbf{VI})] - K_{mix} \cdot \left([\mathbf{S}(\mathbf{VI})] - [\mathbf{S}(\mathbf{VI})]_{(bck)}\right)$$
(13)

$$\frac{d[\mathbf{S}(\mathbf{VI})]}{dt} = k_{\mathrm{OH}+\mathrm{SO}_2} \cdot [\mathbf{SO}_2][\mathrm{OH}] + \left(\sum_j K_j^{l-g} \cdot [\mathbf{S}(\mathbf{IV})]_{aq.}^{l-g} [\mathbf{C}_j]_{aq.}^{l-g}\right) - (\mathbf{14}) - k_{dep} \cdot [\mathbf{S}(\mathbf{VI})] - K_{mix} \cdot \left([\mathbf{S}(\mathbf{VI})] - [\mathbf{S}(\mathbf{VI})]_{(bck)}\right)$$

where  $K_j^{l-g}$  is the gas phase equivalent (meaning conversion into gas-phase units) of the aqueous rate constant of reaction j,  $[S(IV)]^{l-g}$  is the gas-phase equivalent of the S(IV) aqueous species concentration,  $[C_j]^{l-g}$  is the gas phase equivalent of the oxidant j aqueous concentration.

In both model scenarios deposited S(VI) ( $S(VI)_{dep}$ ) is a prognostic variable of the system, and it is parametrised as:

$$\frac{d}{dt}[S(VI)]_{dep} = k_{dep} \cdot [S(VI)]$$
(15)

For both plume conditions, the value of  $k_{dep}$  is a first-order loss constant derived from the average lifetime of sulphate in the free troposphere (Stevenson et al., 2003a).

### 3.3 Tracking S(VI) oxygen isotopic signatures

### 3.3.1 Isotopic chemistry equations

Sulphate mass balance equations of CiTTyCAT are limited to mass tracking of atoms, not isotopes. As a result, they cannot monitor S(VI) and S(VI)<sub>dep</sub> evolving concentrations. In order to track sulphate  $\Delta^{17}$ O, the continuity equations describing sulphate production are combined to isotopic transfer equations, and a new variable called anomaly product ([S(VI)]· $\Delta^{17}$ O(S(VI))) is introduced in the model. Its continuity equation is given by (Morin et al., 2008, 2011; Galeazzo et al., 2018):

$$\frac{d}{dt} \left( [\mathrm{S}(\mathrm{VI})] \cdot \Delta^{17} \mathrm{O}(\mathrm{S}(\mathrm{VI})) \right) = \sum_{j} [P_j \cdot \Delta^{17} \mathrm{O}(\mathrm{S}(\mathrm{VI})_{\mathrm{prd}})_j] - k_{dep} \cdot \Delta^{17} \mathrm{O}(\mathrm{S}(\mathrm{VI}))$$
(16)

where  $\Delta^{17}O(S(VI))$  is the O-MIF of S(VI), P<sub>j</sub> is the S(VI) production via oxidation pathway j, and  $\Delta^{17}O(S(VI)_{prd})_j$  is the specific transfer of O-MIF to S(VI) during the oxidation of S(IV) via reaction j.

As  $S(VI)_{dep}$  is also a variable in the model, the  $[S(VI)_{dep}] \cdot \Delta^{17}O(S(VI))$  anomaly product is also a prognostic variable, whose continuity equation is given by:

$$\frac{d}{dt} \left( [S(VI)_{dep}] \cdot \Delta^{17} O(S(VI)) \right) = k_{dep} \cdot [S(VI)] \cdot \Delta^{17} O(S(VI))$$
(17)

The isotopic balance equations define the isotopic anomaly acquired by S(VI) molecules during their production. Each reaction pathway generates, indeed, a specific O-MIF on the specific produced sulphate. Peculiar signatures for each oxidation pathway are determined by the isotopic anomalies of reactants and the number of oxygen atoms transferred to sulphate during S(IV) oxidation. As a result, the overall sulphate isotopic composition reflects the relative contribution of different sulphate production pathways  $(P_j)$  weighted by their specific transferred isotopic anomaly  $\Delta^{17}O(S(VI))_j)$ .

On top of the oxygen isotopes scheme recently implemented in CiTTyCAT for S(IV) oxidation in cloud water droplets (Galeazzo et al., 2018), the isotopic continuity equations for S(IV) and S(VI) are modified to account for halogens chemistry, including  $SO_2$  oxidation by HOX on sulphate particles and cloud droplets. An HOX isotopic balance equation is derived and the isotopic balance equation for OH is also modified to account for halogens presence. Isotopic balance equations determine sulphate products O-MIF considering the origins of oxygen atoms inherited by S(VI) during S(IV) oxidation. Therefore, O-MIFs of reactants involved in S(VI) production are constrained very precisely.

It is worth stressing that in the model the continuity equations of S(VI) and  $S(VI)_{dep}$  anomaly products are integrated with an external 4th order Runge-Kutta method algorithm, instead of through CiTTyCAT chemistry solver. Preliminary simulations have shown that model results are not significantly affected by the

external integration method, with the advantage that while using this approach the chemistry module is totally independent from the oxygen isotopic scheme.

## 3.3.2 Oxidation by O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub> /TMI, and HOX

In a first place, it is important to assess the isotopic signatures and fractionations generated by single SO<sub>2</sub> oxidation pathways. It is assumed that volcanic SO<sub>2</sub> and H<sub>2</sub>O do not carry any significant O-MIF. The oxygen isotopic composition of magmatic SO<sub>2</sub>, indeed, is mass-dependent and no  $\Delta^{17}$ O (SO<sub>2</sub>) has been observed so far in volcanic SO<sub>2</sub> (Eiler, 2001; Martin, 2018). Finally, to our knowledge no study covering the isotopic composition of volcanic water emissions has been conducted. Therefore, it is assumed that volcanic water has the same isotopic composition as atmospheric water, whose  $\Delta^{17}$ O(H<sub>2</sub>O) is about 0% (Uemura et al., 2010).

Ozone is a key atmospheric reactant, characterised by an intrinsic high O-MIF generated during its formation in the atmosphere (Marcus, 2013). Tropospheric ozone has a large  $\Delta^{17}O(O_3, bulk)$  of about 26 % (Vicars and Savarino, 2014), but the isotopes distribution within the molecular structure is not stochastic. It has been suggested, indeed, that heavier oxygen isotopes are located at its molecular extremities which are therefore isotopically enriched (Bhattacharya et al., 2008; Marcus, 2013). Assuming that generally terminal atoms are more likely to be involved in chemical reactions (i.e., only one chemical bond needs to be broken) a mean reactive ozone MIF ( $\Delta^{17}O(O_3^*)$ ) can be defined. This term encompasses the isotopic enrichments of ozone terminal sites (i.e. about 40 \%) and their enhanced reactivity. In relation to typical tropospheric ozone O-MIF, a  $\Delta^{17}$ O (O<sub>3</sub><sup>\*</sup>) of about 36 % is derived (Morin et al., 2007, 2008; Bhattacharya et al., 2008; Savarino et al., 2008; Vicars and Savarino, 2014). This method for ozone evaluation was also used in previous modelling simulations, whose outcomes were in good agreement with experimental observations (Morin et al., 2008). As ozone reacts in the atmosphere part of its isotopic anomaly can be transmitted to the reaction products, hence generating a reaction specific isotopic signature on final products. In the case of  $SO_2$  oxidation by  $O_3$ , one out of four S(IV) oxygen atoms is inherited on sulphate during the oxidation. Therefore, the final sulphate product has a  $\Delta^{17}O(S(VI))_{O_3+S(IV)} = 9 \%$ .

Remarkably, other atmospheric oxidants can inherit O-MIF directly or indirectly from atmospheric ozone via photochemical reactions (Thiemens, 2006). Notably, among SO<sub>2</sub> atmospheric oxidants, H<sub>2</sub>O<sub>2</sub> carries a significant O-MIF ( $\Delta^{17}O(H_2O_2)$ ) equal to 1.75% (Savarino and Thiemens, 1999a). H<sub>2</sub>O<sub>2</sub> transfers two oxygen atoms to S(IV) via a nucleophilic substitution, resulting in a produced sulphate with  $\Delta^{17}O(S(VI))_{H_2O_2+S(IV)}$ ) equal to 0.87%. Atmospheric O<sub>2</sub> is another SO<sub>2</sub> oxidant characterised by a peculiar O-MIF equal to -0.34% (Young et al., 2002; Barkan and Luz, 2003). The oxidation of S(IV) by O<sub>2</sub> occurs via a chain of radical reactions catalysed by TMI. It is assumed here that only one oxygen atom is transferred from O<sub>2</sub> to S(IV), since there are large uncertainties

regarding the mechanism of S(IV) oxidation. The resulting final sulphate product has a  $\Delta^{17}$ O (S(VI))<sub>O<sub>2</sub>/TMI+S(IV)</sub>  $\approx -0.09\%$ . This value is within errors interval of experimental oxygen isotopes measurements, thus being classified possibly as mass-dependent in relation to experimental measurements.

