

1 Stratospheric eruptions from tropical and extra-tropical volcanoes constrained
2 using high-resolution sulfur isotopes in ice cores

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13

14 **Abstract**

15 The record of volcanic forcing of climate over the past 2500 years is based
16 primarily on sulfate concentrations in ice cores. Of particular interest are large
17 volcanic eruptions with plumes that reached high altitudes in the stratosphere,
18 as these afford sulfate aerosols the longest residence time in the atmosphere, and
19 thus have the greatest impact on radiative forcing. Sulfur isotopes measured in
20 ice cores can be used to identify these large eruptions because stratospheric
21 sulfur is exposed to UV radiation, which imparts a time-evolving mass
22 independent fractionation (MIF) that is preserved in the ice. However sample
23 size requirements of traditional measurement techniques mean that the MIF
24 signal may be obscured, leading to an inconclusive result. Here we present a new
25 method of measuring sulfur isotopes in ice cores by multi-collector inductively

26 coupled plasma mass spectrometry, which reduces sample size requirements by
27 three orders of magnitude. Our method allows us to measure samples
28 containing as little as 10 nmol of sulfur, with a precision of 0.11‰ for $\delta^{34}\text{S}$ and
29 0.10‰ for $\Delta^{33}\text{S}$, enabling a high-temporal resolution over ice core sulfate peaks.
30 We tested this method on known tropical (Tambora 1815 and Samalas 1257)
31 and extra-tropical (Katmai/Novarupta 1912) stratospheric eruptions from the
32 Tunu2013 ice core in Greenland and the B40 ice core from Antarctica. These
33 high-resolution sulfur isotope records suggest a distinct difference between the
34 signatures of tropical versus extra-tropical eruptions. Furthermore, isotope
35 mass balance on extra-tropical eruptions provides a means to estimate the
36 fraction of sulfate deposited that was derived from the stratosphere. This
37 technique applied to unidentified eruptions in ice cores may thus improve the
38 record of explosive volcanism and its forcing of climate.

39

40 **Keywords:** volcanoes, sulfur, mass-independent fractionation, stratosphere,
41 Katmai, ice cores

42

43 **1 Introduction**

44

45 Volcanic eruptions are the main natural external forcing of climate over
46 the past millennium (Schurer, 2013). The SO_2 erupted from volcanoes is
47 oxidized to sulfate in the atmosphere, and these sulfate aerosols reflect incoming
48 radiation, and cool the planet. The largest climatic impacts occur when volcanic
49 eruption columns reach high altitudes in the stratosphere, as the aerosols remain
50 in the atmosphere for longer, with a residence time of a couple of years (Robock,

51 2000). In contrast, sulfate aerosols that are erupted into the troposphere are
52 efficiently removed on the order of weeks. Accurate reconstruction of climate
53 forcing by large volcanic eruptions is fundamental for deconvolving forced from
54 internal climate variability and for better understanding climate sensitivity to
55 greenhouse gases.

56 Current state-of-the art volcanic forcing records are based on sulfate
57 concentrations in ice cores, which show peaks above background levels due to
58 volcanic eruptions (e.g. Gao et al., 2007; Sigl et al., 2015). Sulfate concentrations
59 from several cores are spatially averaged to determine the total mass deposition
60 rate (i.e. “flux”) of sulfate to the ice sheet for a given eruption, and this is then
61 scaled to a total stratospheric burden of sulfate, which can be used to calculate
62 radiative forcing changes or aerosol optical depth fields (e.g. Toohey and Sigl,
63 2017). However, sulfate concentrations in ice can also be elevated due to local,
64 smaller eruptions that did not make it to high altitudes in the stratosphere and
65 thus would not have had a large climatic impact. To address this complication,
66 ice core sulfate records from Greenland and Antarctica have been synchronized
67 and compared to determine which sulfate peaks occur in both hemispheres.
68 These peaks are called ‘bipolar events’, and are attributed to large, tropical
69 eruptions whose plumes made it to the stratosphere and thus were distributed
70 globally, allowing for deposition of sulfate aerosols in both hemispheres (e.g.
71 Plummer et al., 2012; Sigl et al., 2013). These events are then scaled to have a
72 larger effect on the radiative forcing of climate compared to sulfate events that
73 occur in only one of hemispheres (Gao et al., 2008; Sigl et al., 2015; Toohey and
74 Sigl, 2017). However, this approach is not without its difficulties: the attribution
75 of a bipolar event relies on very precise ice core age models, and typical age

76 uncertainties over the past two thousand years can be of the order of 2-4 years
77 (McConnell et al., 2018; Sigl et al., 2015). Thus, based on sulfate concentration
78 alone it is not possible to distinguish between a bipolar event, and two
79 hemispheric events that occur within age model uncertainty of each other. For
80 mid-to-high latitude eruptions (producing unipolar sulfate signals), it is also not
81 possible to determine how much of the sulfate deposited on the ice sheet came
82 via the stratosphere since a large proportion could be transported
83 tropospherically. Given the large difference in the radiative forcing following
84 eruptions with high stratospheric injection height (i.e. 24 km or higher)
85 compared to eruptions with lower injection heights (Toohey et al., 2019), there
86 is a need for a means to independently constrain volcanic sulfate injections to the
87 high stratosphere.

88 Sulfur isotopes have been used in polar snow (Baroni et al., 2007) and ice
89 cores (e.g. Baroni et al., 2008; Cole-Dai et al., 2009; Gautier et al., 2019; Savarino,
90 2003) to distinguish between eruptions whose plumes reached the stratosphere
91 at or above the ozone layer and those that remained below. This approach is
92 possible because the sulfur that makes it up to the ozone layer is exposed to UV
93 radiation, which imparts a mass independent fractionation (MIF) of the S
94 isotopes (Farquhar et al., 2001). This fractionation is then recorded in the ice
95 cores as a non-zero $\Delta^{33}\text{S}$ value, where

96
$$\Delta^{33}\text{S} (\text{‰}) = \delta^{33}\text{S} - ((\delta^{34}\text{S} + 1)^{0.515} - 1) \text{ (Equation 1)}$$

