

Technical Notes

Comparison of $\delta^{18}\text{O}$ Measurements in Nitrate by Different Combustion Techniques

Kinga Révész* and John-Karl Böhlke

U.S. Geological Survey, 431 National Center, Reston, Virginia 20192

Three different KNO_3 salts with $\delta^{18}\text{O}$ values ranging from about -31 to $+54\text{‰}$ relative to VSMOW were used to compare three off-line, sealed glass tube combustion methods (widely used for isotope studies) with a more recently developed on-line carbon combustion technique. All methods yielded roughly similar isotope ratios for KNO_3 samples with $\delta^{18}\text{O}$ values in the midpoint of the $\delta^{18}\text{O}$ scale near that of the nitrate reference material IAEA-NO-3 (around $+21$ to $+25\text{‰}$). This reference material has been used previously for one-point interlaboratory and intertechnique calibrations. However, the isotope ratio scale factors by all of the off-line combustion techniques are compressed such that they are between 0.3 and 0.7 times that of the on-line combustion technique. The contraction of the $\delta^{18}\text{O}$ scale in the off-line preparations apparently is caused by O isotope exchange between the sample and the glass combustion tubes. These results reinforce the need for nitrate reference materials with $\delta^{18}\text{O}$ values far from that of atmospheric O_2 , to improve interlaboratory comparability.

Since the paper of Rittenberg and Ponticorvo¹ was published in 1956, various techniques have been developed to analyze the oxygen isotope ratios of nitrate.^{2–6} These techniques are used extensively to study the sources and fate of nitrate in hydrologic systems.^{7–12} In general, the developers of these techniques used IAEA-NO-3 KNO_3 nitrogen isotope reference material or some

other laboratory nitrate reagent for interlaboratory and intertechnique calibration. All of these materials typically have oxygen isotope compositions close to that of atmospheric O_2 : $\delta^{18}\text{O} = 23.8\text{‰}$.^{13–15} The lack of international nitrate reference materials with a wide range of $\delta^{18}\text{O}$ values prevented more than one-point calibration. The proper calibration of the different techniques is essential so that oxygen isotope ratios of the same sample reported by different laboratories will be identical within analytical uncertainty. The purpose of this paper is to document some potential discrepancies among these techniques and the importance of the international distribution of reference materials with a wider range in oxygen isotopic composition than what is available now.

MATERIALS AND METHODS

In this experiment, we used three different KNO_3 salts with greatly different $\delta^{18}\text{O}$ values. One of the three salts is a laboratory reagent (RSIL N-11), with a $\delta^{18}\text{O}$ value close to that of IAEA-NO-3 and atmospheric O_2 .⁵ The other two salts (N-34a and N-35a) have $\delta^{18}\text{O}$ values that are substantially lower and higher than that of IAEA-NO-3. In the experiment, we compared three off-line, sealed glass tube combustion methods^{3–5} and one on-line carbon combustion method.⁶ We attempted to reproduce these methods as described in previous publications. The off-line methods are based on the reaction of KNO_3 or AgNO_3 with various C-bearing reducing reagents at different temperatures in sealed silica glass tubes. Varieties of glass tubing used in our experiment included high-purity “quartz” glass 99.995% SiO_2 from two manufacturers (Heraeus Amersil; GE-214), “Vycor” 96% silica and Pyrex glass manufactured by Corning. The main combustion product is CO_2 that was analyzed for $\delta^{18}\text{O}$ by a DuPont double-collecting dual-inlet isotope-ratio mass spectrometer. The $\delta^{18}\text{O}$ values were calibrated with respect to Vienna Standard Mean Ocean Water (VSMOW) on a scale normalized to $\delta^{18}\text{O}$ of Standard Light Antarctic Precipitation (SLAP) = -55.5‰ ,¹⁶ and the oxygen

* To whom correspondence should be addressed. Fax: 703-648-5274. E-mail: Krevesz@usgs.gov. JKbohlke@usgs.gov.