No investigation regarding  $\Delta^{17}O(HOX)$  has been conducted so far. Nonetheless, it is suggested that any potential O-MIF carried by HOX would not affect the final isotopic signature of S(VI), since the new oxygen atom transferred to HSO<sub>3</sub><sup>-</sup> and SO<sub>3</sub><sup>2-</sup> originates from water and not from hypohalous acids (Fogelman et al., 1989; Troy and Margerum, 1991; Chen et al., 2016). Therefore, the isotopic mass-balance equation for HOX oxidation takes the following form:

$$\Delta^{17}O(S(VI))_{HOX+S(IV)} = \frac{1}{2} \cdot \Delta^{17}O(SO_2) + \frac{1}{2} \cdot \Delta^{17}O(H_2O)$$
(18)

Assuming that no isotopic anomaly is carried by volcanic H<sub>2</sub>O and SO<sub>2</sub>, it is expected that sulphates generated via S(IV) oxidation by HOX would be mass-dependent and with O-MIF equal to 0 % (Chen et al., 2016). A summary of the isotopic signatures of different oxidation channels is reported in Table:2.

Table 2: O-MIF signatures of S(IV) oxidation pathways in the model

Oxidant	O-MIF pathway ( $\%$ )
OH	calculated (0 to a maximum of 4.5)
$H_2O_2$	0.87
O <sub>3</sub>	9
$O_2/TMI$	-0.09
HOX	0

### 3.3.3 Oxidation by OH

In the atmosphere OH is a major oxidant generated mostly by ozone photochemistry. Specifically it is produced by the reaction between  $O^1(D)$  and  $H_2O$ . OH is initially formed with a relatively high O-MIF because it has a 50% chance of inheriting an oxygen atom from  $O_3$ . However, OH MIF is the result of the competition between OH rates of destruction (i.e. reaction with CH<sub>4</sub> and CO) and the isotopic exchange with  $H_2O$ , which depends, notably, on specific environmental and atmospheric conditions (Dubey et al., 1997; Lyons, 2001). Commonly, it is assumed that for average tropospheric conditions the inherited isotopic anomaly is rapidly lost by the quick O-isotopic exchange between OH and  $H_2O$ , which usually happens before the hydroxyl radical could have the time to react with other species. In the core of volcanic plumes, however, large amounts of volcanic SO<sub>2</sub> and HCl can react with OH, thus pushing significantly the OH destruction rate. In contrast to background atmospheric conditions, OH formed in volcanic plume may conserve some of its initial O-MIF, which then could be further transmitted to its reaction products. As a result, in the model  $\Delta^{17}O(OH)$  is considered a prognostic variable, and it is evaluated by the following equation (Morin et al., 2011; Galeazzo et al., 2018):

$$\Delta^{17}\mathcal{O}(\mathcal{OH}) = x \cdot \Delta^{17}\mathcal{O}(\mathcal{OH}_{prod.}^*)$$
(19)

with

$$\Delta^{17} O(OH_{prod.}^{*}) = \frac{1}{2} \cdot \Delta^{17} O(O_{3}^{*})$$
<sup>(20)</sup>

and

$$=\frac{D}{D+k_{\rm OH+H_2O}^*\cdot[\rm H_2O]}$$
(21)

$$D = k_{\text{OH}+\text{CO}} \cdot [\text{CO}] + k_{\text{OH}+\text{CH}_4} \cdot [\text{CH}_4] + k_{\text{OH}+\text{SO}_2} \cdot [\text{SO}_2] + k_{\text{OH}+\text{HCl}} \cdot [\text{HCl}]$$
(22)

x

The isotopic signature transmitted to sulphate via this channel of oxidation is therefore given by (Savarino et al., 2000):

$$\Delta^{17}O(S(VI))_{OH+SO_2} = \frac{1}{2} \cdot \Delta^{17}O(SO_2) + \frac{1}{4} \cdot \Delta^{17}O(OH) + \frac{1}{4} \cdot \Delta^{17}O(H_2O)$$
(23)

Since  $\Delta^{17}O(H_2O)$  and  $\Delta^{17}O(SO_2)$  are thought to be negligible the equation is finally simplified to:

$$\Delta^{17}O(S(VI))_{OH+SO_2} = \frac{1}{4} \cdot \Delta^{17}O(OH)$$
 (24)

As a result, in volcanic plumes the OH O-MIF ( $\Delta^{17}O(OH)$ ) can vary between 0 % and 18 %. Finally, depending on HCI, SO<sub>2</sub> and water vapour levels within the plume product sulphate can have an O-MIF spanning from 0 % to a max value of 4.5 %.

In order to illustrate how  $\Delta^{17}O(OH)$  can vary in relation to SO<sub>2</sub> and HCl loadings, OH O-MIF is investigated at standard conditions for increasing SO<sub>2</sub> and/or HCl concentration. As shown in **Fig.:3**.  $\Delta^{17}O(OH)$  is calculated for 3 different conditions. The first two cases are rather hypothetical because one concerns a volcanic plume with varying sulphur levels but no halogens, and the other case concerns a volcanic plume with varying halogen levels but no sulphur. Nonetheless, the results give some idea about the levels of SO<sub>2</sub> and HCl required to affect significantly the OH O-MIF. The third case is more realistic, and it is about a plume with varying halogen levels and 1 ppmv of SO<sub>2</sub>.

The first two cases show that only when SO<sub>2</sub> or HCl concentration is greater than tens of ppbv OH carries an O-MIF sufficiently high (O-MIF > 0.4 %) to generate sulphate with an O-MIF greater than 0.1 % (i.e. typical margin of error for oxygen isotopic measurement). This result implies that OH loss by reaction with SO<sub>2</sub> or HCl can compete to the isotopic exchange with H<sub>2</sub>O at concentrations  $\approx 0.1$  ppmv. Finally, the last case scenario shows that, in presence of 1 ppmv of SO<sub>2</sub>, HCl needs to be above 50 ppbv to influence



Figure 3: Variation of  $\Delta^{17}O(OH)$  in relation to initial halogens and SO<sub>2</sub> loading within a non-condensing plume.

significantly OH O-MIF. In this case, indeed, halogens reaction with OH is competing with both the isotopic exchange with  $H_2O$ , and the  $SO_2$  gas-phase reaction which dominates OH consumption.

# 4 Box model set up

# 4.1 Standard initial conditions

All simulations are run for springtime conditions and start at midday at a tropical location (i.e.  $115.5^{\circ}E 8.3^{\circ}S$ , Mt. Agung, Indonesia). In order to reach stable chemical compositions, notably for medium- and short-lived reactive species, the model is run for 3 days before injection of halogens and/or SO<sub>2</sub> (i.e. plume injection). The evolution of the chemical composition is then followed for 7 days in order to cover the evolution from highly concentrated to highly diluted plumes in the troposphere.

Since most large volcanoes are situated in remote areas with their peaks often close to the free troposphere, volcanic plumes tend to end up in the free troposphere at relatively high altitudes. The base model is set at 3 km of altitude and background concentrations of reactive species are set to typical atmospheric levels observed in the tropical free troposphere (Wang et al., 2001; Pan et al., 2015). In the standard conditions, initial concentrations are set to:  $O_3 = 35$  ppbv and  $H_2O_2 = 0.1$  ppbv (Herrmann et al., 2000). Within water droplets and sulphate aerosols, it is assumed that TMI concentrations are correlated with

each other, i.e. that  $[Mn(II)] = 0.1 \cdot [Fe(III)]$ , as observed in tropospheric aerosols and atmospheric hydrometeors (Seinfeld and Pandis, 2016).

Typical halogens emissions within volcanic plumes are not well characterised, because they vary from one volcanic system to another, and even between different phases of the same erupting event. Modelling and field observations suggest typical HCI/SO<sub>2</sub> ratios of about 0.5, and mean HBr/SO<sub>2</sub> ratio of about  $\approx 1 \times 10^{-3}$  for arc-volcanoes (Gerlach, 2004; Witt et al., 2008; Roberts et al., 2009). These initial ratios (HCI/SO<sub>2</sub>, HBr/SO<sub>2</sub>) are used in almost all simulations when halogens are injected, except when sensitivity to SO<sub>2</sub> or halogens loading is explored.

In both condensing (water droplets) and non-condensing (sulphate aerosols) plume standard simulations  $SO_2$  concentration is set to 1.5 ppmv, a value commonly observed at the proximity of volcanic vents during passive degassing (Robock, 2000; Rose et al., 2006; Mather et al., 2006; Roberts et al., 2012; De Moor et al., 2013; Voigt et al., 2014).

## 4.1.1 Specific input parameters: condensing volcanic plumes

In all condensing plume simulations, volcanic water is assumed to condense either forming water droplets, or coating ash particles. It constitutes the bulk of the liquid phase, quantified by the liquid water content (LWC). At standard conditions the LWC is set to 0.3 g m<sup>-3</sup>, a value commonly observed for tropospheric clouds (Korolev et al., 2007; Carey et al., 2008). It is assumed that water droplets have a fixed radius of 5  $\mu$ m. The droplets concentration is then derived from the specific LWC. The initial pH of the aqueous phase is set to 4.5, but it has no impact on the overall model results, since water droplets pH is almost immediately driven by SO<sub>2</sub>, HBr and HCl uptake, and by S(IV) oxidation.

Large uncertainties are pertaining to iron release from volcanic ashes in aqueous phase (Hoshyaripour et al., 2015; Maters et al., 2016). At standard conditions, TMI concentrations in water droplets are set to: [Fe(III)] = 0,5  $\mu$ M, and hence [Mn(II)] = 0,05  $\mu$ M. Standard TMI concentrations correspond to the lower range of tropospheric conditions (Herrmann et al., 2000; Parazols et al., 2006). This value is also within the range of model calculations regarding iron release within volcanic plumes (Hoshyaripour et al., 2015).

