WAIS Divide ice core suggests sustained changes in the atmospheric formation pathways of sulfate and nitrate since the 19th century in the extratropical Southern Hemisphere

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Abstract. The $^{17}$O excess ($\Delta^{17}$O = $\delta^{17}$O – 0.52 × $\delta^{18}$O) of sulfate and nitrate reflects the relative importance of their different production pathways in the atmosphere. A new record of sulfate and nitrate $\Delta^{17}$O spanning the last 2400 years from the West Antarctic Ice Sheet Divide ice core project shows significant changes in both sulfate and nitrate $\Delta^{17}$O in the most recent 200 years, indicating changes in their formation pathways. The sulfate $\Delta^{17}$O record exhibits a 1.1 ‰ increase in the early 19th century from (2.4 ± 0.2) ‰ to (3.5 ± 0.2) ‰, which suggests that an additional 12–18 % of sulfate formation occurs via aqueous-phase production by O$_3$, relative to that in the gas phase. Nitrate $\Delta^{17}$O gradually decreases over the whole record, with a more rapid decrease between the mid-19th century and the present day of 5.6 ‰, indicating an increasing importance of RO$_2$ in NO$_x$ cycling between the mid-19th century and the present day in the mid- to high-latitude Southern Hemisphere. The former has implications for the climate impacts of sulfate aerosol, while the latter has implications for the tropospheric O$_3$ production rate in remote low-NO$_x$ environments. Using other ice core observations, we rule out drivers for these changes other than variability in extratropical oxidant (OH, O$_3$, RO$_2$, H$_2$O$_2$, and reactive halogens) concentrations. However, assuming OH, H$_2$O$_2$, and O$_3$ are the main oxidants contributing to sulfate formation, Monte Carlo box model simulations require a large (≥ 260 %) increase in the O$_3$ / OH mole fraction ratio over the Southern Ocean in the early 19th century to match the sulfate $\Delta^{17}$O record. This unlikely scenario points to a deficiency in our understanding of sulfur chemistry and suggests other oxidants may play an important role in sulfate formation in the mid- to high-latitude marine boundary layer. The observed decrease in nitrate $\Delta^{17}$O since the mid-19th century is most likely due to an increased importance of RO$_2$ over O$_3$ in NO$_x$ cycling and can be explained by a 60–90 % decrease in the O$_3$ / RO$_2$ mole fraction ratio in the extratropical Southern Hemisphere NO$_x$-source regions.

1 Introduction

The formation pathways of tropospheric sulfate (SO$_4^{2-}$) and nitrate (NO$_3^-$) impact atmospheric chemistry and climate in a number of ways. The importance of gas-phase versus aqueous-phase sulfate formation will impact the contribution of sulfate aerosols to direct scattering of solar radiation and indirect radiative effects via changes in cloud
microphysics. Gas-phase $\text{SO}_4^{2-}$ production has the potential to increase sulfate aerosol and CCN concentrations (Langner et al., 1992), while aqueous-phase production in existing droplets can enhance the ability of those particles to act as CCN at lower supersaturations (Kaufman and Tanre, 1994). Changes in nitrogen oxides (NO$_x$ = NO + NO$_2$) cycling and nitrate aerosol formation impact $\text{O}_3$ production rates and the lifetime of NO$_x$, with implications for the oxidizing capacity of the atmosphere. Oxygen isotope measurements from ice cores can provide insight into the formation pathways of sulfate and nitrate aerosol and how they change over time (Alexander et al., 2002, 2003, 2004; Hastings et al., 2005). Quantitatively connecting changes in the oxygen isotopes of sulfate and nitrate to changes in atmospheric conditions remains a key challenge in the application of these measurements to paleo-chemistry.

A key control on the formation pathways of sulfate and nitrate is the abundance of the oxidants involved in their formation. Atmospheric oxidants such as ozone (O$_3$) and the hydroxyl radical (OH) play a central role in determining the chemical makeup of the troposphere, as their concentrations determine the lifetime and fate of reduced trace gases and the formation of aerosols including sulfate and nitrate, with implications for climate and air pollution. Atmospheric oxidant concentrations are strongly influenced by emissions of O$_3$ precursors such as carbon monoxide (CO), methane (CH$_4$), volatile organic carbon (VOC) species, and nitrogen oxides, and are fundamentally coupled to each other via oxidant cycling. Reactive halogens (e.g., BrO) also impact the chemistry of oxidants, sulfate, and nitrate in a number of ways (von Glasow et al., 2004; Morin et al., 2007; Saiz-Lopez and von Glasow, 2012).

Our knowledge of past variability in the abundance of atmospheric oxidants is very limited. Global chemical transport models (CTM) have been used to investigate oxidant changes based on emissions changes between the preindustrial (prior to 1750, 1800, or 1850 CE) and the present day (between 1990 and 2010 CE). Most models suggest an increase in global tropospheric O$_3$ (+25% to +63%), an even larger increase in H$_2$O$_2$ (+44% to +130%), but no consistent agreement in the sign or magnitude of the change in OH (−33% to +14%), although most suggest OH has decreased slightly (Sofen et al., 2011; John et al., 2012, and references therein). These global averages largely reflect changes in the tropics and Northern mid-latitudes where oxidant concentrations are the highest. The lifetime of CH$_4$, which is controlled by OH, is also largely determined in the tropics (Holmes et al., 2013). However, the abundance and isotopic composition of shorter-lived species such as sulfate and nitrate preserved in Antarctic ice cores is determined by processes in mid-to-high southern latitudes. Ice core measurements of hydrogen peroxide (H$_2$O$_2$) indicate a 50% increase in its Antarctic boundary layer concentration during the 20th century due to a combination of the large-scale influence of increases in CO and CH$_4$ emissions and the local increase in tropospheric O$_3$ photolysis (producing HO$_2$, a precursor of H$_2$O$_2$) over Antarctica due to the stratospheric ozone hole since the 1970s (Lamarque et al., 2011). Late 19th century measurements of surface O$_3$ using the Schönbein method suggest very low preindustrial surface ozone mole fraction x(O$_3$) around 10 nmol mol$^{-1}$ (Sandroni et al., 1992; Pavelin et al., 1999) at a number of sites in both hemispheres, implying that human activity in the 20th century has increased surface x(O$_3$) by approximately 100% in remote regions, although there is considerable uncertainty surrounding the reconstruction of these historic measurements. Because oxidants are generally not well preserved in any paleo-archive, there is no other direct evidence of the magnitude of past oxidant changes. The triple oxygen isotopes of sulfate and nitrate from ice cores have been suggested as a potential constraint on local to regional paleo-oxidant changes because the sulfate and nitrate preserve the isotopic composition of the oxidants involved in their formation. However, their interpretation is complicated by other factors influencing sulfate and nitrate chemistry and uncertainty in the spatial scale reflected by measurements at a single location.

The first measurements of the triple-oxygen isotopes of sulfate from the West Antarctic Ice Sheet (WAIS) Divide ice coring project (http://www.waisdivide.unh.edu/) spanning 1774–2005 CE show an increase in the early 19th century, with stable values from the mid-19th century to the present (Kunasek et al., 2010). The lack of changes since the mid-19th century is consistent with increases in both O$_3$ and H$_2$O$_2$, because they have offsetting effects on the sulfate isotopes (Kunasek et al., 2010; Sofen et al., 2011). The present work extends this record back another 2000 years and includes the complementary measurement of nitrate isotopes. We compare these isotope records to other ice core chemical records and consider possible explanations for the observed variability in the $\delta^{17}$O record.

2 Background

The $^{17}$O excess ($\Delta^{17}$O = $\delta^{17}$O − 0.52 × $\delta^{18}$O) is an approximate measure of the deviation from mass-dependent fractionation of $\delta^{17}$O and $\delta^{18}$O. The formation of ozone produces a large positive $\Delta^{17}$O (Thiemens and Heidenreich, 1983) that is then passed to other atmospheric species through oxidation reactions (Thiemens, 2006).

The mean and standard deviation of all $\Delta^{17}$O(O$_3$) observations is 25 ± 5‰ (Krankowsky et al., 1995; Johnston and Thiemens, 1997; Vicars et al., 2012), although due to the low abundance of ozone and potential interfering gases, all of these methods may be subject to low biases (Brenninkmeijer et al., 2003). Because of the possible low bias in the observations, studies of sulfate or nitrate $\Delta^{17}$O have assumed $\Delta^{17}$O(O$_3$) ranging between 25‰ and 35‰ (Michalski et al., 2003; Morin et al., 2007; Kunasek et al., 2010; Morin et al., 2011; Sofen et al., 2011; Alexander et al.,
A global modeling study suggests that $\Delta^{17}O(O_3) = 35 \%e$ agrees best with global observations of $\Delta^{17}O(NO_2)^{(-)}$ (Alexander et al., 2009). In this study, we use $\Delta^{17}O(O_3) = 25 \%e$ to be consistent with observations, but do sensitivity studies assuming 35\%. The isotopic anomaly in ozone is preferentially distributed to the terminal oxygen atoms such that $\Delta^{17}O(O_3)_{\text{terminal}} = 1.5 \times \Delta^{17}O(O_3)_{\text{bulk}}$ (Savarino et al., 2008). Depending on the reaction involving ozone, the resulting isotopic composition may reflect either that of the $\Delta^{17}O(O_3)_{\text{terminal}}$ or $\Delta^{17}O(O_3)_{\text{bulk}}$.

Observations show $\Delta^{17}O(H_2O_2) = (1.3 \pm 0.3) \%e$ (Savarino and Thiemens, 1999). Generally, $\Delta^{17}O(OH) = 0 \%e$ due to rapid isotopic exchange with water vapor (Dubey et al., 1997; Lyons, 2001), but in polar regions where water vapor concentrations are low, OH may retain a small fraction of the positive $\Delta^{17}O$ acquired from O$_3$ (Morin et al., 2007). Observations show $\Delta^{17}O(O_2) = -0.34 \%e$ (Barkan and Luz, 2005).

Sulfate and nitrate both acquire a mass-independent (non-zero $\Delta^{17}O$) oxygen isotopic composition from the oxidants involved in their formation. The main oxidants relevant to nitrate formation are O$_3$, RO$_2$ (R=H atom or organic group), OH, and BrO, while sulfate formation involves primarily O$_3$, H$_2$O$_2$, and OH. Hypohalous acids (HOCl and HOBr) may also be important oxidants for sulfate formation in the marine boundary layer (Vogt et al., 1996; von Glasow et al., 2002), but the rate constant for the reactions HOBr/HOCl + HSO$_3^-$ are unknown (Liu, 2002). Sulfate and nitrate $\Delta^{17}O$ is influenced solely by the relative importance of their formation pathways (Savarino et al., 2000; Michalski et al., 2003), which depends upon the relative abundance of the different oxidants, the isotopic composition of each oxidant, and the number of oxygen atoms transferred during oxidation.