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isotope fractionation factor between water and CO₂ gas was taken to be 1.0412. The on-line method is based on the high-temperature reaction of KNO₃ in a glassy carbon reactor in a continuous He flow, which was done by a ThermoQuest/Finnigan Thermal Conversion Elemental Analyzer (TC/EA) inlet system. The oxygen-bearing product was CO, which was cleaned by gas chromatograph and transferred in a He carrier gas to a Finnigan Delta Plus continuous-flow isotope-ratio mass spectrometer for $\delta^{18}\text{O}$ analysis. These analyses were calibrated by analyzing the sample KNO₃ against aliquots of IAEA-NO-3, which was assumed to have a $\delta^{18}\text{O}$ value of either +22.7 ‰ or +25.3‰.⁶ In this case, no adjustments were made in the $\delta^{18}\text{O}$ scale factors.

Mercury Cyanide Off-Line Combustion Method.³ KNO₃ and Hg(CN)₂ [KNO₃/Hg(CN)₂ = 3/4 molar ratio] sufficient for five analyses were mixed and homogenized gently in an agate mortar. Aliquots containing 100 μmol of KNO₃ were weighed into 9-mm glass tubes, evacuated overnight at 100 °C, and sealed. The sealed tubes were baked at 560 °C for 6 h, and then cooled by removing power from the oven, after which the temperature decreased by 60 °C in the first hour, 50 °C in the second hour, etc., to room temperature in ~24 h. Gases from the combustion tubes were separated cryogenically; then the CO₂ gas was transferred by cryogenic distillation into a sample tube for $\delta^{18}\text{O}$ analysis.

Low-Temperature Graphite Off-Line Combustion Method.⁵ KNO₃ and catalyzed C sufficient for five analyses were mixed and homogenized in an agate mortar. The C/KNO₃ mole ratio was 4, and we used two different kinds of catalyzed carbon, containing ~1 wt % of either Pd or Ni, respectively. Aliquots containing 100 μmol of KNO₃ were weighed into 9-mm glass tubes, and a small slab of 0.0025-mm-thick gold foil was added to each tube. The tubes were evacuated overnight at 100 °C, sealed, baked at 520 °C for 24 h, and then cooled slowly. Gases from the combustion tubes were separated cryogenically; the CO₂ gas was transferred by cryogenic distillation into a sample tube for $\delta^{18}\text{O}$ analysis. The remaining solid in the combustion tube (K₂CO₃) was reacted with phosphoric acid at 25 °C to release CO₂. The CO₂ yield was determined, and the sample was analyzed for $\delta^{18}\text{O}$. The results for the CO₂ and K₂CO₃ were combined to obtain the $\delta^{18}\text{O}$ value of the original KNO₃.⁵

High-Temperature Graphite Off-Line Combustion Method.⁴ Because this technique requires AgNO₃, our KNO₃ samples were converted to AgNO₃ by AG MP-50 cation-exchange resin in the Ag form. Amounts of AgNO₃ and pure spectrographic graphite (C) sufficient for five analyses were mixed and homogenized in an agate mortar. The C/AgNO₃ mole ratio was 4. Aliquots containing 100 μmol of AgNO₃ were weighed into 9-mm glass tubes, which were evacuated overnight, sealed, heated in a programmable oven to 850 °C at its maximum rate, and then cooled slowly. Gases from the combustion tubes were separated cryogenically, and the CO₂ gas was transferred into a sample tube for $\delta^{18}\text{O}$ analysis.

On-Line Carbon Combustion Method.⁶ KNO₃ samples were dried in a 90 °C oven overnight and then capped to prevent moisture contamination. Aliquots of 0.3 mg (~3 μmol) were weighed into silver capsules and combusted in a ThermoQuest/Finnigan TC/EA unit. The samples were dropped into a reaction

tube held at 1450 °C, and a continuous He flow of 70 mL/min transported the product to a GC column (5-Å molecular sieve, 80–100 mesh, 2 ft) held at 70 °C for separation of CO from other gases. From there, the reaction products, mainly N₂ and CO, were transferred to a Finnigan Delta Plus mass spectrometer via a ConFloII open-split interface for measurement of $\delta^{18}\text{O}$.