#### 4.1.2 Specific input parameters: non-condensing volcanic plumes

In all non-condensing plume simulations, the radius of primary volcanic sulphate aerosols is fixed at 0.5  $\mu$ m in the accumulation mode, while aerosols concentration is fixed at 1000 particles per cm<sup>3</sup> of air. Both values are chosen in relation to atmospheric observations of primary sulphate emissions at volcanic vents (Mather et al., 2003).

In non-condensing volcanic plumes, the liquid phase is composed by sulphuric acid, as it is assumed that water vapour pressure does not reach the point of saturation. The relative humidity (RH) is fixed and sulphate aerosol composition (i.e. sulphuric acid weight percentage, wt) is calculated depending on values of RH, temperature, and pressure (DeMore et al., 1997). The aerosol composition is a critical factor for gas-liquid partitioning of species and also for the liquid phase chemistry. During non-condensing plume simulations, RH is set to 45%, the average value observed for volcanic plumes degassing (Mather et al., 2006; Kroll et al., 2015).

Aerosols TMI concentration is set to 0.001  $\mu$ M, the lowest iron mobilization value suggested by volcanic plumes model simulations (Hoshyaripour et al., 2015).

### 4.2 Model experiments

#### 4.2.1 Standard simulations

The objective of the first set of numerical experiments is to assess the competition among SO<sub>2</sub> oxidants in presence or absence of halogens. Seven simulations (C<sub>gas</sub>, C<sub>het</sub>, C<sub>0</sub><sup>halo</sup>, C<sub>het</sub><sup>halo</sup>, and N<sub>gas</sub>, N<sub>het</sub>, N<sub>het</sub><sup>halo</sup>) are run with oxidation schemes of increasing complexity for both condensing and non-condensing volcanic plumes. The different SO<sub>2</sub> oxidation schemes considered in the simulations are oxidation by: only OH in gas phase (C<sub>gas</sub>; N<sub>gas</sub>), OH in gas phase, and H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub> and O<sub>2</sub> /TMI in liquid phase (C<sub>het</sub>; N<sub>het</sub>), and by OH in gas phase, and H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, O<sub>2</sub> /TMI and HOX in liquid phase (C<sub>0</sub><sup>halo</sup>-C<sub>het</sub><sup>halo</sup>; N<sub>het</sub><sup>halo</sup>). C<sub>gas</sub>, N<sub>gas</sub>, C<sub>het</sub> and N<sub>het</sub> do not have halogens within their chemical scheme, whereas C<sub>0</sub><sup>halo</sup>, C<sub>het</sub><sup>halo</sup> and N<sub>het</sub><sup>halo</sup> include halogens injection with plumes. C<sub>0</sub><sup>halo</sup> and C<sub>het</sub><sup>halo</sup> simulations differ between each other: during C<sub>0</sub><sup>halo</sup> halogens heterogeneous chemistry is not active (i.e.  $\gamma_r = 0$ ), while in C<sub>het</sub><sup>halo</sup> halogens heterogeneous chemistry in water droplets is activated (i.e  $\gamma_r \approx 10^{-5}$ ). The standard simulations are designed to explore the effect of different chemical reactions on the plume environment.

#### 4.2.2 Sensitivity simulations

Initial SO<sub>2</sub> levels, LWC, TMI and halogens concentrations are key model inputs, but they are subjected to large uncertainties and variability. The sensitivity of the model to input conditions varying within plausible ranges is explored in additional simulations. Notably, preliminary simulations have shown that TMI catalysed oxidation is negligible in non-condensing plumes, while it is a key parameter for condensing plumes chemistry.

The sensitivity studies for condensing plumes focus (S1) on the sensitivity of SO<sub>2</sub> oxidation to TMI concentrations. It is supposed to cover the possible range of TMI aqueous concentrations resulting from mineral dissolution. Volcanic eruptions can inject some solid material (i.e. ash), which commonly is composed by minerals with different proportions of Fe(II) and Fe(III) within their crystalline structure (Rose and Durant, 2009; Langmann, 2014). Depending on ash content

and plume chemical composition, TMI concentrations can vary for different volcanic plumes (Hoshyaripour et al., 2015). However, the extent to which halogen halides and sulphate can promote iron dissolution is rather uncertain. During S1, [Fe(III)] varies from 0.1 to 2  $\mu$  M, based on model simulations and laboratory experiments on iron release from volcanic ash (Hoshyaripour et al., 2015; Maters et al., 2016, 2017). Further sensitivity studies exploring plumes model sensitivity to LWC and RH values, and initial SO<sub>2</sub> loadings are explored in the Supplementary Material section.

The sensitivity studies for non-condensing plumes (H1) concern plumes chemistry responses to the initial halogens loading. The amounts of halogens emitted vary greatly from one volcanic system to another, and it influences significantly non-condensing plumes gas phase chemistry and therefore SO<sub>2</sub> oxidation in presence of sulphate aerosols. Major differences in halogens emissions are observed for between rift and arc volcanoes (Aiuppa et al., 2009). Intraplate systems (e.g. rift and hotspot volcanic systems) are characterised, indeed, by HBr/SO<sub>2</sub> emission ratios of the order of  $10^{-5}$ , while arc volcanic systems exhibit HBr/SO<sub>2</sub> ratios as high as  $10^{-2}$  (Aiuppa, 2009; Aiuppa et al., 2009; Mather et al., 2012). Finally, halogens rich emissions can reach HCl/SO2 ratios of about 1, such in the case of peculiar arc volcanoes (Aiuppa et al., 2005; Witt et al., 2008). As a result, the H1 sensitivity set explores HX/SO<sub>2</sub> ratios between 0.01 and 0.8. Initial SO<sub>2</sub> remains at 1 ppmv, HBr and Br radicals concentrations are varied considering average HBr/HCI ratios of about  $\approx 10^{-2}$ . In the supplementary material section, further sensitivity studies investigate non-condensing plume model responses to initial SO<sub>2</sub> loading.

A summary of all simulations, and relative specific conditions, is reported in Table: 3-4.

Input Parameters	Condensing plume	Non-condensing plume
LWC (g m <sup>-3</sup> )	0.3	< 0.005
RH (%)	100	40
Radius ( $\mu$ M)	5	0.5
N (particles $cm^{-3}$ )	$\approx$ 550	1000
[TMI] (µ M)	0.5	< 0.01
[SO <sub>2</sub> ] <sub>(0)</sub> (ppmv)	1.5	1.5
[HX] <sub>(0)</sub> (ppmv)	0.75	0.75
[O <sub>3</sub> ] <sub>(0)</sub> (ppmv)	35	35
$[H_2O_2]_{(0)}$ (ppmv)	0.12	0.12

Table 3: Standard input parameters for the condensing and non condensing plume scenario; T = 283.15 K, p = 691 mbar.

)	ХОН			$x \; (\gamma_r = 0)$	x ( $\gamma_r pprox 10^{-5}$ )			×	range	0.1 - 2		0.05 - 5		0.2 - 2		0.05 - 0.8		0.05 - 5		
)	O <sub>2/</sub> TMI		×	×	×		×	×	[HX] <sub>0</sub> /[SO <sub>2</sub> ] <sub>0</sub>							×				
-	$H_2O_2$		×	×	×		×	×	[SO <sub>2</sub> ] <sub>0</sub> (ppmv)			×						×		
	0 <sup>3</sup>		×	×	×		×	×	TMI ( $\mu$ M)	×										
	НО	×	×	×	×	×	×	×	LWC (g m <sup><math>-3</math></sup> )					×						
	sulphate aerosols					×	×	×	sulphate aerosols							×		×		
	water droplets	×	×	×	×				water droplets	×		×		×						
)	Standard set	$C_{gas}$	$C_{het}$	$C_0^{halo}$	$C_{het}^{halo}$	$N_{gas}$	$N_{het}$	$N_{het}^{halo}$	Sensitivity set*	S1	([TMI])	S2†	(SO <sub>2</sub> loading)	S3 <sup>†</sup>	(LWC)	Z1	(HX/SO <sub>2</sub> ratio)	Z2†	(SO <sub>2</sub> loading)	

Table 4: Investigated standard and sensitivity simulations (parameters, related oxidation pathways, and range of investigations).

\* During sensitivity simulations all sulphur oxidation channels are active in both condensing and non-condensing plumes. <sup>†</sup> Model sensitivity to the former parameters are investigated in the Supplementary Material section.

# 5 Results and discussion

# 5.1 Isotopic constraints on S(IV) oxidation: condensing volcanic plumes (water droplets)

#### 5.1.1 Standard simulations

The C<sub>gas</sub> standard simulation investigates O-MIF transfer to sulphate in absence of heterogeneous chemistry (with only activated gas-phase SO<sub>2</sub> oxidation by OH). The C<sub>het</sub> standard simulation has the same scheme as C<sub>gas</sub>, but on top it includes also the liquid phase oxidation of S(IV) by O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and O<sub>2</sub>/TMI. For C<sub>het</sub> simulation, TMI concentration is fixed at 0.5  $\mu$ M, and LWC is set to 0.3 g · m<sup>-3</sup>. C<sub>gas</sub> and C<sub>het</sub> simulations do not include halogens in their chemical scheme, the results and isotopic signatures reproduce correctly the ones obtained previously with CiTTyCAT for the halogens-poor condensing plume scenario (Galeazzo et al., 2018).