In addition to the uncertainty in the present-day value of $\Delta^{17}O(O_3)$, it is possible that $\Delta^{17}O(O_3)$ has varied with time due to variations in the relative importance of the flux of stratospheric O$_3$ to the troposphere compared with in situ tropospheric ozone production. In situ production has become increasingly important for the tropospheric ozone burden in the industrial era due to anthropogenic emissions of ozone precursors (Lelieveld and Dentener, 2000). Measured stratospheric and tropospheric $\Delta^{17}O(O_3)$ show considerable overlap, with the tropospheric $\Delta^{17}O(O_3)$ observations ranging from 17 to 37 \%e and stratospheric $\Delta^{17}O(O_3)$ ranging from 25 to 41 \%e (mean and standard deviation of 33 $\pm$ 4 \%e) (Krankowsky et al., 2007, and references therein). The higher $\Delta^{17}O(O_3)$ value for O$_3$ formed in the stratosphere is due to pressure and temperature effects during O$_3$ formation (Feilberg et al., 2013; Guenther et al., 1999). As an upper bound, we estimate the change in $\Delta^{17}O(O_3)$ by assuming a shift from 60 \% stratospheric to 40 \% stratospheric contribution to high southern latitude O$_3$ during the transition from the preindustrial to industrial period following Lelieveld and Dentener (2000) and assuming a stratospheric $\Delta^{17}O(O_3) = 33 \%e$ and tropospheric $\Delta^{17}O(O_3) = 25 \%e$. Such a change in $\Delta^{17}O(O_3)$ would lower $\Delta^{17}O(O_3)$ by up to 2.6 \%e from the preindustrial to the industrial period. Using more recent calculations from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP) (Young et al., 2013) suggests a change in $\Delta^{17}O(O_3)$ of 0.4 \%e to 1.8 \%e. These calculations are highly uncertain due to uncertainties in the preindustrial ozone budget and stratosphere–troposphere exchange; however, the influence on $\Delta^{17}O(O_3)$ is are small compared to the uncertainty in $\Delta^{17}O(O_3)$ and the magnitude of the observed changes in nitrate $\Delta^{17}O$. Lacking further information, we assume that $\Delta^{17}O(O_3)$ is constant over the time period studied here.

2.1 Sulfate chemistry and $\Delta^{17}O$

While anthropogenic emissions dominate the present-day Northern Hemisphere sulfur budget, marine biogenic emissions of dimethyl sulfide (DMS) and sea-salt sulfate represent the majority of Southern Hemisphere sulfur emissions (Bates et al., 1992; Seinfeld and Pandis, 2006). Poleward of 35°S, > 75 \% of sulfur emissions are from marine sources (Spiro et al., 1992). Most DMS is oxidized by OH, NO$_3$, and BrO to SO$_2$ and then to SO$_4^{2-}$, and most of the remainder forms methanesulfonic acid (MSA). The yield of MSA relative to SO$_2$ from DMS oxidation is enhanced at lower temperatures (Arsene et al., 1999) or when the oxidant is BrO rather than OH (Read et al., 2008).

The main tropospheric sulfate formation pathways are summarized in Fig. 1a. The rate of sulfate production by each oxidation pathway is determined by oxidant concentrations and several other factors. SO$_2$ is oxidized by OH in the gas phase, forming sulfuric acid (H$_2$SO$_4$). SO$_2$ may also dissolve into cloud droplets, speciating into S(IV) (= SO$_2$·H$_2$O+HSO$_3^-$+SO$_3^{2-}$), where it may react with H$_2$O, O$_3$, hypohalous acids or O$_2$ catalyzed by transition metals Fe(III) and Mn(II) to form sulfate. Cloud cover and liquid water content impact the relative importance of gas versus aqueous-phase sulfate production. Cloud water pH influences S(IV) speciation and therefore the sulfate production rate by O$_3$. Finally, heterogeneous sulfate formation by O$_3$ may occur on the surface of sea salt and dust aerosols, and thus depends upon the available aerosol surface area. The lifetime of sulfate to loss via wet and dry deposition is about one week (Park et al., 2004). The $\Delta^{17}O$ of SO$_4^{2-}$ of sulfate formed by OH oxidation is approximately 0 \%e, that by H$_2$O$_2$ is approximately 0.65 \%e, and O$_2$ is ~−0.09 \%e. Here, we assume the bulk $\Delta^{17}O(O_3) = 25 \%e$, resulting in a sulfate isotopic composition of 6.25 \%e, but also conduct sensitivity studies using $\Delta^{17}O(O_3) = 35 \%e$, forming sulfate with $\Delta^{17}O$ of SO$_4^{2-}$ of 8.75 \%e. Sulfate formed by HOCl or HOBr has $\Delta^{17}O$ of SO$_4^{2-}$ near 0 \%e, as the reaction proceeds via hydrolysis, so the oxygen atom comes from a water molecule (Fogelman et al., 1989; Troy and Margerum, 1991).
2.2 Nitrate chemistry and $\Delta^{17}$O

Nitrogen oxides are emitted into or produced in the atmosphere via high-temperature processes including fossil fuel combustion, biomass burning, and lightning as well as via soil microbes and the atmospheric oxidation of ammonia. Reaction of $N_2O$ with $O(^1D)$ in the stratosphere produces NO$_x$ that enters the polar troposphere either via gas-phase stratosphere–troposphere mixing or, after conversion to nitrate, via sedimentation of stratospheric aerosols (Salawitch et al., 1989). Finally, photolysis of snowpack nitrate releases NO$_x$ to the polar boundary layer that may re-deposit locally or elsewhere in Antarctica (Blunier et al., 2005; Frey et al., 2009; Erbland et al., 2013). Isotopic evidence suggests that nitrate at an East Antarctic coastal site is derived from snowpack NO$_x$ emissions upslope on the East Antarctic plateau (Savarino et al., 2007). Antarctic boundary layer meteorology suggests that WAIS Divide is located in an area of low-level divergence of the katabatic winds and likely sees little transport across the Transantarctic Mountains from East Antarctica (Parish and Bromwich, 2007), suggesting that WAIS Divide is not strongly influenced by fluxes of NO$_x$ and NO$_3^-$ from East Antarctica in the present day. Recent trace gas observations combined with NOAA Hysplit back-trajectory analysis starting from 10 km above the surface at WAIS Divide find that during a three-week study period, 27% of air masses came from the East Antarctic Plateau, with an additional 41% contribution from lower elevations (<2500 m) East Antarctic locations (Masclin et al., 2013). However, they find that the lifetime of NO$_x$ and HNO$_3$ is short enough that East Antarctica is not expected to be a major source of NO$_x$ or nitrate to WAIS Divide in the present day. The relative importance of these NO$_x$ sources to nitrate deposited in West Antarctica and how they may have varied on long timescales is not well quantified (Wolff et al., 2008) and remains a topic of active research.

In sunlight (daytime or polar summer), NO$_x$ cycles rapidly via oxidation of NO by O$_3$, RO$_2$, or BrO and photolysis of NO$_2$. Figure 1b illustrates the major nitrate formation pathways. NO$_2$ is oxidized in the daytime by OH to form HNO$_3$ or by BrO to BrONO$_2$. Formation of BrONO$_2$ is followed by hydrolysis to form HNO$_3$ on the surface of aerosols. At night, NO$_2$ is oxidized by O$_3$ to form the nitrate radical (NO$_3$), followed by conversion to HNO$_3$ via hydrocarbon abstraction of either DMS or hydrocarbons (HC) or by N$_2$O$_5$ hydrolysis on the surface of aerosols. During daytime, NO$_3$ is photolyzed back to NO$_x$, preventing significant daytime nitric acid production by these latter reactions. Once formed, aerosol thermodynamics determine the partitioning of nitric acid between the gas phase and aerosol phase. In the aerosol phase, HNO$_3$ may dissolve in water and dissociate into H$^+$ + NO$_3^-$.

The oxygen isotopic compositions of HNO$_3$ and NO$_3^-$ are indistinguishable, as gas–aerosol partitioning will only produce a mass-dependent fractionation. References to “nitrate” and $\Delta^{17}$O(NO$_3^-$) refer to the sum of HNO$_3$ + NO$_3^-$ and its isotopic composition, unless otherwise specified. The global average lifetime of nitrate is 4–6 days and is lost from the atmosphere via dry and wet deposition to the surface (Xu and Penner, 2012).

The oxygen isotopic composition of nitrate ($\Delta^{17}$O(NO$_3^-$)) is determined by the isotopic composition of NO$_2$ ($\Delta^{17}$O(NO$_2$)) and the oxidation pathways of NO$_2$ to nitrate. The $\Delta^{17}$O(NO$_2$) is determined by the relative abundance of O$_3$, RO$_2$, and BrO. NO$_2$ formed by O$_3$ exhibits a higher isotopic value than the bulk $\Delta^{17}$O(O$_3$), as the isotopic anomaly in O$_3$ is preferentially positioned in the terminal oxygen atoms that are transferred to NO$_2$ (Savarino et al., 2008). Since, two of the three oxygen atoms in nitrate come from NO$_2$, $\Delta^{17}$O(NO$_3^-$) equals $\frac{2}{3}\Delta^{17}$O(NO$_2$), plus the isotopic anomaly transferred in the oxidation of NO$_2$ to nitrate. For a given value of $\Delta^{17}$O(NO$_2$), NO$_2$+OH produces the lowest $\Delta^{17}$O(NO$_3^-$) value, and NO$_3$+DMS/HC or BrONO$_2$ hydrolysis produce the highest $\Delta^{17}$O(NO$_3^-$). Observations of $\Delta^{17}$O(NO$_3^-$) from Antarctic aerosol range from 20 to 43.1 ‰ (Savarino et al., 2007). Postdepositional processing also impacts $\Delta^{17}$O(NO$_3^-$). When snowpack NO$_3^-$ is photolysed, released to the boundary layer as NO$_x$, and oxidized back to NO$_3^-$, it acquires a $\Delta^{17}$O reflecting...
oxidant abundances local to the sunlit Antarctic boundary layer.

2.3 Nitrate $\delta^{15}N$

The nitrogen isotopic composition of nitrate ($\delta^{15}N(NO_3^-)$) in snow and ice is thought to be mainly influenced by the source of NO$_x$ and the extent of post depositional loss of nitrate from the snowpack (Morin et al., 2009; Savarino et al., 2007). NO$_x$ sources span a range of $\delta^{15}N(NO_3^-) = -49$ to $+25\%e$ (Felix et al., 2012, and references therein), but are uncertain due in part to fractionation during NO$_x$ collection (Fibiger and Hastings, 2012). Mid-latitude aerosol measurements of $\delta^{15}N(NO_3^-)$ suggest a narrower range, with anthropogenically influenced $\delta^{15}N(NO_3^-) = 0–6\%e$, while nitrate from natural NO$_x$ sources has $\delta^{15}N(NO_3^-) = (-4 \pm 2)\%e$ (Morin et al., 2009).

Photolysis of nitrate in snowpack followed by ventilation of the released NO$_x$ enriches snowpack $\delta^{15}N(NO_3^-)$ and is a source of low-$\delta^{15}N$ NO$_x$ to the boundary layer (Honrath et al., 1999; Blunier et al., 2005). However, the magnitude of the fractionation factor due to photolysis remains uncertain (Erbland et al., 2013), and the actual impact on snowpack $\delta^{15}N(NO_3^-)$ depends on the extent to which NO$_x$ is exported from a site before redeposition. The amount of post depositional loss, and therefore the extent of snowpack $\delta^{15}N(NO_3^-)$ enrichment, depends upon snow accumulation rate (Frey et al., 2009) and the concentration of UV absorbing impurities in the snow (Zatko et al., 2013). The extent to which snowpack NO$_x$ is emitted from the snow to the overlying atmosphere and the extent to which NO$_x$ is transported before oxidation and redeposition remains highly uncertain due to challenges in both the measurement and modeling of snowpack and polar boundary layer NO$_x$. Low-accumulation rate (0.027–0.035 m a$^{-1}$ water equivalent at Dome C) East Antarctic Plateau sites have snowpack $\delta^{15}N(NO_3^-)$ up to $340\%e$ (Erbland et al., 2013).