Sample Size and Silica Additive Experiments with Low- and High-Temperature Graphite Off-Line Combustion Methods. Samples were prepared as described above, but aliquots containing 50 μmol of KNO₃ or AgNO₃ (rather than 100 μmol) were weighed into 9-mm quartz glass tubes. The set of aliquots was then divided into two subsets: one subset was finished as described above; the other subset received the addition of 20 mg of quartz glass powder per aliquot and then was finished as described above. The quartz glass powder was prepared by crushing the same type of quartz glass tube (Heraeus Amersil) that was used for the sealed-tube combustions.

Pure CO₂ Gas/Quartz Glass Isotope-Exchange Experiment. CO₂ gases with two different $\delta^{18}\text{O}$ values were introduced to two sets of nine evacuated quartz glass tubes, ~10 μmol in each tube. The gas in each tube was frozen in the bottom by liquid N₂ while the tube was flame-sealed to avoid isotope fractionation during sealing. Three tubes were analyzed without further treatment, three after being baked at 520 °C for 24 h and cooled slowly and three after being heated to 850 °C and cooled slowly. This experiment was repeated with addition of reagents (C or catalyzed carbon) in the amounts that were used in the off-line nitrate preparations.

RESULTS AND DISCUSSION

The results of experiments with nitrate (Tables 1 and 2, and Figure 1) indicate that the $\delta^{18}\text{O}$ values of the three nitrate samples covered a wide range from about -31 to +54‰ with respect to VSMOW (assuming IAEA-NO-3 has $\delta^{18}\text{O}$ = +22.7‰⁵) when analyzed by the on-line carbon combustion technique (TC/EA). All methods yielded roughly similar results for the sample with $\delta^{18}\text{O}$ near the midpoint (sample N-11 in Table 1); therefore, all techniques gave comparable data when only a single midpoint sample was used for calibration.^{3–6} However, the results differ substantially for the samples with $\delta^{18}\text{O}$ values far from the midpoint. In every case, the apparent off-line $\delta^{18}\text{O}$ values for the endpoint samples are closer to the midpoint values than are the on-line $\delta^{18}\text{O}$ values. The relative $\delta^{18}\text{O}$ scale factor for each set of analyses is defined by the slope of a linear fit to the data: $\delta^{18}\text{O}_{\text{sealed tube combustion}} = m\delta^{18}\text{O}_{\text{TC/EA}} + b$, where m is the slope (or scale factor) and b is the y intercept. The average $\delta^{18}\text{O}$ scale factors for the off-line sealed-tube combustion techniques are compressed such that they are between 0.33 and 0.68 times that of the on-line combustion technique, and the compression depends on the sample size and combustion temperature (Table 2). Consequently, the nitrate $\delta^{18}\text{O}$ values further from that of the midpoint value differ substantially from the TC/EA values and also have large uncertainties (Table 1; Figure 1). Because the on-line technique has the largest scale factor and is the only one that does not involve glass, we hypothesized that an isotope-exchange reaction between the product CO₂ and glass reaction tube could be mainly

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Table 1. $\delta^{18}\text{O}$ Values of Three Nitrates Determined by Using Different Combustion Techniques