The evolution of SO<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and S(VI) concentrations during C<sub>gas</sub> and C<sub>het</sub> simulations are shown in **Fig.:4**. In C<sub>gas</sub> S(VI) production follows a diurnal cycle, and H<sub>2</sub>O<sub>2</sub> concentration increases throughout the run, reaching a final value of about 10 ppbv. Within 7 days from injection SO<sub>2</sub> concentration drops from 1.5 ppmv to 0.05 ppmv, and both produced and deposited S(VI) are equal to about 0.3 ppmv. In C<sub>het</sub> H<sub>2</sub>O<sub>2</sub> concentration drops immediately below pptv levels following plume injection and SO<sub>2</sub> dissolution in the liquid phase. It reaches again significant concentration (> 50 pptv) after 4 days from plume injection and only during daytime hours. The H<sub>2</sub>O<sub>2</sub> concentration drop is due to the fast reaction with S(IV), which is largely in excess in the liquid phase of the plume. Notably, S(VI) production still follows a diurnal cycle, suggesting significant contribution of gas-phase SO<sub>2</sub> oxidation to the overall S(VI) production.

The evolution of  $\Delta^{17}O(S(VI)_{prd.})$  and  $\Delta^{17}O(S(VI)_{dep.})$  for standard simulations  $C_{gas}$  and  $C_{het}$  are reported in **Fig.:5**. During  $C_{gas}$  simulation S(VI) is formed only via SO<sub>2</sub> gas-phase oxidation by OH. Consequently, S(VI) O-MIF depends only on the  $\Delta^{17}OH$  generated within the plume, and therefore mostly on SO<sub>2</sub> dilution. Deposited sulphate is initially formed with  $\Delta^{17}O(S(VI)_{dep.})$  of about 1.4 ‰, and during the simulation it decreases steadily to a final value of 0.75 ‰. Afterwards, as the pH of the water phase decreases due to S(VI) production, less S(VI) dissolves into the liquid phase. From the third day onward, S(IV) chemical consumption is significantly driven by gas-phase oxidation with OH, and by aqueous oxidation with  $H_2O_2$ . However, by the time OH becomes a main pathway of in-plume oxidation,  $\Delta^{17}O(OH)$  has decreased from its initial value because of SO<sub>2</sub> dilution, S(IV) deposition and in-plume reactions. Overall, in presence of 0.5  $\mu$ M of TMI and in absence of halogens chemistry,  $H_2O_2$  and OH contribute the most to S(VI) production, thus  $\Delta^{17}O(S(VI)_{dep})$  is equal to 0.7 ‰.

Simulation  $C_0^{halo}$  is the same of  $C_{het}$  but it includes halogen injection and



Figure 4: Gas-phase concentrations of atmospheric species during the  $C_{gas}$ ,  $C_{het}$ ,  $C_0^{halo}$ ,  $C_{het}^{halo}$  simulations. The runs start at 0:00 p.m.;  $C_{gas}$ , no halogens and no heterogeneous chemistry is active in the system;  $C_{het}$  no halogens, S(IV) heterogeneous oxidation included in the chemical scheme;  $C_0^{halo}$ , S(IV) heterogeneous chemistry, no halogens heterogeneous chemistry ( $\gamma_r = 0$ ); HX/SO<sub>2</sub> = 0.5;  $C_{het}^{halo}$ , S(IV) heterogeneous chemistry, halogens heterogeneous chemistry activated ( $\gamma_r = 10^{-5}$ ); HX/SO<sub>2</sub> = 0.5.

all the major pathways of sulphur oxidation, including S(IV) aqueous reactions with HOX. Due to the large uncertainty linked to the values of halogens reactive uptakes on water droplets,  $C_0^{halo}$  includes halogens injection but no halogens activation reactions (i.e.  $\gamma_r = 0$ ). For this scenario, it is assumed that halogens heterogeneous reactions would be rather slow and that halogens mobilization from the liquid phase would be very inefficient in cloud droplets. The evolution of SO<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and S(VI) concentrations during  $C_0^{halo}$  simulation is shown in **Fig.:4**. There is no significant difference in species concentration trends between  $C_{het}$  and  $C_0^{halo}$ . By the end of the simulation SO<sub>2</sub> concentration drops from 1.5 ppmv to 0.07 ppmv, while atmospheric S(VI) is around 0.04 ppmv and deposited sulphate is about 0.03 ppmv. Once again most of initial SO<sub>2</sub> is lost due to washing out and mixing with background atmosphere. The major differences with  $C_{het}$  are observed for O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> concentrations. Ozone concentration is



Figure 5: Time evolution of  $\Delta^{17}O(S(VI))_{dep.}$  during  $C_{gas}$  (only OH ox.),  $C_{het}$  (OH + het. oxidation, without halogens),  $C_0^{halo}$  (OH + het. oxidation, with halogens;  $\gamma_r = 0$ ), and  $C_{het}^{halo}$  simulations (OH + het. oxidation, with halogens;  $\gamma_r \approx 10^{-5}$ ).

slightly lower in  $C_0^{halo}$  due to the initial injection of reactive halogens generated by hot phase chemistry within the vent. Notably, radical halogens can react with ozone inducing a small decrease in its concentration. Following plume injection H<sub>2</sub>O<sub>2</sub> is quickly consumed by the reaction with S(IV) in the liquid phase. Most of the initial BrO from the young plume reacts with HO<sub>2</sub> leading to HOBr formation, causing a faster H<sub>2</sub>O<sub>2</sub> depletion and a slower recover. Because of the absence of halogens heterogeneous chemistry, HOBr accumulates quickly in the plume, participating significantly to S(IV) oxidation. Overall, less sulphate is formed in the plume compared to C<sub>het</sub>, and by the end of the run 54% of sulphate is formed via SO<sub>2</sub> oxidation by OH in the gas phase, 20% is formed by S(IV) reaction with H<sub>2</sub>O<sub>2</sub>, and 14% and 12% by S(IV) reaction with O<sub>2</sub> /TMI and HOX respectively. Remarkably, in absence of ODEs formation the O<sub>2</sub> /TMI and HOX sulphur oxidation pathways have comparable contributions to sulphate production.

In **Fig.:5** the evolution of  $\Delta^{17}O(S(VI)_{prd.})$  and  $\Delta^{17}O(S(VI)_{dep.})$  for standard simulation  $C_0^{halo}$  is compared to those of  $C_{gas}$ ,  $C_{het}$  and  $C_{het}^{halo}$ . Sulphate is initially formed with  $\Delta^{17}O(S(VI)_{dep.})$  of about 0.5 ‰, decreasing quickly to 0.3 ‰ during the first night. It increases to 0.7 ‰ during the second day, thus decreasing steadily to 0.6 ‰ by the end of the run. Initially, S(VI) O-MIF depends strongly on  $\Delta^{17}OH$  value and on the competition between SO<sub>2</sub> gas-phase oxidation and with the HOX oxidation in the liquid phase. HOX contribute significantly to SO<sub>2</sub> oxidation during the first day because of fast HOX accumulation, however from the second day onward the O<sub>2</sub> /TMI oxidation pathway contribution increases steadily until the end of the run. By the end of the simulation the major fraction of sulphate is produced by OH, followed by comparable contributions of the H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub> /TMI and HOX liquid phase oxidation pathways. Overall, the evolution of the isotopic signature in  $C_0^{halo}$  follows the trends observed for the  $C_{het}$  simulation.



Figure 6: The evolution of the BrO/SO<sub>2</sub> ratios during  $C_{het}^{halo}$  (purple) and  $N_{het}^{halo}$  (orange) simulations following plume injection and halogens activation.

The initial lower O-MIF value is due to major contribution of HOX and  $O_2$  /TMI to SO<sub>2</sub> oxidation.

Simulation  $C_{het}^{halo}$  is the same of  $C_0^{halo}$ , it includes halogen injection and all the major pathways of sulphur oxidation. However, this time halogens heterogeneous chemistry and activation within water droplets are operational (i.e.  $\gamma_r \approx 10^{-5}$ ). In this scenario, it is assumed that halogens heterogeneous reactions would be slow but faster enough to mobilize some halogens from the liquid phase. The evolution of SO<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and S(VI) concentrations during  $C_{het}^{halo}$ simulation is shown in **Fig:.4**. By the end of the simulation SO<sub>2</sub> concentration drops from 1.5 ppmv to 0.09 ppmv, while atmospheric S(VI) is around 0.02 ppmv and deposited sulphate is about 0.01 ppmv. Once again most of initial SO<sub>2</sub> is lost due to washing out and mixing with background atmosphere.

Remarkably, this time S(VI) is produced in significantly less amounts compared to  $C_{gas}$ ,  $C_{het}$  and  $C_0^{halo}$  simulations. Furthermore, in  $C_{het}^{halo}$  S(VI) production does not follow a diurnal cycle, indicating that HO<sub>x</sub> compounds produced by photochemistry are not major sulphur oxidants in the plume. After halogens injection, the O<sub>3</sub> concentration drops dramatically due to injection of radical bromine and HBr activation. A first ODE (ozone depletion event) is observed within half an hour from plume release. O<sub>3</sub> reaches less than ppbv levels during the first day when the plume is very concentrated, and massive drops in OH and H<sub>2</sub>O<sub>2</sub> concentrations are also observed. OH is reformed in significant amounts only after 5 days from plume injection, while H<sub>2</sub>O<sub>2</sub> concentration recovers to pptv levels only after 3.5 days. Within 30 minutes from plume injection only very small HOX concentrations are formed in the plume, because of massive depletion of HO<sub>x</sub> species and halogens mobilization. As a result, HOX (HOX = HOCI + HOBr) is found in extremely low concentrations in both aqueous and gas phases, remaining well below pptv levels throughout  $C_{het}^{halo}$  simulation. In **Fig.:6** the evolution of BrO/SO<sub>2</sub> ratio during the  $C_{het}^{halo}$  simulation is reported. Following halogens injection, BrO/SO<sub>2</sub> ratio keeps increasing during the first minutes of plume development, reaching a maximum value of about  $2.3 \times 10^{-4}$  after 30 minutes from plume release. Throughout  $C_{het}^{halo}$ , BrO/SO<sub>2</sub> ratio fluctuates significantly following a diurnal cycle. However, for the whole simulation the ratio remains within the range of experimental measurements and previous modelling simulations, reaching a max value of  $9 \times 10^{-4}$  after 7 days from plume injection (Bobrowski et al., 2003; Oppenheimer et al., 2006; Bobrowski and Platt, 2007; Bobrowski et al., 2007).

