Uncertainties in the oxygen isotopic composition of barium sulfate induced by coprecipitation of nitrate

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Coprecipitation of nitrate and sulfate by barium has probably resulted in significant error in numerous studies dealing with the oxygen isotopic composition of natural sulfates using chemical/thermal conversion of BaSO4 and analysis by isotope ratio mass spectrometry. In solutions where NO3−/SO42− molar ratios are above 2 the amount of nitrate coprecipitated with BaSO4 reaches a maximum of approximately 7% and decreases roughly linearly as the molar ratio decreases. The fraction of coprecipitated nitrate appears to increase with decreasing pH and is also affected by the nature of the cations in the precipitating solution. The size of the oxygen isotope artifact in sulfate depends both on the amount of coprecipitated nitrate and the δ18O and Δ17O values of the nitrate, both of which can be highly variable. The oxygen isotopic composition of sulfate extracted from atmospheric aerosols or rain waters are probably severely biased because photochemical nitrate is usually also present and it is highly enriched in 18O (δ18O ~ 50–90‰) and has a large mass-independent isotopic composition (Δ18O ~ 20–32‰). The sulfate δ18O error can be 2–5‰ with Δ17O artifacts reaching as high as 4.0‰. Copyright © 2008 John Wiley & Sons, Ltd.

Stable oxygen isotopes are important tools that can be used to trace the production, and removal, of atmospheric sulfate, arguably the most important compound in the global sulfur cycle and one that has a profound influence on global climate. Atmospheric sulfate (SO42− found in aerosols and precipitation) plays an important role in climate because it is one of the most abundant compounds found in aerosols,1,2 which in turn contribute to the direct (light scattering) and indirect (cloud formation) aerosol effect. It is also the main end product of the oxidation of reduced sulfur species and results in the formation of acid rain.3,4 The pioneering work of Holt and Kumar,5–9 along with others,10 demonstrated that the δ18O values in atmospheric sulfate can be used to trace the different pathways that oxidize reduced sulfur. These studies showed that the δ18O value of atmospheric sulfate was largely controlled by the δ18O of tropospheric water because S(IV) rapidly achieves isotopic equilibrium with liquid water. However, the subsequent oxidation pathways that convert S(IV) species into S(VI), referred to as ‘secondary’ sulfates, also influence the ultimate δ18O value of atmospheric sulfate.11 The main oxidation pathway for secondary sulfate is the gas-phase oxidation of SO2 via the OH radical.12 Aqueous phase heterogeneous oxidation of dissolved SO2 by O3, H2O2 or O3 is also an important source of SO42− in clouds, fog and precipitation.13,14 ‘Primary’ sulfate formed via high-temperature O2 oxidation of SOx in smoke stacks of coal-fired power plants is also thought to be regionally important.15,16,17 Observations of atmospheric sulfate δ18O values above those expected from only gas and aqueous oxidation processes have been attributed to the mixing of primary and secondary sulfates and isotopic disequilibrium.

Recently, there has been much interest in anomalous 17O enrichments in sulfate that is produced photochemically and subsequently deposited to surfaces.17–23 The standard notation for these anomalous enrichments is the capital delta notation:

\[ \Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O \] (1)

where δ18O is the standard notation for the difference between the ratio of the minor (17,18) to major (16) oxygen isotope in a sample relative to the same ratios in standard mean ocean water (SMOW).24 It has been suggested that the origin of positive Δ17O values observed in atmospheric sulfate, and the seasonal trends, are a result of shifts in the relative importance of homogenous (gas phase) and heterogeneous (aqueous) SO2 oxidation pathways.19 Therefore, both the δ18O and the Δ17O values in atmospheric sulfate may provide clues as to which chemical pathways are important for atmospheric sulfate production.

