# Isotopic composition of Antarctic Dry Valley nitrate: Implications for NO$_y$ sources and cycling in Antarctica

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[1]   Nitrates minerals from the Dry Valleys of Antarctica have been analyzed for their oxygen and nitrogen isotopic compositions. The $^{15}$N was depleted with $\delta^{15}$N values ranging from $-9.5$ to $-26.2$‰, whereas the $^{17}$O and $^{18}$O isotopes were highly enriched (with excess $^{17}$O) with $\delta^{18}$O values spanning $62-76$‰ and $\Delta^{17}$O values from 28.9 to 32.7‰. These are the largest $^{17}$O enrichments observed in any known mineral. The oxygen isotopes indicate that nitrate is from a combination of tropospheric transport of photochemically produced HNO$_3$ and HNO$_3$ formed in the stratosphere. **Citation:** Michalski, G., J. G. Bockheim, C. Kendall, and M. Thiemens (2005), Isotopic composition of Antarctic Dry Valley nitrate: Implications for NO$_y$ sources and cycling in Antarctica, *Geophys. Res. Lett.*, *32*, L13817, doi:10.1029/2004GL022121.

## 1.  Introduction

[2]   The McMurdo Dry Valleys (MDV), in Victoria Land, Antarctica, though surrounded by a frozen water continent, are amongst the driest places on Earth. The exoreic conditions have limited the transport of soluble compounds out of the valleys and led to the build up of various salts including chloride, sulfate and nitrate minerals [*Claridge and Campbell*, 1968; *Campbell and Claridge*, 1987; *Bockheim*, 1997; *Campbell et al.*, 1998; *Beyer et al.*, 1999; *Hall et al.*, 1993; *Marchant et al.*, 1996]. Chloride and some sulfates have been recognized as originating from seawater evaporation in low elevation basins, deposition of sea salt aerosols, weathering of sulfide minerals and the deposition of aerosol sulfate derived from the oxidation of biogenic sulfur gases (primarily DMS) emitted from coastal waters [*Campbell and Claridge*, 1987; *Bao et al.*, 2000]. Nitrate salts have mainly been attributed to the sublimation of windblown snow originating from the Antarctic interior, but evidence of this has always been tangential [*Claridge and Campbell*, 1968; *Campbell and Claridge*, 1987; *Wada et al.*, 1981].

[3]   The origin of nitrate found in the Antarctic ice sheet and snow is unclear. Studies have indicated that continental aerosols transported to the Antarctic are the primary source [*Savoie et al.*, 1992]. Others have suggested that the transport of HNO$_3$ from tropic and subtropical oceans dominates

the Antarctic nitrate budget [*Wada et al.*, 1981]. The sedimentation of polar stratospheric clouds (PSCs), which are primarily HNO$_3$ hydrates and NO$_3^-$/SO$_4^{2-}$ hydrates, has also been suggested as an important source of nitrate to the Antarctic interior [*Mulvaney and Wolff*, 1993]. The oxidation of oceanic organic matter containing N has also been cited as the main source of the MDV nitrates (and ice sheet) as evident from the nitrates association with iodate [*Campbell et al.*, 1998]. Additional confusion in constraining NO$_3^-$ sources arises from the dynamics of the recycling of NO$_x$ and HNO$_3$ in the surface layers of newly deposited snow through re-volatilization and solid/liquid phase photolysis of snowpack NO$_3^-$ [*Dominé and Shepson*, 2002].

