

# SO 2 Oxidation Kinetics Leave a Consistent Isotopic Imprint on Volcanic Ice Core Sulfate

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1	SO <sub>2</sub> oxidation kinetics leave a consistent isotopic imprint on volcanic ice core					
2	sulfate					
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12	(joel.savarino@cnrs.fr)					
13						
14	Key Points:					
15	• Aerosols are physically separated from the $SO_2$ pool during the oxidation process, and					
16	they preserve the isotopic signature during transport and deposition.					
17						
18	• Volcanic sulfate of stratospheric origin scatter on $\Delta^{33}$ S vs. $\Delta^{36}$ S and $\delta^{34}$ S vs. $\Delta^{33}$ S					
19	slopes of - 1.56 ( $1\sigma = 0.25$ ) and 0.09 ( $1\sigma = 0.02$ ) respectively.					
20						
21 22	• The mechanism generating S-MIF in stratospheric sulfate remains uncertain; a combination of several mechanisms is needed to reproduce the observed signature.					

#### 24 Abstract

This work presents measurements of time-resolved mass-independently fractionated sulfate 25 (S-MIF) of volcanic origin, from Antarctic ice core records that cover the last 2600 years. 26 27 These measurements are used to evaluate the time-dependence of the deposited isotopic signal and to extract the isotopic characteristics of the reactions yielding sulfate from stratospheric 28 volcanic eruptions in the modern atmosphere. Time evolution of the signal in snow (years) 29 with respect to the fast SO<sub>2</sub> oxidation in the stratosphere suggests that photochemically-30 produced condensed phase is rapidly and continuously separated from the gas phase and 31 preserved during transportation and deposition on the polar ice cap. On some eruptions, a 32 non-zero isotopic mass balance highlights that a part of the signal can be lost during transport 33 and/or deposition. The large number of volcanic events studied allows the  $\Delta^{33}$ S vs.  $\Delta^{36}$ S and 34  $\delta^{34}$ S vs.  $\Delta^{33}$ S slopes to be constrained at - 1.56 (1 $\sigma$  = 0.25) and 0.09 (1 $\sigma$  = 0.02), respectively. 35 The  $\triangle^{33}S$  vs.  $\triangle^{36}S$  slope refines a prior determinations of  $\triangle^{36}S/\triangle^{33}S = -4$  and overlaps the 36 range observed for sulfur seen in early earth samples (Archean). In recent volcanogenic 37 sulfate, the  $\Delta^{33}$ S vs.  $\delta^{34}$ S differs, however, from the Archean record. The similitude for 38  $\Delta^{36}$ S/ $\Delta^{33}$ S and the difference for  $\Delta^{33}$ S/ $\delta^{34}$ S suggest similar S-MIF processes to the Archean 39 atmosphere. Using a simple model, we highlight that a combination of several mechanisms is 40 41 needed to reproduce the observed isotopic trends, and suggest a greater contribution from mass dependent oxidation by OH in the modern atmosphere. 42

43

#### 44 Plain Language Summary

Large volcanic eruptions inject sulfurous gases in the stratosphere, where they rapidly form 45 sulfuric acid aerosols. These aerosols can reside in the stratosphere for years, cover the entire 46 47 globe, and profoundly modify the climate by scattering and absorbing solar radiation. Sulfuric acid aerosols formed by this process acquire an isotopic anomaly that traces these processes 48 and allows identification of these eruptions in ice core records, providing a means to 49 distinguish between high and low climatic impact eruptions in ice-core volcanic deposits. 50 This study provides a characterization of this time-dependent isotopic signature that is used to 51 constrain its origin and to understand the processes underlying its production and evolution. 52

53

#### 54 **1. Introduction**

The formation of sulfate aerosols, following stratospheric injection of sulfur dioxide by large, 55 plinian volcanic eruptions influences the Earth's radiation balance and has a documented 56 impact on climate and stratospheric ozone (Robock, 2000). Studies of the 1991 Mount 57 Pinatubo eruption indicate that sulfate aerosols form within the lower and middle stratosphere 58 within months (Bauman et al., 2003; Bekki & Pyle, 1994; Bluth et al., 1997; Dhomse et al., 59 60 2014), were first lofted by the heating resulting from the absorbtion of radiation, and then transported zonally (east-west) and meridionally (poleward) in both hemispheres (Aquila et 61 al., 2012), resulting in a detectable cooling effect on the troposphere that lasted two years. 62 This eruption also led to deposition of an anomalous, mass-independent sulfur isotope 63 signature (S-MIF) in polar snow (Baroni et al., 2007; Savarino et al., 2003). 64

Other eruptions, of even larger magnitude such as Tambora in 1816 CE (the year without a 65 summer) and the 1809 CE unknown eruption (Cole-Dai et al., 2009), the Samalas 1259 CE 66 eruption(s) (Baroni et al., 2008; Savarino et al., 2003) have shown a combination of S-MIF 67 signatures and spikes in sulfate concentration, indicating that similar events are also captured 68 and preserved in ice core archives. These larger eruptions are episodic in nature, occurring on 69 intervals of decades to centuries, with the largest eruptions being more infrequent, and 70 71 sometimes having significant climate impacts (Sigl et al., 2015). For example, while Pinatubo's effects persisted for several years (Liu et al., 2015; Parker et al., 1996; Trenberth 72 & Dai, 2007), a decade of cooling has been attributed to the larger Tambora and 1809 CE 73 events (Cole-Dai et al., 2009). 74

