RCM

Effects of nitrate and water on the oxygen isotopic analysis of barium sulfate precipitated from water samples[†]

Janet E. Hannon, John Karl Böhlke[*] and Stanley J. Mroczkowski

U.S. Geological Survey, 431 National Center, 12201 Sunrise Valley Drive, Reston, VA 20192, USA

$BaSO_4$ precipitated from mixed salt solutions by common techniques for SO_4^{2-} isotopic analysis may contain quantities of H_2O and NO_3^- that introduce errors in O isotope measurements. Experiments with synthetic solutions indicate that $\delta^{18}O$ values of CO produced by decomposition of precipitated $BaSO_4$ in a carbon reactor may be either too low or too high, depending on the relative concentrations of SO_4^{2-} and NO_3^- and the $\delta^{18}O$ values of the H_2O, NO_3^-, and SO_4^{2-}. Typical $\delta^{18}O$ errors are of the order of 0.5 to 1‰ in many sample types, and can be larger in samples containing atmospheric NO_3^-, which can cause similar errors in $\delta^{17}O$ and $\Delta^{17}O$. These errors can be reduced by (1) ion chromatographic separation of SO_4^{2-} from NO_3^-, (2) increasing the salinity of the solutions before precipitating $BaSO_4$ to minimize incorporation of H_2O, (3) heating $BaSO_4$ under vacuum to remove H_2O, (4) preparing isotopic reference materials as aqueous samples to mimic the conditions of the samples, and (5) adjusting measured $\delta^{18}O$ values based on amounts and isotopic compositions of coexisting H_2O and NO_3^-. These procedures are demonstrated for SO_4^{2-} isotopic reference materials, synthetic solutions with isotopically known reagents, atmospheric deposition from Shenandoah National Park, Virginia, USA, and sulfate salt deposits from the Atacama Desert, Chile, and Mojave Desert, California, USA. These results have implications for the calibration and use of O isotope data in studies of SO_4^{2-} sources and reaction mechanisms. Published in 2008 by John Wiley & Sons, Ltd.

Combined analyses of S and O isotopes in SO_4^{2-} are useful for distinguishing sources of SO_4^{2-} (e.g., seawater, evaporites, sulfide weathering, photochemistry, etc.) and for documenting effects of SO_4^{2-}-consuming reactions (e.g., biologic assimilation, sulfate reduction, etc.) in the environment.[1–4] The preparation of dissolved SO_4^{2-} for isotopic analysis commonly involves acidification of the sample to neutralize carbonic acid species, followed by addition of $BaCl_2$ to precipitate $BaSO_4$. For dilute samples, the SO_4^{2-} may be preconcentrated on an anion-exchange resin such as IRA-400[5] before being precipitated as $BaSO_4$. Isotopic analyses of O ($\delta^{18}O$, $\delta^{17}O$, $\Delta^{17}O$) in $BaSO_4$ prepared by these methods have provided much useful information over the last several decades, but there are still significant discrepancies in the calibration of $BaSO_4$ isotopic reference materials analyzed by different methods,[6–9] and there may be additional uncertainties related to impurities such as NO_3^- in the $BaSO_4$ precipitated from aqueous environmental samples.[10,11]

The current paper is focused mainly on the problem of impurities in the prepared materials. For example, if NO_3^- is

Correspondence to: J. K. Böhlke, U.S. Geological Survey, 431 National Center, 12201 Sunrise Valley Drive, Reston, VA 20192, USA.
E-mail: jkbohlke@usgs.gov

present in the sample solution, NO_3^- may co-precipitate with the $BaSO_4$, possibly as $Ba(NO_3)_2$.[12] In addition, a minor amount of H_2O typically is incorporated in the precipitated phase(s)[13] and may be difficult to remove by heating without causing O isotope exchange with other substances. When $BaSO_4$ is decomposed to release O for isotopic analysis, some fraction of the total released O may be derived from NO_3^- and H_2O impurities. If the O isotopic compositions of the NO_3^- and H_2O are different from that of the dissolved SO_4^{2-}, the apparent measured O isotopic composition of the precipitated $BaSO_4$ may be different from the isotopic composition of the original dissolved SO_4^{2-} by more than the usual reproducibility of the isotopic analytical method. Although H_2O and NO_3^- impurities in $BaSO_4$ precipitates have been known for a long time, their effects on O isotopic analyses of SO_4^{2-} samples and reference materials commonly are ignored. The objectives of the current study were to (1) determine the amounts of NO_3^- and H_2O impurities in $BaSO_4$ prepared by common methods for isotopic analysis; (2) test data correction procedures for samples containing impurities; and (3) test methods to eliminate impurities. In this paper, we demonstrate that errors associated with these impurities may be substantial, we show that correction procedures may be applied in some cases to pre-existing samples, and we describe our method for separating NO_3^-, NO_2^-, and SO_4^{2-} in large samples by ion chromatography.

EXPERIMENTAL

Mass spectrometry and isotopic reference materials

Experiments were performed with varying combinations of H_2O, Na_2SO_4, $BaSO_4$, and $NaNO_3$ reagents with known isotopic compositions (Table 1). The $\delta^{18}O$ of H_2O was measured by CO_2 equilibration and isotope-ratio mass spectrometry (IRMS) in dual-inlet mode, and normalized to the VSMOW-SLAP scale by analyses of laboratory reference waters.[14] Concentrations and $\delta^{18}O$ values of dissolved NO_3^- were measured by bacterial reduction to N_2O, followed by gas chromatography and IRMS in continuous-flow mode.[15,16] Nitrate $\delta^{18}O$ values were calibrated by analyzing NO_3^- isotopic reference materials as aqueous samples and normalized to 25.6‰ for IAEA-N3, −27.9‰ for USGS34 and 57.5‰ for USGS35.[8] For $\delta^{18}O$ of SO_4^{2-} salts, weighed aliquots of Na_2SO_4 or $BaSO_4$ (each containing 7.5 µmol of O) were weighed into Ag foil capsules along with 0.5 mg of powdered graphite (reaction catalyst). Capsules were dropped from a He-flushed Costech Zero-Blank autosampler (Valencia, CA, USA) into a high-temperature conversion elemental analyzer (TC/EA) (Thermo Electron, Bremen, Germany) with the reactor temperature controller set to 1325°C, as described previously.[8] CO produced by reaction of SO_4^{2-} with C in the reactor was separated from N_2 in a mol-sieve gas chromatograph internal to the TC/EA, and analyzed in continuous-flow mode with a Delta XP isotope-ratio mass spectrometer (Thermo-Electron) (method referred to as CO-CFIRMS). The reacting sample capsules fell into a carbon cup (crucible, within the reaction furnace), which collected residues (including Ag and C) that were cleaned out after each batch of samples analyzed (≤50 sample aliquots). Although we do not know exactly the reaction temperature in the carbon crucible (nominally 1325°C), complete transfer of O from $BaSO_4$ to CO was indicated by (1) reproducibility of $\delta^{18}O$ values within daily runs and between days, (2) absence of memory effects when analyzing multiple aliquots of reference materials with contrasting $\delta^{18}O$ values, and (3) CO peak areas accounting for approximately 100% of the SO_4^{2-} O (see Results and Discussion). Values of $\delta^{18}O$ for Na_2SO_4 and $BaSO_4$ samples were derived from the measured m/z 30/28 ratios of the CO and normalized to 8.59‰ for NBS-127 and −11.34‰ for IAEA-SO6 $BaSO_4$

Table 1. Isotopic compositions of materials used in experiments

Name	Material	$\delta^{18}O$ (‰)
DIW[a]	H_2O	−7
HDIW[b]	H_2O	240, 252, 253
N12766	$NaNO_3$	23.4
N35	$NaNO_3$	57.5
S3744	Na_2SO_4	13.02
NBS 127	$BaSO_4$	8.59[c]
IAEA SO6	$BaSO_4$	−11.34

[a] Deionized water.
[b] 18O enriched or 'heavy' deionized water.
[c] from Ref. 8.

reference materials that were analyzed along with the samples.[8] Typical reproducibilities of normalized $\delta^{18}O$ values were ±0.1–0.15‰. Uncertainties in this paper are expressed as 1σ, defined by $Sqrt[\sum(x - X)^2/(n - 1)]$.

In addition to the CO peak at m/z 28 and 30, we also monitored the N_2 peak at m/z 28 to determine the relative amounts of N-bearing contamination (e.g. from NO_3^-) in the analyzed $BaSO_4$ samples. The magnitudes of the N_2 and CO peaks from NO_3^- were calibrated by analyzing a known amount of KNO_3 along with the $BaSO_4$ samples. The average peak area ratio 28(CO)/28(N_2) for KNO_3 was 6.4. The peak area of N_2 from each sample was used to estimate the contribution of O_{NO3} to the total O analyzed as CO. The contribution of O_{H2O} was estimated independently from analyses of $BaSO_4$ precipitated in H_2O with differing $\delta^{18}O$ values (see below).

Preparation of SO_4^{2-} for isotopic analysis

Direct precipitation of BaSO4 from water samples

$BaSO_4$ was precipitated directly from solution by a common method.[5] Each solution containing dissolved SO_4^{2-} was acidified with HCl to pH 3.5–3.9 to neutralize (protonate) carbonic acid species, then heated and stirred at 80°C for 30 to 60 min. To precipitate $BaSO_4$, 6 mL of 1.0 mol/L (M) $BaCl_2$ was introduced, drop by drop, onto the inside wall of the beaker. The solution containing suspended $BaSO_4$ was heated and stirred for an additional 30 min, cooled to room temperature, and vacuum-filtered onto a 0.2 µm polycarbonate filter. The filter with $BaSO_4$ was dried overnight in air at 60°C and then the $BaSO_4$ was dislodged from the filter, weighed to determine the approximate yield, dried further at 60°C for 2 h in a vacuum oven, and stored in a glass scintillation vial with a watertight polyseal cap.

