Research Article

Purification of $BaSO_4$ precipitate contaminated with organic matter for oxygen isotope measurements ($\delta^{18}O$ and $\Delta^{17}O$)

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RATIONALE: Sulfate precipitates are often contaminated with nitrates and organic materials (OM), which reduce the precision and accuracy of measurements of $\delta^{18}O$ and $\Delta^{17}O$ values in the sulfate. Although nitrates can be effectively removed using diethylenetriaminepentaacetic acid solution, removing OM from the precipitates is often difficult. One effective approach is to heat powdered precipitates to high temperatures. In this study, the effect of this procedure on the $\delta^{18}O$ and $\Delta^{17}O$ values of $BaSO_4$ precipitate was fully examined.

METHODS: OM-contaminated $BaSO_4$ precipitates and ^{18}O- and ^{17}O-labeled purified $BaSO_4$ precipitates were loaded into alumina and gold crucibles and heated at 450 °C, 600 °C and 800 °C for 2 h. The nitrogen and carbon contents in the initial and the final $BaSO_4$ were measured using an elemental analyzer. The values of $\delta^{18}O$ and $\Delta^{17}O$ were measured using a temperature conversion/elemental analyzer coupled with an isotope ratio mass spectrometer, and a CO_2 laser system coupled with an isotopic ratio mass spectrometer.

RESULTS: OM was effectively (88 ± 17%) removed from the $BaSO_4$ precipitates by this treatment, and heating at 800 °C had the highest removal efficiency (98%). The differences in $\delta^{18}O$ and $\Delta^{17}O$ values between the final and initial $BaSO_4$ precipitates was −0.6‰ to 0.3‰ (average of −0.1‰) and −0.24‰ to 0.10‰ (average of −0.02‰), respectively. Significant positive relationships between the $\delta^{18}O$ and $\Delta^{17}O$ values of the initial $BaSO_4$ precipitate and those of the high-T-treated aliquots were found, with slopes having mean values of 0.96 ± 0.06 and 1.04 ± 0.01, respectively.

CONCLUSIONS: The result demonstrates high removal efficiency for OM in $BaSO_4$ precipitates and no significant differences in the oxygen isotopic compositions between high-T treated $BaSO_4$ and initial $BaSO_4$. This study indicates that the modified high-T treatment (800 °C, 2 h) is an effective method for purifying $BaSO_4$ precipitated from geological and environmental samples with a high OM content for $\delta^{18}O$ and $\Delta^{17}O$ measurements. Copyright © 2016 John Wiley & Sons, Ltd.

Oxygen isotope ratios ($\delta^{18}O$, $\delta^{17}O$ and $\Delta^{17}O$ values, where $\delta = (R_{sample}/R_{standard} - 1)$, R is the ratio of $^{18}O/^{16}O$ or $^{17}O/^{16}O$, and $\Delta^{17}O = \delta'^{17}O - 0.52\delta'^{18}O$, where $\delta' = \ln(R_{sample}/R_{standard})$ and the standard is VSMOW (Vienna Standard Mean Ocean Water)) in sulfates of natural samples and/or in laboratory experiment are useful tracers of sulfur oxidization processes,[1–13] sulfate sources,[1,5,10] and biogeochemical cycles,[13–16] as well as the abundance of earth O_3,[1,2,4–6,10,11] H_2O,[12] O_2,[7,14,17,18] and CO_2,[17,18] in present and past atmospheres and hydrospheres. This is because the oxygen in sulfates contains isotopic fingerprints of different sources and processes, and because sulfates extracted from environmental samples (aerosol, water), or from geological samples, are major, minor or trace components in various minerals,[1–17] and have a slow rate of exchange with oxygen

under the low-temperature conditions prevailing on most of the Earth's surface.[19] Sulfate $\delta^{18}O$ and $\Delta^{17}O$ studies have been comprehensively reviewed by van Stempvoort and Krouse,[20] Krouse and Mayer,[21] and Bao.[22]

The oxygen isotopic compositions ($\delta^{18}O$ and $\Delta^{17}O$ values) of sulfate have been determined mainly from $BaSO_4$ and Ag_2SO_4 precipitates, using isotope ratio mass spectrometry (IRMS). The methods for sulfate $\delta^{18}O$ and/or $\Delta^{17}O$ measurements by IRMS have been reviewed by Krouse and Mayer[21] and Bao,[22] and are briefly described here. A $BaSO_4$ precipitate is reacted with BrF_5 by CO_2-laser fluorination[23] with approximately 25–35% O_2 yield.[23] The produced O_2 is then purified and analyzed on a dual-inlet isotope ratio mass spectrometer with a precision of 0.7‰ and 0.05‰ for $\delta^{18}O$ and $\Delta^{17}O$ values, respectively.[23] The $\delta^{18}O$ values are corrected by 9.4‰ (a kinetic effect) due to the non-quantitative O_2 yield,[23] and accurate values can be obtained by analysis with a temperature conversion/elemental analyzer (TC/EA) coupled with IRMS, with a errors within ±0.5‰.[24] On the other hand, Ag_2SO_4 produced from samples with a low concentration of sulfate has been used for both $\delta^{18}O$ and

