Determination of the Total Oxygen Isotopic Composition of Nitrate and the Calibration of a $\Delta^{17}O$ Nitrate Reference Material

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A thermal decomposition method was developed and tested for the simultaneous determination of $\delta^{18}O$ and $\delta^{17}O$ in nitrate. The thermal decomposition of $AgNO_3$ allows for the rapid and accurate determination of $^{18}O/^{16}O$ and $^{17}O/^{16}O$ isotopic ratios with a precision of $\pm1.5‰$ for $\delta^{18}O$ and $\pm0.11‰$ for $\Delta^{17}O$ ($\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$). The international nitrate isotope reference material IAEA-NO3 yielded a $\delta^{18}O$ value of $+23.6‰$ and $\Delta^{17}O$ of $-0.2‰$, consistent with normal terrestrial mass-dependent isotopic ratios. In contrast, a large sample of $NaNO_3$ from the Atacama Desert, Chile, was found to have $\Delta^{17}O = 21.56 \pm 0.11‰$ and $\delta^{18}O = 54.9 \pm 1.5‰$, demonstrating a substantial mass-independent isotopic composition consistent with the proposed atmospheric origin of the desert nitrate. It is suggested that this sample (designated USGS-35) can be used to generate other gases (CO_2, CO, N_2O, O_2) with the same $\Delta^{17}O$ to serve as measurement references for a variety of applications involving mass-independent isotopic compositions in environmental studies.

The environmental impacts of anthropogenic fixed nitrogen on the biosphere, hydrosphere, and atmosphere have been the focus of scientific research for decades. In many ecosystems, the bioavailability of fixed nitrogen regulates productivity and controls the overall biodiversity of the system. The anthroprogenic contribution of fixed nitrogen (primarily NH_3 and NO_3^-) currently equals the amount of naturally fixed nitrogen and is expected to double worldwide by 2050.[1] Nitrate is a common groundwater and surface water contaminant whose anthropogenic sources include the cultivation of nitrogen-fixing crops, the use of synthetic and manure fertilizers, and fossil fuel/biomass combustion. It is important to be able to identify sources and resolve fates of nitrate in order to understand nitrogen cycling and the effect of human activity upon the cycle. Tracing the contribution of atmospheric nitrate ($NO_3^-_{atm}$) is particularly complex because of long-range transport from various point sources. The use of $\delta^{18}O$ as a tracer of $NO_3^-_{atm}$ has recently gained acceptance because $NO_3^-_{atm}$

typically is enriched in $\delta^{18}O$ compared to other NO_3^- sources.[2] Although the use of $\delta^{18}O$ has had success in some biogeochemical applications,[3] its use is limited in many complex systems because of the large spread in $\delta^{18}O$ of various sources, overlapping $\delta^{18}O$ values in mixed reservoirs, and postdepositional isotopic modifications.[2]

Nitrate oxygen isotope investigations have not yet explored variations in $\delta^{17}O$, primarily because kinetic and equilibrium fractionation processes alter the two minor isotopes in a predictable manner based on their relative mass differences.[4] For these mass-dependent fractionations, $\delta^{17}O$ and $\delta^{18}O$ are highly correlated with $\delta^{17}O \simeq 0.52 \times \delta^{18}O$, making the $\delta^{17}O$ measurement unnecessary and redundant. However, certain photochemical systems do not follow this mass-dependent relationship ($\delta^{17}O \neq 0.52 \times \delta^{18}O$), and are termed mass-independent fractionations (MIF).[5] MIF are quantified by the term $\Delta^{17}O$ ($\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$), and the chemical physics of MIF has been the subject of much theoretical interest.[6] Recently, mass-independent isotopic compositions have been detected in atmospheric nitrate aerosols and rainwater with $\Delta^{17}O$ as high as 31‰.[7,8] Fertilizer and bacterial nitrate have $\Delta^{17}O \simeq 0‰$ because their formation is governed by kinetic and equilibrium isotope fractionation processes. Mass-dependent fractionation associated with postdepositional nitrate transformation (transport, chemical, and biologic reactions) that can alter $\delta^{18}O$ values will not effect the value of $\Delta^{17}O$. Therefore, $\Delta^{17}O$ has the potential to be a more sensitive and reliable tracer for $NO_3^-_{atm}$ in the environment than traditional $\delta^{18}O$ measurements.