In **Fig.:5** the isotopic composition of atmospheric and deposited sulphates of simulation  $C_{het}^{halo}$  are compared to those of  $C_{gas}$ ,  $C_{het}$  and  $C_{het}^{halo}$ . During the first minutes of simulation atmospheric sulphate carries an O-MIF of about 0.2‰. However, within the first 24 hours from plume injection the isotopic anomaly drops to about 0.05‰, and by the end of the simulation  $\Delta^{17}O(S(VI)_{dep.})$  is equal to 0.08‰. The low  $\Delta^{17}O(S(VI)_{prd})$  value indicates that sulphate production is predominantly driven by aqueous phase oxidation pathways, producing sulphate with  $\Delta^{17}O\approx 0\%$ . The only S(IV) oxidation channel which does not exhibit diurnal variation and independent from HO<sub>x</sub> concentration in the plume is the O<sub>2</sub>/TMI oxidation pathway. This oxidation pathway is responsible for most of sulphate production during  $C_{het}^{halo}$  simulation, because of very low HOX concentrations.

The results from these simulations indicate that in condensing plumes halogens activation results in a quick decay of H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, and OH concentrations. In this scenario, the main pathway of  $SO_2$  oxidation is the reaction with  $O_2$  /TMI in the liquid phase. Without halogens activation SO<sub>2</sub> oxidation depends strongly on OH gas phase oxidation, and on H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub> /TMI liquid phase oxidation pathways. Meanwhile, more sulphate is produced in the plume when no ODEs occur. Sensitivity studies have been carried to investigate model responses to the most critical inputs: the amount of SO<sub>2</sub> injected, the assumed TMI concentrations and the LWC of the condensing plume. In occurrence of halogens activation, sulphate isotopic signatures are not significantly influenced by the plume LWC and by the overall SO<sub>2</sub> concentration of halogens rich and sulphur rich plumes (i.e. HX/SO<sub>2</sub>  $\approx$  0.5).Preliminary results suggest, indeed, that volcanic sulphate isotopic signatures are particularly sensitive to [TMI] concentrations. For this reason, here further sensitivity studies are conducted to investigate the impact of different dissolved iron concentrations on the final sulphate signatures. Other sensitivity studies regarding volcanic SO<sub>2</sub> and LWC influence on sulphate isotopic signature are illustrated in the Supplementary Material section.

#### 5.1.2 Influence of TMI concentration

This set of sensitivity studies (S1) covers the system response to different TMI aqueous concentrations. Note that, for these simulations  $SO_{2(0)}$  and HX(0) are set to 1.5 and 0.75 ppmv respectively, and that LWC is fixed at 0.3 g  $\cdot$  m<sup>-3</sup>. The temporal evolution of  $\Delta^{17}O(S(VI)_{dep.})$  for TMI concentrations in the range of 0.1-2  $\mu$  M is presented in **Fig.:7**. In all S1 simulations, an ODE occurs after 30 minutes from plume release.

For TMI equal to 0.1  $\mu$  M, deposited sulphate reaches an O-MIF of about 0.3 ‰ within the first hours from injection, it decreases gradually to 0.28 ‰, and finally it rises to 0.31 ‰ by the end of the run. Interestingly, during the first 6 hours of simulation, HOX contribution to S(IV) oxidation is somehow significant (i.e.  $\approx$ 10%), while H<sub>2</sub>O<sub>2</sub> contribution is low because it is quickly depleted due to its rapid reaction with S(IV). Overall, O<sub>2</sub>/TMI contribution to sulphate production is high throughout the simulation, and 50% of S(VI) has been produced via this oxidation pathway by the end of the run. The remaining S(VI) is mostly generated via H<sub>2</sub>O<sub>2</sub> oxidation during daytime, and to a lower extent by HOX and OH during the second half of the run.

For 0.5  $\mu$  M of TMI, the O-MIF in deposited sulphate initially rises towards 0.15 % and from the first day onward it gradually decreases to a final  $\Delta^{17}O(S(VI)_{dep})$  of about 0.08 %. Overall, by the end of the simulation the O<sub>2</sub> /TMI oxidation pathway is responsible for the 83% of total S(IV) produced, with only 17% of S(VI) generated by S(IV) oxidation by H<sub>2</sub>O<sub>2</sub> and OH.



Figure 7: Left panel: Temporal evolution of  $\Delta^{17}O(S(VI)_{dep.})$  for different TMI concentrations. Other initial parameters are: LWC = 0.3 g m<sup>-3</sup>, [SO<sub>2</sub>]<sub>0</sub> = 1.5 ppmv, [HX]<sub>0</sub> = 0.75 ppmv; Right panel: isotopic signatures measured in volcanic sulphates from small tropospheric eruptions of the current era.

For TMI concentrations above 0.5  $\mu$  M, the O-MIF in deposited sulphates remains mostly below 0.05 % for the whole duration of the runs. By the end of simulations more than 90% of S(VI) have been produced by the reaction with O<sub>2</sub> /TMI, and remaining sulphates are produced by a mix of OH, H<sub>2</sub>O<sub>2</sub> and HOX oxidants. Notably, at TMI concentration of 2  $\mu$  M the final  $\Delta^{17}O(S(VI)_{dep})$  has a negative O-MIF equal to -0.02 %.

Results from these simulations indicate that when TMI concentration is higher than 0.5  $\mu$  M, O<sub>2</sub> /TMI oxidation vastly dominates sulphur oxidation. The resulting O-MIF is lower than 0.1 ‰, in agreement with measurements observed in tropospheric tropospheric volcanic sulphates from ash-deposits (Martin, 2018). For TMI concentrations below 0.2  $\mu$  M, only half of the sulphate is produced via the O<sub>2</sub> /TMI oxidation pathway. The remaining sulphate product is generated via S(IV) oxidation by H<sub>2</sub>O<sub>2</sub> and OH mostly, and the corresponding O-MIF is around 0.3 ‰. Remarkably, when in presence of TMI, SO<sub>2</sub> oxidation by HOX is always negligible with regards to overall sulphate production. This result suggests that in the long term, even for low TMI concentrations (i.e.  $\approx$  0.1  $\mu$  M), the HOX oxidation pathway cannot drive sulphate production.

In conclusion, results from this set of simulations suggest that in a tropospheric condensing plume the only way to generate volcanic sulphate with negative O-MIF is via dominant contribution of  $O_2$ /TMI to S(IV) oxidation. Nonetheless, more detailed investigations are needed to assess the role of iron dissolution from volcanic ash and to assess in-plume TMI concentrations. Physico-chemical processing of suspended ash and mineral particles can vary, indeed, depending on multiple factors, such as ash mineral composition and/or aqueous phase evaporation and condensation cycles. In particular, transport to the upper troposphere and low temperatures can promote major iron mobilization from the solid phase, and possibly an overall enhanced contribution of the  $O_2$ /TMI sulphur oxidation pathway to volcanic SO<sub>2</sub> processing in the atmosphere (Jeong et al., 2012; Langmann, 2014).

# 5.2 Non-condensing volcanic plumes (sulphate aerosols)

### 5.2.1 Standard simulations

Simulations N<sub>gas</sub>, N<sub>het</sub>, and N<sup>halo</sup><sub>het</sub> reproduce the same sulphur and halogens chemical schemes of simulations C<sub>gas</sub>, C<sub>het</sub> and C<sup>halo</sup><sub>het</sub> respectively. This time, however, volcanic particles are composed by concentrated sulphuric acid (primary volcanic sulphate aerosols), and SO<sub>2</sub> heterogeneous reactions are modelled via reactive uptake coefficients.

The time evolution of SO<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and S(VI) concentrations for N<sub>gas</sub> and N<sub>het</sub> are presented in **Fig.:8**. In simulation N<sub>gas</sub> heterogeneous chemistry is not activated and halogens are absent from the plume. In simulation N<sub>het</sub> heterogeneous chemistry is active and halogens are absent from the chemical scheme (see Table:4). In both simulations, SO<sub>2</sub> is depleted from 1.5 ppmv to



Figure 8: Gas-phase concentrations of atmospheric species during the  $N_{gas}$ ,  $N_{het}$  and  $N_{halo}$  simulations. The simulations start at 0:00 p.m., and SO<sub>2</sub> is injected after 3 days;  $N_{gas}$ , only the OH oxidation pathway activated;  $N_{het}$ , heterogeneous and gas-phase oxidation pathways activated, no halogens;  $N_{halo}$ , heterogeneous and gas-phase oxidation pathways activated, halogens emissions and chemistry included.