Pre-concentration of SO_4^{2-} with IRA-400

One of the resins commonly used for the solid-phase extraction and pre-concentration of SO_4^{2-} from dilute solutions is Amberlite IRA-400 (Aldrich, Milwaukee, WI, USA) in Cl^- form.[5] For our experiments, IRA-400 resin with 16–50 mesh size (~300–1200 µm) was pre-cleaned in 500 g batches with 2 L of 3.0 M KCl and rinsed with 2 L deionized water (DIW), then stored in DIW. To prepare columns for SO_4^{2-} extraction, the clean resin was suspended in DIW and the slurry was pipetted into a glass chromatography column (Bio-Rad, Hercules, CA, USA) filled with DIW and with the stopcock partially open until the desired volume of resin had been loaded. The columns were fitted with porous polymer beds at the bottom to retain fine particles, and had inside diameters (ID) of 1.0 or 1.5 cm and lengths from 10 to 50 cm depending on the volume of resin used. For experiments with synthetic solutions, the volume of the resin varied from 6 to 45 mL and the SO_4^{2-} was eluted with various amounts and concentrations of KCl (0.5 or 3 M).

For the collection of SO_4^{2-} from multiple liters of atmospheric deposition, 25 mL of resin was loaded into a plastic drying tube (1.5 cm ID and 15 cm length).[5] DIW (3 L) was pumped at a rate of about 50 mL/min upward through the tube to pre-rinse the resin, then a measured amount of sample was pumped through. The loaded resin was emptied

Table 2. Ion exchange strategies

Sample loaded	Resin used	Sample loading procedure	Typical sample volume	Collection method	Elution pump speed	Elution method
Reagent solutions	IRA-400(Cl)	Gravity feed	10–20 mL	Single aliquot	n/a	0.5 or 3.0 M KCl by gravity
Reagent solutions	AG1-X8 (Cl)	Gravity feed	10–20 mL	Single aliquot and multi-aliquot collections with fraction collector	~3 mL/min	0.5 M KCl with peristaltic pump
Atmospheric deposition	IRA-400(Cl)	Peristaltic pump ~50 mL/min	8–20 L	Single aliquot	n/a	3.0 M KCl by gravity
Atmospheric deposition	AG1-X8 (Cl)	Peristaltic pump ~3 mL/min	8–20 L	Multi-aliquot collections with fraction collector	~3 mL/min	0.5 M KCl with peristaltic pump

into a beaker, suspended in DIW, and the slurry pipetted as above into a glass column with a 1.5 cm ID and 30 cm length. The SO_4^{2-} was eluted by gravity flow of 100 mL of 3.0 M KCl, followed by 100 mL of DIW. The SO_4^{2-} in the total eluent solution was then precipitated by the addition of HCl and $BaCl_2$ as described above (see Direct precipitation). Table 2 summarizes the loading and elution procedures used in this study for small-volume (10–20 mL, high-concentration) synthetic solutions and large-volume (8–20 L, low concentration) samples of atmospheric deposition.

### Chromatographic separation of SO_4^{2-}, NO_2^-, and NO_3^- with AG1-X8

Another resin tested for the collection and chromatographic separation of oxyanions was AG1-X8 (Bio-Rad) in Cl^- form with 100–200 mesh size (~75–150 μm). This resin was pre-cleaned in 500 g batches with 2 L of 1.0 M NaOH, followed by 1 L DIW, 1 L of 2.0 M HCl, 2 L DIW, and 500 mL methanol, then allowed to dry for storage. To prepare columns for anion-exchange chromatography, the resin was resuspended in water, and the slurry was pipetted into glass chromatography columns filled with water (as described above for IRA-400). The resin was further cleaned in each column with 100 mL of 3.0 M KCl followed by 500–1000 mL DIW. Collection of SO_4^{2-} and NO_3^- from multiple liters of atmospheric deposition was accomplished by pumping a known volume through a column containing 30 mL of AG1-X8 at a rate of 2–3 mL/min using a model RP-1 peristaltic pump (Rainin, Woburn, MA, USA) with Tygon tubing with 1/16'' (1.59 mm) ID and 1/32'' (0.79 mm) wall.

Anions were eluted from the AG1-X8 resin column by pumping 0.5 M KCl through the column using the peristaltic pump at a rate of 2–3 mL/min. An automated fraction collector was used to divide the eluent into 6-mL aliquots. Figure 1 shows a typical set of breakthrough curves for a synthetic mixture of 542 μmol SO_4^{2-}, 32 μmol NO_2^-, and 426 μmol NO_3^- dissolved in 10 mL DIW and pipetted onto the top of the column. The anions were eluted, collected in 6-mL aliquots, and analyzed by ion chromatography for SO_4^{2-} and NO_3^- and by colorimetry (segmented flow analysis) for NO_2^-.[17]

Using 30 mL AG1-X8 resin, 0.5 M KCl as the eluent, and a pumping rate of 2–3 mL/min, SO_4^{2-} eluted first, followed by NO_2^-, then NO_3^-, with complete separation between each of the peaks (Fig. 1). For isotopic analysis, aliquots were combined as follows: (1) for SO_4^{2-}, all aliquots from the

beginning of the elution until the first appearance of NO_2^-; (2) for NO_2^-, all aliquots from the first appearance of NO_2^- until the last appearance of NO_2^-; (3) for NO_3^-, all aliquots from the first appearance of NO_3^- until the last appearance of NO_3^-.

The presence or absence of NO_2^- and NO_3^- in the eluent was determined by qualitative colorimetric 'drop' tests on each eluted 6-mL fraction. The reagents for the drop tests were prepared according to a modification of standard colorimetric methods for NO_2^- and NO_3^- analysis[18] (Terry B. Councell, US Department of Agriculture, personal communication, 2003). The NO_2^- coloring solution was made with 10 mL concentrated HCl, 1.0 g sulfanilamide, and 50 mg N-(1-naphthyl)ethylenediamine dihydrochloride diluted to 100 mL with water. This solution was kept refrigerated. The NO_3^- reductant solution was made with 1.35 mL hydrazine solution (1.375 g hydrazine sulfate in 50 mL water)
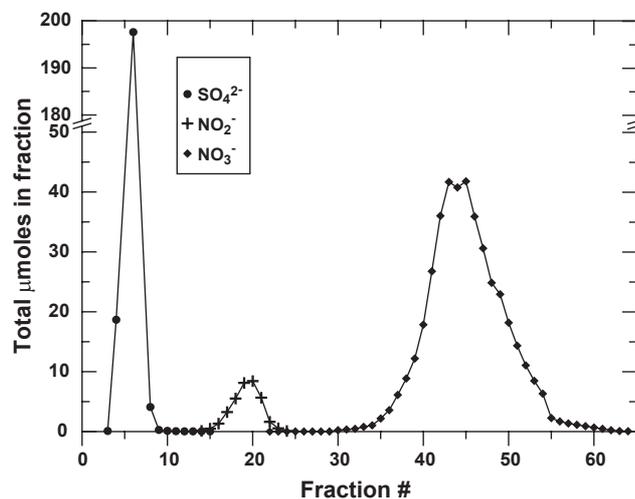
Figure 1. Breakthrough curves for SO_4^{2-}, NO_2^-, and NO_3^- from a mixed solution that was sorbed onto 30 mL AG1-X8, eluted with 0.5 M KCl, and captured with a fraction collector in 6 mL aliquots. The original solution contained 542 μmol Na_2SO_4, 32 μmol $NaNO_2$, and 426 μmol $NaNO_3$. The amounts of solutes in each aliquot were calculated using the concentration and volume of each aliquot. The total recovered yields, determined by integrating the breakthrough curves, were approximately 98% for SO_4^{2-}, 110% for NO_2^-, and 99% for NO_3^-.

and 0.80 mL $CuSO_4$ solution (1.00 g $CuSO_4$ in 250 mL water), diluted to 100 mL with water and stored at room temperature. To test for the presence of NO_2^-, one drop of each eluted fraction was pipetted into a well of a spot test plate and treated with one drop of NO_2^- coloring reagent. In the presence of NO_2^-, the solution turned pink or purple in a few seconds. The presence of SO_4^{2-} had no effect on this test. To test for the presence of NO_3^- in subsequent fractions, one drop of each eluted fraction was pipetted into a well of a spot test plate, and one drop of NO_3^- reductant solution and one drop of 0.30 M NaOH were added to each well. After 15 min, one drop of the NO_2^- coloring reagent was added. NO_3^-, if present, was reduced to NO_2^-, and the coloring reagent turned the sample drop in the well from clear to pink.

