

Sulfur and Oxygen Isotope Analysis of Sulfate at Micromole Levels Using a Pyrolysis Technique in a Continuous Flow System

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The discovery of a mass-independent isotopic composition ($\Delta^{17}\text{O} = (\delta^{17}\text{O} - 0.512 \cdot \delta^{18}\text{O}) \neq 0$) in aerosol sulfate and the identification of its origin (aqueous-phase oxidation by O_3 and H_2O_2) have renewed interest in measuring the oxygen isotopic content of sulfate. In this paper, we present a new method to measure both $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in SO_4 , with the possibility of sulfur isotope analysis on the same sample. The technique takes advantage of the easy pyrolysis of Ag_2SO_4 to SO_2 , O_2 , and Ag metal in a continuous flow system. Because the technique is not quantitative in oxygen (yield $\sim 45\%$ for O_2), a calibration is needed. Correction factors of $+0.87$ and $+0.44\%$ were obtained for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$, respectively. A technique to convert micromole levels of sulfate in any form to silver sulfate is described. To reach this goal, a solid electrolyte (Nafion membrane) is used in an electrolysis apparatus. Reproducibilities for micromole sample sizes are (1σ) 0.5, 0.3, and 0.1‰ for $\delta^{18}\text{O}$, $\delta^{17}\text{O}$, and $\Delta^{17}\text{O}$, respectively. No memory effects or isotopic exchange during the treatment of the sample is observed. The main advantages of this new method over the existing ones are no fluorinating agent is needed, both oxygen and sulfur isotopes can be measured on the same sample, only very small amounts of sulfate are needed (down to 100 μg (1 μmol)), it is relatively fast and inexpensive, and the possibility exists to couple this technique to an on-line analysis.

Sulfate is a ubiquitous species on Earth, present in all environments (e.g. biosphere, atmosphere, hydrosphere, pedospheres, etc.). Although sulfate is important for life as a source of energy and nutrients, it can also be harmful to human health when inhaled. For years, it has been recognized as a contributor to rain acidification and as a significant climatological component of the atmosphere interacting with the radiative budget of the Earth.¹ On geological time scales, buried sulfate partly controls the oxygenation of the atmosphere.^{2,3} Sulfur and oxygen isotopes of sulfate have been used for decades as a mechanism to understand the sulfur cycle.⁴ Today, the sulfur isotopic composition of sulfate is commonly used to estimate the strength, mixing,

and origin of different atmospheric sources. $\delta^{34}\text{S}$ has been commonly used to attain these goals, mainly because of the relatively high natural abundance of ^{34}S ($\sim 4.2\%$) and the significant differences in isotopic signature between sources.^{5–14} Despite the pioneering works of Holt and others,^{15–20} less attention has been paid to the oxygen isotopic composition of sulfates. The fact that the $\delta^{18}\text{O}$ values of non-seasalt sulfates are quite similar on average ($\sim 12\%$) limits interpretation.^{8,21} However, recently, the extension of oxygen isotopic measurements to the low-abundance ^{17}O isotope has reactivated the oxygen isotope analysis. The measurement of $\delta^{17}\text{O}$ was previously believed to be unnecessary because, until recently, $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ were highly correlated for terrestrial materials through the mass-dependent relationship $\delta^{17}\text{O} = 0.52 \delta^{18}\text{O}$,²² and only meteoritic material did not obey this relationship. Deviation from the purely mass-dependent effect is defined as $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \delta^{18}\text{O}$. Samples with $\Delta^{17}\text{O} = 0\%$ possess a mass-dependent isotopic composition, whereas samples with $\Delta^{17}\text{O} \neq 0\%$ are mass-independently fractionated.