The S-MIF signatures of plinian volcanic origin have a characteristic time evolution in ice 75 core records: while  $\Delta^{33}$ S and  $\delta^{34}$ S evolve from positive in first-deposited sulfate to negative in 76 the last,  $\angle A^{36}$ S displays a complementary, but opposite sign signature (Baroni et al., 2007). This 77 typical pattern provides a signature that identifies stratospheric volcanic events with global 78 climatic impact of unknown past eruptions. The absence of such signatures in ice can also be 79 used to weed out near-field tropospheric or below stratospheric ozone layer events for 80 81 volcanic records assembled using evidence from bipolar correlations such as that of Sigl et al. (2015). This time evolution can thus provide a more finely resolved and accurate record of 82 stratospheric eruptions from ice core records (Savarino et al., 2003). 83

Here, we have undertaken a systematic analysis of the isotopic composition of sulfate ascribed to volcanic events that are recorded in a series of five 100 m long ice cores collected in 2010 – 2011 at Dome C, Antarctica. The resultant data set is used to reconstruct and understand the time-dependence of the sulfate isotopic signal ( $\delta^{34}$ S,  $\Delta^{33}$ S and  $\Delta^{36}$ S) and to evaluate the S-MIF producing mechanisms in the context of published laboratory experiments. We present a conceptual model for these data to quantify the contributions of photolysis, photo-excitation and OH oxidation in volcanic stratospheric sulfate.

### 91 2 Methods

- 92 2.1 Sampling and analysis
- 93

A series of five ice cores were drilled at Concordia station (Antarctica, 75°06'S, 123°21'E, 94 elevation 3220 m, mean annual temperature -54.5°C) to give enough sulfate for isotopic 95 analysis. Sulfate concentrations were quantified for each core with an ion chromatograph and 96 all depth-concentration profiles were synchronized using tie points of well-known volcanic 97 horizons (Gautier et al., 2016). A peak detection algorithm was applied to each profile. Each 98 portion of the five ice cores containing the same volcanic sulfate peak was cut, 99 decontaminated and subsampled at least in 5 portions, composed of two backgrounds (before 100 and after the peak) and at least 3 parts for the volcanic peak. The choice of sub-sampling 101 meets two needs: Firstly, the background samples allow for the correction of the volcanic 102 peak isotopic composition from the background contribution. Secondly, the peak subdivision 103 allows following the time-evolution of the volcanic isotopic signal. All portions of the same 104 stage of a given volcanic horizon were melted together (volume > 11) before following a 105 semi-preparative ion chromatography for further purification and concentration of the sulfate 106

in a small volume (<10 ml water solution). From that point, the samples were shipped to the University of Maryland where they were processed to  $SF_6$  following the standard Thode's reduction (Thode et al., 1961) and fluorination (Farquhar et al., 2001). Sulfur isotope ratios were measured using the dual inlet and micro-volume of a mass spectrometer (ThermoFinnigan, MAT 253).

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114

113 2.2 Corrections and uncertainties

Raw isotope data associated with the volcanic sulfate deposition were corrected for 115 background sulfate. Background sulfate imbedded into a volcanic peak was estimated using 116 117 the concentration and isotopic composition of the background sulfate surrounding the volcanic event (i.e. before and after the sulfate peak). After averaging the background data, a 118 simple isotopic mass balance correction was applied to extract the volcanic isotopic 119 composition (see SI for details). It is important to mention that this background correction 120 121 implicitly takes into account all possible sources of background sulfate, which in central Antarctica are dominated by sea-salt and biogenic sulfate (Legrand & Mayewski, 1997) for 122 which no S-MIF exists (Savarino et al., 2003), further confirmed by the isotopic composition 123 of our multitude background samples. 124

To estimate the uncertainty associated with the mass spectrometer internal error, the external 125 error due to sample treatment and the background correction, we used a Monte-Carlo routine. 126 Results showed that when the volcanic contribution did not exceed 20 % of the total sulfate, 127 the uncertainty on  $\varDelta^{33}S$  exceeds 0.2 ‰, an unacceptable uncertainty for establishing the 128 isotope systematics of the volcanic sulfate. For this reason, samples with a volcanic 129 contribution lower than 20 % were not corrected for background contributions, and only 130 samples with large volcanic contribution (above 65 %) were used to determine the isotopic 131 systematics of the stratospheric sulfate associated with individual volcanic events (Figs. 1 and 132 3). With such criteria, uncertainty is better than 1.3 ‰, 0.05 ‰ and 0.55 ‰ for  $\delta^{34}$ S,  $\Delta^{33}$ S and 133  $\Delta^{36}$ S, respectively. 134

- The isotopic values are defined as follows:  $\Delta^{33}S = \delta^{33}S ((1 + \delta^{34}S)^{0.515} 1), \Delta^{36}S = \delta^{36}S ((1 + \delta^{34}S)^{1.9} 1), \delta^{x}S = ({}^{x}S/{}^{32}S)_{sample} / ({}^{x}S/{}^{32}S)_{reference} 1$ , with x = 33, 34 or 36. Results are reported against the international reference standard V-CDT, on a scale where IAEA-S1 yields -0.3%, 0.0944%, and -0.69% for  $\delta^{34}S$ ,  $\Delta^{33}S$ , and  $\Delta^{36}S$  (Wing & Farquhar, 2015).
- 139

140 Additional details of the method are given in supporting information online materials (SI).

141

## 142 **3 Results**

143 A total of 46 volcanic eruptions (156 samples) were identified using changes in the

144 concentration and isotopic composition of sulfate in Dome C ice cores. Concentration, raw

isotopic data and background corrected data are presented in Dataset S1.