3 Methods

3.1 Description of the WAIS Divide site and cores

The West Antarctic Ice Sheet Divide (WAIS Divide) ice core site is located at 79.467° S, 112.085° W at a surface elevation of 1176 m. The site was selected due to its proximity 24 km downslope from the ice flow divide – providing good ice stratigraphy – and its present-day annual accumulation rate of (0.22 ± 0.04) m a$^{-1}$ water equivalent – comparable to Greenland summit ice cores. The accumulation rate is calculated based on annual layer thickness corrected for ice flow strain and densification and is found to have declined gradually over the past 2400 years from a maximum of 0.28 m a$^{-1}$, with very little change since 1700 CE (Fegyveresi et al., 2011). An accumulation rate comparable to that in Greenland allows for direct comparison of many ice core records between hemispheres. The high accumulation rate at the site also has the potential to mitigate the impact of post depositional processes on many chemical species such as H$_2$O and nitrate. In addition to a long core (WDC06A) that almost reaches the ice sheet bed, a number of short cores of approximately 100 m were drilled to provide greater ice volume for studies of the recent past and development of new analytical techniques.

3.2 Ice core sampling

The upper 577 m of the WAIS Divide ice core, spanning the time period from 427 BCE to 2006 CE with a dating uncertainty of approximately ±2 % (McGwire et al., 2011), was sampled for measurement of the isotopic composition of sulfate and nitrate. Ice samples from the WAIS Divide ice cores were cut at the National Ice Core Lab (NICL; Denver, CO, USA). Each section consisted of a 3 cm × 3 cm cross section pieces, generally 1 m in length. Based upon concentration measurements, 1 m sections were combined to achieve sample sizes adequate for isotopic analysis. Low sulfate concentrations in the ice required the combination of 7–15 m of ice per isotopic analysis, corresponding to 27–68 a of snow accumulation per sample.

Table 1 summarizes the sampling and isotopic measurement scheme. Sulfate isotope measurements were conducted on six samples from the WDC05A core between the surface and 69.80 m and were previously published (Kunasek et al., 2010). Nitrate $\delta^{15}N$ was measured on 70 samples of approximately 1 m length from the surface to 69.80 m in the WDC05A core. Nitrate $\Delta^{17}O$ was measured at 1 m resolution on 121 samples between the surface and 129.196 m in the WDC05Q core. The 1 m resolution $\delta^{15}N(NO_3^-)$ and $\Delta^{17}O(NO_3^-)$ were measured on separate ice cores because the process of evaporating the melted ice sample on a low (60° C) hot plate in a laminar flow clean hood to concentrate the nitrate for $\Delta^{17}O(NO_3^-)$ analysis was found to fractionate $\delta^{15}N(NO_3^-)$. Upon adoption of a new method of concentrating nitrate using an anion exchange resin following Frey et al. (2009), all three sets of isotopes, $\Delta^{17}O(SO_4^{2-})$, $\Delta^{17}O(NO_3^-)$, and $\delta^{15}N(NO_3^-)$, were measured on thirty-two samples from the WDC06A core between 114 m and 577 m.

3.3 Isotopic analysis

3.3.1 Nitrate isotopes

For the 32 samples measured on the WDC06A core, after melting the ice samples in a laminar flow clean hood, 500 mL aliquots were taken for nitrate isotope analysis. All nitrate isotope measurements on the WDC06A core were conducted in triplicate. The melt water samples are concentrated using the anion exchange resin prior to conversion of nitrate to N$_2$O via bacterial denitrification using
Table 1. Ice core sampling resolution and isotopic measurements.

<table>
<thead>
<tr>
<th>Core</th>
<th>Depth range (m)</th>
<th>Depth res. (m)</th>
<th>No. of samples</th>
<th>Measurements</th>
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<tbody>
<tr>
<td></td>
<td>Time range</td>
<td>Time res. (m)</td>
<td>(No. of replicates)</td>
<td></td>
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<tr>
<td>WDC05A</td>
<td>0–69.8</td>
<td>7.03–12.86</td>
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<td></td>
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<tr>
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<td>0–69.8</td>
<td>0.875–1.12</td>
<td>70</td>
<td>$\delta^{15}$N(NO$_3^{-}$)</td>
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<tr>
<td></td>
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<td>1.8–4.8</td>
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<tr>
<td>WDC05Q</td>
<td>0–129.17</td>
<td>0.546–1.37</td>
<td>121</td>
<td>$\Delta^{17}$O(NO$_3^{-}$)</td>
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<td></td>
<td>1521–2000 CE</td>
<td>2.3–6.1</td>
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<tr>
<td>WDC06A</td>
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<td>12–15</td>
<td>32</td>
<td>$\Delta^{17}$O(SO$_4^{2-}$)</td>
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<td>427 BCE–1586 CE</td>
<td>50–68</td>
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<tr>
<td>WDC06A</td>
<td>114–577</td>
<td>12–15</td>
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<td>$\Delta^{17}$O(NO$_3^{-}$)</td>
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<td>427 BCE–1586 CE</td>
<td>50–68</td>
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Table 2. Sulfate model isotope assumptions.

<table>
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<tr>
<th>Pathway</th>
<th>Sulfate $\Delta^{17}$O (%)</th>
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<td>SO$_3$ + OH</td>
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</tr>
<tr>
<td>S(IV) + HOCl/HOBr</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Pseudomonas aureofaciens. The N$_2$O is then decomposed into O$_2$+N$_2$ in a heated gold tube in a quantitative manner for isotopic analysis of $\delta^{15}$N and $\Delta^{17}$O (Sigman et al., 2001; Kaiser et al., 2007).

The samples at 1 m resolution were measured prior to those from the WDC06A core and underwent a slightly different process.

The upper 69.80 m of the WDC05A core was sampled at 1 m resolution for $\delta^{15}$N(NO$_3^{-}$) analysis. Seventy ice samples were melted in a laminar flow clean hood, and aliquots were taken (without pre-concentration) for conversion of nitrate to N$_2$O via bacterial denitrification using *Pseudomonas chlororaphis*, which allows for smaller samples than *P. aureofaciens*, and measured via continuous flow isotope ratio mass spectrometry. Duplicates were conducted at 10 depths.

For the 114 $\Delta^{17}$O(NO$_3^{-}$) measurements on the WDC05Q core, ice samples were melted and then pre-concentrated by evaporation on a hot plate in the laminar flow clean hood. The sample nitrate was then converted to N$_2$O and $\Delta^{17}$O(NO$_3^{-}$) was measured as described above for the WDC06A samples, although only $\Delta^{17}$O(NO$_3^{-}$) measurements were used, not $\delta^{15}$N.

Nitrate $\Delta^{17}$O(NO$_3^{-}$) and $\delta^{15}$N(NO$_3^{-}$) are measured relative to VSMOW and air N$_2$, respectively. Their values are corrected for nonlinearity associated with sample size based on replicate measurements of international (USGS-34: $\Delta^{17}$O(NO$_3^{-}$) = −0.1‰ and $\delta^{15}$N(NO$_3^{-}$) = 1.8‰; USGS-35: $\Delta^{17}$O(NO$_3^{-}$) = 21.6‰; and IAEA-N-3: $\delta^{15}$N(NO$_3^{-}$) = 4.7‰) and in-house laboratory standards over a range of sizes. Uncertainty in the $\delta^{15}$N(NO$_3^{-}$) from the WDC06A core and all $\Delta^{17}$O(NO$_3^{-}$) measurements is the maximum of the standard deviation of the triple measurement due to inter-sample variability or uncertainty in the yield correction. A fixed uncertainty of ±0.55‰ is used for $\delta^{15}$N(NO$_3^{-}$) from the WDC05A core, based on the 1σ error in the 10 duplicate measurements.

3.3.2 Sulfate isotopes

The rest of the melt water (approximately 6–14 L), intended for sulfate isotope analysis, was heated on a hot plate to 60 °C in a laminar flow hood to concentrate the sample by evaporation to approximately 50 mL volume. Sulfate was separated from other anions using a Dionex 2000 ion chromatograph with an IonPac AG15 column (4 × 50 mm) for anion preconcentration, IonPac AG19 guard column (4 × 50 mm), IonPac AS19 separation column (4 × 250 mm), ASRS-Ultra II suppressor (4 mm), and Dionex conductivity detector. The extracted sulfate (as H$_2$SO$_4$ solution) was frozen and shipped to UCSD where it was converted to Ag$_2$SO$_4$ using an Ag$^+$ exchange resin. The $\Delta^{17}$O(SO$_4^{2-}$) was measured at UCSD using the silver salt pyrolysis method described by Kunasek et al. (2010) and Savarino et al. (2001), except that sulfur isotopes were not measured beyond the upper 70 m as they proved difficult to interpret (Kunasek et al., 2010). Due to sample size requirements, only a single $\Delta^{17}$O(SO$_4^{2-}$) analysis was performed for each depth interval.

Sulfate $\Delta^{17}$O is first corrected for isotopic exchange with quartz (Schauer et al., 2012) then for sea-salt sulfate based on high-resolution Na$^+$ measurements from continuous-flow analysis (performed at the Desert Research Institute (DRI)) averaged to the resolution of the isotope measurements. We assume a sulfate-to-sodium ratio of $k = 0.25$ (Holland,
1978). An uncertainty in the $\Delta^{17}O(SO_4^{2-})$ measurements of $\pm 0.3\%_o$ is determined from the 1σ error in the repeated measurement of standards.

3.4 Box model description

To interpret the observations of $\Delta^{17}O(SO_4^{2-})$ and $\Delta^{17}O(NO_3^-)$ to changes in mid- to high-latitude Southern Hemisphere oxidant abundances, we developed a Monte Carlo modeling framework for box models of the production and isotopic composition of sulfate and nitrate.

3.4.1 Model design

The nitrate box model chemistry was previously described by Kunasek et al. (2008). The sulfate box model chemistry scheme is the same as that used in sulfate isotope simulations in the GEOS-Chem (http://www.geos-chem.org) global three-dimensional chemical transport model (Bey et al., 2001; Park et al., 2004; Alexander et al., 2012). Both box models calculate monthly mean production rates for each pathway described in Sects. 2.1 and 2.2 and shown in Fig. 1. The sulfate model goes a step further to calculate concentrations based on the production rates from the box model using Southern Ocean boundary conditions and the global mean lifetime for each form of sulfate (gas-phase, aqueous, or heterogeneous) based on a global sulfate aerosol simulation (Alexander et al., 2009). This step is not necessary for nitrate, because the thermodynamic partitioning of nitrate between gas and aerosol phases means that the lifetime of nitrate is independent of its production mechanism.

Convolving the models monthly mean production rates (nitrate) and concentrations (sulfate) associated with each formation mechanism, the oxidant isotopic composition, and isotopic transfer associated with each pathway shown in Tables 2 and 3 allows the calculation of the monthly and annual mean isotopic compositions of sulfate and nitrate. The sulfate $\Delta^{17}O$ calculation utilises the concentration of sulfate formed by each oxidation pathway and its corresponding isotopic composition as shown in Table 2. The $\Delta^{17}O(SO_4^{2-})$ values shown in Table 2 are based on the experimental results of Savarino et al. (2000). The nitrate calculation is somewhat complicated by the two-step oxidation of NO to NO$_3^-$.