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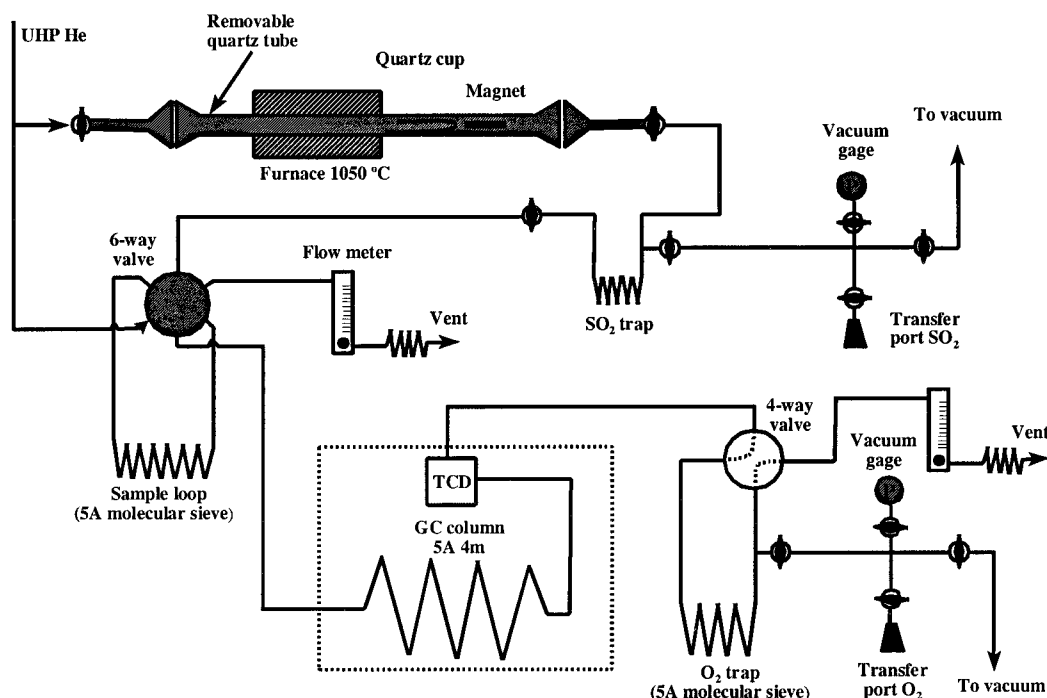


Figure 1. Schematic representation of the pyrolysis system.

Lee and Thiemens²³ were the first to report this anomaly in sulfate. This finding was confirmed with positive $\Delta^{17}\text{O}$ values ranging from 0.2 to 3‰.^{24–26} The origin of the anomaly has been attributed to the ozone and hydrogen peroxide oxidation of S(IV) in atmospheric water droplets.²⁷ These recent findings have generated interest in sulfate $\Delta^{17}\text{O}$ measurements. First, $\Delta^{17}\text{O}$ becomes a powerful new tool to investigate the mechanism of sulfur oxidation and has the potential to quantify the relative oxidation pathways in our atmosphere. Second, the conservation of sulfate isotopes through time in archives such as ice cores opens, for the first time, an opportunity to connect atmospheric chemistry and climate evolution. However, as a result of the extremely low concentration of sulfate in the free troposphere ($\sim 0.003 \mu\text{mol m}^{-3}$) and in ice cores ($0.001 \mu\text{mol g}^{-1}$ of water), a new analytical method is needed to reach this goal.

Conventional methods used the well-established graphite-reduction technique.^{28–31} Sulfate is extracted from solution as solid BaSO_4 . After filtration and purification, the precipitate is mixed with pure graphite and combusted under vacuum at 1100°C to generate CO_2 . At this point, only $\delta^{18}\text{O}$ may be measured by this technique because of isobaric interference of ^{13}C with ^{17}O . Only the coupling of the graphite-reduction method with a fluorination technique³² provides access to both $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ as O_2 is

quantitatively generated from CO_2 . More recently, Bao and Thiemens²⁴ proposed a method to generate O_2 directly from BaSO_4 . The method is based on a CO_2 -laser fluorination system used for silicate and oxides, with the BaSO_4 thermally decomposed in a BrF_5 environment. Contrary to the previous method, the laser fluorination is not quantitative (yield $\sim 30\%$) and must be calibrated against known standards; however, the above techniques share the same following limitations:

- (1) The size limitation of the samples ($20 \mu\text{mol}$ and above), which is unrealistic for atmospheric studies;
- (2) The difficulty in adapting these techniques to state-of-the-art isotopic techniques, such as the continuous flow-combustion-IRMS; and
- (3) The need of a fluorinating agent, which is expensive, difficult to purify, and highly lethal.

