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1           **Regional characteristics of atmospheric sulfate formation in East Antarctica**  
2                                   **imprinted on  $^{17}\text{O}$ -excess signature**

3  
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18  
19 **Key Points:**

- 20       • Regional characteristics of atmospheric sulfate formation were probed by  $^{17}\text{O}$ -excess  
21       ( $\Delta^{17}\text{O}$ ) of sulfate at inland and coastal East Antarctica.
- 22       • Specifically high  $\Delta^{17}\text{O}$  in spring–summer at inland suggests that chemical destruction of  
23       methanesulfonate ( $\text{MS}^-$ ) on the Antarctic Plateau produces sulfate.
- 24       • Existing gap between  $\Delta^{17}\text{O}$  of sulfate in the atmosphere and ice can be reconciled by  
25        $\text{MS}^-$  destruction in snow.

## 28 Abstract

29  $^{17}\text{O}$ -excess ( $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ) of sulfate trapped in Antarctic ice cores has been  
 30 proposed as a potential tool for assessing past oxidant chemistry, while insufficient  
 31 understanding of atmospheric sulfate formation around Antarctica hampers its interpretation. To  
 32 probe influences of regional specific chemistry, we compared year-round observations of  $\Delta^{17}\text{O}$   
 33 of non-sea-salt sulfate in aerosols ( $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$ ) at Dome C and Dumont d'Urville, inland and  
 34 coastal sites in East Antarctica, throughout the year 2011. Although  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  at both sites  
 35 showed consistent seasonality with summer minima ( $\sim 1.0$  ‰) and winter maxima ( $\sim 2.5$  ‰)  
 36 owing to sunlight-driven changes in the relative importance of  $\text{O}_3$ -oxidation to OH- and  $\text{H}_2\text{O}_2$ -  
 37 oxidation, significant inter-site differences were observed in austral spring–summer and autumn.  
 38 The co-occurrence of higher  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  at inland ( $2.0 \pm 0.1$  ‰) than the coastal site ( $1.2 \pm$   
 39  $0.1$  ‰) and chemical destruction of methanesulfonate ( $\text{MS}^-$ ) in aerosols at inland during spring–  
 40 summer (October to December), combined with the first estimated  $\Delta^{17}\text{O}(\text{MS}^-)$  of  $\sim 16$  ‰, implies  
 41 that  $\text{MS}^-$  destruction produces sulfate with high  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  of  $\sim 12$  ‰. If contributing to the  
 42 known post-depositional decrease of  $\text{MS}^-$  in snow, this process should also cause a significant  
 43 post-depositional increase in  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  over 1 ‰, that can reconcile the discrepancy  
 44 between  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  in the atmosphere and ice. The higher  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  at the coastal site  
 45 than inland during autumn (March to May) may be associated with oxidation process involving  
 46 reactive bromine and/or sea-salt particles around the coastal region.

## 48 Plain Language Summary

49 It has been proposed that the past variations of atmospheric oxidants (e.g., ozone) might be  
 50 estimated using  $^{17}\text{O}$ -excess, an unique isotopic signature, of sulfate trapped in polar ice cores.  
 51 However, chemical processes altering  $^{17}\text{O}$ -excess of sulfate in the atmosphere and also in snow  
 52 after deposition has not been fully understood, limiting the practicality of the signature. We  
 53 investigated regional differences in  $^{17}\text{O}$ -excess of sulfate in aerosol particles at inland and coastal  
 54 sites in East Antarctica. Our results suggest that the chemical destruction of atmospheric  
 55 methanesulfonate, the second abundant sulfur compound in Antarctic aerosols, produces sulfate  
 56 with significantly high  $^{17}\text{O}$ -excess signature at inland Antarctica. If also occurring in snow, this  
 57 process can explain the existing gap of the signature between the atmosphere and ice. These  
 58 results should be taken into account through future studies investigating the past atmospheric  
 59 compositions using this signature in ice cores.

## 61 1 Introduction

62 Sulfate is a major component of impurities trapped in Antarctic ice cores and widely  
 63 used for reconstruction of paleoclimate conditions (e.g., Legrand and Mayewski, 1997). For  
 64 instance, since the main source of sulfate in Antarctica is oxidation of dimethyl sulfide (DMS)  
 65 emitted by marine biota (Minikin et al., 1998; Cosme et al., 2005), sulfate in the Antarctic ice  
 66 cores are often discussed in light of the past bioproductivity of the Southern Ocean (Legrand et  
 67 al., 1988; Wolff et al., 2006; Azuma et al., 2019). In addition to the use of sulfate content in ice  
 68 cores,  $^{17}\text{O}$ -excess ( $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ ) of sulfate ( $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ ) is expected to be a  
 69 potential tool assessing past oxidant chemistry involving ozone ( $\text{O}_3$ ) and hydroxyl radicals (OH),  
 70 those playing central roles in tropospheric chemistry but not directly preserved in ice cores

71 (Alexander and Mickley, 2015; Kunasek et al., 2010; Sofen et al., 2014; Murray et al., 2014).  
 72  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  is generally assumed to reflect relative importance of different sulfate formation  
 73 pathways, since the sulfate produced via gas-phase oxidation of  $\text{SO}_2$  by OH possesses  $\Delta^{17}\text{O} = 0$   
 74 ‰ (Dubey et al., 1997; Barkan and Luz, 2005), whereas those produced via aqueous-phase  
 75 oxidations of dissolved  $\text{SO}_2$  ( $\text{S(IV)} = \text{SO}_2 \cdot \text{H}_2\text{O} + \text{HSO}_3^- + \text{SO}_3^{2-}$ ) by  $\text{O}_3$  or hydrogen peroxide  
 76 ( $\text{H}_2\text{O}_2$ ) possess  $\Delta^{17}\text{O} > 0$  ‰ (Savarino et al., 1999, 2000; Vicars and Savarino, 2014). Sofen et al.  
 77 (2014) observed a 1.1 ‰ increase of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  within the early 19th century in West Antarctic  
 78 Ice Sheet Divide ice cores, probably suggesting an increase of  $\text{O}_3$ -oxidation relative to OH- and  
 79  $\text{H}_2\text{O}_2$ -oxidation in sulfate formation in the mid- to high-southern latitude region. However, they  
 80 estimated by their box model that a 1.1 ‰ increase of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  requires a 260% increase of  
 81 relative abundance of  $\text{O}_3/\text{OH}$ , which they concluded was highly implausible given a 26%  
 82 increase of  $\text{O}_3/\text{OH}$  from a chemistry transport model estimate for the Southern Hemisphere  
 83 extra-tropics. Based on such results, they pointed out deficiencies in the understanding of sulfate  
 84 formation other than the recognized  $\text{SO}_2$  oxidation by OH,  $\text{H}_2\text{O}_2$ , and  $\text{O}_3$ . Furthermore, there is  
 85 increasing evidence for a significant difference between the  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  in aerosol samples (ca.  
 86 1.5 ‰; Hill-Falkenthal et al., 2013; Ishino et al., 2017; Walters et al., 2019) and those in ice-  
 87 cores corresponding to the present-day climate conditions (ca. 3 ‰; Alexander et al., 2002, 2003;  
 88 Kunasek et al., 2010; Sofen et al., 2014). Despite the significance of this ~1.5 ‰ shift in  
 89  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  compared to the observed variability in ice cores (1.3–4.8 ‰ for glacial-interglacial  
 90 time scale), there has been no study pointing it out so far. Thus, the interpretation of ice-core  
 91  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  records requires a better understanding of atmospheric sulfate formation in  
 92 Antarctica.

93 In Antarctica, where the impact of anthropogenic emissions is still insignificant, there  
 94 exist unique oxidative conditions associated with natural emissions of reactive trace gases from  
 95 snow and sea-ice surfaces (Grannas et al., 2007; Simpson et al., 2007). One characteristic is  
 96 drastic enhancements of photochemical oxidants, represented by OH and  $\text{O}_3$ , over the Antarctic  
 97 Plateau after polar sunrise to the austral mid-summer (Grannas et al., 2007; Crawford et al.,  
 98 2001; Mauldin et al., 2001), which is mainly triggered by nitrate photolysis within snowpack  
 99 (Frey et al., 2009; Erbland et al., 2013; Noro et al., 2018) emitting reactive nitrogen species (e.g.,  
 100  $\text{NO}_x$ ) to the atmosphere (Davis et al., 2008). It has been recently found that the concentration of  
 101 methanesulfonate ( $\text{MS}^-$ ), a second abundant product of DMS oxidation after sulfate, suddenly  
 102 decreased in the highly oxidative atmosphere in mid-summer at Dome C, inland Antarctica  
 103 (Legrand et al., 2017b). It was hypothesized that this may be due to a chemical destruction of  
 104  $\text{MS}^-$ , possibly into sulfate, but the hypothesis needs confirmation and quantification. Since it is  
 105 also known that  $\text{MS}^-$  is partially lost in snow after its deposition (Wagon et al., 1999; Delmas et  
 106 al., 2003; Weller et al., 2004), it is important to examine the impact of  $\text{MS}^-$  destruction on sulfate  
 107 formation and  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  values in snow and ice. Another characteristic is the elevated  
 108 reactive bromine over coastal Antarctica during austral spring, as indicated from satellite  
 109 observations of tropospheric BrO columns (Theys et al., 2011). Hypobromous acids (HOBr),  
 110 which is produced from the  $\text{BrO} + \text{HO}_2$  reaction, was proposed to represent up to 50% of total  
 111 sulfate production in the summertime marine boundary layer over the southern ocean (Chen et  
 112 al., 2016). The contribution of this reaction is thus expected to be also significant in the Antarctic  
 113 troposphere.

114 There are only a few reports of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  observations in the present Antarctic  
 115 atmosphere, and little is known about the influence of characteristic oxidation processes in

116 Antarctica on  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ .  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  observations of aerosols at three different sites, Dome C  
117 (Hill-Falkenthal et al, 2013) and South Pole (Walters et al., 2019) on the Antarctic Plateau and  
118 coastal Antarctic station Dumont d'Urville (DDU) (Ishino et al., 2017), show similar seasonality  
119 with minima in the austral summer and higher values in the autumn to spring, which likely  
120 reflects a seasonal shift from OH- and H<sub>2</sub>O<sub>2</sub>- to O<sub>3</sub>-dominated chemistry. In addition, Ishino et  
121 al. (2017) and Walters et al. (2019) suggested the possibility of an increased contribution of  
122 S(IV) + HOBr during austral spring at DDU and summer at South Pole, respectively, based on  
123 the relatively low  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  in those seasons. However, the importance of S(IV) + HOBr  
124 remains inconclusive, since both results in those two previous works can also be explained by the  
125 contribution of OH- and H<sub>2</sub>O<sub>2</sub>-oxidation. Meanwhile, there is no study investigating the possible  
126 impact of MS<sup>-</sup> destruction to  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  so far. To evaluate the consequences of characteristic  
127 chemical processes to  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  in Antarctica, a comparison of the isotope signatures at inland  
128 and coastal sites can be helpful, since the MS<sup>-</sup> destruction appears most significant on the  
129 Antarctic Plateau (Legrand et al., 2017b) while reactive bromine is more abundant in coastal  
130 regions (Theys et al., 2011). Here, we conduct an inter-site comparison of year-round  
131  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  values of atmospheric sulfate, using weekly  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  observations newly  
132 obtained for the inland site Dome C in this study and those previously obtained for coastal site  
133 DDU (Ishino et al., 2017) in the same year 2011. We also compare the observations with the  
134  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  values estimated using a global chemical-transport model GEOS-Chem, which  
135 includes reactive bromine production from sea-salt aerosols that originate from both the open  
136 ocean and blowing snow sublimation over sea-ice (Huang et al., 2020).

137

## 138 2 Materials and Methods

### 139 2.1 Aerosol sampling and measurement of soluble species

140 Aerosol samples were collected at Dome C (75°10'S, 123°30'E; 3233 m above sea  
141 level), located on the East Antarctic Plateau 1100 km from the nearest coast. The aerosol  
142 sampling is performed continuously at Dome C from the year 2010 as a part of Sulfate and  
143 Nitrate Evolution at Dome C (SUNITEDC) program (e.g., Erbland et al., 2013). Bulk aerosol  
144 was collected on glass fiber filters using high-volume air sampler (HVAS; General Metal Works  
145 GL 2000H Hi Vol TSP; Tisch Environmental, Cleves, OH, USA) at the flow rate of 1.7 m<sup>3</sup> min<sup>-1</sup>  
146 with time resolution of 1–2 week. The HVAS was placed at ~1 km distant from the main  
147 building of research activity at Dome C. A field blank was checked once per month by mounting  
148 filters onto the filter holder and running for 1 min. After each collection run, filters were  
149 removed from the HVAS and wrapped in aluminium foil, which were sealed in plastic bags,  
150 stored at -20 °C, and shipped to Institut des Géosciences de l'Environnement (Grenoble, France)  
151 for chemical analyses. Samples collected during January to December 2011 were used in this  
152 study.

153 The procedures for extraction and quantification of soluble species concentrations in  
154 aerosols are detailed in Ishino et al. (2019). Some anions (NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) and cations (K<sup>+</sup>, Mg<sup>2+</sup>,  
155 Ca<sup>2+</sup>) were measured at Tokyo Tech using ion chromatograph ICS2100, DIONEX with a guard  
156 column (Dionex IonPac AG19) and a separation column (Dionex IonPac AS19) for anions, and  
157 881 Compact IC Pro, Metrohm with a guard column (Metrosep C4 S-Guard/4.0) and a separation  
158 column (Metrosep C 4-150/4.0) for cations. Considering high blank loading on filters or the lack

159 of ion standard materials at Tokyo Tech., the concentration of other ions ( $\text{MS}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , oxalate  
 160 ( $\text{C}_2\text{O}_4^{2-}$ ), and  $\text{Na}^+$ ) were obtained from other aerosol samples as described in Legrand et al.  
 161 (2017a, 2017b). The measured ion concentrations were corrected for blank values, and reported  
 162 as atmospheric concentration in standard temperature and pressure ( $T = 273.15 \text{ K}$ ,  $p = 101325$   
 163 Pa) based on meteorological data of Dome C provided by IPEV/PNRA ([www.climantartide.it](http://www.climantartide.it)).  
 164 The uncertainties were estimated based on the typical uncertainty of the ion chromatography  
 165 analysis (5%).  
 166

## 167 2.2 Oxygen isotope measurements of sulfate ( $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ )

168  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  values were measured with an isotope ratio mass spectrometer (IRMS)  
 169 (MAT253; Thermo Fisher Scientific, Bremen, Germany), coupled with an in-house measurement  
 170 system built following original setup by Savarino et al. (2001) and a series of improvements  
 171 (Schauer et al., 2012; Geng et al., 2013). The detailed method is described in Ishino et al. (2017).  
 172 Briefly, ca.  $1 \mu\text{mol}$  of  $\text{SO}_4^{2-}$  was separated from other anions using ion chromatography, and  
 173 chemically converted to silver sulfate ( $\text{Ag}_2\text{SO}_4$ ) using ion exchange resin.  $\text{O}_2$  produced via  
 174 thermal decomposition of the  $\text{Ag}_2\text{SO}_4$  at  $1000 \text{ }^\circ\text{C}$  within a high temperature conversion  
 175 elemental analyzer (TC/EA; Thermo Fisher Scientific, Bremen, Germany) was analysed for  
 176 isotopic compositions with the IRMS system. The inter-laboratory calibrated standards (Sulf- $\alpha$ ,  
 177  $\beta$  and  $\epsilon$ ; Schauer et al., 2012) were used to assess the accuracy of our measurements of our  
 178 working standards. Measured  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  was corrected for oxygen isotope exchange with  
 179 quartz ( $\Delta^{17}\text{O} = 0 \text{ }^\circ\text{‰}$ ; Matsuhisa et al., 1978) by estimating the magnitude of isotopic exchange  
 180 based on the set of working standard measurements along with the sample measurement runs as  
 181 described in Schauer et al. (2012). The precision ( $1\sigma$ ) of corrected  $\Delta^{17}\text{O}$  was  $\pm 0.2 \text{ }^\circ\text{‰}$  based on  
 182 replicate analyses ( $n = 35$ ) of our working standard C ( $\Delta^{17}\text{O} = 8.4 \text{ }^\circ\text{‰}$ ).  
 183