CO_2 and CO generated by current $\delta^{18}O$ analytical methods are not suitable for $\Delta^{17}O$ measurements because of the isobaric interference of the ^{13}C at m/e 45 ($^{16}O^{13}C^{16}O$ and $^{16}O^{12}C^{17}O$), and thus, O_2 is required for $\Delta^{17}O$ analysis. Here we will present a rapid

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(1) Galloway, J. N. *Environ. Pollut.* **1998,** *102*, 15−24.

(2) Kendall, C., McDonnell, J. J., Eds. *Isotope Tracers in Catchment Hydrology*; Elsevier: New York, 1998.
(3) Durka, W.; Schulze, E. D.; Gebauer, G.; Voerkelius, S. *Nature (London)* **1994,** *372*, 765−767.
(4) Urey, H. C. *J. Chem. Soc.* **1947,** 562−581.
(5) Thiemens, M. H.; Savarino, J.; Farquhar, J.; Bao, H. *Acc. Chem. Res.* **2001,** *34*, 645−652.
(6) Gao, Y. Q.; Marcus, R. A. *Science (Washington, DC)* **2001,** *293*, 259−263.
(7) Michalski, G. M.; Thiemens, M *EOS, Trans., Am. Geophys. Union* **2000,** *81*, 120.
(8) Galanter, M.; Sigman, D. M.; Levy, H., II; Böhlke, J. K.; Lipschultz, F.; Steig, E. *EOS, Trans., Am. Geophys. Union* **2000,** *81*, 191.
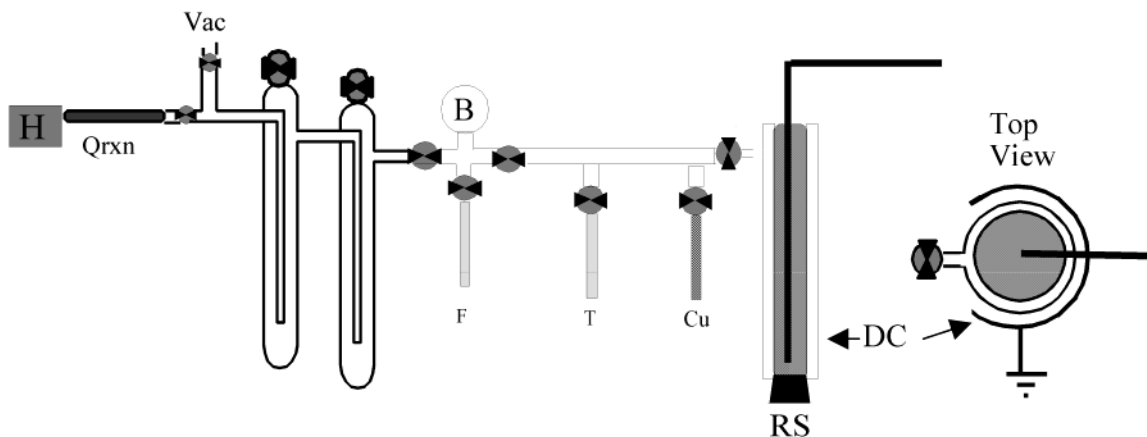
Figure 1. Schematic diagram of the thermal decomposition system with the electrical discharge chamber attached. H, heater; B, Baratron gauge; F, finger (calibrated); RS, rubber stopper; Qrxn, quartz reaction vessel; T, O_2 sample tube; XX, 5 M NaCl solution; Cu, copper reduction (not used); DC, discharge chamber. A top view of the discharge chamber is on the right. Details of the discharge chamber construction and its use are given by Bes[15].

