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# Stratospheric ozone changes from explosive tropical volcanoes: Modelling and ice core constraints

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## Key Points:

- The tropical volcanic eruption in the model shows that the sign of the ozone change is highly sensitive to stratospheric chlorine amounts.
- $\delta^{15}\text{N}(\text{NO}_3^-)$  (a proxy for surface ultra-violet radiation) from the Samalas eruption is obscured by inter-annual variability in the ice core.
- $\delta^{15}\text{N}(\text{NO}_3^-)$  changes are unlikely to be synchronous with volcanic sulphate peaks due to different pathways for these signals to reach the ice.

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**Abstract**

Major tropical volcanic eruptions have emitted large quantities of stratospheric sulphate and are potential sources of stratospheric chlorine although this is less well constrained by observations. This study combines model and ice core analysis to investigate past changes in total column ozone. Historic eruptions are a good analogue for future eruptions as stratospheric chlorine levels have been decreasing since the year 2000. We perturb the pre-industrial atmosphere of a chemistry-climate model with high and low emissions of sulphate and chlorine. The sign of the resulting Antarctic ozone change is highly sensitive to the background stratospheric chlorine loading. In the first year, the response is dynamical, with ozone increases over Antarctica. In the high HCl (10 Tg emission) experiment, the injected chlorine is slowly transported to the polar regions with subsequent chemical ozone depletion. These model results are then compared to measurements of the stable nitrogen isotopic ratio,  $\delta^{15}\text{N}(\text{NO}_3^-)$ , from a low snow accumulation Antarctic ice core from Dronning Maud Land (recovered in 2016-17). We expect ozone depletion to lead to increased surface ultraviolet (UV) radiation, enhanced air-snow nitrate photo-chemistry and enrichment in  $\delta^{15}\text{N}(\text{NO}_3^-)$  in the ice core. We focus on the possible ozone depletion event that followed the largest volcanic eruption in the past 1000 years, Samalas in 1257. The characteristic sulphate signal from this volcano is present in the ice-core but the variability in the  $\delta^{15}\text{N}(\text{NO}_3^-)$  dominates any signal arising from changes in UV from ozone depletion. Whether Samalas caused ozone depletion over Antarctica remains an open question.

**Plain Language Summary**

Chlorine in the stratosphere destroys ozone that protects the Earth from harmful ultraviolet radiation. Volcanic eruptions in the tropics can emit sulphate and chlorine into the stratosphere. Chlorine levels are currently decreasing and to understand the impact of a volcanic eruption on stratospheric ozone in a future climate, historical eruptions are a useful analogue since the pre-industrial climate also had low chlorine levels. Using a chemistry climate model, we run a set of experiments where we inject different amounts of sulphate and chlorine into the stratosphere over the tropics to simulate different types and strengths of explosive volcanoes and we find that the ozone over Antarctica initially increases over the first year following the eruption. If the volcano emits a large amount of chlorine, ozone then decreases over Antarctica in years two to four following the eruption. We also compare our results to ice-core data around a large historic volcanic eruption, Samalas (1257).

**1 Introduction**

The ozone layer protects life on Earth from ultraviolet (UV) radiation. Explosive tropical volcanic eruptions can inject volcanic gases into the stratosphere which can disrupt the complex stratospheric chemistry and lead to substantial changes in total column ozone (Solomon, 1999; Robock & Oppenheimer, 2003, for a comprehensive review). Over the last 1000 years, a number of explosive tropical volcanoes have injected copious volumes of sulphur dioxide ( $\text{SO}_2$ ) and hydrochloric acid (HCl) into the stratosphere. Injection of sulphur dioxide into the stratosphere from an explosive volcanic eruption increases the number of sulphate aerosol particles, providing a larger surface area for heterogeneous reaction to take place on. The impact of this change in stratospheric aerosol loading on ozone is dependent on the stratospheric chlorine loading (e.g., Timmreck, 2012). In a low chlorine atmosphere,  $\text{N}_2\text{O}_5$  reacts with water vapour on the surfaces of these volcanic aerosols to form  $\text{HNO}_3$ , effectively sequestering reactive  $\text{NO}_x$  species into a long-lived reservoir and limiting the availability of  $\text{NO}_x$  radicals to take part in catalytic reactions which deplete stratospheric ozone (Crutzen, 1970; Johnston, 1971). However, in a high chlorine atmosphere, while the heterogeneous reaction of  $\text{N}_2\text{O}_5$  on aerosol sur-

68 faces has the same effect, halogenated reservoir species also undergo heterogeneous re-  
69 actions, liberating reactive  $\text{ClO}_x$  and  $\text{BrO}_x$  species from long-lived reservoirs (e.g., Solomon,  
70 1999). As a result, a large sulphur dioxide injection is expected to cause polar ozone loss  
71 when the chlorine loading of the stratosphere is high (e.g. Tie & Brasseur, 1995), while  
72 in a low chlorine environment, such as a pre-industrial atmosphere or a future atmosphere  
73 where the chlorine loading of the stratosphere has declined, it is widely accepted that  
74 an injection of sulphate from an explosive tropical volcanic eruption will lead to ozone  
75 gain over polar regions (Langematz et al., 2018, and references therein). To understand  
76 the future atmospheric impact of volcanic eruptions, studying historic eruptions is a use-  
77 ful analog.

78 Estimates of the amount of sulphur dioxide emitted into the stratosphere from erup-  
79 tions over the past 1000 years are highly variable. For example, sulfate mass concentra-  
80 tion records from ice core data give the following estimates for recent tropical eruptions:  
81  $\sim 10$  to  $20$  Tg  $\text{SO}_2$  from Mount Pinatubo in 1991 (Timmreck et al., 2018),  $\sim 60$  Tg  $\text{SO}_2$   
82 from Mount Tambora in 1815 (Zanchettin et al., 2016) and  $\sim 100$  to  $140$  Tg  $\text{SO}_2$  from  
83 the Samalas 1257 series of eruptions (1257,  $8.4^\circ$  S,  $116.5^\circ$  E) (Toohey & Sigl, 2017). Samalas  
84 is the largest eruption over the last 1000 years and part of a series of 4 large eruptions  
85 occurring over a period of about 26 years.

86 Some types of explosive volcanoes also emit chlorine and other halogen compounds.  
87 Volcanic stratospheric chlorine emissions are important for ozone destruction reactions  
88 (Kutterolf et al., 2013) but are less well constrained, since the highly soluble HCl is scav-  
89 enged by processes in the volcanic plume (Halmer et al., 2002). In the stratosphere, HCl  
90 is the dominant chlorine reservoir species and a source of reactive halogen such as chlo-  
91 rine monoxide, ClO, that destroys ozone. A sophisticated plume model (Textor et al.,  
92 2003) suggest that 10% to 20% of the HCl emitted would enter the stratosphere and re-  
93 cent satellite observations have detected HCl injection into the stratosphere from explo-  
94 sive volcanoes (Theys et al., 2014). Geo-chemical evidence by Vidal et al. (2016) sug-  
95 gests that the Samalas eruption could have injected as much as  $\sim 230$  Tg HCl into the  
96 atmosphere. In contrast, observations during the 1991 Pinatubo eruption show that the  
97 efficiency of the scavenging is highly dependent on atmospheric conditions with barely  
98 detectable increases in stratospheric HCl following the eruption (Wallace & Livingston,  
99 1992). Volcanic HCl emissions and the fraction of HCl mass entering the stratosphere  
100 are hence highly variable as these depend on the geochemistry of the eruption and the  
101 efficiency of the scavenging processes respectively. The type and location of the erup-  
102 tion also play a role.

103 The impact of an explosive eruption on stratospheric ozone also depends on dy-  
104 namical processes. Variability arising from the El Niño-Southern Oscillation (ENSO),  
105 the quasi-biennial oscillation (QBO) and the variability in the Brewer-Dobson circula-  
106 tion are able to affect the ozone response following the eruption (Lehner et al., 2016; Telford  
107 et al., 2009). In addition, the radiative heating from the aerosol injection and associated  
108 changes to the planetary wave flux from the troposphere are able to alter the stratospheric  
109 circulation and hence the transport of aerosols and trace gases (Poberaj et al., 2011).  
110 Since the precise time of the year of the historic eruption is often not known, these fac-  
111 tors have to be taken into account in the model simulations (Stevenson et al., 2017).