RESULTS AND DISCUSSION

Analyses of the solid Na_2SO_4 reagent (S3744) by CO-CFIRMS yielded a mean $\delta^{18}O$ value of 13.02 ± 0.11‰ (1σ, n = 28) when normalized to 8.59‰ for NBS-127 ($BaSO_4$) and -11.34‰ for IAEA-SO6 ($BaSO_4$) analyzed with the samples (Table 1). In contrast, $BaSO_4$ samples precipitated by adding $BaCl_2$ to aqueous solutions of S3744 in H_2O with $\delta^{18}O = -7$‰, some of which also contained NO_3^- with $\delta^{18}O = 23.4$ or 57.5‰, had measured $\delta^{18}O$ values ranging from about 12.0 to 14.5 ‰ (Table 3). These data can be explained by assuming that the $BaSO_4$ contained varying amounts of two different contaminants that contributed to the total O analyzed by the CO-CFIRMS method: (1) H_2O, possibly incorporated in fluid inclusions or sorption/exchange sites, which decreased the measured $\delta^{18}O$, and (2) NO_3^-, possibly co-precipitated in solid solution as $Ba(NO_3)_2$, which increased the measured $\delta^{18}O$. Assuming that there was no isotopic fractionation associated with these processes, and no other processes altering the O isotopic composition of the sample, the measured isotopic composition of a contaminated sample can be described approximately by:

$$\delta^{18}O_{measured} = \delta^{18}O_{SO4} * x[O_{SO4}] + \delta^{18}O_{H2O} * y[O_{H2O}] \\ + \delta^{18}O_{NO3} * z[O_{NO3}] \qquad (1)$$

where $x[O_{SO4}]$, $y[O_{H2O}]$, and $z[O_{NO3}]$ are the fractional contributions of O atoms from each of the three components of the bulk solution from which the $BaSO_4$ was precipitated ($x + y + z = 1$). Other data confirm that SO_4^{2-}, NO_3^-, and H_2O yield O quantitatively to form CO during typical CO-CFIRMS analysis[8] (see Results and Discussion). Although it is possible that isotopic fractionations could occur for various reasons, such as the selective incorporation of ion-associated H_2O with $\delta^{18}O$ different from that of the bulk H_2O source,[19] results from a variety of experiments described below indicate that Eqn. (1) gives a good approximation of the effects of H_2O and NO_3^- on measured values of $\delta^{18}O$ in our preparations.

$BaSO_4$ direct precipitation from SO_4^{2-} solutions without NO_3^-

Incorporation of H_2O
Samples of $BaSO_4$ precipitated directly from solutions of S3744 in normal water (DIW with $\delta^{18}O = -7$‰) by the normal

procedure at 80°C had a mean $\delta^{18}O_{measured}$ value of 12.31 ± 0.20‰ (1σ, n = 4), approximately 0.7‰ lower than the mean value of the Na_2SO_4 reagent. A sample of $BaSO_4$ precipitated directly from a solution of S3744 in ^{18}O-enriched ('heavy') water (HDIW, $\delta^{18}O = 240$‰) had a much higher value of $\delta^{18}O_{measured}$ (21.6‰), indicating O from the HDIW was present in the $BaSO_4$. The amount of O from H_2O in the sample can be estimated from these data by mass balance using a version of Eqn. (1):

$$y[O_{H2O}] = (\delta^{18}O_{measured} - \delta^{18}O_{SO4} * x[O_{SO4}] - \delta^{18}O_{NO3} \\ * z[O_{NO3}])/\delta^{18}O_{H2O} \qquad (2)$$

where $\delta^{18}O_{SO4} = 13.02$‰, $\delta^{18}O_{H2O} = -7$‰ (DIW) or 240–253‰ (HDIW), $x[O_{SO4}] = (1 - y[O_{H2O}] - z[O_{NO3}])$, and $z[O_{NO3}] = 0$. The HDIW experiment described above, evaluated with Eqn. (2), yields a value of $y[O_{H2O}] = 0.037$. Additional aliquots of S3744, each dissolved in 100 mL HDIW ($\delta^{18}O = 240$–253‰) and precipitated as $BaSO_4$, also had elevated $\delta^{18}O$ values ($\delta^{18}O_{measured} = 21.0$–27.0‰) indicating $y[O_{H2O}] = 0.046 \pm 0.010$ (1σ, n = 8) (Fig. 2). Values of $y[O_{H2O}]$ estimated from experiments with DIW ($\delta^{18}O = -7$‰) range from about 0.026 to 0.045. The similarity of $y[O_{H2O}]$ values derived from systems with $\delta^{18}O_{H2O}$ ranging from -7‰ to 253‰ seems to indicate that the H_2O trapped in the $BaSO_4$ was not fractionated substantially with respect to the bulk H_2O. Minor ^{18}O enrichment (by a few ‰) of trapped H_2O could be consistent with the lower mean calculated $y[O_{H2O}]$ values derived from experiments with DIW ($\delta^{18}O = -7$‰), but additional experiments would be required to investigate this possibility. The overall mean value of $y[O_{H2O}]$ calculated from DIW and HDIW precipitations was 0.043 ± 0.011 (1σ, n = 12).

Effect of salinity on the incorporation of H_2O
To determine the effect of salinity on the incorporation of H_2O in $BaSO_4$, three aliquots of S3744 were dissolved in 100 mL HDIW ($\delta^{18}O = 253$‰) with the addition of KCl to produce a 3.0 M solution. $BaSO_4$ precipitated from these solutions by the normal $BaCl_2$ technique had $\delta^{18}O_{measured} = 17.9$, 16.3, and 17.4‰, distinctly lower than that of the $BaSO_4$ precipitated in HDIW without KCl. These data correspond to $y[O_{H2O}]$ values of 0.020, 0.014, and 0.018. Additional experiments with varying concentrations of KCl yielded similar results for KCl concentrations down to 0.5 M (Fig. 2). These results indicate that the presence of a salt such as KCl can decrease the amount of water trapped in the $BaSO_4$. Above 0.5 M, the concentration of KCl does not appear to be related to the amount of trapped H_2O. From experiments with normal and heavy H_2O, without NO_3^-, and with KCl = 0.5–3 M, the mean value of $y[O_{H2O}]$ was 0.018 ± 0.007 (1σ, n = 17).

Support for our interpretation of H_2O contamination was given in an independent study by Gregory Wandless (US Geological Survey (USGS), unpublished data, 2007). Differential thermal analysis of $BaSO_4$ precipitated from a concentrated SO_4^{2-} solution (100–200 mg $Fe_2(SO_4)_3$ in 200 mL H_2O) resulted in approximately 2.5% weight loss between 100 and 1100°C, with a peak in the mass

**Table 3.** Results for solutions of salts with known isotopic composition

Resin used (mL)	NO₃ added	N/S molar ratio	Solution for precipitation	$\delta^{18}O$ of H₂O measured separately	$\delta^{18}O$ of NO₃ measured separately	$\delta^{18}O$ BaSO₄ measured	z[O$_{NO3}$] calculated (Equation 3)	y[O$_{H2O}$] calculated (Equation 2)
				BaSO4 precipitated directly				
n.a.	none	0	DIW	−7	n.a.	12.13	0.000	0.045
n.a.	none	0	DIW	−7	n.a.	12.14	0.000	0.044
n.a.	none	0	DIW	−7	n.a.	12.49	0.000	0.026
n.a.	none	0	DIW	−7	n.a.	12.49	0.000	0.026
n.a.	none	0	HDIW	240	n.a.	21.44	0.001	0.037
n.a.	none	0	HDIW	240	n.a.	21.00	0.001	0.035
n.a.	none	0	HDIW	253	n.a.	24.14	0.001	0.046
n.a.	none	0	HDIW	253	n.a.	23.99	0.000	0.046
n.a.	none	0	HDIW	253	n.a.	27.03	0.001	0.058
n.a.	none	0	HDIW	252	n.a.	25.71	0.000	0.053
n.a.	none	0	HDIW	252	n.a.	21.65	0.000	0.036
n.a.	none	0	HDIW	252	n.a.	26.97	0.000	0.058
n.a.	none	0	0.5 M KCl	−7	n.a.	12.93	0.001	0.004
n.a.	none	0	0.5 M KCl	−7	n.a.	12.61	0.000	0.020
n.a.	none	0	0.5 M KCl	−7	n.a.	12.74	0.000	0.014
n.a.	none	0	0.5 M KCl	252	n.a.	17.26	0.000	0.018
n.a.	none	0	0.5 M KCl	252	n.a.	15.30	0.000	0.010
n.a.	none	0	0.5 M KCl	252	n.a.	18.76	0.000	0.024
n.a.	none	0	1.5 M KCl	252	n.a.	17.31	0.000	0.018
n.a.	none	0	1.5 M KCl	252	n.a.	18.30	0.000	0.022
n.a.	none	0	1.5 M KCl	252	n.a.	17.08	0.000	0.017
n.a.	none	0	3.0 M KCl	252	n.a.	19.58	0.000	0.027
n.a.	none	0	3.0 M KCl	252	n.a.	19.45	0.000	0.027
n.a.	none	0	3.0 M KCl	252	n.a.	20.01	0.000	0.029
n.a.	none	0	3.0 M KCl	253	n.a.	17.91	0.001	0.020
n.a.	none	0	3.0 M KCl	253	n.a.	16.34	0.000	0.014
n.a.	none	0	3.0 M KCl	253	n.a.	17.41	0.001	0.018
n.a.	N35	2.0	DIW	−7	57.5	13.80	0.031	0.029
n.a.	N35	10	DIW	−7	57.5	14.12	0.043	0.040
n.a.	N12766	2.0	DIW	−7	23.4	12.54	0.033	0.041
n.a.	N12766	10	DIW	−7	23.4	12.74	0.043	0.036
n.a.	N12766	21	0.5 M KCl	−7	23.4	12.92	0.049	0.030
n.a.	N35	1.0	0.5 M KCl	−7	57.5	14.27	0.038	0.021
n.a.	N35	2.0	0.5 M KCl	−7	57.5	13.95	0.030	0.019
n.a.	N35	2.0	3.0 M KCl	−7	57.5	13.55	0.018	0.013
n.a.	N35	10	3.0 M KCl	−7	57.5	14.54	0.038	0.009
n.a.	N12766	2.0	3.0 M KCl	−7	23.4	13.00	0.017	0.010
n.a.	N12766	10	3.0 M KCl	−7	23.4	13.30	0.033	0.003
				BaSO4 precipitated after elution from IRA-400				
25	none	0	1.5 M KCl [1]	−7	n.a.	12.71	0.001	0.016
6	N12766	21	0.5 M KCl [2]	−7	23.4	13.54	0.089	0.020
22	N12766	21	0.5 M KCl [2]	−7	23.4	12.95	0.024	0.016
22	N12766	21	0.5 M KCl [2]	−7	23.4	13.18	0.027	0.006
25	N35	2.0	1.5 M KCl [1]	−7	57.5	13.53	0.021	0.020
25	N35	1.8	1.5 M KCl [1]	−7	57.5	13.39	0.014	0.012
				BaSO4 precipitated after elution from AG1-X8				
30	none	0	0.5 M KCl [2]	−7	n.a.	12.88	0.001	0.007
22	N12766	21	0.5 M KCl [2]	−7	23.4	12.00	0.002	0.051
25	N12766	21	0.5 M KCl [2]	−7	23.4	12.74	0.001	0.014
30	N12766	21	0.5 M KCl [3]	−7	23.4	12.35	0.000	0.034
30	N35	2.0	0.5 M KCl [3]	−7	57.5	12.62	0.002	0.023
30	N35	1.8	0.5 M KCl [3]	−7	57.5	12.92	0.001	0.005

[1] Eluted with 3.0 M KCl, followed by DIW, whole eluent used.
[2] Collected initial aliquots (100–150 mL).
[3] Collected 6 mL fractions and tested for NO₃⁻, used NO₃⁻ fraction only.

spectrometer response at around 500°C at *m/z* 18 (H₂O). The amount of weight loss and the identification of H₂O in the reaction product are consistent with our isotope tracer results for solutions with relatively high total solute concentrations.