and precise technique for determining both the $\delta^{18}O$ and $\delta^{17}O$ in nitrate by generating O_2 through the thermal decomposition of $AgNO_3$. We have utilized IAEA-NO3, an internationally distributed KNO_3 isotope reference material with $\delta^{15}N = +4.7‰$[9] and with reported $\delta^{18}O$ values ranging from about +22.7 to +25.3‰ depending on the C reduction technique.[10,11] In addition, two local laboratory standards, RSIL-N11 (USGS laboratory KNO_3 with $\delta^{15}N = +3.5‰$ and $\delta^{18}O \sim 26‰$) and GMSTD-1 (UCSD laboratory $AgNO_3$, Fisher brand, lot 987703), were also used for calibration purposes. In contrast to those three reagents, which exhibited only mass-dependent O isotope variations ($\Delta^{17}O \sim 0$), we also tested the new analytical method on a large sample of natural nitrate salt from the Atacama Desert in Chile and detected a substantial positive value of $\Delta^{17}O$. This nitrate salt (designated as USGS-35) has been prepared for international distribution as a nitrate O isotope reference material (Böhlke et al., in preparation) and may be used as a reference material for MIF isotope studies.

METHODS

Nitrate Purification and $AgNO_3$ Preparation. Samples containing large amounts of nitrate (>50 μmol) either in aqueous form (rainwater, surface water, or well water) or solid form (soils, aerosols collected on filters) are extracted in Millipore water and converted to $AgNO_3$ by a series of purification steps that have been described elsewhere.[12] This NO_3^- purification technique is not suitable for samples containing small amounts of NO_3^- (<10 μmol) because it is subject to contamination from the large quantity of reagents required. Therefore, a modified system utilizing ion chromatographic purification and isolation was constructed for small NO_3^- samples (SO_4^{2-} maybe simultaneously isolated in pure form). A Dionex 2020i ion chromatograph is used to pump aqueous solutions (prefiltered at 0.22 μm) containing 20 μmol or less of total soluble ions (Cl^-, NO_3^-, SO_4^{2-}) through a

preconcentration column (Dionex AS9-HC) and a Dionex Ionpac AS4A anion column, which traps all anions and allows uncharged dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) to pass through. After anion trapping, the flow is reversed and the anions are eluted using a 9.6 mM Na_2CO_3/ 8.5 mM $NaHCO_3$ solution and separated on a Dionex HPIC-AS3 high-capacity anion column. The anions are sequentially eluted from the column and pass through a Dionex AMMS-4ml suppression column that exchanges Na^+ and other cations for H^+, converting the salt solutions into HCl, HNO_3, and H_2SO_4 solutions and converting the eluent into CO_2 and water. HCl and acidified DOC and DON are allowed to elute, and the HNO_3 and H_2SO_4 solutions (~ 6 mL) are collected in separate containers by monitoring the elution peaks on a conductivity detector. The HNO_3 is converted to $AgNO_3$ by anion exchange using a second AMMS column (Ag form) and using 0.002 M Ag_2SO_4 as the regenerant. The resulting $AgNO_3$ solution is then either freeze-dried or oven-dried at 70 °C.

The bulk nitrate reference materials (IAEA-NO3, RSIL-N11, USGS-35) were converted to $AgNO_3$ by hydrating with Millipore water, passing the solution through a cation exchange resin (BioRad AG-50W-X12, hydrogen form), and then neutralizing the product HNO_3 with Ag_2O to form $AgNO_{3(aq)}$.