[4]   Stable isotopes are often used as indices to isolate source and sink strengths as well as for detecting transformation and transportation dynamics. For example, previous $\delta^{15}$N measurements of the MDV nitrates showed large depletions (relative to air N$_2$) and were attributed to removal processes that preferentially eliminated NO$_2$ containing the $^{15}$N [*Wada et al.*, 1981]. Recent measurements of oxygen isotopes in nitrate collected from urban atmospheres have shown anomalous enrichments in $^{17}$O with $\Delta^{17}$O values ranging from $20-31$‰ ($\Delta^{17}$O $= \delta^{17}$O $- .52*$ $\delta^{18}$O) [*Michalski et al.*, 2003]. Enrichments in $^{18}$O have been observed in aerosol, precipitation and snow nitrate with $\delta^{18}$O from 40 to 80‰ [*Michalski et al.*, 2003, 2004b; *Hastings et al.*, 2003; *Kendall*, 1998; *Kendall et al.*, 1995; *Durka et al.*, 1994]. The oxygen isotopic enrichments are attributed to oxidation reactions involving ozone and the ratio of homogeneous to heterogeneous HNO$_3$ formation pathways [*Michalski et al.*, 2003; *Hastings et al.*, 2003]. The $\Delta^{17}$O signal found in atmospheric nitrate has recently been used to constrain the amount of atmospherically deposited NO$_3^-$ in mineral nitrate deposits found in another exoreic region, the Atacama Desert of Chile [*Michalski et al.*, 2004a]. Here we present oxygen and nitrogen isotopic data that places new limitations on possible source and cycling dynamics of atmospheric N that resulted in the formation of the MDV nitrate salts.

## 2.  Methods and Results

[5]   MDV soils, which exhibited no biologic activity and had low moisture content ($\sim$10%), were stored at room temperature in sealed plastic bags and showed no nitrate loss over time. Complete mineralogical and site descriptions can be found elsewhere [*Bockheim*, 1997] and the isotopic, anion and location data of individual samples can be found in the auxiliary material[1]. Soluble ions where extracted in Millipore water in a roughly 1:5 mass ratio (soil to H$_2$O). Sulfate was

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[1]Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2004GL022121.
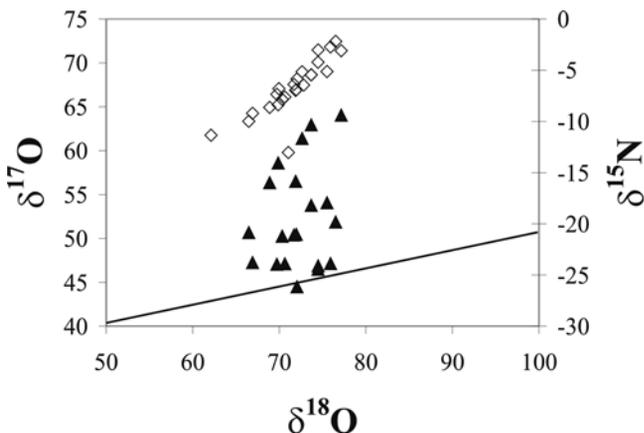
**Figure 1.** MDV nitrate oxygen ($\diamond$) and nitrogen ($\blacksquare$) isotope correlation plots. Equilibrium or kinetic fractionations result in $\delta^{15}N$, $\delta^{17}O$ and $\delta^{18}O$ values that follow the mass dependent arrays, which for oxygen is the terrestrial fraction line, $\Delta^{17}O = 0$ (solid line). The slope of the $\delta^{17}O$ vs. $\delta^{18}O$ (.72) is the result of mixing between the two main reservoirs of $NO_x$ oxidation, $O_3$ and tropospheric $H_2O$. The high depletions in $^{15}N$ may be due to the different $\delta^{15}N$ of various nitrate sources whereas the enriched oxygen isotopes are due to oxidation pathways related to ozone and are independent of the $NO_x$ point source oxygen isotopic composition.

precipitated using $BaCl_2$ in slight excess and $NO_3^-$ was purified and converted to $AgNO_3$ [*Michalski et al.*, 2004a] and decomposed and the evolved $O_2$ that was analyzed on a Finnigan-Mat 251 isotope ratio mass spectrometer [*Michalski et al.*, 2002] ($\delta^{18}O \pm 2.0‰$, $\Delta^{17}O \pm 0.2‰$) and reported with respect to SMOW. Nitrogen isotopes ($\delta^{15}N \pm .1‰$) were analyzed using the CO pyrolysis method [*Chang et al.*, 2004] and are reported with respect to air $N_2$.

[6] The MDV nitrates have three prominent isotopic signatures (Figure 1). First there is a large mass-independent component with $\Delta^{17}O$ values ranging from 28.9 to 32.7‰. Secondly the $\delta^{18}O$ values are also highly enriched with respect to SMOW (62–76 ‰). Finally the nitrate $\delta^{15}N$ values are significantly depleted with respect to $N_2$ (−9.5 to −26.2‰), which are in agreement with $\delta^{15}N$ values found previously [*Wada et al.*, 1981].