0.06 ppmv. Deposited S(VI) and atmospheric S(VI) reach roughly 0.06 ppmv each, with the latter following a diurnal pattern of production. The total produced sulphate in N<sub>gas</sub> is 120 ppbv, while for N<sub>het</sub> it is around 130 ppbv. Remarkably, only 10 ppbv more of S(VI) is produced when in N<sub>het</sub> heterogeneous chemistry is activated. Therefore, in N<sub>het</sub> the heterogeneous SO<sub>2</sub> oxidation has a rather negligible contribution to sulphur oxidation. The only noticeable difference between N<sub>gas</sub> and N<sub>het</sub> is a small depletion in H<sub>2</sub>O<sub>2</sub> observed during the first 3 days of the N<sub>het</sub> simulation. This result contrasts significantly with results from C<sub>gas</sub> and C<sub>het</sub> simulations, where in C<sub>het</sub> a sharp drop in H<sub>2</sub>O<sub>2</sub> is observed due to the fast reaction with S(IV) in the aqueous phase. The temporal evolution of O-MIFs of atmospheric and deposited S(VI) from N<sub>gas</sub> and N<sub>het</sub> simulations are reported in **9**. As expected, there are no significant differences between



Figure 9: Time evolution of  $\Delta^{17}O(S(VI))_{dep.}$  during N<sub>gas</sub> (only OH ox.), N<sub>het</sub> (OH + het. oxidation, without halogens), N<sup>halo</sup><sub>het</sub> (OH + het. oxidation, with halogens).

 $\Delta^{17}O(S(VI)_{prd})$  and  $\Delta^{17}O(S(VI)_{dep})$  of the first two standard simulations. Initially, produced sulphate carries a large O-MIF at  $\approx$  2.3  $\%_0$ , which declines to about 1.2 % towards the end of N<sub>gas</sub> and N<sub>het</sub>. For both N<sub>gas</sub> and N<sub>het</sub> simulations the main SO<sub>2</sub> oxidant is OH, and sulphate O-MIFs reflect mostly the isotopic anomaly carried by OH during the reaction.

Simulation N<sup>halo</sup>, includes heterogeneous chemistry but this time halogens are also included within the plume chemical scheme. The evolution of SO<sub>2</sub>, O<sub>3</sub>,  $H_2O_2$ , and S(VI) in  $N_{het}^{halo}$  is shown in Fig.:8. Like  $N_{gas}$  and  $N_{het}$  simulations, during N<sup>halo</sup> simulation the concentration of SO<sub>2</sub> decays below 1 ppmv, reaching roughly 0.85-0.9 ppmv by the end of the run. Remarkably, this time much less sulphate is produced: only 1.9 ppbv of sulphate compared to at least 120 ppbv generated during other standard simulations ( $C_{qas}$ ,  $C_{het}$ ,  $C_0^{halo}$ ,  $N_{qas}$  and  $N_{het}$ ). Notably, in  $N_{het}^{halo}$  about half of sulphate is also produced within the first hour from plume injection. The first ODE develops in  $N_{het}^{halo}$  only after  $\approx$ 15 min. from halogens and SO<sub>2</sub> release, being triggered by very efficient halogens mobilization and bromine activation on sulphuric acid aerosols. The BrO/SO2 ratio reaches a value of about  $1 \times 10^{-4}$  within 5-10 minutes from plume release, in agreement with BrO/SO<sub>2</sub> experimental observations in volcanic plumes from passive degassing (Bobrowski et al., 2003; Oppenheimer et al., 2006; Bobrowski and Platt, 2007; Bobrowski et al., 2007). Within half an hour from plume release  $O_3$  levels drop to roughly 0.01 ppbv, inducing the deactivation of the HO<sub>x</sub> cycle and, notably, blocking OH production. Throughout the simulation the BrO/SO2 values remain within the range of observed measurements, as shown in Fig.:6.

After 2 days from plume injection, ozone levels recover to more appreciable concentrations, reaching  $\approx$  4-5 ppbv during daytime. By this time, OH is produced again in the plume because of ozone recover. From the third day onward, the gas-phase sulphur oxidation by OH drives sulphate production. During the first day H<sub>2</sub>O<sub>2</sub> decreases slowly to 0.1 ppbv, and from the second

day onward its concentration remains quite stable for the whole run. From the second day onward the photochemical production of H<sub>2</sub>O<sub>2</sub> is prevented due to O<sub>3</sub> destruction, and the only significant source of H<sub>2</sub>O<sub>2</sub> is mixing with the background atmosphere. The influx of background air, however, is sufficient to maintain reasonable H<sub>2</sub>O<sub>2</sub> levels within the plume ( $\approx 0.2$  ppbv). Remarkably, much higher H<sub>2</sub>O<sub>2</sub> concentrations are maintained in N<sup>halo</sup><sub>het</sub> if compared to C<sup>halo</sup><sub>0</sub>, where the very fast S(IV) oxidation in water droplets results in immediate H<sub>2</sub>O<sub>2</sub> consumption. Meanwhile, HO<sub>x</sub> destruction is also responsible for very low HOX (HOCI+HOBr) production. Notably, hypohalous acids are formed in very negligible amounts, and they react immediately with X<sup>-</sup> (Cl<sup>-</sup>+Br<sup>-</sup>) to promote halogens mobilization. As a result, during N<sup>halo</sup><sub>het</sub> there is no direct contribution of HOX to the overall S(VI) production.

The atmospheric and deposited sulphate O-MIF evolution during N<sup>halo</sup> is shown in **Fig.:9**, along with those of simulations  $N_{qas}$  and  $N_{het}$ . In  $N_{het}^{halo}$ , initially atmospheric sulphate is produced with an O-MIF of about 1.5 ‰, a slightly lower value if compared to N<sub>gas</sub> and N<sub>het</sub> simulations. This time, indeed, OH is quickly depleted from the gas-phase and a much higher fraction of SO<sub>2</sub> is oxidised by  $H_2O_2$  before the 1st ODE full development. Since the  $H_2O_2$  O-MIF is lower than the one carried by OH in a dense volcanic plume, sulphate O-MIF is smaller during the first few days of  $N_{\it het}^{\it halo}.$  Within few days from plume injection OH becomes again the main SO<sub>2</sub> oxidant within the plume. By this time SO<sub>2</sub> and HX levels have declined because of plume dilution and chemical reactions. As a result,  $\Delta^{17}O(OH)$  and sulphate O-MIF decline according to Eq.:19 and Eq.:24. During  $N_{het}^{halo} \Delta^{17}O(OH)$  varies from an initial value of 11.2 % to a final value of 1.7 %, which correspond to  $\Delta^{17}(S(VI)_{prd.})$  values of 2.8 and 0.4 % respectively. By the end of  $N_{het}^{halo}$ , both atmospheric and deposited sulphates carry an O-MIF of  $\approx$  1 %. Overall, after 7 days from plume injection 59% of S(VI) is produced via  $SO_2$  heterogeneous oxidation by  $H_2O_2$  on sulphate aerosols, and the remaining 41% is generated in the gas phase via oxidation by OH.

Results from these simulations indicate that in non-condensing volcanic plumes  $H_2O_2$  and OH are major  $SO_2$  oxidants. Unlike condensing plume simulations, the oxidation of  $SO_2$  on sulphuric acid is very slow because of low  $H_2O_2$  and  $SO_2$  solubilities in highly concentrated sulphuric acid solutions. During daytime, halogens concentrations can cause fast ODEs via fast bromine activation on sulphate aerosols. Meanwhile, halogens contribution to sulphate production via  $SO_2$  oxidation by HOX is negligible, because there is no sufficient accumulation of hypohalous acids due to the HO<sub>x</sub> cycle suppression.

Notably, it is possible to distinguish three different phases of SO<sub>2</sub> oxidation in presence of halogens. The first stage corresponds to SO<sub>2</sub> oxidation before the 1st ODE full development and it is dominated by the gas-phase oxidation by OH. The second phase extends for the time of the 1st ODE and it is characterised by the SO<sub>2</sub> oxidation by H<sub>2</sub>O<sub>2</sub>. The third and last phase covers from O<sub>3</sub> recover in diluted plumes to the end of simulation, and it is marked by SO<sub>2</sub> oxidation by both H<sub>2</sub>O<sub>2</sub> and OH. Overall, sulphate O-MIF is relatively high and close to 1 %,

suggesting that sulphates formed in volcanic plumes during passive degassing should have <sup>17</sup>O-anomalies very close to anthropogenic sulphates O-MIFs (Lee et al., 2001; Lee and Thiemens, 2001). Similarly to the condensing plume scenario, sensitivity studies are conducted in order to assess the variability of results to key input parameters, and to explore the ability of the model to reproduce measured O-MIF in sulphate.

#### 5.2.2 Influence of initial halogens concentration (H1)

The second set of sensitivity studies (H1) concerns model sensitivity to the initial halogens loading. It investigates mostly the impacts of in-plume  $[HX]_{(0)}/[SO_2]_0$  ratios on  $\Delta^{17}O(OH)$ , and on sulphate O-MIF. In addition, it also explores the impacts of  $HX_{(0)}$  loadings on ODE formation within the core of non-condensing plumes. In the H1 sensitivity set,  $[SO_2]_0$  is fixed at 1 ppmv, while  $[HX]_0$  is changed progressively from 0 to 0.8 ppmv, hence covering halogen-to-sulphur ratio varying from 0 to 0.8.

