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## A record of ozone variability in South Pole Antarctic snow: Role of nitrate oxygen isotopes

Justin R. McCabe,<sup>1</sup> Mark H. Thiemens,<sup>1</sup> and Joel Savarino<sup>2</sup>

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[1] The information contained in polar nitrate has been an unresolved issue for over a decade. Here we demonstrate that atmospheric nitrate's oxygen isotopic composition ( $\Delta^{17}\text{O-NO}_3$ ) reflects stratospheric chemistry in winter and tropospheric chemistry in summer. Surface snow isotope mass balance indicates that nitrate oxygen isotopic composition is the result of a mixture of 25% stratospheric and 75% tropospheric origin. Analysis of trends in  $\Delta^{17}\text{O-NO}_3$  in a 6 m snow pit that provides a 26-year record reveals a strong 2.70-year cycle that anticorrelates ( $R = -0.77$ ) with October–November–December column ozone. The potential mechanisms linking the records are either denitrification or increased boundary layer photochemical ozone production. We suggest that the latter is dominating the observed trend and find that surface ozone and  $\Delta^{17}\text{O-NO}_3$  correlate well before 1991 ( $R = 0.93$ ). After 1991, however, the records show no significant relationship, indicating an altered oxidative environment consistent with current understanding of a highly oxidizing atmosphere at the South Pole. The disappearance of seasonal  $\Delta^{17}\text{O-NO}_3$  trends in the surface layer at depth remain unresolved and demand further investigation of how postdepositional processes affect nitrate's oxygen isotope composition. Overall, the findings of this study present a new paleoclimate technique to investigate Antarctic nitrate records that appear to reflect trends in stratospheric ozone depletion by recording tropospheric surface ozone variability.

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### 1. Introduction

[2] The ability of polar nitrate to record changes in the oxidizing potential of the atmosphere have been suggested [Wolff, 1995] and shown with a multiple oxygen isotope ( $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ ) study in Greenland [Alexander *et al.*, 2004]. The primary source of nitrogen to Antarctica remains relatively uncertain but is suggested to be a combination of transport from midlatitudes, galactic cosmic ray production, volcanic emissions, lightning, stratospheric  $\text{N}_2\text{O}$  oxidation and denitrification of the stratosphere [Wolff, 1995]. Mayewski and Legrand [1990] were the first to propose a link between South Polar nitrate and ozone depletion over Antarctica. However, consistent findings of near-surface nitrate increases [Röthlisberger *et al.*, 2000; Wolff, 1995] along with unexpectedly high  $\text{NO}_x$  concentrations in the polar boundary layer [Davis *et al.*, 2001] implicated significant influence of postdepositional effects thereby limiting the ability to interpret snow/ice nitrate in terms of atmospheric air concentration. Laboratory and field experiments

demonstrated the role of photochemistry [Honrath *et al.*, 1999]. Volatilization of nitric acid is also suspected to play a significant role in the distribution of nitrate in the air-snow boundary [Wolff *et al.*, 2002; Blunier *et al.*, 2005]. In recent years, a large number of studies have been dedicated to understanding these processes to derive a means of elucidating the information contained in polar nitrate records [Domine and Shepson, 2002]. The oxygen isotope measurements of nitrate presented here reveal a connection to October, November, December total column ozone levels providing new information from Antarctic nitrate and offering a potential means to reconstruct the dynamics of the stratospheric ozone layer beyond ground and satellite observations.

[3] The ozone hole first appeared in the early 1980s and since then reappears every Austral spring (September and October) with varying intensity [Farman *et al.*, 1985]. As the result of a dynamic combination of physical and chemical factors, the nonlinear decrease in ozone levels remains an area of intense research in efforts to understand the recovery of ozone levels over Antarctica [Bodeker *et al.*, 2005; Solomon *et al.*, 2005]. The physical conditions are manifest by the formation of the polar vortex every July and August when extremely cold stratospheric temperatures of 188–193 K (−80 – −85°C) result in polar stratospheric clouds (PSCs) containing nitric acid trihydrate (NAT) and sulfuric acid trihydrate (SAT) ice crystals [Hamill *et al.*,

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1988]. On the surface of these ice particles, inactive chlorine gas species are converted to active  $\text{ClO}_x$  species. In early spring, these species are readily photolyzed to chlorine atoms that catalyze ozone destruction [Solomon *et al.*, 1986; Crutzen and Arnold, 1986]. During the polar vortex of the preceding winter, extreme temperatures can promote ice crystal, PSC, growth up to 10 microns in size leading to their descent from the stratosphere and deposition on the snow surface. This process is known as denitrification and dehydration of the stratosphere. Several studies attribute Antarctic nitrate to this source [Mayewski and Legrand, 1990; Mulvaney and Wolff, 1993; Wagenbach *et al.*, 1998]. In the following discussion, we implement isotopic measurements of nitrate to probe denitrification of the Antarctic stratosphere and its link to ozone depletion.