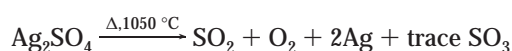
The following paper describes a new, safe, fast, and inexpensive way to analyze the complete isotopic content of SO_4 , including all three oxygen isotopes and all four sulfur isotopes. This technique takes advantage of the perfluorinated polymer membranes such as Nafion to convert any sulfate form to Ag_2SO_4 and also the low temperature thermal decomposition of Ag_2SO_4 to SO_2 , O_2 , and Ag in a continuous flow system.

EXPERIMENTAL SECTION

The Pyrolysis System. A schematic representation of our pyrolysis system is displayed in Figure 1. Our system consists of two main components. The first is a line that includes the pyrolysis system and a trapping system for SO_2 and O_2 . The second line includes a gas chromatograph and an oxygen sample collector. The lines are in stainless steel (except the quartz pyrolysis tube) and are coupled via a 6-way 2-position valve. Molecular sieves (5A Alltech, 80/100 mesh) are used to trap any noncondensable gas at liquid nitrogen temperature (LN_2). An ultrahigh-purity He tank equipped with an oxygen purification trap (Fisher) flows at a rate

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of 30 mL min⁻¹ in both lines. Blanks of the helium stream show no measurable O₂ and only a trace of N₂ (~10 ppmv). The pyrolysis tube is attached to the line via two flat O-ring joints, thus allowing quick and easy sample loading. The tube is first pumped to vacuum through the SO₂ trap. When vacuum is attained and leak tests are performed, the SO₂ trap is isolated from vacuum, and the pyrolysis system is flushed with He for 10 min at 2 atm, thus preventing any air leak contamination. The silver sulfate sample, contained in a quartz cup, is then pushed by a magnet contained in a sealed quartz tube into the furnace maintained at 1050 ± 10 °C. Ag₂SO₄ is quickly decomposed, and yields are consistent with the following reaction.



Repetitive measurements show yields close to 45 ± 7% for O₂. Fluctuations in the yields are probably the consequence of temperature fluctuations of the furnace (±10 °C) and the size of Ag₂SO₄ crystals. In our current system, these parameters cannot be controlled and are partially responsible for the reproducible uncertainty in yields and isotopic ratio measurements. Evolved gases are cryofocused in two successive traps for SO₂ and O₂, respectively. During this time, the GC line is continuously flushed with helium. The 6-way valve is then switched to the GC mode, the sample loop is thawed, and the oxygen sample is sent to the GC for yield measurements and further purification. The GC is equipped with a 4-m 5A molecular sieve column held at 32 °C and a TCD detector. One minute before the oxygen peak appears, the 4-way valve is switched to the trapping mode. After the O₂ sample has been trapped on molecular sieve, the 4-way valve is switched back to bypass mode, and the isolated O₂ trap is pumped to vacuum. The chromatogram reveals generally small traces of N₂ and CO. Finally, O₂ is transferred to a sample tube containing molecular sieve at liquid nitrogen temperature and brought to the IRMS for δ¹⁷O and δ¹⁸O measurement. Samples smaller than 3 μmol are cryofocused in an isotope ratio mass spectrometer microinlet. Meanwhile, the helium flow is stopped in the pyrolysis line and the SO₂ trap is isolated and pumped to vacuum. Condensable gases at LN₂ are cryotransferred to a sample tube containing a 30% H₂O₂ solution. The sample is thawed, and sulfur species are oxidized to sulfate. This sulfate is converted to SF₆ following the well-established procedures.^{33–35} Using SF₆ as the working gas allows the measurement of all four sulfur-stable isotopes. SO₂ may also be directly analyzed if only δ³⁴S is desired. This new method is quantitative in regard to the sulfur but not for oxygen. Ideally, only 50% of the original sulfate oxygen may be recovered as O₂. Therefore, the fractionation between O₂ and SO₄ requires calibration.