The nitrate model first calculates the ratio of the steady-state production rates of NO$_2$ by O$_3$ and RO$_2$ and the isotopic composition of NO$_2$ is calculated based on this ratio and the isotopic composition of O$_3$ and RO$_2$. This represents 2/3 of the final isotopic composition of the nitrate. This is followed by the oxidation of NO$_2$ to NO$_3^-$ by OH or to NO$_3^-$ by O$_3$ followed by N$_2$O$_5$ formation and hydrolysis or hydrogen abstraction by DMS or hydrocarbons to form NO$_3^-$.

In oxidation of NO$_2$ by OH, since we assume $\Delta^{17}O(OH)$ is 0, $\Delta^{17}O(NO_3^-)$ is simply $\frac{2}{3}\Delta^{17}O(NO_2)$. The isotopic transfer functions associated with the other oxidation pathways are shown in Table 3.

To account for the internal isotopic distribution of ozone, we use the isotopic transfer function of Savarino et al. (2008) for NO + O$_3$ and that of Berhanu et al. (2012) for NO$_2$ + O$_3$ and assume that for reactions involving BrO, the oxygen comes entirely from the terminal oxygen atom of ozone (Morin et al., 2007; Viccars et al., 2012).

Halogen chemistry is included in both nitrate and sulfate models as a sensitivity study. In the nitrate model, we include both NO + BrO and NO$_2$ + BrO followed by the hydrolysis of BrONO$_2$ on aerosols as in Kunasek et al. (2008). In the sulfate model, we include aqueous-phase sulfate production by both HOBr and HOCl using assumed (for HSO$_3^-$) and measured (for SO$_3^{2-}$) reaction rate constants (Fogelman et al., 1989; Troy and Margerum, 1991).

3.4.2 Model boundary conditions

Box model boundary conditions are generally taken from a GEOS-Chem simulation of the year 2005 for the geographical region of interest (Southern Ocean and South American boundary layers for sulfate and nitrate, respectively). For the nitrate model, the fraction of the month in daylight is calculated based on latitude (50° S).

Sulfate model boundary conditions include concentrations of SO$_2$, HNO$_3$, O$_3$, OH, H$_2$O$_2$, dust (in four size bins: 0.1–1.0, 1.0–1.8, 1.8–3.0, 3.0–6.0 µm), and sea salt (in two size bins: 0.1–0.5, 0.5–10 µm). Physical parameters include air density, temperature, specific humidity, and surface pressure.

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Table 3. Nitrate model isotope assumptions.

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Product $\Delta^{17}O$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO + HO$_2$ → NO$_2$</td>
<td>0.0</td>
</tr>
<tr>
<td>NO + O$_3$ → NO$_2$</td>
<td>$1.18 \times \Delta^{17}O(O_3)_{bulk} + 6.6$</td>
</tr>
<tr>
<td>NO + BrO → NO$_2$</td>
<td>$1.5 \times \Delta^{17}O_{bulk}$</td>
</tr>
<tr>
<td>NO$_2$ + O$_3$ ↔ HNO$_3$</td>
<td>$\frac{1}{2}(1.23 \times \Delta^{17}O(O_3)_{bulk} + 9.0) + \frac{3}{2}\Delta^{17}O(NO_2)$</td>
</tr>
<tr>
<td>NO$_2$ + N$_2$O$_5$ ↔ HNO$_3$</td>
<td>$\frac{1}{2}[\frac{1}{2}(1.23 \times \Delta^{17}O(O_3)_{bulk} + 9.0) + \frac{3}{2}\Delta^{17}O(NO_2)] + \frac{1}{2}\Delta^{17}O(NO_2)$</td>
</tr>
<tr>
<td>NO$_2$ + BrO → HNO$_3$</td>
<td>$\frac{1}{2}(1.5 \times \Delta^{17}O(O_3)_{bulk}) + \frac{2}{3}\Delta^{17}O(NO_2)$</td>
</tr>
<tr>
<td>NO$_2$ + OH → HNO$_3$</td>
<td>$\frac{2}{3}\Delta^{17}O(NO_2)$</td>
</tr>
</tbody>
</table>
For aqueous phase chemistry, cloud water pH is varied between 4.5 and 6.0 to span the pH range across which aqueous sulfate formation and $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ are highly sensitive to pH. Observations of cloud water pH in clean marine environments span a range of 3.8–6.1 (Faloona, 2009, and references therein). We neglect consideration of pH < 4.5 because it is unlikely to occur over the remote Southern Ocean and these acidic conditions are unlikely to produce sulfate with a $\Delta^{17}\text{O}$ consistent with observations, as sulfate formation by $\text{O}_3$ will be suppressed. Cloud liquid water content is taken from GEOS-Chem, where it is calculated based on temperature, and cloud fraction from GEOS-Chem is scaled to Southern Ocean low cloud fraction observations (Eastman et al., 2011) while retaining its calculated vertical structure.

Nitrate model boundary conditions include concentrations of NO, NO$_2$, HO$_2$, O$_3$, OH, NO$_3$, VOCs (aldehydes, $\geq$ C$_4$ alkanes, $>$ C$_2$ aldehydes), DMS, and N$_2$O$_5$, as well as the photolysis rate of NO$_2$, NO$_2$ production rates by RO$_2$ and O$_3$, and aerosol surface area from GEOS-Chem. Physical parameters include air temperature and air density. When BrO is included, we assume a fixed concentration of 1 pmol mol$^{-1}$.

### 3.4.3 Monte Carlo approach

The mean and standard deviation ($\sigma_{\text{ox}}$) of each monthly oxidant concentration is calculated based on the spatial variability across the region of interest (Southern Ocean for $\Delta^{17}\text{O}(\text{SO}_4^{2-})$; extratropical South America for $\Delta^{17}\text{O}(\text{NO}_3^-)$) in a present-day simulation using the GEOS-Chem global chemical transport model. Each iteration of the Monte Carlo model encompasses a year-long simulation of sulfate or nitrate chemistry. To span a large range of oxidant conditions, each oxidant is independently varied over 3 $\sigma_{\text{ox}}$ to produce a wide Gaussian distribution of possible oxidant conditions (preserving the seasonal cycle), while all other boundary conditions are held constant (Sect. 5.4 justifies these assumption that other boundary conditions are held constant). In each iteration, the monthly mean oxidant concentrations from GEOS-Chem that serve as boundary conditions are scaled by a factor drawn from the 3 $\sigma_{\text{ox}}$ distribution. For each simulation, the monthly and annual $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ or $\Delta^{17}\text{O}(\text{NO}_3^-)$ is calculated. The box model is run repeatedly for approximately 10,000 simulations. We then search for pairs of simulations that match the observed change in $\Delta^{17}\text{O}$. These pairs of simulations that match the $\Delta^{17}\text{O}$ observations provide the corresponding changes in annual mean oxidant concentrations required to match the ice core observations.

### 3.4.4 Model limitations

There is uncertainty in the assumed $\Delta^{17}\text{O}$ of oxidants, the isotopic transfer from oxidants to products, and the chemical mechanisms in the box models, all of which could bias the calculation of $\Delta^{17}\text{O}(\text{NO}_3^-)$ or $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ and concentrations in any given time period. Therefore, we focus on the magnitude of the change in $\Delta^{17}\text{O}$ between time periods of interest, since the potential biases in the isotopic assumptions will be similar for each time period.

The above box model approach does not include coupling between oxidants as if they are in a photochemical box model. However, a photochemical box model will not provide an accurate representation of the relationships between oxidants on the time or spatial scales of interest because of the stiffness of the system as determined by the large difference in lifetimes between OH and O$_3$ (Seinfeld and Pandis, 2006). Furthermore, the model does not allow for the mixing of sulfate or nitrate from multiple regions/sources that is likely representative of samples from WAIS Divide. While a global model would provide this, it would be less flexible for exploring how chemistry changes impact $\Delta^{17}\text{O}$.

### 4 WAIS Divide ice core observations

Figure 2 shows the WAIS Divide ice core measurements of $\Delta^{17}\text{O}(\text{SO}_4^{2-})$, $\Delta^{17}\text{O}(\text{NO}_3^-)$, and $\delta^{15}\text{N}(\text{NO}_3^-)$. This record represents the first ice core record of $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ and $\Delta^{17}\text{O}(\text{NO}_3^-)$ sampled continuously over the past 2400 years. $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ is sampled at 7–15 m (27–68 years) resolution and varies between 1.8‰ and 3.7‰ over the entire record (Table 1 summarizes the sampling and isotopic measurement scheme). Prior to 1810 CE, $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ is less than 2.8‰. From 1810–2005 CE, $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ is greater than 3‰, with a maximum of 3.7‰ between 1837 and 1880 CE. There is a 1.1‰ difference in the mean $\Delta^{17}\text{O}(\text{SO}_4^{2-})$ between the period prior to 1810 and that after 1837. The 1810–1837 sample is excluded from this analysis because it is strongly influenced by the 1810 and Tambora volcanic eruptions (Kunasek et al., 2010). At the same time as the increase in $\Delta^{17}\text{O}(\text{SO}_4^{2-})$, there is a decrease in [MSA] and a slight, but not statistically significant, decrease in the [MSA]/[nssSO$_4^{2-}$] ratio, although MSA records may be compromised by acid-driven mobilization of MSA around volcanic peaks. This is suggestive of a change in the chemistry of DMS oxidation at the same time as the observed change in the chemistry of SO$_2$ oxidation. However, changes in the [MSA]/[nssSO$_4^{2-}$] ratio could be driven by either temperature (influencing reaction rates), oxidant abundances (OH).

$\Delta^{17}\text{O}(\text{NO}_3^-)$ is sampled at 1 m (1.8–4.8 years) resolution in the upper part of the core (0–129 m depth, spanning 1521–2000 CE) and varies between 21.4‰ and 43.7‰. Figure 4 includes an expanded version of the 1 m resolution data from Fig. 2. Large intersample variability in the high-resolution $\Delta^{17}\text{O}(\text{NO}_3^-)$ record highlights its local nature, in that it represents the signal of NO$_x$ cycling and nitrate formation in the NO$_x$ source regions. Prior to 1586 CE,
$\Delta^{17}$O(NO$_3^-$) and $\delta^{15}$N(NO$_3^-$) are sampled at the same resolution as $\Delta^{17}$O(SO$_4^{2-}$). For the consideration of long-term trends and comparison to $\Delta^{17}$O(SO$_4^{2-}$), the 1 m resolution $\Delta^{17}$O(NO$_3^-$) and $\delta^{15}$N(NO$_3^-$) records are smoothed by calculating a concentration-weighted average of the 1 m resolution nitrate isotope data to the temporal resolution of the $\Delta^{17}$O(SO$_4^{2-}$) measurements. Considering these low-resolution $\Delta^{17}$O(NO$_3^-$) data, the maximum $\Delta^{17}$O(NO$_3^-$) of 37.8 ‰ occurs between 802 and 865 CE. The minimum of 26.7 ‰ occurs between 1977 and 2006 CE.

The ice core $\delta^{15}$N(NO$_3^-$) at 1 m resolution (0–69.8 m; 1774–2005 CE) varies between 1.0 ‰ (1787–1791 CE) and 15.7 ‰ (1961–1964 CE and 1998–2000 CE). The low-resolution $\delta^{15}$N(NO$_3^-$) varies between 1.5 ‰ (316–370 CE) and 9.9 ‰ (1422–1481 CE), with a gradual upward trend since 370 CE. WAIS Divide $\delta^{15}$N(NO$_3^-$) does not exhibit the large enrichments observed in East Antarctic sites and are similar in range to $\delta^{15}$N(NO$_3^-$) from Greenland summit ice cores (−15.3–16.7 ‰) (Hastings et al., 2004). The similarity to Greenland is likely due to comparable snow accumulation rates (0.22–0.25 m a$^{-1}$ water equivalent Fegyveresi et al., 2011) that limit the degree of postdepositional processing.