[4] Oxygen isotopes of nitrate contain a nonmass-dependent relationship between oxygen 17 ( $\delta^{17}\text{O}$ ) and oxygen 18 ( $\delta^{18}\text{O}$ ) that is defined by  $\Delta^{17}\text{O-NO}_3$ . Typical mass-dependent fractionation processes result in a relationship of  $\delta^{17}\text{O} \approx 0.5 \times \delta^{18}\text{O}$  while mass-independent fractionation (MIF) does not and is defined by the linear approximation  $\Delta^{17}\text{O} \approx \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$  where  $\Delta^{17}\text{O} = 0$  is a mass-dependent process. The origin of  $\Delta^{17}\text{O-NO}_3$  is oxygen atom transfer from the mass-independent composition of ozone during  $\text{NO}_x$  ( $\text{NO}$ ,  $\text{NO}_2$ ) oxidation. Laboratory experiments showed that ozone production leads to MIF of oxygen isotopes,  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  [Thiemens and Heidenreich, 1983] confirmed by tropospheric ozone measurements of  $\Delta^{17}\text{O} = 27.1 \pm 4.8\text{‰}$  [Johnston and Thiemens, 1997; Krankowsky *et al.*, 1995], and stratospheric ozone being more enriched, with a range from 25.0 to 38.9‰ [Krankowsky *et al.*, 2000; Mauersberger *et al.*, 2001]. Several atmospheric species contain MIF:  $\text{CO}$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{ClO}_4$  and stratospheric  $\text{CO}_2$  [Thiemens, 2006]. Studies of urban atmospheres have shown  $\Delta^{17}\text{O-NO}_3 = 20 - 30\text{‰}$  [Michalski *et al.*, 2003]. Measurements of  $\Delta^{17}\text{O-NO}_3$  have already generated a wealth of information regarding the N cycle or the past oxidative capacity of the atmosphere [Michalski *et al.*, 2004, 2005]. In this study, we utilize the difference between tropospheric and stratospheric-generated nitrate as reflected in South Pole aerosol nitrate to identify the two sources (tropospheric photochemistry and stratosphere denitrification) and show how multiple oxygen isotope measurement in nitrate preserved in snow record changes in oxidative conditions of the overlying atmosphere and thereby record stratospheric ozone variations.

## 2. Methods

[5] In December of 2003, we began a yearlong campaign to investigate how oxygen isotopes of nitrate could improve our understanding of polar chemistry. The South Pole Atmospheric Nitrate Isotopic Analysis (SPANIA) program consisted of a suite of three complimentary collection and measurement efforts: 3.5 to 4.0 kg samples of snow every 5 cm from a 6 m snow pit, weekly high-volume aerosol collections, and monthly surface snow samples containing 3.0–3.6 kg. All snow samples were stored in sealed polyethylene bags at NICL until analysis at UCSD's Stable Isotope Laboratory.

[6] Surface snow and snow pit samples were evaporated to 50 ml at 70°C and separated on a Dionex AS9-HC column. Aerosols collected on prewashed  $8 \times 10''$  ( $20.3 \times 25.4$  cm) Grasbey glass fiber filters were sent to UCSD, solubilized in 40 mL of Millipore water and separated as above. Purified nitrate was converted to  $\text{AgNO}_3$  using a Dionex AMMS-III suppressor membrane with 2.5 mM  $\text{Ag}_2\text{SO}_4$  as regenerant.  $\text{AgNO}_3$  was then combusted at 520°C and analyzed for oxygen isotopes,  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ , on a Finnigan Mat 251 multiple collector mass spectrometer according to the methods of Michalski *et al.* [2002]. The standard deviation of this method is  $\pm 0.3\text{‰}$ .

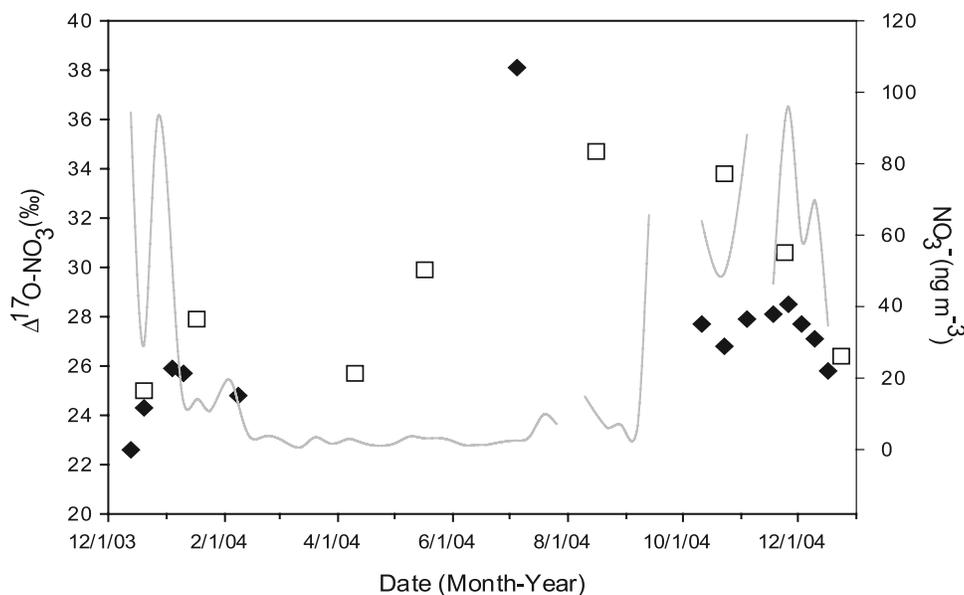
[7] The chronology of the 6 m snow pit was derived from trace chemical analysis ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ ) conducted via ion chromatography at LGGE in Grenoble, France. A Dionex DX500 with AS11 column and Dionex DX100 with CS12 column were used for anion and cation measurements, respectively. Mt. Pinatubo produces fivefold increases in sulfate concentrations in snow and was used to establish the year 1993 [Dibb and Whitlow, 1996; Cole-Dai *et al.*, 1997]. Seasonal trends in  $\text{Na}^+$ ,  $\text{Cl}/\text{Na}$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were then utilized to date individual years [Whitlow *et al.*, 1992; Legrand *et al.*, 1992]. The result was a record of  $\Delta^{17}\text{O-NO}_3$  spanning from 1977–2003.