Preparation of the Standards. Four different silver sulfate standards were made for the analysis tests. Only reagent grade chemicals were used when possible. Standards 1 and 2 were prepared by mixing AgNO₃ salt in a 50-mL concentrated solution

(~1 mol l⁻¹) of H₂SO₄ and Na₂SO₄, respectively. The high concentration of sulfate ensures that the solubility of Ag₂SO₄ in water (0.03 mol l⁻¹) is exceeded. The white Ag₂SO₄ precipitate was filtered and washed with Millipore water. Standard 3 was prepared from a natural sample (Akron-S, gypsum from glacial till deposit, Ohio) with known δ¹⁸O composition.²⁴ A 0.5-g portion of the sample was crushed and completely dissolved in 200 mL of water. The solution was then filtered and passed through a H⁺ exchange resin (Bio-Rad, AG 50W-X8) to replace any cations by H⁺. This acid solution was further filtered through a Ag⁺ exchange resin (Alltech, Maxi-clean IC-Ag Plus cartridge) to eliminate chlorine and any other contaminants. At this point, an ion chromatograph (Dionex DX2000) test revealed a pure sulfuric acid solution with small traces of nitrate. This solution was then converted to Ag₂SO₄ using the same procedure as for the previous standards. To mimic our method as closely as possible to real samples, standard 4 possesses a mass-independent isotopic composition (i.e., a small excess of ¹⁷O). The full procedure to prepare this specific standard has been described elsewhere.²⁷ Briefly, a vessel containing a solution of Na₂SO₃ is frozen at LN₂ temperatures and evacuated. Ozone produced by electrical discharges is cryotransferred to the vessel. Ozone possesses a large mass-independent composition. During the oxidation of sulfite by ozone, the anomaly is partially transferred to the sulfate. Standard 4 was further processed as standard 2. For all of the standards, ion chromatography tests revealed a pure silver sulfate powder. Powders were stored in amber bottles, because silver sulfate is photosensitive.

Calibration of the Method. Low quantities ranging from 1.8 to 11 μmol of Ag₂SO₄ powder were poured into a small quartz cup (o.d., 8 mm; i.d., 6 mm; length, 4 cm) and placed in the pyrolysis tube. Quartz cups were previously passivated by immersing them for 5 min in a 10% HF solution and, after rinsing, placing them in an oven at 1000 °C for 5 h. Multiple runs for each standard were performed. The results are reported in Table 1. Our method gives good reproducibility (1σ = 0.5‰ and = 0.3‰ for δ¹⁸O and δ¹⁷O, respectively, including all data) over a wide range of isotopic compositions. As expected, the reproducibility for Δ¹⁷O is better (1σ = 0.1‰) than for δ measurements. This is due to the fact that experimental fractionations are mass-dependent processes and, therefore, do not affect the Δ¹⁷O. Any technique set up to measure the Δ¹⁷O must be tested using a mass-independent standard. Indeed, any isotopic exchange (e.g., with quartz) or mixing will only be observed if an anomalous standard is used (see tests and controls section). Figure 2 is a plot of the δ¹⁸O deviation of each individual analysis from its respective mean versus the size of the sample. Over the size range, no trend is observed. In general, the graphite-reduction method is more accurate, with reproducibilities around 0.2‰.³⁰ However, this is only obtained for sample sizes that are 1–2 orders of magnitude higher than our samples. For the three mass-dependent standards, the δ¹⁷O versus δ¹⁸O has been plotted (Figure 3). As expected, the standards align along a slope of 0.512, in accord with mass dependent compositions. The nonzero y intercept (−0.12‰) is within the statistical uncertainty.