| type of combustion | type of glass | T (°C) | $\delta^{18}\text{O}^a$ | | | $mX + b$ |
|---------------------|----------------|-------------|-------------------------------|------------------------------|-------------------------------|----------------|
| | | | N-34a σ ($n = 3$) | N-11 σ ($n = 3$) | N-35a σ ($n = 3$) | |
| NiC | quartz Hereaus | 520 | -5.3 ± 2.7 | 22.0 ± 0.3 | 36.9 ± 0.4 | $0.50X + 10.0$ |
| PdC | quartz Hereaus | 520 | -10.3 ± 2.7 | 22.0 ± 0.2 | 39.8 ± 1.4 | $0.59X + 7.8$ |
| PdC | quartz GE-214 | 520 | lost | 21.8 ± 0.2 | 39.4 ± 0.2 | $0.58X + 8.1$ |
| PdC | Pyrex | 520 | -16.6 ± 2.8 | 22.7 ± 0.6 | 40.4 ± 0.9 | $0.69X + 4.8$ |
| C | quartz Hereaus | 850 | -0.9 ± 2.6 | 23.3 ± 0.3 | 40.3 ± 0.2 | $0.48X + 13.3$ |
| C | quartz GE-214 | 850 | -8.5 ± 0.2 | 21.3 ± 0.0 | 42.7 ± 1.3 | $0.60X + 6.6$ |
| Hg(CN) ₂ | quartz Hereaus | 560 | -12.9 ± 3.4 | 22.6 ± 1.0 | 39.4 ± 0.8 | $0.62X + 6.6$ |
| Hg(CN) ₂ | Vycor | 560 | -14.9 ± 2.8 | 21.0 ± 0.2 | 42.8 ± 0.7 | $0.67X + 5.6$ |
| CFIRMS | none | 1450 | $-30.6^b \pm 0.2$ | $23.7^b \pm 0.2$ | $54.2^b \pm 0.3$ | |

^a The $\delta^{18}\text{O}$ values by sealed tube techniques are reported relative to VSMOW on a scale normalized to $\delta^{18}\text{O}$ of SLAP = -55.5‰ .¹⁶
^b $\delta^{18}\text{O}_{\text{TC/EACalibrated}}$ to IAEA-NO-3 = 22.7‰ .⁵

Table 2. Effects of Varying Sample Size and SiO₂ Additive on the Apparent Values of $\delta^{18}\text{O}$ of Nitrates

| type of combustion | sample size (μmol) | T (°C) | $\delta^{18}\text{O}\text{‰}^a$ | | | $mX + b$ |
|------------------------|------------------------------------|-------------|---------------------------------|------------------------------|-------------------------------|----------------|
| | | | N-34a σ ($n = 3$) | N-11 σ ($n = 3$) | N-35a σ ($n = 3$) | |
| PdC | 100 | 520 | -10.3 ± 2.7 | 22.0 ± 0.2 | 39.8 ± 1.4 | $0.57X + 9.4$ |
| PdC | 50 | 520 | -1.5 | 20.2 ± 0.4 | 33.1 ± 1.3 | $0.41X + 14.9$ |
| PdC + SiO ₂ | 50 | 520 | -0.4 ± 0.5 | 18.7 ± 0.1 | 29.2 ± 1.0 | $0.36X + 14.5$ |
| C | 100 | 850 | -0.9 ± 2.6 | 23.3 ± 0.3 | 40.3 ± 0.2 | $0.53X + 12.1$ |
| C | 50 | 850 | 3.2 ± 1.3 | 21.3 ± 0.8 | 31.3 ± 0.5 | $0.33X + 14.0$ |
| C + SiO ₂ | 50 | 850 | 5.1 ± 0.5 | 24.3 ± 0.5 | 44.1 ± 0.9 | $0.45X + 18.2$ |

^a The $\delta^{18}\text{O}$ values by sealed tube technique are reported relative to VSMOW on a scale normalized to $\delta^{18}\text{O}$ of SLAP = -55.5‰ .¹⁶

Table 3. Effect of Baking, with or without Reagents, on the Apparent $\delta^{18}\text{O}$ Values of CO₂ Gas in Quartz Glass Tubes

| T (°C) | $\delta^{18}\text{O}\text{‰}^a$ | | $mX + b$ | $\delta^{13}\text{C}\text{‰}^b$ | |
|-----------|---------------------------------|-----------------------|---------------|---------------------------------|-----------------------|
| | heavy CO ₂ | light CO ₂ | | heavy CO ₂ | light CO ₂ |
| not baked | 70.1 ± 0.2 | 6.2 ± 0.2 | | -4.2 | -40.9 |
| 520 | 58.0 ± 2.7 | 6.0 ± 0.2 | $0.81X + 1.0$ | -4.2 | -41.0 |
| 520 + PdC | 48.0 ± 0.2 | 7.6 ± 2.1 | $0.65X + 2.1$ | -4.2 | -40.8 |
| 850 | 51.8 ± 2.1 | 5.9 ± 0.0 | $0.71X + 1.5$ | no data | no data |
| 850 + C | 40.7 ± 0.3 | 10.3 ± 0.3 | $0.48X + 7.4$ | -3.2 | -40.0 |