While there is significant variability in the low-resolution $\Delta^{17}$O data in the early part of the ice core record, the largest changes in both $\Delta^{17}$O(NO$_3^-$) and $\Delta^{17}$O(SO$_4^{2-}$) occur in the period after 1800 CE. The maximum $\Delta^{17}$O(SO$_4^{2-}$) occurs in the sample spanning 1837–1880 CE with slightly lower values in the more recent samples, but the entire period 1837–2008 has a higher $\Delta^{17}$O(SO$_4^{2-}$) than any earlier sample and the post-1837 samples are indistinguishable from each other within the laboratory precision (±0.3 ‰). In contrast to the step increase in $\Delta^{17}$O(SO$_4^{2-}$), $\Delta^{17}$O(NO$_3^-$) gradually declines throughout the past 1000 years, with a more rapid decline beginning in the 1860s. While there is short-term variability in the 1 m resolution $\Delta^{17}$O(NO$_3^-$) record in the 1500s that is comparable in magnitude to the recent decline in $\Delta^{17}$O(NO$_3^-$), on the 100 to 200 year timescale, the downward trend in $\Delta^{17}$O(NO$_3^-$) between 1863 and 2000 CE is statistically distinct from any other centennial trends in the 1 m resolution record (1521–2000 CE). Trends for all 100 year intervals with starting dates of 1521–1859 CE have a mean slope of $(-0.5 \pm 2.3)$ ‰ century$^{-1}$, while those trends starting after 1863 CE have a mean slope of $(-6.7 \pm 0.8)$ ‰ century$^{-1}$. Similarly, the decrease in $\Delta^{17}$O(NO$_3^-$) when averaged to the resolution of the $\Delta^{17}$O(SO$_4^{2-}$) data is $-5.6$ ‰ from 1878 to 2000 CE.

Finally, there is a downward excursion in $\Delta^{17}$O(SO$_4^{2-}$), $\Delta^{17}$O(NO$_3^-$), and $\delta^{15}$N(NO$_3^-$) around the year 360 CE. The magnitude of the excursion in $\Delta^{17}$O(NO$_3^-$) is comparable in magnitude to the changes observed between the 1860s and the present day. There is no evidence of contamination in these samples and the deviation in both $\Delta^{17}$O(NO$_3^-$) and $\delta^{15}$N(NO$_3^-$) spans multiple samples. However, no other chemical tracers from the WAIS Divide ice core show a similar excursion. At this time, we do not attempt to explain the observed isotopic deviation around 360 CE and instead focus on the sustained changes in $\Delta^{17}$O(SO$_4^{2-}$) and $\Delta^{17}$O(NO$_3^-$) between 1800 CE and the present.

5 Comparison of $\Delta^{17}$O to other ice core records

To try to constrain the interpretation of the observed $\Delta^{17}$O changes, we compare the sulfate and nitrate isotope to other ice core measurements (listed below in Sections 5.1 and 5.2) from WAIS Divide that are related to sulfate and nitrate formation (Figs. 3 and 4). These measurements are made using continuous-flow analysis (CFA) at DRI, following methods adapted from McConnell et al. (2002, 2007), providing centimeter-scale resolution, which are averaged to the resolution of the isotope records presented here.

The continuous-flow measurement of MSA has not been previously published, and is briefly described here. MSA was analyzed by pumping a portion of the degassed CFA melt stream to an electrospray ionization triple-quadrupole mass spectrometer (ThermoFinnigan Quantum). The meltwater (150 µL min$^{-1}$) was mixed with HPLC grade methanol (50 µL min$^{-1}$) that was spiked with deuterated MSA as an internal standard (CD$_3$SO$_4$). MSA and deuterated MSA were
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5.1 $\Delta^{17}O(SO_4^{2-})$ comparison

Measurements of ice core acidity (Fig. 3) or calculated [$H^+$] based on sulfate, nitrate, and ammonium concentrations provide the best available insight into possible changes in cloud water pH, which impacts S(IV) speciation and the relative importance of oxidation by $O_3$ and $H_2O_2$. However, the acidity record shows little variability, and $\Delta^{17}O(SO_4^{2-})$ does not correlate with either ice core acidity or [$H^+$], making it unlikely that a change in cloud water pH could explain the observed change in $\Delta^{17}O(SO_4^{2-})$.

Similarly, $\Delta^{17}O(SO_4^{2-})$ shows no correlation with concentrations of transition metals (Fe or Mn) (Fig. 3) that may impact the aqueous-phase oxidation of S(IV) by $O_3$. Furthermore, CTM studies indicate that metal-catalyzed oxidation of S(IV) is a minor sulfate production pathway in the extratropical Southern Hemisphere (Alexander et al., 2009; Sofen et al., 2011). The lack of a relationship between $\Delta^{17}O(SO_4^{2-})$ and transition metal concentrations or acidity is notable, as it has been demonstrated that metal-catalyzed oxidation of S(IV) by $O_3$ is important for describing the observed variability of $\Delta^{17}O(SO_4^{2-})$ in a Greenland ice core over the same time period (Sofen et al., 2011).

$\Delta^{17}O(SO_4^{2-})$ does not show a statistically significant correlation with [$Na^+$], a proxy for sea salt (Fig. 3). Sea-salt sulfate represents 15–22% of the total sulfate in these samples. However, [$Na^+$] does not change in the early 1800s in a similar way to $\Delta^{17}O(SO_4^{2-})$. The step change in $\Delta^{17}O(SO_4^{2-})$ is present in the record prior to correction for sea-salt sulfate.

$\Delta^{17}O(SO_4^{2-})$ and sulfur concentrations (Fig. 3) are not correlated. This suggests that variability in $\Delta^{17}O(SO_4^{2-})$ is not controlled by changes in the magnitude of the sulfur source or the sulfur source region, as a change in the source region that impacted sulfate formation would likely be accompanied by a change in the amount of sulfate transported to WAIS Divide.

Hydrogen peroxide is the one oxidant species that can be directly measured in ice cores. Oxidation of S(IV) by $H_2O_2$ is thought to be the dominant sulfate formation pathway globally. Since $\Delta^{17}O(SO_4^{2-})$ of sulfate formed by $H_2O_2$ is only 0.65%, an increase in $H_2O_2$ in the southern high latitudes should decrease $\Delta^{17}O(SO_4^{2-})$ at WAIS Divide. We find that the WAIS Divide $\Delta^{17}O(SO_4^{2-})$ and [$H_2O_2$] records (Fig. 3) are not correlated. Ice core [$H_2O_2$] does not significantly change during the early 19th century when $\Delta^{17}O(SO_4^{2-})$ undergoes a step increase. However, $H_2O_2$ increases by approximately 60% in the period after 1837 CE, when $\Delta^{17}O(SO_4^{2-})$ remains relatively constant.

There is no available ice core proxy for fractional cloud cover or cloud liquid water content, both of which impact sulfate formation and thus $\Delta^{17}O(SO_4^{2-})$. We assume no change in these parameters based on the fact that climate has been relatively stable over this time period, as indicated by temperature proxies (e.g., $\delta^{18}O(H_2O)$).

Figure 3. Low-resolution sulfate and nitrate isotopes compared to measurements of accumulation rate, nitrate concentration, MSA concentration, sulfur concentration, sodium concentration, acidity, and $\delta^{18}O(H_2O)$ from the WDC06A core (except for nssSO$_4^{2-}$, from WDC05Q) averaged to the resolution of the sulfate isotope data.

detected in negative ion mode at the 95/80 and 98/80 m/z transitions (Saltzman et al., 2006). The internal standard was calibrated against aqueous MSA standards and the concentration of MSA in the ice core was determined from the ratio of the undeuterated and deuterated signals after minor blank corrections.

Records that come from the same core as the isotope record of interest are averaged with respect to depth. For comparison of measurements between different cores, high-resolution data is divided into segments to match the resolution of the isotope data in the time domain and then averaged based on depth.

We calculate correlation coefficients and determine their statistical significance using the $p$ value ($\leq 0.05$) with the number of degrees of freedom adjusted based upon the autocorrelation in the time series (Bretherton et al., 1999).
5.2 \(\Delta^{17}O(NO_3^-)\) comparison

Due to the fact that \(H_2O_2\) forms via the self-reaction of \(HO_2\), we would expect the large-scale increase in \(H_2O_2\) to be reflected in a decrease in \(\Delta^{17}O(NO_3^-)\) due to the increased importance of \(HO_2\) in \(NO_3\) cycling as long as the relative increase in \(x(HO_2)\), where \(x\) represents the mole fraction, is greater than the increase in \(x(O_3)\). We would expect a larger change in \(\Delta^{17}O(NO_3^-)\) than \(H_2O_2\) if organic peroxides were also increasing, since \(H_2O_2\) may not be influenced as strongly by changes in organic peroxide concentration \(x(RO_2)\) as it is by \(HO_2\). However, this may be alleviated by a simultaneous increase in \(x(O_3)\), since \(\Delta^{17}O(NO_3^-)\) reflects \(x(O_3)/x(RO_2)\). If \(\Delta^{17}O(NO_3^-)\) is influenced by local Antarctic boundary layer chemistry, we expect \(\Delta^{17}O(NO_3^-)\) to decrease at a more rapid rate beginning in the 1970s due to the impacts of the recent increase in UV flux on \(H_2O_2\) (Lamarque et al., 2011).

Indeed, \([H_2O_2]\) (Fig. 4) is anti-correlated with the 1 m resolution \(\Delta^{17}O(NO_3^-)\) between 1521 and 2000 CE \((R = -0.36)\), consistent with an increase in the importance of \(RO_2\) in \(NO_3\) cycling. The temporal resolution in \(\Delta^{17}O(NO_3^-)\) observations is not high enough to test whether the ozone hole impacts \(\Delta^{17}O(NO_3^-)\) through snowpack photodenitrification or the oxidizing capacity of the Antarctic boundary layer. The trend in \(\Delta^{17}O(NO_3^-)\) over the last thirty years \((-4 ± 4){\%}\ century^{-1}\) is indistinguishable from that of the last 100 years \((-5 ± 1){\%}\ century^{-1}\), further suggesting that postdepositional loss does not have a strong influence on ice core nitrate or its isotopes at WAIS Divide.

Ice core observations of \([MSA]\) (Fig. 3), indicative of DMS emissions, show a downward trend over the past 1800 years, but the correlation with the low-resolution \(\Delta^{17}O(NO_3^-)\) is not significant. A reduction in DMS would diminish the fraction of nitrate formed through the hydrogen abstraction pathway, reducing the \(\Delta^{17}O(NO_3^-)\). Therefore, the trend in MSA is consistent with the long-term trend in \(\Delta^{17}O(NO_3^-)\). However, there are a number of complicating factors in the interpretation of the MSA record. First, it assumes a constant relationship between DMS and MSA concentrations in the atmosphere, which could vary with changing oxidants. Second, MSA is also sensitive to postdepositional loss from the snowpack through volatilization (Weller et al., 2004), and the downward trend in MSA is consistent with increasing postdepositional processing as accumulation declines (see Fig. 3; as is the case for \(\Delta^{17}O(NO_3^-)\) and \(\delta^{15}N(NO_3^-)\)), although it has been argued that postdepositional loss of MSA is insignificant when snow accumulation is higher than 0.1 m water equivalent (Weller et al., 2004). Finally, the past 150 years in the MSA record do not show a change in \([MSA]\) akin to that observed in \(\Delta^{17}O(NO_3^-)\) (Fig. 4) and the two records are not significantly correlated over this time period (using 1 m resolution measurements).