97 and $\delta^{33}\text{S} = ({}^x\text{S}/{}^{32}\text{S})_{\text{sample}} / ({}^x\text{S}/{}^{32}\text{S})_{\text{reference}} - 1$, with x either 33 or 34. Almost all
98 physical, chemical and biological processes fractionate isotopes based on mass,
99 and thus have $\Delta^{33}\text{S}$ values that are zero. Sulfur photochemistry is one of the few

100 processes that produces mass-independent fractionation, even though the exact
101 photochemical mechanism for this fractionation is still debated (e.g. Gautier et
102 al., 2018). The presence of non-zero $\Delta^{33}\text{S}$ in sulfate in ice therefore indicates that
103 the sulfate formation occurred at a height in the stratosphere where it is possible
104 to interact with UV radiation. Although sulfur isotopes have previously been
105 used as a means to distinguish between stratospheric and tropospheric
106 eruptions (e.g. Lanciki et al., 2012), an important caveat is that at high latitudes,
107 the lower stratosphere lies below the ozone layer (Fig. 1), and so it is possible to
108 have a high latitude eruption that reaches the lower stratosphere that does not
109 result in a MIF signature in polar ice (Schmidt et al., 2012). However, recent
110 modelling work (Toohey et al., 2019) shows that high latitude eruptions that
111 only penetrate into the upper troposphere/lower stratosphere (UT/LS) have
112 reduced radiative forcings because of shorter sulfate aerosol residence times.
113 The unambiguous identification of volcanic events that had plumes that reached
114 altitudes in the stratosphere at or above the ozone layer, and thus had long
115 atmospheric residence times, would represent a major improvement of the
116 record of volcanic forcing of climate.

117 Sulfur isotopes are traditionally measured by gas-source mass
118 spectrometry. These methods require a micromole of sulfur for analysis and
119 thus entire sulfate peaks were analyzed from a single ice core (Baroni et al.,
120 2008) or multiple ice cores were synchronized and combined (Gautier et al.,
121 2019; 2018) to get enough sulfate from an individual eruption . Since the $\Delta^{33}\text{S}$
122 signature is time-evolving from positive to negative over the course of the sulfate
123 deposition on the ice sheet (Baroni et al., 2007), the integration over an entire
124 peak may give $\Delta^{33}\text{S} = 0$ (Baroni et al., 2008), resulting in ambiguity in the

125 fingerprinting of stratospheric eruptions. To resolve this issue we applied a new
126 technique of S isotope measurement by MC-ICP-MS to ice cores (McConnell et al.,
127 2017; Paris et al., 2013). This method requires only 10 nmol of sulfate, allowing
128 up to bi-monthly resolution. We applied this technique to two known tropical
129 stratospheric eruptions (Tambora 1815 and Samalas 1257), as well as a known
130 high latitude stratospheric eruption (Katmai/Novarupta 1912) to test the
131 applicability of this approach for volcanic eruptions proximal to the ice sheet.

132

133 **2 Methods**

134

135 Ice core samples were collected from the Tunu2013 core from Greenland
136 (78° 2.1' N 33° 52.8' W, 2105 m; 213 m deep; collected May 2013 (Sigl et al.,
137 2015)) for three large volcanic eruptions: the 1815 eruption of Tambora
138 (Indonesia), the 1257 eruption of Samalas (Indonesia), and the 1912 eruption of
139 Katmai/Novarupta, henceforth Katmai (Alaska, US). The eruption of Samalas
140 was also replicated from the B40 core from Antarctica (75° 0' S 0° 4.1' E, 2890 m;
141 200 m deep; collected December 2012 (Sigl et al., 2014)). The age models and
142 continuous sulfur concentration measurements from these ice cores (Sigl et al.,
143 2015) were used to identify the volcanic peaks. Samples were cut from the wings
144 of cores at a resolution of ~2-3 cm over the course of each volcanic event and a
145 resolution of 5 cm for background analyses pre- and post-event. Each sample
146 was measured twice, so a total of 20 nmol was used (only 4 mL for event samples
147 (5 uM) to 40 mL for background samples (0.5 uM)), making this method
148 preferable for high-resolution work on precious sample material. Outside edges
149 of the ice core were scraped clean and the samples were melted. Sulfate

150 concentration was determined by ion chromatography on a 500 μL aliquot.
151 These concentrations (circles, Fig 2 a,b, Fig 3 a) were compared to continuous
152 sulfur measurements (Sigl et al., 2015) to validate which part of the peak was
153 sampled in the discrete samples, and to determine the amount of sample needed
154 for two isotope measurements (20 nmol total). The appropriate amount of
155 sample was then dried down and redissolved in 70 μL of 0.01% v/v distilled HCl
156 under clean laboratory conditions. The samples were passed through Teflon
157 columns made from 4:1 PTFE heat shrink tubing (11 mm expanded diameter)
158 that were loaded with 35 μl of clean AG1X8 anion-exchange resin in order to
159 separate out the sulfate from the sample matrix. Prior to sample loading, the
160 resin was cleaned with 350 μl of 1.6 M HNO_3 , 350 μl of 1.2 M HCl, and 350 μl of
161 0.6 M HCl. Samples were then loaded and cations were removed by rinsing the
162 column with 3 times 175 μl of MilliQ water, followed by sulfate elution in 3 \times 70 μl
163 of 0.5 M HNO_3 . The eluted samples were evaporated to dryness, resuspended in
164 0.5 M HNO_3 , and NaOH was added to the sample to match the concentration and
165 matrix of the in-house Na_2SO_4 bracketing standard (Paris et al., 2013).

166 Triple sulfur isotopes (^{32}S , ^{33}S , ^{34}S)¹ were measured by MC-ICP-MS using
167 sample-standard bracketing with an in-house Na_2SO_4 standard (Paris et al.,
168 2013) at both Caltech and the STAiG lab at the University of St Andrews, and are
169 reported relative to Vienna-Canyon Diablo Troilite (V-CDT). Each sample was
170 measured at least twice. Long-term external reproducibility on the Caltech
171 Switzer Falls secondary river water standard (Burke et al., 2018) was $\delta^{34}\text{S} =$

¹ Although ^{36}S provides further information about the oxidation process in the atmosphere (Gautier et al., 2018), it is not possible to measure ^{36}S by MC-ICP-MS because the argon plasma results in an interference from ^{36}Ar .