184 Since sea-salt sulfate aerosols (ss- $\text{SO}_4^{2-}$ ) are not impacted by atmospheric oxidation  
 185 processes (i.e.,  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{ss}} = 0 \text{ }^\circ\text{‰}$ ), both total sulfate concentrations and  $\Delta^{17}\text{O}$  values were  
 186 corrected for their ss- $\text{SO}_4^{2-}$  component to obtain their non-sea-salt sulfate (nss- $\text{SO}_4^{2-}$ ) content,  
 187 using the following Eq. (1) and (2).

$$187 \quad [\text{SO}_4^{2-}]_{\text{nss}} = [\text{SO}_4^{2-}]_{\text{total}} - k \times [\text{Na}^+] \quad (1)$$

$$188 \quad \Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}} = \frac{[\text{SO}_4^{2-}]_{\text{total}}}{[\text{SO}_4^{2-}]_{\text{nss}}} \times \Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{total}} \quad (2)$$

189 where “total” is the sum of ss- and nss- $\text{SO}_4^{2-}$  components; and  $k$  is the mass ratio of  
 190  $[\text{SO}_4^{2-}]_{\text{ss}}/[\text{Na}^+]$  in seawater (0.25; Holland et al., 1986). To take into account sea salt chemical  
 191 fractionation processes that occurs in the Antarctic region in winter, when temperatures drop  
 192 below  $-8 \text{ }^\circ\text{C}$  in the presence of sea-ice (Wagenbach et al., 1998),  $k$  value of  $0.16 \pm 0.05$  (Legrand  
 193 et al., 2017a) was applied from May to October. Eq. (2) represents the isotope mass balance  
 194 equation between ss- and nss- $\text{SO}_4^{2-}$ , with  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{ss}} = 0 \text{ }^\circ\text{‰}$ . Note that the sea salt  
 195 fractionation is a chemical fractionation and should not shift  $\Delta^{17}\text{O}$ . The uncertainties of ion  
 196 concentration measurement ( $\pm 5\%$ ),  $\Delta^{17}\text{O}$  measurement ( $\pm 0.2 \text{ }^\circ\text{‰}$ ), and the  $k$  value were  
 197 propagated to  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$ . The obtained uncertainty of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  was  $\pm 0.3 \text{ }^\circ\text{‰}$  on  
 198 average, while reaches  $\pm 1.1 \text{ }^\circ\text{‰}$  at maximum in the austral mid-winter when the  $[\text{SO}_4^{2-}]_{\text{nss}}/[\text{SO}_4^{2-}]_{\text{total}}$   
 199 is minimum.  
 200

## 201 2.3 Complementary data

202 The  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  at Dome C were compared to those previously obtained at DDU  
 203 (Ishino et al., 2017) in the same year 2011. The inter-site difference was evaluated at weekly  
 204 resolution by subtracting the  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  of each DDU sample from that of each Dome C  
 205 sample collected in the closest time period, hereafter denoted  $\Delta_{\text{DC-DDU}}$ . Note that, at DDU,  
 206 aerosol samples were collected separately for coarse ( $>1 \mu\text{m}$ ) and fine ( $<1 \mu\text{m}$ ) mode particles  
 207 and the  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  was measured for fine mode (Ishino et al., 2017). The results were also  
 208 compared to datasets of oxidants available year-round at both Dome C and DDU,  $\text{O}_3$  mixing  
 209 ratios (Legrand et al., 2016a) and an estimate of total gaseous inorganic bromine ( $[\text{Br}_y^*] = [\text{HBr}]$   
 210  $+ [\text{HOBr}] + 0.9[\text{Br}_2] + 0.4[\text{BrO}] + [\text{BrNO}_2] + [\text{BrONO}_2] + [\text{Br}]$ ) (Legrand et al., 2016b), as  
 211 indicators of regional characteristic processes. Furthermore,  $[\text{MS}^-]/[\text{SO}_4^{2-}]_{\text{nss}}$  mass ratios at  
 212 Dome C (Legrand et al., 2017b) and DDU (Ishino et al., 2017) for the same year were used to  
 213 examine the influence of chemical destruction of  $\text{MS}^-$  on sulfate formation in the mid-summer.

214 Additionally, to explore other possible processes influencing the  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  values,  
 215 we investigated the relationship of  $\Delta_{\text{DC-DDU}}$  to various chemical species observed at both sites.  
 216 They include ion concentrations and acidity in aerosols ( $[\text{H}^+]$ ), ratios of respective sulfur  
 217 components,  $[\text{SO}_4^{2-}]_{\text{ss}}/[\text{SO}_4^{2-}]_{\text{total}}$  ratio ( $= 1 - [\text{SO}_4^{2-}]_{\text{nss}}/[\text{SO}_4^{2-}]_{\text{total}}$ , cf., Eq. (1)), and sulfur  
 218 isotopic composition of non-sea-salt sulfate ( $\delta^{34}\text{S}_{\text{nss}}$ ) (Ishino et al., 2019).  $[\text{H}^+]$ , estimated by  
 219 using the following equation, was used to consider the contribution of aqueous-phase  $\text{S(IV)} + \text{O}_3$   
 220 pathway, which is highly dependent on pH of liquid water in the atmosphere (Seinfeld and  
 221 Pandis, 2006).

$$222 \quad [\text{H}^+] = ([\text{Cl}^-] + [\text{Br}^-] + [\text{NO}_3^-] + 2[\text{SO}_4^{2-}] + 2[\text{C}_2\text{O}_4^{2-}]) - ([\text{Na}^+] + [\text{NH}_4^+] +$$

$$223 \quad [\text{K}^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}]) \quad (3)$$

224 Also  $[\text{SO}_4^{2-}]_{\text{ss}}/[\text{SO}_4^{2-}]_{\text{total}}$  was used to consider the potential importance of aqueous-phase  $\text{S(IV)}$   
 225  $+ \text{O}_3$  reaction, since it has been recognized that  $\text{S(IV)} + \text{O}_3$  proceeds rapidly in alkaline (pH  $\sim 8$ )  
 226 deliquescent solution in fresh sea-salt particles, subsequently shutting off due to acidification of  
 227 sea salt aerosol by the produced sulfate as well as by uptake of acidic gases such as  $\text{SO}_2$ ,  $\text{HNO}_3$ ,  
 228 and  $\text{H}_2\text{SO}_4$  (Alexander et al., 2005).  $\delta^{34}\text{S}_{\text{nss}}$  was used to test the impact of sulfur sources on  
 229  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$ , since it reflects the relative contributions of marine biogenic (i.e., DMS-sourced)  
 230 sulfate and non-marine sulfate (nmb- $\text{SO}_4^{2-}$ ) including volcanic and continental sulfur sources  
 231 (Patris et al., 2000; Pruet et al., 2004; Ishino et al., 2019). Additionally,  $^{210}\text{Pb}$  was used to trace  
 232 the contribution of long-range transport of continental submicron aerosols (Elsasser et al., 2011;  
 233 Legrand et al., 2017b). The relationships were examined separately for each season: December-  
 234 January-February (DJF), March-April-May (MAM), June-July-August (JJA), September-  
 235 October-November (SON), as well as October 29th to December 23rd (OND), where the last one  
 236 was defined based on the specifically positive  $\Delta_{\text{DC-DDU}}$  values as explained later in Section 3.1.  
 237 The obtained correlation coefficients ( $r$  and  $p$  values) are summarized in Table S1.

## 241 2.4 Model description and limitations

242 We used v11-02d of the GEOS-Chem global chemical-transport model of coupled  
 243 aerosol-oxidant chemistry (Park et al., 2004; <http://www.geos-chem.org/>) to estimate the relative  
 244 importance of sulfate formation processes and  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  in Antarctica. The model was run

245 at  $4^\circ \times 5^\circ$  (latitude  $\times$  longitude) horizontal resolution and 47 vertical levels up to 0.01 hPa, using  
246 the MERRA-2 assimilated meteorological data developed by the Global Modeling and  
247 Assimilation Office (GMAO) at NASA Goddard Space Flight Center. Simulations were  
248 performed for January to December 2011 after spinning up the model for 6 months prior to  
249 January 2011.

250 GEOS-Chem v11-02d includes detailed bromine chemistry as described in Parrella et al.,  
251 (2012), Schmidt et al. (2016), Sherwen et al. (2016a, 2016b), and Chen et al. (2017). We also  
252 applied the reactive bromine emission scheme from sea-salt aerosols produced by blowing snow  
253 sublimation over sea-ice as described in Huang et al. (2018, 2020), with surface snow salinity of  
254 0.1 psu and 0.03 psu over the Arctic and the Antarctic, respectively, for both first-year-ice and  
255 multi-year-ice. We assumed an enrichment factor of 9 for  $\text{Br}^-/\text{Na}^+$  ratio in surface snow on sea-  
256 ice relative to seawater. Sea-salt emission from open ocean is simulated as a function of sea  
257 surface temperature and wind speed (Jaeglé et al., 2011), with updates from Huang and Jaeglé  
258 (2017) for cold ocean waters ( $\text{SST} < 5^\circ\text{C}$ ). The model is able to reproduce observed  $\text{Br}_y^*$   
259 concentrations at DDU from winter to spring (June to November), within the range of standard  
260 deviations of the monthly mean observations (Legrand et al., 2016b; Fig. S1). DMS emission is  
261 parameterized as a function of sea surface temperature, wind speed, and DMS concentration in  
262 seawater obtained from Lana et al. (2011). Note that the model does not include reactive nitrogen  
263 emissions from snow nitrate photolysis (Grannas et al., 2007). This would lead to underestimates  
264 in oxidants over large area of the Antarctic continents, as exhibited by the underestimates in  
265 surface  $\text{O}_3$  concentrations at both Dome C and DDU by a factor of  $\sim 1.5$  (Fig. 1e). Zatzko et al.  
266 (2016) previously simulated that the inclusion of their snow  $\text{NO}_x$  emission scheme in GEOS-  
267 Chem model will increase surface  $\text{O}_3$  concentrations over the Antarctic continent by factors of  
268 1.1–1.8. It is also recently pointed out that the underestimates in  $\text{O}_3$  over the Southern Ocean is  
269 improved by the inclusion of a new  $\text{O}_3$  deposition scheme associated with chemical reaction of  
270  $\text{O}_3$  with iodide on the ocean surface (Pound et al., 2020), which is not implemented in this study.  
271 Thus, the model has limitations in reproducing oxidants abundances, even though the general  
272 seasonality in  $\text{O}_3$  with increases in winter and decreases in summer was reproduced (Fig. 1e). We  
273 therefore note that our estimates in the relative contributions of sulfate formation processes bear  
274 an uncertainty associated with oxidant abundances despite good reproducibilities in  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$   
275 as shown later in Section 3.2 (Fig. 2). The further precise prediction of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  will  
276 require improvements in oxidants reproducibility in the future.

277 This version of the model includes gas phase oxidation of  $\text{SO}_2$  by OH, in-cloud aqueous  
278 phase oxidations of S(IV) by  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$  (Park et al., 2004), and HOBr (Chen et al., 2017), and  
279 oxidation of S(IV) by  $\text{O}_3$  on sea salt particles (Alexander et al., 2005). For in-cloud reactions, the  
280 cloud fraction and the liquid water content of cloud are obtained from MERRA-2 meteorological  
281 fields. For pH-dependent reactions such as in-cloud S(IV) +  $\text{O}_3$  and S(IV) + HOBr, the effect of  
282 heterogeneity of cloud pH on S(IV) partitioning is accounted as described in Alexander et al.  
283 (2012). The model assumes in-cloud sulfate formations are prohibited at temperature  $< -15^\circ\text{C}$  as  
284 originally designed by Park et al. (2004). We confirmed that this assumption limits the annual  
285 tropospheric sulfate production via aqueous-phase reactions to 13.8 Gg-S on the Antarctic  
286 Plateau ( $> 68^\circ\text{S}$ ) in contrast to 137.0 Gg-S on the Southern Ocean ( $60\text{--}68^\circ\text{S}$ ) within longitudes  
287 of  $0\text{--}180^\circ\text{E}$  (Fig. S3). This result is consistent with the limited occurrence frequency of super-  
288 cooled-liquid-water containing cloud (0–10%) over the Antarctic Plateau compared to over the  
289 Southern Ocean (20–60%) (Listowski et al., 2019). S(IV) +  $\text{O}_3$  in sea-salt is assumed as a  
290 function of  $\text{SO}_2$  transfer rate constant from the gas to the aerosol phase, because the rate limiting



291 step is not the aqueous-phase reaction rate of S(IV) + O<sub>3</sub> in alkaline solution on fresh sea-salt but  
 292 is gas-phase diffusion of SO<sub>2</sub> to the aerosol surface (Alexander et al., 2005). This reaction is  
 293 calculated only within MBL column, where the newly emitted sea-salt is available, assuming that  
 294 sea-salt alkalinity is rapidly consumed by this reaction in addition to the uptake of gas form  
 295 H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> (Alexander et al., 2005).