146 147 3.1  $\varDelta^{33}$ S vs.  $\delta^{34}$ S

- Figure 1 illustrates a positive correlation between  $\delta^{34}S$  and  $\Delta^{33}S$  for samples from different eruptions, where a volcanic contribution greater than 65 % of the total sulfate is measured. The  $\Delta^{33}S$  vs.  $\delta^{34}S$  slope equals 0.09 ( $1\sigma = \pm 0.02$ ) and is very similar for various volcanic eruptions taken individually (Figure S3b). The same slope although constrained by less data was obtained in previous studies of ices core sulfate in very different locations (Antarctica (et al., 2008) and Greenland (Lanciki et al., 2012)).
- 154

155 Figure 2 illustrates that the relationships between ( $\delta^{33}$ S and  $\delta^{34}$ S) and ( $\delta^{36}$ S and  $\delta^{34}$ S) yield

arrays with slopes that are steeper than and less steep than, respectively, the mass-dependent

- 157 fractionation arrays of 0.515 and 1.90.
- 158
- 159  $3.2 \varDelta^{36}S \& \varDelta^{33}S$ : Characterization of S-MIF processes

Figure 3a is a typical example of the time-evolution of the concentration and isotopic characteristics of the volcanic sulfate during its deposition (additional examples are available Figure S3a). During the plume deposition,  $\Delta^{33}$ S and  $\Delta^{36}$ S display opposite sign, with a clear time dependence already documented by Baroni et al., (2007). This characteristic pattern is observed on every stratospheric eruption, even if the negative part is sometimes muted and seems to be lost during transport and deposition processes.

Figure 3b illustrates the negative relationship between  $\Delta^{36}S$  and  $\Delta^{33}S$ . In order to obtain a 166 trend as robust as possible, we plot only data with a volcanic contribution above 65 %. This 167 reduces uncertainties in  $\triangle^{36}$ S at a reasonable level (1  $\sigma \le \pm 0.5$  %), but retains enough points 168 to constrain the slope. The  $\Delta^{36}$ S /  $\Delta^{33}$ S slope thus obtained is -1.56 (1 $\sigma$  = ± 0.25), with a 0.59 169  $(1\sigma = \pm 0.21)$  intercept. There are several possibilities that may explain the nonzero intercept, 170 including measurement uncertainty, uncertainty in the intercept for the earth, and mixing of 171 sulfur by two or more processes having different fractionation relationships. (Labidi et al., 172 2012) have shown that the composition of the mantle should be near zero for both  $\Delta^{33}$ S and 173  $\Delta^{33}$ S, thus we do not favor that explanation, but the other two explanations remain viable. 174 Additional uncorrected data are plotted in Figure S4. 175

176

#### 177 4 Discussion

The production of S-MIF occurs when chemical reactions for chemically-identical, but isotopically unique reactants, yield rates that do not scale with the isotopic mass. This occurs when factors in addition to those associated with molecular translation, vibration and rotation contribute to the reaction rates. Such factors include, but are not limited to, how states along a reaction path are coupled and differences in the spectrum of radiation that are available for photolysis.

Sulfur dioxide has a rich excited state chemistry, which results in many state to state transitions and complex isotopologue-specific absorption spectra (Endo et al., 2015), and complicates attempts to model the isotopic effects. Sulfur dioxide photolysis has also been shown to generate a variety of different types of S-MIF signatures (Endo et al., 2016; Farquhar et al., 2001; Lyons, 2007; Whitehill & Ono, 2012), and is thus implicated as a likely source for the effects seen in ice core sulfate and other carriers of S-MIF. The current

- 190 proposed mechanisms (Ono, 2017) include a spectral isotope effect (Danielache et al., 2008;
- 191 Endo et al., 2015), a self-shielding effect (Endo et al., 2016; Lyons, 2009; Ono et al., 2013),
- an intersystem crossing during  $SO_2$  photo-excitation (Hattori et al., 2013; Whitehill et al.,
- 193 2013) or a combination of these effects. However, lack of clear agreement in the literature on 194 the processes that explain S-MIF in modern and ancient atmospheres requires a more
- 195 complete characterization of the natural isotopic signals.
- Observations for a variety of different scale stratospheric eruptions can thus help to constrain 196 the different scenario for the production of S-MIF in the atmosphere. So far, uncertainty in 197  $\Delta^{36}$ S /  $\Delta^{33}$ S arising from a combination of analytical uncertainty and small number statistics 198 has prevented knowledge of whether there is a single array or many, and a precise 199 determination of  $\Delta^{36}$ S /  $\Delta^{33}$ S. The range of slopes that can be extracted from these data is too 200 large, and results in fits which range from -2 to -4 (Hattori et al., 2013; Muller et al., 2016; 201 Ono et al., 2013). The  $\Delta^{33}$ S/ $\delta^{34}$ S slope is better constrained and varies in a smaller range, 202 between 0.07 and 0.1. Understanding this isotopic variability is of interest because it can be 203 used to identify the source of S-MIF and possibly be connected to specific eruption features 204 such as plume height and the magnitude of plinian volcanic eruptions, which is crucial to 205 understand the role of volcanic forcing on climate. Making this connection requires an 206 understanding of the factors that control the expression of the signal as it is preserved in the 207 ice, and also those that link it to the atmospheric chemical reactions. 208
- 209