172 4.11±0.24 and $\Delta^{33}\text{S} = 0.05 \pm 0.18 \text{ ‰}$ (2 s.d., n = 10) at Caltech and $\delta^{34}\text{S} = 4.17 \pm$
173 0.11 and $\Delta^{33}\text{S} = 0.01 \pm 0.10 \text{ ‰}$ (2 s.d., n = 16) at St Andrews (Supplemental Data
174 Table 3). Procedural blanks were run with each set of columns at Caltech and St
175 Andrews, and the values were $0.12 \pm 0.02 \text{ nmol}$ with a $\delta^{34}\text{S}$ value of $-0.2 \pm 2.8 \text{ ‰}$
176 (2 s.d., n = 3) for Caltech and $0.14 \pm 0.04 \text{ nmol}$ with a $\delta^{34}\text{S}$ value of $5.5 \pm 1.9 \text{ ‰}$ (2
177 s.d., n = 9) for St Andrews (Supplemental Data Table 4). All reported $\delta^{34}\text{S}$ and
178 $\delta^{33}\text{S}$ values were blank corrected with the long-term blank averages, and errors
179 were propagated. $\Delta^{33}\text{S}$ values were calculated following Equation 1.

180 Background ice core samples were measured prior to the volcanic sulfate
181 events. These background samples were used to correct the measured sulfate
182 isotope values (δ_{meas}) for background sulfate to determine the isotope values of
183 the volcanic sulfate (δ_{volc}) following equation 2 (Baroni et al., 2007) :

184
$$\delta_{\text{volc}} = (\delta_{\text{meas}} - f_{\text{bkgd}}\delta_{\text{bkgd}})/f_{\text{volc}} \quad (\text{Equation 2})$$

185 where δ_{bkgd} is the $\delta^{34}\text{S}$ or $\delta^{33}\text{S}$ of the background sample, f_{bkgd} is the mass
186 fraction of the total sulfate that can be attributed to the background ($f_{\text{bkgd}} =$
187 $[\text{SO}_4]_{\text{bkgd}}/[\text{SO}_4]_{\text{sample}}$), and f_{volc} is the mass fraction of the total sulfate that can
188 be attributed to volcanic sulfate ($f_{\text{volc}} = 1 - f_{\text{bkgd}}$). Following Gautier et al.
189 (2018) we only plotted those samples with more than 65% volcanic sulfate (f_{volc}
190 > 0.65).

191

192 **3 Results**

193

194 Each of the three volcanic events show non-zero $\Delta^{33}\text{S}$ (Figs 2 and 3,
195 Supplementary Data Table 1), with an evolution from positive to negative over

196 the course of the sulfate deposition (Baroni et al., 2007), and there is good
197 agreement (Fig 4) between the records of the Samalas eruption in Greenland
198 (Tunu2013) and Antarctica (B40). In the Tunu2013 core, the magnitude of the
199 $\Delta^{33}\text{S}$ is larger for sulfate associated with the Samalas and Tambora eruptions
200 (1.9‰ and 1.7‰, respectively; Fig 2) than it is for the Katmai eruption, which
201 only has a magnitude of 0.4‰ (Fig 3). The lowest $\Delta^{33}\text{S}$ values for the Samalas
202 and Tambora eruptions are negative (-1.8 and -0.8 ‰), whereas the lowest $\Delta^{33}\text{S}$
203 values for the Katmai eruptions are within uncertainty of 0‰. In B40, the $\Delta^{33}\text{S}$
204 values for Samalas range from 1.4 to -1.5‰.

205 In the two tropical eruptions (Fig 2), $\delta^{34}\text{S}$ follows the same shape as the
206 $\Delta^{33}\text{S}$, with an initial increase to 27.5‰ for Samalas and 20.6‰ for Tambora,
207 dropping to -19.1‰ and -5.9‰ respectively over the course of the deposition of
208 the sulfate. In contrast, for the Katmai eruption the $\delta^{34}\text{S}$ initially decreases from
209 its background value of 7.2‰ down to 0.6‰, before increasing back up to 4.6‰
210 (Fig 3). In B40, the $\delta^{34}\text{S}$ values for Samalas range from 17.3 to -12.5‰
211 (Supplementary Data Table 1).

212 Pre-event background samples were measured for both the Samalas and
213 Katmai eruptions. $\delta^{34}\text{S}$ values prior to the Samalas event in Tunu2013 ranged
214 from 9.1 to 11.1 ‰ with an average concentration of 0.4 μM , and prior to the
215 Katmai event were 7.2 ‰ at a concentration of 1.3 μM . The $\delta^{34}\text{S}$ value prior to
216 the Samalas event in B40 was 13.9‰ at a concentration of 0.6 μM . All
217 background samples had $\Delta^{33}\text{S}$ values within uncertainty of 0‰. Although we
218 attempted to measure a pre-event background for Tambora, the sample that was
219 cut from the ice core included the onset of the volcanic sulfate peak, and had a

220 $\Delta^{33}\text{S}$ value of 0.5‰. Thus, the average of 13 non-volcanic pre-industrial
221 background samples from other intervals of the Tunu2013 ice core ($\delta^{34}\text{S} = 9.2 \pm$
222 0.93‰ , $\Delta^{33}\text{S} = 0.03 \pm 0.09$, $[\text{S}] = 0.5 \pm 0.2 \mu\text{M}$; Supplementary Data Table 2) was
223 used to make a background correction for the Tambora samples. This average
224 excludes the background sample for Katmai deposited in 1912, which likely has
225 significant anthropogenic sulfate, supported by its higher concentration and
226 lower isotopic value. The standard deviation of these background samples was
227 used to calculate the final uncertainty on the background-corrected volcanic
228 sulfate $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ values by Monte Carlo simulations.