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Since sulfate is isotopically preserved in soils and water, the unique oxygen isotope signature of atmospheric sulfate has been utilized as a proxy for detecting atmospheric deposition. In a recent study on soils from the Atacama Desert in northern Chile, we observed large $\Delta^{17}O$ values (1–5%) in soil sulfates. In a subsequent study using sulfates obtained from Rech et al., it was found that some of the samples showed a much higher degree of $\delta^{18}O$ and $\Delta^{17}O$ deviation between replicate analyses (~5% for $\delta^{18}O$, 1–2% for $\Delta^{17}O$) than would be expected from the analytical uncertainty of 1% ($\delta^{18}O$) and 0.1% ($\Delta^{17}O$). This only occurred when the extracts also had a significant amount of nitrate. Atacama soil nitrate has $\delta^{18}O$ and $\Delta^{17}O$ values of ~50% and ~19%, respectively, which is attributed to the accumulation of atmospheric nitrate. Since the precision of the sulfate oxygen isotopic analysis deteriorated only in samples that also contained nitrate we initiated a series of control experiments to test the precision and accuracy of $SO_4^{2-}$ isotopic analysis when samples are prepared by barium precipitation in the presence of nitrate. These test sulfates were then analyzed using three common isotope ratio mass spectrometry techniques: (1) the CO pyrolysis method, (2) the offline C reduction (and fluorination) method, and (3) the BrF$_5$ laser fluorination system. The objective of the experiments was to assess whether the presence of nitrate in a nitrate/sulfate solution had an impact on the $\delta^{18}O$ and $\Delta^{17}O$ values of the BaSO$_4$ precipitate.

**EXPERIMENTAL**

The experimental design was to obtain BaSO$_4$ from two sulfate solutions, one that was nitrate-free and the other that contained various amounts of an isotopically unique nitrate salt. A lab standard sulfate (Na$_2$SO$_4$; Fisher Scientific, Pittsburgh, PA, USA) was mixed to a concentration of 1.5 M and aliquoted in order to obtain ~100 μmol of SO$_4^{2-}$ in 30 mL. A control set of BaSO$_4$ was prepared by heating the sulfate solutions at 80°C followed by precipitation using a slight excess of 1 M BaCl$_2$. Some samples were acidified after the heating step using a few drops of 1 M HCl. Heating and acidification are carried out on natural samples to eliminate possible interference by barium carbonate precipitation and to help form idealized BaSO$_4$ crystals. Precipitations of BaSO$_4$ were also carried out in the presence of the nitrate isotope standard USGS35 (NaNO$_3$ form), the first $\Delta^{17}O$ standard, which has an established $\delta^{18}O$ value of 51% and a $\Delta^{17}O$ value of ±21.6%. USGS35 was added in order to produce solutions with NO$_3^-$/SO$_4^{2-}$ molar ratios ranging from 0.05 to 10, similar to those found in natural samples from aerosols, precipitation, and runoff. Each BaSO$_4$ precipitate was centrifuged, decanted and rinsed with Millipore water, three times. Ion chromatography analysis of the final rinse indicated that, at most, only a few nanomoles of NO$_3^-$ remained in solution (e.g. ~0.001%) that could crystallize with the BaSO$_4$ upon drying. After being dried, several of the samples were ground and onceagain rinsed in Millipore water before the final drying.

In order to evaluate our data in the context of numerous prior studies on sulfate oxygen isotopes we chose to utilize three different isotope ratio mass spectrometry (IRMS) methods. The first method tested is currently the standard means for sulfate $\delta^{18}O$ analysis, thermal conversion elemental analysis (TC/EA). The second method is the offline graphite reduction of BaSO$_4$ to CO and CO$_2$ followed by disproportionating the CO into C and CO$_2$ followed by analysis of the CO$_2$ using dual-inlet IRMS. The third analytical approach uses laser fluorination to generate O$_2$ from BaSO$_4$ as described by Bao and Thiemens.