## 3. Results

[8] The seasonal composition of nitrate aerosol and surface snow is noticeably different between Austral winter and summer as shown in Figure 1. Summer  $\Delta^{17}\text{O-NO}_3$  in aerosol ranges from 22.6 to 28.5‰ while combined winter (July and August)  $\Delta^{17}\text{O-NO}_3 = 38.1\text{‰}$ . The monthly surface snow also shown in Figure 1, reflects this change in isotopic composition despite a 1–2 month lag in early spring, with summer/fall (December–April)  $\Delta^{17}\text{O-NO}_3 = 25.0$  to 27.9‰ and winter/spring (May–November)  $\Delta^{17}\text{O-NO}_3 = 29.9$  to 34.7‰. The 6 m snow pit preserves this seasonal variation in the top 18 cm, equivalent to 1 year of deposition, shown in Figure 2a during 2003 where  $\Delta^{17}\text{O-NO}_3 = 24.6$  to 33.1‰. However, beneath the top 18 cm (prior to 2003), the seasonal trend disappears giving rise to the appearance of longer cycles and an average  $\Delta^{17}\text{O-NO}_3 = 25.4 \pm 1.9\text{‰}$ . Nitrate concentrations are also displayed in Figure 2a and show no correlation to  $\Delta^{17}\text{O-NO}_3$  suggesting the isotopic variability is not significantly influenced by postdepositional effects, as is the case for the concentrations [Röthlisberger *et al.*, 2000]. At depth, the variation in  $\Delta^{17}\text{O-NO}_3$  appears to vary on multiyear timescales with some periodicity.

## 4. Discussion

[9] In comparing the seasonal cycle observed in aerosol and surface snow to the interannual variations in the snow pit record, we suggest that local oxidation conditions controlling nitrate formation are reflected in the isotope record and indicative of changes in surface ozone and UV flux associated with ozone depletion in Austral spring as shown by corresponding periods at 2.7 years in Figure 3.



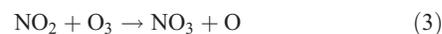
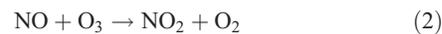
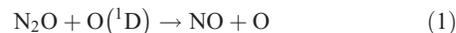
**Figure 1.** Seasonal trend in  $\Delta^{17}\text{O-NO}_3$  aerosol (solid diamonds) and surface snow (open squares) shown for samples collected at the South Pole during 2004. Nitrate aerosol concentrations ( $\text{ng m}^{-3}$ ) are shown on the right axis by a solid gray line.

Seasonal variations in  $\Delta^{17}\text{O-NO}_3$  confirm stratospheric nitrate as an important winter and early spring source of Antarctic nitrate. However, the role of local photochemical nitrate production in spring and summer appears to dominate both the isotope record in surface snow during 2004 and the range in isotopic values found in the snow pit. Changes in local conditions of the overlying atmosphere occurring on similar timescales appear to result in yearly variations in the average  $\Delta^{17}\text{O-NO}_3$  preserved in South Pole snow. While postdepositional effects do not affect the isotopic record in the same way as the concentrations, the influence of photochemical recycling of  $\text{NO}_x$  and nitrate in the boundary layer is important to any interpretation of nitrate records snow. Here we argue that trends in spring-time total column ozone are reflected in interannual variations found in nitrate's oxygen isotopes. The relationship between the records appears to be driven in part by fluctuations in summer UV flux associated with ozone depletion and may provide evidence of recent changes in the production and destruction of surface ozone at South Pole.

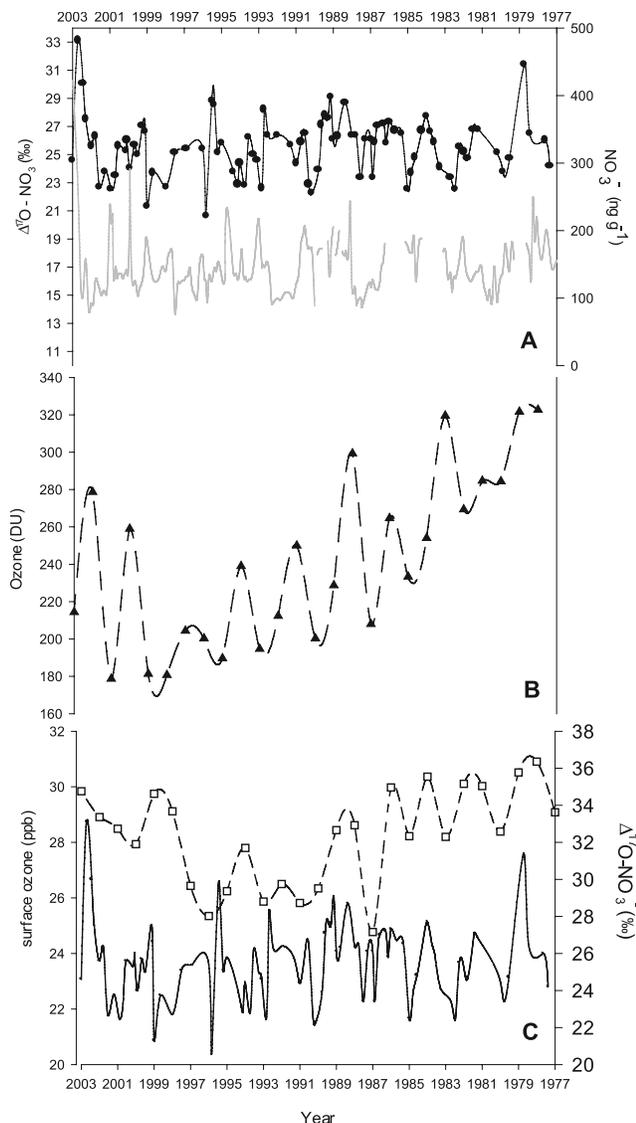
#### 4.1. Seasonal Composition of $\Delta^{17}\text{O-NO}_3$