229 The background-corrected volcanic sulfate $\Delta^{33}\text{S}$ values for the Samalas
230 and Tambora eruptions have a similar positive to negative temporal evolution as
231 the non-background corrected values, but with a larger range (Fig 2). In
232 Tunu2013, the volcanic sulfate $\Delta^{33}\text{S}$ values for Samalas and Tambora range from
233 2.8 to -2.5‰ and from 2.2 to -0.85‰, respectively. The volcanic sulfate $\delta^{34}\text{S}$
234 values for Samalas and Tambora range from 29.7 to -31.1‰ and 23.4 to -7.9‰,
235 respectively. In contrast, the background-corrected volcanic sulfate for the
236 Katmai eruption in Tunu2013 has $\delta^{34}\text{S}$ values between 4.4 and -4.3‰ and $\Delta^{33}\text{S}$
237 values between 0.3 and 0.6‰, with a different temporal trend (Fig 3). In B40,
238 the Antarctic core, the volcanic sulfate $\Delta^{33}\text{S}$ and $\delta^{34}\text{S}$ values for Samalas is very
239 similar to that found in Greenland in Tunu2013, with a range from 1.7 to -2.2‰
240 and from 19.2 to -24.2‰, respectively (Supplementary Data Table 1).

241

242 **4 Discussion**

243

244 4.1 $\Delta^{33}\text{S}$ constraints on eruptive plume height

245 The presence of non-zero $\Delta^{33}\text{S}$ in each of these eruptions implies that
246 some of the SO_2 from the eruptive plume reached a height in the stratosphere at
247 least as high as the ozone layer (Fig 1). At these altitudes in the atmosphere the
248 SO_2 was exposed to UV radiation imparting a MIF signal, and this signal was
249 preserved in the sulfate deposited on the ice sheet. For the two tropical
250 eruptions (Tambora and Samalas), this puts a rough constraint of $> 20\text{km}$ for the
251 eruptive plume. This height constraint is consistent with estimates of the
252 Tambora and Samalas column height of up to 43 km (Sigurdsson and Carey,
253 1989; Vidal et al., 2016), which would mean that the SO_2 was transported well
254 above the ozone layer.

255 For the extra-tropical Katmai eruption (58°N), the presence of non-zero
256 $\Delta^{33}\text{S}$ puts a height constraint of $>15 \text{ km}$ for the eruptive plume, consistent with
257 estimates of a column height of 17-26 km for this eruption (Fierstein and
258 Hildreth, 1992). Previous studies (e.g. Schmidt et al., 2012) have questioned
259 whether MIF signals from high latitude eruptions (i.e. proximal to ice sheets)
260 could be preserved in ice, given that a substantial amount of sulfate would be
261 transported directly to the ice sheet via the troposphere or lower stratosphere
262 below the ozone layer with $\Delta^{33}\text{S} = 0\text{‰}$. It was hypothesized that this upper
263 tropospheric/lower stratospheric (UT/LS) transport may overwhelm the signal
264 of any MIF from sulfate from at or above the ozone layer. However, our results
265 suggest that the MIF signature can be preserved in ice for high latitude eruptions,
266 albeit more muted (maximum $\Delta^{33}\text{S}$ values of $\sim 0.5\text{‰}$) than in tropical eruptions
267 (maximum $\Delta^{33}\text{S}$ values of $\sim 2\text{‰}$) where none of the sulfate was delivered to the
268 ice sheets directly via the troposphere. Thus, the presence of non-zero $\Delta^{33}\text{S}$ in

269 volcanic sulfate in ice cores provides a minimum height of the eruptive plume
270 into the stratosphere above the ozone layer, even if the volcano was from the
271 high latitudes. This minimum height will be useful in characterizing the climatic
272 forcing of unknown eruptions because volcanic aerosols that make it to higher
273 altitudes in the stratosphere have a longer residence time, and thus a greater
274 negative radiative forcing, than aerosols that remain in the troposphere (or in
275 the lower levels of the stratosphere below the ozone layer) (Toohey et al., 2019).

276

277 **4.2 Time evolving signature of $\Delta^{33}\text{S}$ and $\delta^{34}\text{S}$ and fingerprinting of tropical** 278 **and extratropical eruptions**

279 For all three eruptions, the $\Delta^{33}\text{S}$ follows a time evolving signature where
280 the initial sulfate deposited has a positive $\Delta^{33}\text{S}$, and the later sulfate has a
281 negative $\Delta^{33}\text{S}$ (Fig 2). This time evolution has been observed before (Baroni et al.,
282 2007) from measurements of sulfate from the 1991 eruption of Pinatubo
283 (Philippines) and the 1963 eruption of Agung (Indonesia) collected from snow
284 pits in Antarctica, and more recently from combined multiple ice cores (Gautier
285 et al., 2018). The initial fractionation process generates a positive $\Delta^{33}\text{S}$, and the
286 following negative $\Delta^{33}\text{S}$ is a result of mass balance (Baroni et al., 2007), with the
287 $\Delta^{33}\text{S}$ excursion evolving over a timescale of about 3 to 4 years (Fig 2). Given that
288 the timescale over which sulfur dioxide is oxidized to sulfate in the atmosphere
289 is approximately a month, in order to generate the observed isotopic signature
290 that is deposited in the ice over the course of several years there needs to be a
291 spatial separation of these sulfur pools with a differing $\Delta^{33}\text{S}$ signature (Gautier et
292 al., 2018).

293 We can use the timing and the shape of the $\Delta^{33}\text{S}$ and $\delta^{34}\text{S}$ signatures to
294 fingerprint whether the sulfate from a volcanic event in an ice core was purely
295 stratospheric (and thus likely tropical) or if some of the sulfate was transported
296 to the ice sheet via the troposphere (or lower stratosphere below the ozone
297 layer), and thus likely came from an extra-tropical eruption in the hemisphere of
298 the ice sheet. In the case of the two tropical eruptions (Fig 2), the peak in the
299 $\Delta^{33}\text{S}$ comes at the very start of the sulfate deposition; this was also observed in
300 the case of the Pinatubo and Agung eruptions (Baroni et al., 2007). In contrast,
301 for the Katmai eruption (Fig 3), the initial sulfate deposited to the ice sheet has a
302 $\Delta^{33}\text{S} = 0\text{‰}$ because in the case of this high latitude eruption the first sulfate to
303 arrive to the ice sheet was transported via the troposphere (or lower
304 stratosphere below the ozone layer) and thus was not fractionated.