The evolutions of  $\Delta^{17}O(S(VI)_{dep})$  for six different initial  $[HX]_0$  (0, 0.05, 0.1, 0.2, 0.4, 0.8 ppmv) are shown in **Fig.:10**. Note that, the reported simulation without halogens (i.e.  $[HX]_0 = 0$ ) is the N<sub>het</sub> standard simulation. Moreover, recall that for such scenario there is no ODE, and that OH is the dominant SO<sub>2</sub> in-plume oxidant throughout the simulation. Consequently, it is important to remark that sulphate O-MIF reflects mostly the evolution of OH O-MIF in relation to SO<sub>2</sub> loading, and in particular in relation to plume dilution (see Eq.:24). This simulation is used as a parameter of comparison for halogens influence on sulphate O-MIF.

The model responses to low halogens loadings (i.e. below 0.2 ppmv) are very similar. The low halogens loadings simulations include H1a ([HX]<sub>0</sub> = 0.05 ppmv) and H1b ([HX]<sub>0</sub> = 0.1 ppmv). Remarkably, already 50 pbbv of halogens are sufficient to generate an ODE within 2 and a half hours from halogens injection, as observed in H1a. A doubling in initial halogens loading (i.e. H1b) induce faster ODE formation, with ozone destruction occurring within an hour from plume injection. In H1a and H1b the initial stage of SO<sub>2</sub> oxidation is driven by the reaction with OH. In both simulations, initially deposited sulphates carry an O-MIFs of about 1.95 %. These O-MIFs are very close to the 1.9 % value found in the no-halogen simulation (N<sub>het</sub>), hence confirming that in presence of  $SO_2$  concentrations of  $\approx$  1 ppmv, low halogens loadings do not affect significantly in-plume OH O-MIF (see **Fig.:3**). In more details, in H1a and H1b  $\Delta^{17}$ O(OH) is equal to 7.8 and 8 % respectively, resulting in sulphates with 1.95 and 2 % O-MIFs respectively. By the time the ODEs are fully developed (i.e. 1 and 3 hours roughly), OH formation is suppressed and the second stage of SO<sub>2</sub> oxidation begins. At this stage SO<sub>2</sub> oxidation by H<sub>2</sub>O<sub>2</sub> becomes the dominant pathway of sulphate production, tehrefore generating sulphate with lower O-MIF at 0.87 %. Obviously, in H1b the faster formation of the 1st ODE results in a slightly enhanced contribution of H<sub>2</sub>O<sub>2</sub> to sulphate production during the first day. In both H1a and H1b simulations, large amounts of sulphates are produced by OH oxidation before the formation of the first ODEs. As a result, during the second phase the addition of brand new sulphate produced via oxidation by H<sub>2</sub>O<sub>2</sub> affects weakly the overall O-MIFs of deposited sulphates. From the second day onward, O<sub>3</sub> concentrations and OH formations resume, and a third phase for SO<sub>2</sub> oxidation begins. This third last SO<sub>2</sub> oxidation stage is characterised by prevailing oxidation by OH in the gas-phase. By this time in both H1a and H1b  $\Delta^{17}$ O(OH) have decreased from early peak values, generating sulphates with O-MIF of about 1.6 and \% (see Eq.:19-21). The overall effect on deposited sulphates O-MIFs, however, is moderate, since the rate of sulphate production in this third phase drops continuously because of decreasing SO<sub>2</sub> concentrations due to dilution. Remarkably, in H1a and H1b simulations the amount of sulphate produced during the third stage is much smaller than during the first stage of SO<sub>2</sub> oxidation. In H1b less sulphate is also produced initially by OH because of faster 1st ODE development. Overall, the final sulphate O-MIF for H1b is slightly lower compared to H1a, because of the faster 1st ODE formation. The final O-MIFs is about 1.75 and 1.7 \% for H1a and H1b respectively. By the end of the H1a run, 13% of the sulphate is produced by H<sub>2</sub>O<sub>2</sub> oxidation and the remaining 87% by OH. Meanwhile, by the end of the H1b 19% of S(VI) is formed by SO<sub>2</sub> oxidation via  $H_2O_2$ , and the remaining 81% by  $SO_2$  oxidation via OH.

For  $[HX]_0 = 0.2 \text{ ppmv}$  (H1c), the first ODE occurs within half an hour from plume injection, significantly faster than H1a and H1b simulations. During the first phase of oxidation, deposited sulphate carries a high O-MIF of about 1.95 %, like H1a and H1b simulations. However, this time the second phase



Figure 10: Left panel: Temporal evolution of  $\Delta^{17}O(S(VI)_{dep})$  at different values of [HX]<sub>0</sub> in non-condensing plumes; Right panel: isotopic signatures measured in volcanic sulphates from small tropospheric eruptions of the current era.

of oxidation begins earlier, hence H<sub>2</sub>O<sub>2</sub> becoming faster the dominant SO<sub>2</sub> oxidant. Remarkably, in H1c the first ODE is considerably stronger and more pervasive than previous H1 simulations, therefore H<sub>2</sub>O<sub>2</sub> contribution to sulphate production is larger compared to H1a and H1b simulations. Consequently, this second SO<sub>2</sub> oxidation phase corresponds to a steep decline in sulphate O-MIF. Within 3 days from plume injection sulphate production enters finally its third stage. As expected, like previous simulations OH becomes again the main SO<sub>2</sub> oxidant. By this time, however, OH O-MIF has considerably lowered (i.e.  $\Delta^{17}O(OH) \approx 0.7\%$ ) because of the dilution-driven decline in SO<sub>2</sub> and HCl concentrations. Meanwhile, compared to previous H1 simulations, ozone recover is lower, so is the overall rate of OH formation. As a result, less sulphate is produced in this third phase of SO<sub>2</sub> oxidation, and the relative decrease in O-MIF is less stark, resulting in a final O-MIF of about 1.3 ‰. Overall, 42% of S(VI) is formed by SO<sub>2</sub> oxidation via H<sub>2</sub>O<sub>2</sub> and the remaining 58% is formed by SO<sub>2</sub> oxidation via OH.

The model response to high halogens loadings above 0.2 ppmv are very similar. The high halogens loading simulations include H1d ( $[HX]_0 = 0.4 \text{ ppmv}$ ) and H1e ([HX]<sub>0</sub> = 0.8 ppmv). For H1d the first ODE fully develops in 20 minutes, while in H1e the first ODE occurs within 15 minutes from plume injection. The first stages of SO<sub>2</sub> oxidation are significantly shorter compared to the ones observed at low halogens loadings. In both simulations, the initial deposited sulphate O-MIFs peak at about 1.4 %, a markedly lower level than what observed in low H1a and H1b simulations. While the initial OH O-MIF is higher than low halogens simulations, ozone destruction is very fast and SO<sub>2</sub> heterogeneous oxidation by  $H_2O_2$  becomes quickly the main  $SO_2$  oxidation pathway. Remarkably, the amounts of sulphate produced in H1d and H1e in this first phase of oxidation are very small. Within an hour H<sub>2</sub>O<sub>2</sub> becomes the overwhelmingly dominant SO<sub>2</sub> oxidant, inducing a sharp O-MIFs drop towards 1.1 \% during the second phase of oxidation. Finally, by the third day the final phase of SO<sub>2</sub> oxidation begins for both H1c and H1d. Once again, OH becomes the dominant pathway of  $SO_2$ oxidation, but OH formation is weaker due to more pervasive ODEs. Meanwhile,  $\Delta^{17}$ O(OH) values have significantly decreased because of plume dilution. As a result, the combination of lower OH O-MIFs and plume dilution produces little variation in sulphate O-MIFs, which stabilizes at 1.1 \% during this final stage of SO<sub>2</sub> oxidation. Finally, for H1d ([HX]<sub>0</sub> = 0.4 ppmv), 51% of S(VI) is formed by  $H_2O_2$  oxidation, and the remaining 49% by OH oxidation; while for H1e ([HX]<sub>0</sub> = 0.8 ppmv), 56% of S(VI) is formed by  $H_2O_2$  oxidation and the remaining 44% is formed by OH oxidation.

Results from the H1 set of sensitivity simulations suggest that volcanic halogens concentrations have multiple effects on the plume chemical development. Remarkably, even relatively small halogen loadings (i.e. 50 ppbv) induce ODEs, and suppression of in-plume OH production. Notably, the speed of formation, amplitude and duration of in-plume ODEs increase with halogens loading. At the same time stronger ODEs result in enhanced  $H_2O_2$  contribution to sulphate production, and, overall in lower amounts of sulphate produced within the plume. As for the H1 sensitivity simulations, halogens loading does not have a major impact on the O-MIF of volcanic sulphate produced in non-condensing plumes. The final deposited sulphate O-MIF, indeed, varies between 1 and 1.4 % for halogen-to-sulphur ratio between 0 and 1. Notably, the sulphate O-MIF is only marginally affected by increasing halogens concentrations because, while OH O-MIF increases proportionally with halogens loading, the overall contribution of OH to SO<sub>2</sub> oxidation is inversely proportional to halogens concentrations. Finally, like all previous non-condensing plume simulations, modelled sulphate O-MIF of H1 are not at all consistent with most O-MIF measurements in sulphate collected on volcanic ash.

# 6 Summary and concluding remarks

Volcanic plumes are peculiar chemical environments, radically different from background air. They are mostly composed by a mix of water, sulphur and halogens species. While sulphur is almost entirely emitted as  $SO_2$ , with a very small fraction (typically 1%) emitted at vents as primary sulphate aerosols, most tropospheric volcanic sulphate is produced in the atmosphere as a result of  $SO_2$  processing. Remarkably, most tropospheric volcanic sulphates extracted from volcanic ash-deposits of small tropospheric eruptions of the current geological era have an oxygen mass-independent fractionation equal to 0 % (Martin, 2018), indicating that peculiar  $SO_2$  oxidation pathways should take place within the plume.