296 We modified the model to tag sulfate produced via each oxidation pathway as different  
 297 tracers which are transported, as originally described in Alexander et al. (2005). As atmospheric  
 298 SO<sub>2</sub> rapidly attains isotopic equilibrium with H<sub>2</sub>O ( $\Delta^{17}\text{O} = 0 \text{ ‰}$ ) (Barkan and Luz, 2005; Holt et  
 299 al., 1981),  $\Delta^{17}\text{O}$  value of sulfate produced via each formation pathway is determined by  $\Delta^{17}\text{O}$   
 300 value of corresponding oxidant and their transferring factors (Savarino et al., 2000). Since OH  
 301 also efficiently exchanges its oxygen isotopes with water vapor (Dubey et al., 1997),  $\Delta^{17}\text{O}(\text{OH})$   
 302 is also 0 ‰ under regions where water vapor is abundant (e.g., throughout most of the  
 303 troposphere) (Lyons, 2001; Morin et al., 2007). Therefore, gas-phase SO<sub>2</sub> + OH produces sulfate  
 304 with  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  is assumed to be 0 ‰. Note that it has been previously suggested that  
 305  $\Delta^{17}\text{O}(\text{OH})$  can be 1–3 ‰ at Dome C (Savarino et al., 2016) due to the limited availability of  
 306 water vapor in inland Antarctica. We also conducted the calculation with  $\Delta^{17}\text{O}(\text{OH}) = 3 \text{ ‰}$  as a  
 307 maximum case, which is expected to produce sulfate with  $\Delta^{17}\text{O}(\text{SO}_4^{2-}) = 0.75 \text{ ‰}$  with assuming  
 308 oxygen atom transferring factor of 0.25. We note that there remains possibility that  $\Delta^{17}\text{O}(\text{OH})$  is  
 309 higher than 3 ‰ (Savarino et al., 2016), that might cause underestimates in  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$ . The  
 310  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  value of sulfate produced via aqueous-phase S(IV) + H<sub>2</sub>O<sub>2</sub> is assumed to be  $0.8 \pm$   
 311  $0.2 \text{ ‰}$  based on  $\Delta^{17}\text{O}(\text{H}_2\text{O}_2)$  of  $1.6 \pm 0.3 \text{ ‰}$  (Savarino and Thiemens, 1999) with a transferring  
 312 factor of 0.5 (Savarino et al., 2000). Note that the  $\Delta^{17}\text{O}(\text{H}_2\text{O}_2)$  is derived from only one set of  
 313 observations at La Jolla, California, and thus needs further verification in various environment in  
 314 the future. For  $\Delta^{17}\text{O}(\text{O}_3)$ , among the whole sets of observations to the present, the two early  
 315 studies using cryogenic technique had shown large variabilities ( $24.7 \pm 11.4 \text{ ‰}$  and  $26.5 \pm 5.0$   
 316  $\text{‰}$ ; Krankowsky et al., 1995; Johnston and Thiemens, 1997). Such variabilities were much  
 317 greater than those expected from the experimentally determined pressure and temperature  
 318 dependency of  $\Delta^{17}\text{O}(\text{O}_3)$ , e.g., a decrease of only  $\sim 2 \text{ ‰}$  for an pressure increase from 500 to 760  
 319 Torr (Morton et al., 1990; Thiemens and Jackson, 1990) and a increase of only  $\sim 5 \text{ ‰}$  for an  
 320 temperature increase from 260 to 320 K (Morton et al., 1990; Janssen et al., 2003). Based on  
 321 these experimental data, it has been pointed out that these observations would have random  
 322 errors associated with sampling artifacts (Mauersberger et al., 2003). Therefore, we exclude the  
 323 data of these two studies from the consideration. Given the consistency of the  $\Delta^{17}\text{O}(\text{O}_3)$   
 324 observations using nitrite-coated method among various locations and seasons including at  
 325 Dome C and DDU (Vicars and Savarino et al., 2014; Savarino et al., 2016; Ishino et al., 2017),  
 326 we decided to use the average value of the  $\Delta^{17}\text{O}(\text{O}_3)$  observations, which comes to  $25.6 \pm 1.3 \text{ ‰}$ .  
 327 The  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  for S(IV) + O<sub>3</sub>, both in cloud and in sea salt, is assumed to be  $6.4 \pm 0.3 \text{ ‰}$ , by a  
 328 transferring factor of 0.25 (Savarino et al., 2000). Since aqueous-phase S(IV) oxidation by HOBr  
 329 gives an oxygen atom from liquid water to produce sulfate (Fogelman et al., 1989; Troy and  
 330 Margerum, 1991; Liu et al., 2001), the obtained  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  is expected to be 0 ‰. Therefore,  
 331 the  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  values in the model were calculated by adding all sulfate isotope tracers  
 332 following the mass-balance equation:

$$333 \quad \Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}} = 0 \cdot F_{\text{SO}_2+\text{OH}} + 0.8 \cdot F_{\text{S(IV)+H}_2\text{O}_2} + 6.4 \cdot F_{\text{S(IV)+O}_3} + 0 \cdot F_{\text{S(IV)+HOBr}}, \quad (4)$$

334

$$F_i = \frac{[\text{SO}_4^{2-}]_i}{[\text{SO}_4^{2-}]_{\text{SO}_2+\text{OH}} + [\text{SO}_4^{2-}]_{\text{S(IV)}+\text{H}_2\text{O}_2} + [\text{SO}_4^{2-}]_{\text{S(IV)}+\text{O}_3} + [\text{SO}_4^{2-}]_{\text{S(IV)}+\text{HOBr}}, \quad (5)$$

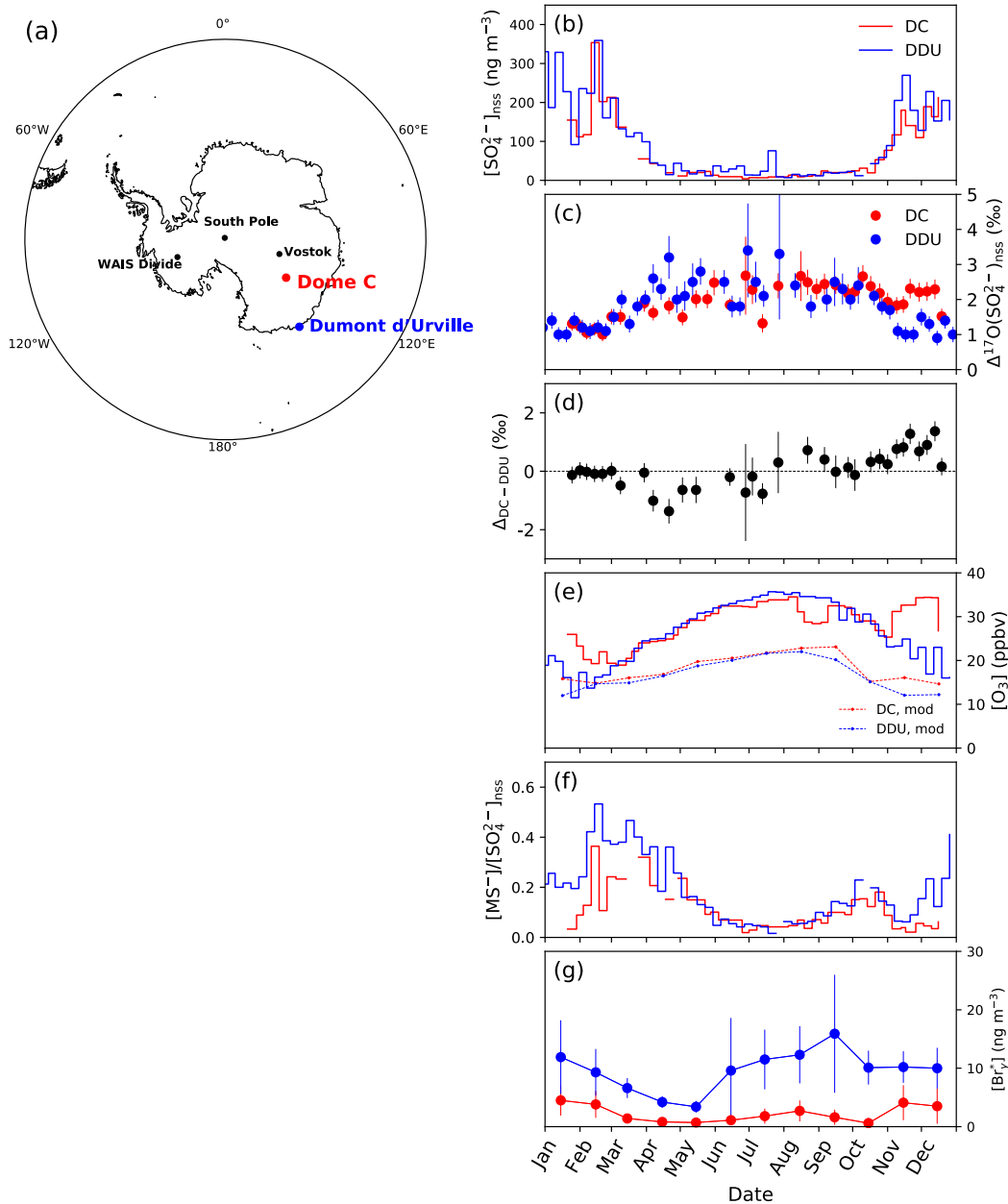
336 where  $F_i$  represents the relative fraction of sulfate produced via each formation pathway  $i$ ,  
 337 respective to total sulfate concentration in each model grid. To calculate the  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$   
 338 values and compare to the observations, the modeled  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  values of each grid  
 339 including Dome C and DDU were mass-weighted averaged within the planetary boundary layer.  
 340  
 341

### 342 **3 Results**

#### 343 3.1 $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$ values observed at Dome C and comparison to DDU

344 Figure 1 shows nss- $\text{SO}_4^{2-}$  concentrations ( $[\text{SO}_4^{2-}]_{\text{nss}}$ ) and  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  at Dome C  
 345 throughout 2011 in comparison to those previously reported for DDU (Ishino et al., 2017). Note  
 346 that the concentration data are presented in Ishino et al. (2019). It is well-established that  
 347  $[\text{SO}_4^{2-}]_{\text{nss}}$  is enhanced during austral summer and reduced during winter, a seasonality that is  
 348 driven by marine biogenic emission of DMS (Preunkert et al., 2007, 2008; Legrand et al.,  
 349 2017b). This seasonal cycle in  $[\text{SO}_4^{2-}]_{\text{nss}}$  is partially intensified by atmospheric dynamics due to  
 350 enhanced efficiency of meridional long-range transport and the weakened inversion layer on the  
 351 Antarctic Plateau during summer, as previously suggested by the similar seasonal cycle with  
 352  $^{210}\text{Pb}$  (Elsässer et al., 2011; Legrand et al., 2017b).  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  show lower values in austral  
 353 summer and higher values in winter, with monthly-mean values ranging from  $1.1 \pm 0.1$  ‰ in  
 354 February to  $2.5 \pm 0.2$  ‰ in August, with a mass-weighted annual average of  $1.7 \pm 0.1$  ‰ (Table  
 355 1). These trends and values are generally consistent with previous observations at Dome C in  
 356 2010 (Hill-Falkenthal et al., 2013) as well as at DDU in 2011 (Ishino et al., 2017).

357 Figure 1d shows  $\Delta_{\text{DC-DDU}}$ , the differences in weekly  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  values between the  
 358 two sites in the year 2011. Throughout most of the year,  $\Delta_{\text{DC-DDU}}$  is 0 ‰ within the range of the  
 359 estimated uncertainty. However, there are two specific time periods exhibiting  $\Delta_{\text{DC-DDU}}$  values  
 360 different from 0 ‰. One is from October to December, a transition from the austral spring to  
 361 summer, when a group of positive  $\Delta_{\text{DC-DDU}}$  values ranging  $0.4 \pm 0.3$  ‰ to  $1.4 \pm 0.3$  ‰ are  
 362 observed. The second is found from March to May, the austral autumn, when negative  $\Delta_{\text{DC-DDU}}$   
 363 values ranging  $-1.4 \pm 0.6$  ‰ to  $-0.5 \pm 0.3$  ‰ are observed. These  $\Delta_{\text{DC-DDU}}$  values different from  
 364 zero suggest that sulfate at Dome C and DDU experienced different oxidation processes during  
 365 their transport from source regions. The possible processes corresponding to these  $\Delta_{\text{DC-DDU}}$   
 366 values are discussed in Section 4.  
 367



368

**Figure 1.** (a) Map of stations cited in this study. (b-g) Observed seasonal variations of (b) non-sea-salt sulfate concentrations, (c)  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  values (from this study and Ishino et al., 2017), (d) residual  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  values between Dome C and DDU ( $\Delta_{\text{DC-DDU}}$ , see section 3.1), (e) ozone mixing ratios (Legrand et al., 2016a), (f)  $[\text{MS}^-]/[\text{SO}_4^{2-}]_{\text{nss}}$  ratios (Legrand et al., 2017b; Ishino et al., 2017), and (g) total gaseous reactive bromine species ( $\text{Br}_y^*$ ) (Legrand et al., 2016b) at Dome C (red) and DDU (blue). Error bars in (b) and (c) represent the uncertainties propagated from analytical errors of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  and concentration, and the uncertainty in  $k$  value ( $[\text{SO}_4^{2-}]_{\text{ss}}/[\text{Na}^+]$  mass ratio) in sea-salt. The modeled ozone mixing ratios are also shown in (d). The red and blue shaded areas indicate the time periods showing positive and negative  $\Delta_{\text{DC-DDU}}$  values, respectively.

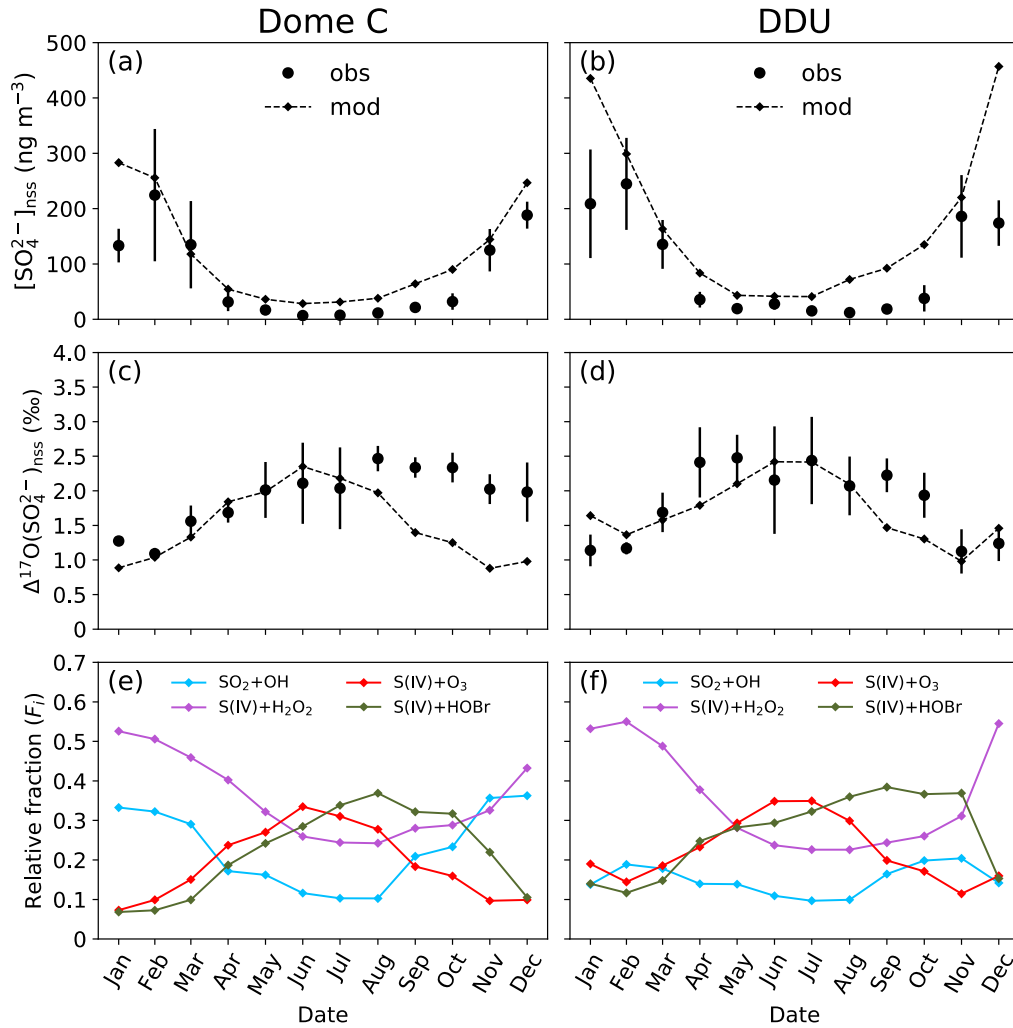
379

### 3.2 Modeled sulfate formation processes and $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$ values

Figure 2 shows the modeled monthly  $[\text{SO}_4^{2-}]_{\text{nss}}$  and mass-weighted  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  averaged within planetary boundary layer in the model grids including Dome C and DDU, with comparison to the monthly-mean observations ( $\pm 1\sigma$ ). The modeled  $[\text{SO}_4^{2-}]_{\text{nss}}$  reproduces the seasonality of the observations with austral summer maxima and winter minima, but the model overestimates  $[\text{SO}_4^{2-}]_{\text{nss}}$  observations for summer (DJF) and winter (JJA) by a factor of 2 and 4 at Dome C, and 2 and 3 at DDU, respectively. Chen et al. (2018) reported that GEOS-Chem model run with DMS concentration in seawater from Lana et al. (2011) and without DMS oxidation by BrO, the condition used in this study, overestimates mixing ratio of DMS by a factor of 5 and 21 during summer and winter at DDU, respectively. This is likely a main reason for the overestimate of  $[\text{SO}_4^{2-}]_{\text{nss}}$  at DDU and Dome C, as DMS oxidation is thought to be the main source of sulfate in these locations (e.g., Minikin et al., 1998; Ishino et al., 2019). We note that the overestimate of  $[\text{SO}_4^{2-}]_{\text{nss}}$  could lead to an underestimate of  $F_{\text{S(IV)+O}_3}$  and thus  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  in the model as we discuss in Section 4.