The TC/EA method utilized a Costec Autoanalyzer (Valencia, CA, USA) interfaced to a Thermo Delta XP (ThermoFinnigan, Bremen, Germany) continuous flow IRMS instrument (also called CO-CFRMS). BaSO$_4$ (~0.2–0.3 mg) is loaded into silver cups that are dropped into a high temperature (1425°C) carbon reduction chamber. The subsequent product CO is purified on a fused-silica Molsieve 5A chromatography column (Varian #CP7536; Palo Alto, CA, USA) and injected into the IRMS instrument using a Thermo Conflow open split. $\delta^{18}O$ determinations are made by calibration using isotopic reference materials such as NBS127 (BaSO$_4$), NIST 8549 (KNO$_3$), and NIST 8542 (Sucrose). Because of isotopic interface between $^{13}CO$ and $^{17}CO$, $\delta^{17}O$ determinations were not possible using CO-CFRMS.

The offline carbon reduction method was carried out in vacuum using a device described by Sakai and Krouse. A mixture of graphite and BaSO$_4$ is heated to 400–500°C in a platinum foil boat connected to a resistance heater for 5 min to drive off water before raising the temperature to 1100°C. Evolved CO$_2$ is cryogenically separated using liquid nitrogen and residual CO is disproportionated to C and CO$_2$ using parallel platinum foil discharge plates and a current controlled by a Variac. The discharge product CO$_2$ is combined with the initial pyrolysis CO$_2$ giving yields that are typically >95% of sulfate on an oxygen basis. The CO$_2$ was analyzed using a dual-inlet Thermo Delta XP IRMS instrument for $\delta^{18}O$ determination. We used the nitrate-free Fisher Scientific BaSO$_4$ as our internal standard for these samples. For $\Delta^{17}O$ determination, one sample of CO$_2$ was fluorinated with BrF$_5$ using standard protocols resulting in an O$_2$/CF$_4$ mixture that was cryogenically purified and the O$_2$ was analyzed using a Finnigan-Mat 251 (ThermoFinnigan) dual-inlet IRMS instrument. This method was only tested using BaSO$_4$ precipitated from a 1:1 NO$_3^-$/SO$_4^{2-}$ molar solution.

Details of the laser fluorination procedure can be found elsewhere. Briefly, ~10 mg of BaSO$_4$ are weighed into a stainless steel sample target and loaded into the laser fluorination chamber that is then heated to 100°C and pumped to 10$^{-8}$ Torr overnight. The following day the chamber is etched at room temperature with ~30 Torr of BrF$_5$ that will react with any absorbed water that is not eliminated during the pumping stage. The samples are lased in the presence of 30 Torr BrF$_5$ and the resulting O$_2$ is then purified and analyzed using a Finnigan MAT 251 dual-inlet IRMS instrument.
RESULTS

The results of the oxygen isotopic analysis of the test sulfates are given in Figs. 1 and 2. For the CO-CFIRMS method the BaSO₄ derived from the pure SO₄²⁻ solutions had δ¹⁸O values of 13.1% relative to VSMOW with a precision of ±0.2‰, typical of continuous flow techniques. For BaSO₄ samples derived from solutions with NO₃⁻/SO₄²⁻ molar ratios of 0.5 and higher there is a clear positive δ¹⁸O bias, reaching as high as 3.8% at the highest molar ratios. There are similar δ¹⁸O biases in the CO₂ produced from BaSO₄ using the offline graphite reduction technique (solid circles).

Figure 1. δ¹⁸O values for CO and CO₂ derived from BaSO₄ precipitated out of solutions with various NO₃⁻/SO₄²⁻ molar ratios using USGS35 NO₃⁺ (δ¹⁸O = 57.5‰)²⁷ and analyzed using (CO-CFIRMS) (stars) and the offline graphite reduction technique (solid circles).