The tropospheric photochemical box-model CiTTyCAT is used to simulate sulphur oxidation in presence of halogens in the core of volcanic plumes, and the resulting oxygen isotopic compositions in produced and deposited sulphates. An heterogeneous chemistry scheme for halogens has been implemented in the model. In addition, a new heterogeneous chemistry scheme has been added to account also for SO<sub>2</sub> oxidation on sulphate aerosols. This work is a follow-on of a modelling study on sulphur oxidation in a volcanic plume and the resulting secondary sulphate isotopic composition (Galeazzo et al., 2018). The present study aims at extending the investigation to cover previously missing processes. Here, the focus is on the role of halogens in plume chemistry and the implications for the isotopic composition of volcanic secondary sulphate. In more details, two typical volcanic plumes scenarios are investigated: the condensing plume (i.e. made of water droplets) and the non-condensing plume (i.e. made of water droplets) and the non-condensing plume (i.e. made of sulphate aerosols) scenarios.

With regards to condensing plumes, the first finding is that ozone depletion events (ODE) catalysed by halogens might occur in presence of water droplets even for very slow halogens reactions ( $\gamma_r \approx 10^{-5}$ ). The ODE is initiated by emitted bromine and chlorine radicals, and then it develops via heterogeneous

chemistry and halogens mobilization from water droplets. The second salient finding is that, in presence of halogens activation, SO<sub>2</sub> oxidation by both H<sub>2</sub>O<sub>2</sub> in water droplets and OH in the gas-phase are negligible. Within a condensing plume, indeed, H<sub>2</sub>O<sub>2</sub> is immediately consumed by sulphur reaction between SO2 and S(IV) in the aqueous phase, while the gas-phase OH concentration is severely depressed by ozone destruction. At the same time, O<sub>3</sub> is a negligible oxidant because the ozone concentration is very low and, more importantly, because the aqueous phase is much too acidic. In addition, HOCI and HOBr (i.e. HOX) do not contribute significantly to sulphur oxidation because their concentrations are very low under the effects of the fast halogens heterogeneous reactions. Consequently, according to model calculations, in condensing plumes SO<sub>2</sub> oxidation is dominated by S(IV) aqueous reaction with O<sub>2</sub>/TMI, even for relatively low TMI aqueous concentrations. As the plume mixes with the background air and becomes more diluted, halogens radical cycling weakens and the  $O_3$ , OH and  $H_2O_2$  concentrations increase substantially. Nonetheless, the O<sub>2</sub> /TMI oxidation remains the overall dominant oxidation pathway. Notably, even in absence of halogens, this sulphate production channel can be dominant for TMI concentrations around 2  $\mu$ M (i.e. high spectrum of typical atmospheric concentrations) (Galeazzo et al., 2018). As a result, volcanic sulphate carries a low oxygen mass-independent isotopic anomaly, and in some cases, the sulphate O-MIF is equal to 0 % (i.e. mass-dependent sulphate). These results are consistent with most isotopic measurements on sulphate collected on volcanic ash, which indicate mass-dependent sulphate within the typical measurement error (0.1 %). Finally, the model calculates sulphate O-MIF below 0.1 % only if the concentration of TMI is significant (i.e. above 0.5  $\mu$ M). Model calculations, however, would be much better constrained, if more information on TMI concentrations in volcanic water phases would be available.

With regards to non-condensing plumes (i.e. only sulphate aerosols), the first finding is that even for relatively low halogen loadings (about 50 ppbv) an ODE occurs; the speed of formation, amplitude and duration of the ODE depend on the initial halogens loading. In addition, the rate of SO<sub>2</sub> oxidation, and hence the amount of sulphate produced, is much lower in non-condensing plume simulations than in condensing plume ones. Overall, sulphate production is found to be inversely correlated to in-plume halogens concentrations, because of ODEs magnitude and duration. The second finding is that, the SO<sub>2</sub> reactions with O<sub>2</sub>/TMI and HOX on sulphate aerosols are totally negligible, and that sulphur oxidation is dominated by H<sub>2</sub>O<sub>2</sub> oxidation on sulphate aerosols and OH oxidation in the gas-phase. The H<sub>2</sub>O<sub>2</sub> contribution to SO<sub>2</sub> oxidation is very significant because, contrary to a condensing plume, the H<sub>2</sub>O<sub>2</sub> concentration does not drop instantaneously. Notably, H<sub>2</sub>O<sub>2</sub> is consumed very slowly because of the low solubility of  $H_2O_2$  in concentrated sulphuric acid solutions. Within a non-condensing volcanic plume gas-phase SO<sub>2</sub> oxidation is severely reduced after the formation of the 1st ODE (within 15 min. to 2-3 hr. depending on the halogens loading), in particular because of the OH concentration drop generated by the ozone depletion. The relative contributions of OH and H<sub>2</sub>O<sub>2</sub> to the total sulphur oxidation vary depending on the initial sulphur and halogens loadings. When the sulphur loading is small and the halogens loading is large, the relative contribution of H<sub>2</sub>O<sub>2</sub> to sulphur oxidation increases to the detriment of the OH oxidation. Typically, at low halogens loading, the contribution of OH oxidation is higher than the H<sub>2</sub>O<sub>2</sub> contribution and, at high halogens loading, it is the reverse. As a result, the third finding is that the O-MIFs of sulphates formed within a non-condensing plume is high. For all non-condensing plume simulations (including the sensitivity), the final deposited sulphate O-MIF varies between 0.8 and 1.4 \%. It is not at all consistent with most isotopic measurement on sulphate collected on volcanic ash. Recently, it has been demonstrated that OH  $\Delta^{17}$  O is large within volcanic plumes in presence of large SO<sub>2</sub> concentrations (Galeazzo et al., 2018). The present model calculations indicate that OH MIF is further enhanced by typical HCl in-plume concentrations. Overall, the net effect on the final  $\Delta^{17}$ O on sulphate is affected by the relative contribution of OH and H<sub>2</sub>O<sub>2</sub> on sulphur oxidation. However, while sulphur oxidation by H<sub>2</sub>O<sub>2</sub> generates sulphate with O-MIF of 0.87 %, the  $\Delta^{17}$  O in sulphate generated by OH varies strongly with the sulphur and halogen loadings, hence in relation to plume dilution. Recall that, however, the rate of SO<sub>2</sub> heterogeneous oxidation by H<sub>2</sub>O<sub>2</sub> on sulphate particles is quite uncertain, but that model calculated O-MIF would be considerably higher for non-condensing plumes without considering this sulphur oxidation pathway. In conclusion, these results suggest that sulphates collected in volcanic ash-deposits are not produced in non-condensing plumes, and it is possibly generated in condensing plumes or within water phases at the surface of ash.

There are a number of uncertainties associated with the present modelling work, arising notably from the chosen model inputs, such as kinetic data and the isotopic signatures of SO<sub>2</sub> oxidation pathways. In a first place, a certain degree of uncertainty is related to the SO<sub>2</sub> liquid phase oxidation by O<sub>2</sub> catalysed by transition metal ions. The oxidation, indeed, results form a series of complex radical reactions, and a significant limit is imposed by the number of oxygen atoms transferred to final sulphate product via the reaction. In this study, indeed, it has been assumed that only one oxygen atom would be transferred during SO<sub>2</sub> oxidation out of the two oxygen atoms of O<sub>2</sub>. Therefore sulphate isotopic signatures might be slightly overestimated. Another source of uncertainty arise from the values of kinetic data used for the SO<sub>2</sub> + OH and the H<sub>2</sub>O + OH reactions. The reaction rate constants for both reactions are quite outdated (Calvert et al., 1978; Dubey et al., 1997), and new kinetic data from laboratory experiments or ab-initio calculations would provide better constraints for modelled OH O-MIF signature, hence for secondary volcanic sulphate modelled signatures. Another limit of current model simulations is related to halogens chemistry. In this study, similar halogens reactive uptakes have been used to cover all halogens heterogeneous reactions in sulphate aerosols. All reactive uptakes have been set to a rather low value of  $\gamma_r \approx 10^{-5}$ , but this assumption is a quite crude

approximation. However, it is challenging to treat differently halogens chemistry in model simulations, notably because of the lack of experimental data on the subject, and in particular for atmospheric temperatures above 273.15 K and water droplets. Ideally, the results from this study would gain in robustness in presence of a qualitative and significant revision of current kinetic data, notably with regards to halogens chemistry and sulphur oxidation in liquid phase.

There are, however, several ways of testing these model predictions. First of all, the occurrence of a high  $\Delta^{17}$  O in volcanic sulphate produced by OH oxidation should be first tested. In principle, laboratory chamber experiments should be able to do it, notably in a controlled setting (i.e. humidity, ozone, SO<sub>2</sub> or halogen loadings) where OH chemical sources and losses are well constrained. It would also be desired to collect sulphate aerosols in the atmosphere during field campaigns, preferably far from volcanic vents (where the secondary sulphate dominates the composition of sulphate), and analyse their isotopic composition. A designated field campaign should take place in a location where the contribution of background non-volcanic sulphur aerosols (e.g. anthropogenic or sea-salt sulphates) to the total sulphate budget can be subtracted. This can be done easily for sea-salt sulphate; therefore, a campaign around a strong halogen and sulphur-rich degassing volcano in the middle of an ocean (such as on Ambrym, Vanuatu) would be the ideal location.

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