The model also reproduces the seasonality of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  in the observations with austral summer minima and austral winter maxima, ranging from 0.9 ‰ (0.8–1.3 ‰, November and January) to 2.4 ‰ (2.2–2.6 ‰, June) and from 1.0 ‰ (0.9–1.2 ‰, November) to 2.4 ‰ (2.3–2.6 ‰, June–July) at Dome C and DDU, respectively. The modeled seasonality results from changes in the relative fractions of sulfate formed via different processes,  $F_i$  in Eq. (5) (Figure 2e, f; Table 1). During austral summer at Dome C, the relative fractions of sulfate formed by OH ( $F_{\text{SO}_2+\text{OH}}$ ) and  $\text{H}_2\text{O}_2$  ( $F_{\text{S(IV)+H}_2\text{O}_2}$ ) increase to 34% and 49%, respectively (Table 1), because solar radiation induces production of these oxidants. In contrast, the  $F_{\text{S(IV)+O}_3}$  increases to 31% during winter, when production of OH and  $\text{H}_2\text{O}_2$  is diminished. Since S(IV) + O<sub>3</sub> is the only sulfate-formation pathway that leads to  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}} > 1$  ‰, the modeled  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  values (> 2 ‰ in winter) mainly reflect the change in the relative importance of this pathway. The sulfate formed via S(IV) + HOBr ( $F_{\text{S(IV)+HOBr}}$ ), which has  $\Delta^{17}\text{O}(\text{SO}_4^{2-}) = 0$  ‰, also increases to 33% during winter, limiting the increase of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  in the model. Although similar seasonal trends for sulfate formation pathways are found for DDU (Fig. 2f),  $F_{\text{SO}_2+\text{OH}}$  is significantly higher at Dome C (34% in summer) than DDU (16% in summer) (Table 1). This is because the model prohibits aqueous-phase sulfate production at temperatures lower than  $-15^\circ\text{C}$  and therefore most sulfate formation along with the transport of precursors towards inland Antarctica occurs through gas-phase  $\text{SO}_2 + \text{OH}$  pathway.

As a result of these estimates in sulfate formation pathways, the model roughly reproduces the observed seasonality and magnitude of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  (Fig. 2c, d). However, the model largely underestimates observed  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  from August to December at Dome C by 0.5 to 1.1 ‰ (Fig. 2c), partially overlapping the period when the significantly positive  $\Delta_{\text{DC-DDU}}$  values were observed in October to December. This underestimate implies that the model might lack sulfate formation processes that causes  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  of higher than  $2.0 \pm 0.3$  ‰ at the inland site (Table 1) and thus the positive  $\Delta_{\text{DC-DDU}}$  in this time period. Meanwhile for DDU, the model also underestimates  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  from September to October by 0.6 to 0.8 ‰, but rather slightly overestimates in January by 0.5 ‰ (Fig. 2d). This result is further discussed in the following sections within the focus of the observed inter-site differences.



424

425 **Figure 2.** Comparison of observed and modeled values of (a, b) non-sea-salt sulfate  
 426 concentration and (c, d)  $\Delta^{17}O(SO_4^{2-})_{nss}$ , and (e, f) calculated relative fraction of sulfate produced  
 427 via different formation pathways ( $F_i$ , see Section 2.4), in the model. Left and right columns show  
 428 results for Dome C and DDU, respectively.

429

430 **Table 1.** Model calculation of relative fraction of sulfate produced via different formation  
 431 pathways and  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  values in each season in comparison to the observed  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$   
 432 values (seasonal mean).

Site	Period	Observation		Model				
		Number	$\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}(\text{‰})$	$\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}(\text{‰})^b$	$F_{\text{SO}_2+\text{O}_3}$	$F_{\text{S(IV)+H}_2\text{O}_2}$	$F_{\text{S(IV)+O}_3}$	$F_{\text{S(IV)+HOBr}}$
Dome C	Annual	37	$2.0 \pm 0.5$ ( $1.7 \pm 0.1$ ) <sup>a</sup>	1.5 (1.4-1.8)	0.23	0.34	0.18	0.25
	DJF	8	$1.5 \pm 0.5$	1.0 (0.8-1.4)	0.34	0.46	0.07	0.12
	MAM	9	$1.8 \pm 0.3$	1.7 (1.6-2.0)	0.21	0.38	0.21	0.20
	JJA	8	$2.2 \pm 0.5$	2.2 (2.0-2.4)	0.11	0.24	0.29	0.36
	SON	12	$2.2 \pm 0.2$	1.2 (1.1-1.5)	0.27	0.26	0.13	0.34
	OND	9	$2.0 \pm 0.3$	1.0 (0.9-1.4)	0.32	0.32	0.11	0.26
DDU	Annual	46	$1.8 \pm 0.7$ ( $1.4 \pm 0.1$ ) <sup>a</sup>	1.7 (1.6-2.0)	0.15	0.34	0.21	0.29
	DJF	13	$1.2 \pm 0.2$	1.5 (1.3-1.8)	0.16	0.52	0.13	0.18
	MAM	12	$2.2 \pm 0.5$	1.8 (1.7-2.1)	0.15	0.37	0.23	0.24
	JJA	10	$2.2 \pm 0.8$	2.3 (2.2-2.5)	0.10	0.22	0.32	0.34
	SON	11	$1.8 \pm 0.6$	1.3 (1.2-1.5)	0.19	0.25	0.15	0.41
	OND	9	$1.3 \pm 0.3$	1.3 (1.1-1.5)	0.18	0.35	0.13	0.34

Note. <sup>a</sup> Mass-weighted average. <sup>b</sup> Values shown in parenthesis are possible ranges in case taking variabilities in  $\Delta^{17}\text{O}$  of oxidants into account (see Section 2.4).

433

#### 434 4 Discussion

435 The  $\Delta_{\text{DC-DDU}}$  values different from 0 ‰ during the austral spring to summer (October–  
 436 December) and during the austral autumn (March–May) (Fig. 1d) suggest that some fractions of  
 437 sulfate existing at these inland and coastal sites experienced different oxidation processes. The  
 438 possible processes may include long-range transport of sulfate produced above the other  
 439 continents or in the stratosphere (i.e., nmb- $\text{SO}_4^{2-}$ ), in addition to DMS-sourced sulfate produced  
 440 within the troposphere above the Antarctic continents and the Southern Ocean. In the former  
 441 case, it is expected that  $\delta^{34}\text{S}_{\text{nss}}$  values in the same aerosol samples would specifically decrease  
 442 during the corresponding periods, since nmb- $\text{SO}_4^{2-}$  has lower  $\delta^{34}\text{S}_{\text{nss}}$  values than DMS-sourced  
 443 sulfate (Patris et al., 2000; Pruet et al., 2004; Ishino et al., 2019). Indeed, Ishino et al. (2019)  
 444 found an unexpected decrease of  $\delta^{34}\text{S}_{\text{nss}}$  at Dome C in November, suggesting a significant input

445 of nmb-SO<sub>4</sub><sup>2-</sup>, which is likely attributed to long-range transport of continental submicron  
 446 aerosols based on a significant correlation with <sup>210</sup>Pb tracer. This input of nmb-SO<sub>4</sub><sup>2-</sup> in  
 447 November overlaps the period of the positive Δ<sub>DC-DDU</sub> values. However, there were not  
 448 significant correlations observed for the Δ<sub>DC-DDU</sub> compared to δ<sup>34</sup>S<sub>nss</sub> (*p* = 0.39) and <sup>210</sup>Pb (*p* =  
 449 0.15) at Dome C (Fig. 3a, 3b, and Table S1). Therefore, this nmb-SO<sub>4</sub><sup>2-</sup> is not likely the main  
 450 factor causing the positive Δ<sub>DC-DDU</sub>, while it may dilute or perturb the high Δ<sup>17</sup>O(SO<sub>4</sub><sup>2-</sup>)<sub>nss</sub>  
 451 signature in that period. Since δ<sup>34</sup>S<sub>nss</sub> values were homogeneous between Dome C and DDU for  
 452 the rest period of the year (Ishino et al., 2019), the negative Δ<sub>DC-DDU</sub> values during the autumn  
 453 would neither be associated with the contribution of nmb-SO<sub>4</sub><sup>2-</sup>. Additionally, whereas the  
 454 deposition of polar stratospheric clouds (PSCs) is thought to be a potential source of tropospheric  
 455 sulfate in Antarctica, it is likely to occur during mid-winter (July–August) (Savarino et al., 2007),  
 456 not coinciding with the positive and negative Δ<sub>DC-DDU</sub> values. Furthermore, the relative  
 457 abundance of <sup>35</sup>S, a radioactive tracer often used as an indicator of stratospheric sulfate, relative to  
 458 total sulfate is maximized in June (Hill-Falkenthal et al., 2013). Therefore, the intrusion of  
 459 stratospheric sulfate is not the likely reason for the Δ<sub>DC-DDU</sub> values discussed here. Thus, below  
 460 we discuss possible influences of regional characteristic chemistry taking place at the scale of the  
 461 Antarctic continent on Δ<sup>17</sup>O(SO<sub>4</sub><sup>2-</sup>)<sub>nss</sub> during these periods.  
 462

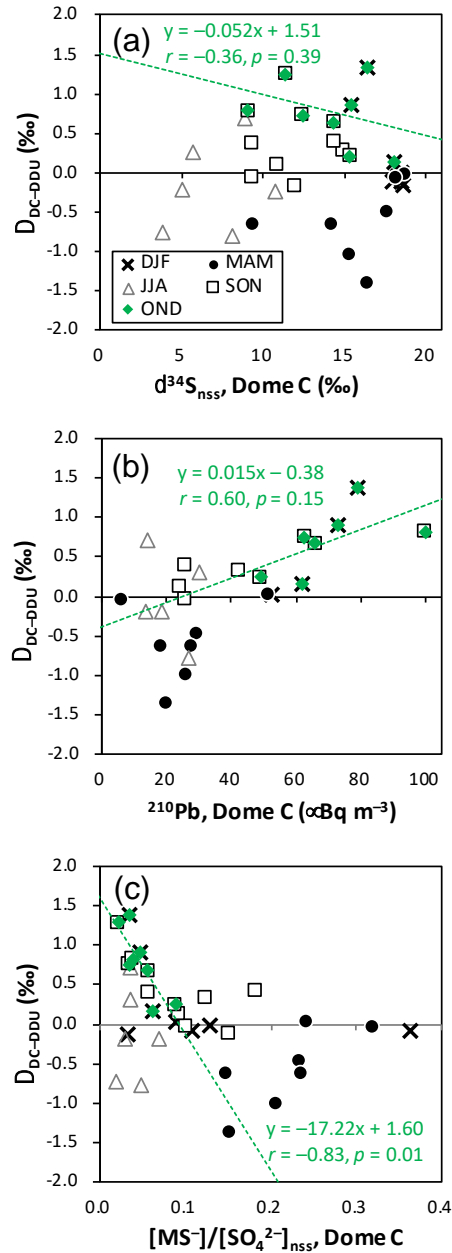
#### 463 4.1 Positive Δ<sub>DC-DDU</sub> values in austral spring to summer

464 Positive Δ<sub>DC-DDU</sub> in spring–summer coincides with a [O<sub>3</sub>] increase from 25 ppb to 34 ppb  
 465 at Dome C (Fig. 1e) and a significant drop of [MS<sup>-</sup>]/[SO<sub>4</sub><sup>2-</sup>]<sub>nss</sub> ratios at Dome C (Fig. 1f) from  
 466 0.13 ± 0.04 (October) to 0.05 ± 0.02 (January). [MS<sup>-</sup>]/[SO<sub>4</sub><sup>2-</sup>]<sub>nss</sub> generally shows a bimodal  
 467 seasonal cycle with slight increase from winter (July–August; 0.06 ± 0.01) to spring (October;  
 468 0.13 ± 0.04), followed by a significant drop in summer (January; 0.05 ± 0.02) and then increases  
 469 to maximum values in autumn (March; 0.25 ± 0.09) at Dome C (Legrand et al., 2017b). Legrand  
 470 et al. (2017b) found that the decline of [MS<sup>-</sup>]/[SO<sub>4</sub><sup>2-</sup>]<sub>nss</sub> during summer coincides with periods of  
 471 high photochemical activity as indicated by high O<sub>3</sub> levels, suggesting the occurrence of  
 472 chemical destruction of MS<sup>-</sup>. Legrand et al. (2017b) also showed that the decrease in [MS<sup>-</sup>  
 473 ]/[SO<sub>4</sub><sup>2-</sup>]<sub>nss</sub> at DDU is less significant than Dome C, while MS<sup>-</sup> destruction may also occur at  
 474 DDU where is frequently exposed to the highly oxidative atmosphere from the interior  
 475 Antarctica during summer due to katabatic wind (Legrand et al., 2016a). The co-occurrence of  
 476 MS<sup>-</sup> destruction at Dome C and positive Δ<sub>DC-DDU</sub> (Fig. 1d and 1f) is striking, suggesting the  
 477 possibility that MS<sup>-</sup> destruction produces sulfate with significantly high Δ<sup>17</sup>O(SO<sub>4</sub><sup>2-</sup>)<sub>nss</sub> at Dome  
 478 C and leads to the high Δ<sub>DC-DDU</sub>. This possibility is supported by the negative co-variation  
 479 between the Δ<sub>DC-DDU</sub> and [MS<sup>-</sup>]/[SO<sub>4</sub><sup>2-</sup>]<sub>nss</sub> at Dome C for October to December with *p* value of  
 480 0.01 (Fig. 3c and Table S1), where Δ<sub>DC-DDU</sub> tends to be higher as [MS<sup>-</sup>]/[SO<sub>4</sub><sup>2-</sup>]<sub>nss</sub> becomes  
 481 lower.