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$\Delta^{17}O$ measurements by pyrolysis–IRMS at micromole[25] or even sub-micromole[26] levels of sulfate, with the advantage of requiring 2 orders of magnitude less SO_4^{2-} than the CO_2-laser fluorination-IRMS method (>10 μmol).[23] The pyrolysis–IRMS method for $\Delta^{17}O$ measurement has a significantly worse precision (0.1–0.6‰)[25–27] than CO_2-laser fluorination coupled with high-precision dual-inlet IRMS (0.05‰).[23] Both $\delta^{18}O$ and $\Delta^{17}O$ pyrolysis–IRMS measurements in sulfates have to be corrected using empirical equations obtained from the analysis of multiple isotopic standards, because of the non-quantitative O_2 yield (45 ± 7%)[25] and oxygen isotopic exchange (approximately 15%).[27]

Mineral or aerosol sulfates are normally extracted with deionized water,[1,2,4] acid (generally HCl),[6,14,17,28] NaClO,[28] or H_2O_2,[12,28] and then precipitated as $BaSO_4$ by adding excess acidic $BaCl_2$[19] or precipitated as Ag_2SO_4 by using an ion-exchange resin.[26,27] For water samples (atmospheric precipitation, surface water, porewater, and groundwater), excess acidic $BaCl_2$ and $AgNO_3$ is added to precipitate $BaSO_4$[1–7,14–17] and Ag_2SO_4,[8–13] respectively. Contaminants, such as nitrate, organic material (OM), water, metal oxides, phosphate, and chloride, are generally released during the extraction processes and are then present in the precipitated $BaSO_4$ and Ag_2SO_4. These contaminants in the precipitates have to be removed prior to measuring oxygen isotope ratios.[24,29,30] This is because such contaminants, particularly for oxygen-bearing material which have different oxygen isotope compositions, affect the O_2 yield and cause errors. For example, high levels of OM in porewater[14] and shale would be incorporated into the $BaSO_4$ precipitate. It has been reported that organic carbon amounted to 25% by weight of a $BaSO_4$ precipitate even after using ion-exchange resin before precipitation, thereby reducing the O_2 yield and causing low-precision measurements.[12] Moreover, photochemical nitrate is enriched in ^{18}O ($\delta^{18}O$ value of 50–90‰[31]) and has a high $\Delta^{17}O$ value (20–32‰),[31] which causes errors in the sulfate $\delta^{18}O$ and $\Delta^{17}O$ values that can reach 2–5‰[30] and 4.0‰,[30] respectively, when nitrate is trapped in the precipitate. Furthermore, in addition to nitrate, other N-containing species, i.e. organic N from OM trapped in $BaSO_4$ and the NF_3 produced by the CO_2-laser fluorination system, will interfere with the $^{17}O/^{16}O$ analysis.[32–34]

Nitrate and OM are the two major contaminants in $BaSO_4$ and Ag_2SO_4 precipitated from waters and other sulfur-containing materials. Although nitrates in sulfate precipitates and sulfate solutions can be effectively removed by DTPA (diethylenetriaminepentaacetic acid) dissolution and re-precipitation (DDARP)[24] and ion chromatography,[25–27] respectively, the OM is often difficult to remove. However, there are several commonly used approaches for removing OM trapped in precipitated $BaSO_4$ and/or Ag_2SO_4, or co-existing with sulfate in solution before precipitation. (1) High-T treatment. It is well known that organics can be removed from glassware by heating at an appropriate temperature (typically 450 °C, called high-T treatment). Mandernack et al.[14] heated $BaSO_4$ at 500 °C for 1–3 h in the open air to purify $BaSO_4$ precipitated from porewater. (2) Wet oxidization: using an oxidant such as H_2O_2[12,26,28] and NaClO[28] to oxidize the OM before precipitation. (3) Solid-phase adsorption: OM can be adsorbed onto other phases such as C-18 resin[12,26] or cross-linked polyvinylpyrrolidone[26]

before precipitation. However, the sulfate produced from sulfite during wet oxidization pretreatment[28] will contain oxygen from a different source (water and dissolved O_2[7,13]). In addition, solid-phase adsorption has only a low removal efficiency (18–48%),[26] while both wet oxidization and solid-phase extraction are time-consuming pretreatments. In contrast, high-T treatment at 500 °C for 2 h[14] is an easier, faster, and better controlled method for removing a high OM content from $BaSO_4$ precipitates without ^{18}O exchange ($\delta^{18}O$ difference < 0.2‰). However, the authors of this study[14] used only one $\delta^{18}O$ $BaSO_4$ standard, baked only at one temperature (500 °C, 1–3 h).