# 210 4.1 $\Delta^{33}$ S vs. $\delta^{34}$ S: Proportion between mass dependent and mass-independent processes

211 The expression and evolution of the signal in the ice preserves information about the respective contributions of stratospheric volcanogenic sulfate and tropospheric background 212 sulfate. The plot of  $\Delta^{33}$ S vs.  $\delta^{34}$ S for a volcanic event illustrates the systematic evolution of 213 the isotopic signature preserved in the ice. Figure 4 depicts the typical pattern for 1259 CE 214 Samalas eruption, a pattern that is common to all volcanic events observed (four typical 215 events are given in Figure S3b). Several first-order observations can be made. First, no clear 216 slope is observed when all raw data are plotted together (blue dots); but a similar pattern is 217 observed for each volcanic event: the isotopic signal traces a cyclic counter-clockwise path. 218

The beginning (dot 1 on Figure 4) and end (dot 9 on Figure 4) of this path correspond to the 219 background signal, situated around +15  $\% \pm 1.4 \%$  (1 $\sigma$ , n = 17), 0.05  $\pm 0.05 \%$  and 0.34  $\pm$ 220 0.67 % for  $\delta^{34}$ S,  $\Delta^{33}$ S and  $\Delta^{36}$ S, respectively (see SI), consistent with a background sulfate 221 primarily derived from oxidation of biogenic gases such as DMS (Oduro et al., 2011), with 222 only minor contributions for more <sup>34</sup>S-enriched mass dependent sea salt sources (Patris et al., 223 2000). The evolution of the isotopic signal from, and then back to, the background biogenic 224 values, (described by the blue trajectory in Figure 4) reflects the physical mixing of 225 background sulfate with variable amounts of a stratospheric volcanic sulfate pool (or pools). 226 Higher values of  $\delta^{34}$ S,  $\Delta^{33}$ S correspond to early parts of the event, and lower (more negative) 227 values of  $\delta^{34}$ S,  $\Delta^{33}$ S are associated with continued deposition, five to ten years after the 228 eruption. The <sup>34</sup>S enrichment in first formed sulfates (and its depletion in latter formed 229 sulfates) is in agreement with the measurements conducted on volcanic sulfate directly in the 230 stratosphere (Castleman et al., 1974). 231

# 233 4.2 $\Delta^{33}S$ vs. $\Delta^{36}S$ : Signal time-evolution preserved in the ice

As seen in figure 3a, the first part of the deposited sulfate has positive  $\Delta^{33}$ S (and negative 234  $\Delta^{36}$ S), which reflects the <sup>33</sup>S enrichment (and <sup>36</sup>S depletion) in first deposited aerosols, while 235 the SO<sub>2</sub> pool becomes more and more  ${}^{33}$ S depleted ( ${}^{36}$ S enriched), as a result of mass balance. 236 The last formed and thus deposited  $H_2SO_4$  aerosols result from a <sup>33</sup>S-depleted pool, hence the 237 sign shift at the end. The pattern is clearly asymmetric. While the positive phase is long, and 238 smooth, the negative phase is generally weaker, shorter and sharper and often missing as 239 underlined by the isotopic budget calculation (Table S4). This missing part in the signal 240 reflects a partial deposition of the plume (due to transport, meteorological conditions or 241 sedimentation processes). Last aerosols fractions seem to be subjected to stronger 242 loss/dilution, probably as a result of their longer atmospheric residence time. Assuming that 243 sulfate aerosols are formed and deposited following the same chronology, the sign inversion 244 and the asymmetric isotopic signals are two important constrains for the dynamics of the 245 volcanic cloud. 246

Observations of disappearance of the stratospheric SO<sub>2</sub> cloud as sulfate aerosol formation 247 proceeds following the Pinatubo eruption have indicated rapid, near-complete conversion of 248 sulfur dioxide to sulfate within 1-month of injection into the stratosphere for Pinatubo-size 249 eruption (Baran & Foot, 1994; Bluth et al., 1992; Read et al., 1993). Such time-scale seems to 250 be compatible with modeling studies that include only the OH sink of SO<sub>2</sub> in their 251 stratospheric chemical code (Bekki & Pyle, 1994; Dhomse et al., 2014). Yet the time 252 evolution of the isotopic signal we measure implies more than one oxidation scheme and is 253 preserved in a depositional record that can span more than a year. This implies that the whole 254 isotopic oscillation observed is the result of approximately one month of photo-oxidation 255 reactions (i.e. not only OH) and that some process imparted isotopic variability on a timescale 256 of weeks to months that was then preserved and sampled over a period of more than a year. 257 Physical separation of aerosol from the sulfur dioxide from which it forms is a secondary 258 requirement of the observed isotopic variability. 259