482 This hypothesis requires that MS<sup>-</sup> possesses significantly high Δ<sup>17</sup>O signature or MS<sup>-</sup>  
 483 destruction occurs via its oxidation by O<sub>3</sub> to produce sulfate. It is known that MS<sup>-</sup> formation in  
 484 the marine boundary layer involves O<sub>3</sub> as well as BrO, which is produced via Br + O<sub>3</sub> (Zhang et  
 485 al., 1997), as important oxidants (von Glasow and Crutzen, 2004; Hoffmann et al., 2016). These  
 486 oxidants would imprint a high Δ<sup>17</sup>O value on MS<sup>-</sup>. To date, however, there are no observations  
 487 or estimates of Δ<sup>17</sup>O(MS<sup>-</sup>). The mechanism and the subsequent products of MS<sup>-</sup> destruction in  
 488 inland Antarctica remain unclear. While MS<sup>-</sup> oxidation by OH, SO<sub>4</sub><sup>-</sup>, Cl, and Cl<sub>2</sub><sup>-</sup> have been

489 proposed so far (Zhu et al., 2003a, 2003b; Zhu, 2004), there is no evidence for a reaction with  
490  $O_3$ . A previous box model study simulating multi-phase sulfur chemistry (Hoffmann et al., 2016)  
491 indicated that aqueous-phase oxidation of  $MS^-$  by OH to produce sulfate (Zhu et al., 2003a) is  
492 the dominant pathway under typical pristine marine boundary layer (MBL) conditions (Bräuer et  
493 al., 2013). Furthermore, it is also shown by a flow tube chamber experiment that  $MS^-$  can be  
494 oxidized on deliquesced aerosols to form sulfate, which may lead to shorter lifetime of  $MS^-$  than  
495 in condensed aqueous-phase in MBL (Mungall et al., 2018). Legrand et al. (2017b) mentioned  
496 that, although the chance of aerosol experiencing aqueous-phase chemistry is far lower than in  
497 the marine boundary layer, far more acidic conditions on the Antarctic Plateau compared to the  
498 marine boundary layer would favor the production of OH via the reaction of  $O_3$  with  $O_2^-$  (Ervens  
499 et al., 2003). Thus, here we assume  $MS^-$  oxidation by OH in aqueous-phase or on aerosols as the  
500 mechanism for  $MS^-$  destruction, and for the first time estimate  $\Delta^{17}O$  transferred from DMS  
501 oxidation to  $MS^-$  and then to sulfate.  
502

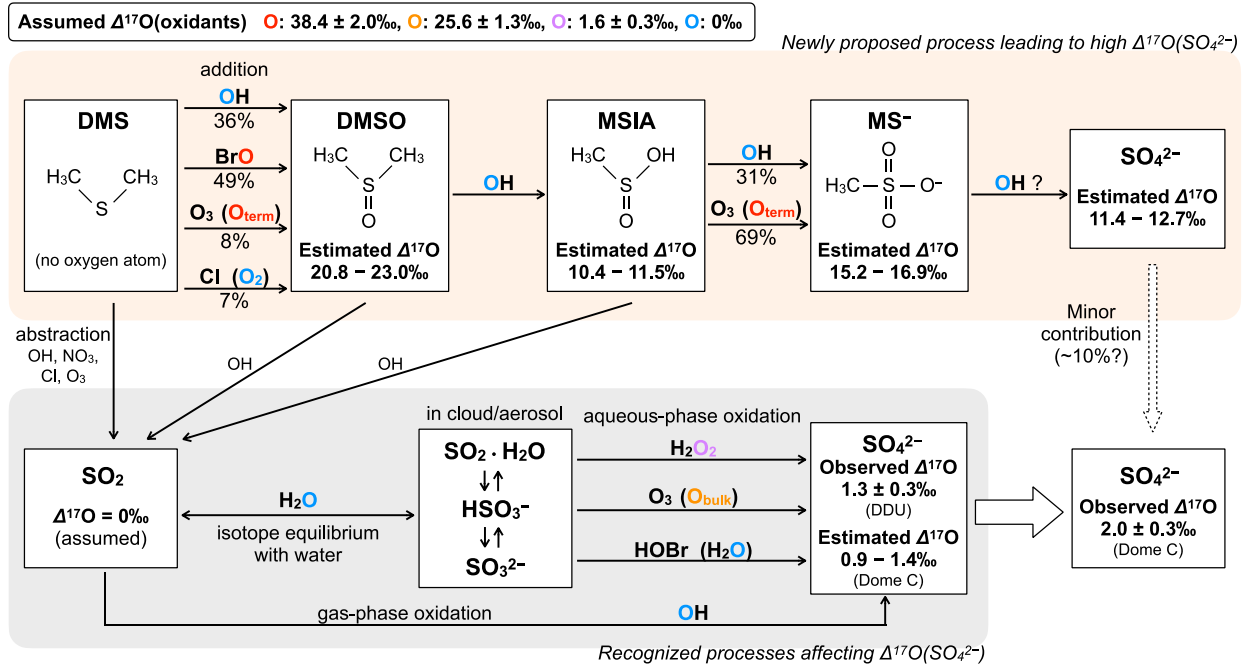




503

504 **Figure 3.** Variations of  $\Delta_{DC-DDU}$  against (a)  $\delta^{34}S_{nss}$ , (b)  $^{210}Pb$ , and (c)  $[MS^-]/[SO_4^{2-}]_{nss}$ , at Dome  
 505 C. Data for summer (DJF), autumn (MAM), winter (JJA), and spring (SON) are plotted with  
 506 crosses, circles, triangles, and squares, respectively. Data for October 29th to December 23rd  
 507 (OND) are plotted with green diamonds, with the linear least-squares fit shown by green dashed  
 508 lines.

509



**Figure 4.** Schematic of sulfate formation processes affecting  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  considered in this study. The processes in upper row (orange shaded) are described in Section 4.1, whereas those in lower row (grey shaded) are described in Section 2.4. The  $\Delta^{17}\text{O}$  of oxidants are indicated by different colors. The  $\Delta^{17}\text{O}$  of sulfur species shown in the figure represent the mean values for October to December. The percentages shown under arrows are the relative contributions of each pathway averaged within the troposphere in 60–90°S during October to December, which are estimated by the model with detailed DMS chemistry by Chen et al. (2018).

**Table 2.** Expected  $\Delta^{17}\text{O}$  values of sulfur species produced through oxidation of DMS from different reaction mechanisms.

Reaction	$\Delta^{17}\text{O}(X)_j$	Reference
DMS + OH (add)	$\Delta^{17}\text{O}(\text{DMSO})_{\text{DMS}+\text{OH}} = \Delta^{17}\text{O}(\text{OH})$	Barnes et al. (2006)
DMS + BrO	$\Delta^{17}\text{O}(\text{DMSO})_{\text{DMS}+\text{BrO}} = \Delta^{17}\text{O}(\text{BrO}) = \Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$	Ingham et al. (1999)
DMS + O <sub>3</sub>	$\Delta^{17}\text{O}(\text{DMSO})_{\text{DMS}+\text{O}_3} = \Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$	Gershenzon et al. (2001)
DMS + Cl (+ O <sub>2</sub> )	$\Delta^{17}\text{O}(\text{DMSO})_{\text{DMS}+\text{Cl}} = \Delta^{17}\text{O}(\text{O}_2)$	Barnes et al. (2006)
DMSO + OH	$\Delta^{17}\text{O}(\text{MSIA})_{\text{DMSO}+\text{OH}} = 1/2 \Delta^{17}\text{O}(\text{DMSO}) + 1/2 \Delta^{17}\text{O}(\text{OH})$	Wang and Zhang (2002)
MSIA + OH	$\Delta^{17}\text{O}(\text{MS}^-)_{\text{MSIA}+\text{OH}} = 2/3 \Delta^{17}\text{O}(\text{MSIA}) + 1/3 \Delta^{17}\text{O}(\text{OH})$	Gonzalez-Garcia et al. (2007); Tian et al. (2007)
MSIA + O <sub>3</sub>	$\Delta^{17}\text{O}(\text{MS}^-)_{\text{MSIA}+\text{O}_3} = 2/3 \Delta^{17}\text{O}(\text{MSIA}) + 1/3 \Delta^{17}\text{O}(\text{O}_3)_{\text{term}}$	Flyunt et al. (2001); Kukui et al. (2000)
MS <sup>-</sup> + OH	$\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{MS}+\text{OH}} = 3/4 \Delta^{17}\text{O}(\text{MS}^-) + 1/4 \Delta^{17}\text{O}(\text{OH})$	Zhu et al., (2003a); Hoffmann et al. (2016)

521

522 Figure 4 summarizes the hypothesized sulfate formation processes via  $MS^-$  oxidation  
 523 possibly transferring high  $\Delta^{17}O$  to sulfate, in addition to the recognized processes explained in  
 524 Section 2.4. The reaction scheme includes DMS oxidation into dimethyl sulfoxide (DMSO;  
 525  $CH_3S(O)CH_3$ ), methyl sulfinic acid (MSIA;  $CH_3S(O)OH$ ), and then to  $MS^-$ , as well as  
 526 production of  $SO_2$  from each species, whose importance in the marine boundary layer are  
 527 recognized (Barnes et al., 2006; von Glasow and Crutzen, 2004; Hoffmann et al., 2016; Chen et  
 528 al., 2018). Note that gas-phase and aqueous-phase reactions using the same oxidants are  
 529 considered as one pathway for simplification, since they will result in the same  $\Delta^{17}O(SO_4^{2-})$ . We  
 530 also summarize the formula for calculating the  $\Delta^{17}O$  value of each sulfur species  $X$  (DMSO,  
 531 MSIA,  $MS^-$ , and  $SO_4^{2-}$ ) produced by each reaction  $j$  ( $\Delta^{17}O(X)_j$ ) in Table 2, which is determined  
 532 based on mechanisms of respective oxidation pathways as follows.

533 At the first step, DMS oxidation into DMSO includes four different oxidation pathways  
 534 reacting with OH, BrO,  $O_3$ , and Cl. These reactions generally occur through adduct of the  
 535 oxidant to the sulfur atom of DMS (Barnes et al., 2006; Ingham et al. 1999; Gershenzon et al.,  
 536 2001), transferring oxygen atoms of oxidants to the produced DMSO. Therefore, the  $\Delta^{17}O$   
 537 transferred to DMSO via  $DMS + OH$ ,  $DMS + BrO$ , and  $DMS + O_3$  reflect  $\Delta^{17}O$  values of each  
 538 oxidant.  $\Delta^{17}O$  of DMSO produced via  $DMS + OH$  is assumed to be equal to  $\Delta^{17}O$  of OH, i.e., 0  
 539 ‰. Since  $^{17}O$  excess is located at the two terminal O atoms of  $O_3$  ( $O_3$ -terminal) (Bhattacharya et  
 540 al., 2008; Janssen and Tuzson, 2006),  $\Delta^{17}O(O_3)_{term}$  is assumed to be  $38.4 \pm 2.0$  ‰ ( $= 3/2 \times$   
 541  $\Delta^{17}O(O_3)_{bulk}$ ). In addition, BrO receives  $O_3$ -terminal via  $Br + O_3$  (Zhang et al., 1997).  $DMS + O_3$   
 542 and  $DMS + BrO$  are thus expected to produce DMSO with  $\Delta^{17}O$  of 39 ‰. Since  $DMS + Cl$   
 543 pathway is expected to form  $CH_3S(Cl)CH_3$ , which is followed by subsequent oxidation by  $O_2$   
 544 (Barnes et al., 2006),  $\Delta^{17}O_{DMS+Cl}$  is assumed to be equal to  $\Delta^{17}O(O_2)$  ( $= -0.3$  ‰; Barkan and Luz,  
 545 2005). During DMSO oxidation by OH into MSIA, one of the two oxygen atoms of produced  
 546 MSIA is from DMSO while another comes from OH (Bardouki et al., 2002), suggesting that  
 547  $\Delta^{17}O(MSIA)_{DMSO+OH}$  is determined as the sum of  $1/2 \Delta^{17}O(DMSO)$  and  $1/2 \Delta^{17}O(OH)$ . MSIA is  
 548 oxidized into  $MS^-$  by OH or  $O_3$ . In  $MSIA + OH$ , O-atom added to  $MS^-$  is assumed to come from  
 549 OH, since OH is added to S-atom of MSIA to form  $CH_3S(O)(OH)_2$  adduct before its reaction  
 550 with  $O_2$  to form  $MS^-$  (Bardouki et al., 2002). In  $MSIA + O_3$ , it is experimentally indicated that  
 551  $O_3$ -terminal transfers to  $MS^-$  (Flyunt et al., 2001). In both reactions, two of three O-atoms of  
 552  $MS^-$  are preserved from MSIA. Therefore,  $\Delta^{17}O$  transferring to  $MS^-$  via each reaction is  
 553 determined as sum of  $2/3 \Delta^{17}O(MSIA)$  and  $1/3 \Delta^{17}O(oxidant)$ . Finally, assuming  $MS^- + OH$   
 554 provides one O-atom from OH to produce sulfate,  $\Delta^{17}O(MS^-)_{MS+OH}$  is determined as the sum of  
 555  $3/4 \Delta^{17}O(MS^-)$  and  $1/4 \Delta^{17}O(OH)$  (Table 2).

556 With the above assumptions on  $\Delta^{17}O$  transferring processes,  $\Delta^{17}O$  value of species  $X$  is  
 557 determined by the isotopic mass balance as the following equation:

558

$$559 \quad \Delta^{17}O(X) = \sum \Delta^{17}O(X)_j f_j \quad , \quad (6)$$

$$560 \quad f_j = P(X)_j / \sum P(X)_j \quad , \quad (7)$$

561

562 where  $f_j$  is relative contribution of reaction  $j$  for production of  $X$  ( $P(X)$ ). To obtain  $\Delta^{17}O(MS^-)$ ,  
 563 we here used  $P(X)_j$  and thus  $f_j$  estimated by the previous simulation using GEOS-Chem by Chen  
 564 et al. (2018), which incorporated whole sulfur chemistry shown in Figure 4. We used the mean  
 565  $P(X)_j$  within the troposphere in 60–90°S during October to December. For production of DMSO,

566  $f_{\text{DMS}+\text{OH}}$ ,  $f_{\text{DMS}+\text{BrO}}$ ,  $f_{\text{DMS}+\text{O}_3}$ , and  $f_{\text{DMS}+\text{Cl}}$  are estimated to be 36%, 49%, 8%, and 7%, respectively.  
 567 By applying these estimated  $f_j$  with  $\Delta^{17}\text{O}(X)_j$  defined in Table 2 and Eq. (6), the  $\Delta^{17}\text{O}(\text{DMSO})$  is  
 568 estimated to be 20.8–23.0 ‰. Since MSIA production occurs via  $\text{DMSO} + \text{OH}$  only ( $f_{\text{DMSO}+\text{OH}} =$   
 569 100%),  $\Delta^{17}\text{O}(\text{MSIA})$  is equivalent to  $\Delta^{17}\text{O}(\text{MSIA})_{\text{DMSO}+\text{OH}} = 10.4\text{--}11.5$  ‰. For production of  
 570  $\text{MS}^-$ ,  $f_{\text{MSIA}+\text{OH}}$  and  $f_{\text{MSIA}+\text{O}_3}$  are estimated to be 31% and 69%, respectively, consequently leading  
 571 to  $\Delta^{17}\text{O}(\text{MS}^-)$  of 15.2–16.9 ‰. Finally,  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$  derived via  $\text{MS}^-$  destruction,  $\Delta^{17}\text{O}_{\text{MS}+\text{OH}}$ , is  
 572 estimated to be 11.4–12.7 ‰.

573 If the oxidation of  $\text{MS}^-$  into sulfate fully corresponds to the difference in  $[\text{MS}^-]/[\text{SO}_4^{2-}]_{\text{nss}}$   
 574 of 0.09 between Dome C ( $0.05 \pm 0.02$ ) and DDU ( $0.14 \pm 0.07$ ) during October to December,  
 575  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  can increase by 1.1 ‰ ( $= \Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{MS}+\text{OH}} \times 0.09$ ), which is close to the  
 576 observed  $\Delta_{\text{DC-DDU}}$  of ca. 0.7 ‰. Additionally, the intercept of the slope of  $\Delta_{\text{DC-DDU}}$  versus  $[\text{MS}^-]$   
 577  $[\text{SO}_4^{2-}]_{\text{nss}}$  relationship (Fig. 3) suggests that  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  can increase by 1.6 ‰ if all  $\text{MS}^-$   
 578 observed at DDU was converted to sulfate at Dome C (i.e.,  $[\text{MS}^-]/[\text{SO}_4^{2-}]_{\text{nss}}$  decreases from  $0.14$   
 579  $\pm 0.07$  to 0), which is consistent with  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{MS}+\text{OH}} \times 0.14 \pm 0.07 = 1.7 \pm 0.9$  ‰. These  
 580 consistencies imply that the positive  $\Delta_{\text{DC-DDU}}$  observed in the austral spring–summer is mainly  
 581 caused by  $\text{MS}^-$  destruction. We therefore conclude that  $\text{MS}^-$  destruction and subsequent sulfate  
 582 production along with transport over the Antarctic Plateau is the most likely process responsible  
 583 for the positive  $\Delta_{\text{DC-DDU}}$  in the austral spring–summer at inland Antarctica.