In some studies,[35,36] a higher temperature treatment consisting of loading $BaSO_4$ into an alumina crucible and heating at 800 °C under air in an oven for 2 h has been used to remove OM trapped in precipitated $BaSO_4$ and to remove the cellulose filter used for precipitating $BaSO_4$. The OM removal efficiency during such high-T (800 °C) combustion[35,36] is expected to be higher than that at 500 °C. However, at higher temperature (>500 °C), partial decomposition of $BaSO_4$ followed by isotopic exchange with the oxygen in air (O_2 and water vapor, among others) and/or container wall may occur, especially during high-T treatment for several hours (personal communications from H. Bao and S. Halas in 2014 and 2015, respectively).

In this paper, we describe tests of the OM removal efficiency and potential oxygen isotopic effects determined on $BaSO_4$ precipitates: between $BaSO_4$ and air O_2, and the effects of the containers (alumina and gold crucibles) during high-T treatments (450–800 °C for 2 h). Five $BaSO_4$ precipitates, labeled with ^{18}O and ^{17}O, were studied.

EXPERIMENTAL

Test materials

Six samples of $BaSO_4$ precipitate were prepared by adding OM to sulfate solutions or $BaSO_4$ powder to test the efficiency of the high-T treatment for removing OM. The experiments were conducted at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (Guangzhou, China). Three of the contaminated $BaSO_4$ precipitate samples (S1, S2 and S3) were prepared to achieve a low OM content, as follows: a mixture of L-phenylalanine (98%, CAS 63–91-2, TCI, Shanghai, China), benzoic acid (65–85-0, Merck, Darmstadt, Germany), and urea (99%, Fuchen, Tianjin, China) was added to HCl (37%, K39343417 841, Merck) acidified Na_2SO_4 (99%, Guangzhou Chemical Reagent Factory, Guangzhou, China) solution (pH <2) in a 50-mL polypropylene (PP) centrifuge tube (430828, Corning Inc., Corning, NY, USA). The solution was equilibrated for 24 h, precipitated using a 10% HCl-acidified $BaCl_2$ (99.9%, CAS 10361–37-2, Alfa Aesar, Ward Hill, MA, USA) solution (pH <2), centrifuged and washed with Milli-Q water (18.2 MΩ, MUL-9000, Zongxin Ltd, Nanjing, China). The Milli-Q water used in this treatment had $\delta^{18}O$ and $\Delta^{17}O$ values of −6.7‰ and 0‰, respectively. The other three highly OM-contaminated $BaSO_4$ samples (S4, S5, and S6) were prepared by directly adding organic acids or a mixture of other OMs into $BaSO_4$ powder. These contaminated $BaSO_4$ powders were dried at 75 °C for 48 h and ground before the high-T treatment.

Five BaSO$_4$ samples with anomalous Δ^{17}O values were prepared as follows. (1) Three BaSO$_4$ samples with negative anomalous Δ^{17}O values were prepared by equilibration, oxidation and precipitation, as modified from Schauer et al.[27] First, three sodium sulfite solutions with negative Δ^{17}O values were made by equilibrating commercial sodium sulfite powder (≈ 0.3 g each of Na$_2$SO$_3$, 98.5%, CAS 7757–83-7, Fisher Chemicals, Pittsburgh, PA, USA) with three 10-mL ^{17}O-labeled water reference materials with varied Δ^{17}O values for >12 h. The first ^{17}O-labeled water reference material (Δ^{17}O ≈ −6‰) was prepared using distilled and deionized water (DD water, 18.2 MΩ locally produced from tap water with δ^{18}O ≈ −7‰ and Δ^{17}O ≈ 0‰) into 99% ^{18}O-labeled water (Cat. No. IO6490, Icon Services, Summit, NJ, USA), and the other two water reference materials were then made by adding varied volumes of DD water to the first ^{17}O-labeled water reference material. Excess 30% H$_2$O$_2$ (CAS 7722–84–1, Fisher Chemicals) was then added to oxidize the Na$_2$SO$_3$ to Na$_2$SO$_4$ at room temperature (22 °C). Excess acidified saturated BaCl$_2$ (99%, CAS 10326–27-9, Alfa Aesar) solution was added to the three Na$_2$SO$_4$ solutions to precipitate the BaSO$_4$ samples (BaSO$_4$–1, BaSO$_4$–2, BaSO$_4$–3). The BaSO$_4$ powder was analyzed using an Empyrean X-ray diffractometer (PANalytical, Almelo, The Netherlands) at the Department of Geology and Geophysics, Louisiana State University (Baton Rouge, LA, USA), and no contaminants were detected. (2) The other two BaSO$_4$ samples used in this test were: one commercial BaSO$_4$ powder with a high δ^{18}O value (LSU-SO$_4$, 99%, CAS 7727–43-7, Sigma-Aldrich) and another BaSO$_4$ precipitate mixture (BaSO$_4$–4) with a positive Δ^{17}O value prepared from three Antarctic samples after double DDARP treatment. The DDARP method followed that of Bao:[24] BaSO$_4$ powder was dissolved in DTPA solution (0.05 M DTPA, 98%, CAS 67–43-6, Alfa Aesar, in 1 M NaOH, ≥ 97%, CAS 1310–73-2, Fisher Chemicals), shaken overnight, with 10% HCl (37%, CAS 7647–01-0, Fisher Chemicals) then added to reach pH <2, and subsequently acidified saturated BaCl$_2$ solution added for re-precipitation. The re-precipitated BaSO$_4$ was washed with DD water after centrifuging three times. All the BaSO$_4$ precipitates were collected in PP centrifuge tubes and dried at 75 °C for 48 h, ground to fine powder, and stored in glass containers at room temperature before the high-T treatment and geochemical analysis. The pretreatment of the δ^{18}O- and Δ^{17}O-labeled BaSO$_4$ samples was conducted at the Oxy-Anion Stable Isotope Consortium at Louisiana State University.