Conversion of $AgNO_3$ to O_2 by Thermal Decomposition. The conversion of $AgNO_3$ to O_2 utilizes the thermal decomposition reaction, $AgNO_3 \rightarrow \frac{1}{2}O_2 + NO_2 + Ag_{(s)} + (N_2, NO$ in trace amounts). The decomposition apparatus (Figure 1) was constructed out of borosilicate (Pyrex) glass except for the decomposition tube, which is quartz glass and is attached to the line with a Cajon 9-mm Ultratorr fitting. The quartz decomposition tubes (9 mm o.d. $\times$ 120 mm) are precleaned by soaking in 7 M HNO_3 and subsequently etched for 10 min in 10% HF solution to remove surface impurities. The tubes are thoroughly rinsed with Millipore water and annealed at 900 °C while exposed to air for 24 h. $AgNO_3$ (1−7 mg) is weighed into silver foil capsules, and the top of each capsule is pinched and twisted closed. For small samples, purified $AgNO_3$ is redissolved with 100 μL of Millipore water, directly transferred into large silver foil capsules (Elemental Microanalysis Ltd., 12.5 $\times$ 5 mm, 99.9% pure) using a micropipet, and then freeze-dried. The capsules containing the $AgNO_3$ solid

(9) Böhlke, J. K.; Coplen, T. B. *Int. At. Energy Agency* **1995**, *IAEA TECDOC 825*, 51−66.
(10) Kornexl, B. E.; Gehre, M.; Hofling, R.; Werner, R. A. *Rapid Commun. Mass Spectrom.* **1999**, *13*, 1685−1693.
(11) Revesz, K.; Böhlke, J. K.; Yoshinari, T. *Anal. Chem.* **1997**, *69*, 4375−4380.
(12) Silva, S. R.; Kendall, C.; Wilkison, D. H.; Ziegler, A. C.; Chang, C. C. Y.; Avanzino, R. J. *J. Hydrol. (Amsterdam)* **2000**, *228*, 22−36.

Table 1. $\delta^{18}O$, $\delta^{17}O$, and $\Delta^{17}O$ Values for Reference Material IAEA-NO3, RSIL-N11, GMSTD-1, and USGS-35[a]

	% nitrate oxygen	$\delta^{18}O$	$\delta^{17}O$	$\Delta^{17}O$	$\delta^{18}O$ CO-CFIRMS[b]	$\Delta^{17}O$ fluorination
			Thermal Decomposition			
RSIL-N11 ($n = 5$)	37 ± 1	13.0 ± 0.87	6.57 ± 0.43	-0.21 ± 0.08	24.6 ± 0.5	na[c]
IAEA-NO3 ($n = 5$)	38 ± 1	11.8 ± 0.81	6.0 ± 0.40	-0.18 ± 0.12	23.6	na
GMSTD-1 ($n = 8$)	37 ± 1	3.03 ± 0.47	1.49 ± 0.29	-0.10 ± 0.10	17.3 ± 0.5	-0.2 ($n = 3$)
USGS-35 ($n = 10$)	36.7 ± 1.2	42.41 ± 1.5	43.61 ± 0.75	21.56 ± 0.11	$+54.9 \pm 0.5$	na
			Thermal + Electrical Decomposition			
RSIL-N11 ($n = 5$)	92 ± 0.2	24.90 ± 0.42	12.63 ± 0.25	-0.32 ± 0.29	24.6 ± 0.5	na
IAEA-NO3 ($n = 5$)	91 ± 0.2	23.59 ± 0.73	12.01 ± 0.38	-0.25 ± 0.14	23.6	na
GMSTD-1 ($n = 7$)	94 ± 0.3	15.42 ± 0.63	8.2 ± 0.31	-0.18 ± 0.10	17.3 ± 0.5	-0.2 ($n = 3$)
USGS-35 ($n = 8$)	92 ± 0.02	53.23 ± 1.14	48.01 ± 0.98	20.33 ± 0.46	$+54.9 \pm 0.5$	na

[a] Carbon reduction $\delta^{18}O$ values of the same standards are provided to compare accuracy of techniques. Fluorination refers to offline conversion to CO_2 followed by fluorination to produce O_2. CO-CFIRMS refers to on-line conversion to CO with continuous-flow isotope mass spectrometry. [b] $\delta^{18}O$ values from CO-CFIRMS were calibrated by assuming $\delta^{18}O$[IAEA-NO3] = +23.6‰ (this study); the range of reported $\delta^{18}O$ values of IAEA-NO3 is +22.7 to +25.3‰[10-12] [c] na, not available.