584 The model underestimate of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  for Dome C during August to December by  
 585 0.5–1.1 ‰ (Fig. 2c) are also within the possible range of the expected shift in  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  by  
 586  $\text{MS}^-$  destruction, i.e., 1.6‰ at maximum (Fig. 3). Note that the  $\text{MS}^-$  destruction becomes  
 587 significant from November (Fig. 1f), only for the latter period of this underestimate of  
 588  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  in the model. Additionally, the model also underestimates  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  for  
 589 DDU during September to October by 0.6–0.8 ‰, while does not during November to  
 590 December. The absence of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  underestimate for DDU during November–December  
 591 is expected because  $\text{MS}^-$  destruction in the mid-summer is less significant at DDU than Dome C  
 592 (Legrand et al., 2017b). On the other hand, the underestimates of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  in early spring at  
 593 both sites indicate the other missing processes such that impacts both sites. One idea that might  
 594 cause the underestimates of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  is the underestimates of  $F_{\text{S(IV)}+\text{O}_3}$  due to the excessive  
 595 sulfur loading (Fig. 2a and 2b). Since  $\text{S(IV)} + \text{O}_3$  reaction prefers higher pH condition, the  
 596 excessive acidification of cloud water and sea-salt aerosols induced by the overestimates of  
 597  $[\text{SO}_4^{2-}]_{\text{nss}}$  may result in suppression of  $\text{S(IV)} + \text{O}_3$ . This idea is uncertain because the  
 598 overestimate of  $[\text{SO}_4^{2-}]_{\text{nss}}$  is not specific for early spring but seen for year-round. Additionally,  
 599 there remains possibility that  $\Delta^{17}\text{O}(\text{OH})$  is higher than 3 ‰ (Savarino et al., 2016), that might  
 600 partially correspond to the underestimates in  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$ . Future modeling work incorporating  
 601 DMSO, MSIA,  $\text{MS}^-$ , and sulfate possessing different  $\Delta^{17}\text{O}$  signatures is necessary to examine if  
 602 this underestimate in  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  at Dome C corresponds to the lack of  $\text{MS}^-$  destruction in the  
 603 model.

604 This finding that confirms the suspected occurrence of an efficient atmospheric oxidation  
 605 of  $\text{MS}^-$  into sulfate over the Antarctic plateau has an important implication for the interpretation  
 606 of ice-core  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  records. Previous studies revealed that, in Antarctica,  $\text{MS}^-$  in snow is  
 607 largely lost after deposition (Wagon et al., 1999; Delmas et al., 2003; Weller et al., 2004).  
 608 While the mechanism of this  $\text{MS}^-$  loss in snow is under debated, there are two proposed ideas:  
 609 physical migration of  $\text{MS}^-$  within firn layers and possibly by  $\text{MS}^-$  oxidation by OH in quasi-  
 610 brine layer of snow grain. If being viable, the latter  $\text{MS}^-$  oxidation should increase  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$

611 values in snow after deposition of  $\text{MS}^-$  and sulfate. Indeed, the previous measurements of  
 612  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  in Antarctic ice corresponding to the present-day warm climate period (Holocene)  
 613 average  $2.8 \pm 0.4$  ‰ (Alexander et al., 2002, 2003; Kunasek et al., 2010; Sofen et al., 2014),  
 614 which is significantly higher than the annual mass-weighted average of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  of  $1.7 \pm$   
 615  $0.1$  ‰ in aerosols at Dome C (Table 1). Even the maximum monthly mean  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  of  $2.5$   
 616  $\pm 0.1$  ‰ in July cannot reach the ice-core  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  of  $2.8 \pm 0.4$  ‰, indicating the additional  
 617 sulfate production with the higher  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  in snow after deposition. The degree of post-  
 618 depositional loss of  $\text{MS}^-$  tends to be higher at sites with lower snow accumulation rates (Delmas  
 619 et al., 2003), and reaches 80–90% at Vostok where the present-day snow accumulation rate is  $2.2$   
 620  $\text{g cm}^{-2} \text{ yr}^{-1}$  (Wagon et al., 1999). Assuming 90% of  $\text{MS}^-$  in snow is converted into sulfate at  
 621 Dome C where the accumulation rate ( $2.7 \text{ g cm}^{-2} \text{ yr}^{-1}$ ) is similar to the one in Vostok, combined  
 622 with the annual mean  $[\text{MS}^-]/[\text{SO}_4^{2-}]_{\text{nss}}$  in aerosols of 0.11 (Legrand et al., 2017b),  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$   
 623 can increase by 1.1–1.3 ‰ ( $= \Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{MS+OH}} \times 0.11 \times 0.9$ ) at maximum. This estimated post-  
 624 depositional shift in  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  is in agreement with the difference between atmosphere and  
 625 snow  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$ , indicating the significance of the post-depositional oxidation of  $\text{MS}^-$  to  
 626 sulfate as a controlling factor of ice-core  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$ . Thus, we argue that, to use ice-core  
 627  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  for assessing past atmospheric oxidant chemistry, it is necessary to correct the  
 628 ice-core  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  for this process. For this purpose, the investigation of the relationship  
 629 between  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  and  $[\text{MS}^-]/[\text{SO}_4^{2-}]_{\text{nss}}$  in snow at various sites with different snow  
 630 accumulation rates over Antarctica will be required as a future step. Additionally, observations  
 631 of  $\Delta^{17}\text{O}(\text{MS}^-)$  in aerosols, snow, and ice will provide useful information to prove the proposed  
 632 mechanisms as well as to constrain the sulfur chemistry in atmospheric chemical transport  
 633 models.

634

#### 635 4.2 Negative $\Delta_{\text{DC-DDU}}$ values in austral autumn

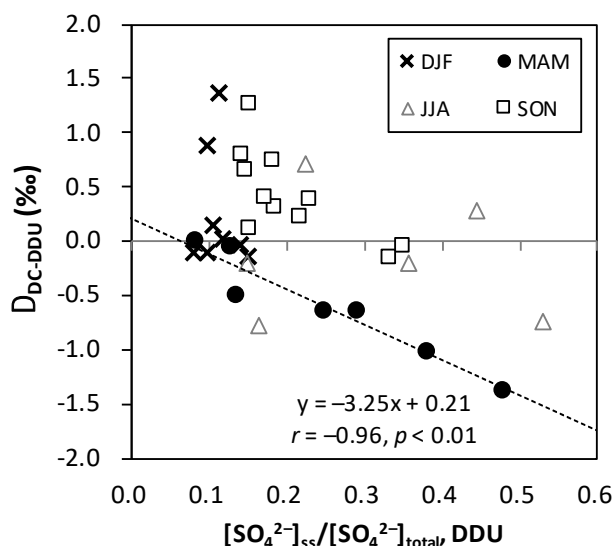
636 The negative  $\Delta_{\text{DC-DDU}}$  values ranging  $-1.4 \pm 0.6$  ‰ to  $-0.5 \pm 0.3$  ‰ were observed in  
 637 austral autumn (March to May) (Fig. 1d), suggesting that sulfate with higher  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  is  
 638 produced at or transported to DDU, compared to Dome C. The largest negative  $\Delta_{\text{DC-DDU}}$  value of  
 639  $-1.4 \pm 0.6$  ‰ was observed in April. Meanwhile, the model in the present study slightly  
 640 underestimates the observed  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  at DDU in April (modeled: 1.6–2.1 ‰, observed:  $2.4$   
 641  $\pm 0.5$  ‰), but reproduces the observed  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  at Dome C (modeled: 1.7–2.1 ‰,  
 642 observed:  $1.7 \pm 0.1$  ‰) within the range of standard deviation of observations (Fig. 2). Below we  
 643 consider processes that possibly lead to high  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  at DDU in this period and that also  
 644 can explain the underestimate of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  at DDU in the model.

645 The negative  $\Delta_{\text{DC-DDU}}$  values in March to May coincide with the period when  $[\text{Br}_y^*]$  is  
 646 minimal at both sites (Fig. 1g). This  $[\text{Br}_y^*]$  minimum in autumn is thought to be a result of the  
 647 decrease in  $\text{Br}_y$  emission from sea-salt provided from both open ocean and sea-ice related  
 648 process (Legrand et al., 2016b). Since  $\text{Br}_y^*$  includes HOBr that reacts with S(IV) to produce  
 649 sulfate with  $\Delta^{17}\text{O}(\text{SO}_4^{2-}) = 0$  ‰ as mentioned in Section 2.4, the decrease in  $[\text{Br}_y^*]$  may cause the  
 650 reduction of  $F_{\text{S(IV)+HOBr}}$  and the increase in  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$ . Since  $\text{Br}_y^*$  emission sources are close  
 651 to coastal regions, the decrease of  $[\text{Br}_y^*]$  during autumn compared to the other period is larger at  
 652 DDU ( $4.7 \pm 1.7 \text{ ng m}^{-3}$  for MAM compared to  $8.9 \pm 1.8 \text{ ng m}^{-3}$  for JJA) than Dome C ( $1.0 \pm 0.4$   
 653  $\text{ng m}^{-3}$  for MAM compared to  $1.9 \pm 0.8 \text{ ng m}^{-3}$  for JJA). Given the larger decrease of  $[\text{Br}_y^*]$  at

654 DDU than Dome C during autumn, it seems that  $F_{S(IV)+HOBr}$  might decrease and  $\Delta^{17}O(SO_4^{2-})_{nss}$   
 655 might increase at larger degree at DDU than Dome C, resulting in the negative  $\Delta_{DC-DDU}$  values.  
 656 However, although the model also shows the larger decrease in  $[Br_y^*]$  during autumn at DDU  
 657 ( $3.5 \pm 1.4 \text{ ng m}^{-3}$  for MAM compared to  $12.8 \pm 2.7 \text{ ng m}^{-3}$  for JJA) than Dome C ( $5.1 \pm 1.4 \text{ ng}$   
 658  $\text{m}^{-3}$  for MAM compared to  $2.2 \pm 0.5 \text{ ng m}^{-3}$  for JJA) (Fig. S1), the change in the modeled  
 659  $F_{S(IV)+HOBr}$  were smaller at DDU (23% for MAM compared to 33% for JJA) than Dome C (18%  
 660 for MAM compared to 33% for JJA) (Table 1). Therefore, the larger decrease in  $[Br_y^*]$  at DDU  
 661 than Dome C does not lead to a larger decrease in  $F_{S(IV)+HOBr}$  at DDU in the model. Furthermore,  
 662 despite the good reproducibility of  $[Br_y^*]$  at DDU during MAM by the model (observed:  $4.7 \pm$   
 663  $1.7 \text{ ng m}^{-3}$ , modeled:  $3.5 \pm 1.4 \text{ ng m}^{-3}$ ), the model tends to underestimate tropospheric BrO  
 664 vertical column density in 60 to 90°S during March to April by a factor of  $\sim 4$  (Fig. S2), implying  
 665 that the model could also underestimate HOBr abundance. The underestimate of HOBr  
 666 abundance would lead to underestimate of  $F_{S(IV)+HOBr}$  and overestimate of  $\Delta^{17}O(SO_4^{2-})_{nss}$ , which  
 667 is opposed to the obtained result of underestimate in  $\Delta^{17}O(SO_4^{2-})_{nss}$  during autumn at DDU.  
 668 Rather, given that BrO in 60 to 90°S is underestimated year-round (Fig. S2), it could be a reason  
 669 for overestimate of  $\Delta^{17}O(SO_4^{2-})_{nss}$  such that seen for DDU in January (Fig. 2d). We note that,  
 670 based on the kinetics of  $HSO_3^- + HOCl$  investigated by a flow tube experiment, Liu and Abbatt  
 671 (2020) recently determined reaction rate constant of  $HSO_3^- + HOBr$  ( $k_{HOBr+HSO_3^-}$ ) which was  
 672 estimated to be two orders of magnitude lower than the values used in atmospheric models  
 673 including GEOS-Chem. However, Chen et al. (2017) had performed a sensitivity test with the  
 674 two orders of magnitude lower  $k_{HOBr+HSO_3^-}$  and showed that the contribution of S(IV) + HOBr  
 675 reaction to the global sulfate formation does not change because this reaction is limited by gas  
 676 diffusion of HOBr into cloud droplets. Thus, it seems that the current understanding in  
 677 S(IV)+HOBr pathway and related reactive bromine chemistry cannot explain the underestimate  
 678 of  $\Delta^{17}O(SO_4^{2-})_{nss}$  at DDU during the autumn in the model.

679 Another possible explanation is the increase in  $\Delta^{17}O(SO_4^{2-})_{nss}$  at DDU associated with  
 680 the aqueous-phase S(IV) +  $O_3$  pathway in sea-salt aerosol. As mentioned in Section 2.3, fresh  
 681 sea-salts typically contain alkaline solution (pH  $\sim 8$ ) where the S(IV) +  $O_3$  pathway is efficient  
 682 prior to aerosol acidification (Alexander et al., 2005). It is thus expected that, while sea-salt  
 683 loading in autumn ( $0.9 \pm 0.4 \mu\text{g m}^{-3}$  for MAM) is lower than in summer ( $1.1 \pm 0.4 \mu\text{g m}^{-3}$  for  
 684 DJF) by only a factor of 1.2, the  $[SO_4^{2-}]_{nss}$  level in autumn ( $57 \pm 46 \text{ ng m}^{-3}$ ) is a factor of 4 lower  
 685 than that in summer ( $215 \pm 79 \text{ ng m}^{-3}$ ), leading to slower sea-salt acidification, possibly allowing  
 686 S(IV) +  $O_3$  to proceed. This possibility seems to be supported by the negative covariation  
 687 between the  $\Delta_{DC-DDU}$  and  $[SO_4^{2-}]_{ss}/[SO_4^{2-}]_{total}$  at DDU, an assumed index of the degree of sea-salt  
 688 acidification, for the data during March to May with  $r = -0.96$  and  $p < 0.01$  (Fig. 5 and Table  
 689 S1), where the  $\Delta_{DC-DDU}$  tends to be lower as  $[SO_4^{2-}]_{ss}/[SO_4^{2-}]_{total}$  becomes higher. Note that,  
 690 however, since both  $\Delta^{17}O(SO_4^{2-})_{nss}$  and  $[SO_4^{2-}]_{ss}/[SO_4^{2-}]_{total}$  are determined as functions of  $k \times$   
 691  $[Na^+]$  in Eq. (1), the correlation between the  $\Delta_{DC-DDU}$  and  $[SO_4^{2-}]_{ss}/[SO_4^{2-}]_{total}$  could be an  
 692 artefact of the calculation. If we assume  $[Na^+]/[SO_4^{2-}]_{total}$  as an index of sea-salt loading relative  
 693 to titrating acids without using  $k$  value, the correlation coefficient compared to  $\Delta_{DC-DDU}$  becomes  
 694 less significant ( $r = -0.74$  and  $p = 0.06$ ; Table S1). Hence, it is currently difficult to conclude the  
 695 role of sea-salt controlling  $\Delta^{17}O(SO_4^{2-})_{nss}$  and  $\Delta_{DC-DDU}$  values based on the available data. In the  
 696 meantime, the sea-salt aerosol in the model may be acidified excessively because of the  
 697 overestimate of  $[SO_4^{2-}]_{nss}$  (Fig. 2a and 2b), while the model fairly reproduces the abundances of  
 698 sea-salt aerosols at DDU by implementing sea-salts production from blowing snow sublimation  
 699 (Huang and Jaeglé, 2017; Fig. S1). The excessive acidification of sea-salt in the model would