Conditions of precipitation and drying
A sample of BaSO₄ precipitated at room temperature (22°C) from a solution of S3744 in HDIW ($\delta^{18}O_{H2O} = 240‰$) yielded a $\delta^{18}O_{measured}$ value of 21.0‰, similar to those of
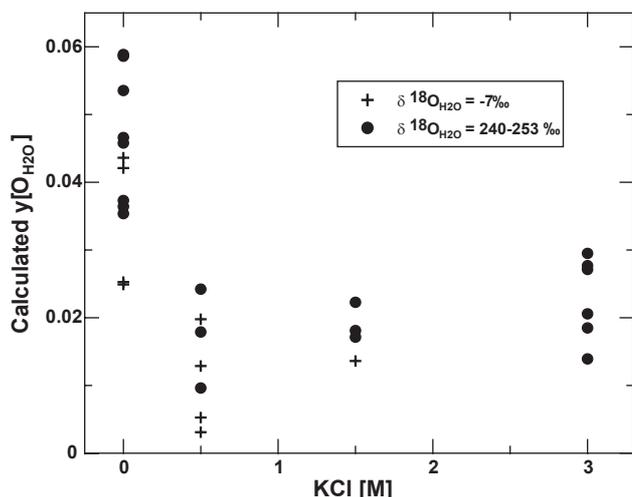
Figure 2. Effect of varying KCl concentrations (M = mol L^{-1}) on the amount of H_2O trapped in $BaSO_4$ precipitated from solutions containing Na_2SO_4 (data from Table 3, no NO_3^- added). The mole fraction of O derived from H_2O (y[O_{H2O}]) in each sample of $BaSO_4$ analyzed by CO-CFIRMS was calculated using Eqn. (2).

seven samples precipitated in HDIW at 80°C (21.4–27.0‰), indicating that precipitation temperature was not a major factor controlling the amount of H_2O incorporated in the $BaSO_4$. To test the significance of the $BaSO_4$ precipitation process, three aliquots of S3744 Na_2SO_4 were dissolved in 20 mL of HDIW ($\delta^{18}O = 240$‰), evaporated to dryness at room temperature, then dried overnight in an oven at 60°C followed by 2 h in a vacuum oven at 40°C. The recovered Na_2SO_4 had $\delta^{18}O_{measured} = 13.3$–14.0‰, only slightly higher than the original salt and consistent with y[O_{H2O}] = 0.001–0.004, indicating that Na_2SO_4 produced by evaporation did not incorporate as much H_2O as $BaSO_4$ precipitated with $BaCl_2$. Heating the 14.0‰ Na_2SO_4 sample at 600°C in a quartz tube under vacuum reduced the $\delta^{18}O_{measured}$ value to 13.2‰, indicating that most of the heavy H_2O was removed.

Experiments were performed to evaluate the possibility of exchange between trapped water and external water after precipitation. An aliquot of $BaSO_4$ containing ^{18}O-enriched

H_2O ($\delta^{18}O_{measured} = 21.4$‰) was suspended in DIW ($\delta^{18}O = -7$‰) overnight and refiltered. A second aliquot of the $BaSO_4$ was suspended in DIW overnight, and this suspension was agitated in an ultrasonic bath for 2 min before filtering. Neither experiment produced a measurable change in the $\delta^{18}O$ (Table 4). To determine if acidic conditions (pH 1) would facilitate exchange of the trapped water with water in which it was suspended, a third aliquot of the $BaSO_4$ was stirred in 0.1 M HCl for 30 min, filtered, and dried. The $\delta^{18}O$ did not change. This pH experiment was repeated with a reagent $BaSO_4$ with $\delta^{18}O = 17.3$‰. The measured $\delta^{18}O$ of the recovered $BaSO_4$ after acid treatment was 17.5‰. These results indicate that $BaSO_4$ precipitated from solution by addition of $BaCl_2$ contains H_2O that does not exchange readily with external H_2O after precipitation.

To test the effectiveness of high-temperature drying for removing H_2O, an aliquot of $BaSO_4$ from a HDIW experiment was heated in a quartz glass crucible open to air for 2 h at 700°C. The value of $\delta^{18}O_{measured}$ of the heated sample was 20.3‰, which was slightly lower than the value before heating (21.4‰) but higher than the value of $\delta^{18}O_{SO4}$ in the original solution (Table 4). Heating similar aliquots of $BaSO_4$ containing HDIW for 4 h at 1000°C reduced $\delta^{18}O_{measured}$ from 21.0–21.4‰ down to 3.2–4.9‰, with little change in the apparent yield of CO, perhaps indicating O exchange with the glass container or with air.[13,20]

Another set of experiments was performed to determine the effects of heating under vacuum. Six 3-mg aliquots of $BaSO_4$ from one of the HDIW experiments were weighed into quartz glass tubes. Each tube was heated under vacuum at one of six different temperatures (400, 500, 600, 700, 800, or 900°C) for 2 h. The heat was removed, and the sample was allowed to cool to room temperature before being removed from vacuum and prepared for CO-CFIRMS analysis. Results (Table 4) indicate that heating may have removed some of the trapped heavy water, but at no temperature was the $\delta^{18}O_{measured}$ of the heated sample equal to the $\delta^{18}O_{SO4}$ value of the original solution. Partial O isotopic exchange within the glass tubes may have occurred at the higher temperatures (≥ 700°C) where $\delta^{18}O_{measured}$ increased slightly while the CO yields remained constant ($\pm 1.3\%$, 1σ). Offline techniques for conversion of $BaSO_4$ into CO_2 commonly involve a pre-heating step under vacuum in an inert metal

Table 4. Selected results of experiments on water removal and exchange

Drying conditions of $BaSO_4$ precipitated from HDIW	$\delta^{18}O$ $BaSO_4$ measured before treatment[a]	$\delta^{18}O$ $BaSO_4$ measured after treatment
2 h in glass crucible at 700°C	21.44	20.30
4 h in glass crucible at 1000°C	21.44	4.94
4 h in glass crucible at 1000°C	21.00	3.15
suspended in −7‰ H_2O overnight, filtered, dried	21.44	21.59
suspended in −7‰ H_2O overnight, sonicated, filtered, dried	21.44	21.62
stirred in 0.1 M HCl (light H_2O) for 30 minutes, filtered, dried	21.44	21.42
2 h under vacuum at 423°C	26.15	20.73
2 h under vacuum at 499°C	26.15	17.91
2 h under vacuum at 591°C	26.15	16.41
2 h under vacuum at 702°C	26.15	16.71
2 h under vacuum at 814°C	26.15	18.21
2 h under vacuum at 898°C	26.15	18.21

[a] S3744 precipitated from HDIW, dried in vacuum oven for 2 h at 60°C.

(e.g. Pt) container at temperatures of 400–500°C or more,[20–22] which presumably removes at least some of the H_2O while precluding exchange with other O-bearing substances.

Direct precipitation of $BaSO_4$ from mixed solutions containing SO_4^{2-} and NO_3^-

Measured $\delta^{18}O$ values of $BaSO_4$ precipitated from solutions containing mixtures of SO_4^{2-} and NO_3^- typically were higher than those of $BaSO_4$ precipitated from solutions without NO_3^- (Table 3, Fig. 3). The measured $\delta^{18}O$ values of the samples were directly related to the $\delta^{18}O$ values of the NO_3^- and the amounts of NO_3^- contamination in the precipitated $BaSO_4$ samples.

The fraction of O contributed by NO_3^- in each sample was estimated from the relative magnitudes of the GC-separated N_2 and CO peaks monitored at m/z 28:

$$z[O_{NO3}] = (CO/N_2)_{KNO3} * [(N_{2,measured}/CO_{measured})$$
$$- (N_{2,blank}/CO_{measured})] \qquad (3)$$

where $(CO/N_2)_{KNO3}$ is the measured peak area ratio for KNO_3 analyzed under the same conditions, and $N_{2,blank}$ represents a small signal for N_2 that appeared during analysis of Ag capsules containing samples with no known source of NO_3^-. The mean value of $(N_{2,blank}/CO_{measured})$ used

in this equation was 3×10^{-4}, which would correspond to $z[O_{NO3}] = 0.0015$ if this N_2 represented NO_3^-. This is the mean value of $(N_{2,measured}/CO_{measured})$ for $BaSO_4$ precipitated directly from H_2O-Na_2SO_4 solutions with 0–0.5 M KCl and no NO_3^- added. Independent measurements of NO_3^- in reagent solutions by the bacterial reduction method indicate that the H_2O had $NO_3^- \leq 0.2\,\mu mol/L$, the Na_2SO_4 had $NO_3^-/SO_4^{2-} \leq 6 \times 10^{-5}\,\mu mol/\mu mol$, and the KCl had $NO_3^-/Cl^- \leq 3 \times 10^{-6}\,\mu mol/\mu mol$. Analyses of these blank solutions before and after $BaSO_4$ precipitation indicate that no more than 30% of the trace dissolved NO_3^- was incorporated in the $BaSO_4$. These results indicate that the mean value of $(N_{2,blank}/CO_{measured})$ was caused by a source of N other than NO_3^- incorporated from the reagent solutions. Therefore, only values of $(N_{2,measured}/CO_{measured}) > 3 \times 10^{-4}$ were attributed to NO_3^-.