## 3. Discussion

[7] The oxygen isotopes provide a strong constraint on the possible origin of the MDV soil nitrate. The large $\Delta^{17}O$ and $\delta^{18}O$ values indicate that the nitrate is solely atmospheric in origin ($NO_3^-{}_{atm}$) with little or no nitrate produced by nitrification, which has been known to occur in soils located in the wetter areas of the MDV [*Barrett et al.*, 2002] and in other exoreic regions [*Michalski et al.*, 2004a; *Walvoord et al.*, 2003]. It has been previously suggested that the source of the $\Delta^{17}O$ values observed in $NO_3^-{}_{atm}$ can be interpreted using a isotopic/photochemical model, which is summarized as [*Michalski et al.*, 2003]

$$\Delta^{17}O\ NO_3^-{}_{atm} = \beta\left(\tfrac{2}{3}\alpha^\Delta O_3\right) + \chi\left(\tfrac{2}{3}\alpha^\Delta O_3 + \tfrac{1}{3}{}^\Delta O_3\right)$$
$$+ \varepsilon\left(\tfrac{2}{3}\alpha^\Delta O_3 + \tfrac{1}{6}{}^\Delta O_3\right) \quad (1)$$

[8] Here the $\Delta^{17}O$ values ($35 \pm 2‰$) in ozone ($^\Delta O_3$) are solely determined by temperature and pressure dependant rate constants [*Janssen et al.*, 2003]. The $\alpha$ parameter is the proportion of NO oxidized by $O_3$ relative to $HO_2$ ($RO_2$). At latitudes greater than 60°S, tropospheric $[O_3]$ is $\sim20$–50 ppb and $[OH] \sim 4 \times 10^5$ molecules $cm^{-3}$, with $HO_2/OH$ ratios of $\sim5$ [*Spivakovsky et al.*, 2000; *Horowitz et al.*, 2003; *Lanzendorf et al.*, 2001]. Considering the $\sim10^5$ concentration difference (0.2 ppt versus 20 ppb) and that the $[O_3 + NO]/[HO_2 + NO]$ rate constant ratio is $2.2 \times 10^{-3}$, an $\alpha \sim0.98$ is expected. This may decrease to 0.92 for the four fold increase in $HO_2$ near mid latitudes [*Horowitz et al.*, 2003; *Lanzendorf et al.*, 2001], which is in good agreement with the estimated global $\alpha$ value of 0.9 by *Rockmann et al.* [2001]. The $\beta$, $\chi$ and $\varepsilon$ parameters are the fractions of $HNO_3$ produced by the $OH + NO_2 + M$, $NO_3\cdot$ hydrogen abstraction, and $N_2O_5$ heterogeneous hydrolysis reaction pathways respectively. Except in rare cases, the $NO_3$ abstraction pathway is trivial relative to the OH and heterogeneous pathways and we can approximate $\chi = 0$ and $\alpha = 1$ to yield

$$\Delta^{17}O\ NO_3^-{}_{atm} \approx \beta\left(\tfrac{2}{3}{}^\Delta O_3\right) + \varepsilon(5/6^\Delta O_3) = \beta\left(\tfrac{2}{3}{}^\Delta O_3\right)$$
$$+ (1-\beta)(5/6^\Delta O_3) \quad (2)$$

[9] The $HNO_3$ branching ratios ($\beta$ and $\varepsilon$) can vary significantly depending on $NO_x$ concentrations, temperature, aerosol surface area and amount of sunlight. For $HNO_3$ produced in the tropics where $\beta$ approaches 1 ($\varepsilon \sim 0$) [*Dentener and Crutzen*, 1993; *Derwent et al.*, 2003] the $HNO_3$ $\Delta^{17}O$ values are $\sim23‰$. These $HNO_3$ $\Delta^{17}O$ estimates are upper bounds because including the NO oxidation parameter ($\alpha$) would result in decreases of $1-2‰$ in the $\Delta^{17}O$ values. The mid latitude $HNO_3$ $\Delta^{17}O$ values are clearly below those found in the MDV nitrates and dispute the suppositions that tropical, subtropical or continental transport of $NO_3^-{}_{atm}$ produced in the troposphere is the dominant source of the nitrate. Since the nitrate formation passes through the $NO_x$ cycle, the $\Delta^{17}O$ data also refute the hypothesis that the nitrate is derived from direct oxidation of oceanic nitrogenous matter [*Campbell et al.*, 1998].