[10] The oxygen isotopes of nitrate in snow/ice will record the influence of three processes: the stratospheric chemistry, the tropospheric chemistry, and in situ photochemistry. Therefore we must first recognize how tropospheric versus stratospheric chemistry appears to be controlling the difference in  $\Delta^{17}\text{O-NO}_3$  observed in summer and winter. The unusually large enrichment in  $\Delta^{17}\text{O-NO}_3$  observed during late winter is best explained by stratospheric chemistry. Nitrate and nitric acid in the stratosphere are largely the result of  $\text{N}_2\text{O}$  oxidation via

$\text{O}(^1\text{D})$  followed by  $\text{NO}_x$  oxidation by ozone according to the following reactions:

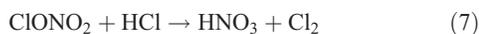


[11] Reaction (5) will yield  $\text{HNO}_3$  and nitrate with a  $\Delta^{17}\text{O-NO}_3 = 5/6 \alpha \Delta^{17}\text{O-O}_{3\text{strat}}$  [Michalski *et al.*, 2003], where  $\alpha$  represents the anomaly transfer from  $\text{O}_3$  to  $\text{NO}_2$ . The distribution of heavy oxygen atoms within ozone is not statistical with higher enrichment for asymmetric ( $\text{O}^{16}\text{-O}^{16}\text{-O}^{18}$ ) than symmetric ( $\text{O}^{16}\text{-O}^{18}\text{-O}^{16}$ ) isotopomers above 170 K [Janssen, 2005]. Considering that contributions from the central and terminal atoms of ozone must be accounted in oxygen atom transfer during reactions (2) and (3), laboratory experiments reveal  $\alpha \approx 0.8$  for reaction (2) [Savarino *et al.*, 2006a]. Using this value of  $\alpha$  for reactions (2) and (3) results in  $\Delta^{17}\text{O-NO}_3$  values of 19.5–25.9‰ on the basis of stratospheric ozone values,  $\Delta^{17}\text{O-O}_{3\text{strat}} = 34.1 \pm 4.8 \text{‰}$  [Mauersberger *et al.*, 2001]. Without  $\alpha$ ,  $\Delta^{17}\text{O-NO}_3 = 24.4\text{--}36.3\text{‰}$ . The higher observed value in winter nitrate aerosol (38.1‰) suggests that either the nitrate has acquired all oxygen atoms from stratospheric



**Figure 2.** (a) Yearly  $\Delta^{17}\text{O}-\text{NO}_3$  (‰) and  $\text{NO}_3^-$  concentrations ( $\text{ng g}^{-1}$ ) from the South Pole snow pit, (b) October–November–December total column ozone concentrations (Dobson Units (DU)) from the CMDL Data Archive (<http://www.cmdl.noaa.gov/infodata/ftpdata.html>), and (c) surface ozone concentrations in ppb from CMDL Data Archive with spline of  $\Delta^{17}\text{O}-\text{NO}_3$ .

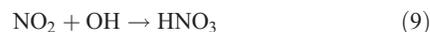
ozone when  $\text{ClONO}_2$  is the dominant source, or polar stratospheric ozone contains a higher enrichment than the presently known values.  $\text{ClONO}_2$  forms in polar vortex conditions and leads to  $\text{HNO}_3$  via the following reactions:



The isotopic composition of  $\text{ClO}$  will be more enriched than bulk ozone because of contribution from asymmetrically enriched end members of ozone,  $\Delta^{17}\text{O}-\text{O}_{3\text{endmembers}}$  [Zhang *et al.*, 1997; Toohey *et al.*, 1988]. The overall composition of  $\text{ClONO}_2 = 2/3 \Delta^{17}\text{O}-\text{O}_{3\text{strat}} + 1/3 \Delta^{17}\text{O}-\text{O}_{3\text{endmembers}}$ , where

$\Delta^{17}\text{O}-\text{O}_{3\text{endmembers}} = 46.6\text{‰}$  at 240 K and 200 Torr total pressure [Janssen, 2005], which results in  $\Delta^{17}\text{O}$  of  $\text{ClONO}_2 = 38.7\text{‰}$ . Similar values of  $\Delta^{17}\text{O}-\text{NO}_3$  are observed July through September at a coastal site, Dumont d'Urville, Antarctica [Savarino *et al.*, 2006b].

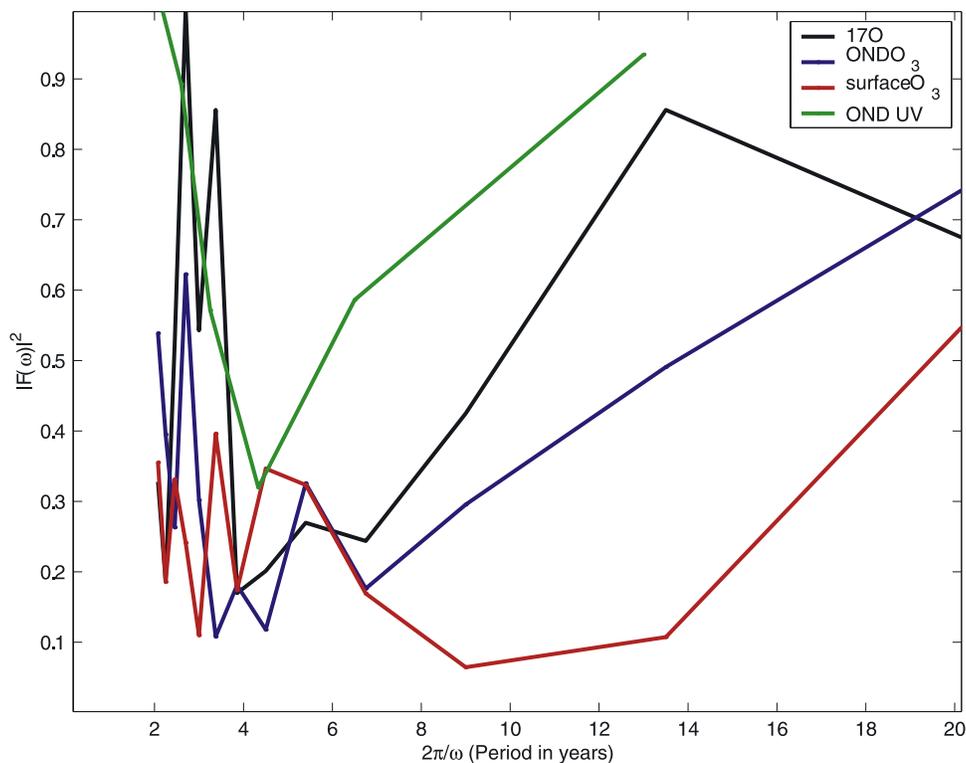
[12] In the troposphere,  $\Delta^{17}\text{O}-\text{NO}_3$  will have lower values as a result of lower tropospheric ozone enrichments,  $\Delta^{17}\text{O}-\text{O}_{3\text{tropo}} = 27.1 \pm 4.9\text{‰}$ , and the addition of the following reactions:



$\text{OH}$  and  $\text{HO}_2$  are assumed to contain  $\Delta^{17}\text{O} = 0\text{‰}$  because the lifetime of  $\text{OH}$  over Antarctica is long enough to isotopically exchange with water before oxidation via  $\text{CO}$  [Michalski *et al.*, 2003]. Measurements of high  $\text{OH}$  concentrations ( $2 \times 10^6$  molecules  $\text{cm}^{-3}$ ) similar to that of the marine boundary layer have been observed at South Pole during summer [Mauldin *et al.*, 2001], which is consistent with lower  $\Delta^{17}\text{O}-\text{NO}_3 = 26.3\text{‰}$  observed during summer (Figure 1) and similar to observations in the midlatitude troposphere,  $26.4 \pm 2.0\text{‰}$  [Michalski *et al.*, 2003]. Therefore winter and summer aerosol isotopic composition is explained by a transition from winter stratospheric denitrification to summer photochemical surface snow release of  $\text{NO}_x$  followed by ozone and hydroxyl oxidation, and nitric acid redeposition.

#### 4.2. Air-Snow Isotope Transfer

[13] Comparison between seasonal composition in aerosol and surface snow indicates efficient transfer of the isotopic composition of the atmosphere to surface snow (Figure 1). In July–August and September–October nitrate in surface snow contain 91% and 87%, respectively, of the  $\Delta^{17}\text{O}-\text{NO}_3$  observed in winter aerosol, 38.1‰. However, during early spring (October) dramatic fivefold to sixfold nitrate aerosol concentration increases see a significant reduction in  $\Delta^{17}\text{O}-\text{NO}_3$  compared to surface snow. This 6.0‰ difference cannot be explained by in situ photochemical isotope effects [McCabe *et al.*, 2005] and is better explained by the information contained in aerosol filter versus surface snow collections. Surface snow will contain integrated deposition of  $\Delta^{17}\text{O}-\text{NO}_3$  while filters will record the oxidation and source conditions only during the period of collection. The presence of this initial disparity is possible evidence that winter nitrate from the stratosphere is the primary source for nitrate photochemically released from surface snow in spring. According to Muscari *et al.* [2003], the total loss of  $\text{NO}_y$  during denitrification is  $6.3 \pm 2.3 \times 10^7$  kg N, which corresponds to a stratospheric nitrogen flux of  $2.4\text{--}5.7$  kg N  $\text{km}^{-2}$   $\text{yr}^{-1}$  assuming homogeneous deposition across the plateau. This is a significant flux when compared to the net flux of  $2.1$  kg N  $\text{km}^{-2}$   $\text{yr}^{-1}$  based on ice core analysis [Legrand and Kirchner, 1990]. Of the stratospheric nitrate preserved in the ice record, nearly half ( $1.0$  kg N  $\text{km}^{-2}$   $\text{yr}^{-1}$ ) is estimated to be affected