are inserted into the quartz reaction tubes, attached to the vacuum decomposition line, and evacuated to 10^{-7} (Torr) for 20 min. Decomposition is initiated by sliding a ceramic resistance heater (preheated to 520 °C) over the quartz reaction tube. The gas products ($\sim36\%$ O_2, 55% NO_2, 9% NO) evolve after several minutes and pass through two liquid nitrogen (LN_2) traps, which cryogenically remove the NO_x. The O_2 is then collected in a calibrated volume finger containing 5A molecular sieves (precleaned at 300 °C in vacuo for 30 min) at 77 K. The finger is thawed, and the stoichiometric yield is determined manometrically with a Baratron pressure gauge. O_2 yields vary from 36 to 39% of the original nitrate oxygen. Analyses of the noncondensable gas that passes through the LN_2 traps indicate that it is primarily O_2 and only trace amounts of N_2 ($\ll1\%$) and NO ($\ll1\%$). Heating of the finger containing molecular sieve (200 °C) did not release detectable amounts of NO, indicating that the NO generated during the decomposition formed N_2O_3 and was frozen in the LN_2 traps. The O_2 is then transferred to a sample tube containing 5A molecular sieve, and the oxygen isotope ratios are determined using a Finnigan-Mat 251 isotope ratio mass spectrometer with Faraday cup detectors at m/e 32, 33, and 34 amu.

RESULTS

The $\delta^{18}O$ and $\Delta^{17}O$ values of the O_2 produced from IAEA-NO3, RSIL-N11, and GMSTD-1 and USGS-35 by the partial thermal decomposition of $AgNO_3$ are presented in Table 1. Because the O_2 yields were less than 100% and the O_2 will be isotopically fractionated during the partitioning of the oxygen atoms into the O_2 and NO_x products, the $\delta^{18}O$ of the O_2 will depend on the initial isotopic composition of the nitrate and the fractionation factor for the decomposition reaction, which depends on the decomposition temperature. However, the O isotope fractionation is consistent during decomposition at a given temperature, and the $\delta^{18}O$ can be determined by applying a correction based on analysis of nitrate reference materials. Decomposition is a thermodynamic process, which is a mass-dependent process and has no effect on the $\Delta^{17}O$. The $\delta^{18}O$ values of the nitrate salts were also determined independently by continuous-flow isotope ratio mass spectrometry on CO gas (CO-CFIRMS).[10] The CO was produced by the reaction of nitrate with carbon at 1450 °C in a carrier gas of He, separated by gas chromatography, and directed into the mass spectrometer

(Finnigan Delta Plus). Calibrations were made by analyzing IAEA-NO3 as a sample and assigning it a $\delta^{18}O$ value of +23.6‰ with respect to VSMOW, as determined in this study (see below). A comparison of $\delta^{18}O$ values measured by the thermal decomposition method and the CO-CFIRMS method for IAEA-NO3, GMSTD-1, and USGS-35 is shown in Figure 2. A line of slope 1 with an offset of 11.7 $\pm$ 1.4‰ indicates the consistency of the $\delta^{18}O$ fractionation between the O_2 and NO_2 products over a 40‰ range. Each of these reference materials has a $\Delta^{17}O \sim -0.2 \pm 0.1$‰, except the USGS-35. These values are consistent with the common commercial process for producing nitrate reagents by catalytic oxidation of ammonia by air O_2, which has a $\Delta^{17}O = -0.155$‰.[13] As discussed above, common C reduction methods are unsuitable for $\Delta^{17}O$ measurements because of isobaric interference; therefore, no $\Delta^{17}O$ comparison can be made between our method and the C reduction methods. However, several samples of GMSTD-1 were reacted with graphite to produce CO_2, which was then fluorinated to O_2.[14] The $\Delta^{17}O$ values obtained with the CO_2 fluorination method agree with the thermal decomposition results to within the standard errors, indicating that the two techniques have similar accuracies and precisions for $\Delta^{17}O$ values near zero.

