Isotopic composition of Antarctic Dry Valley nitrate: Implications for NO$_3^-$ 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 $^{18}$O values ranging from $-9.5$ to $-26.2\%$, whereas the $^{17}$O and $^{18}$O isotopes were highly enriched (with excess $^{17}$O) with $^{18}$O values spanning $62-76\%$ and $^{17}$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 compounds observed 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$_3^-$ 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 stratigraphic 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$_3^-$ [Domine 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 $^{15}$N measurements of the MDV nitrate 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 $^{17}$O values ranging from 20-31% $^{17}$O = $^{17}$O - .52* $^{18}$O) [Michalski et al., 2003]. Enrichments in $^{18}$O have been observed in aerosol, precipitation and snow nitrate with $^{17}$O from 40 to 80% $^{17}$O [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 $^{17}$O signal found in atmospheric nitrate has recently been used to constrain the amount of atmospherically deposited NO$_2$ 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 (~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
precipitated using BaCl2 in slight excess and NO3 was purified and converted to AgNO3 [Michalski et al., 2004a] and decomposed and the evolved O2 that was analyzed on a Finnigan-Mat 251 isotope ratio mass spectrometer [Michalski et al., 2002] (δ18O ± 2.0‰, Δ17O ± 0.2‰) and reported with respect to SMOW. Nitrogen isotopes (δ15N ± 1‰) were analyzed using the CO pyrolysis method [Chang et al., 2004] and are reported with respect to air N2.

The MDV nitrates have three prominent isotopic signatures (Figure 1). First there is a large mass-independent component with Δ17O values ranging from 28.9 to 32.7‰. Secondly the Δ18O values are also highly enriched with respect to SMOW (62–76 ‰). Finally the nitrate δ15N values are significantly depleted with respect to N2 (−9.5 to −26.2‰), which are in agreement with δ15N values found previously [Wada et al., 1981].

3. Discussion

The oxygen isotopes provide a strong constraint on the possible origin of the MDV soil nitrate. The large Δ17O and Δ18O values indicate that the nitrate is solely atmospheric in origin (NO3) 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 Δ17O values observed in NO3 can be interpreted using an isotopic/photochemical model, which is summarized as [Michalski et al., 2003]

\[
\Delta^{17}O_{NO_3} = \beta(\frac{2}{3}\alpha^{18}O) + \chi(\frac{2}{3}\alpha^{17}O + \frac{1}{3}\delta O_2) + \epsilon(\frac{2}{3}\alpha^{17}O + \frac{1}{3}\delta O_2)
\]

Here the Δ17O values (35 ± 2‰) in ozone (δ18O) are solely determined by temperature and pressure dependant rate constants [Janssen et al., 2003]. The α parameter is the proportion of NO oxidized by O3 relative to HO2 (RO2). At latitudes greater than 60°S, tropospheric [O3] is ~20–50 ppb and [OH] ~ 4 × 10^5 molecules cm^-3, with HO2/ OH ratios of ~5 [Spivakovksy et al., 2000; Horowitz et al., 2003; Lanzendorf et al., 2001]. Considering the ~10^3 concentration difference (0.2 ppt versus 20 ppb) and that the [O3 + NO]/[HO2 + NO] rate constant ratio is 2.2 × 10^-3, an α ~0.98 is expected. This may decrease to 0.92 for the four fold increase in HO2 near mid latitudes [Horowitz et al., 2003; Lanzendorf et al., 2001], which is in good agreement with the estimated global α value of 0.9 by Rockmann et al. [2001]. The β, χ and ε parameters are the fractions of HNO3 produced by the OH + NO2 + M, NO2 hydrogen abstraction, and N2O5 heterogeneous hydrolysis reaction pathways respectively. Except in rare cases, the NO2 abstraction pathway is trivial relative to the OH and heterogeneous pathways and we can approximate χ = 0 and α = 1 to yield

\[
\Delta^{17}O_{NO_3} \approx \beta(\frac{2}{3}\alpha^{18}O) + \epsilon(\frac{2}{3}\delta^{17}O) = \beta(\frac{2}{3}\alpha^{18}O) + (1-\beta)(\frac{2}{3}\delta^{17}O)
\]

The HNO3 branching ratios (β and ε) can vary significantly depending on NOx concentrations, temperature, aerosol surface area and amount of sunlight. For HNO3 produced in the tropics where β approaches 1 (ε ~ 0) [Dentener and Crutzen, 1993; Derwent et al., 2003] the HNO3 Δ17O values are ~23‰. These HNO3 Δ17O estimates are upper bounds because including the NO oxidation parameter (α) would result in decreases of 1–2‰ in the Δ17O values. The mid latitude HNO3 Δ17O values are clearly below those found in the MDV nitrates and dispute the suppositions that tropical, subtropical or continental transport of NO3 from the troposphere is the dominant source of the nitrate. Since the nitrate formation passes through the NO2 cycle, the Δ17O data also refute the hypothesis that the nitrate is derived from direct oxidation of oceanic nitrogenous matter [Campbell et al., 1998].