In Fig. 3, values of $\delta^{18}O_{measured}$ for $BaSO_4$ prepared from solutions to which NO_3^- was deliberately added are compared with hypothetical curves corresponding to Eqn. (1) for six different scenarios. In each case, $\delta^{18}O_{SO4} = 13.02‰$ (S3744) and $\delta^{18}O_{H2O} = -7‰$. The curves correspond to hypothetical mixing between SO_4^{2-} and NO_3^- with two different values of $\delta^{18}O_{NO3}$ (57.5‰ for N35 and 23.4‰ for N12766) and three different values of $y[O_{H2O}]$ (0 for no added water, 0.18 representing $BaSO_4$ precipitated from
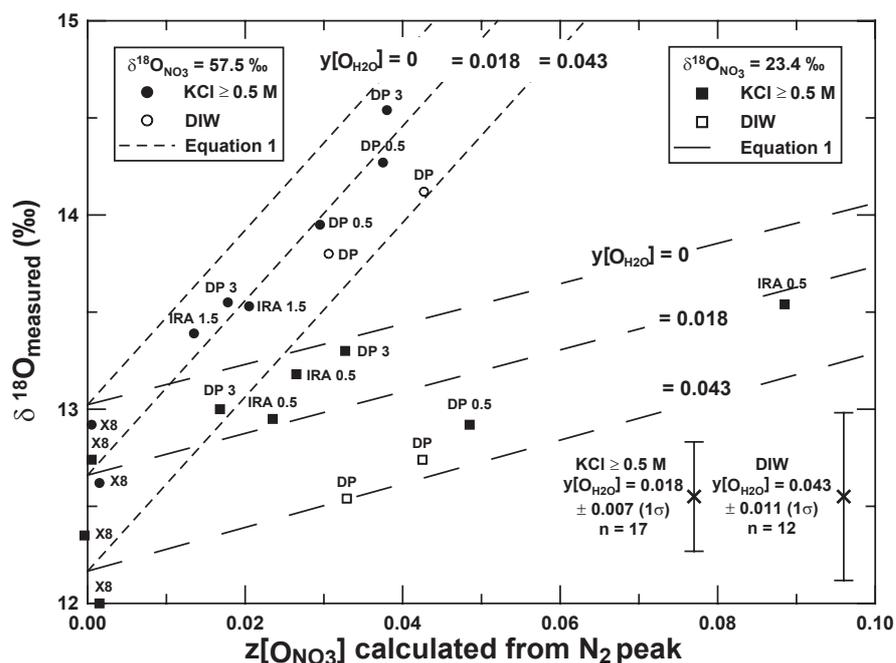
Figure 3. Relationship between measured and hypothetical values of $\delta^{18}O$ for $BaSO_4$ containing varying amounts of H_2O and NO_3^-. The calibrated ('true') value for the SO_4^{2-} used in the experiments is $13.02 \pm 0.11‰$ (1σ). Points on the graph represent data from Table 3 (experiments with NO_3^- added). DP = direct precipitation with no resin. IRA = eluted from IRA-400 resin with 0.5–3.0 M KCl. X8 = eluted from AG1-X8 resin with 0.5 M KCl. Curves on the graph represent hypothetical values of mixtures calculated using Eqn. (1) with mean values of $y[O_{H2O}]$ from data in Fig. 2 (0.018 for KCl solutions and 0.043 for DIW, with 0.0 for comparison). Error bars show the magnitude of uncertainty in adjusted $\delta^{18}O_{SO4}$ values due to uncertainties in the amounts of H_2O ($y[O_{H2O}] \pm 1\sigma$) for samples prepared in DIW or KCl solutions.

solutions with KCl ≥ 0.5 M, and 0.43 representing $BaSO_4$ precipitated from solutions with no KCl). In most of the experiments, values of $\delta^{18}O_{measured}$ are approximately consistent with the hypothetical values represented by the relevant curves, indicating that Eqn. (1) can provide a useful description of the combined effects of H_2O and NO_3^- contamination in $BaSO_4$ samples precipitated from solution, and approximately consistent with the mean values of $y[O_{H2O}]$ derived from Fig. 2. For comparison, individual values of $y[O_{H2O}]$ were calculated for the samples in Fig. 3, with $z[O_{NO3}]$ determined from Eqn. (3) (Table 3). The mean values of $y[O_{H2O}]$ for the NO_3^--bearing samples were 0.037 ± 0.005 (1σ) for DIW solutions and 0.020 ± 0.012 (1σ) for KCl solutions, similar to those determined above for samples without NO_3^-. Discrepancies between the data and models in Fig. 3 can be attributed largely to variability in the amount of H_2O incorporated in different $BaSO_4$ precipitates (real variability in $y[O_{H2O}]$).

There is evidence that the value of $z[O_{NO3}]$ may depend in part on the NO_3^-/SO_4^{2-} ratio of the solution from which the $BaSO_4$ is precipitated, as might be expected if the NO_3^- precipitated in solid solution with $BaSO_4$. Solutions with NO_3^-/SO_4^{2-} molar ratio of 10 precipitated $BaSO_4$ with a higher $z[O_{NO3}]$ than solutions prepared with a ratio of 2. Although the data are limited, the relationship between the NO_3^-/SO_4^{2-} ratio in solution and the NO_3^-/SO_4^{2-} ratio in precipitated $BaSO_4$ appears to be nonlinear, with the most rapid increase in $z[O_{NO3}]$ occurring at relatively low values of aqueous NO_3^-/SO_4^{2-} molar ratio (between about 0 and 2; Table 3, see also Ref. 11).

$BaSO_4$ precipitation following pre-concentration with IRA-400 resin columns

A common method for pre-concentrating SO_4^{2-} from dilute solutions prior to $BaSO_4$ precipitation is by collection on IRA-400 (Cl$^-$ form) and bulk elution with 3 M KCl,[5] which returns both SO_4^{2-} and NO_3^- quantitatively. Two $BaSO_4$ samples prepared in this way from solutions with $NO_3^-/SO_4^{2-} = 2$ yielded $z[O_{NO3}] = 0.021$ and 0.014, similar to the values obtained by direct precipitation from KCl solutions with similar concentrations (Table 3). Preliminary experiments were performed with lower eluent concentration (0.5 M) to test the separation of SO_4^{2-} from NO_3^- with this resin. An affinity sequence of $NO_3^- > SO_4^{2-}$ for IRA-400 (Cl$^-$) was predicted thermodynamically and confirmed experimentally.[23] Thus, the elution sequence with a dilute eluent would be SO_4^{2-} eluting before NO_3^-, as shown for AG1-X8 in Fig. 1. Mixed solutions containing S3744 and NO_3^- ($NO_3^-/SO_4^{2-} = 21$) were loaded into columns containing various amounts of resin and eluted gradually with 0.5 M KCl. The early aliquots (first 100–150 mL) were combined and precipitated as $BaSO_4$. Results evaluated with Eqn. (3) yielded $z[O_{NO3}] = 0.089$ for a 6 mL resin column (1.0 cm ID and 7.6 cm length) and 0.024–0.027 for 22 mL resin columns (1.0 cm ID and 28 cm length). The lower $z[O_{NO3}]$ values are attributed to better separation of NO_3^- and SO_4^{2-} with larger resin exchange capacity and column length. Samples containing NO_3^- after elution from IRA-400 yielded $\delta^{18}O_{measured}$ values that are consistent with the mixing relations derived from direct precipitations (Fig. 3).

$BaSO_4$ precipitation following pre-concentration with AG1-X8 resin columns

Improved separation of oxyanions was obtained with AG1-X8 (Cl$^-$) resin (Fig. 1), which has the same polystyrene skeleton and quaternary ammonium groups at the exchange sites as IRA-400 (Cl$^-$), but smaller grain size and analytical grade purity. Six experiments with mixed solutions of SO_4^{2-} and NO_3^- collected on AG1-X8 and eluted gradually with 0.5 M KCl into a fraction collector while monitoring the appearance of NO_2^- and NO_3^- with a colorimetric drop test yielded $BaSO_4$ with $z[O_{NO3}] \leq 0.002$ (Table 3). This amount of NO_3^- contamination is too small to affect the $\delta^{18}O_{measured}$ of the $BaSO_4$ substantially, even when $\delta^{18}O_{NO3}$ was relatively high (Fig. 3). All six experiments with AG1-X8 gave $\delta^{18}O_{measured}$ values less than 13.02 indicating varying amounts of trapped H_2O ($\delta^{18}O_{DIW} = -7$‰) (Table 3). For comparison, solutions with $NO_3^-/SO_4^{2-} = 21$ were eluted from 22 mL of AG1-X8 and from 22 mL of IRA-400, both using 0.5 M KCl. The precipitated $BaSO_4$ had $z[O_{NO3}] = 0.002$ in the first 100 mL of eluent from AG1-X8, compared with 0.024–0.027 from the first 125 mL of eluent from IRA-400. The same solution captured on a 44-mL column of AG2-X8 (Bio-Rad) resin and eluted similarly yielded $z[O_{NO3}] = 0.005$ (not reported).