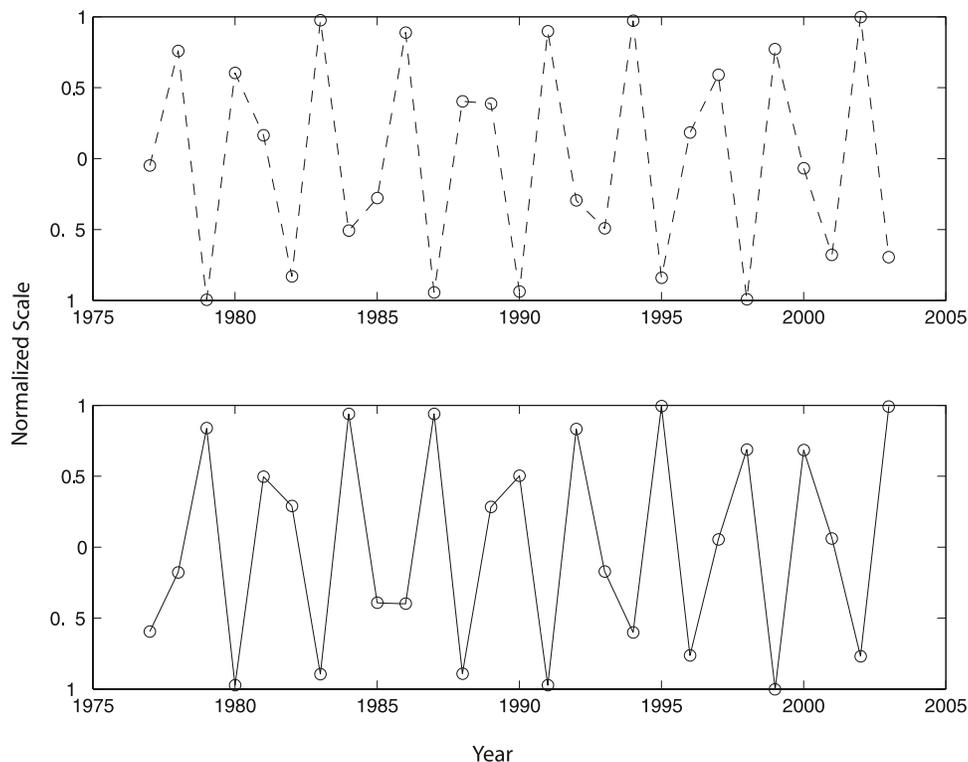


**Figure 3.** Fourier analysis of  $\Delta^{17}\text{O}\text{-NO}_3$  (black line); October, November, December column ozone (blue line); surface ozone (red line); and October, November, December UV from the CMDL Data Archive (green line), demonstrating the ability of oxygen isotopes in nitrate to preserve trends in column and surface ozone in the ice core record.

by photochemical recycling [Davis *et al.*, 2004]. This process involves  $\text{NO}_x$  release from the snowpack, transport across the plateau undergoing oxidation via OH and tropospheric  $\text{O}_3$  in the boundary layer, and redeposition [Davis *et al.*, 2004]. Therefore surface snow  $\Delta^{17}\text{O}\text{-NO}_3$  will reflect the relative stratospheric and tropospheric isotopic contributions. The amount of stratospheric nitrate preserved in surface snow is dictated by this redistribution across the plateau due to photochemical and oxidative recycling in the boundary layer and is particularly important at the South Pole where connections between wind speed and  $\text{NO}_x$  concentrations argues for the transport of  $\text{NO}_x$  from the eastern upslope plateau [Davis *et al.*, 2004]. The highest observed atmospheric  $\text{NO}_x$  [Davis *et al.*, 2001] and snow nitrate concentrations across the plateau have been observed at the South Pole [Wolff, 1995] suggesting that this location may contain nitrate produced largely at other locations across the plateau and record changes in boundary layer oxidation conditions over Antarctica.

[14] Significant in situ postdepositional effects in the snow pit isotope record would likely result in near surface increases similar to nitrate concentrations. However, the top 18 cm of the snow pit preserves a seasonal cycle ranging from 24.6‰ in the top 5 cm to 33.1‰ in the next 5 cm (Figure 2a) similar to the range in surface snow observed in 2004 (25.0 to 34.7‰). The disappearance of the seasonal trend below the top 18 cm may be the result of sampling protocol that unintentionally smoothed the seasonal trends or diffusion of nitric acid within the interstitial air. The in situ photochemical isotope effect, however, appears negli-

gible. The annual average  $\Delta^{17}\text{O}\text{-NO}_3 = 28.8\text{‰}$  in 2003 as preserved in the top 18 cm of the snow pit. When compared to 29.3‰ observed the following year in total surface snow, we see a 0.5‰ reduction in  $\Delta^{17}\text{O}\text{-NO}_3$  between 2003 and 2004, which is close to the uncertainty in our measurements (0.3‰). However, long-term multiple year aerosol and surface snow sampling efforts are necessary to define the actual range and variability in the isotopic values. If the discrepancy in 2003 and 2004 surface snow is purely the result of a postdepositional isotope effect, it is consistent with a  $-0.5 \pm 0.3\text{‰}$  change in  $\Delta^{17}\text{O}\text{-NO}_3$  with 40% nitrate loss observed during photolysis experiments at  $-30^\circ\text{C}$  [McCabe *et al.*, 2005]. Flux model studies suggest the same fraction of photochemical loss (40%) [Wolff *et al.*, 2002]. In addition,  $\delta^{18}\text{O}$  isotope effects evaluated using the methods of Blunier *et al.* [2005] for  $\delta^{15}\text{N}$  result in a fractionation factor,  $\varepsilon = -6.8\text{‰}$  in the top 18 cm, compared to a fractionation factor,  $\varepsilon = -3.5\text{‰}$  in photolysis experiments. Without knowledge of the fractionation factor for diffusion, however, the quantitative roles of these processes cannot be determined. The potential importance of diffusion and volatilization is evident in the disappearance of seasonal trends below the surface layers. However, it remains unclear how diffusion of nitric acid in interstitial air of the snow would affect  $\Delta^{17}\text{O}\text{-NO}_3$ . Surface snow temperatures at South Pole will be no greater than  $-20^\circ\text{C}$  and postdepositional photochemical effects will not reach below 20 cm given a 3.7 cm *e*-folding depth for UV absorption [Jones and Wolff, 2003]. Therefore in situ postdepositional isotope effects resulting from photochemistry appear to be insignif-



**Figure 4.** Isolated frequency components corresponding to the 2.7-year cycle of (top) October–November–December column ozone and (bottom)  $\Delta^{17}\text{O-NO}_3$  plotted on a normalized scale versus year.

icant for  $\Delta^{17}\text{O-NO}_3$  in snow and do not limit the ability to preserve trends in stratospheric and tropospheric fluxes. The role of diffusion and other potential processes, however, need further investigation to properly elucidate the information contained in  $\Delta^{17}\text{O-NO}_3$  records.