112 Ground-based observations of total column ozone (TCO) commenced in the 1920s  
113 and captured the severe decline in the ozone layer resulting from anthropogenic produc-  
114 tion of long-lived ozone destroying-halocarbons e.g., Harris et al. (2015, and references  
115 therein). However, beyond the relatively short instrumental period, records of total col-  
116 umn ozone are non-existent and thus paleo-reconstructions are required to understand  
117 how natural phenomena, such as volcanic eruptions, can impact the variability of total  
118 column ozone.

Recent research has focused on novel Antarctic ice core proxies of surface UV radiation, which can provide constraints on past ozone variability as changes in total column ozone affect the surface UV over Antarctica. The UV proxy is based on the stable isotopic composition of nitrate ( $\delta^{15}\text{N}(\text{NO}_3^-)$ ) at low accumulation sites in Antarctica (Frey et al., 2009). Theory, laboratory and field experiments have shown that nitrate ( $\text{NO}_3^-$ ) loss from snow and associated isotopic enrichment of  $\delta^{15}\text{N}(\text{NO}_3^-)$  in the  $\text{NO}_3^-$  fraction remaining in the snow is driven by UV photolysis (Shi et al., 2019; Berhanu et al., 2014, 2015; Frey et al., 2009). The presence of the heavier isotope of nitrogen in  $\text{NO}_3^-$  leads to an increase in reduced mass which causes a red shift in the vibrational frequencies and a reduction in zero point energy. The UV absorption peak of the heavier isotope is then narrower and blue shifted resulting in a difference in isotopic fractionation. Further details of this process can be found in Frey et al. (2009). The photolytically-induced fractionation of the  $\delta^{15}\text{N}(\text{NO}_3^-)$  signal is eventually archived in firn and ice. This depends on a number of site-specific factors aside from the UV irradiance including the snow physical properties and the amount and timing of snow accumulation (Erbland et al., 2015, 2013; Noro et al., 2018; Shi et al., 2018). The largest enrichment of  $\delta^{15}\text{N}(\text{NO}_3^-)$  is observed at low accumulation sites on the East Antarctic Plateau, where near surface snow is exposed for more than one summer season to incoming UV radiation (Erbland et al., 2013; Shi et al., 2018).

Winton et al. (2019) carried out a comprehensive field and modelling study of the air-snow transfer of  $\text{NO}_3^-$  at the low snowfall accumulation site at Kohnen Station in Dronning Maud Land (DML), East Antarctica as part of the ISOL-ICE (ISotopic constraints of past Ozone Layer in polar ICE) project. At the DML site,  $\text{NO}_3^-$  is recycled three times before it is archived in the snowpack below a depth of 15 cm and within 0.75 years. Sensitivity analysis with a 1D air-snow model, TRANSITS (TRansfer of Atmospheric Nitrate Stable Isotopes To the Snow) (Erbland et al., 2015), of  $\delta^{15}\text{N}(\text{NO}_3^-)$  at DML showed that the dominant factors controlling the archived  $\delta^{15}\text{N}(\text{NO}_3^-)$  signature are the snow accumulation rate and e-folding depth of the surface snowpack for incident UV, with a smaller role from changes in the snowfall timing and TCO. The Winton et al. (2019) study sets the framework for the interpretation of a  $\delta^{15}\text{N}(\text{NO}_3^-)$  record from the new ISOL-ICE ice core drilled in January 2017 at Kohnen Station in Dronning Maud Land, henceforth referred to as the DML site following the terminology in Winton et al. (2019). The DML region experiences low annual accumulation rates ( $< 10 \text{ g cm}^{-2} \text{ yr}^{-1}$ ) but ice cores from the area still record seasonal, centennial and millennial scale variability in glaciochemistry (Göktas et al., 2002; Oerter et al., 2000; Sommer et al., 2000), as well as highly-resolved tropical volcanic eruptions (Hofstede et al., 2004; Severi et al., 2007). This site offers useful potential to investigate the impact of volcanic eruptions on TCO, surface UV radiation and its imprint in the  $\delta^{15}\text{N}(\text{NO}_3^-)$  ice core signature.

The aim of this study is to combine modelling studies with ice core evidence to understand the impact on the total column ozone of explosive tropical volcanic eruptions in a low chlorine stratosphere. The first part of this study will explore the sensitivity of ozone over Antarctica to different volcanic emission scenarios using a state-of-the-art chemistry-climate model (UM-UKCA) with additional key heterogeneous and photolysis reactions. The second part of the study examines the  $\delta^{15}\text{N}(\text{NO}_3^-)$  signal for the tropical volcanic eruption, Samalás. Section 2 described the methods used in this paper. We provide a brief overview of the UM-UKCA chemistry-climate model and the additional key heterogeneous and photolysis reactions that were added to improved the representation of stratospheric ozone. A Pinatubo eruption test case is used to validate the response to a present day volcanic eruption. We also provide a brief description of the ice core data and the isotopic analysis. In Section 3.1, we use the model to investigate the response of stratospheric ozone to various volcanic emission scenarios in a pre-industrial atmosphere. The isotopic constraints offered on past ozone change from the ice core evidence are presented in Section 3.2. Finally, Section 4 combines the model results and ice core

172 analysis to discuss the implications for past and future ozone changes from explosive trop-  
 173 ical volcanoes.

## 174 2 Data and methods

### 175 2.1 Model description, changes

176 We make use of the coupled chemistry-climate model which consists of the United  
 177 Kingdom Chemistry and Aerosol (UKCA) module together with the UK Met Office Uni-  
 178 fied Model (UM) (Walters et al., 2019; Morgenstern et al., 2009; O’Connor et al., 2014).  
 179 The model is free running and with prescribed sea ice and sea surface temperatures. The  
 180 original configuration is similar to the Atmospheric Model Intercomparison Project (AMIP)  
 181 simulation of UK Earth system model (UKESM) submission to the Coupled Model In-  
 182 tercomparison Project Phase 6 (CMIP6) (Eyring et al., 2016). The resolution is  $1.875^\circ$   
 183 longitude by  $1.25^\circ$  latitude with 85 vertical levels extending from the surface to 85 km.  
 184 The UKCA module is run with the combined stratosphere and troposphere chemistry  
 185 (CheST) option at version 10.9. The model has an internally generated QBO and the  
 186 dynamics of the stratosphere is well represented (Osprey et al., 2013). The model includes  
 187 the aerosol scheme, GLOMAP-mode, to simulate the direct and indirect radiative effects  
 188 (Mann et al., 2010). Aerosol optical properties are computed online as the particle size  
 189 distributions evolve due to micro-physical processes.

190 Stratospheric ozone concentrations are determined by sets of photo-chemical reac-  
 191 tions first described by Chapman (1930) plus ozone destroying catalytic cycles involv-  
 192 ing chlorine, nitrogen, hydrogen and bromine radical species (Solomon, 1999). The pho-  
 193 tolysis reactions in the model make use of rates calculated from a combination of the FAST-  
 194 JX scheme (Wild et al., 2000; Bian & Prather, 2002; Neu et al., 2007) and look-up ta-  
 195 bles. FAST-JX wavelengths range from 177 to 850 nm over 18 bins and calculates scat-  
 196 tering for all bands (Telford et al., 2013). Above about 60 km, a look-up table of pho-  
 197 tolysis rates (Lary & Pyle, 1991; Morgenstern et al., 2009) is used when wavelengths be-  
 198 low 177 nm become important. Heterogeneous reactions are also important for deter-  
 199 mining stratospheric ozone concentrations in the presence of polar stratospheric clouds  
 200 in the polar lower stratosphere or in the presence of sulphate aerosol following explosive  
 201 volcanic eruptions. Ozone depleting radicals are produced by the photolysis of the prod-  
 202 ucts formed from halogen containing compounds reacting on the surface of stratospheric  
 203 aerosol such as polar stratospheric clouds. These species include hydrochloric acid (HCl),  
 204 chlorine nitrate (ClONO<sub>2</sub>), hydrogen bromide (HBr) and bromine nitrate (BrONO<sub>2</sub>).  
 205 Three types of aerosol are considered by the model: ice, nitric acid trihydrate and sul-  
 206 fate aerosol. Above a temperature of about 195 K, reactions occur on liquid sulfate aerosol,  
 207 around 195 K to 188 K, the model forms nitric acid trihydrate particles and below about  
 208 188 K, ice particles form.