[10] The MDV nitrates also have highly depleted $\delta^{15}N$ values, which has been previously attributed to isotopic fractionations occurring during $NO_x$ transport [*Wada et al.*, 1981]. The authors suggested that $NO_2$ behaved in a similar fashion as $NH_3$, which has been shown to preferentially partition $^{15}N$ into the aerosol phase during $NH_3$ gas-liquid and particle-gas kinetic and equilibrium reactions [*Moore*, 1977]. This leaves isotopically light $NH_{3(g)}$ available to be transported out of the source region where it is converted into aerosol $NH_4^+$. The assertion that the main source of $NO_3^-$ is from $NO_2$ reacting in a water droplet [*Moore*, 1977] shows that this hypothesis was put forth prior to our complete understanding of how $NO_3^-$ is formed in the atmosphere. It is now well established that $HNO_3$ formation is dominated by homogenous and heterogeneous gas phase reactions of $NO_x$ followed by nucleation, cloud uptake, or washout, of the $HNO_3$ [*Seinfeld and Pandis*, 1998]. It is therefore unlikely that $NO_2$ equilibrium with water droplets is the source of the negative $\delta^{15}N$ values in the MDV nitrates.

[11] The fractionation effect of photolysis and the kinetic reactions on N isotopes in the $NO_x$ cycle is poorly developed, so estimations on the magnitude and sign of these fractionations would be imprudent. Likewise the limited numbers of $\delta^{15}N$ studies on $NO_x$ are restricted to urban regions, with highly perturbed $NO_x$ cycles [*Heaton*, 1986], and no studies have been made in clean, oceanic environments, which are more representative of air masses transported to Antarctica. In addition the $\delta^{15}N$ of nitrate in the free troposphere or stratosphere has not been measured so nothing can be said about possible $\delta^{15}N$ signatures of these important sources. In the absence of data it is difficult to try and reconcile the extremely negative $\delta^{15}N$ with sources or fractionation mechanisms occurring during transport.

[12] However, in the case of normal mass dependent fractionations that arise from kinetic or equilibrium rate differences for isotopomers, $HNO_3$ $\delta^{15}N$ depletions (or enrichments) would parallel those observed in $\delta^{18}O$ (and $\delta^{17}O$). Processes such as diffusion, where the isotopes fractionate based on relative differences in molecular mass, the $\delta^{15}N$ is expected to be $\sim\frac{1}{2}$ $\delta^{18}O$, which has been observed in denitrification zones where the dual isotope plot of $\delta^{15}N$ versus $\delta^{18}O$ form a slope $\sim\frac{1}{2}$ [*Kendall*, 1998]. Kinetic fractionations normally preferentially utilize the lighter isotope, so correlations between $\delta^{18}O$ and $\delta^{15}N$ should also be expected, though not strictly in the $\frac{1}{2}$ scheme. Therefore, if kinetic or equilibrium isotope effects occurring during transport were controlling the $\delta^{15}N$ we expect $NO_3^-{}_{atm}$ $\delta^{18}O$ values to also be depleted ($\sim30-40‰$) relative to their tropospheric values of $\sim70‰$ [*Michalski et al.*, 2003; *Hastings et al.*, 2003; *Kendall*, 1998]. This is not found in our measurements; this also suggests that mid latitude $NO_3^-{}_{atm}$ is not the main source of the MDV nitrates nor is mid-latitude transport driving the negative $\delta^{15}N$ values.