305 The $\delta^{34}\text{S}$ of the tropical eruptions show a strong positive correlation
306 between the $\Delta^{33}\text{S}$ and the $\delta^{34}\text{S}$ ($r^2 > 0.99$; Fig 5); the initial sulfate $\delta^{34}\text{S}$ increases
307 and then decreases over the same timeframe as the $\Delta^{33}\text{S}$ changes. The strong
308 correlation is because the same process that causes the non-zero $\Delta^{33}\text{S}$
309 fractionation in the stratosphere also drives fractionation observed in $\delta^{34}\text{S}$, and
310 since the sulfate in these peaks from tropical eruptions is derived purely from
311 the stratosphere, this signature is preserved. In contrast, for the Katmai eruption,
312 the initial volcanic sulfate decreases the $\delta^{34}\text{S}$ values compared to background
313 $\delta^{34}\text{S}$ values. This feature can be understood by mass balance: background sulfate
314 is around 10‰ as it is a mixture of marine (21‰) and volcanic emissions
315 ($\sim 0\text{‰}$), and thus the addition of more volcanic sulfate with low $\delta^{34}\text{S}$ (that has
316 not been fractionated by stratospheric processes as in the case of the tropical

317 eruptions) would act to decrease the $\delta^{34}\text{S}$. This is the opposite of what is
318 measured in the initial $\delta^{34}\text{S}$ in the tropical eruptions and thus can provide an
319 additional means of distinguishing between unknown tropical and extra-tropical
320 events recorded in ice cores. In contrast to the tropical eruptions, the correlation
321 between $\delta^{34}\text{S}$ and $\Delta^{33}\text{S}$ in the sulfate from the Katmai eruption is weak ($r^2 = 0.37$)
322 and negative (slope is -0.05).

323 Distinguishing between tropical and extra-tropical eruptions in the ice
324 core record of volcanism is important for improving the volcanic radiative
325 forcing record for two reasons. Firstly, constraining the latitudinal band of
326 eruptions has implications for transport and residence time of climatically
327 important aerosols. Secondly, if a fraction of the sulfate deposited in the ice core
328 was delivered through the troposphere, then the associated radiative forcing for
329 that event should be adjusted, as current reconstructions assume that all sulfate
330 deposited in the ice reached the stratosphere (e.g. Toohey and Sigl, 2017). High-
331 resolution sulfur isotope measurements in ice cores thus can potentially provide
332 an additional means of distinguishing between unknown tropical and extra-
333 tropical events recorded in ice cores if this observation is corroborated by
334 further studies.

335

336 **4.3 Agreement of isotope records between hemispheres**

337 There is good agreement between the two $\Delta^{33}\text{S}$ records from Greenland
338 (Tunu2013) and Antarctica (B40) for the Samalas eruption (Fig 4). This
339 agreement suggests that the isotopic signature is primary and is not significantly
340 affected or altered by transport or depositional processes. Furthermore, all
341 three records of tropical eruptions (Tambora from Tunu2013, and Samalas from

342 Tunu2013 and B40) plot along the same line in $\Delta^{33}\text{S}$ versus $\delta^{34}\text{S}$ space within
343 uncertainty (Fig 5; Table 1). The slope of this line is 0.089 ± 0.003 and is the
344 same as the slope of the line derived from eight eruptions from Antarctic ice
345 (0.09 ± 0.02) (Gautier et al., 2018), but is more precisely constrained. When
346 plotted in $\ln(\delta^{33}\text{S} + 1)$ versus $\ln(\delta^{34}\text{S} + 1)$ space, the slope of the line is $0.608 \pm$
347 0.006 , significantly different from the terrestrial mass dependent slope of 0.515 .
348 Thus, the relationship between $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ for volcanic sulfate derived from
349 the stratosphere is predictable and does not appear to differ between ice cores
350 or eruptions. Differences in aerosol transport or deposition, or indeed the
351 timing, hemisphere, or magnitude of the eruption, therefore do not appear to
352 significantly affect the fractionation process (Gautier et al., 2018). This
353 predictable relationship between $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ for volcanic sulfate derived from
354 the stratosphere proves useful in estimating the proportion of stratospheric
355 sulfate from extra-tropical eruptions (see section 4.4).

356 It remains an open question as to what exact process causes this sulfur
357 isotope fractionation. Gautier et al.(2018) use both $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ data from ice
358 cores to estimate the proportion of different oxidation pathways that could
359 explain the isotopic trends. While their data cannot rule out or unambiguously
360 confirm an oxidation pathway, they show that mass independent oxidation
361 pathways (e.g. photolysis or photoexcitation) could account for at least 21% and
362 as much as 91% of the oxidation. Furthermore, they argue that the small
363 variations in the slope in $\Delta^{33}\text{S}$ versus $\delta^{34}\text{S}$ space (further confirmed in this study)
364 imply that the relative contribution of different oxidation pathways is similar
365 across eruptions. If the oxidation pathways are similar across different
366 eruptions, then the differences in the magnitude of the mass independent

367 fractionation between eruptions need to be explained by another process. A
368 recent study (Lin et al., 2018) that considered the correlation between
369 cosmogenic ^{35}S and $\Delta^{33}\text{S}$ in modern aerosols proposed that the $\Delta^{33}\text{S}$ signature is
370 altitude dependent, with greater fractionation occurring higher in the
371 stratosphere. If true, this would prove a useful metric for estimating eruptive
372 plume height in past eruptions, and improving the record of the volcanic forcing
373 of climate.