209 We add 8 new heterogeneous reactions to the model involving chlorine and bromine  
 210 species in a similar way to Dennison et al. (2019), following the previous work by (Yang  
 211 et al., 2014), with the main difference being the explicit treatment of the reactions of 4  
 212 additional chemical species: Cl<sub>2</sub>, Br<sub>2</sub>, ClNO<sub>2</sub> and BrNO<sub>2</sub>. These species are also pho-  
 213 tolysed to produce Cl and Br radicals. Reaction rates depend on the probability of a gas  
 214 molecule colliding irreversibly with the surface of the aerosol and this is given by an up-  
 215 take coefficient. We update the calculation of the uptake coefficients using the same scheme  
 216 as Dennison et al. (2019) with the differences listed in Table A1 in the Appendix.

217 Klobas et al. (2017) show that stratospheric bromine from natural, very shortlived  
 218 biogenic compounds is critically important in determining the sign of the ozone change  
 219 from eruptions when stratospheric chlorine levels are low. Stratospheric bromine is about  
 220 100 times more efficient at removing ozone in the high latitudes than chlorine. Yang et  
 221 al. (2014) showed that a 5 pptv increase in Br<sub>y</sub> from very short-lived substances (VSLS)

(a doubling of the emissions in a present day experiment) resulted in an ozone decrease in the Southern Hemisphere lowermost stratosphere of about 10 DU. This suggests interhalogen reactions are likely to be important for Pinatubo sized eruptions in a low background chlorine environment (as shown by Klobas et al. (2017)) but we expect the ozone response to be largely dominated by chlorine for larger Samalás sized eruptions where the background chlorine loading approaches present-day values. Hence, we explicitly add the emissions of five very short-lived bromocarbon species ( $\text{CH}_3\text{Br}$ ,  $\text{CH}_2\text{BrCl}$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_2\text{Cl}$ ,  $\text{CHBrCl}_2$ ). These represent estimates of pre-industrial natural emissions of the species (Yang et al., 2014) and are modified from Warwick et al. (2006). For large injections of chlorine, the ozone response will still be dominated by chlorine rather than the details of the interhalogen reactions. Further details of the model setup are described in Appendix A.

## 2.2 Model validation

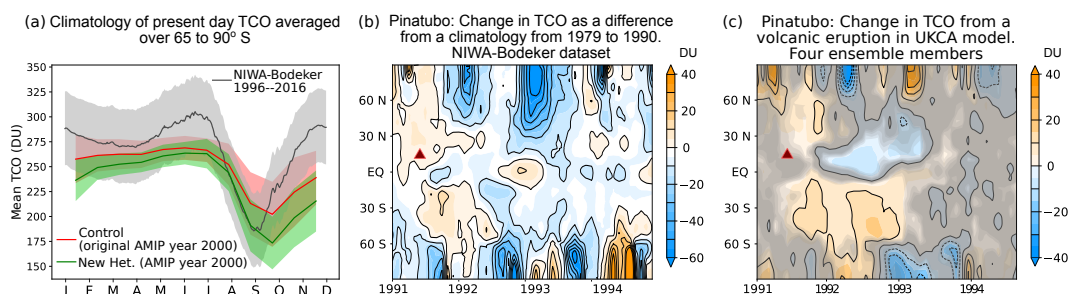
The changes to the stratospheric chemistry are tested by running the model for 30 years in a year 2000 time slice experiment using CMIP6 prescribed trace gases and sea surface temperature forcings. The model is mostly able to reproduce the observed total column ozone and the results are similar to those found by Dennison et al. (2019) in which a more thorough discussion of the changes can be found. The improved match with observed TCO resulting from our model updates is shown in Figure 1(a). The spring ozone hole over Antarctica is deeper than the original model with total column ozone values reaching about 175 DU (65 to 90° S average) in October compared to about 200 DU in the original model. These values are closer to those in the ozone values from the satellite ozone dataset from the National Institute of Water and Atmospheric Research – Bodeker Scientific (NIWA-BS) satellite dataset (version 3.4; see <http://www.bodekerscientific.com/data/total-column-ozone>). The ozone hole minimum in the satellite data reaches about 185 DU although this happens earlier in September. The modified model still underpredicts the summer ozone values which take longer to recover compared to observations. This could be due to the vortex breakup being delayed and is a known issue in a number of comprehensive chemistry climate models (Eyring et al., 2010; Butchart et al., 2011; McLandress et al., 2012). Overall, our changes to the chemistry scheme lead to an ozone distribution that is very similar to Dennison et al. (2019).

To assess the model response to a volcanic perturbation in the present atmosphere we run an experiment that simulates the eruption of Mount Pinatubo. The model is first spun up using CMIP6 present day forcings, including changing trends in trace gases. We then initialize four ensemble runs using the climate state taken from four different years of the spun up model state. The runs use the CMIP6 trace gas forcings from 1979 to 1994 with the eruption happening in 1991. Although the exact climate state at the time of the Pinatubo eruption is known from observations, the four ensemble runs are done so as to span over the variability arising from the QBO and ENSO. This allows the Pinatubo run to be compared to the pre-industrial volcanic runs in Section 3.1. The timing of historical volcanic eruptions is not well constrained and we do not know the phases of the QBO and ENSO in which the eruptions occurred. The ensemble is designed to average over this variability. We simulate the Pinatubo eruption as an emission of 10 Tg  $\text{SO}_2$  and 0.02 Tg HCl on 1 June 1991 into the stratosphere as a single vertical plume between 19 and 24 km altitude (the neutral buoyancy height of the plume) at 15.1° N and 120.2° E. Mills et al. (2016) discuss the justification for various choices of modelling parameters for Pinatubo. The aim of this experiment is not to reproduce the observations after the Pinatubo eruption exactly but to check that, with the additional chemical reactions and emissions, our model is still able to simulate the broad pattern of the ozone response after a current day explosive volcano.

Figure 1(b) shows change in total column ozone from the Pinatubo eruption in the NIWA-Bodeker dataset as the difference between a 1991 to 1994 average and a clima-

274 tology taken from 1979 to 1990. Similarly, the same change in the model runs is shown  
 275 in Figure 1(c) but using the average of the four ensemble runs. A non parametric per-  
 276 mutation test is used to determine if the changes seen are larger than the natural vari-  
 277 ability; changes below the level of the noise is represented by the grey fog which is plot-  
 278 ted as overlaid contours at confidence levels of 95, 90, 80, 70 and 60%. The same test  
 279 is used in all subsequent model plots. The red triangle marks the volcanic eruption in  
 280 this and subsequent plots.

281 The initial, low latitude, increase in total column ozone south of the volcano in the  
 282 year following the eruption and the decrease in ozone in Jan 1992 over the North Pole  
 283 are captured by the model although the changes are shorter lived than in the satellite  
 284 data. Note that the Antarctic ozone hole is not as prominent a feature in model runs  
 285 due to the averaging of four ensemble members. Our model ozone changes are qualita-  
 286 tively similar to the Pinatubo case study by Aquila et al. (2012) using a different chemis-  
 287 try-climate model. Aquila et al. (2012) also discuss, in more detail, the possible mechan-  
 288 isms for the stratospheric ozone changes. This experiment demonstrates that our modified  
 289 model is able to satisfactorily stimulate the ozone changes associated with a present-day  
 290 volcanic eruption.



**Figure 1.** (a) Climatology of total column ozone (TCO) (DU) for the present climate from the NIWA-Bodeker satellite dataset (1996–2016) in black, a 30 year timeslice run of the year 2000 from the original AMIP model setup in red and the corresponding timeslice with the modified model with new heterogeneous reactions and emission files in green. Shaded bands show  $\pm 1$  standard deviation. (b) Change in Bodeker ozone following the Pinatubo eruption (red triangle) as a difference from a climatology taken from years 1979 to 1990. The QBO signal filtered out. (c) Change in TCO (DU) following a Pinatubo eruption (10 Tg  $\text{SO}_2$ , 0.02 Tg HCl) in the model. The plot shows the difference from a climatology (1979 to 1990) and is the average of four ensemble members. The grey fog illustrates regions where the signal is below the level of the noise (see the main text for further details). The red triangle marks the volcanic eruption. Note the different colour scales between (b) and (c).