Other studies have employed ion-exchange procedures for separating SO_4^{2-} from mixed solutions for isotopic analysis. One method involves the extraction of SO_4^{2-} from rainwater on a ZrOOH ion-exchange column prior to precipitation as $BaSO_4$.[24,25] Another method uses anion-exchange chromatography to separate small amounts of SO_4^{2-} and NO_3^- (<10 μmol) from mixed solutions, followed by acidification and conversion into Ag salts.[26–28] In addition, $BaSO_4$ samples containing NO_3^- can be redissolved, treated with a chelating reagent to remove NO_3^-, then reprecipitated as $BaSO_4$.[10]

Our chromatographic separation procedure provides excellent separation of SO_4^{2-} and NO_3^- using a resin (AG1-X8) that is used commonly to extract NO_3^- from water samples,[29] but our method differs by having a larger column and using a lower concentration of Cl$^-$ in the eluent, 0.5 M KCl in our case, compared with 3 M HCl in Ref. 29. The more dilute eluent permits controlled (and monitored) elution and separation of the different oxyanions (Fig. 1). In addition to separating SO_4^{2-} and NO_3^-, the AG1-X8 can be used to separate any NO_2^- that may be present from both SO_4^{2-} and NO_3^- (Fig. 1). Samples of ground water and surface water may contain small amounts of NO_2^-. We used this technique previously to separate NO_2^- and NO_3^- for $\delta^{15}N$ analysis in a ^{15}N tracer study in a stream[30] and an N isotope fractionation study in ground water.[31] Collecting and combining the intermediate fractions, where NO_2^- would appear, produced no $BaSO_4$ when $BaCl_2$ was added, confirming the separation indicated in Fig. 1.

Gradual monitored elution with dilute KCl also appears to have the advantage of leaving a large fraction of charged dissolved organic carbon (DOC) on the resin column. Elution of O-bearing DOC from the anion-exchange resins with 3 M HCl can cause contamination problems for the O isotopic analysis of NO_3^-,[32] and possibly also for analysis of SO_4^{2-}. Our procedure takes advantage of the fact that non-polar organic molecules largely pass through the AG1-X8 resin

during loading when organic anions are held on the resin. Then, with controlled dilute KCl elution, organic anions largely are left on the resin and the DOC content of the eluent is reduced from that of the original sample solution. This was indicated in part by brownish discoloration that accumulated and remained in the upper few cm of the resin columns during collection and elution of SO_4^{2-} from large volumes of atmospheric deposition (see below).

Implications for sulfate isotopic reference materials

Reported $\delta^{18}O$ values of internationally distributed $BaSO_4$ isotopic reference materials analyzed by different methods are variable,[6–9] possibly reflecting either analytical biases or problems with the reference materials. According to James O'Neil (USGS, Emeritus, personal communication, 2007), NBS-127 was prepared from seawater (major solute $\sim$0.5 M NaCl) that was obtained approximately 10 km off the coast of Monterey, California, USA. The seawater was passed through an anion-exchange column to remove PO_4^{3-}. $BaCl_2$ was added and the mixture was allowed to 'cure' for several days to promote growth of larger crystals of $BaSO_4$, then the $BaSO_4$ was filtered out and dried in air. According to Stanislaw Halas (Marie Curie-Sklodowska University, Lublin, Poland, personal communication, 2008), IAEA-SO5 was prepared from H_2SO_4 reagent, whereas IAEA-SO6 was prepared from natural sphalerite (ZnS) by heating in O_2 to produce SOx gases, then reaction of these SOx gases with chilled H_2O_2 to produce H_2SO_4. For SO5 and SO6, the H_2SO_4 solutions were diluted to pH 3 (major solute $\sim$0.002 M H_2SO_4), then $BaCl_2$ was added at room temperature to precipitate $BaSO_4$. The mixtures were allowed to 'cure' (unspecified time) to promote isotopic homogenization, then the $BaSO_4$ was filtered out and dried by heating in air at around 120°C. For IAEA-SO6, the SO_4^{2-} solution was produced using snowmelt water with relatively low $\delta^{18}O$ to increase the probability of yielding SO_4^{2-} with low $\delta^{18}O$ (Stansilaw Halas, personal communication, 2008).

Carefully weighed aliquots of the $BaSO_4$ reference materials were analyzed by CO-CFIRMS against each other and against aliquots of H_2O, KNO_3, $KClO_4$, and Na_2SO_4 under identical conditions[8] to determine the efficiency of conversion of the different materials into CO. The relative CO yields were estimated from the measured CO peak area per μmol O in the sample, assuming that the weighed sample was pure reagent, and normalized to 100.0% for H_2O (Table 5). Mean relative CO yields from H_2O, KNO_3, and $KClO_4$ reference materials were indistinguishable with uncertainties of around 0.5–0.7% (uncertainties are ±1σ, n = 4–12, from batches of analyses with NBS-127 as common reference). Slightly lower CO yield from $NaNO_3$ (USGS35) may be due to minor Cl or other impurities in this purified natural product.[8] Slightly elevated yields (around 101%) were indicated for NBS-127 ($BaSO_4$), IAEA-SO5 ($BaSO_4$), and S-4744 (Na_2SO_4), whereas the yield from IAEA-SO6 was significantly higher (around 105%). The amounts of excess O released from $BaSO_4$ reference materials are roughly similar to the range of $y[O_{H2O}]$ values determined in this study, and it is possible that some of the relatively high yields are related to H_2O in the $BaSO_4$ reference materials. If so, it is then

Table 5. Relative yields of O (as CO)[a] from different reference materials analyzed by CO-CFIRMS

material	Yield[b]	Yield[c]
H_2O	100.0 ± 0.7	na
KNO_3 (IAEA-NO3, USGS34, N11)	99.9 ± 0.5	na
$NaNO_3$ (USGS35)	98.4 ± 0.9	na
$KClO_4$ (USGS37, 38, 39)	100.3 ± 0.6	na
$BaSO_4$ (NBS127)	101.0 ± 0.7	99.9 ± 0.6
$BaSO_4$ (IAEA-SO5)	101.5 ± 0.9	na
$BaSO_4$ (IAEA-SO6)	105.0 ± 1.2	100.0 ± 1.0
Na_2SO_4 (S3744)	100.8 ± 0.7	100.0 ± 1.7

[a] CO peak area per μmole of O expected in sample assuming pure compound stoichiometry, normalized to 100.0% for H_2O.
[b] First yield is for reagent salt dried in vacuum oven at 60°C.
[c] Second yield is after heating in vacuum at 600°C, based on the sample weight before heating.

possible that the measured values of $\delta^{18}O$ of total O in these materials are slightly different from the $\delta^{18}O$ values of the SO_4^{2-} in the materials. Impurities (including H_2O) would not necessarily affect the performance of these solid reference materials for calibration purposes, provided the analytical technique used to calibrate samples or lab standards with respect to the solid reference materials is comparable with that used to calibrate the solid reference materials with respect to VSMOW. This may be possible for the CO-CFIRMS technique, but it may not always be the case.

Aliquots of NBS-127, IAEA-SO6, and S3744 were pre-weighed in Ag capsules and then heated at 600°C in quartz glass tubes under vacuum. Relative CO yields after heating were near 100% (Table 5), approximately consistent with release of H_2O to produce purer salts, though the uncertainties for NBS127 and S3744 are similar in magnitude to the differences. Measured $\delta^{18}O$ values of IAEA-SO6 increased from $-11.34 \pm 0.10‰$ to $-10.81 \pm 0.08‰$ (1σ, n = 4) as a result of heating at 600°C, whereas changes in measured $\delta^{18}O$ values of NBS-127 and S3744 caused by heating were within the uncertainties of the analyses (±0.1‰). Because IAEA-SO6 was produced by oxidation of ZnS, it may contain other impurities in addition to H_2O (Stanislaw Halas, personal communication, 2008). Nevertheless, the decrease in CO yield and increase in $\delta^{18}O_{measured}$ of IAEA-SO6 after heating at 600°C are consistent with removal of H_2O with $\delta^{18}O_{H2O} \approx -19‰$. This $\delta^{18}O_{H2O}$ value was derived by assuming that the unheated material was a mixture of $BaSO_4$ and H_2O and contained 1.05 times the O content of pure $BaSO_4$ for a given aliquot mass (this is equivalent to $z[O_{H2O}] = 0.069$), and that all of the H_2O was removed during heating. Halas et al.[22] report $\delta^{18}O$ values of $-10.43 \pm 0.12‰$ for IAEA-SO6 and $8.73 \pm 0.05‰$ for NBS-127, following thermal vacuum dehydration ($\geq$400°C) and high-temperature conversion into CO_2. At least qualitatively, those data also could be consistent with H_2O loss during thermal vacuum dehydration of IAEA-SO6. The relatively small apparent excess O yield and H_2O isotope effect indicated by our data for NBS-127 may be related in part to the relatively high salinity ($\sim$0.5 M) of the solution from which it was precipitated (Fig. 2). In addition, incorporation of seawater from which NBS-127 was precipitated (with $\delta^{18}O = 0‰$)

would have less effect on the bulk $\delta^{18}O_{measured}$ value than would meteoric water with $\delta^{18}O \ll 0‰$. Thus, the current results do not address the cause of higher $\delta^{18}O$ values (>9‰) reported previously for NBS-127, e.g.,[6] which are more likely to be related to different methods or calibrations, than to impurities in the material.