An additional test was conducted by decomposing the residual NO_x product in an electrical discharge chamber[15] and separating the product N_2 and O_2 by gas chromatography. Combining the thermal decomposition O_2 with the discharged O_2 gave greater than 93% of the original NO_3^- oxygen and $\delta^{18}O$ and $\Delta^{17}O$ values that were in reasonable agreement with the results from CO-CFIRMS and our thermal decomposition values (Table 1). Minor discrepancies between the discharge values and the CO-CFIRMS and thermal decomposition values are attributed to partial isotopic exchange on the glass surface of the electrical discharge chambers. Evidence of this isotopic exchange was given by the observation of a small memory effect between mass-dependent and mass-independent analysis. The combined thermal decomposition and electrical discharge method yielded a $\delta^{18}O$ value for IAEA-NO3 of +23.6‰. This value is within the range of values

(13) Luz, B.u; Barkan, E.; Bender, M. L.; Thiemens, M. H.; Boering, K. A. *Nature (London)* **1999**, *400*, 547−550.
(14) Bhattacharya, S. K.; Thiemens, M. H. *Z. Naturforsch., A: Phys. Sci.* **1989**, *44*, 435−44.
(15) Bes, R.; Lacoste, G.; Mahenc, J. *Methodol. Phys. Anal.* **1970**, *6*, 109−112.

Table 2. $\Delta^{17}O$ Values for USGS-35 Nitrate Samples in the 10–30-μmol (NO_3^-) Size Range[a]

μmol AgNO$_3$	μmol O$_2$	% nitrate oxygen	$\delta^{18}O$	$\delta^{17}O$	$\Delta^{17}O$
		Sample: USGS-35			
30.61	17.39	37.87	43.98	44.35	21.48
27.55	14.83	35.89	44.91	44.88	21.52
19.01	10.36	36.32	43.38	44.21	21.65
26.20	14.74	37.51	43.55	44.07	21.43
13.61	9.63	39.37	41.75	43.36	21.65
33.44	18.24	36.36	42.81	43.63	21.37
23.61	12.92	36.49	41.22	43.12	21.69
23.19	12.60	36.22	40.81	42.88	21.66
10.48	5.51	35.06	41.57	43.10	21.48
12.24	6.63	36.07	40.13	42.50	21.63
av/SD		36.7 ± 1.2	42.41 ± 1.5	43.61 ± 0.75	21.56 ± 0.11

[a] No correlations were observed between $\Delta^{17}O$ and sample size or percent of nitrate oxygen collected. The ±0.11 standard deviation includes the variation of $\Delta^{17}O$ due to blank, possible exchange reactions, and mass spectrometer noise.

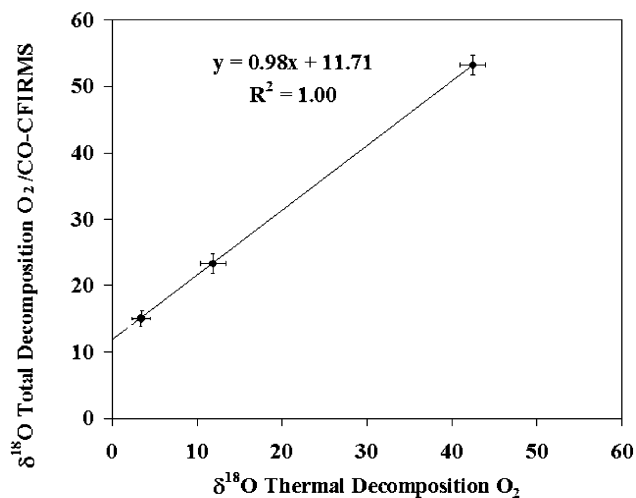**Figure 2.** $\delta^{18}O$ values of USGS-35, GMSTD-1, and IAEA-N3 from carbon reduction method and discharge method versus $\delta^{18}O$ values from the thermal decomposition (Table 1). Error bars indicate standard deviations for 5–10 analyses by the thermal decomposition method.
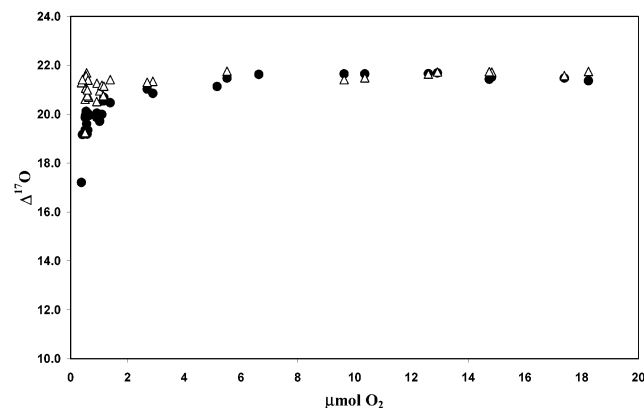