374

375 **4.4 Proportion of stratospheric sulfate from Katmai**

376 We can use the high-resolution isotope record from the Katmai eruption
377 and isotope mass balance to calculate the proportion of sulfate that was
378 deposited in the Greenland ice core via the stratosphere. This calculation will
379 improve volcanic forcing indices since these indices typically make the
380 assumption that all of the sulfate deposited on the ice sheets was stratospheric
381 (Toohey and Sigl, 2017), which is likely incorrect in the case of high latitude
382 eruptions such as Katmai. This calculation is based on the following two isotope
383 mass balance equations:

$$384 \quad \delta^{34}\text{S}_{\text{meas}} = \delta^{34}\text{S}_{\text{strat}} f_{\text{strat}} + \delta^{34}\text{S}_{\text{trop}} (1 - f_{\text{strat}}) \quad (\text{Equation 3})$$

$$385 \quad \delta^{33}\text{S}_{\text{meas}} = \delta^{33}\text{S}_{\text{strat}} f_{\text{strat}} + \delta^{33}\text{S}_{\text{trop}} (1 - f_{\text{strat}}) \quad (\text{Equation 4})$$

386 where the subscript *meas* refers to measured isotopic values, f_{strat} refers to the
387 fraction of sulfate deposited that came from the stratosphere, and the subscripts
388 *strat* and *trop* refer to the isotopic composition of the sulfate coming from the
389 stratosphere and troposphere respectively. Since sulfate formed in the

390 troposphere (and lower stratosphere below the ozone layer) follows terrestrial
391 mass dependent fractionation, we can use the following relationship:

$$392 \quad \delta^{33}\text{S}_{\text{trop}} = \left((\delta^{34}\text{S}_{\text{trop}} + 1)^{0.515} - 1 \right) \quad (\text{Equation 5})$$

393 to reduce the number of unknowns in those paired equations. We can further
394 reduce the number of unknowns since the stratospheric sulfate measured in ice
395 cores follows the following relationship (see Section 4.3):

$$396 \quad \delta^{33}\text{S}_{\text{strat}} = \left((\delta^{34}\text{S}_{\text{strat}} + 1)^{0.608} - 1 \right) \quad (\text{Equation 6})$$

397 with an uncertainty on the exponent $\lambda = 0.608$ of 0.006. Combining equations 3
398 to 6 gives two equations with three unknowns: $\delta^{34}\text{S}_{\text{strat}}$, $\delta^{34}\text{S}_{\text{trop}}$, and f_{strat} . Thus if
399 we make an assumption of the isotopic composition of the volcanic $\delta^{34}\text{S}_{\text{trop}}$, we
400 can solve for f_{strat} and $\delta^{34}\text{S}_{\text{strat}}$. The sulfur isotopic composition of volcanic SO_2
401 can vary significantly away from a mantle value (0‰, V-CDT) as a function of the
402 mantle source and the oxygen fugacity of the magma (e.g. de Moor et al., 2010;
403 Mather et al., 2006). To address this, we calculate the f_{strat} and corresponding
404 uncertainty using a 500 iteration Monte Carlo simulation for a uniformly
405 distributed range of $\delta^{34}\text{S}_{\text{trop}}$ values from -10 to 10‰. The uncertainties on the
406 measured values and exponent λ are assumed to be normally distributed. We
407 find that the f_{strat} values for the Katmai samples range from 0.26 to 0.88, and that
408 when integrated over the whole peak, the proportion of the sulfate peak that
409 came from the stratosphere was 0.55, with an uncertainty range of 0.35 to 0.62.
410 Constraints on the $\delta^{34}\text{S}_{\text{trop}}$ for this specific eruption would help to narrow the
411 range of uncertainty of the fraction of stratospheric sulfate deposited in
412 Greenland. Even so, this estimate improves upon the assumption that all of the
413 sulfate deposited came from the stratosphere (Toohey and Sigl, 2017). It also

414 helps to reconcile estimates of stratospheric sulfate loading from studies using
415 pyrhelometric optical depth perturbations with estimates based purely on the
416 sulfate deposition in Greenland, which are greater than the optical depth
417 estimates by a factor of three (11 Tg compared to 30 Tg (Hammer et al., 1980;
418 Stothers, 1996)). This approach may thus be used in future studies to improve
419 volcanic forcing indices.

420

421 **5. Conclusion**

422

423 Sulfur isotopes of volcanic sulfate deposited in ice cores can be used to
424 identify if the sulfate came from above the ozone layer in the stratosphere, since
425 exposure to UV radiation imparts a mass independent fractionation, recorded as
426 a non-zero $\Delta^{33}\text{S}$ (Savarino et al., 2003). There is good agreement between
427 isotope records from Greenland and Antarctica over the same volcanic event,
428 indicating that sulfur isotopes are not significantly affected by transportation or
429 depositional processes. Our method of analysis by MC-ICPMS requires only 10
430 nmol of sulfur, allowing for up to bi-monthly resolution over the volcanic sulfate
431 peak in the ice cores from samples as small as 4 mL. These high-resolution
432 records show distinct differences between tropical (Samalas and Tambora) and
433 extra-tropical (Katmai) eruptions. In the case of the tropical eruptions, all of the
434 sulfate deposited on the ice sheet came via the stratosphere, and thus the $\delta^{34}\text{S}$
435 and $\Delta^{33}\text{S}$ values are strongly correlated, with the initial sulfate deposited
436 showing an increase in both values. In contrast, for the extra-tropical eruption,
437 some of the sulfate was deposited in Greenland via the troposphere or lower
438 stratosphere below the ozone layer, and thus the initial signal of the volcanic

439 sulfate is a decrease in its $\delta^{34}\text{S}$ value, with $\Delta^{33}\text{S}$ values within error of zero.
440 Isotope mass balance on extra-tropical eruptions such as Katmai can be used to
441 estimate the proportion of the volcanic sulfate deposited in the ice core that
442 came via the stratosphere. These measurements will help to improve the record
443 of the volcanic forcing of climate for unidentified eruptions in the past, which
444 should in turn improve simulations of historical climate change.