The \(\Delta^{17}O(NO_3^-)\) is not correlated with nitrate concentrations (Fig. 4) at 1 m resolution between 1521 CE and present, and there is little trend in the concentration of nitrate over the past 200 years. This, in conjunction with the absence of large changes in \([NO_3^-]\) or \(\delta^{15}N(NO_3^-)\) all suggest that sources of nitrate to WAIS Divide have likely remained constant over this period, as a major shift in source regions would likely be accompanied by a change in the amount of nitrate transported to WAIS Divide and possibly the isotopic composition.

In addition to nitrate that forms at lower latitudes, \(NO_3\) emitted in mid-latitude continental regions could be transported to Antarctica via the reservoir molecule peroxyacetyl nitrate (PAN), which then thermally decomposes, releasing \(NO_3\), which will then be oxidized to \(NO_3^-\) in the local Antarctic atmosphere. While there is no proxy for PAN, mean PAN concentration of \((13 ± 7) pmol mol^{-1}\) with a slow decomposition rate of 0.05 pmol mol^{-1} h^{-1} are found at Neumayer (Jacobi et al., 2000). More recent measurements at Neumayer suggest that PAN varies between a net sink (spring) and a net source (summer) of \(NO_3\), with PAN loss rates of between 0.17 and 0.58 pmol mol^{-1} h^{-1} (Jones et al., 2011). PAN concentrations and loss rates are an order of magnitude lower than in the Arctic (Beine and Krognes, 2000), suggesting that PAN decomposition is an unimportant factor in WAIS Divide nitrate formation. Furthermore, while atmospheric PAN concentrations can be higher than inorganic nitrogen species during winter, snowpack nitrate concentrations correlate with inorganic reactive nitrogen (Jones...
et al., 2011), likely due to the longer lifetime to deposition of organic nitrate than inorganic nitrate (Wolff et al., 2008).

Finally, stratospheric denitrification is a potential source of high-$\Delta^{17}O$ nitrate to Antarctica, although its magnitude in West Antarctica is unknown. While it may impact the magnitude of the average $\Delta^{17}O(NO_3^-)$ observed in the WAIS Divide ice core, there is no reason to expect systematic changes in the polar stratospheric nitrate flux prior to the formation of the ozone hole in the 1970s. Furthermore, the lower elevation of West Antarctica likely means that stratospheric deposition is less important than on the East Antarctic Plateau.

5.3 Influence of postdepositional processing on $\Delta^{17}O(NO_3^-)$

The magnitude of nitrate postdepositional processing impacts the extent to which $\Delta^{17}O(NO_3^-)$ reflects regional oxidants from where the NO$_3^-$ is originally formed versus local oxidants from snowpack NO$_x$ being oxidized back to NO$_3^-$ in the Antarctic boundary layer. The 2400 year $\delta^{15}N(NO_3^-)$ record is negatively correlated with snow accumulation rate (Fegyveresi et al., 2011) ($R = -0.62$) and positively correlated with [NO$_3^-$] ($R = 0.58$; Fig. 3). Similarly, at low resolution, $\delta^{18}O(H_2O)$ (Fig. 3), a temperature proxy, is anti-correlated with $\delta^{15}N(NO_3^-)$ ($R = -0.63$) over the entire 2400 year record. However, $\Delta^{17}O(NO_3^-)$ and $\delta^{15}N(NO_3^-)$ are not correlated with each other. The correlations between $\delta^{15}N(NO_3^-)$, [NO$_3^-$], snow accumulation, and temperature suggests that on long timescales some degree of postdepositional processing of snowpack NO$_3^-$ is occurring at WAIS Divide. Increasing postdepositional processing due to the long-term decline in snow accumulation over the past 2000 years is likely responsible for the gradual downward trend in $\Delta^{17}O(NO_3^-)$ and upward trend in $\delta^{15}N(NO_3^-)$. However, the magnitude of the $\delta^{15}N(NO_3^-)$ values (1.0–15.7‰) is comparable to Greenland snowpack nitrate (Hastings et al., 2004, 2009) and only slightly enriched compared to NO$_x$ emissions and mid-latitude aerosol observations (Morin et al., 2009; Felix et al., 2012), suggesting that the majority of nitrate is well preserved in the snowpack. This is in contrast to East Antarctica where snowpack $\delta^{15}N(NO_3^-)$ enrichments on the order of 300‰ are observed. A flux of NO$_x$ emitted from East Antarctic snowpack and transported to WAIS Divide could also contribute to the low $\delta^{15}N(NO_3^-)$ values observed at WAIS Divide, but the similarity in $\delta^{15}N(NO_3^-)$ at WAIS Divide and Greenland summit sites with comparable snow accumulation rate suggest that this is not the case. Furthermore, while the 1 m resolution $\delta^{15}N(NO_3^-)$ between 1774 and 2008 CE is anti-correlated with the snow accumulation rate (Fig. 4; $R = -0.35$), the 1 m resolution $\Delta^{17}O(NO_3^-)$ is not correlated with snow accumulation, [NO$_3^-$], or $\delta^{15}N(NO_3^-)$ over the period 1521–2000 CE, suggesting that postdepositional processing does not have a controlling influence on higher frequency variability, such as the downward trend in $\Delta^{17}O(NO_3^-)$ since the 1860s.

5.4 Non-oxidant influences on $\Delta^{17}O$

The above comparisons between sulfate and nitrate isotopes and other tracers from the WAIS Divide ice cores include several related to the non-oxidant influences on $\Delta^{17}O$. These measurements include ice core acidity (proxy for cloud water pH) (Pastoris et al., 2012), [Mn] and [Fe] (impacting metal-catalyzed S(IV) oxidation by O$_2$, [Na$^+$] (proxy for sea-salt aerosol), [MSA] (a proxy for DMS), [S] and [SO$_4^{2-}$] (proxy for sulfate sources and sulfate aerosol abundance), [NO$_3^-$] (proxy for nitrate sources and nitrate aerosol abundance), snow accumulation rate (related to postdepositional loss of nitrate), and $\delta^{18}O(H_2O)$ (temperature proxy). We find that most of these records either show no significant correlation with either nitrate or sulfate isotopes or are correlated only on long timescales (the entire 2400 year record) with the low-resolution isotopes. While non-oxidant factors may contribute to the long-term variability in the WAIS Divide sulfate and nitrate isotopes, visually and statistically, none of the records representing non-oxidant factors exhibit changes similar to the observed changes in $\Delta^{17}O(NO_3^-)$ and $\Delta^{17}O(SO_4^{2-})$ over the past 200 years. This analysis suggests that variability in oxidant concentrations is the only possible explanation for the observed 1.1‰ increase in $\Delta^{17}O(SO_4^{2-})$ in the early 19th century and the 5.6‰ decrease in $\Delta^{17}O(NO_3^-)$ since the mid-19th century.

6 Monte Carlo box models of oxidant influences on $\Delta^{17}O$

To consider what changes in oxidants could cause the observed changes in $\Delta^{17}O$ since 1800 CE, we employ Monte Carlo box model simulations of sulfate and nitrate chemistry to investigate the magnitude of the oxidant changes implied in two time periods: the observed 1.1‰ increase in $\Delta^{17}O(SO_4^{2-})$ in the early 19th century and 5.6‰ decrease in $\Delta^{17}O(NO_3^-)$ between the 1860s and the present day. Based on the evidence of little postdepositional processing at WAIS Divide, NO$_x$ emissions and nitrate formation likely occur over Southern Hemisphere extratropical continental regions. The model uses boundary conditions from the extratropical South American boundary layer to calculate nitrate formation, reflecting the likely dominant source region for Antarctic nitrate (Lee et al., 2014). The sulfate box model uses boundary conditions from the Southern Ocean marine boundary layer (MBL), reflecting the dominant source region for Antarctic sulfate (Patris et al., 2000; Cosme et al., 2005; Sofen et al., 2011).
6.1 Model $^{17}\text{O}$-oxidant sensitivity

The box models are first used to assess the sensitivity of $^{17}\text{O}(\text{SO}_4^{2-})$ and $^{17}\text{O}(\text{NO}_3^-)$ to changes in the concentration of each oxidant. Figure 5 shows the sensitivity of $^{17}\text{O}(\text{SO}_4^{2-})$ and $^{17}\text{O}(\text{NO}_3^-)$ to a relative change in the concentration of each oxidant normalized to the mean conditions extracted from GEOS-Chem for the boundary conditions described above (Southern Ocean and South American boundary layers, respectively) (Sofen et al., 2011). The slope of each curve represents the response of $^{17}\text{O}$ to a change in a particular oxidant.

$^{17}\text{O}(\text{SO}_4^{2-})$ is sensitive to changes in O$_3$, OH, and H$_2$O$_2$ over the Southern Ocean, with $^{17}\text{O}(\text{SO}_4^{2-})$ increasing with increasing O$_3$ and increasing with decreasing OH or H$_2$O$_2$. $^{17}\text{O}(\text{SO}_4^{2-})$ becomes insensitive to changes in H$_2$O$_2$ at H$_2$O$_2$ concentrations greater than or equal to those of the present-day Southern Ocean marine boundary layer. The sensitivity of $^{17}\text{O}(\text{SO}_4^{2-})$ to H$_2$O$_2$ and O$_3$, as measured by the slope in Fig. 5, varies with their abundances, with higher sensitivity at lower x(H$_2$O$_2$) and x(O$_3$), respectively. The sensitivity of $^{17}\text{O}(\text{SO}_4^{2-})$ to x(OH) is nearly linear over the range of OH concentrations considered.

$^{17}\text{O}(\text{NO}_3^-)$ is most sensitive to O$_3$ and RO$_2$, because $^{2}$ of the $^{17}\text{O}$ of nitrate is determined during the NO$_x$-cycling step. $^{17}\text{O}(\text{NO}_3^-)$ increases with increasing O$_3$ and decreases with increasing RO$_2$. Changes in $^{17}\text{O}(\text{NO}_3^-)$ mainly reflect changes in x(O$_3$)/x(RO$_2$); that is, the variability in $^{17}\text{O}(\text{NO}_3^-)$ is dominated by the NO$_x$-cycling step. Except at extremely low OH concentrations, $^{17}\text{O}(\text{NO}_3^-)$ only weakly depends on x(OH) because NO$_2$+OH is always the dominant nitrate formation pathway during daytime. Including BrO in NO$_x$ cycling and the oxidation of NO$_2$ to NO$_3^-$ via the hydrolysis of BrONO$_2$ changes the sensitivity of $^{17}\text{O}(\text{NO}_3^-)$ to each of the oxidants (dashed lines; Fig. 5). BrO oxidation of NO leads to an overall upward shift in $^{17}\text{O}(\text{NO}_3^-)$, as well as increasing the sensitivity of $^{17}\text{O}(\text{NO}_3^-)$ to changes in OH concentrations by providing a competing daytime NO$_2$-oxidation pathway. Increasing x(BrO) further increases the sensitivity of $^{17}\text{O}(\text{NO}_3^-)$ to OH. However, note that with or without bromine chemistry, the box model underestimates the mean $^{17}\text{O}(\text{NO}_3^-)$ of the observations when we assume $^{17}\text{O}(\text{O}_3)$ is 25\%.