Figure 3. $\Delta^{17}O$ values of USGS-35 as a function of the amount (μmol) of the O$_2$ generated from the thermal decomposition. Solid dots indicate uncorrected values; open triangles indicate samples corrected for a mass-dependent blank of 50 nmol. Standard deviation ($\Delta^{17}O$) for samples of >5 μmol are ±0 0.11‰ and for samples of <5 umol and ±1 (uncorrected) and ±0.58‰ (corrected).

reported previously (+22.7 to +25.3‰), based on various carbon reduction methods.[10–12]

Table 2 lists the $\delta^{18}O$ and $\Delta^{17}O$ values from 10 analyses of USGS-35 obtained by thermal decomposition. The results indicate a large MIF with $\Delta^{17}O = 21.56 \pm 0.11$‰, which is close to the values observed in tropospheric nitrate aerosols[7] and rainwater.[8] The $\Delta^{17}O$ data provide an independent confirmation of the atmospheric origin of this nitrate that was previously suggested based on the $\delta^{18}O$ enrichment.[16]

DISCUSSION

The accuracy of $\delta^{17}O$ measurement is limited by the low isotopic abundance of ^{17}O (0.038%) and lack of recognized standards possessing nonzero values of $\Delta^{17}O$. Testing analytical techniques without a mass-independent standard is difficult for $\Delta^{17}O$ measurements because minor, but critical exchange reactions that may be taking place during analytical processes may be undetectable. All analytical material and possible contaminants (glass, quartz, metal oxide, air O$_2$) have mass-dependent oxygen $\Delta^{17}O \sim 0$; therefore. any possible exchange or contamination with the sample oxygen, which may be *mass independent*, results in a dilution of the $\Delta^{17}O$. The reduction of the $\Delta^{17}O$ value is equal to the degree of exchange, or contamination, relative to sample size. The degree of exchange is also important for ^{18}O measurements but the isotopic composition of the exchangeable reservoirs are often similar and the fractionation factor (α) is typically small, resulting in less exchange sensitivity for $\delta^{18}O$ analysis.

Exchange and memory effects involving the product O$_2$ and the quartz reaction tube were observed when decomposition temperatures exceeded 650 °C and became more pronounced at temperatures above 850 °C (data not shown). The 520 °C decomposition temperature permitted rapid decomposition while eliminating detectable isotopic exchange.

There was good consistency in the USGS-35 $\Delta^{17}O$ values for samples larger than 5 μmol (Table 2), but $\Delta^{17}O$ values decreased

as sample sizes decreased below 5 μmol (Figure 3). This decrease is attributed to contamination from silver oxides on the surface of the silver capsules that either exchanged[17] with the O$_2$ sample or desorbed during the decomposition.[18] To evaluate the size of this blank, it is assumed that the source of the oxygen on the silver surface is from atmospheric O$_2$ ($\Delta^{17}O \sim 0$) and that the $\Delta^{17}O$ of USGS-35 = 21.6‰. The following mass balance equation is solved for USGS-35 samples of varying size:

$$O_{2\,\text{blank/exchange}\,(moles)} = \left(\frac{\Delta^{17}O_{\text{USGS-35}} - \Delta^{17}O_{\text{measured}}}{\Delta^{17}O_{\text{USGS35}}} \right) \times O_2\,(moles)$$

Here O$_2$ (moles) is the total number of moles of O$_2$ generated during the decomposition. Analysis of USGS-35 samples smaller

(16) Böhlke, J. K.; Ericksen, G. E.; Revesz, K. *Chem. Geol.* **1997**, *136*, 135–152.