Our isotopic observations suggest, therefore, that production of volcanogenic sulfate aerosols 260 in the stratosphere happens with spatially-resolved isotopic heterogeneity and imply their 261 physical separation within few weeks after the eruption. We rule out the possibility of side to 262 side (N-S and E-W) heterogeneity because north-south and east-west mixing is rapid (Hall & 263 Waugh, 1997), which leaves the possibility of a vertically distributed isotopic variation in 264 volcanogenic aerosols, which would set up during the Brewer-Dobson circulation. The signal 265 that is recorded in the ice core would therefore reflect the time it takes for aerosols at different 266 stratospheric altitudes to be transported to the Antarctic site of deposition. The exact process 267 that produced the hypothesized vertical stratification of aerosols with different isotopic 268 compositions and different stratospheric residence times is not clear. Physical separation of 269 aerosols with different isotopic composition during a unidirectional process is required to 270 explain the positive to negative oscillation for  $\Delta^{33}$ S, thus a process that separates residual SO<sub>2</sub> 271 from aerosols is required. Several processes are known that could have contributed to the 272 separation of sulfur dioxide from product aerosols and also led to vertical distribution of 273 different populations of aerosols. These are gravitational settling which would affect the 274

275 largest aerosols, and radiative/thermal effects that generate vertical motion arising from 276 thermal heating of the aerosols (Santachiara et al., 2012). It appears clear, however, that this 277 process results in deposition of sulfate to the surface that records the chemical process and 278 also a process associated with the separation of sulfur dioxide from aerosols during the 279 stratospheric Brewer-Dobson circulation.

- 280
- 4.3 Implications of isotopic data for aerosol production
- 282

After background correction (details in SI), the volcanic sulfate isotopic composition forms a 283 linear array in the ( $\Delta^{33}$ S,  $\delta^{34}$ S) space, that may be possible to fit with a single straight line (red 284 dots in Figure 4), and that in principle, characterizes the transformation of the volcanic 285 products from the point source up to the deposition site. In other words, as  $\delta^{34}$ S fractionates 286 during the conversion of SO<sub>2</sub> to sulfate,  $\Delta^{33}$ S is generated in parallel. The simultaneous time-287 evolution of  $\Delta^{33}$ S and  $\delta^{34}$ S and robust correlation between these two variables strongly 288 indicates that they arise during the same process. The absence of break in the slope leads to 289 the conclusion that processes subsequent to the oxidation step (such as transport and 290 291 depositional effect) play a minor role in the imprint of the isotopic composition of volcanic sulfate. 292

More surprisingly, the very small variations in the slope  $(0.09 \pm 0.02)$  suggest that the relative 293 contributions of S-MIF and S-MDF is similar for every volcanic event. Since oxidation of 294 SO<sub>2</sub> by OH is the only reaction that is normally taken into account in stratospheric chemistry 295 models (Bekki & Pyle, 1994; Dhomse et al., 2014) and has been identified as a S-MDF 296 process (Harris et al., 2012), the non-zero and linearity of the slope implies that the current 297 scheme of sulfur oxidation in stratospheric models is incomplete and the proportion of sulfate 298 produced by OH oxidation and by the S-MIF processes is almost invariant during the whole 299 oxidation process. After background correction, the line crosses the origin, which is in 300 agreement with previous studies, on Mount Etna fumaroles reporting a  $\delta^{34}$ S range of  $0 \pm 1$ ‰ 301 in emitted SO<sub>2</sub> (Liotta et al., 2012) and on sulfate collected near volcanic vents showing 302 isotopic compositions of  $\Delta^{33}S = 0$  % (Mather et al., 2006). The background corrected data 303 also yield a  $\Delta^{36}$ S /  $\Delta^{33}$ S of -1.6 (Figure 3b) that is similar to some slopes observed for the 304 well-known Archean sulfur isotope dataset which has a most common value of - 0.9, but 305 sometimes rotates to -1.5 (Kaufman et al., 2007; Zerkle et al., 2012). 306

Several studies (Hattori et al., 2013; Whitehill et al., 2015) have compared experimental slopes and natural slopes obtained from ice-core sulfate to test hypothesized mechanisms. So far, lab experiments that better reproduce stratospheric sulfate composition observed in ice cores samples, as described by Lanciki et al., (2012), are the Farquhar et al., (2001) photolysis experiments with a Xe lamp (<200nm) with a -1.2 slope for  $\Delta^{36}$ S/  $\Delta^{33}$ S. While these experiments could capture a possible atmospheric mechanism, the experimental conditions are quite far from real stratospheric conditions.

More recent photolysis experiments of Whitehill et al., (2015) are closer to the stratospheric conditions in terms of illuminating conditions. The pressure in the experimental cell (SO<sub>2</sub> partial pressure above 10 mbar) is sufficient to combine spectral effects and the self-shielding