[13] According to our model, the high $\Delta^{17}O$ values imply that $N_2O_5$ hydrolysis is the dominant $HNO_3$ formation pathway. $\Delta^{17}O$ values in $NO_3^-{}_{atm}$ produced solely by heterogeneous hydrolysis in the troposphere are expected to approach $29-30‰$ in agreement with most of our data. However, complete heterogeneous $HNO_3$ production seems unreasonable in light of most tropospheric $HNO_3$ modeling studies [*Stroud et al.*, 2003; *Derwent et al.*, 2003; *Dentener and Crutzen*, 1993]. A possible explanation is the assumed $\Delta^{17}O$ value of tropospheric ozone, where it was implicit that the $O_3$ was produced in the troposphere through photolysis of $NO_2$ and the $O(^3P) + O_2 + M$ recombination reaction ($\Delta^{17}O \sim 35‰$). Cross tropopause mixing of $O_3$ produced in the stratosphere is known to be a significant source of tropospheric $O_3$ in the natural atmosphere and measurements have shown stratospheric ozone $\Delta^{17}O > 40‰$ [*Lämmerzahl et al.*, 2002]. Fitting our MDV nitrate $\Delta^{17}O$ values using stratospheric ozone as the primary oxidant gives $\beta$ values between .44 (using approximation (2)) which are still well below the branching ratio predicted by models [*Stroud et al.*, 2003; *Derwent et al.*, 2003; *Dentener and Crutzen*, 1993]. In addition, attributing all of the $NO_3^-{}_{atm}$ to stratospheric mixing of $NO_x$ and $O_3$ does not seem reasonable given that lightning, biomass burning and tropospheric chemistry produce considerable amounts of tropospheric $NO_x$ and ozone.

[14] In the absence of in situ measurements, assigning a $\Delta^{17}O$ value to polar stratospheric $NO_3^-{}_{atm}$ would be tenu-ous. However, the predominance of $N_2O_5$ hydrolysis in the polar stratosphere [*Seinfeld and Pandis*, 1998] should give nitrate $\Delta^{17}O$ values of $\sim40‰$ (ozone $\Delta^{17}O > 40$, $\varepsilon = 1$) and we have observed similar values in the aerosols collected at the South Pole during the late winter/early spring (G. Michalski, Isotopic composition of nitrate and sulfate aerosols from the South Pole, manuscript in preparation, 2005, hereinafter referred to as Michalski, manuscript in preparation, 2005). A reasonable interpretation of the $\Delta^{17}O$ values observed in the MDV nitrate would be a mixing of two sources; the transport of $NO_3^-{}_{atm}$, from mid latitudes ($\Delta^{17}O \sim 24‰$) and the stratospheric $HNO_3$ ($\Delta^{17}O \sim 40‰$) derived from either the sedimentation/evaporation of PSCs or mixing of stratospheric air masses containing gas phase $HNO_3$. The MDV nitrate average of $31‰$ would correspond to a tropospheric:stratospheric partitioning of roughly 43:57. If the tropospheric portion had $\delta^{15}N$ values similar to those of modern wet deposited $NO_3^-{}_{atm}$ ($-9‰$) [*Heaton*, 1986] then the MDV nitrate $\delta^{15}N$ variability could be explained by a variable stratospheric $NO_3^-{}_{atm}$ source with $\delta^{15}N$ of $\sim-23‰$. Such $\delta^{15}N$ depletions in stratospheric nitrate have recently been suggested as the source of depleted $^{15}N$ in snow nitrate in Greenland [*Hastings et al.*, 2004; *Heaton et al.*, 2004] and we have observed such depletions from nitrate originating from the Antarctic interior (Michalski, manuscript in preparation, 2005). The distribution of anions and cations within the MDV also suggests a two-source deposition flux [*Stenberg et al.*, 1998], but our $\delta^{15}N$ data is too minimal to determine if it correlates with the spatial gradients suggested in that study.

## 4. Conclusion

[15] Nitrate from the McMurdo Dry Valleys have been analyzed for their N and O isotopic composition. The $\Delta^{17}O$ values show that the nitrate is exclusively atmospheric in origin and is the result of $NO_x$ oxidation. The large enrichments can possibly be explained by the mixing of tropospheric and stratospheric nitrate in roughly equal amounts. These nitrates are deposited on the Antarctic ice cap and transported to the MDV by katiabatic winds or are transported in from oceanic air masses. The accumulation of the nitrate salts over million year timescales [*Campbell and Claridge*, 1987] suggests that stratospheric and tropospheric chemistry followed by deposition is important for landform and soil evolution in the McMurdo Dry Valleys. The large depletions and variability in $\delta^{15}N$ remain unresolved as to their origin but the variability maybe the result of mixing between two $NO_3^-{}_{atm}$ sources (stratospheric and tropospheric) with distinct $\delta^{15}N$ values.

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