High-T treatment

One aliquot (10 mg) of BaSO$_4$ powder was loaded into either an alumina or a gold crucible, and placed in an approximately 40 cm long custom-made quartz tube with one end sealed. The quartz tube was inserted into a preheated tube furnace at 450 ± 5 °C or 800 ± 5 °C and heated in air for 2 h. The tube furnace was then removed and the sample in the quartz tube allowed to cool to room temperature (within 20 min) in air. Further details of the quartz tube and tube furnace at Louisiana State University were given by Hayles and Bao.[37] Aliquots of these BaSO$_4$ powders before and after heat treatment were analyzed for their δ^{18}O and Δ^{17}O values.

To determine the nitrogen and carbon content, approximately 40 mg of OM-contaminated BaSO$_4$ powder was loaded into alumina crucibles and heated at 450 ± 10 °C,

600 ± 10 °C and 800 ± 10 °C for 2 h in a similar custom-made quartz tube and furnace (SK2–2-10, Rongfeng Ltd, Shanghai, China) in air at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry. In addition, 0.2-μm pieces of cellulose filter (Xinya Inc., Shanghai, China) with a few drops of Milli-Q water were loaded into alumina crucibles and subjected to the same high-T treatment to determine the removal efficiency of the cellulose filter.

Nitrogen and carbon contents analysis

The contents (wt. %) of nitrogen and carbon in the contaminated BaSO$_4$ before and after the high-T treatment were determined using an elemental analyzer (PYRO cube, Elementar Analysensysteme GmbH, Hanau, Germany) at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry. Approximately 20 mg of each BaSO$_4$ sample was loaded into a tin capsule (8 × 5 mm, Elemental Microanalysis, Okehampton, UK) and weighed, and a 5-fold larger amount of finely ground V$_2$O$_5$ (11.02–0017, Elementar) was then added. The samples were combusted at 920 °C in a furnace containing CuO (Elementar) under a stream of O$_2$ for 90 s. The SO$_2$ released from BaSO$_4$ was absorbed by lead chromate (03 679 914, Elementar) at the bottom of the combustion tube. The other gases (NO$_x$, CO$_2$, water vapor, etc.) were passed through a reduction tube containing hot Cu (CHNOS Ltd, Taiyuan, China) at 600 °C, dried by P$_2$O$_5$ (ZC869943 945, Merck). Finally N$_2$ (product of NO$_x$) and CO$_2$ were separated by chromatography and determined using a thermal conductivity detector. The precision for both nitrogen and carbon determinations was better than 5% (relative standard deviation (RSD)) for multiple runs of pure sulfanilamide (059 k0045, Elementar).

Oxygen isotope analysis

For δ^{18}O analysis, aliquots of 180–220 μg of BaSO$_4$ powder were loaded into silver capsules (4 × 3.2 mm, EA Consumables, Inc., Pennsauken, NJ, USA) and pyrolysed with glass carbon chips (C7015, Elemental Microanalysis Ltd) to produce CO under 1450 °C in a TC/EA (Thermo Electron, Bremen, Germany) coupled with a Finnigan MAT253 isotope ratio mass spectrometer (Thermo Electron).[17] The δ^{18}O value (reported relative to V-SMOW) of the sample was corrected with respect to the international reference material NBS 127 (8.6‰, supplied by NIST, Gaithersburg, MD, USA) with a precision of ±0.5‰ (1 SD, thereafter).