- effect of photolysis. The slope obtained (-3.8) is steeper than the volcanic slope obtained here. 317 It is also interesting to compare the observed  $\Delta^{33}$ S vs.  $\delta^{34}$ S, slopes of 0.09 with what has been 318 proposed by Whitehill et al., (2015). Photolysis experiments in the presence of O<sub>2</sub> gives a 319 slope of 0.06. These values might seem in close agreement with our data, but in contradiction 320 with Whitehill et al., (2015) who assume purely mass independent fractionation. Our sulfate 321 composition results from a mixing between mass independent and mass dependent processes. 322 Mass dependent processes ( $\Delta^{33}$ S /  $\delta^{34}$ S slope = 0) tend to dilute the mass independent signal 323 and induce a lowering of the  $\Delta^{33}$ S vs.  $\delta^{34}$ S slope. The slope in natural samples should 324 therefore logically lie between the lab experimental slope and the x-axis, which is not the 325 case. We suggest two possible explanations. First, mass dependent processes are also present 326 in Whitehill's experiments, and the fractionation observed is not representative of the mass 327 independent fractionation process. Second, in the stratosphere, an additional stratospheric 328 process steepens the slope of volcanic sulfate. Photo-excitation could be a candidate for this. 329 Photo-excitation yields positive  $\Delta^{36}S / \Delta^{33}S$ , but the exact slope is still uncertain and 330 dependent on environmental conditions, such as the atmospheric pressure at which it occurs. 331 Whitehill & Ono, (2012) determine the  $\Delta^{36}$ S /  $\Delta^{33}$ S of SO<sub>2</sub> photo-excitation to be  $\approx +$  0.6, 332 while this value is determined to range between 1.3 and 2.25 in Whitehill et al., (2013) and as 333 high as + 2.5 in Whitehill et al., (2015). 334
- So far, no experiment truly reproduces conditions of the current atmosphere, although efforts 335 are made in this direction. A recent study by Endo et al., (2016), tests optically-thin SO<sub>2</sub> 336 photolysis (1-10 Pa) in reducing atmospheric conditions (presence of CO in the bath gas). 337 They find only a relatively small contribution of the photolysis spectral effect, but a 338 significant self-shielding effect ( $\Delta^{36}$ S /  $\Delta^{33}$ S  $\approx$  -2.4), even in optically thin conditions. The 339 oxidation state of their experiment is more relevant to the Archean case than to the present-340 day stratospheric case but we will nonetheless test their data in the following, in the idea that 341 the oxidation state impacts more on the sulfur form and the anomaly preservation, rather than 342 the fractionation itself. 343
- 344

## 345 4.4 Source of S-MIF

In light of our results, we argue that none of the experimental trends obtained from lab 346 experiments can strictly reproduce both the  $\Delta^{36}$ S /  $\Delta^{33}$ S slope (-1.56) and the  $\Delta^{33}$ S /  $\delta^{34}$ S slope 347 (0.09) observed in stratospheric sulfate. This mismatch does not rule out any of the proposed 348 mechanisms (photolysis, through spectral effect and/or self-shielding effect, photo-excitation 349 and mass dependent OH oxidation), but it shows that in the present state of knowledge, none 350 of them is likely to be the only mechanism. It is possible that they all contribute in different 351 proportions to the observed isotopic composition, as it can be observed through a simple 352 modeling of sulfur isotopic composition in the oxidation product, during the stratospheric 353 process (details given in SI). Starting from an unfractionated initial SO<sub>2</sub> reservoir ( $\delta^{33}S = \delta^{34}S$ 354  $\delta^{36}S = 0$ , using the fractionation factors for OH oxidation, photolysis and photo-excitation 355 available in the literature, and involving the mechanisms in different proportion, we evaluate 356 what combinations can reproduce the natural data in Table 1 using constraints on the two sets 357

of fractionation factors taken from Endo et al., (2016); Harris et al., (2012); Whitehill et al.,

359 (2015); Whitehill & Ono, (2012).

360

With four possible combinations of fractionation factors, we found that the proportion of mass 361 dependent (vs. mass independent) process is ranging from 9 % to 79 %. Choosing one 362 fractionation factor rather than another can therefore drastically change the interpretations of 363 atmospheric chemistry. A minor contribution of OH oxidation contradicts our current 364 knowledge of the oxidation pathway in the stratosphere (Bekki, 1995; Seinfeld & Pandis, 365 1998), which pinpoint one combination likely to describe the stratospheric case: using Endo et 366 al., (2016) fractionation factors for photolysis, Whitehill & Ono, (2012) for photo-excitation, 367 and Harris et al., (2012) results for OH oxidation, we need 79 % of MDF process (i.e. OH 368 oxidation) and 21 % of MIF process (i.e. photo-oxidation), in a proportion of 7:1 for 369 photolysis and photo-excitation respectively, to obtain the volcanic slopes. Sensitivity tests 370 highlight that to stand below the uncertainty of our slopes (- 1.6 ( $1\sigma = 0.2$ ) and 0.09 ( $1\sigma =$ 371 372 0.02)), MIF processes must account for 15 to 35 % of the oxidation, and that the proportion of photo excitation is 5 to 9 times smaller than photolysis. The time evolution pattern of  $\Delta^{33}$ S 373 and  $\Delta^{36}$ S during deposition is well reproduced by the modeling (Figure S1a). 374