### 291 2.3 Ice core analysis

292 The first high-resolution record of  $\delta^{15}\text{N}(\text{NO}_3^-)$  was obtained for the last 1.3 kyr from  
 293 the 120 m ISOL-ICE ice core. The core was drilled in the clean air sector at Kohnen Sta-  
 294 tion, DML on the high-elevation East Antarctic Plateau (2892 m above sea-level; 74.9961° S, 0.094717° E)  
 295 in January 2017. A full description of the methods for the ISOL-ICE ice core can be found  
 296 in Winton et al. (2019) and only a brief summary is given here. The core was analysed  
 297 for i) continuous flow analysis (CFA) of nitrate ( $\text{NO}_3^-$ ), sodium (Na) and magnesium (Mg)  
 298 mass concentrations and electrolytic meltwater conductivity at the British Antarctic Sur-  
 299 vey (BAS), Cambridge, and ii) discrete sections for the  $\delta^{15}\text{N}(\text{NO}_3^-)$  composition at the  
 300 Institute of Environmental Geosciences (IGE), University of Grenoble. Here we report



301 the dated section of the ice core from 1227 to 1350 AD (69.8 to 79.4 m) covering the Samalas  
 302 eruption in 1257. Dating was achieved by annual layer counting of measured concentra-  
 303 tions of Na and Mg following previous studies at DML (Göktas et al., 2002; Weller &  
 304 Wagenbach, 2007; Weller et al., 2008) constrained by well-dated volcanic horizons (fur-  
 305 ther details can be found in Table B1). An age uncertainty of  $\pm 3$  years is estimated at  
 306 the base of the ice core. High-resolution sampling for  $\delta^{15}\text{N}(\text{NO}_3^-)$  analysis was carried  
 307 out i) across volcanic horizons with a sample resolution of 5 to 30 cm, and ii) in 10 cm  
 308 resolution baseline samples 1 m either side of the volcanic peak. A total of 119 discrete  
 309 measurements of  $\delta^{15}\text{N}(\text{NO}_3^-)$  are reported here. Discrete  $\delta^{15}\text{N}(\text{NO}_3^-)$  samples were pre-  
 310 concentrated and analysed using the denitrifier method following Frey et al. (2009) and  
 311 Morin et al. (2009). The nitrogen isotopic ratio was referenced against  $\text{N}_2$ -Air (Mariotti,  
 312 1983). We report  $^{15}\text{N}/^{14}\text{N}$  of  $\text{NO}_3^-$  ( $\delta^{15}\text{N}(\text{NO}_3^-)$ ) as  $\delta$ -values:  $\delta^{15}\text{N}(\text{NO}_3^-) = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right)$   
 313 where R is the elemental isotopic ratio in the sample and standard respectively. The over-  
 314 all accuracy of the method for  $\delta^{15}\text{N}(\text{NO}_3^-)$  is 3 per mil.

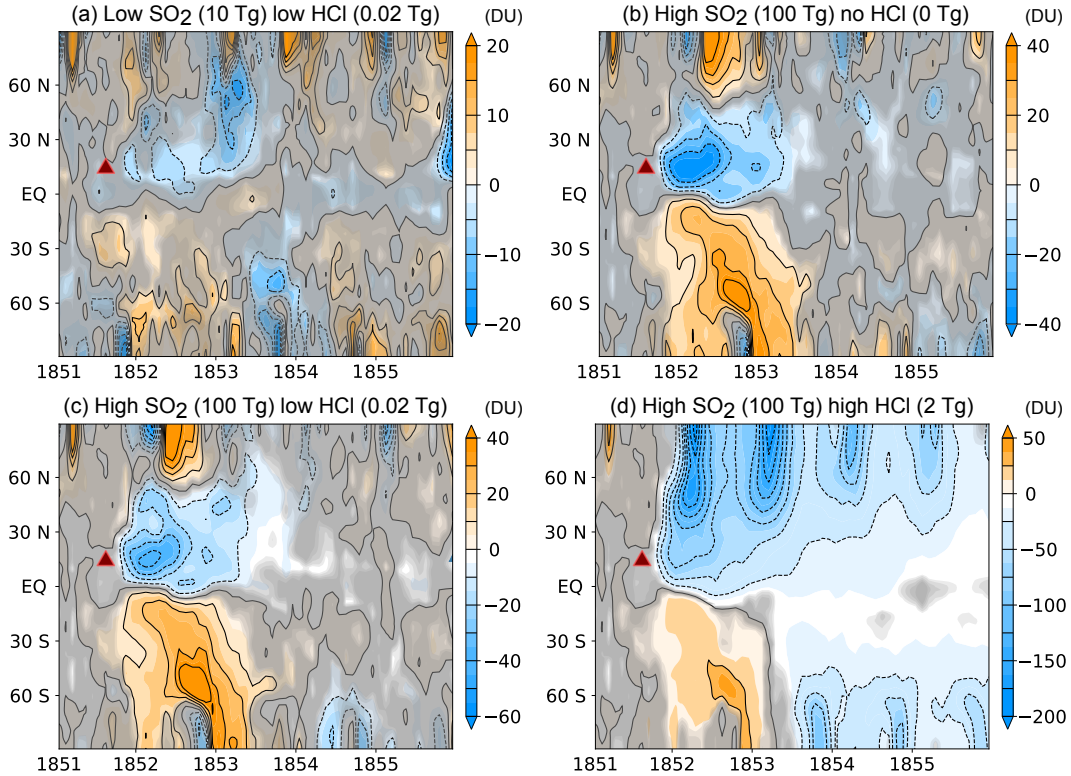
### 315 3 Results

#### 316 3.1 Volcanic perturbations in model

317 Using the CMIP6 pre-industrial forcings, a year 1850 control run is produced. The  
 318 control run is 60 years long excluding 10 years of spin up which are discarded. The ef-  
 319 fect from explosive volcanoes on the stratosphere is investigated by running a series of  
 320 four volcanic perturbation runs spun off from four different years of the control run to  
 321 represent the variability arising from different ENSO and QBO states in a similar way  
 322 to the Pinatubo case study in Section 2.2. The volcanic emissions are prescribed in a sim-  
 323 ilar way to the Pinatubo eruption on 1 September of the first year of the run. Since his-  
 324 torical volcanic eruptions are variable and HCl emissions are less well constrained, we  
 325 develop a matrix of simulations that span the uncertainty in emissions. The six sets of  
 326 experiments have one of low  $\text{SO}_2$  (10 Tg) or high  $\text{SO}_2$  (100 Tg) paired with no HCl, low  
 327 HCl (0.02 Tg) and high HCl (2 Tg). Changes are plotted as the difference between the  
 328 average of the four perturbation runs and a climatology derived from the control run.

329 Figure 2 shows the change in total column ozone in the (a) low  $\text{SO}_2$  + low HCl,  
 330 (b) high  $\text{SO}_2$  + no HCl, (c) high  $\text{SO}_2$  + low HCl and (d) high  $\text{SO}_2$  + high HCl cases.  
 331 The low  $\text{SO}_2$  + no HCl case and high  $\text{SO}_2$  + no HCl cases are found to be qualitatively  
 332 similar to two further experiments (not shown): the low  $\text{SO}_2$  + low HCl and high  $\text{SO}_2$   
 333 + low HCl cases, respectively. This is expected since the stratospheric chlorine loading  
 334 is low ( $< 0.4$  ppbv of HCl over the polar region averaged between  $65$  to  $90^\circ$  S), as it is  
 335 in a pre-industrial atmosphere. We do not observe large depletion of ozone depletion events  
 336 by chlorine radicals during spring to form ozone holes.