700 lead to the underestimate of  $F_{S(IV)+O_3}$  and then  $\Delta^{17}O(SO_4^{2-})_{nss}$ . Therefore, the small underestimate  
 701 of  $\Delta^{17}O(SO_4^{2-})_{nss}$  at DDU during autumn might be partly compensated by correcting  $[SO_4^{2-}]_{nss}$ .  
 702



703  
 704 **Figure 5.** Relationship between  $[SO_4^{2-}]_{ss}/[SO_4^{2-}]_{total}$  at DDU and  $\Delta_{DC-DDU}$ . Symbols for different  
 705 seasons are same as Fig. 3. The dashed line shows the linear least-squares fit for autumn (MAM).  
 706

707 In both cases, to obtain the negative  $\Delta_{DC-DDU}$  values, sulfate with high  $\Delta^{17}O(SO_4^{2-})_{nss}$  of  
 708  $1.9 \pm 0.2$  ‰ during autumn at DDU needs to be reduced and sulfate with lower  $\Delta^{17}O(SO_4^{2-})_{nss}$   
 709 needs to be increased along with the transport of sulfate and its precursors towards inland  
 710 Antarctica. It is reasonable that, since liquid water content becomes zero at  $-40^\circ\text{C}$  (Jeffery and  
 711 Austin, 1997; Pruppacher, 1995), aqueous-phase S(IV) oxidation is strictly limited and sulfate  
 712 produced via gas-phase  $SO_2 + OH$  pathway with  $\Delta^{17}O(SO_4^{2-})_{nss} = 0$  ‰ is more important at  
 713 inland Antarctica, represented by Dome C where the annual mean temperature is  $-50^\circ\text{C}$   
 714 (Argentini et al., 2014). Additionally, given that  $[Na^+]$  is two orders of magnitude lower at Dome  
 715 C (ca.  $5 \text{ ng m}^{-3}$ ; Legrand et al., 2017a) than DDU (ca.  $300 \text{ ng m}^{-3}$ ; Jourdain and Legrand, 2002),  
 716 it is expected that the sea-salt particles preferentially deposit during transport towards inland  
 717 Antarctica together with sulfate produced in sea-salt, possibly leading to sulfate with lower  
 718  $\Delta^{17}O(SO_4^{2-})_{nss}$  values at Dome C. Thus, it seems qualitatively reasonable to observe lower  
 719  $\Delta^{17}O(SO_4^{2-})_{nss}$  at Dome C than DDU.

720 Thus, the changes in sulfate formation processes responsible for the negative  $\Delta_{DC-DDU}$   
 721 values during March to May are uncertain. Considering the small but significant underestimate in  
 722  $\Delta^{17}O(SO_4^{2-})_{nss}$  at DDU in the model despite of the good reproducibility at Dome C in that period,  
 723 we looked into the processes that would be more important around coastal regions than inland  
 724 such as the decrease in  $F_{S(IV)+HOBr}$  and the increase in  $F_{S(IV)+O_3}$  in sea-salt particles at DDU.  
 725 However, both of them are not decisive. Given the larger abundances of reactive bromine at  
 726 coastal regions of West Antarctica than those of East Antarctica (Theys et al., 2011; Saiz-Lopez  
 727 et al., 2007; Grilli et al., 2013), further observations of  $\Delta^{17}O(SO_4^{2-})_{nss}$  at different coastal sites  
 728 around Antarctica would help to constrain the importance of those processes.  
 729

730 **5 Conclusions**

731 We investigated the consequences of characteristic oxidation chemistry in Antarctica for  
 732 sulfate formation processes and  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  by comparing weekly  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  observations  
 733 at inland site Dome C and those previously obtained at coastal site DDU in the same year 2011.  
 734 The  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  at Dome C showed lower values in austral summer ( $1.1 \pm 0.1$  ‰ in February)  
 735 and higher values in winter ( $2.5 \pm 0.2$  ‰ in August), with a mass-weighted annual average of  $1.7$   
 736  $\pm 0.1$  ‰, which are generally consistent with previous observations at DDU. This seasonality in  
 737  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  at Dome C is roughly reproduced by the GEOS-Chem atmospheric chemistry  
 738 transport model, reflecting the increased relative fraction of sulfate produced via  $\text{SO}_2 + \text{OH}$   
 739 (34%) and  $\text{S(IV)} + \text{H}_2\text{O}_2$  (48%) in summer in contrast to the increased fraction of  $\text{S(IV)} + \text{O}_3$   
 740 (30%) and  $\text{S(IV)} + \text{HOBr}$  (34%) in winter. The model also reproduces the  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  at  
 741 DDU with estimated sulfate formation processes similar to Dome C but with lower fraction of  
 742 gas-phase OH oxidation for DDU (16% in summer).

743 Aside from those general seasonal trends, we found that there are significant differences  
 744 in  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  at Dome C and DDU during the austral spring–summer (October to December)  
 745 and the austral autumn (March to May), indicating the contribution of specific oxidation  
 746 chemistry to sulfate at each site. For spring–summer, the higher  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  at Dome C than  
 747 DDU was observed, which coincides with the period when chemical  $\text{MS}^-$  destruction is  
 748 enhanced under the high photochemical activity at Dome C. Combined with the first estimate of  
 749  $\Delta^{17}\text{O}(\text{MS}^-)$  based on the isotopic mass balance calculations, we conclude that  $\text{MS}^-$  destruction  
 750 producing sulfate with  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  as high as 12 ‰ is the most likely process responsible for  
 751 the observed high  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  at Dome C, and suggests that  $\text{MS}^-$  destruction is responsible for  
 752 ca. 10% of total sulfate during spring–summer at this inland Antarctic location. This finding has  
 753 important implications for the interpretation of ice-core  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  records, since it is known  
 754 that  $\text{MS}^-$  can be also chemically destroyed in snow. This process may lead to a significant post-  
 755 depositional increase in  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  of over 1 ‰ and reconcile the existing discrepancy  
 756 between the  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  in the atmosphere and ice. For a precise interpretation of ice-core  
 757  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  records, future works investigating the relationship between  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  and  
 758  $[\text{MS}^-]/[\text{SO}_4^{2-}]_{\text{nss}}$  in snow at various sites over Antarctica are required to formulate the post-  
 759 depositional shift of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$ . Additionally, the calculation of  $\Delta^{17}\text{O}(\text{MS}^-)$  should be  
 760 implemented into the model that is used for simulation of the past  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$ . Developments  
 761 of analytical methods for  $\Delta^{17}\text{O}(\text{MS}^-)$  are also necessary to prove the proposed mechanisms as  
 762 well as to constrain the models. Meanwhile, the higher  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  at DDU than Dome C  
 763 during autumn may be associated with decreased contribution of  $\text{S(IV)} + \text{HOBr}$  due to the  
 764 limited reactive bromine availability and/or the increased contribution of  $\text{S(IV)} + \text{O}_3$  due to the  
 765 insufficient acidification of sea-salt at DDU. Further observations of  $\Delta^{17}\text{O}(\text{SO}_4^{2-})_{\text{nss}}$  at various  
 766 coastal sites over Antarctica will help to constrain the impact of these processes.

767



768 **Conflict of Interest**

769 The authors declare no conflicts of interest.

770 **Data Availability Statement**

771 Data presented in this article are available at <http://dx.doi.org/10.17632/xfr8ffn9xv.1>.

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793

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**Figure1.**

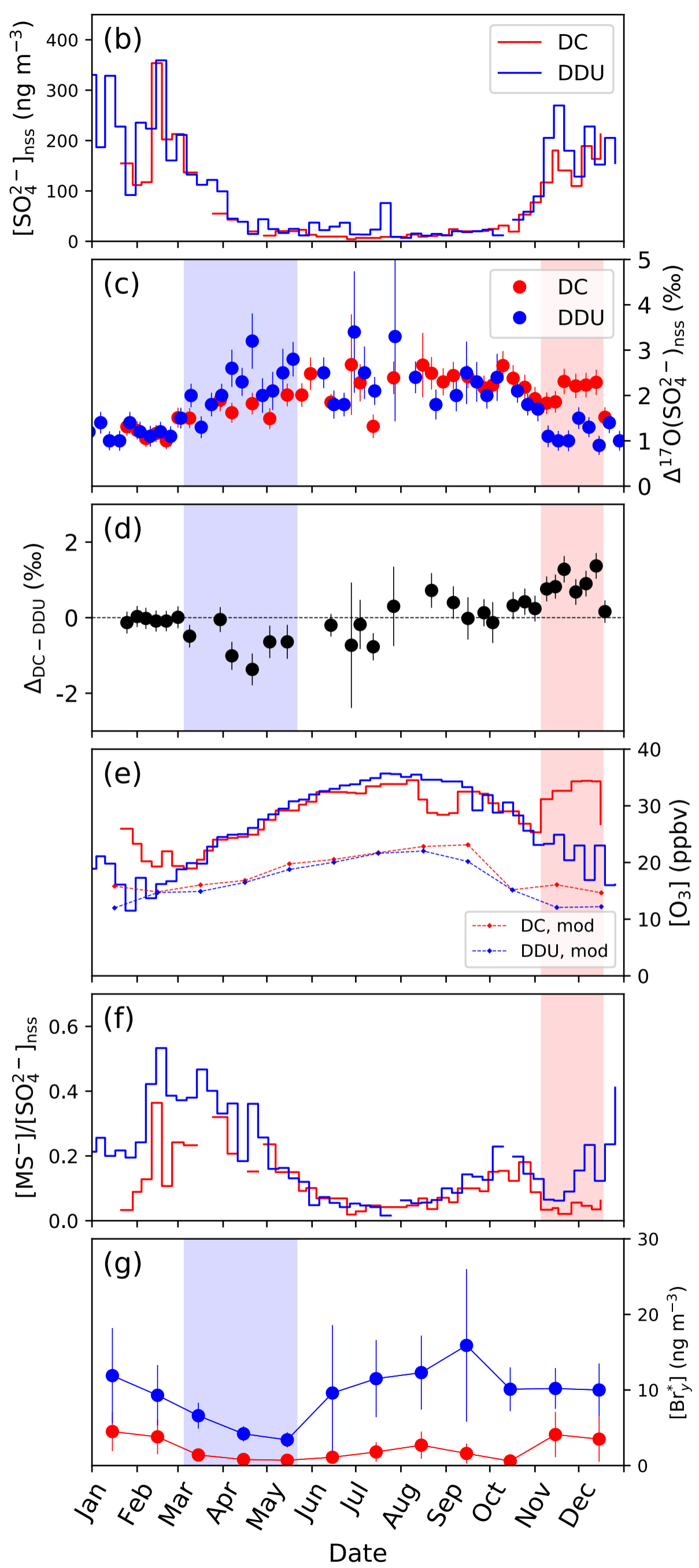
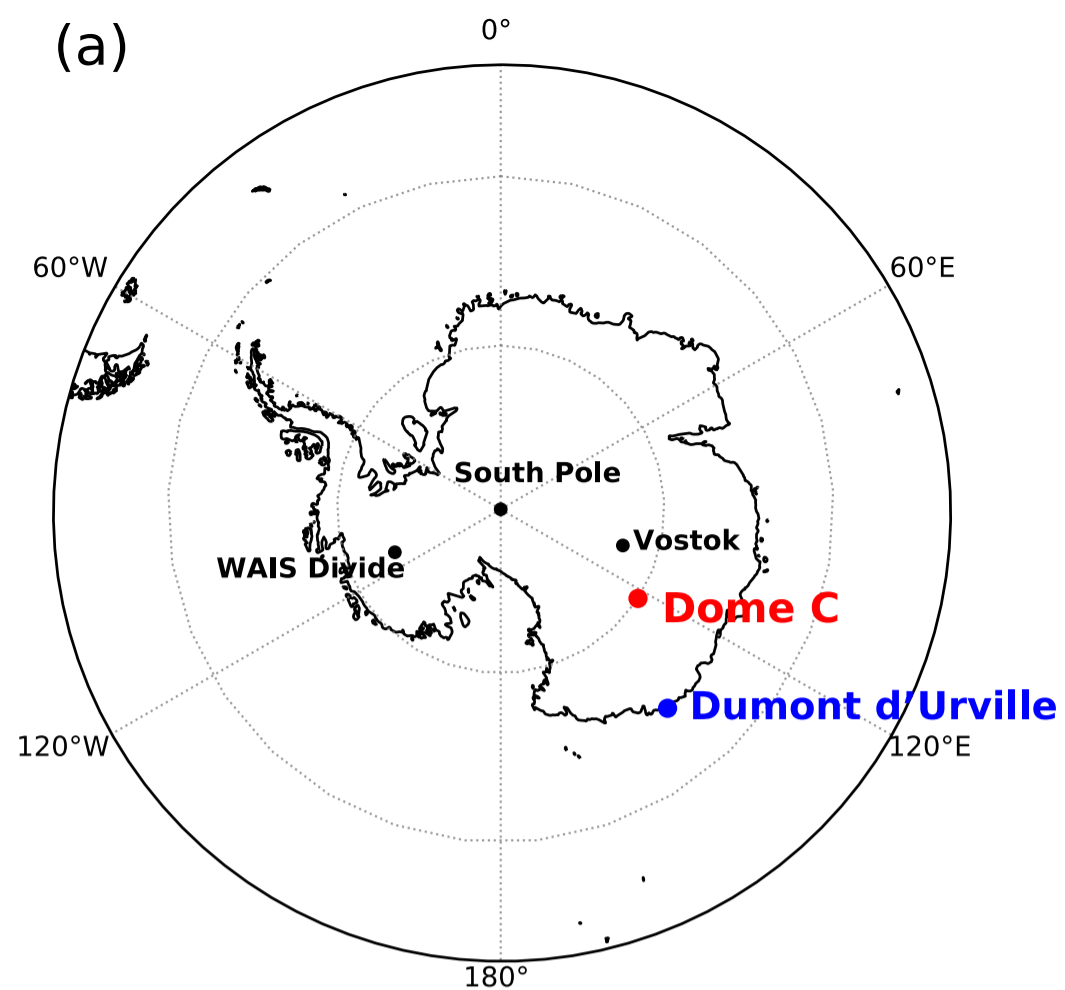
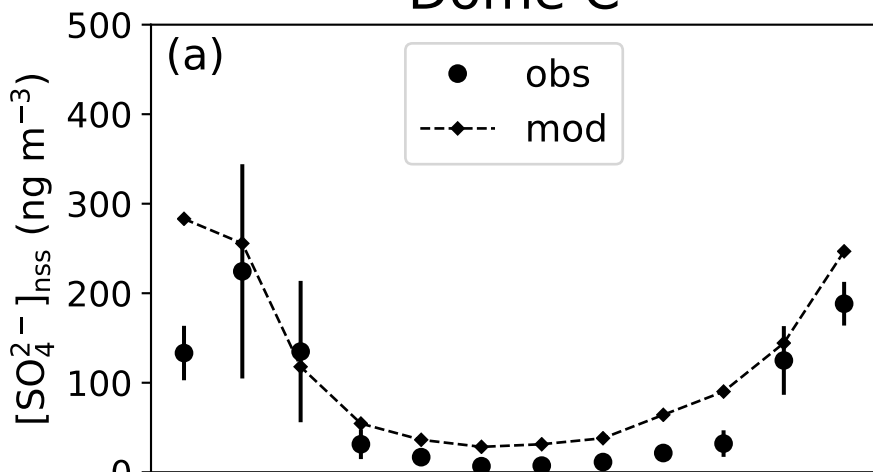


Figure2.