^a The $\delta^{18}\text{O}$ values are reported relative to VSMOW on a scale normalized to $\delta^{18}\text{O}$ of SLAP = -55.5‰ .¹⁶ ^b The $\delta^{13}\text{C}$ values are reported relative to Vienna Pee Dee belemnite (VPDB), such that $\delta^{13}\text{C}_{\text{NBS19/VPDB}} = +1.95\text{‰}$.¹⁹

responsible for these discrepancies.^{17,18} This hypothesis was tested in part by analyzing the same set of samples using half the amount of nitrate that was used before and adding crushed quartz glass powder to enhance the effect of the possible oxygen exchange with the quartz glass. The isotope ratio scale is more compressed when 50 μmol of nitrate was used than it is when 100 μmol of nitrate was used (Figure 1; Tables 1 and 2). The SiO₂ additive enhanced the exchange reaction in the case of low-temperature-catalyzed carbon combustion so that the isotope ratio scale factor

became even smaller (Table 2). The CO₂-exchange experiment yielded roughly similar, though somewhat subdued results: the CO₂ gas with $\delta^{18}\text{O} = 6\text{‰}$ (relatively close to the midpoint value) was changed only slightly by baking the tubes, whereas the CO₂ gas with $\delta^{18}\text{O} = 70\text{‰}$ was changed substantially, with a larger shift at 850 °C than at 520 °C. When this experiment was repeated with reagents in the tubes, the per mil scale factor changed from 0.8 to 0.5 (Figure 2 ; Table 3), indicating that the oxygen-exchange reaction between the CO₂ gas and SiO₂ was enhanced significantly. In contrast, the $\delta^{13}\text{C}$ of CO₂ gas was not altered significantly during the heating period. This indicates that there was no carbon isotope-exchange reaction between C reagent and CO₂ gas and that the reagent carbon did not react with the glass oxygen to produce CO₂.

These experimental results indicate that the CO₂ produced from nitrate samples by off-line combustion reactions in glass

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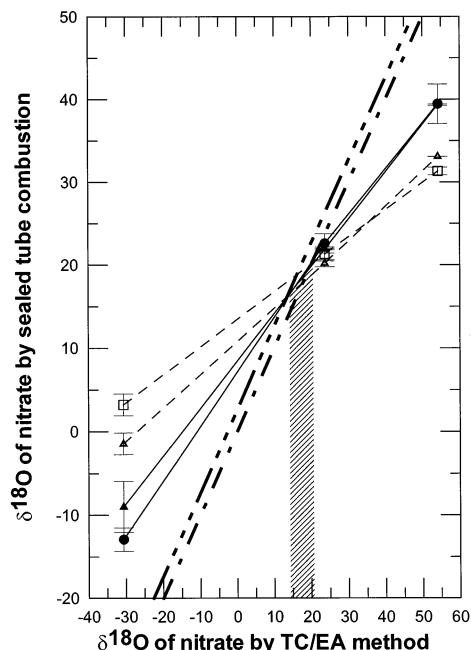