Initial model results provide a qualitative explanation for how the change in $^{17}\text{O}(\text{SO}_4^{2-})$ and $^{17}\text{O}(\text{NO}_3^-)$ can have opposite signs between 1800 CE and the present given likely increases in both O$_3$ and H$_2$O$_2$ (and therefore RO$_2$), and a small decrease in OH in the extratropical Southern Hemisphere. In sum, the increase in $^{17}\text{O}(\text{SO}_4^{2-})$ and decrease in $^{17}\text{O}(\text{NO}_3^-)$ can be explained by an increase in the x(O$_3$)/x(OH) ratio over the Southern Ocean and a decrease in the x(O$_3$)/x(RO$_2$) ratio over Southern Hemisphere extratropical continents respectively, which is qualitatively consistent with our expectations.

6.2 Oxidant changes suggested by $^{17}\text{O}(\text{NO}_3^-)$

The nitrate Monte Carlo box model simulations indicate that to match the observed decrease in $^{17}\text{O}(\text{NO}_3^-)$, assuming no change ($\leq 5\%$) in Southern Hemisphere extratropical x(OH) between the 1860s and 2000 CE, the x(O$_3$)/x(RO$_2$) ratio must decrease by 60–90\% in the NO$_3^-$ formation region. As shown in Fig. 6b, x(O$_3$) can increase by up to 80\% and x(RO$_2$) must increase by 130–350\% to be consistent with the $^{17}\text{O}(\text{NO}_3^-)$ observations. If x(OH) decreases by 33\% (the lower bound of CTM studies), x(O$_3$)/x(RO$_2$) must decrease by an even larger amount (−62 to −94\%). An increase in x(O$_3$)/x(RO$_2$) is only possible if x(OH) increases by > 250\%, which is highly unlikely over this time period due to increasing CH$_4$, which is a major sink of OH. If we assume a 25–63\% increase in x(O$_3$) since the preindustrial period based on global models and no change in
x(OH), this implies a local 180–350 % increase in x(RO2) in high-latitude Southern Hemisphere NOx source regions. CTM studies of preindustrial oxidant chemistry generally do not report changes in HO2 or RO2 species. If future model studies report changes in RO2 in addition to O3, they can use these ice core observations of \( \Delta^{17}O(\text{SO}_4^{2-}) \) as an additional constraint on paleo-oxidant modeling.

### 6.3 Oxidant changes suggested by \( \Delta^{17}O(\text{SO}_4^{2-}) \)

Monte Carlo box model simulations are used to find changes in oxidant abundances that reproduce the observed 1.1 % increase in \( \Delta^{17}O(\text{SO}_4^{2-}) \) in the early 19th century. Further constraints are imposed that x(H2O2) does not change, as ice core observations indicate that H2O2 does not begin to increase until the late 19th century, and x(O3) cannot decrease. To match the observed increase in ice core \( \Delta^{17}O(\text{SO}_4^{2-}) \), the fractional increase in the \( x(O_3)/x(OH) \) ratio in the Southern Ocean MBL must be at least 260 %, corresponding to an 18 % increase in the fraction of sulfate formed by O3 in the aqueous phase. As shown in Fig. 6a, there is a steep, near-linear relation between the required fractional changes in \( x(OH) \) (−50 to −80 %) and \( x(O_3) \) (0 to +120 %); simulations that match the observed \( \Delta^{17}O(\text{SO}_4^{2-}) \) change due to a large increase in \( x(O_3) \) correspond to a small decrease in \( x(OH) \). The minimum \( x(OH) \) decrease (−50 %), which is a much larger decrease than calculated by global models (−33 % to +14 %), corresponds to a 17 nmol mol⁻¹ (125 %) increase in \( x(O_3) \). This fractional change in \( x(O_3) \) is greater than the global average change since the preindustrial period in most global models and is comparable in magnitude to that based on the Schönbein \( x(O_3) \) observations in the Southern Hemisphere extratropics. A global model sensitivity study suggests that a doubling in \( x(CH_4) \), which is much greater than the observed \( x(CH_4) \) increase in the early 1800s, leads to only a 26 % increase in \( x(O_3)/x(OH) \) and changes in \( x(OH) \) and \( x(O_3) \) individually of ≤ 15 % in the Southern Hemisphere extratropics (Fig. A1; see Appendix A).

Overall, the early timing and large magnitude of the oxidant changes required to explain the observed \( \Delta^{17}O(\text{SO}_4^{2-}) \) seem highly implausible. This, combined with the fact that ice core observations suggest no significant influence of the non-oxidant factors on sulfate formation, suggests that the change in \( \Delta^{17}O(\text{SO}_4^{2-}) \) may be due to changes in oxidants not considered in the box model analysis. In particular, this analysis points to a decreasing importance of another low-\( \Delta^{17}O(\text{SO}_4^{2-}) \)-producing oxidant on this timescale. This is discussed further in Sect. 6.5.

The negligible changes in \( \Delta^{17}O(\text{SO}_4^{2-}) \) from 1837 to 2005 CE were previously shown to be consistent with the increases in extratropical Southern Hemisphere \( x(O_3) \) (25 to 27 %) and \( x(H_2O_2) \) (45 to 51 %), and a decrease in \( x(OH) \) (−15 %) in a CTM between the preindustrial and present day mainly due to the offsetting effects of increasing \( x(O_3) \) and \( x(H_2O_2) \) on \( \Delta^{17}O(\text{SO}_4^{2-}) \) (Kunasek et al., 2010; Sofen et al., 2011). Monte Carlo model results for the time period 1837–2005 CE, when \( \Delta^{17}O(\text{SO}_4^{2-}) \) is constant and \( x(H_2O_2) \) increases by 40–50 %, are consistent with the oxidant changes mentioned above. However, uncertainties in cloud water pH and \( \Delta^{17}O(O_3) \) leads to a wide range in \( x(O_3) \) and \( x(OH) \) changes in the Monte Carlo model that match the \( \Delta^{17}O(\text{SO}_4^{2-}) \) observations from 1837 to 2005 CE (Fig. 6b; red and yellow regions). At a pH of 5.0, there is a linear relationship between changes in \( x(O_3) \) and \( x(OH) \). At a higher pH, when \( O_3 \) dominates, \( \Delta^{17}O(\text{SO}_4^{2-}) \) is less sensitive to oxidant changes. Ice core observations suggest a pH of Antarctic precipitation of 5.4 (Cragin et al., 1987); however, it is difficult to directly link ice core acidity to cloud pH. Snow precipitation may overestimate cloud water
pH due to dilution of $[H^+]$ in large droplets. On the other hand, “bulk” cloud water chemistry schemes can underestimate cloud water pH of large droplets, effectively underestimating the importance of O$_3$ in sulfate formation and $\Delta^{17}O(SO_4^{2−})$ (Roelofs, 1993). Better observational constraints on cloud water pH and $\Delta^{17}O(O_3)$ may improve the ability of $\Delta^{17}O(SO_4^{2−})$ to be used to constrain $x(O_3)$ over this time period. That said, the model (Fig. 6) does suggest that changes in $x(O_3)$ of 100% since the late 1800s, as inferred from remote Southern Hemisphere Schönbein measurements (Sandroni et al., 1992), while not impossible, are difficult to reconcile with the ice core record of $\Delta^{17}O(SO_4^{2−})$, given our present understanding of sulfate formation mechanisms.

### 6.4 Sensitivity to ozone isotopic assumption

As a sensitivity study, we assume $\Delta^{17}O(O_3)$ is 35%. The higher isotopic signature of ozone makes it a stronger “lever” on the isotopic composition of nitrate or sulfate, so it slightly reduces the fractional changes in oxidant abundances required to match the observed changes in ice core nitrate and sulfate isotopes. Assuming $\Delta^{17}O(O_3)=35%$, the absolute agreement between the modeled and observed isotopic composition of both sulfate and nitrate. When we assume $\Delta^{17}O(O_3)=35%$, the $x(O_3)/x(RO_2)$ ratio must decrease by 48–84 %, with $x(O_3)$ increasing by up to 110% and $x(RO_2)$ increasing by 100–350 % between the 1860s and 2000 CE to match the observed decrease in $\Delta^{17}O(NO_3^−)$. If $x(OH)$ decreases by 33%, then $x(O_3)/x(RO_2)$ must decrease by 51–91%. As above, if we consider the range of preindustrial-to-present changes in $x(O_3)$ from global models and no change in $x(OH)$, a 140–300 % increase in high-latitude Southern Hemisphere $x(RO_2)$ is implied. In the sulfate model, assuming $\Delta^{17}O(O_3)$ is 35% reduces the magnitude of the change in sulfate formation pathways. To match the observed increase in $\Delta^{17}O(SO_4^{2−})$, an additional 12% of sulfate formed must be formed via oxidation by ozone, compared to 18% if $\Delta^{17}O(O_3)=25%$. This slightly lowers the required change in the $x(O_3)/x(OH)$ ratio to 210%, rather than 260%. The fractional change in $x(OH)$ also includes slightly smaller changes (−40 to −80%) than in the base case simulations.

In this sensitivity study, we find that, while unlikely, the nitrate isotope record can be consistent with the 100% increase in ozone suggested by the late-19th century measurements of surface ozone. In the base case ($\Delta^{17}O(O_3)=25%$), the modeled oxidant changes are not consistent with the late-19th century ozone measurements. Otherwise, the results of the base case and sensitivity study are quite similar, as the model analysis is focused on fractional changes in oxidant abundances.

### 6.5 Impact of reactive halogens on $\Delta^{17}O$

Reactive halogens may also impact the formation of both sulfate and nitrate, and hence, their $\Delta^{17}O$. There is no observation-based information about how the abundance of reactive halogens has changed in the recent past. Here we examine the sensitivity of sulfate and nitrate $\Delta^{17}O$ and our above conclusions regarding oxidant abundances to reactive halogens.

Including 1 pmol mol$^{−1}$ BrO as an oxidant of both NO and NO$_2$ increases the sensitivity of $\Delta^{17}O(NO_3^−)$ to changes in other oxidants (Fig. 5). If $x(OH)$ does not change between 1863 and 2000 CE, then including BrO in NO$_x$ cycling slightly reduces the fractional decrease in $x(O_3)/x(RO_2)$ (−58 to −84 %, or −46 to −79 % if $\Delta^{17}O(O_3)=35%$) required to match the observed change in $\Delta^{17}O(NO_3^−)$. This is because oxidation by BrO is a high-$\Delta^{17}O$ pathway, and with increases in $x(O_3)$ and $x(RO_2)$, the relative importance of BrO declines, reducing $\Delta^{17}O(NO_3^−)$. However, reactive Br will also reduce $x(O_3)$ through its catalytic destruction. While this could potentially further alter $\Delta^{17}O(NO_2)$, the changes associated with NO$_x$ cycling have little impact on $\Delta^{17}O$, as NO$_3$ and NO+BrO have similar isotopic signatures (Savarino et al., 2013). Including BrO also introduces another daytime nitrate formation pathway (BrONO$_2$ hydrolysis), which increases the sensitivity of $\Delta^{17}O(NO_3^−)$ to changes in $x(OH)$, partially offsetting the impact of BrO+NO on the sensitivity of $\Delta^{17}O(NO_3^−)$ to changes in $x(O_3)/x(RO_2)$. If we assume the largest decrease in $x(OH)$ from global models (−33 %) and no other oxidant changes, $\Delta^{17}O(NO_3^−)$ increases by 1.8% due to the increase in importance of BrONO$_2$ hydrolysis in nitrate formation. If BrO decreases, the primary impact on $\Delta^{17}O(NO_3^−)$ is a decrease due to the decreased importance of the BrONO$_2$ hydrolysis pathway; the changes associated with NO$_x$ cycling have little impact on $\Delta^{17}O(NO_3^−)$, as NO+O$_3$ and NO+BrO have similar isotopic signatures (Savarino et al., 2013).