## Dome C



## DDU

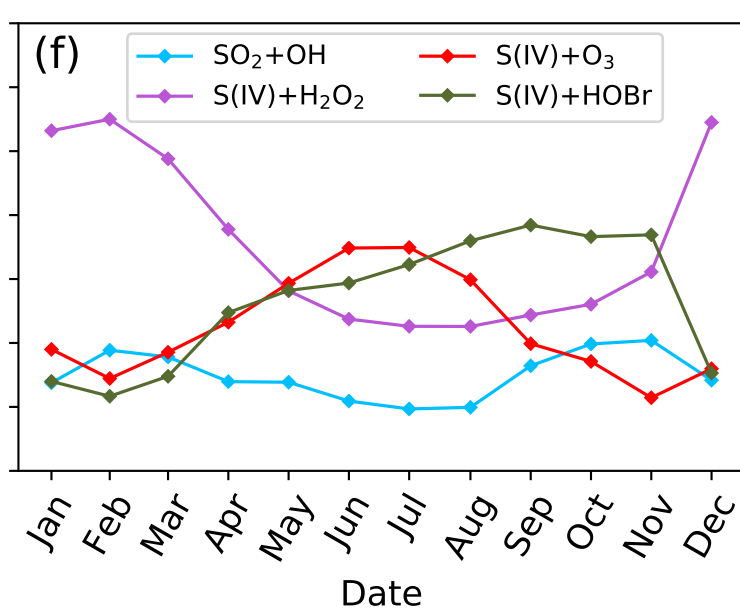
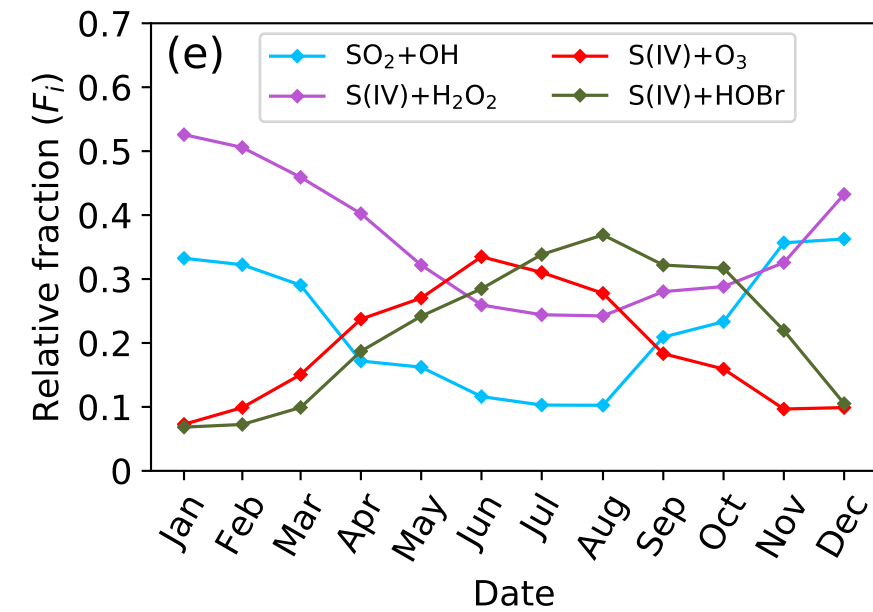
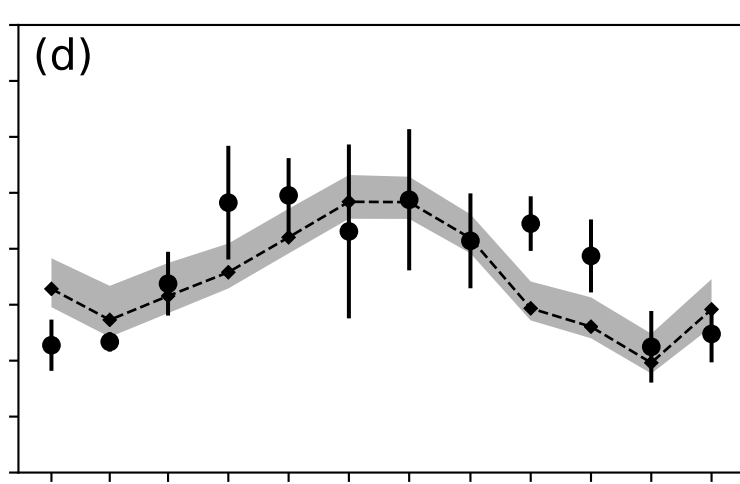
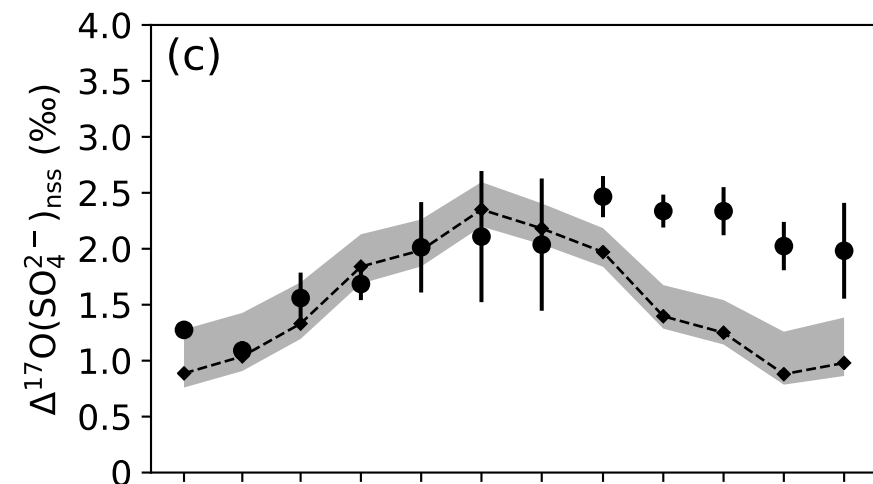
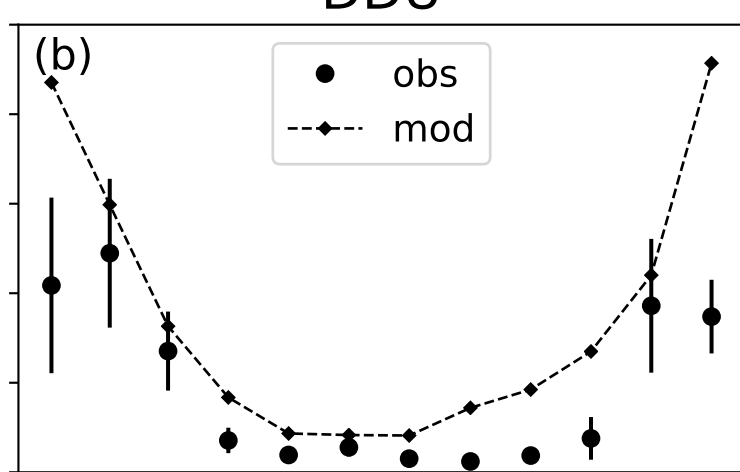


Figure 3.



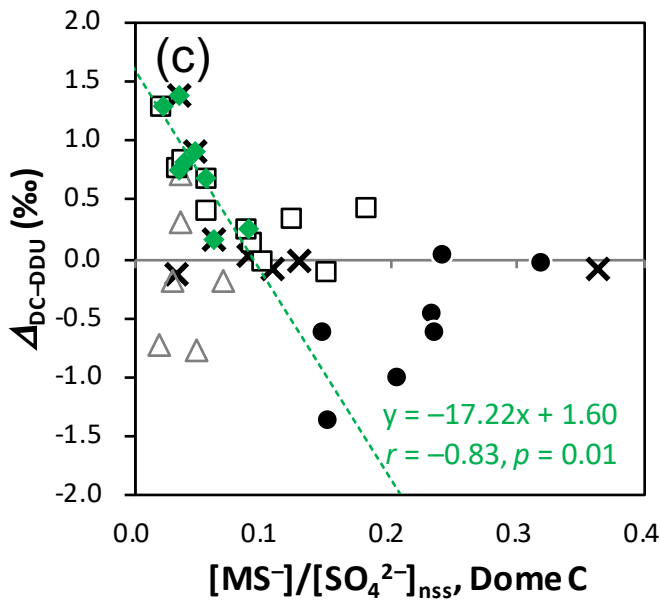
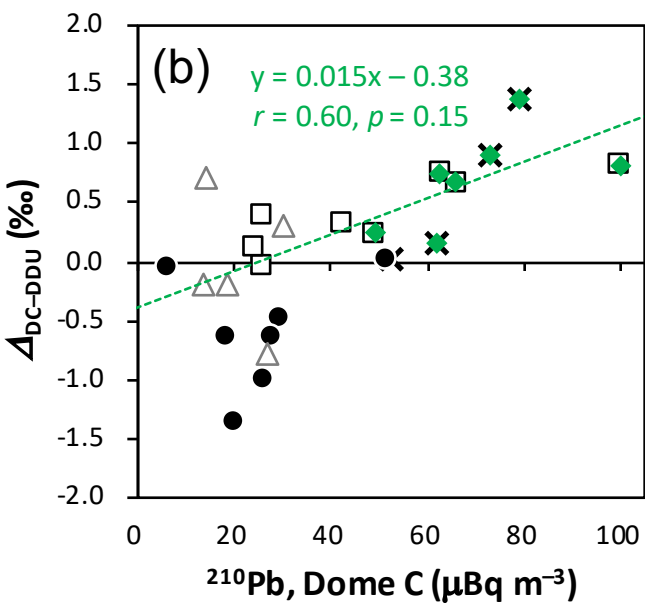
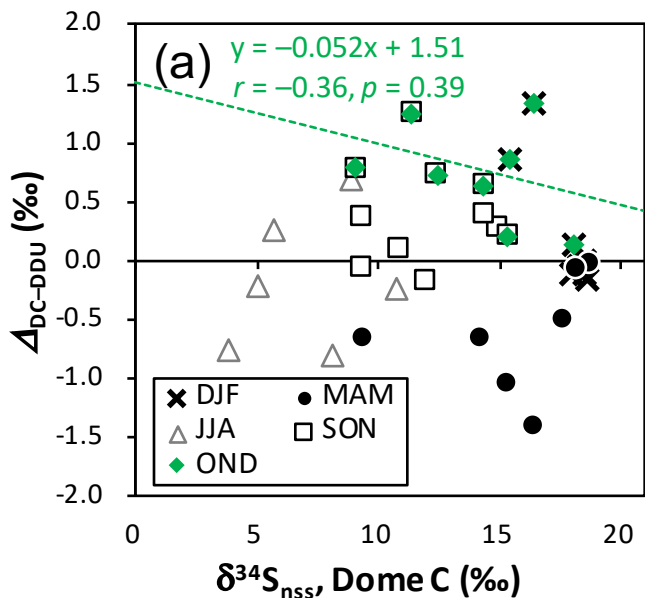
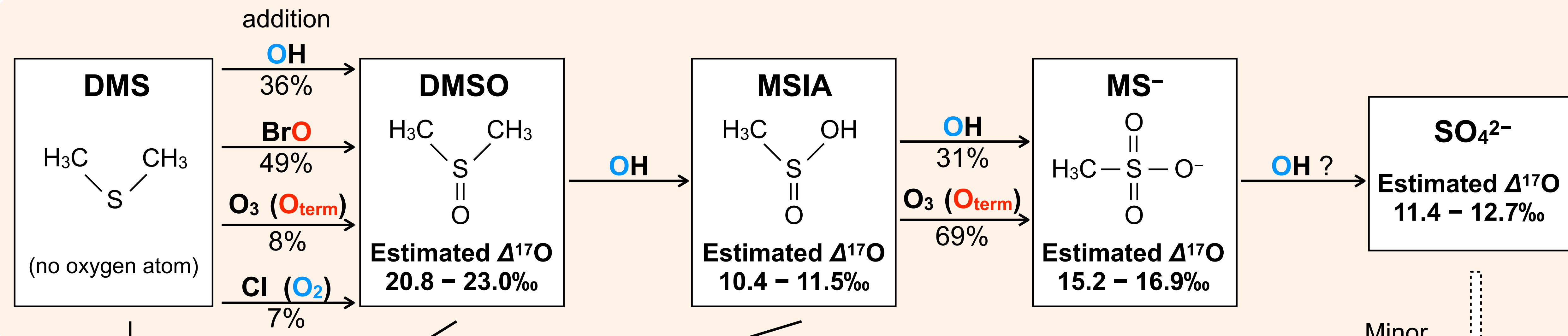


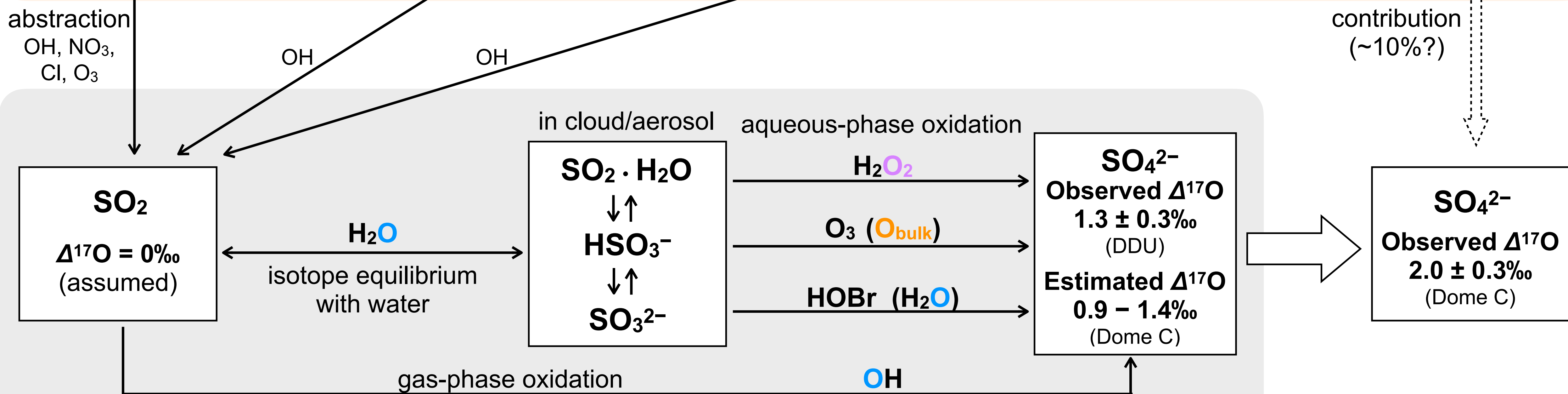
Figure4.

Assumed  $\Delta^{17}\text{O}(\text{oxidants})$  ○:  $38.4 \pm 2.0\text{‰}$ , ○:  $25.6 \pm 1.3\text{‰}$ , ○:  $1.6 \pm 0.3\text{‰}$ , ○:  $0\text{‰}$

*Newly proposed process leading to high  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$*



Minor contribution (~10%?)



*Recognized processes affecting  $\Delta^{17}\text{O}(\text{SO}_4^{2-})$*

Figure 5.