Figure 1. $\delta^{18}\text{O}$ values of nitrate samples prepared by different sealed-tube combustion techniques using different sample sizes versus the $\delta^{18}\text{O}$ values derived from the on-line (TC/EA) combustion technique for the same sample set. $\delta^{18}\text{O}$ values are given relative to VSMOW. Error bars represent the standard deviation for the sealed-tube analyses (typically $n = 3-6$); standard deviations for TC/EA analyses were $\pm 0.2-0.3\text{‰}$. Dashed line with three dots represents analysis by TC/EA normalized to IAEA-NO-3 = 25.3‰ ,⁶ dashed line with one dot represents the analysis by TC/EA normalized to IAEA-NO-3 = 22.7‰ ,⁵ squares represent high-temperature carbon combustion,⁴ triangles represent low-temperature catalyzed graphite combustion,⁵ circles represent low-temperature $\text{Hg}(\text{CN})_2$ combustion.³ Dashed lines represent $50\text{-}\mu\text{mol}$ sample sizes; and solid lines are for $100\text{-}\mu\text{mol}$ sample sizes. Shaded area represents the estimated range of $\delta^{18}\text{O}$ of the glass-exchange component.

tubes was altered by exchange of O with the glass. The mechanism of the exchange reaction cannot be determined from this series of experiments. Other studies indicate that isotope exchange can occur by diffusion of CO_2 molecules into the glass structure, followed by exchange with the oxygen atoms between the CO_2 and the SiO_2 .¹⁷ The relatively small effect for pure CO_2 in comparison with the larger effects for nitrates and for $\text{CO}_2 +$ reagents may indicate that the exchange is facilitated by the presence of the reagents (carbon) and the nitrate salts. The results indicate that the magnitude of the exchange effect is a function of the sample size, the SiO_2 surface area, and temperature, but there is no clear difference in the results from different types of glass tubing (Table 1). Because the deviations from the on-line results are symmetrical and generally disappear between about 10 and 20‰ (Figure 1), it may be inferred that the O components from the glass had $\delta^{18}\text{O}$ values lower than that of atmospheric O_2 and most nitrate chemical reagents. The increased uncertainty in case of samples far from the midpoint $\delta^{18}\text{O}$ value (20 ‰)

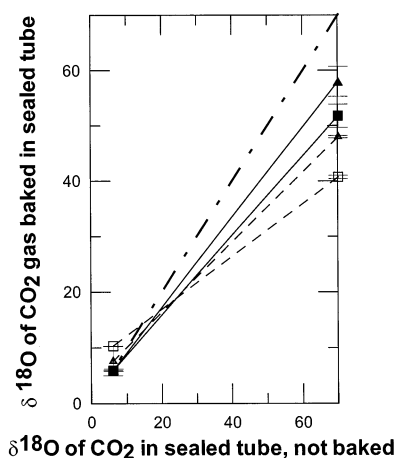


Figure 2. $\delta^{18}\text{O}$ values of CO_2 gases baked at temperatures and times corresponding to the different sealed-tube combustion techniques with or without reagents versus the $\delta^{18}\text{O}$ values of original CO_2 gases. $\delta^{18}\text{O}$ values are given relative to VSMOW. Error bars represent the standard deviations for the baked samples (typically $n = 3$), standard deviations for CO_2 samples not baked were $\pm 0.2\text{‰}$. Dash-dot line is the 1:1 line. Squares represent high-temperature ($850\text{ }^\circ\text{C}$) carbon combustion,⁴ triangles represent low-temperature ($520\text{ }^\circ\text{C}$) catalyzed graphite combustion.⁵ Dashed lines and open symbols represent experiments with reagents (carbon or catalyzed carbon) in tubes.

indicates, however, that the isotope exchange between the oxygen of CO_2 and the oxygen of SiO_2 is not in equilibrium, in agreement with published data.¹⁷

It is possible that we have failed to reproduce exactly the procedures used in some laboratories, so the discrepancies illustrated here may not be typical. Nevertheless, we conclude that because of the potential for isotope exchange between CO_2 product and silica glass, nitrate reference materials with widely varying $\delta^{18}\text{O}$ values are essential to allow laboratories to normalize their $\delta^{18}\text{O}$ scales. For this reason, large aliquots of nitrate salts similar to the ones used in this study have been prepared for distribution as O isotope reference materials (Böhlke et al., in preparation). Future interlaboratory comparisons using these reference materials will be useful for determining more quantitatively the magnitudes of the discrepancies among the techniques and for reevaluating published data.

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