337 The low  $\text{SO}_2$  + low HCl case in Figure 2(a) represents the ozone response to a Pinatubo-  
 338 like explosive volcano in a pre-industrial atmosphere. It shows that the changes in TCO  
 339 are small and dominated by internal variability in most regions. This should be contrasted  
 340 with the Pinatubo case study shown previously in Figure 1(c) where an eruption of an  
 341 equivalent magnitude was able to cause significant ozone changes, including an ozone de-  
 342 pletion of about 20 DU in the year following the eruption over Antarctica. In contrast,  
 343 under scenarios of low or no HCl but when the  $\text{SO}_2$  emitted is high (Figures 2(b) and  
 344 (c)), substantial changes in total column ozone are seen for 1.5 years following the erup-  
 345 tion. These two cases (high  $\text{SO}_2$  and no HCl case, high  $\text{SO}_2$  and low HCl) are qualita-  
 346 tively similar suggesting that transport effects still dominate when the amount of HCl  
 347 is low in a pre-industrial atmosphere and the volcanic chlorine injection is not sufficient  
 348 to make a significant change to the background stratospheric chlorine loading. The pri-  
 349 mary impact of a large injection of  $\text{SO}_2$  is to locally decrease TCO in the tropics and  
 350 increase TCO at high latitudes, via the mechanisms described below.



**Figure 2.** Change in total column ozone (DU) for the pre-industrial volcanic perturbation experiments. The plots show the difference between the average of four ensemble members and a single climatology drawn from a 60 year run. The emission scenarios shown are (a) low  $\text{SO}_2$ , low HCl case (b) high  $\text{SO}_2$ , no HCl (c) high  $\text{SO}_2$ , low HCl and (d) high  $\text{SO}_2$ , high HCl. The red triangle denotes the location of the injection. Note the different colour scales.

351 Since chemical, dynamical and radiative processes are coupled in the model, it is  
 352 difficult to quantify the contribution from individual processes but the results suggest  
 353 that the main driver of the ozone changes is dynamical in the year following the eruption.  
 354 The  $\text{SO}_2$  aerosol leads to both longwave and shortwave heating in the lower strato-  
 355 sphere (Robock, 2000) resulting in a change in the meridional circulation as shown in  
 356 Figure 3(a). The increased upwelling brings more ozone-poor tropospheric air into the  
 357 lower stratosphere leading to lower total column ozone. In contrast, the decreases in up-  
 358 welling outside the initial  $\text{SO}_2$  cloud results in an increase in ozone in the regions pole-  
 359 wards of the  $\text{SO}_2$  cloud in both hemispheres. Compared to the changes in transport, the  
 360 changes to the partitioning between radicals and reservoir species for  $\text{ClO}_x$ ,  $\text{HO}_x$  and  
 361  $\text{NO}_x$  appear to be a second order effect (not shown). The warming in the lower strato-  
 362 sphere results in a warming of the cold point region. This region controls the freeze-drying  
 363 of water vapour entering the lower stratosphere and warmer temperatures will result in  
 364 a moistening of the stratosphere and subsequent changes to  $\text{HO}_x$  chemistry. Changes in  
 365  $\text{SO}_2$  aerosol also change the partitioning between  $\text{NO}_y$  and  $\text{N}_2\text{O}_5$  in the polar regions  
 366 which can result in ozone changes but these have not been quantified in this study.

367 In contrast, when a substantial amount of HCl together with  $\text{SO}_2$  is injected into  
 368 the stratosphere (high  $\text{SO}_2$  and high HCl case, Figure 2(d)), large, chemical ozone de-  
 369 pletion occurs over the polar regions during spring time in the year two to four follow-  
 370 ing the eruption. The initial, low latitude, response still appears to be dynamical but  
 371 when the injected chlorine reaches polar regions (Figure 3(b)), catalytic destruction of

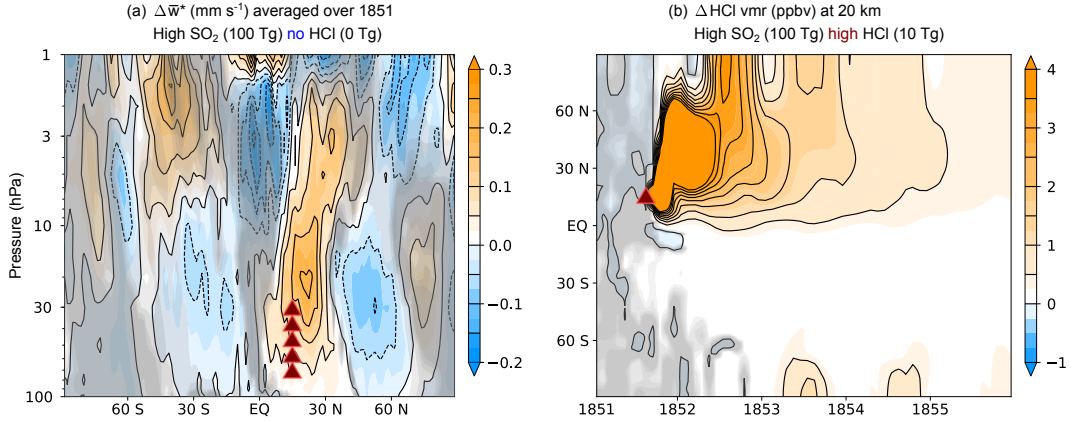
372 ozone occurs in the polar vortex during spring. The mixing ratio of HCl reaches values  
 373 of up to 4 ppbv and 1.3 ppbv at 20 km over the North and South poles respectively. These  
 374 values are comparable to the present day (year 2000) values of the equivalent effective  
 375 stratospheric chlorine of  $\sim 3$  ppbv. The high SO<sub>2</sub> and high HCl scenario is the one ex-  
 376 periment where we observed prolonged ozone destruction occurring over a number of years  
 377 over Antarctica with a maximum decrease in total column ozone of  $\sim 90$  DU in spring  
 378 of the second year after the eruption. Over the North pole, stratospheric ozone is nearly  
 379 completely removed in the spring for at least four years following the eruption.

380 The results are sensitive to the date, location and height of the injection in the trop-  
 381 ics. A discussion of the sensitivity of eruption source parameters on volcanic radiative  
 382 forcing can be found in Marshall et al. (2019). In our experiment, the lower branch of  
 383 the Brewer-Dobson circulation is stronger in the Northern Hemisphere in September and  
 384 hence the injected chlorine is primarily advected to the North pole in the months fol-  
 385 lowing the eruption. It takes about 1.5 years for chlorine to be transported to the South  
 386 pole. Our results are comparable to the experiments by Brenna et al. (2019) who im-  
 387 pose a Central American explosive volcano in a chemistry climate model (CESM1) in  
 388 which the effect of sulphuric acid aerosols are imposed as a modified El Chichòn surface  
 389 area density forcing equivalent to 30 Mt SO<sub>2</sub>. The results from their experiment with 2.93 Mt Cl,  
 390 9.5 Mt Br at 14°N, 89°W with an injection height of 29.7 hPa on January 1 (their Fig-  
 391 ure 3(c)) are qualitative similar to our results in Figure 2(d). Brenna et al. (2019) show  
 392 that the average ozone decreases by more than 120 DU over the polar cap and observe  
 393 a similar ozone increase over Antarctica in the year after that eruption which is followed  
 394 by a series of four years with large spring-time ozone depletion. The duration of the re-  
 395 sponse to a volcanic eruption is controlled by stratospheric dynamics and the material  
 396 that is injected in the lower stratosphere is transported to the troposphere and removed  
 397 within 2 to 5 years.

398 In summary, in a pre-industrial atmosphere with low chlorine levels in the strato-  
 399 sphere, we do not detect a significant ozone response to a Pinatubo strength eruption  
 400 in the model. A large explosive volcano, of similar magnitude to Samalas with no or low  
 401 HCl produces an increase in total column ozone over Antarctica. The change is short-  
 402 lived ( $\sim 2$  years) and primarily driven by transport changes. In contrast, if a volcanic  
 403 injection of HCl (2 Tg in our experiments) is able to raise stratospheric chlorine concen-  
 404 trations closer to present day levels, ozone depleting chemical reactions will occur to pro-  
 405 duce Antarctic ozone depletion in spring as long as sufficient HCl is present. The strato-  
 406 spheric lifetime of chlorine is determined by the age of air and the strength of the strato-  
 407 spheric circulation. When the chlorine reaches the troposphere, it is washed out, giving  
 408 a lifetime of about 5 years for HCl entering in the shallow branch of the Brewer-Dobson  
 409 circulation. The increase in surface UV, resulting from ozone depletion, will affect the  
 410  $\delta^{15}\text{N}(\text{NO}_3^-)$  ratio in the snow pack. The timing of the change in surface UV could lag,  
 411 by a number of years, behind that of the volcanic sulphate signal in ice cores, since sul-  
 412 phate arrives via tropospheric and stratospheric transport whilst the UV signal is de-  
 413 pendent on stratospheric ozone depletion. An additional difficulty is that the timing of  
 414 the arrival of the signal depends on the season of the eruption; a quantity that is unknown  
 415 for most volcanoes over the past 1000 years.