The Δ^{17}O values in BaSO$_4$ were determined using a CO$_2$-laser system coupled with IRMS, as described in Bao and Thiemens,[23] and modified by Bao.[24] Approximately 5 mg of BaSO$_4$ powder was loaded into a custom-made sample holder and reacted with BrF$_5$ in a 25 W CO$_2$ laser (New Wave Research, Merchantek Products, Fremont, CA, USA) vacuum chamber system. The generated O$_2$ was purified by two stainless steel tube liquid nitrogen traps held at −196 °C, and then collected into 5 Å molecular sieve (1/16″, pellets, Spectrum Chemical Mfg. Corp., Gardena, CA, USA) sample tubes at −196 °C for 7 min. Finally the O$_2$ was released into a MAT 253 isotope ratio mass spectrometer for two to three measurements for δ^{18}O and δ^{17}O values to be carried out by dual-inlet mode within 24 h. [δ = (R_{sample}/$R_{standard}$ − 1), where R is the ratio of ^{18}O/^{16}O or ^{17}O/^{16}O, and the

standardis VSMOW.] The $\Delta^{17}O$ value was calculated as $\Delta^{17}O = \delta'^{17}O - 0.52 \times \delta'^{18}O$,[22] where $\delta' = \ln(R_{sample}/R_{standard})$, with a precision of better than $\pm 0.05‰$ for replicates of the $BaSO_4$ working standard via the entire CO_2-laser fluorination processes.[23,24] The $\delta^{18}O$ and $\Delta^{17}O$ measurements of $BaSO_4$ were conducted at the Oxy-Anion Stable Isotope Consortium at Louisiana State University.

Data analysis

The data were analyzed on the basis of isotopic exchange problems during high-T treatment. A paired-sample t-test was used to test the high-T treatment using SPSS 11.5 software (SPSS, Inc., Chicago, IL, USA) and the p-value (p) is reported. A significant difference was noted as p-value ≤ 0.001 (99.9% confidence). A least-squares linear regression for oxygen isotopic composition between the final and the initial $BaSO_4$ was also calculated by SPSS.

RESULTS

The alumina crucible did not contain visible ash after combusting pieces of 0.2-μm cellulose filter at 450 °C, 600 °C and 800 °C for 2 h, indicating that the cellulose filter (used to collect the precipitated $BaSO_4$[35,36]) was completely combusted in an open air system above 450 °C. The results in Fig. 1 show that the average removal efficiency of the OM in the $BaSO_4$ precipitates heated at 450 °C, 600 °C and 800 °C is 80 ± 20%, 88 ± 14% and 98 ± 4%, respectively, demonstrating

that the majority of the OM (88 ± 17%, n = 26) was removed during high-T (450–800 °C) treatment for 2 h. The removal efficiency of the high-T treatment in this study was as high as that of the wet oxidation method (67–100%),[26] and it was considerably higher than that of the solid-phase extraction method (18–48%).[26]