445

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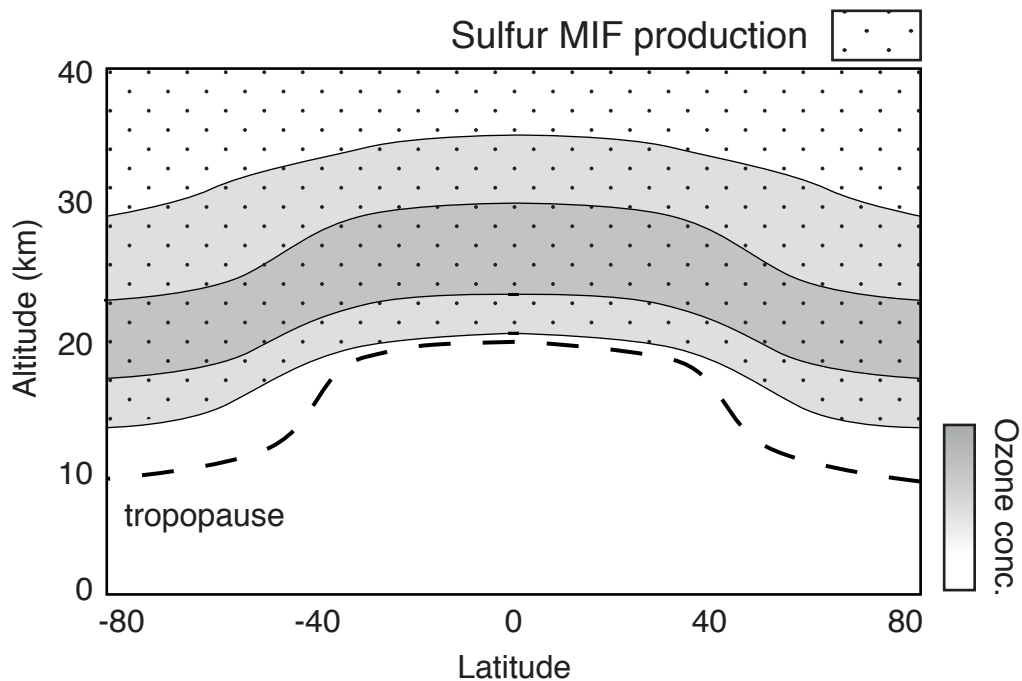
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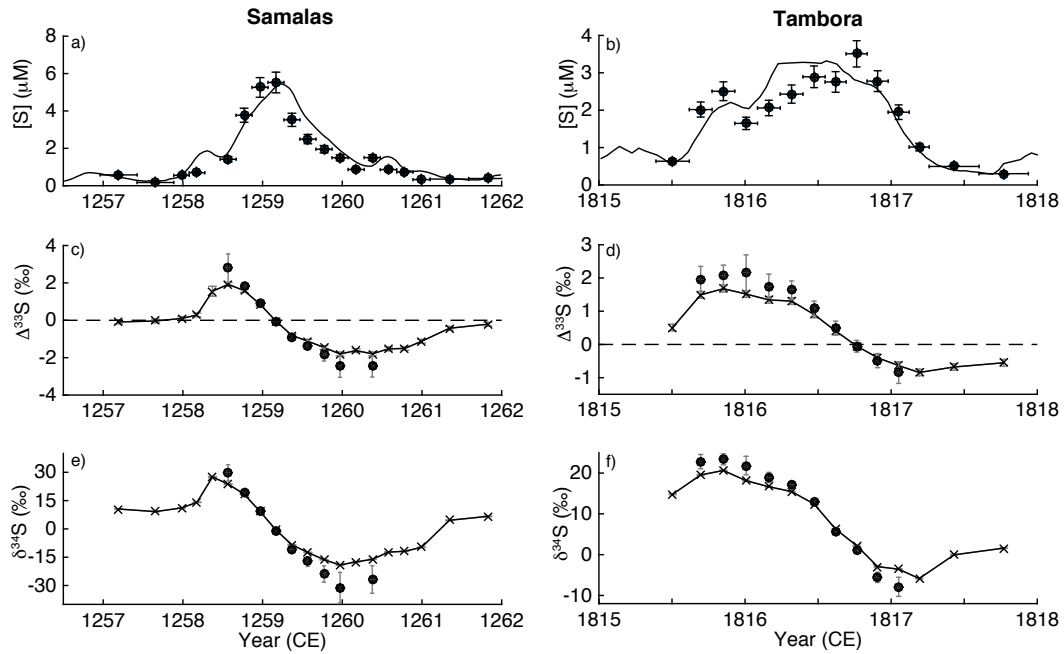
583 **Figures**

584



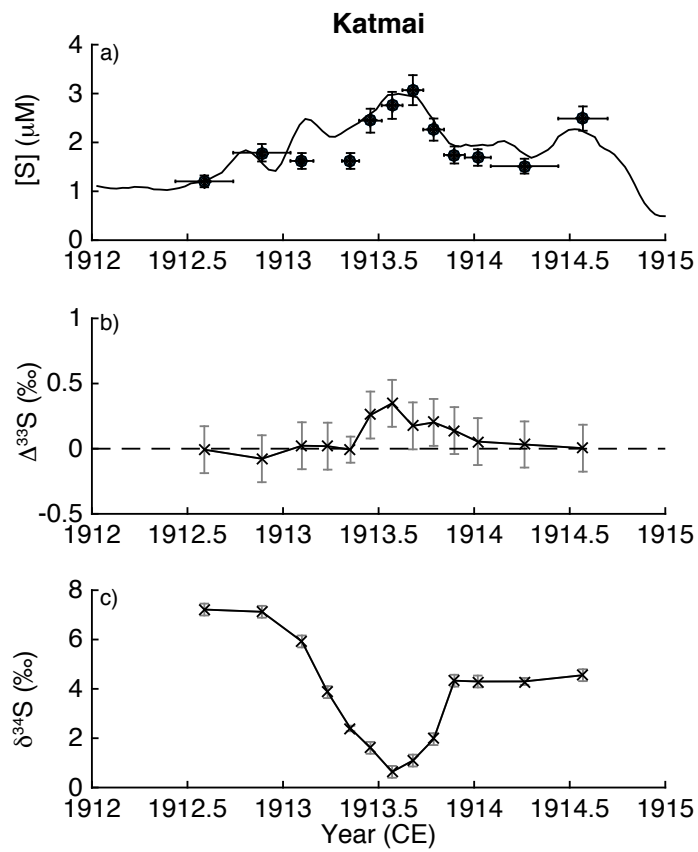
585

586 **Fig 1.** Schematic of sulfur mass independent fractionation (MIF) production. The
587 formation of sulfur MIF requires UV radiation, and therefore it is limited to
588 altitudes in the stratosphere at or above the ozone layer (indicated on schematic
589 by stippling). Without knowing the exact mechanism of sulfur MIF formation it is
590 not currently possible to put more precise altitude constraints on the process. At
591 high latitudes there is a region of the stratosphere that lies below the ozone layer
592 where MIF is not produced. Thus the presence of MIF in polar ice provides a
593 means to identify eruptions whose plumes reached high altitudes in the
594 stratosphere; high latitude eruptions into the lower stratosphere would not
595 produce sulfur MIF.