Figure 2. Artifact sulfate Δ¹⁷O values of BaSO₄ precipitated from solutions with various NO₃⁻/SO₄²⁻ molar ratios of USGS35 nitrate (Δ¹⁷O = 21.6‰) and Fisher brand Na₂SO₄ (■, Δ¹⁷O = −0.1‰) for neutral and acidic solutions. Fit line A is from the experimental data and fit line B is the possible artifact assuming a nitrate Δ¹⁷O = 31‰, typical of Antarctica soils and the high end of nitrate aerosol Δ¹⁷O values. The X markers on the right-hand side are the published Δ¹⁷O values for sulfates from aerosols, rainwater, dusts, soils and minerals as described in the text.

DISCUSSION

The results indicate that a significant amount of NO₃⁻ is coprecipitating with the barite leading to spurious sulfate δ¹⁸O and Δ¹⁷O values. The sulfate δ¹⁸O values, as determined by the TC/EA method, show a clear increase for BaSO₄ that was precipitated in the presence of USGS35. The degree of contamination can be established from the mass balance equation:

\[ \delta^{18}{}^{\text{OCO}} = s \times \delta^{18}{}^{\text{OSO}_4^{2-}} + n \times \delta^{18}{}^{\text{ONO}_3^-} + \epsilon \]  

(2)
where the CO is generated by CO-CFIRMS, s and n correspond to the fractions of CO derived from the sulfate and nitrate anions during reduction, and $\varepsilon$ is the enrichment factor associated with any fractionation of oxygen isotopes by the reduction if there is less than a 100% yield (negligible for the current case where yields are $>90\%$). Taking the pure BaSO$_4$ $\delta^{18}$O value (13.1‰) and USGS35 nitrate $\delta^{18}$O as 51‰, then, using Eqn. (2), the maximum $\delta^{18}$O shift of $\sim 3.5\%$ corresponds to a contamination of about 6.8‰ from USGS35 nitrate. Figure 1 suggests that the fraction of oxygen originating from NO$_3$ decreases as the NO$_3$/SO$_4$ molar ratio decreases and that it is indiscernible at ratios of less than 0.1.

A similar mass balance equation to Eqn. (2) can be derived using $\Delta^{17}$O by replacing $\delta^{18}$O with $\Delta^{17}$O and CO with O$_2$. The $\Delta^{17}$O value of the initial Na$_2$SO$_4$ is $\sim$0.1‰ (relative to our VSMOW normalized O$_2$ standard) and, for USGS35 NO$_3$, the $\Delta^{17}$O value is 21.6‰. Using the $\Delta^{17}$O version of Eqn. (2), estimates of nitrate contamination ranged from 1.2% to 8.0% in neutral solutions and from 6.2 to 7.7% for acidified solutions, which are similar to those obtained using the $\delta^{18}$O mass balance. Again there is a weak correlation between the degree of NO$_3$ contamination and lower molar ratios, but it is not strictly linear and even the NO$_3$/SO$_4$ solutions with 0.1 and 0.05 molar ratios have significant $\Delta^{17}$O artifacts.

The resulting sulfate isotopic artifact (error) can be estimated by:

$$\delta^{18}$$O artifact = $x \times y \times \delta^{18}$$O NO$_3$ + $\varepsilon$  (3)

where $x$ is the mole fraction of nitrate coprecipitated, $y$ is the mole fraction that nitrate converted into CO/CO$_2$/O$_2$ relative to sulfate conversion (method dependent), $\varepsilon$ is an enrichment factor related to the incomplete conversion of NO$_3$ to the gas to be analyzed, and $\delta^{18}$$O$ NO$_3$ is the $\delta^{18}$$O$ value of the nitrate. A similar equation in $\Delta^{17}$$O$ can be formulated but, in this case, $\varepsilon$ is zero as no known non-photochemical process can generate a non-zero $\Delta^{17}$$O$ value. The good precision at a given molarity suggests that the relative amount of oxygen derived from NO$_3$ and SO$_4^-$ is always consistent ($y$ in Eqn. (3)) but the amount of nitrate coprecipitation may be variable ($x$ in Eqn. (3)) depending on solution conditions such as pH, cation species and concentration.