(17) Zemlyanov, D.; Schlogl, R. *Surf. Sci.* **2000**, *470*, L20–L24.

(18) Carlisle, C. I.; Fujimoto, T.; Sim, W. S.; King, D. A. *Surf. Sci.* **2000**, *470*, 15–31.

than 5 μmol yielded an average blank of 50 $\pm$ 5 nmol. Blank-corrected $\Delta^{17}O$ values for other samples are given by

$$\Delta^{17}O_{sample} = \left(\frac{O_2}{O_2 - blank}\right) \times \Delta^{17}O_{measured}$$

Blank-corrected and uncorrected $\Delta^{17}O$ values are compared in Figure 3, which shows that the correction has little effect on samples larger than 5 μmol for which the 50-nmol blank represents less than 1% of the generated oxygen.

The ideal sample sizes for simultaneous measurements of $\Delta^{17}O$ and $\delta^{18}O$ with this method are between 2 and 6 mg (10−40 μmol) of $AgNO_3$. Samples smaller than this require substantial blank correction, and samples larger than 6 mg are subject $AgNO_3$ volatilization. The melting point of $AgNO_3$ is 212 °C, and its vapor pressure increases until decomposition initiates at $\sim$ 440 °C (*CRC Handbook of Chemistry and Physics*; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1996). Samples larger than $\sim$10 mg and in unpinched silver capsules were subject to volatilization and resulted in $\delta^{18}O$ fractionations from 2 to 10‰. The volatized $AgNO_3$ could be observed as it condensed in a clear liquid ring inside the quartz reaction tube outside the heater, which would crystallize upon cooling. Reducing the sample size to less than 7 mg and pinching the Ag capsule closed (but not sealing) eliminated any noticeable condensate and reduced the $\delta^{18}O$ variation to $\pm$1.5‰. The $\Delta^{17}O$ error remained $\pm$0.11‰ regardless of volatilization because this is a kinetic mass dependent process.

CONCLUSION

Our data indicate that the thermal decomposition of $AgNO_3$ to O_2 provides a rapid, accurate, and precise measurement of $\Delta^{17}O$ ($\pm$0.11‰), as well as $\delta^{18}O$ values that are comparable to those obtained by carbon reduction methods when calibrated against reference materials ($\pm$1.5‰). The nitrate salt USGS-35 was found to have $\Delta^{17}O = 21.6$‰ and should be useful as a $\Delta^{17}O$ reference material for future analtyical developments. The USGS-35 reference material presents an opportunity to reexamine various oxygen isotope analytical methods that were developed using mass-dependent standards, high temperatures, and materials such as glass (quartz, Pyrex) and metals (Ni, Pt, stainless steel) that are subject to oxidation, isotopic exchange, and oxygen sorption. Nitrate salts can be converted into most gases of interest by selecting the appropriate salt and combustion technique. NO_2 and O_2 can be generated by the method detailed in this paper: CO_2 and CO by graphite reduction of $AgNO_3$ in a graphite tube, and N_2O and H_2O by thermally decomposing $NH_4NO_3 \rightarrow N_2O + 2$ H_2O. Because the oxygen atoms of each of these processes are derived solely from the nitrate molecule, and because the thermodynamic and kinetic isotopic fractionations are mass dependent, the $\Delta^{17}O$ of the resultant gases will remain at 21.6‰ allowing for interlaboratory calibrations of $\Delta^{17}O$ analytical methods.