Because our method is not quantitative, potential fractionations can occur between the original sulfate and the O₂ that is generated. A calibration is, therefore, needed. Only the Akron-S standard has

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Table 1. Repetitive Isotopic Measurements of Our Silver Sulfate Standards. Data Are Uncorrected (see text)

Standard 1					Standard 2				
run	size μmol	$\delta^{18}\text{O}$ ‰	$\delta^{17}\text{O}$ ‰	$\Delta^{17}\text{O}$ ‰	run	size μmol	$\delta^{18}\text{O}$ ‰	$\delta^{17}\text{O}$ ‰	$\Delta^{17}\text{O}$ ‰
1	4.3	7.9	4.0	0.0	1	2.2	11.6	5.8	-0.1
2	2.7	9.5	4.7	-0.2	2	9.8	11.6	5.8	-0.1
3	6.4	8.2	4.0	-0.2	3	4.5	11.8	5.9	-0.1
4	4.3	9.0	4.3	-0.3	4	1.8	12.2	6.3	-0.0
5	3.7	8.8	4.3	-0.2	5	5.4	10.6	5.4	0.0
6	8.8	7.9	3.9	-0.1					
7	5	8.4	4.1	-0.2					
8	5	9.2	4.6	-0.1					
9	3.4	9.5	4.6	-0.3					
mean		8.7	4.3	-0.2			11.6	5.8	-0.1
σ		± 0.6	± 0.3	± 0.1			± 0.6	± 0.3	± 0.1

Standard 3					Standard 4				
run	size μmol	$\delta^{18}\text{O}$ ‰	$\delta^{17}\text{O}$ ‰	$\Delta^{17}\text{O}$ ‰	run	size μmol	$\delta^{18}\text{O}$ ‰	$\delta^{17}\text{O}$ ‰	$\Delta^{17}\text{O}$ ‰
1	6	-0.9	-0.5	0.0	1	6.8	26.8	17.6	3.9
2	4.2	-0.4	-0.5	-0.3	2	3.9	26.8	17.6	3.9
3	4.2	0.0	0.0	0.0	3	3.3	27.6	18.0	3.9
					4	11	26.8	17.9	4.2
					5	3	26.9	17.7	3.9
mean		-0.45	-0.34	-0.1			27.0	17.8	3.9
σ		± 0.4	± 0.3	± 0.2			± 0.3	± 0.2	± 0.1

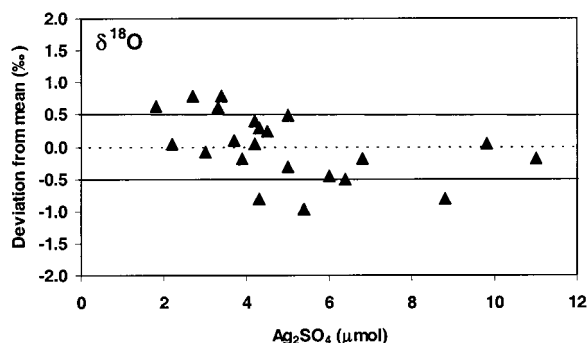


Figure 2. Comparison between the deviation from the mean of the oxygen isotopic composition of the sulfate standards and the size of the sample. The horizontal lines represent the statistical mean \pm one standard deviation.

a known $\delta^{18}\text{O}$ oxygen isotopic composition, which was previously measured by the graphite-reduction technique (see ref 24). To determine the $\delta^{18}\text{O}$ of remaining standards, standards 1, 2, and 4 were converted quantitatively to BaSO_4 . Standards 1 and 2 were processed with the graphite-reduction technique and the CO_2 generated was measured for $\delta^{18}\text{O}$ content. Standard 4 was processed according to Bao and Thieme,²⁴ and the value was corrected for the isotopic shift associated with this technique. The results are displayed in Figure 4. As it is observed, the correlation is near perfect, with a slope very close to 1. The original isotopic composition of the sulfate has no impact on the fractionation process during the combustion, as expected. However, the y intercept is not zero, and a constant correction is applied to our measurements to retrieve the values obtained by the graphite-reduction technique. These corrections are $+0.87\text{‰}$ and $+0.44\text{‰}$ ($= 0.512 \times 0.87$) for $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$, respectively. According to thermodynamic equilibrium for oxygen isotopic exchange between