### 416 3.2 Ice core results

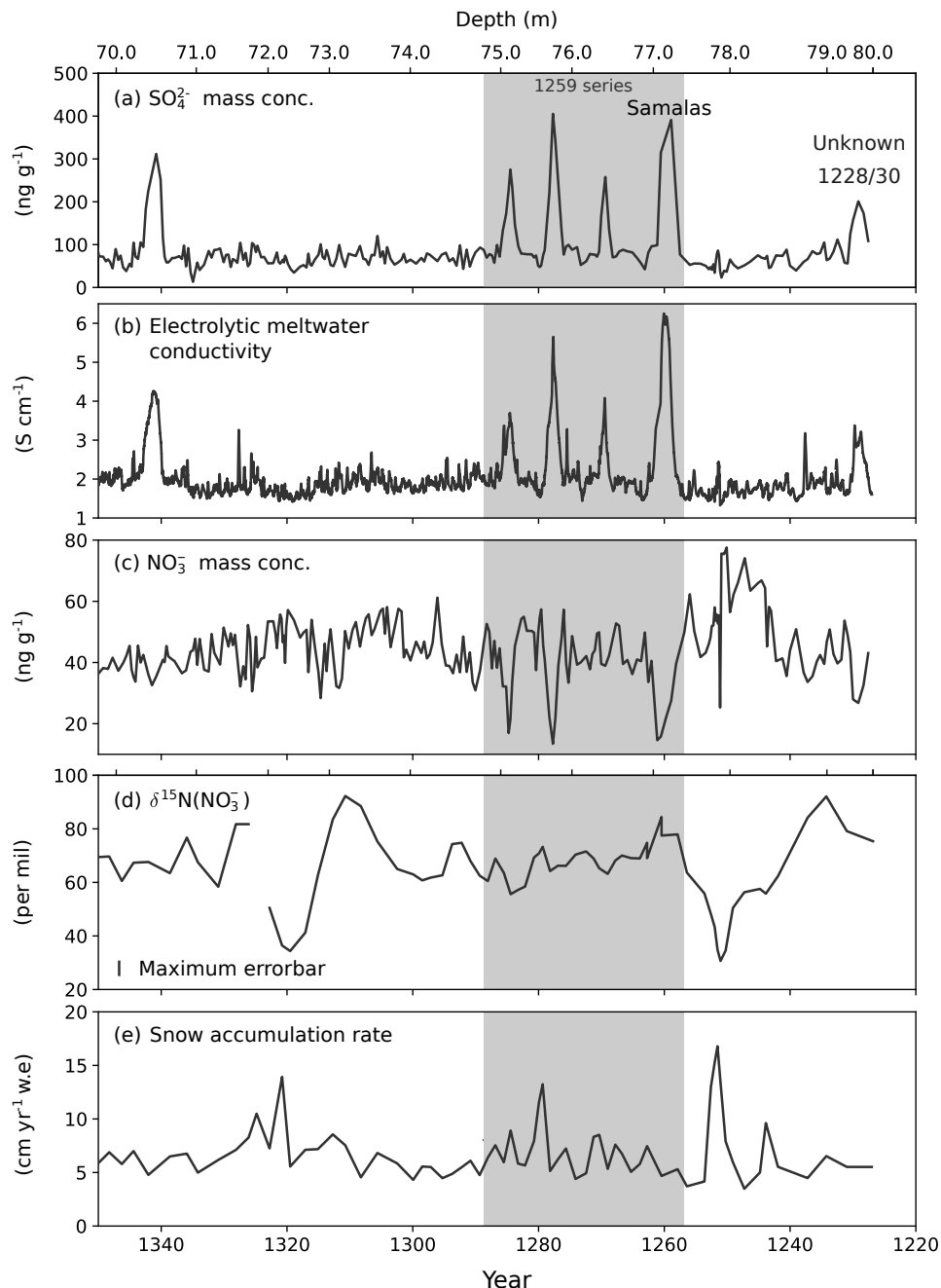
417 We expect a tropical volcanic eruption to lead to a sulphate signal in the ice record.  
 418 The previous modelling studies show that high SO<sub>2</sub> and high HCl eruptions can cause  
 419 a decrease in TCO which would increase the UV dose reaching the surface at the ice core  
 420 site. As a result, stronger photolysis would enhance NO<sub>3</sub><sup>-</sup> loss, redistribution and recy-  
 421 cling from snowpack, decreasing the NO<sub>3</sub><sup>-</sup> mass concentration and enriching the  $\delta^{15}\text{N}(\text{NO}_3^-)$   
 422 signature.



**Figure 3.** (a) Change in the mean residual vertical velocity averaged over one year after the eruption and 4 ensemble members for the high  $\text{SO}_2$  and no HCl case from the control run to show dynamical changes. The red triangles represent the location and vertical extent of the volcanic eruption. (b) Change in HCl volume mixing ratio (ppbv) at 20 km for the high  $\text{SO}_2$  and high HCl case from the control run to show chemical changes.

423 The ISOL-ICE ice core data from 1227 to 1350 AD is illustrated in Figure 4. The  
 424 ice core captures a clear signal of the 1257 Samalas series of four volcanic eruptions as  
 425 indicated by elevated sulphate mass concentrations and electrolytic meltwater conduc-  
 426 tivity levels above the background in the ice core (Figures 4(a) and (b)). This pattern  
 427 is consistently observed in ice cores across DML and across the wider Antarctic region  
 428 (e.g. Hofstede et al. (2004); Göktas et al. (2002)), where sulphate originated from the  
 429 1257 series of eruptions, was transported via the stratosphere to Antarctica (Baroni et  
 430 al., 2008). Nitrate mass concentrations in the ice core decrease coincident with the four  
 431 large volcanic eruptions (Figure 4(c)). This observation has been reported for other vol-  
 432 canic eruptions in Antarctic and Greenland ice cores, and is thought to occur from the  
 433 displacement of  $\text{NO}_3^-$  away from the highly acidic (sulphuric acid) volcanic layers (Wolff,  
 434 1995; Laj et al., 1993; Legrand & Kirchner, 1990). This post-depositional process, un-  
 435 related to photolysis, leads to the anti-correlation between the sulfate peaks and  $\text{NO}_3^-$   
 436 during the volcanic eruptions. Based on other records of  $\text{NO}_3^-$  in Antarctica (Pasteris  
 437 et al., 2014), we expect the  $\text{NO}_3^-$  mass concentration to be correlated to the accumula-  
 438 tion rate outside of the volcanic eruptions. We do not see this positive correlation in the  
 439 background variability in the ISOL-ICE ice core (Figure 4(c) and (e);  $R^2 = 0.04, p <$   
 440  $10^{-3}$  with data from five years either side of the volcanic eruptions is not used). The  $\delta^{15}\text{N}(\text{NO}_3^-)$   
 441 is weakly anti-correlated to the accumulation rate as would be expected from spatial tran-  
 442 sects across Antarctica (Figure 4(d) and (e);  $R^2 = 0.2, p < 10^{-4}$  again with five years  
 443 either side of the volcanic eruptions removed.) (Erbland et al., 2015, 2013; Noro et al.,  
 444 2018; Shi et al., 2018), and sensitivity tests of variable accumulation rate on the  $\delta^{15}\text{N}(\text{NO}_3^-)$   
 445 signal at the DML site (Winton et al., 2019).