Application to sulfate in atmospheric deposition from Shenandoah National Park

The experiments described above indicate that Eqn. (1) provides a reasonable description of the effects of H_2O and NO_3^- on the measured $\delta^{18}O$ values of $BaSO_4$ prepared from solutions of mixed reagents. This observation can be applied to the evaluation of data from environmental samples by rearranging Eqn. (1):

$$\delta^{18}O_{SO4} = (\delta^{18}O_{measured} - \delta^{18}O_{H2O} * y[O_{H2O}] - \delta^{18}O_{NO3}$$
$$* z[O_{NO3}])/x[O_{SO4}] \qquad (4)$$

Experiments were performed to test the application of this equation for correcting analyses of $BaSO_4$ prepared by different methods from samples of atmospheric deposition from Shenandoah National Park, Virginia, USA, which had high and variable $\delta^{18}O_{NO3}$ values. Samples were recovered from continuously open deposition collectors at approximately 4–6-week intervals from February 2004 to April 2006. Each sample was divided into two identical aliquots consisting of 8 to 20 L each that were prepared by two different procedures. One aliquot was pumped through

25 mL of IRA-400 (Cl$^-$) resin and the SO_4^{2-} was eluted with 3 M KCl (no separation of SO_4^{2-} from other anions); and the second aliquot was pumped through 30 mL of AG1-X8 (Cl$^-$) resin and the SO_4^{2-} was eluted with 0.5 M KCl, separating the SO_4^{2-} from NO_2^- and NO_3^-. $BaSO_4$ was precipitated from both eluents by the normal procedure and the $BaSO_4$ samples were dried in a oven at 60°C overnight followed by a vacuum oven at 40°C. The $BaSO_4$ was analyzed by CO-CFIRMS, and Eqn. (4) was used to adjust the data and derive $\delta^{18}O_{SO4}$ from $\delta^{18}O_{measured}$ (Table 6, Fig. 4). Values of $\delta^{18}O_{NO3}$ in the open deposition samples were measured by the bacterial reduction method, $z[O_{NO3}]$ was determined from the N_2/CO ratio of each $BaSO_4$ sample measured by the CO-CFIRMS method, and $y[O_{H2O}]$ was assumed to be 0.018, as described above. The value of $\delta^{18}O_{H2O}$ (−7.0‰) is that of the laboratory H_2O used to make the KCl eluent solutions from which the $BaSO_4$ was precipitated.

The mole fraction of trapped NO_3^- was reduced from $z[O_{NO3}] = 0.013$–0.036 when collected with IRA-400 (eluted with 3 M KCl) to $z[O_{NO3}] \leq 0.008$ when collected by AG1-X8 (eluted with 0.5 M KCl). The results shown in Fig. 4 indicate that the apparent $\delta^{18}O_{measured}$ values of atmospheric SO_4^{2-} prepared by the two resin methods were biased in opposite directions because of the different relative contributions from $y[O_{H2O}]$ and $z[O_{NO3}]$. Before adjustment with Eqn. (4), the apparent values of $\delta^{18}O_{measured}$ derived from IRA-400 and AG1-X8 preparations differed by a mean of $1.61 \pm 1.14‰$, the IRA-400 results being higher because of higher fractions of NO_3^- in the $BaSO_4$. After adjustment with Eqn. (4), using

Table 6. Results for environmental SO_4^{2-} samples prepared by different techniques

| Shenandoah National Park collection date	N/S molar ratio[a]	$\delta^{18}O_{NO3}$	$z[O_{NO3}]$ (Eqn. (3))	$\delta^{18}O_{meas}$	$\delta^{18}O_{SO4}$ (Eqn. (4))	$z[O_{NO3}]$ (Eqn. (3))	$\delta^{18}O_{meas}$	$\delta^{18}O_{SO4}$ (Eqn. (4))
			Collected with IRA-400[b]			Collected with AG1-X8[c]		
2/17/2004	1.68	84.83	0.032	14.05	12.13	0.008	11.70	12.20
4/27/2004	1.60	80.62	0.036	15.88	13.94	0.004	12.74	13.26
6/15/2004	0.74	69.47	0.022	14.20	13.42	0.004	13.37	13.91
8/10/2004	0.69	67.11	0.020	14.03	13.41	0.005	12.48	12.99
9/14/2004	0.63	68.04	0.013	12.59	12.29	0.003	11.85	12.35
10/20/2004	0.88	76.06	0.025	12.91	11.70	0.002	11.51	11.99
12/9/2004	1.64	85.82	0.025	11.34	9.78	0.005	9.45	9.87
2/15/2005	1.45	85.26	0.026	13.23	11.71	0.005	11.31	11.79
4/17/2005	1.81	82.30	0.027	14.04	12.58	0.003	11.74	12.22
5/31/2005	1.49	73.76	0.027	16.65	15.55	0.001	15.09	15.67
9/13/2005	0.85	67.87	0.016	13.62	13.16	0.003	12.74	13.26
11/1/2005	0.73	73.48	0.025	13.42	12.27	0.002	12.13	12.63
12/20/2005	1.83	83.28	0.014	11.74	11.07	0.004	10.92	11.39
2/21/2006	1.77	80.89	0.020	12.27	11.26	0.002	10.69	11.15
4/18/2006	1.93	77.82	0.023	16.13	15.21	0.003	14.32	14.89
Atacama and Mojave Desert salts			Direct precipitation[d]			Collected with AG1-X8[c]		
1221A	18.29	51.44	0.132	5.22	−1.60	0.000	−2.31	−2.20
193	0.38	51.96	0.045	7.24	5.65	0.000	5.49	5.81
87c-20	14.48	44.58	0.107	5.35	0.99	0.002	1.23	1.41
8419-salt	0.71	52.03	0.043	1.51	−0.52	0.000	0.17	0.34
91c-01	1.00	52.80	n/d	n/d	n/d	0.000	4.51	4.80

[a] Shenandoah N/S ratios calculated from IC data; desert salt ratios calculated from yields of $BaSO_4$ and bacterial reduction analysis of NO_3 after separation on AG1-X8.
[b] Eluted with 3.0 M KCl, single aliquot, followed by DIW, calculated assuming $y[O_{H2O}] = 0.018$.
[c] Eluted with 0.5 M KCl using fraction collector, calculated assuming $y[O_{H2O}] = 0.018$.
[d] Direct precipitation from solutions (0.02–0.24 equiv L^{-1}), calculated assuming $y[O_{H2O}] = 0.043$.
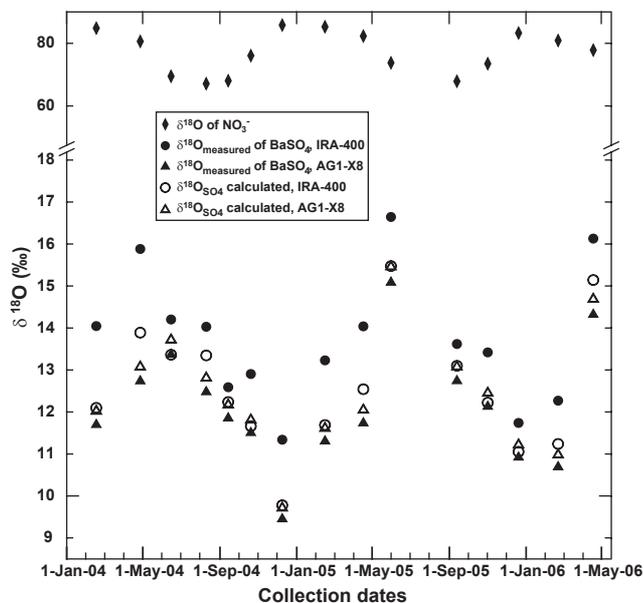
Figure 4. Two-year record of $\delta^{18}O$ values of NO_3^- and SO_4^{2-} in bulk atmospheric deposition at Shenandoah National Park, Virginia, illustrating data adjustment procedures for $BaSO_4$ samples prepared with IRA-400 and AG1-X8 resins. Eluents from IRA-400 contained anion mixtures in 3 M KCl. Eluents from AG1-X8 contained SO_4^{2-} fractions in 0.5 M KCl. Measured $\delta^{18}O$ values of $BaSO_4$ precipitates ($\delta^{18}O_{measured}$) are compared with $\delta^{18}O$ values of SO_4^{2-} ($\delta^{18}O_{SO4}$) calculated using Eqn. (4) with $\delta^{18}O_{NO3}$ as determined by bacterial reduction, $z[O_{NO3}]$ as determined by CO-CFIRMS (Eqn. (3)), and $y[O_{H2O}] = 0.018$ (Table 6).

the individually estimated values of $z[O_{NO3}]$ and a mean assumed value of $y[O_{H2O}]$ (0.018), the $\delta^{18}O_{SO4}$ values from the two resin methods converged to values that plot between the different $\delta^{18}O_{measured}$ values. The adjusted values of $\delta^{18}O_{SO4}$ are significantly lower than the unadjusted values from the IRA-400 preparations (relatively large NO_3^- effect) and slightly higher than the values from the AG1-X8 preparations (mainly H_2O effect). After adjustment with Eqn. (4), the mean difference between the pairs of $\delta^{18}O_{SO4}$ analyses was $+0.01 \pm 0.18‰$, indicating that Eqn. (4) effectively removed the biases from both sets of unadjusted data. Remaining random differences may be largely due to real variability in the amounts of H_2O trapped with the $BaSO_4$ (e.g., Fig. 2), which limits the precision of the adjustments.