However, a minor contribution of OH oxidation (obtained here using the Whitehill et al. 375 (2015) factors for both photolysis and photoexcitation) cannot be completely discarded; 376 Stratospheric ozone can be severely depleted after an eruption (Cadoux et al., 2015; von 377 Glasow, 2010), due to volcanic halogen emissions (chlorine and bromine). OH would in that 378 case be largely depleted during a few weeks after the eruption (Bekki, 1995; Hattori et al., 379 2013; von Glasow, 2010), and could, under these conditions, play a less important role in 380 sulfur dioxide oxidation. OH titration by an excess of SO<sub>2</sub> would also lead to a self-limitation 381 of this pathway, and decrease its role in the oxidation process and extend the life-time of SO<sub>2</sub>. 382 This exercise is not intended to validate one mechanism, it mainly highlights the incomplete 383 chemical reaction scheme currently running in atmospheric chemistry models (i.e. 100 % OH 384 oxidation) and the need of conducting more laboratory experiments to precisely determine the 385 fractionation factors associated with the SO<sub>2</sub> photo-oxidation under more relevant 386 stratospheric conditions. In particular, none of the lab experiments mentioned have used a 387 radiation spectrum matching the solar radiation. Since it is challenging to match the solar 388 spectrum in the laboratory, experiments should be designed to obtain results that could be 389 extrapolated to the solar spectrum. In that sense, laboratory experiments should be conducted 390 in association with at least 1D atmospheric chemistry transport model incorporating a precise 391 atmospheric radiative transfer and microphysical aerosol modules. 392

393

### 394 **5 Conclusions**

Using sulfur isotope data from a set of five parallel ice cores this study reconstructs a timeresolved record of isotopic composition for large volcanic events. Our results show mass independent fractionation relationships that do not match current experimental results, and as a result they do not provide unique insight into the mechanisms that produce the stratospheric S-MIF. The following observations are made:

- 400 1.  $\Delta^{33}$ S and  $\Delta^{36}$ S display opposite sign during the plume deposition and evolve in a 401 characteristic pattern for all stratospheric eruptions. This general pattern can be well 402 reproduced when a combination of OH and photo-oxidation pathways are active 403 simultaneously. The non-zero isotopic budget of a volcanic deposit reflects a 404 missing part in the signal, and therefore a partial deposition of the plume (due to 405 transport, meteorological conditions or sedimentation processes).
- 2. Our results indicate that the oxidation end-products are transported and deposited 406 during several years after the eruption, with a preservation of a temporal isotopic 407 signal formed following the first months of emissions. This observation requires a 408 process that decouples product sulfate from the residual reactant sulfur dioxide 409 during the mass-independent sulfate formation process. It also requires i) conditions 410 that preserve sulfate formed by such a process, and having different mass-411 independent compositions within the atmosphere, ii) a deposition mechanism that 412 transfers the isotopic records a continuous signal of the sulfate generation process. 413 414 We suggest that the preservation reflects a process that produces an altitudinal variation in sulfate sulfur isotopic signatures and the different residence times of 415 sulfate as a function of its altitude. 416
- 3.  $\Delta^{33}$ S and  $\delta^{34}$ S of volcanic sulfate aerosols all spread on a well constrained 0.09 (1 $\sigma$  = 417 0.02) slope. This linearity suggests that the processes behind the sulfate isotopic 418 final composition are mostly operating simultaneously, during the oxidation of  $SO_2$ 419 into H<sub>2</sub>SO<sub>4</sub>. Linearity also implies that OH and photo-oxidation (photolysis + photo-420 excitation of SO<sub>2</sub>) proportions are quasi invariant for all the eruptions analyzed in 421 this study. This slope is around ten times smaller than the one observed for the 422 Archean samples, suggesting that OH radicals were much lower in the Archean than 423 in present-day atmosphere. Our results also indicate that the current chemical 424 scheme used in stratospheric chemistry model lacks the photo-oxidation. Such lack 425 may have impacts on the life-time of volcanic stratospheric aerosol modeled for past 426 eruptions and thus their climatic forcing. 427
- 4. A better constraint for the  $\Delta^{33}$ S vs.  $\Delta^{36}$ S slope yields a slope of -1.56 (1 $\sigma$  = 0.25), a 428 value not much different than the Archean's one (Figure 3b). The similarity of the 429 slopes may be fortuity as oxidation pathways of the activated sulfur compounds also 430 condition the formation rate of the stable products and thus the branching ratio 431 between photolysis and photoexcitation. If this similarity is not accidental, it will 432 suggest that photooxidation conditions of the Archean atmosphere may not have 433 been that much different than the present-day stratospheric photooxidation 434 conditions. 435
- 436 5. Finally, none of the experimental slopes obtained in lab experiments can reproduce 437 both the  $\Delta^{36}$ S /  $\Delta^{33}$ S slope and the  $\Delta^{33}$ S /  $\delta^{34}$ S slope observed in stratospheric sulfate. 438 However, it seems that mixing the mechanisms, acting in different proportions, can 439 potentially explain the observed slopes.

While slopes point to a photochemical process common to all eruptions, the magnitude of the isotopic anomaly differs. This latter feature is potentially linked with the elevation of the eruption or the amount of gas emitted as the strongest isotope anomaly is observed for the Samalas eruption, the greatest eruption of the period covered by our study. To establish a relationship between isotopic anomalies magnitude and one of those parameters, and ultimately link the isotopic signal to the climatic impact of an eruption, a model will be required. Empirical correlation could be used, but a set of well-known volcanoes (in terms of identified location, column elevation, and sulfate amount), and their associated isotopic signal magnitudes are needed to reduce the uncertainties.