446 The accumulation rate is variable at the DML site (2.5 to  $11 \text{ cm yr}^{-1}$  water equiv-  
 447 alent) (Oerter et al., 2000; Sommer et al., 2000) and there is no trend over the last 1000  
 448 years. We speculate that changes in the accumulation rate will lead to changes in e-folding  
 449 depth over time which can account for part of the variability of the  $\delta^{15}\text{N}(\text{NO}_3^-)$  signal  
 450 (Winton et al., 2019), with a smaller contribution from extreme precipitation events (Turner  
 451 et al., 2019). The e-folding depth of the local snowpack depends on snow physical prop-  
 452 erties and contributes to the  $\delta^{15}\text{N}(\text{NO}_3^-)$  signal eventually preserved in local firn and ice  
 453 (Winton et al., 2019). Unfortunately, the variability of e-folding depth in the past is not  
 454 known and may be a source of additional noise in the  $\delta^{15}\text{N}(\text{NO}_3^-)$  signal.



**Figure 4.** 1227 to 1350 AD section of the ISOL-ICE ice core data from DML, Antarctica. Age is plotted along the bottom and the corresponding ice depth along the top. The vertical grey region marks the dates around the 1257 series of volcanoes. (a) Sulphate mass concentrations. (b) Electrolytic melt water conductivity. (c) Nitrate mass concentration (d) Isotopic ratio of  $^{15}\text{N}/^{14}\text{N}$  of  $\text{NO}_3^-$  ( $\delta^{15}\text{N}(\text{NO}_3^-)$ ) given as  $\delta$ -values. (e) Snow accumulation rate in ( $\text{cm yr}^{-1}$  water equivalent (w.e)). Note that the various quantities are available at different time resolutions depending on the analysis method used.

455  
456

We see no enrichment of the  $\delta^{15}\text{N}(\text{NO}_3^-)$  signal above the background variability during the four volcanic eruptions Figure 4(d). We speculate on possible reasons for thus

457 lack of enrichment after the 1257 series. Firstly, the  $\delta^{15}\text{N}(\text{NO}_3^-)$  UV proxy is not sen-  
 458 sitive enough to record TCO and concurrent surface UV changes lasting only a few years.  
 459 (Winton et al., 2019) assessed the sensitivity of the  $\delta^{15}\text{N}(\text{NO}_3^-)$  UV proxy to changes  
 460 in total column ozone using the TRANSITS model (Erbland et al., 2015). We expect  
 461 that a decrease in the total column ozone of 100 DU, estimated for a large eruption on  
 462 the magnitude of Samalás (assuming an eruption in September), would result in a 25 per  
 463 mil increase in  $\delta^{15}\text{N}(\text{NO}_3^-)$  at DML. However, this is below the inter-annual  $\delta^{15}\text{N}(\text{NO}_3^-)$   
 464 variability of 30 to 90 per mil at DML (over the period 1227 to 1350 AD), and thus the  
 465 development of a volcanic induced-large ozone depletion in spring is unlikely to be ob-  
 466 served above the natural background  $\delta^{15}\text{N}(\text{NO}_3^-)$  variability. Note that the inter-annual  
 467 variability of  $\delta^{15}\text{N}(\text{NO}_3^-)$  is larger than the seasonal variability of about  $\pm 25$  per mil of  
 468  $\delta^{15}\text{N}(\text{NO}_3^-)$  seen at the bottom of the snow pits in Winton et al. (2019). Despite DML  
 469 having a relatively low snow accumulation rate, the sensitivity of the  $\delta^{15}\text{N}(\text{NO}_3^-)$  UV  
 470 proxy is low at this site. Secondly, although we observe a significant decrease in the  $\text{NO}_3^-$   
 471 concentration during the volcanic eruptions, we cannot rule out the possibility that the  
 472 lower  $\text{NO}_3^-$  concentrations are due to migration of  $\text{NO}_3^-$  in acidic layers. Lastly, the im-  
 473 pact of acidic volcanic layers on the  $\delta^{15}\text{N}(\text{NO}_3^-)$  has yet to be quantified.

#### 474 4 Discussion and conclusions

475 The aim of this paper is to understand the impact on the total column ozone of  
 476 explosive tropical volcanic eruptions in a low chlorine stratosphere and to search for ev-  
 477 idence of these changes in the ice core record over the last 1000 years. We made use of  
 478 the UM-UKCA chemistry-climate model, with improved heterogeneous reactions and emis-  
 479 sions, to model the evolution of ozone after different injections scenarios of  $\text{SO}_2$  and HCl  
 480 representing possible past volcanic eruptions. We then compare the model results to the  
 481  $\delta^{15}\text{N}(\text{NO}_3^-)$  isotopic ratio from the recently obtained ISOL-ICE ice core. Winton et al.  
 482 (2019) and earlier work (Berhanu et al., 2015; Erbland et al., 2015) suggest that it may  
 483 be possible to use  $\delta^{15}\text{N}(\text{NO}_3^-)$  as a UV proxy for Antarctic ozone changes, after account-  
 484 ing for accumulation rate changes. A decrease in ozone leads to increased surface UV  
 485 which increases the fractionation of  $\delta^{15}\text{N}(\text{NO}_3^-)$  in the photolytically active region of the  
 486 snowpack. The resulting  $\delta^{15}\text{N}(\text{NO}_3^-)$  isotopic signal, which integrates the UV signal seen  
 487 over several years, is then buried. We analyse the  $\delta^{15}\text{N}(\text{NO}_3^-)$  ice core signature around  
 488 the period of the Samalás eruption to reconstruct past UV changes.

489 The model experiments show that a “Pinatubo-like” eruption (low  $\text{SO}_2$ , 10 Tg +  
 490 low HCl, 0.02 Tg) in a pre-industrial atmosphere does not produce a significant response  
 491 in ozone over Antarctica (Figure 2(c)) whilst the high  $\text{SO}_2$  (100 Tg) volcanoes (with no  
 492 or low HCl) both produce increases in ozone over Antarctica that are short-lived, last-  
 493 ing about 1.5 years (Figure 2(b) and (c)). The pattern of ozone changes for the latter  
 494 are primarily caused by transport changes arising from changes to the Brewer-Dobson  
 495 circulation (Figure 3(a)). In contrast, when the amounts of  $\text{SO}_2$  and HCl emitted are  
 496 both high (high  $\text{SO}_2$ , 100 Tg + high HCl, 2 Tg) and the HCl loading over the polar re-  
 497 gions becomes comparable to present day stratospheric values, our model results show  
 498 significant ozone depletion over both poles (Figure 2(d)) for at least four years follow-  
 499 ing the eruption. Note that the chemical reactions that destroy ozone are only able to  
 500 occur when HCl in the stratosphere reaches the polar regions and hence the timing of  
 501 the springtime ozone depletion depends strongly on the date of the eruption. Since we  
 502 model the eruption as occurring on 1 September, we find that it takes about 1 year for  
 503 the injected HCl from the volcano to reach Antarctica (Figure 3(b)). Before the HCl reaches  
 504 Antarctica, the increase in ozone over the Southern Hemisphere is caused by the same  
 505 dynamical changes as in the low HCl model experiments.

506 The model experiments suggest that if a tropical volcano emits a substantial amount  
 507 of  $\text{SO}_2$  and HCl (high  $\text{SO}_2$ , 100 Tg + high HCl, 2 Tg), prolonged ozone depletion, last-  
 508 ing more than four years, will occur over Antarctica. We choose to focus on the ice core

509 record around the Samalas eruption (part of the 1257 series of four volcanoes) since ice  
 510 core and geochemical evidence suggests that this volcano was the largest in the past 1000  
 511 years in terms of SO<sub>2</sub> and HCl emissions although there is significant uncertainty in the  
 512 amount of HCl that was able to reach the stratosphere from this eruption (Halmer et  
 513 al., 2002). The 1257 series of volcanoes that includes Samalas consists of four eruptions  
 514 that occur at intervals of 10, 8 and 8 years. If all four eruptions caused ozone depletion,  
 515 we expect to see a prolonged period of increase in  $\delta^{15}\text{N}(\text{NO}_3^-)$  in the ice core.