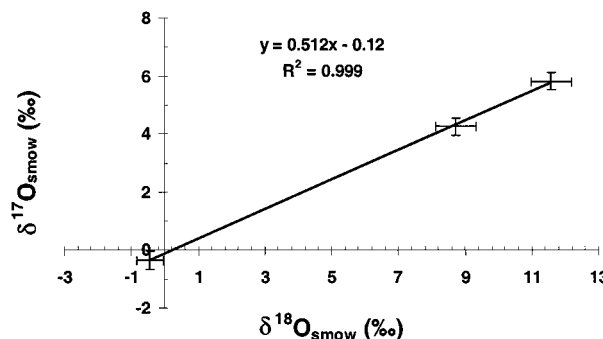


Figure 3. Three-isotope plot of the three mass-dependent standards. The slope of 0.512 confirmed a mass-dependent process formation for these standards.

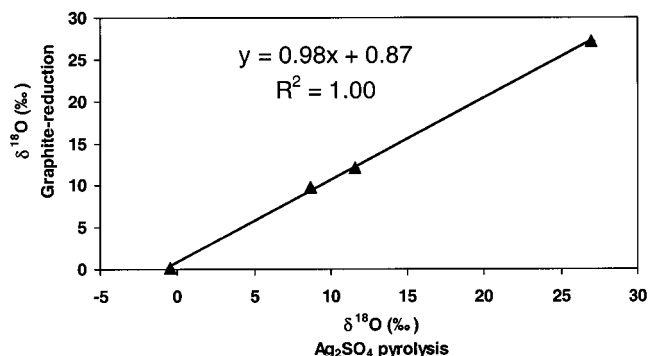
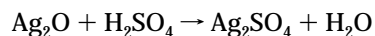


Figure 4. Calibration of the pyrolysis technique against the quantitative oxygen recovery of the graphite-reduction method. The slope (~ 1) shows that the fractionation is independent of the isotopic composition. The y intercept is the correction that should be applied to the pyrolysis technique to obtain the SMOW composition.

SO_2 and O_2 at $1100\text{ }^\circ\text{C}$,³⁶ the $\delta^{18}\text{O}$ of O_2 should be depleted by 1.5‰ relative to SO_2 . Our value, 1.7‰ (2×0.87) is very close to the thermal equilibrium values. This suggests that the isotopic equilibrium is quickly reached, thereby limiting any artifacts that can occur during the thermal decomposition (for instance, due to crystallization level of the sample). These corrections should therefore be valid for any system close to our design.

Conversion of Sulfate Salts to Silver Sulfate. The conversion of any sulfate salts or sulfuric acid to silver sulfate is an important step in the method. This has been a difficult task to realize for micromolar size samples. Today, Ag_2O is commonly used to convert HNO_3 to AgNO_3 for oxygen and nitrogen isotopic analysis of nitrate.^{37,38} A first attempt was made to use Ag_2O to convert H_2SO_4 to Ag_2SO_4 following the reaction:



Ag_2O is only slightly soluble in water. An excess amount of Ag_2O was poured into a 15-mL solution containing $3\text{ }\mu\text{mol}$ of sulfuric acid. The solution was gently evaporated in a clean hood to 3 mL and filtered. The solution was then evaporated to 1 mL

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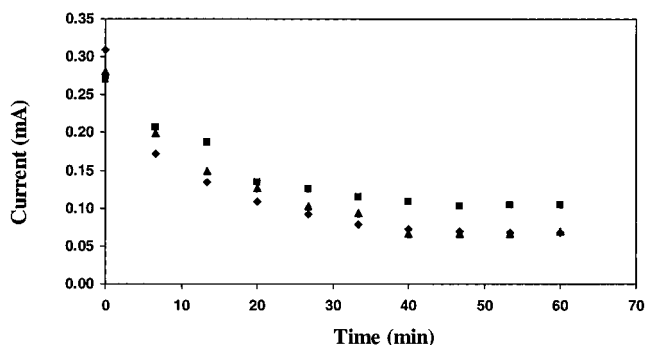


Figure 5. Time evolution of the current in the electrolysis apparatus from three different samples. The reaction is stopped when a plateau is reached.