Introducing a fixed concentration of HOCl and HOBBr in the sulfate box model reduces the sensitivity of $\Delta^{17}O(SO_4^{2−})$ to changes in other oxidants. Inclusion of this low-$\Delta^{17}O$ aqueous-phase pathway reduces the fraction of sulfate formed by O$_3$ in both periods, requiring even larger changes in O$_3$ to match the $\Delta^{17}O(SO_4^{2−})$ observations. On the other hand, at very low concentrations of HOCl and HOBBr (< 2 pmol mol$^{−1}$), $\Delta^{17}O(SO_4^{2−})$ is highly sensitive to changes in $x(HOCl)$ or $x(HOBBr)$, with a halving in $x(HOCl)$ or $x(HOBBr)$ causing a 1% increase in $\Delta^{17}O(SO_4^{2−})$. At higher $x(HOCl)$ or $x(HOBBr)$, these oxidants dominate aqueous-phase sulfate production, leading to very low $\Delta^{17}O(SO_4^{2−})$ values and little change in $\Delta^{17}O(SO_4^{2−})$ with changing $x(HOCl)$ or $x(HOBBr)$ (or other oxidants).

Interestingly, a decrease in the abundance of reactive halogens can qualitatively explain the observed trends in
Δ^{17}O(SO_{4}^{2−})�, Δ^{17}O(NO_{3}^{−})�, and [MSA]/[nssSO_{4}^{2−}] in the most recent part of the record. However, there is little information about the variability in reactive halogens on this timescale. Murray et al. (2014), using the reactive bromine chemistry scheme of Parrella et al. (2012) in the GEOS-Chem global chemical transport model, suggests a small increase in x(BrO_{3}) (BrO_{3} = Br + BrO), but the production mechanisms in the model are highly parameterized and do not include potentially important anthropogenic impacts such as changes in pH. However, ice core observations suggest little change in acidity in the high southern latitudes over this time period. The Δ^{17}O observations will be worth revisiting should new observational and modeling constraints on past reactive halogen abundances be developed.

7 Conclusions

We have measured the Δ^{17}O(SO_{4}^{2−}), Δ^{17}O(NO_{3}^{−}), and δ^{15}N(NO_{3}^{−}) from the upper 577 m of the WAIS Divide ice cores, spanning 2400 years. Based on comparison to other ice core observations, we demonstrate that the long-term increase in δ^{15}N(NO_{3}^{−}) and decrease in Δ^{17}O(NO_{3}^{−}) can be explained by the impact of the long-term decrease in the snow accumulation rate on the postdepositional loss of snowpack nitrate. However, changes in postdepositional processing cannot explain the 5.6% decrease in Δ^{17}O(NO_{3}^{−}) since 1860 CE. The 5.6‰ downward trend in Δ^{17}O(NO_{3}^{−}) since 1860 suggests an increase in the importance of RO_2 relative to O_3 in the oxidation of NO, while there is no apparent change in the formation of nitrate (NO_2 → HNO_3). The decrease in Δ^{17}O(NO_{3}^{−}) can be explained by a 60–90% decrease in the x(O_3)/x(RO_2) ratio in extratropical Southern Hemisphere NO_x source regions, which is qualitatively consistent with our expectations based on global modeling studies. A decrease in the importance of O_3 relative to RO_2 in NO_x cycling also leads to an enhancement in the production of O_3 by NO_x cycling. The 1.1‰ step increase in Δ^{17}O(SO_{4}^{2−}) in the early 19th century suggests a sustained increase in aqueous-phase sulfate production by O_3 (with an additional 12–18% of sulfate being formed by O_3) compared to gas-phase production by OH, reducing the fraction of sulfate that can contribute to new particle formation over the Southern Ocean. However, the 260% increase in x(O_3)/x(OH) required to explain the observed increase in Δ^{17}O(SO_{4}^{2−}) in the early 19th century is much too large to be reconciled with a 26% increase in x(O_3)/x(OH) from a CTM estimate for the Southern Hemisphere extratropics. This suggests deficiencies in our understanding of remote marine boundary layer sulfate formation, possibly related to sulfate formation involving hypohalous acids (HOCl and HOBr). Observations in the remote MBL of cloud water acidity and hypohalous acids in addition to Δ^{17}O(SO_{4}^{2−}) may lead to a better understanding of sulfate formation in the remote MBL and shed light on the record of Δ^{17}O(SO_{4}^{2−}) from the WAIS Divide ice core.

Appendix A: GEOS-Chem sensitivity studies

Global model studies report anthropogenic impacts on tropospheric oxidants due to the combined total changes in emissions of CH_4, CO, VOCs, and NO_x between a preindustrial period (typically 1750–1850) and the present (typically 1985–2010). However, emissions of different oxidant precursors (CH_4, CO, VOCs, NO_x) have some independence in their variability over this time period. For example, changes in wetlands will impact CH_4 without impacting NO_x. x(CH_4) began increasing around 1800 CE (Mitchell et al., 2011), prior to changes in other oxidant precursors due to anthropogenic activity. To investigate how possible emissions changes could impact oxidants since the preindustrial period, we conduct emissions sensitivity studies in which emissions of NO_x, CO, VOCs, or the concentration of CH_4 are independently doubled relative to those in a preindustrial simulation in the GEOS-Chem global three-dimensional atmospheric chemistry model (Bey et al., 2001; Sofen et al., 2011). Note that the model does not include recent updates by Mao et al. (2013) that implement HO_2 uptake on aerosols. The model uses present-day GEOS-4 meteorology. Anthropogenic emissions are turned off and x(CH_4) is set to a preindustrial value of 792 nmol mol^{-1}.

Figure A1. Sensitivity of oxidant concentrations to a doubling in [CH_4] or emissions of CO, NO_x, or VOCs relative to a simulation of preindustrial oxidant chemistry (Sofen et al., 2011). Each bar represents the fractional change in Southern Hemisphere extratropical lower tropospheric (≤ 2 km) oxidant concentration. The checkered segment of the CH_4 sensitivity study indicates the fraction of the oxidant changes for which CH_4-derived CO is responsible.
The evolution of preindustrial Southern Hemisphere NO\textsubscript{x}, CO, and VOC emissions and concentrations and their impact on oxidants are highly uncertain. The magnitude of the changes in CH\textsubscript{4} and NO\textsubscript{x} are similar to the expected changes between the preindustrial and present-day periods, but CO and VOC emissions sensitivity studies likely overestimate actual changes in their emissions. Figure A1 shows the percent change in Southern Hemisphere extratropical lower-tropospheric (five vertical levels; approximately 2 km) annual mean oxidant concentration for each sensitivity study. Doubling methane causes increases in O\textsubscript{3} (+9 %) and HO\textsubscript{2} (+10 %), and a decrease in OH (−14 %) in the Southern Hemisphere extratropical lower troposphere. It causes an even larger increase in H\textsubscript{2}O\textsubscript{2} (+22 %). A portion of the change in oxidants due to doubling methane is due to the change in CO that is an oxidation byproduct of the CH\textsubscript{4} and is shown in the hatched portion of the bar chart. Increasing x(CH\textsubscript{4}) prior to changes in other emissions is qualitatively consistent with the increase in x(O\textsubscript{3}) and decrease in x(OH) suggested by ∆\textsuperscript{17}O(SO\textsubscript{4}\textsuperscript{2−}). However, a doubling in x(CH\textsubscript{4}) (Fig. A1), and certainly the relatively small change in x(CH\textsubscript{4}) by the mid-1800s, is not enough to produce the magnitude of x(O\textsubscript{3})/x(OH) changes inferred from ∆\textsuperscript{17}O(SO\textsubscript{4}\textsuperscript{2−}).

Most CTMs assume that preindustrial biomass burning carbon monooxide emissions were 10 % of those in the present day, but recent ice core and firn air observations of carbon monooxide isotopes and concentration suggest that Southern Hemisphere carbon mono oxide varied widely over the past millennium, including periods when carbon mono oxide was higher than in the present day (Wang et al., 2010). Doubling CO emissions causes small increases in O\textsubscript{3} (+1 %) and HO\textsubscript{2} (+2 %), a small decrease in OH (−3 %) and a larger increase in H\textsubscript{2}O\textsubscript{2} (+5 %).

Doubling NO\textsubscript{x} emissions increases Southern Hemisphere extratropical O\textsubscript{3} (+6 %) and OH (+8 %) with little influence on HO\textsubscript{2} or H\textsubscript{2}O\textsubscript{2} (< 1 %). Emissions inventories suggest that increases in Southern Hemisphere NO\textsubscript{x} emissions are likely restricted to the low latitudes (van Aardenne et al., 2001). Similarly, we see no change in [NO\textsubscript{3}−1] in the WAIS Divide ice core. However, NO\textsubscript{x} emissions at low latitudes may have a larger hemispheric influence on O\textsubscript{3}, as O\textsubscript{3} has a longer lifet ime than NO\textsubscript{x} itself.

We find that increasing VOC emissions produces large increases in HO\textsubscript{2} (+10 %) and H\textsubscript{2}O\textsubscript{2} (+31 %), a decrease in OH (−15 %), and little change in O\textsubscript{3} (−1 %) (because the Southern Hemisphere extra tropics are NO\textsubscript{x} limited). One model study of preindustrial VOC emissions suggests that while on the global scale emissions of isoprene decreased and monoterpenes increased between 1854 and 2000 CE, South American emissions of both VOCs increased, but only by 10 % (Tanaka et al., 2012).

The largest changes in oxidant ratios are a 26 % increase in x(O\textsubscript{3})/x(OH) due to doubling methane and a 9 % decrease in x(O\textsubscript{3})/x(HO\textsubscript{2}) due to doubling VOCs. Considering the likely impact of these emissions scenarios on 1800s oxidants, estimated emissions changes in the Southern Hemisphere are likely too small to produce the large oxidant changes suggested by ∆\textsuperscript{17}O(SO\textsubscript{4}\textsuperscript{2−}), making it difficult to reconcile CTMs with the oxidant changes implied by the ice core ∆\textsuperscript{17}O(SO\textsubscript{4}\textsuperscript{2−}). It is difficult to compare the oxidants implied by ∆\textsuperscript{17}O(NO\textsubscript{3}−) to CTMs directly because x(RO\textsubscript{2}) is not typically diagnosed in global models.

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References


Arsene, C., Barnes, I., and H. Becker, K.: FT-IR product study of the photo-oxidation of dimethyl sulfide: temperature and O\textsubscript{2} partial

www.atmos-chem-phys.net/14/5749/2014/ Atmos. Chem. Phys., 14, 5749–5769, 2014
E. D. Sofen et al.: WAIS Divide sulfate and nitrate isotopes


Liu, Q.: Kinetics of aqueous phase reactions related to ozone depletion in the Arctic troposphere: bromine chloride hydrolysis, bromide ion with ozone, and sulfur(IV) with bromine and hypobromous acid, Ph.D. thesis, Purdue University, Lafayette, IN, 2002.


Savarino, J. and Thiemens, M. H.: Analytical procedure to determine both $\delta^{18}$O and $\delta^{17}$O of H$_2$O$_2$ in natural water and first measurements, Atmos. Environ., 33, 3683–3690, doi:10.1016/S1352-2310(99)00122-3, 1999.