The $\delta^{18}O$ and $\Delta^{17}O$ values of the aliquots of $BaSO_4$ before (initial) and after (final) the high-T treatments (450 °C and 800 °C, 2 h) are listed in Table 1. Including the two data points ($BaSO_4$–5 in Fig. 2(a)) from Mandernack et al.,[14] the differences in the $\delta^{18}O$ values between the final and initial aliquots of $BaSO_4$ (Fig. 2(a)) ranged from −0.6‰ to 0.3‰ (average of −0.1 ± 0.2‰, n = 21), and the variation in the final and initial values of each $BaSO_4$ sample ranged from 0.1‰ to 0.3‰, which is within the instrumental precision (±0.5‰). The differences in the $\Delta^{17}O$ values between the final and initial $BaSO_4$ (Fig. 2(b)) ranged from −0.24‰ to 0.10‰ (average of −0.02 ± 0.09‰, n = 18), and the variation in the $\Delta^{17}O$ values between the final and initial $BaSO_4$ sample ranged from 0.02‰ ($BaSO_4$–3) to 0.10‰ ($BaSO_4$–1), with a mean of 0.05 ± 0.03‰, which is not significantly different from the instrumental precision (± 0.05‰) ($p = 1.0$). The $\delta^{18}O$ and $\Delta^{17}O$ values of the heated $BaSO_4$ were not significantly different ($p > 0.001$) from the initial values at each heating condition (different temperatures or crucibles), indicating that there is no significant change in oxygen isotopes during the high-T treatment process. In addition, the results in Fig. 2 show positive linear correlations ($r^2 > 0.99$) of the $\delta^{18}O$ and $\Delta^{17}O$ values between the thermally treated (in both alumina and gold crucibles) and the untreated (PP tube) $BaSO_4$. This
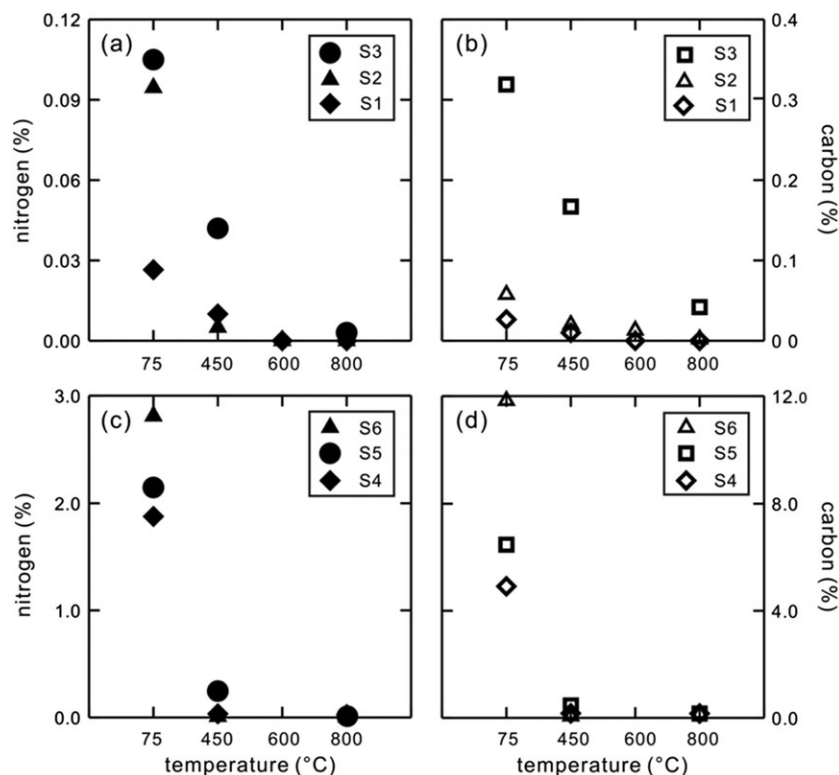

Figure 1. Efficiency of high-T treatment for removal of OM. OM-contaminated $BaSO_4$ samples were made, loaded into alumina crucibles and baked at high temperature (450 °C, 600 °C and 800 °C) for 2 h. The results indicate that most of the OM was removed by heating, especially at 800 °C.

Table 1. The measured $\delta^{18}O$ values and $\Delta^{17}O$ values for the initial and final BaSO$_4$

Sample name	Initial in PP		Final 450 °C in Au		Final 450 °C in Al		Final 800 °C in Au		Final 800 °C in Al	
	$\delta^{18}O$ (‰)	$\Delta^{17}O$ (‰)	$\delta^{18}O$ (‰)	$\Delta^{17}O$ (‰)	$\delta^{18}O$ (‰)	$\Delta^{17}O$ (‰)	$\delta^{18}O$ (‰)	$\Delta^{17}O$ (‰)	$\delta^{18}O$ (‰)	$\Delta^{17}O$ (‰)
BaSO$_4$–1	6.3 ± 0.1	−3.04 ± 0.01	6.4 ± 0.2	−3.08 ± 0.02	6.2 ± 0.7	−3.17 ± 0.01	6.4 ± 0.1	−3.28 ± 0.02	6.4 ± 0.1	−3.20 ± 0.03
BaSO$_4$–2	5.4 ± 0.3	−1.69 ± 0.03	5.6 ± 0.1	−1.71 ± 0.00	5.3 ± 0.1	−1.65 ± 0.01	5.6 ± 0.1	−1.77 ± 0.03	5.6 ± 0.3	−1.72 ± 0.03
BaSO4–3	8.6 ± 0.2	−0.28 ± 0.07	8.4 ± 0.3	N.A.	8.4 ± 0.4	−0.26 ± 0.05	8.9 ± 0.4	N.A.	8.4 ± 0.1	−0.29 ± 0.08
BaSO$_4$–4	10.0 ± 0.5	1.14 ± 0.06	9.8 ± 0.1	1.24 ± 0.00	9.8 ± 0.3	1.15 ± 0.02	9.6 ± 0.3	1.17 ± 0.01	9.7	1.11 ± 0.04
LSU-S	12.5 ± 0.2	−0.20 ± 0.04	12.4 ± 0.0	−0.12 ± 0.04	12.4 ± 0.0	−0.11 ± 0.01	11.9 ± 0.0	−0.19 ± 0.03	12.6 ± 0.3	−0.13 ± 0.02