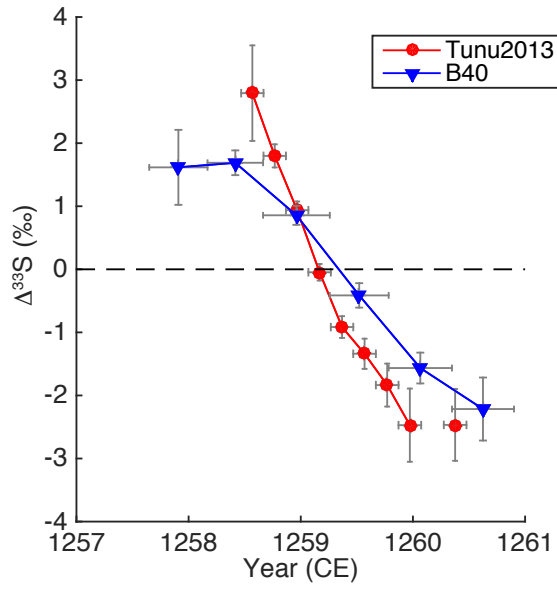
596

597 **Fig 2.** Sulfur concentration (a, b) and isotope curves (c-f) versus time for two
 598 tropical eruptions recorded in Tunu2013 ice core in Greenland: the 1258
 599 eruption of Samalás (a,c,f) and the 1815 eruption of Tambora (b,d,e). The line in
 600 (a,b) is the continuous melting sulfur concentration from (Sigl et al., 2015) and it
 601 is compared to sulfur concentration measurements by ion chromatograph on the
 602 discrete samples that were subsequently measured for isotopes (circles). (c,d)
 603 $\Delta^{33}\text{S}$ (‰) measured in the ice samples (x's) and the background corrected
 604 volcanic $\Delta^{33}\text{S}$ (circles) for samples with more than 65% volcanic sulfate (see
 605 text). (e,f) is the same as (c,d), but for $\delta^{34}\text{S}$ (‰, V-CDT).



606

607 **Fig 3.** Sulfur concentration (a), $\Delta^{33}\text{S}$ (b), and $\delta^{34}\text{S}$ (c) versus time for the high
 608 latitude eruption Katmai/Novarupta in 1912. The symbols are the same as in
 609 Figure 2.



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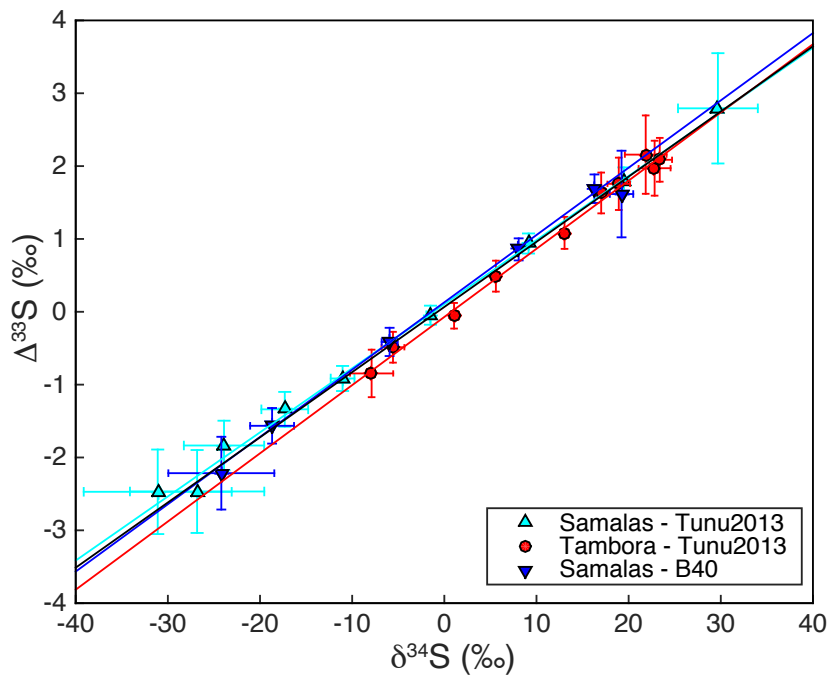
611 **Fig 4.** Background-corrected volcanic $\Delta^{33}\text{S}$ (‰) across the Samalas volcanic
 612 event from the Tunu2013 ice core (Greenland, red circles) and the B40 ice core
 613 (Antarctica, blue triangles).

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619 **Fig 5.** Cross plot of $\Delta^{33}\text{S}$ versus $\delta^{34}\text{S}$ for the background-corrected volcanic
 620 sulfate from tropical eruptions Tambora (red circles) and Samalas (cyan upward
 621 triangle measured in Tunu2013, blue downward triangle measured in B40).
 622 Regression lines are plotted in the color of the symbols. Black line is the
 623 regression considering all of the data. The size of the error bars is driven by
 624 uncertainty in the background correction, as analytical uncertainties are $\sim 0.1\text{‰}$
 625 for both $\Delta^{33}\text{S}$ and $\delta^{34}\text{S}$.

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633 **Table 1. Regression solution parameters.** Slope and intercept values for linear
 634 regressions of $\Delta^{33}\text{S}$ versus $\delta^{34}\text{S}$ data and $\ln(\delta^{33}\text{S}+1)$ versus $\ln(\delta^{34}\text{S}+1)$ data for each
 635 individual tropical eruption and for all data combined. Uncertainties encompass
 636 the 95% confidence interval.

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638

Eruption	Core	$\Delta^{33}\text{S}$ versus $\delta^{34}\text{S}$		$\ln(\delta^{33}\text{S}+1)$ versus $\ln(\delta^{34}\text{S}+1)$	
		slope	intercept	slope	intercept
Samalas	Tunu2013	0.088±0.003	0.10±0.03	0.604±0.003	0.1±0.05
Samalas	B40	0.092±0.007	0.13±0.04	0.610±0.006	0.1±0.1
Tambora	Tunu2013	0.094±0.005	-0.07±0.08	0.609±0.006	-0.08±0.07
All data		0.089±0.003	0.07±0.05	0.608±0.006	0.06±0.07

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