in a Teflon beaker and transferred to a quartz cup. The cup was placed in an 80 °C oven and dried completely. The cup was later introduced into the pyrolysis tube and processed in the same manner as the standards. Despite multiple attempts, we were unable to reproduce the $\Delta^{17}\text{O}$ of our standard 4. In each case, we found a black-silver residue at the bottom of the cup after drying. We speculate that the formation of this deposit (probably due to the re-formation of some Ag_2O) was interfering with the standard by systematically lowering its $\Delta^{17}\text{O}$. The next attempt was to use AgF , which is much more soluble than Ag_2SO_4 in water and does not contain any oxygen. A slight excess of AgF ($3\times$) was added to the sulfuric acid solution and dried completely as before. Again, during this process a black-silver deposit was formed at the bottom of the quartz, and inconsistent results were again obtained, with $\Delta^{17}\text{O}$ always lower than expected. Ion-exchange resin in the form of Ag was also tried for the silver conversion; however, because of the stronger affinity of Ag^+ for the resin, as compared with H^+ , passing the sulfuric acid solution through the silver resin did not neutralize the acidity. The solution to the problem was found with the use of a Nafion N-117 (DuPont) membrane (0.18 mm thick). Nafion is an ion exchange polymer of PTFE backbone chains and pendant perfluorovinyl ether sulfonate anionic side groups. In this solid electrolyte, cations, especially H^+ , move freely and can cross the membrane easily if a differential potential is applied on each side of the membrane. A DC generator equipped with an ammeter and voltmeter supplies the power. The voltage is fixed at 5 V between two electrodes (Pt cathode, Ag anode) plunged in their respective electrolytes (silver nitrate at 10 mM for the cathode, sample solution for the anode) separated by the Nafion membrane. When the current is established, a cationic current is created between the Ag and Pt electrodes. With time (~ 1 h), all of the cations in the sample compartment are replaced by Ag^+ generated at the anode. This system follows the same principles of ion-exchange resins; however, in this case, the DC generator can overturn the normal affinity of cations with the Nafion membrane. Figure 5 presents typical responses of the current with time. At the beginning, the current drops very quickly, and in about 45 min, a steady state is reached. The sample compartment has the strongest resistance in the circuit. The current is therefore limited by the conductivity of the sample solution. We speculate that at the beginning, the current should be controlled by the mobility of H^+ , and the current is relatively high. As H^+ crosses the membrane barrier, a Ag^+ ion is created, and the conductivity decreases slowly with time. Finally, a steady

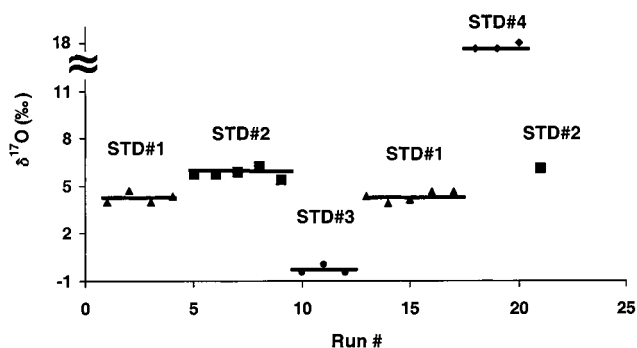


Figure 6. Results of consecutive oxygen isotope analysis of our sulfate standards. No memory effects are observed.

state is reached when no more H^+ is present in the sample compartment. At this point, the sample is in silver form and the pH of the solution is close to neutral. This was later confirmed by titration of the solution for its silver content using the Volhard endpoint ($\text{FeNH}_4\text{SO}_4/\text{KSCN}$). Yields close to 100% show the aptness of our approach. Controls performed by IC show that no anion mixing occurs between the two electrolytes. The Nafion membrane is permeable only to cations. The sample was completely dried in a quartz cup and no black-silver color was observed. This technique gives clean, white silver sulfate crystals that are ready for pyrolysis.