$\Delta^{17}O = \delta'^{17}O - 0.528\delta'^{18}O$, in which $\delta' = \ln(R_{sample}/R_{standard})$, R is the ratio of $^{18}O/^{16}O$ or $^{17}O/^{16}O$, and the standard is VSMOW. The initial BaSO$_4$ samples were prepared and dried at 75 °C within polypropylene (PP) tubes for 48 h, loaded into alumina (Al) and gold (Au) crucibles, baked at 450 °C and 800 °C for 2 h in air, and then cooled to room temperature in air within 20 min for triple oxygen isotope measurements.
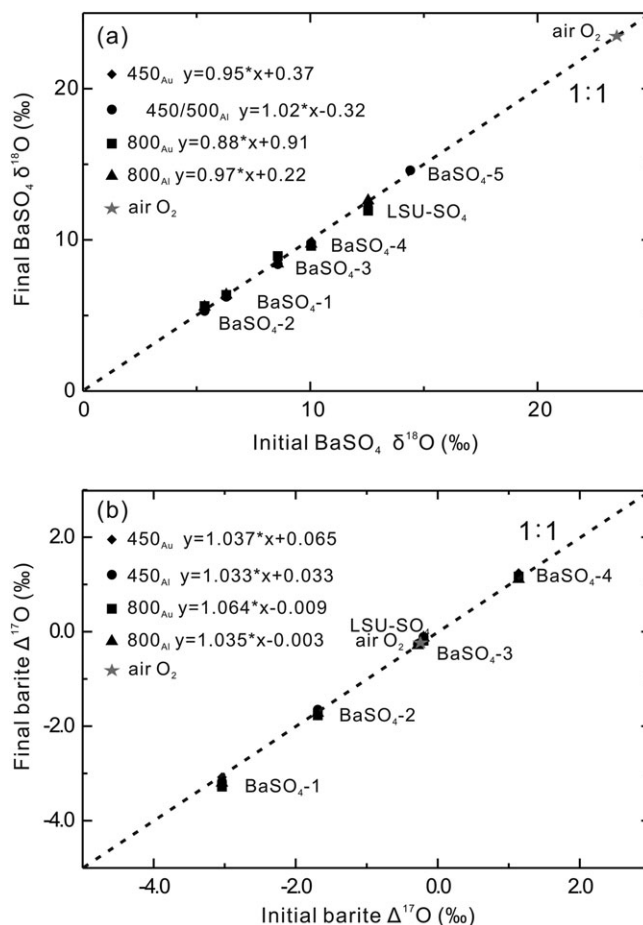N.A. = not available.

Figure 2. Differences in $\delta^{18}O$ and $\Delta^{17}O$ values between the initial and final BaSO$_4$ samples. In (a) and (b) the dashed line is the 1:1 line and the gray star is the air O$_2$ with a $\delta^{18}O$ value of 23.5‰ and a $\Delta^{17}O$ value of −0.23‰. The $\delta^{18}O$ data of BaSO$_4$–5 in (a) are cited from Mandernack et al.[16] The $\delta^{18}O$ and $\Delta^{17}O$ results show no significant oxygen isotopic exchange during high-T treatment (450–800 °C) for 2 h.

common trend indicates that the same isotopic effect controls the isotopic compositions of BaSO$_4$ precipitates during the high-T treatment, and it may be used for oxygen isotopic corrections. The slopes and intercepts (Fig. 2(a)) of the other heating conditions to the PP tube at 75 °C (75$_{PP}$ for short) of the $\delta^{18}O$ values were 0.95, 1.02, 0.88 and 0.97 and 0.37, −0.32, 0.91 and 0.22, with average values of 0.96 ± 0.06 and 0.30 ± 0.51. Moreover, the slopes and intercepts of the $\Delta^{17}O$ results show small differences of 1.037, 1.033, 1.064 and 1.035 and 0.065, 0.033, −0.009 and −0.003, with average values of 1.04 ± 0.01 and 0.02 ± 0.04.

DISCUSSION

Oxygen isotopic exchange

The oxygen isotopic exchange during the high-T treatment process (the percentage of the slope deviating from the 1:1 line), calculated from the $\delta^{18}O$ and $\Delta^{17}O$ results from the BaSO$_4$ precipitate, ranged from −12% to 2% (average of −5 ± 6%) and from 3% to 6% (average of 4 ± 1%), respectively.

These large oxygen isotopic exchange ranges, based on the $\delta^{18}O$ results, may have contributions from the physical parameters of the $BaSO_4$ precipitate (i.e., grain size/surface area and morphology, H. Bao and S. Halas, personal communications, 2015), the analytical precisions (±0.5‰), and the $\delta^{18}O$ range (H. Bao, personal communication, 2015) in the $BaSO_4$ precipitate that was heated. Furthermore, the lower variation (4 ± 1%) of oxygen isotope exchange on the $\Delta^{17}O$ values may suggest a small effect of isotopic mass-dependent fractionation during the high-T treatment process. This effect is similar to those in the CO_2-laser fluorination,[23] DDARP,[24] and pyrolysis[25] processes.