- **Tables, figures and captions**

Fractionation factor for photolysis ( $\alpha^{33}/\alpha^{34}/\alpha^{36}$ )	Fractionation factor for photoexcitation ( $\alpha^{33}/\alpha^{34}/\alpha^{36}$ )	OH propotion / %	Photolysis proportion / %	Photoexcitation proportion / %
Endo <i>et al.</i> 2016 (1.03481/1.054/1.0859)	Whitehill <i>et al.</i> 2015 (1.02529/1.00733/1.06439)	79	20	1
Endo <i>et al.</i> 2016 (1.03481/1.054/1.0859)	Whitehill <i>et al</i> . 2012 (1.0248/1.0184/1.0454)	77	20	3
Whitehill <i>et al.</i> 2015 (1.05085/1.08924/1.15093)	Whitehill <i>et al.</i> 2015 (1.02529/1.00733/1.06439)	9	80	11
Whitehill <i>et al.</i> 2015 (1.05085/1.08924/1.15093)	Whitehill <i>et al</i> . 2012 (1.0248/1.0184/1.0454)	47	40	13

**Table 1.** Proportion of the three mechanisms hypothesized needed to produce the volcanic slope, 463 obtained using fractionation factors from different sources. For the  $SO_2$  + OH reaction, all simulations

464 use the sulfur kinetic isotope fractionation factor obtained from Harris et al., (2012) at 40°c ( $\alpha^{33}/\alpha^{34}/\alpha^{36}$ 465 = 1.0054/1.0105/1.02)



468 **Figure 1.** Cross plot of  $\delta^{34}$ S vs.  $\varDelta^{33}$ S for background-corrected values of samples with an initial 469 volcanic contribution in total sulfate above 65%. Different colors correspond to different eruptions. 470 When error bars are not visible, uncertainty is included in the size of the point.

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- 472
- 473



**Figure 2. (a)** Cross plot of  $\delta^{33}$ S vs.  $\delta^{34}$ S. Slope of stratospheric aerosols are steeper than the mass dependent fractionation slope, which translates systematic <sup>33</sup>S enrichment in the product (for positive  $\delta^{34}$ S), as observed in first deposited aerosols. (b)  $\delta^{36}$ S vs.  $\delta^{34}$ S. Slopes of stratospheric aerosols are less steep than the mass dependent fractionation line. Plotted data points are all background corrected values. Each colour (of dots and lines) is associated with one volcanic eruption.



496 Figure 3.(a)  $\Delta^{36}$ S and  $\Delta^{33}$ S, plotted vs. time, during Samalas eruption (1259 AD) deposition. Grey 497 boxes correspond to the mean sulfate mass fraction (in ng.g<sup>-1</sup>) of each sample analyzed. Red dots 498 (plain line) are  $\Delta^{33}$ S values, blue dots (dashed line) are  $\Delta^{36}$ S, both are background corrected 499 when volcanic sulfate is above 20% in the sample. In the insert, several different volcanic eruptions

- are plotted together to show the reproducibility of the signature pattern (initial positive and latter negative  $\Delta^{33}$ S).
- (b) Cross plot of  $\Delta^{36}$ S vs.  $\Delta^{33}$ S. Plotted data points are background corrected values, with an initial volcanic contribution in total sulfate above 65 %. Uncertainty is included in the size of the point when invisible. Different events are plotted, with different colors. The slope and intercept are given with 1-σ uncertainties of 0.25 and 0.21 respectively, calculated as described in (Taylor, 1997). Archean data (from (Kaufman et al., 2007), samples from the Campbellrand and Kuruman Iron formations in the AD-5 drill core from South Africa. Upper layer) are added for comparison. A similar plot with more, and uncorrected data is available in Fig. S4.
- 509 510





**Figure 4.** a. Cross plot of  $\delta^{34}$ S vs.  $\Delta^{33}$ S during one volcanic event displaying the time dependence of 515 the isotopic signature. Blue data points are measured values of natural samples, dot 1 corresponds to 516 the first deposited sulfate, 9 being the last. The isotopic signal traces a cyclic counter-clockwise path. 517 The beginning (dot 1) and end (dot 9) of this path correspond to the background signal, situated 518 around 15% for  $\delta^{34}$ S, compatible with biogenic sulfur emissions. Data corrected from their 519 background contribution are plotted with red squares, and their order of deposition, when it is given, is 520 written in grey (X'). In this plot, to avoid excessive scattering associated with the error arising from 521 background correction on  $\delta^{34}$ S vs.  $\Delta^{33}$ S, and keep the figure clear, only points with more than 40% 522 volcanic contribution are corrected. Volcanic data points form a line with a slope of 0.09, which 523 crosses the origin. The evolution of the isotopic signal reflects a physical mixing of a (stratospheric) 524 volcanic sulfate pool with an ambient background aerosol pool that originates from (principally) 525 biogenic sources. Uncertainties are included and in cases where no bars are visible, are included in the 526 size of the point. 527

528 b. Cross plot of  $\delta^{34}$ S vs.  $\Delta^{36}$ S during the same volcanic event. The isotopic signal traces here a cyclic 529 clockwise path. In the insert: Cross plot of  $\Delta^{36}$ S vs.  $\Delta^{33}$ S during the same volcanic event. In the ( $\Delta^{36}$ S, 530  $\Delta^{33}$ S) space, corrected and un-corrected data points stand on the same slope, but the magnitude of the 531 anomaly is affected by the correction.

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535 The data used are listed in the supporting information.

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