[15] If we define the stratospheric and tropospheric sources of nitrate as their winter and summer aerosol isotopic compositions, respectively, mass balance can be utilized to estimate the relative influence of these two sources on surface snow according to the following equation:

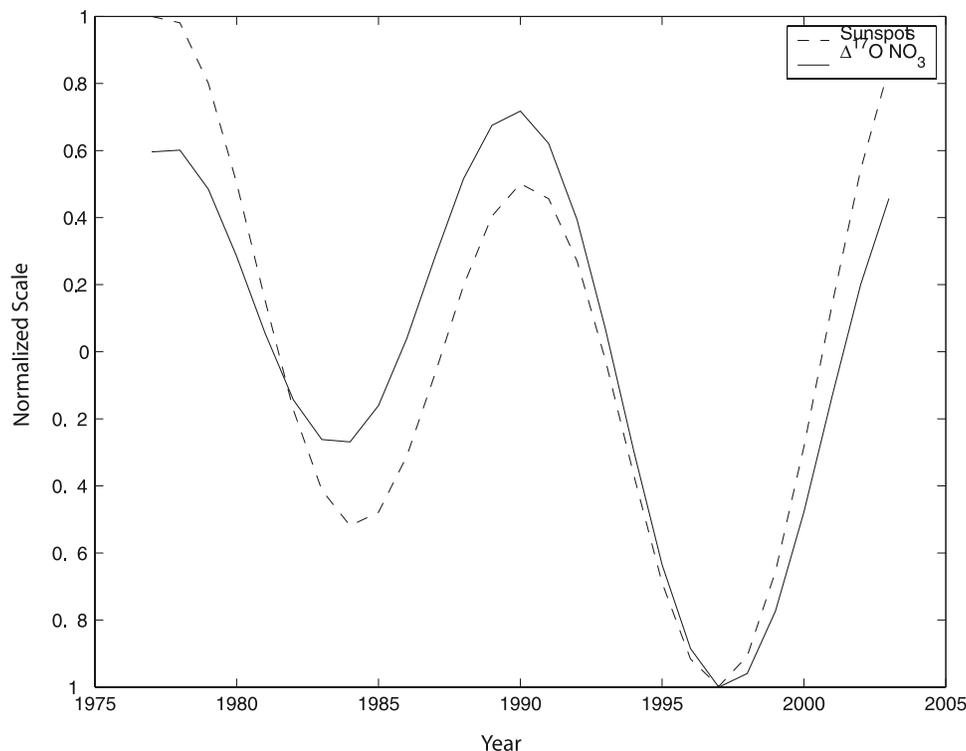
$$\Delta^{17}\text{O-NO}_{3total} = f_{strat} \times \Delta^{17}\text{O-NO}_{3strat} + f_{tropo} \times \Delta^{17}\text{O-NO}_{3tropo} \quad (11)$$

with  $f_{strat} + f_{tropo} = 1$ , where  $\Delta^{17}\text{O-NO}_{3total}$  is the expected value preserved annually in surface snow, and  $\text{NO}_{3strat} = 38.1\text{‰}$  and  $\Delta^{17}\text{O-NO}_{3tropo} = 26.3\text{‰}$  are the stratospheric and tropospheric nitrate isotopic compositions, respectively. Knowing the average surface snow  $\Delta^{17}\text{O-NO}_3 = 29.3\text{‰}$ , we solve  $f_{strat}$  and  $f_{tropo}$  representing the respective stratospheric and tropospheric fractional mass contributions. We find that nitrate in south polar ice preserves 25% of the original stratospheric isotopic composition, where 75% possess the tropospheric isotopic composition, due to nitrate produced from the photochemically recycled  $\text{NO}_x$  on the polar plateau.

#### 4.3. Variations in $\Delta^{17}\text{O-NO}_3$ , the Ozone Hole, and Surface Ozone

[16] In order to assess the influence of trends in total column springtime ozone, we have isolated the frequency

components that describe the 2.7-year cycle in Figure 3. It is clear that column ozone and  $\Delta^{17}\text{O-NO}_3$  are anticorrelated, as shown in Figure 4. For further confirmation, we employed the methods of *Ebisuzaki* [1997] to the 2.7-year components in column ozone and  $\Delta^{17}\text{O-NO}_3$  and found a negative correlation,  $R = -0.77$ , at above 95% confidence. This relationship suggests two possibilities. Either the nitrate oxygen isotopes are being primarily affected by increases in tropospheric ozone levels affected by increased UV from decreased springtime column ozone levels or the oxygen isotopes are recording increases in the stratospheric nitrate flux during years of reduced column ozone as suggested by *Mayewski and Legrand* [1990]. The later case invokes the role of the quasi-biennial oscillation and its influence on lower stratospheric temperatures during westerly phases on a 2.5-year timescale [*Garcia and Solomon*, 1987]. This possibility is consistent with higher values of  $\Delta^{17}\text{O-NO}_3$  during years of less total column ozone and an anticorrelation between the two records. However, given the range in isotopic values found in the snow pit, and the dominance of tropospheric input in the surface snow during 2004, we implicate boundary layer oxidation of  $\text{NO}_x$  released from the snow surface as a result of increased UV to explain the trends observed in the 26-year record. In addition, a negative correlation,  $R = -0.91$ , at 60% confidence is found comparing the 2.5-year trends in westerly QBO (cold phase) and  $\Delta^{17}\text{O-NO}_3$  implicating boundary layer surface chemistry over denitrification. This alternative does not negate the role of the QBO in stratospheric ozone levels but indicates that our observations are indirectly



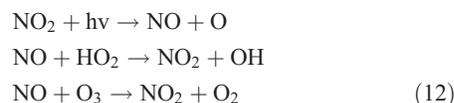
**Figure 5.** Reconstruction of  $\Delta^{17}\text{O-NO}_3$  13.5-year period frequency component (solid line) with the solar cycle (dashed line).

recording this process as it affects local oxidation conditions over the plateau by modulating ozone depletion.