Application to sulfate salts from the Atacama Desert and Mojave Desert

Similar experiments were performed with samples of NO_3^--rich natural salt deposits containing SO_4^{2-} from the Atacama Desert in Chile and the Mojave Desert in California, USA.[33,34] Solutions were prepared by leaching samples of mixed salt and sediment in DIW. Aliquots of the leachates were prepared by two different procedures (Table 6): (1) direct precipitation of $BaSO_4$ by addition of $BaCl_2$ after acidification; and (2) separation of SO_4^{2-} by ion chromatography on AG1-X8, followed by precipitation of $BaSO_4$ from the SO_4^{2-} fraction. $BaSO_4$ precipitated directly from mixed

salt solutions had $z[O_{NO3}] = 0.043–0.13$, whereas $BaSO_4$ precipitated after separation on AG1-X8 had $z[O_{NO3}]$ ≤ 0.002. Because these samples have large positive values of $\delta^{18}O_{NO3}$, the values of $\delta^{18}O_{measured}$ for $BaSO_4$ were substantially higher after direct precipitation than after AG1-X8 separation. For example, when $BaSO_4$ was prepared from sample 1221A by direct precipitation, $z[O_{NO3}]$ was 0.13 and $\delta^{18}O_{measured}$ was 7.5‰ higher than when the sample was eluted gradually from AG1-X8, and NO_3^- was excluded from the precipitation solution. Applying Eqn. (4) to the directly precipitated samples improved the agreement between these results (Table 6). Values of $z[O_{NO3}]$ after separation on AG1-X8 appear to be generally smaller for the desert salt samples than for the atmospheric deposition samples. This may be related to the difference in volume of sample solution loaded onto the ion-exchange columns (8–20 L for the atmospheric deposition, 5–10 mL for the desert salt leachates).

CONCLUSIONS

$BaSO_4$ precipitated from aqueous solutions for O isotopic analysis of SO_4^{2-} may contain substantial amounts of H_2O and NO_3^- impurities. Both contaminants may be expected to have varying effects on the apparent $\delta^{18}O$ (and $\delta^{17}O$) of a sample, depending on the amounts and the isotopic compositions of the H_2O, SO_4^{2-}, and NO_3^-. Experiments with H_2O, SO_4^{2-}, and NO_3^- reagents with known isotopic compositions confirm the applicability of Eqn. (1) for describing the effects of H_2O and NO_3^- contamination on measured values of $\delta^{18}O$ of $BaSO_4$ prepared by different methods from aqueous SO_4^{2-}. Equation (4) can be used to evaluate potential errors, and to make approximate adjustments to measured data. For atmospheric deposition, the effect of the NO_3^- is especially large because the $\delta^{18}O$ value of atmospheric NO_3^- is much higher than that of the SO_4^{2-}. Similarly, for SO_4^{2-} precipitated from high-elevation or high-latitude meteoric waters with large negative values of $\delta^{18}O_{H2O}$ (field or lab H_2O), the effect of the trapped H_2O might be relatively large. Variable amounts of H_2O incorporated in $BaSO_4$ samples and isotopic reference materials (including IAEA-SO6) could cause discrepancies in calibration results, and may limit the overall reproducibility of $\delta^{18}O$ data for aqueous SO_4^{2-} prepared by various methods.

Complete removal of H_2O from $BaSO_4$ is difficult, but the incorporation of H_2O can be minimized by increasing the salinity of the sample solution (e.g., >0.5 M KCl) before precipitating $BaSO_4$. Partial removal of H_2O can be achieved by heating under vacuum at 500–600°C, but higher temperatures in contact with glass or air may cause O isotope exchange. For direct calibrations under identical conditions, it may be preferable in some circumstances to produce $BaSO_4$ from soluble SO_4^{2-} isotopic reference materials dissolved in H_2O with $\delta^{18}O_{H2O}$ values similar to that of the samples, so the H_2O effect is the same in samples and standards (although the amount of incorporated H_2O appears to be variable from sample to sample). Incorporation of NO_3^- can be minimized by separating NO_3^- from SO_4^{2-} on AG1-X8 anion-exchange resin prior to $BaSO_4$ precipitation. Partial separation may be accomplished

with IRA-400 resin, but this was not as effective as AG1-X8 in our experiments. The importance of NO_3^- separation will vary with the NO_3^-/SO_4^{2-} ratio and the isotopic difference between NO_3^- and SO_4^{2-} in the sample. In some cases, it may be possible to adjust measured $\delta^{18}O$ data for $BaSO_4$ containing small amounts of NO_3^- if the $\delta^{18}O$ of the NO_3^- is known and the relative yield of CO from NO_3^- and SO_4^{2-} is measured during the analysis. This can be done as part of the CO-CFIRMS technique by monitoring the N_2 peak and calibrating the $^{28}N_2/^{28}CO$ peak area ratio of NO_3^- analyzed under the same conditions. Regardless of the methods used, it might be helpful if measurements of $\delta^{18}O_{SO4}$ calibrated against analyses of $BaSO_4$ isotopic reference materials such as NBS127, IAEA-SO5, and IAEA-SO6 were accompanied by a description of the procedures used to mitigate errors associated with these contaminants, as well as the measured or assumed $\delta^{18}O$ values of reference materials used to calibrate data.

Acknowledgements

REFERENCES

1. Strebel O, Boettcher J, Fritz P. *J. Hydrol.* 1990; **121**: 155.
2. Bao H, Thiemens MH, Farquhar J, Campbell DA, Lee CC-W, Heine K, Loope DB. *Nature* 2000; **406**: 176.
3. Krouse HR, Mayer B. In *Environmental Tracers in Subsurface Hydrology*, Cook PG, Herczeg A (eds). Kluwer: Dordrecht, 2000; 195–229.
4. Seal RR. In *Environmental Aspects of Mine Wastes*, Jambor JL, Blowes DW, Ritchie AIM (eds). Mineralogical Society of Canada, Short Course: 2003; vol. 31, 303–334.
5. Carmody RW, Plummer LN, Busenberg E, Coplen TB. *Methods for Collection of Dissolved Sulfate and Sulfide and Analysis of Their Sulfur Isotopic Compositions*, U.S. Geological Survey Open-File Report 97-234, 1998.
6. Gonfiantini R, Stichler W, Rozanski K. In *Reference and Intercomparison Materials for Stable Isotopes of Light Elements*. International Atomic Energy Agency, IAEA-TECDOC-825: 1995; 13–29.
7. Kornexl BE, Werner RA, Gehre M. *Rapid Commun. Mass Spectrom.* 1999; **13**: 1248.
8. Böhlke JK, Mroczkowski SJ, Coplen TB. *Rapid Commun. Mass Spectrom.* 2003; **17**: 1835.
9. Boschetti T, Iacumin P. *Rapid Commun. Mass Spectrom.* 2005; **19**: 3007.
10. Bao H. *Anal. Chem.* 2006; **78**: 304.
11. Michalski G, Kasem M, Rech JA, Adieu S, Showers WS, Genna B, Thiemens M. *Rapid Commun. Mass Spectrom.* 2008; **22**: 2971.
12. Willard HH, Furman NH, Bricker CE. *Elements of Quantitative Analysis*, (4th edn.). Van Nostrand: New York, 1950.
13. Blaedel WJ, Meloche VW. *Elementary Quantitative Analysis, Theory and Practice*, (2nd edn). Harper & Row: New York, 1963.
14. Coplen TB. *Chem. Geol. (Isot. Geosci. Sect.)* 1988; **72**: 293.
15. Casciotti KL, Sigman DM, Hastings M, Böhlke JK, Hilkert A. *Anal. Chem.* 2002; **74**: 4905.
16. Coplen TB, Böhlke JK, Casciotti KL. *Rapid Commun. Mass Spectrom.* 2004; **18**: 245.
17. APHA. *Standard Methods for the Examination of Water and Wastewater*, (15th edn). American Public Health Association: Washington DC, 1981.
18. Fishman MJ, Friedman LC. *Methods for Determination of Inorganic Substances in Water and Fluvial Sediments*. U.S. Geological Survey Techniques for Water-Resources Investigations 5 (A1), 1989.
19. O'Neil JR, Truesdell AH. In *Stable Isotope Geochemistry: A Tribute to Samuel Epstein*, Taylor HP, O'Neil JR, Kaplan IR (eds). Special Publication 3, The Geochemical Society: San Antonio, 1991; 17–25.
20. Sakai H, Krouse HR. *Earth Planet. Sci. Lett.* 1971; **11**: 369.
21. Rafter TA. *New Zealand J. Sci.* 1967; **10**: 493.
22. Halas S, Szaran J, Czarnacki M, Tanweer A. *Geostandards and Geoanalytical Research* 2007; **31**: 61.
23. Smith RP, Woodburn ET. *Am. Inst. Chem. Eng. J.* 1978; **24**: 577.
24. Mizutani Y, Rafter TA. *New Zealand J. Sci.* 1969; **12**: 69.
25. Wadleigh MA, Schwartz HP, Kramer JR. *J. Geophys. Res.* 2001; **106**: 20883.
26. Savarino J, Alexander B, Darmohusodo V, Thiemens MH. *Anal. Chem.* 2001; **73**: 4457.
27. Michalski G, Savarino J, Böhlke JK, Thiemens MH. *Anal. Chem.* 2002; **74**: 4989.
28. McCabe JR, Savarino J, Alexander B, Gong S, Thiemens MH. *Geophys. Res. Lett.* 2006; **33**: L05810. DOI: 10.1029/2005GL025164, 1–4.
29. Silva SR, Kendall C, Wilkison DH, Ziegler AC, Chang CCY, Avanzino RJ. *J. Hydrol.* 2000; **228**: 22.
30. Böhlke JK, Harvey JW, Voytek MA. *Limnol. Oceanogr.* 2004; **49**: 821.
31. Böhlke JK, Smith RL, Revesz KM, Yoshinari T. *EOS, Trans. Am. Geophys. Union* 2000; **81**: S186.
32. Chang CCY, Langston J, Riggs M, Campbell DH, Silva SR, Kendall C. *Can. J. Fish. Aquat. Sci.* 1999; **56**: 1856.
33. Böhlke JK, Ericksen GE, Revesz K. *Chem. Geol.* 1997; **136**: 135.
34. Michalski G, Böhlke JK, Thiemens MH. *Geochim. Cosmochim. Acta* 2004; **68**: 4023.