516 Spatial transects across Antarctica (Noro et al., 2018, and references therein), sup-  
 517 ported by air snow-photochemistry modelling (TRANSITS) (Winton et al., 2019; Erb-  
 518 land et al., 2015) show a strong non linear dependence of  $\delta^{15}\text{N}(\text{NO}_3^-)$  on snow accumu-  
 519 lation rate which is not seen in the ice record (60–70 m depth). Deeper ice core records  
 520 in Greenland have observed a dependence of  $\delta^{15}\text{N}(\text{NO}_3^-)$  and accumulation rate on glacial-  
 521 interglacial transition timescales (Freyer et al., 1996). However, in this paper, we present  
 522 the highest resolution record in ice cores and do not observe a clear relationship on cen-  
 523 tennial timescales. Our record of the isotopic ratio of  $\delta^{15}\text{N}(\text{NO}_3^-)$  in the ice core around  
 524 the 1257 series eruptions shows that using  $\delta^{15}\text{N}(\text{NO}_3^-)$  as a proxy for ozone changes is  
 525 inconclusive. Winton et al. (2019) show that for 100 DU change in total column ozone  
 526 (Figure 2(d)), we expect to see a change of about 25 per mil in  $\delta^{15}\text{N}(\text{NO}_3^-)$ . This is be-  
 527 low the level of inter-annual variability in  $\delta^{15}\text{N}(\text{NO}_3^-)$  seen in the ice core of about 60  
 528 to 90 per mil. The maximum uncertainty in our samples is less than  $\pm 3$  per mil over this  
 529 time period. Note that the snow pack also integrates UV changes over a couple of years  
 530 and smooths out seasonal variability. For a  $\delta^{15}\text{N}(\text{NO}_3^-)$  signal to have been detected at  
 531 the DML site from the 1257 eruptions, we suggest that it would require a prolonged pe-  
 532 riod (several years) of near complete ozone destruction, for instance, during the series  
 533 of seven stratospheric volcanic eruptions that occurred over a deglaciation  $\sim 17.7$  ka (McConnell  
 534 et al., 2017). With the additional caveat that the timing and magnitude of ozone changes  
 535 depends on the season of the eruption, the climate model results suggest that this would  
 536 require more than 2 Tg HCl to have been injected into the stratosphere. Since we do not  
 537 see a  $\delta^{15}\text{N}(\text{NO}_3^-)$  signal of this magnitude in the ice core, this provides a constraint on  
 538 the magnitude of past ozone changes caused by the 1257 eruptions.

539 In summary, we have evaluated the impact of various explosive tropical volcanic  
 540 emission scenarios on stratospheric ozone changes in a pre-industrial atmosphere and found  
 541 that the sign of the ozone change over the polar regions depends on the amount of HCl  
 542 injected by the eruption.  $\delta^{15}\text{N}(\text{NO}_3^-)$  can theoretically be used as a proxy for UV and  
 543 thus has the potential to indicate changes in past TCO. Changes in  $\delta^{15}\text{N}(\text{NO}_3^-)$  could  
 544 be positive or negative (indicating either increases or decreased in TCO) depending on  
 545 the type of volcanic eruption and they are unlikely to be synchronous with sulphate peaks  
 546 because of different transport pathways and the different timings of the ozone changes.  
 547 Using a novel high resolution  $\delta^{15}\text{N}(\text{NO}_3^-)$  ice core record, we are unable to detect a sig-  
 548 nal from the largest volcanic eruption (1257 series) in the past 1000 years as there is a  
 549 large inter-annual variability in the  $\delta^{15}\text{N}(\text{NO}_3^-)$  record. We recommend that future stud-  
 550 ies of this nature should first understand why the  $\delta^{15}\text{N}(\text{NO}_3^-)$  record has a large vari-  
 551 ability at DML site. A site with lower variability than 25 per mil in  $\delta^{15}\text{N}(\text{NO}_3^-)$  could  
 552 be considered although increasing the sensitivity of the UV proxy by choosing a site with  
 553 lower annual accumulation comes at the expense of reduced time resolution making it  
 554 less likely to resolve volcanic eruptions.

## 555 Appendix A Model improvements

### 556 A1 Heterogeneous and photolysis reactions

557 Table A1 lists the new heterogeneous reactions added to the UKCA module together  
 558 with the uptake coefficients on ice, nitric acid trihydrate and sulfate aerosol. This can  
 559 be compared to Table 1 in Dennison et al. (2019). We use the method in Shi et al. (2001)

Reaction	Uptake coefficient		
	Ice	Nitric acid trihydrate	Sulphate aerosol
$\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3$	0.3	0.3	<i>f</i>
$\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3$	0.3	0.006	<i>f</i>
$\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$	0.3	0.3	<i>f</i>
$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3$	0.03	0.006	0.1
$\text{N}_2\text{O}_5 + \text{HCl} \rightarrow \text{ClONO}_2 + \text{HNO}_3$	0.03	0.006	0.02
$\text{HOBr} + \text{HCl} \rightarrow \text{BrCl} + \text{H}_2\text{O}$	0.25	0.25	0.1
$\text{BrONO}_2 + \text{HCl} \rightarrow \text{BrCl} + \text{HNO}_3$	0.3	0.3	0.01
$\text{BrONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOBr} + \text{HNO}_3$	0.3	0.001	0.01
$\text{HOBr} + \text{HBr} \rightarrow \text{Br}_2 + \text{H}_2\text{O}$	0.25	0.25	0.1
$\text{HOCl} + \text{HBr} \rightarrow \text{BrCl} + \text{H}_2\text{O}$	0.25	0.25	0.02
$\text{ClONO}_2 + \text{HBr} \rightarrow \text{BrCl} + \text{HNO}_3$	0.56	0.56	0.02
$\text{BrONO}_2 + \text{HBr} \rightarrow \text{Br}_2 + \text{HNO}_3$	0.3	0.3	0.01
$\text{N}_2\text{O}_5 + \text{HBr} \rightarrow \text{BrNO}_2 + \text{HNO}_3$	0.05	0.001	0.02

*f* denotes uptake coefficients calculated using the method in Shi et al. (2001).

**Table A1.** New heterogeneous reactions added to the UKCA module together with the uptake coefficients.

560 to calculate the values of the uptake coefficients that are not constant and are denoted  
561 by *f* in Table A1.

## 562 A2 Bromocarbon emissions

563 The emission flux datasets of the five very short lived bromocarbon species ( $\text{CH}_3\text{Br}$ ,  
564  $\text{CH}_2\text{BrCl}$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_2\text{Cl}$ ,  $\text{CHBrCl}_2$ ) are explicitly included as emission files. These  
565 are similar to the ones used in Yang et al. (2014), which are based on the original work  
566 (scenario 5) of Warwick et al. (2006), except for the emissions of  $\text{CH}_2\text{Br}_2$ . The emissions  
567 of  $\text{CH}_2\text{Br}_2$  were scaled to give a total emission of  $57\text{Gg yr}^{-1}$ , corresponding to 50% of  
568 the original flux and in better agreement with Liang et al. (2010) and Ordóñez et al. (2012).  
569 The combined effect of the bromocarbons is to provide  $\sim 5\text{pptv}$  of inorganic bromine  
570 to the stratosphere (Yang et al., 2014) in a pre-industrial atmosphere.

## 571 Appendix B Ice core analysis

572 Table B1 shows the volcanic horizons identified from the sulfate and electrical melt-  
573 water conductivity records in the ISOL-ICE ice core.

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Volcano	Eruption date	Arrival date	Peak Depth (m)	Start Depth (m)
Kuwa <sup>a</sup>	1450	1454	61.01	61.13
1285 <sup>b</sup>	1285	1285	75.12	75.22
1277 <sup>b</sup>	1277	1277	75.77	75.9
1269 <sup>b</sup>	1269	1269	76.41	77.46
Samalas 1257 <sup>b</sup>	1257	1259	77.12	77.23
Unknown 1228/30 <sup>b</sup>	1229	1229	79.33	79.43

<sup>a</sup> Zielinski et al. (1994) <sup>b</sup> Langway Jr. et al. (1995)

**Table B1.** Volcanic horizons identified from the sulfate and electrical meltwater conductivity records. Eruption date of the volcano and arrival dates of the sulfate in the ice core are obtained from Zielinski et al. (1994) and Langway Jr. et al. (1995) except for the Unknown 1228/30 volcano where the precise eruption date is not known. We choose 1229 as the eruption and arrival date for dating purposes.

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