The MDV nitrates also have highly depleted Δ15N values, which has been previously attributed to isotopic fractionations occurring during NOx transport [Wada et al., 1981]. The authors suggested that NO2 behaved in a similar fashion as NH3, which has been shown to preferentially partition 15N into the aerosol phase during NH3 gas-liquid and particle-gas kinetic and equilibrium reactions [Moore, 1977]. This leaves isotopically light NH3 available to be transported out of the source region where it is converted into aerosol NH4. The assertion that the main source of NO3 is from NO2 reacting in a water droplet [Moore, 1977] shows that this hypothesis was put forth prior to our complete understanding of how NO3 is formed in the atmosphere. It is now well established that HNO3 formation is dominated by heterogeneous gas phase reactions of NOx followed by nucleation, cloud uptake, or washout, of the HNO3 [Seinfeld and Pandis, 1998]. It is therefore unlikely that NO2 equilibrium with water droplets is the source of the negative Δ15N values in the MDV nitrates.
[11] The fractionation effect of photolysis and the kinetic reactions on N isotopes in the NOx cycle is poorly developed, so estimations on the magnitude and sign of these fractionations would be imprudent. Likewise the limited numbers of δ15N studies on NOx are restricted to urban regions, with highly perturbed NOx 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 δ15N of nitrate in the free troposphere or stratosphere has not been measured so nothing can be said about possible δ15N signatures of these important sources. In the absence of data it is difficult to try and reconcile the extremely negative δ15N 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, HNO3 δ15N depletions (or enrichments) would parallel those observed in δ18O (and δ17O). Processes such as diffusion, where the isotopes fractionate based on relative differences in molecular mass, the δ15N is expected to be ~1/2 δ18O, which has been observed in denitrification zones where the dual isotope plot of δ15N versus δ18O form a slope ~1/2 [Kendall, 1998]. Kinetic fractionations normally preferentially utilize the lighter isotope, so correlations between δ18O and δ15N should also be expected, though not strictly in the 1/2 scheme. Therefore, if kinetic or equilibrium isotope effects occurring during transport were controlling the δ15N we expect NO3 atm δ18O values to also be depleted (~30–40%) relative to their tropospheric values of ~70‰ [Michalski et al., 2003; Hastings et al., 2003; Kendall, 1998]. This is not found in our measurements; this also suggests that mid latitude NO3 atm is not the main source of the MDV nitrates nor is mid-latitude transport driving the negative δ15N values.

[13] According to our model, the high Δ17O values imply that N2O5 hydrolysis is the dominant HNO3 formation pathway. Δ17O values in NO3 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 HNO3 production seems unreasonable in light of most tropospheric HNO3 modeling studies [Stroud et al., 2003; Derwent et al., 2003; Dentener and Crutzen, 1993]. A possible explanation is the assumed Δ17O value of tropospheric ozone, where it was implicit that the O3 was produced in the troposphere through photoysis of NOx and the O(3P) + O2 + M recombination reaction (Δ17O ~ 35‰). Cross tropopause mixing of O3 produced in the stratosphere is known to be a significant source of tropospheric O3 in the natural atmosphere and measurements have shown stratospheric ozone Δ17O >40‰ [Lämmerzahl et al., 2002]. Fitting our MDV nitrate Δ17O values using stratospheric ozone as the primary oxidant gives 3 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 NO3 atm to stratospheric mixing of NOx and O3 does not seem reasonable given that lightning, biomass burning and tropospheric chemistry produce considerable amounts of tropospheric NOx and ozone.

[14] In the absence of in situ measurements, assigning a Δ17O value to polar stratospheric NO3 atm would be tenuous. However, the predominance of N2O5 hydrolysis in the polar stratosphere [Seinfeld and Pandis, 1998] should give nitrate Δ17O values of ~40‰ (ozone Δ17O >40, ε = 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 Δ17O values observed in the MDV nitrate would be a mixing of two sources; the transport of NO3 atm from mid latitudes (Δ17O ~ 24‰) and the stratospheric HNO3 (Δ17O ~ 40‰) derived from either the sedimentation/evaporation of PSCs or mixing of stratospheric air masses containing gas phase HNO3. The MDV nitrate average of 31‰ would correspond to a tropospheric: stratospheric partitioning of roughly 43:57. If the tropospheric portion had δ15N values similar to those of modern wet deposited NO3 atm (~9‰) [Heaton, 1986] then the MDV nitrate δ15N variability could be explained by a variable stratospheric NO3 atm source with δ15N of ~23‰. Such δ15N depletions in stratospheric nitrate have recently been suggested as the source of depleted 15N 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 δ15N 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 Δ17O values show that the nitrate is exclusively atmospheric in origin and is the result of NOx 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 katabatic 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 δ15N remain unresolved as to their origin but the variability maybe the result of mixing between two NO3 atm sources (stratospheric and tropospheric) with distinct δ15N values.

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References