[17] Highly variable values of  $\text{NO}_x$ , OH and  $\text{O}_3$  have been observed in the planetary boundary layer at South Pole from year to year [Chen *et al.*, 2004; Davis *et al.*, 2004]. This variability in photochemical oxidation conditions will lead to interannual variations in average aerosol  $\Delta^{17}\text{O-NO}_3$  preserved in ice if tropospheric conditions are controlling the isotope record in the snow. Jones and Wolff [2003] propose that the 50% reduction in Antarctic column ozone levels since the 1970s has increased November  $\text{NO}_2$  concentrations by 43% leading to enhanced oxidizing conditions in the boundary layer as a result of an 87% increase in UV-B irradiance. Stratospheric ozone depletion therefore influences boundary layer photochemistry via higher  $\text{NO}_x$  concentrations and catalytic ozone production. As seen in Figure 2c, surface ozone records correlate well with the isotope record in snow until 1991, after which there is no clear correlation or anticorrelation. The correlation of summer (October–February) surface ozone and  $\Delta^{17}\text{O-NO}_3$  at 2.5 years is 0.93 at 67% confidence before 1991 and insignificant after 1991. This departure between the records may be indicative of an altered oxidizing environment over the polar plateau from ozone destruction before 1991 to ozone production after 1991 as suggested by Crawford *et al.* [2001] and Jones and Wolff [2003]. These authors suggest that  $\text{HO}_x$  destruction dominates before 1991 and gives way to ozone production due to high levels of NO in recent years.

[18] The correlation, and lack thereof after 1991, of nitrate's oxygen isotope record and surface ozone may provide evidence of the altered oxidation conditions that

have switched from ozone destruction to production around 1991. Michalski *et al.* [2003] describes the transfer of the isotopic anomaly in ozone to  $\text{NO}_2$  as a result of the following reactions that come to equilibrium 1000 times faster than the sink reactions (4), (5), (9), and (12):



In the case of low-NO environments, reaction (8) will be slow and allow for the dominance of ozone oxidation in reaction (2) resulting in higher transfer rates of the isotopic anomaly. However, under high-NO conditions (greater than 30 pptv), reaction (8) will increase favoring the role of  $\text{HO}_2$  oxidation in  $\text{NO}_2$  formation and reducing  $\Delta^{17}\text{O}$  in  $\text{NO}_2$  during periods of increased ozone. These possibilities demand further investigation with photochemical models but provide evidence for the altered oxidizing environment as suggested by Jones and Wolff [2003] as reflected by the oxygen isotopes in South Polar nitrate.

[19] In addition to strong Fourier components in  $\Delta^{17}\text{O-NO}_3$  variations at 2.7 and 3.4 years, Figure 3 also reveals a strong component at 13.5 years, close to the 11-year solar cycle. Suggestions that GCRs and SPEs influence mesospheric NO production and as a result of mixing affect the stratospheric nitrogen budget have been suggested to be evident in Antarctic nitrate ice records [Parker *et al.*, 1982]. The possible connection between Antarctic nitrate  $\Delta^{17}\text{O-NO}_3$  and solar variability shown in Figure 5 can be evaluated by comparing phase differences

in the frequency components at 13.5 years according to Ebisuzaki [1997]. The result is a strong correlation,  $R = 0.91$  at greater than 95% confidence. If the connection is due to cosmic ray production, increases in  $\Delta^{17}\text{O-NO}_3$  should be anticorrelated to solar variability as a result of increased shielding of GCRs by the Sun's magnetic field during periods of increased solar activity. The positive correlation, however, does appear to be evidence of fluctuations in UV, which is consistent with a record dominated by tropospheric ozone fluctuations. The short length of both the isotope and UV records does not permit confident conclusions but suggests that  $\Delta^{17}\text{O-NO}_3$  may record variations in solar activity.

## 5. Conclusion

[20] In conclusion, oxygen isotopes of nitrate ( $\Delta^{17}\text{O-NO}_3$ ) identify the relative stratospheric and tropospheric nitrate sources as preserved in South Polar snow during winter and summer, respectively, providing an important improvement toward understanding the polar nitrogen cycle. The preservation of changes in boundary layer oxidation conditions on 2.7-year timescales resulting from stratospheric ozone depletion presents new information from Antarctic nitrate records. The record of  $\Delta^{17}\text{O-NO}_3$  results from changes in tropospheric photochemical recycling of nitrate during summer controlled by UV fluctuations associated with stratospheric ozone loss and suggests a change in local boundary layer oxidation conditions since 1991 consistent with increased  $\text{NO}_x$  concentrations. As a result of its unique location on the plateau and the prevailing meteorological conditions, the South Pole appears to collect the highest amount of  $\text{NO}_x$  and nitrate across Antarctica. Evidence of stratospheric nitrate from oxygen isotopes in Antarctic snow, however, demands the consideration that other locations with lower accumulation and nitrate concentrations may preserve stratospheric nitrate signals and be more suited for finding a proxy of changes in stratospheric ozone and nitrogen, such as the ozone hole or solar variability.

[21] Future work to evaluate how the variations in  $\Delta^{17}\text{O-NO}_3$  reflect changes in ozone and hydroxyl concentrations over Antarctica will improve the understanding of recent changes in boundary layer oxidations conditions resulting from stratospheric ozone depletion. Measurements of air-snow transfer over the course of several years followed by shallow core or snow pit collections will illuminate how changes in aerosol  $\Delta^{17}\text{O-NO}_3$  is preserved in the snow record and affected by postdepositional processes such as diffusion, volatilization and photochemistry. Overall, this work suggests that with continued effort the measurement of multiple oxygen isotopes of nitrate in Antarctica will improve both the understanding of local nitrogen cycling and oxidation in addition to potentially providing knowledge of variations in stratospheric oxidation conditions over time.

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