The high solubility of all nitrate salts would suggest that Ba(NO$_3$)$_2$ precipitation does not occur and that this is an important, with nitrate coprecipitation being greatest in the presence of K$^+$ and decreasing in order with NH$_4^+$, Na$^+$ and Li$^+$. $\Delta^{17}$$O$.

The $\delta^{18}$O and $\Delta^{17}$O results presented here support these coprecipitation conclusions. Our percentages of coprecipitated nitrate, based on $\delta^{18}$O and $\Delta^{17}$O values, are in the same range as those found analytically and we also find that low pH enhances the coprecipitation at low molar ratios. The precise amount of nitrate coprecipitated based on $\delta^{18}$O or $\Delta^{17}$O is difficult to determine because it is less clear how much of the coprecipitated nitrate is actually being converted into CO and O$_2$ during analysis. Oxygen yields for sulfate in the laser fluorination method are only $\sim$30% and lasing pure Ba(NO$_3$)$_2$ as a yield experiment would probably give different results from those from the actual lasing the mixed crystal. Yields for the CO$_2$ fluorination are greater than 90%, but the amount of nitrate converted into CO$_2$ during the pyrolysis portion of the method is also ambiguous because some nitrate may decompose to NO$_2$ which would be cryogenically retained at $\sim$80°C in the water-removal trap. Nitrate salts have been quantitatively converted into CO$_2$ by graphite pyrolysis but this usually occurs in closed vessels, which are allowed to equilibrate, and conversion yields depend on the cation of the salt and the reduction conditions. However, the similarity between the $\Delta^{17}$O artifact in the laser fluorination technique and the CO reduction-CO$_2$ fluorination technique ($\sim$0.3%) suggests that the yield of nitrate oxygen is similar for both methods.

The $\delta^{18}$O bias that we observe in nitrate-contaminated BaSO$_4$ using the TC/EA-IRMS system and offline C reduction raises questions as to the accuracy of numerous sulfate $\delta^{18}$O studies involving aerosol, rainwater, stream and soil sulfates that have the potential to be influenced by nitrate contamination. Nitrate is normally present in the atmosphere as particulate matter or gaseous HNO$_3$, both of which are incorporated into precipitation and bulk aerosols. Nitrate is often the dominant anion in urban areas that are far removed from oceanic and coal combustion sulfate sources. Even in sulfate-dominated regions, such as the upper Midwest region of the United States, the NO$_3$/$\delta^{18}$O ratios in precipitation are still $\sim$1 (see NADP database). Nitrate produced in the atmosphere at mid-latitudes has average $\delta^{18}$O values of approximately 70‰ but which can be lost as high as 90‰ and this would produce sulfate $\delta^{18}$O errors of 4–6‰ based on the nitrate coprecipitation amounts of $\sim$6.5‰. This is significant given that the range of published atmospheric sulfate $\delta^{18}$O data typically varies in the order of 5–10‰. It is likely that this has led to the misinterpretation of seasonal variations in the $\delta^{18}$O values of atmospheric sulfate. It is difficult to establish which
studies may have biases because many of these studies did not report NO₃⁻ concentrations and there are subtle differences in methodology such as the pre-heating temperature/time and concentration/cleanup methods that are too numerous for us to test in a reproducible manner. For example, in a method still used today, Corteci and Longinelli²⁶ pre-concentrated dilute sulfate solutions on the anion exchanger hydrous zirconium oxide that is ‘purified’ using nitric acid. When the pH is raised to desorb the sulfate, nitrate is also likely to desorb but was probably not detected because the control sulfate δ¹⁸O value of 10‰ is similar to the δ¹⁸O values of commercial nitric acids and nitrates (10–18‰).