It is noteworthy that the oxygen isotopic exchange in our high-T treatment of $BaSO_4$ precipitate is considerably lower than that in Ag_2SO_4 pyrolysis.[27] The latter has 15% exchange between Ag_2SO_4 and the wall of the quartz capsule, because the Ag_2SO_4 was completely thermally decomposed at 1000 °C, and the product O_2 could exchange with the wall of the quartz capsule within minutes.[27] However, little decomposition of $BaSO_4$ and/or limited air O_2-$BaSO_4$ exchange occurred due to the formation of a protective layer on the $BaSO_4$ precipitate surface (S. Halas, personal communication, 2015) during the 2-h high-T treatment in our experiment. The actual decomposition temperature of pure $BaSO_4$ or barite is >1400 °C,[38] although this would reduce to 650–700 °C when $BaSO_4$ is mixed with regents such as $NaPO_3$ and V_2O_5.[39] Therefore, the $BaSO_4$ precipitate heated at 800 °C[35,36] can be used for $\delta^{18}O$ and/or $\Delta^{17}O$ measurements with little to no correction.

Causes of isotopic effect

The major oxygen-bearing species in air, O_2 ($\delta^{18}O \approx 23.5‰$ and $\Delta^{17}O \approx -0.23‰$[17,37]), H_2O vapor ($\delta^{18}O \approx -15‰$ and $\Delta^{17}O \approx 0‰$ in Baton Range, LA, USA),[37] and in the alumina crucible were the potential oxygen sources for exchange with $BaSO_4$ during the high-T treatment process. The exchange percentage (f) of source i (air O_2, alumina crucible and/or H_2O) can be calculated by the mass balance of $\delta^{18}O$ or $\Delta^{17}O$:

$$f = \frac{\delta^{18}O_{Final} - \delta^{18}O_{Initial}}{\delta^{18}O_i - \delta^{18}O_{Initial}} \text{ or } f = \frac{\Delta^{17}O_{Final} - \Delta^{17}O_{Initial}}{\Delta^{17}O_i - \Delta^{17}O_{Initial}}$$

The calculated f of the air O_2 source to $BaSO_4$ after heating, based on the $\delta^{18}O$ and $\Delta^{17}O$ results, ranges from −5.5% to 2.2% with an average of −0.5 ± 1.8% ($n = 21$) and from −8.5% to 2.7% with an average of −2.9 ± 3.5% ($n = 12$), respectively. The $\Delta^{17}O$ data of the $BaSO_4$–3 and LSU-SO_4 samples were not used for the calculation of f due to their $\Delta^{17}O$ values being close to that of air O_2. The small negative values of f obtained for both $\delta^{18}O$ and $\Delta^{17}O$ in the initial and final $BaSO_4$ suggest that air O_2 is not the isotopic source to $BaSO_4$ during the heating process, despite the $\delta^{18}O$ and $\Delta^{17}O$ values of the air O_2 falling on straight lines in Figs. 2(a) and 2(b).

Although the oxygen isotopic values of the alumina crucible used for high-T treatment were unknown, the fact that there were no significant differences ($p = 0.8$ and 0.9, respectively) between the $\delta^{18}O$ and $\Delta^{17}O$ values of the $BaSO_4$ samples loaded into alumina and those loaded into gold (no oxygen and exchange-free[27]) crucibles (Table 1) suggests that the alumina crucible is not the oxygen source for $BaSO_4$ during high-T treatment.

SUMMARY AND CONCLUSIONS

We have conducted a series of high-T heating experiments on $BaSO_4$ containing labeled oxygen isotopes and contaminated with organic matter. The samples were loaded into alumina and gold crucibles and heated at 450 °C, 600 °C and 800 °C for 2 h under air. The results demonstrate that a high proportion (88 ± 17%) of the OM in $BaSO_4$ contamination can be removed by heating at 450–800 °C for 2 h with no significant difference in the oxygen isotopic values from the initial $BaSO_4$ because of a lack of decomposition and a small amount of oxygen exchange (<5%). Moreover, the efficiency of OM removal from heated $BaSO_4$ at 800 °C is 18% higher than at 450 °C, and without significant oxygen isotopic exchange at both temperatures. Therefore, we suggest purifying $BaSO_4$ (precipitated from geological and environmental samples) with a high OM content by heating the samples in an alumina crucible at 800 °C, instead of 450 °C or 500 °C, for 2 h before carrying out $\delta^{18}O$ and $\Delta^{17}O$ measurements.

Acknowledgements

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