Tests and Controls. Memory effects and isotopic exchange are two possible artifacts that can degrade the performance of any isotopic method. We have conducted a set of tests to determine the integrity of our method. Figure 6 displays the evolution of the $\delta^{17}\text{O}$ isotopic composition of standards versus the run number. No memory effect is found, but this was true only when a new quartz cup was used for each separate analysis. Indeed, the quartz cup is etched during the pyrolysis and we found that this phenomenon had a profound effect on the $\delta^{17}\text{O}$ measurements, and to a smaller extent on the $\delta^{18}\text{O}$ measurement. We speculate that an etched quartz surface may create sites where oxygen isotopic exchange can easily occur. This effect was found to be negligible for the $\delta^{18}\text{O}$, but particularly sensitive for the $\delta^{17}\text{O}$, and therefore, for the calculation of $\Delta^{17}\text{O}$. To ensure that no isotopic exchange occurs between the water solvent and the sample during the treatment of samples, the following test was performed. Acid forms of standard 4 were processed through the same steps as for the natural samples. Natural samples are a combination of many soluble species from which sulfate must be extracted, purified, and concentrated. This goal is best reached by ion chromatography.³⁹ The standards were loaded in a 1-mL sample loop and injected into a separation column (Dionex AS4). After separation, sulfate standards were collected at the outlet of the conductivity detector and processed through the steps previously described. The results are presented in Table 2. The values obtained are in excellent agreement with the direct pyrolysis of the powder, showing that the entire procedure to treat the sample from the sample solution to Ag_2SO_4 does not corrupt its original isotopic composition. No isotopic exchange occurs

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Table 2. Comparison of Isotopic Composition between the Processed and Nonprocessed Standard 4

	standard 4 through IC/electrolysis/pyrolysis				standard 4 powder
	run 1	run 2	run 3	ave	ave
$\delta^{18}\text{O}$, ‰	26.5	27.3	26.8	26.9	27.0
$\delta^{17}\text{O}$, ‰	17.5	17.8	17.8	17.7	17.8
$\Delta^{17}\text{O}$, ‰	3.9	3.9	4.0	3.9	3.9

Table 3. Comparison of the Oxygen Isotopic Composition of Antarctica Sulfate between Our Method and the Literature

	coastal Antarctic aerosols, this study		Antarctic soil deposits ²⁵	Antarctica Vanda lake ⁴⁰
	run 1	run 2	range	range
$\delta^{18}\text{O}_{\text{snow}}$ (‰)	1.3	1.0	−10.4 to +2.8	−9.4 to −3.6
$\delta^{17}\text{O}_{\text{snow}}$ (‰)	1.4	1.1	−3.4 to +4.5	N/A
$\Delta^{17}\text{O}$ (‰)	0.7	0.6	0.6 to 3.4	N/A

between the water and the sample at any step. Finally, an aerosol collection filter from the coast of Antarctica was analyzed following our procedure. Enough sulfate was present on the filter to duplicate the isotopic measurements. The results are presented in Table 3, along with the only published data available for comparison. The replicate measurements of our sample are in good agreement, and compare well with the scant measurements of the oxygen isotopic composition of Antarctic sulfate published in the literature. The principal features are retrieved, especially the low $\delta^{18}\text{O}$ values and the mass independent isotopic composition. Our data has not been corrected for the sea salt content and may explain the low value of $\Delta^{17}\text{O}$ observed.

CONCLUSION

We have presented a new analytical method to investigate the complete isotopic composition of sulfate. The calibration and necessary tests for the oxygen isotopes have been presented. The results show that using silver sulfate as the working sulfate salt allows us to analyze all oxygen and sulfur isotopes on the same sample at the micromole level without the need of a fluorinating agent. This technique represents an advance in the isotopic analysis of sulfate, because it is faster than the graphite-reduction–fluorination method, although slightly slower than the CO_2 -laser fluorination. Starting from the electrolysis, 4 to 5 samples can be processed in 2 days. However, we point out that this new technique can be easily improved and adapted to a state-of-the-art CF-pyrolysis–IRMS system. We are confident that in this configuration, submicromole-level analysis can be reached. There is also no doubt that the electrolysis system can be improved to accommodate this level and to reduce the time required to process each sample. Our technique opens new frontiers in the analysis of $\Delta^{17}\text{O}$ of sulfate, from the background atmosphere to the valuable analysis of ice cores.

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