The nitrate contamination can also produce Δ¹⁷O values that are equal to those found in sulfate minerals and aerosols.¹⁹-²³,⁵¹-⁵³ Atmospheric nitrate from mid-latitudes has Δ¹⁷O values from 20–30‰,⁴⁶ which could generate Δ¹⁷O biases as high as 3‰, based on the percentage of coprecipitation that we observe. Aerosol and rainwater sulfate Δ¹⁷O values were previously attributed to SO₄ oxidation by ozone in the aqueous phase, but there could be a Δ¹⁷O bias if nitrate, another common aerosol anion, is present in the precipitation solution. Similar biases may be present in mineral sulfates that were extracted from soils that contain significant amounts of nitrate such as those from the Atacama Desert⁵⁴ and the McMurdo Dry Valleys of Antarctica.⁵⁵ Bao et al. recently reported Δ¹⁷O values of 1–5‰ for Antarctic Dry Valley soil sulfate²² that coexist with % levels of nitrate, which have Δ¹⁷O values of ~30‰.⁵⁶ A reanalysis of these samples revealed a Δ¹⁷O bias in excess of 4% for NO₃⁻/SO₄²⁻ molar ratios as low as 0.28.⁵⁷ Due to the variable amounts of nitrate coprecipitated depending on solution conditions (pH, cation content, temperature) it is unlikely that the artifacts can be corrected based on nitrate concentration data alone. A method for eliminating nitrate contamination has recently been published⁵⁷ that should be adopted as part of the preparation procedure of BaSO₄ for solutions containing nitrate and sulfate. Nitrate contamination would not affect studies¹⁷,¹⁸ that used analytical methods that avoid the BaSO₄ precipitation step, such as the thermal decomposition of Ag₂SO₄,⁵⁸ and thus would not have the isotopic bias.

**CONCLUSIONS**

We have shown that the standard preparation of sulfate samples for oxygen isotopic analysis by precipitation with barium can be significantly influenced by coprecipitation of the nitrate anion. Three different isotopic techniques show that up to 7% of the oxygen derived from BaSO₄ can actually be originating from coprecipitated NO₃⁻. The degree of contamination depends on the precipitation conditions including NO₃⁻/SO₄²⁻ molar ratios, pH, solution cations and overall solution concentrations. The magnitude of the isotope error depends not only on the degree of contamination, but also on the δ¹⁸O and Δ¹⁷O values of the nitrate in solution, which can be highly variable. It is likely that many studies examining δ¹⁸O and/or Δ¹⁷O values and trends in atmospheric sulfates (aerosols, precipitation, snow) that used the BaSO₄ methodology are positively biased because of the failure to eliminate NO₃⁻ during sample preparation. This is because NO₃⁻/SO₄²⁻ molar ratios are significant (~0.5–10) in atmospheric samples and because atmospheric NO₃⁻ has uncharacteristically high δ¹⁸O and Δ¹⁷O values. Terrestrial samples are likely to be less severely influenced by the contamination because NO₃⁻ is typically only available in trace amounts and has low δ¹⁸O and Δ¹⁷O values. However, in systems where terrestrial sulfate and nitrate are highly influenced by the atmosphere, and BaSO₄ is the isotopic analyte, the positive bias is likely to be significant.

Possible solutions to the coprecipitation problem are: barite digestion, heating BaSO₄ above the Ba(NO₃)₂ decomposition temperature, or removal of the nitrate prior to precipitation by chemical reduction, precipitation (Nitron) or bacterial reduction. Ba₅⁷ has recently reported that the contamination can be eliminated by repeated precipitation and dissolution using a chelating agent. Alternatively, one can avoid BaSO₄ precipitation and use the chromatographic separations and thermal decomposition of Ag₂SO₄ as described by Savarino et al.⁶⁰ Any of these nitrate-removal processes should be carefully tested for isotope effects and a sulfate Δ¹⁷O and Δ³⁴S standard, similar to USGS53, should be developed to better control the accuracy of oxygen and sulfur isotope analytical techniques. New, more accurate analysis of δ¹⁸O and Δ¹⁷O variations in atmospheric sulfate using improved analytical techniques may yield more interesting seasonal and special variability that was previously masked by nitrate-induced artifacts.

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