Discovery and measurement of an isotopically distinct source of sulfate in Earth's atmosphere

Gerardo Dominguez, Terri Jackson, Lauren Brothers, Burton Barnett, Bryan Nguyen, and Mark H. Thiemens*

Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, CA 92093

Sulfate (SO_4) and its precursors are significant components of the atmosphere, with both natural and anthropogenic sources. Recently, our triple-isotope (^{16}O, ^{17}O, ^{18}O) measurements of atmospheric sulfate have provided specific insights into the oxidation pathways leading to sulfate, with important implications for models of the sulfur cycle and global climate change. Using similar isotopic measurements of aerosol sulfate in a polluted marine boundary layer (MBL) and primary sulfate (p-SO_4) sampled directly from a ship stack, we quantify the amount of p-SO_4 found in the atmosphere from ships. We find that ships contribute between 10% and 44% of the non-sea-salt sulfate found in fine [diameter (D) < 1.5 μm] particulate matter in coastal Southern California. These fractions are surprising, given that p-SO_4 constitutes ≈2–7% of total sulfur emissions from combustion sources [Seinfed JH, Pandis SN (2006) *Atmospheric Chemistry and Physics* (Wiley–Interscience, New York)]. Our findings also suggest that the interaction of SO_2 from ship emissions with coarse hydrated sea salt particles may lead to the rapid removal of SO_2 in the MBL. When combined with the longer residence time of p-SO_4 emissions in the MBL, these findings suggest that the importance of p-SO_4 emissions in marine environments may be underappreciated in global chemical models. Given the expected increase of international shipping in the years to come, these findings have clear implications for public health, air quality, international maritime law, and atmospheric chemistry.

maritime vessels | triple oxygen isotope | aerosols | polluted marine boundary layer | sea salt spray

Although there are natural sources of aerosol sulfate and its precursors in the atmosphere, the global sulfur budget is dominated by anthropogenic contributions (1). Despite decades of research, however, our understanding of the global sulfur cycle remains unsatisfactory, in part because of the complexity of the multivalence states of sulfur as well as the variety of sources. Emissions of fully oxidized sulfate (SO_4) at the source, also known as primary sulfate, and sulfur dioxide (SO_2), a gas phase precursor that may eventually be oxidized in the atmosphere to become sulfate (secondary sulfate), have decreased in North America because of regulatory activities, although contributions from the developing world continue to rise (2).

Recently, marine vessels, which consume sulfur-rich (up to 5% S by weight) bunker oils, have been recognized to be globally significant sources of S in the atmosphere (3, 4). These emissions are in general not regulated, although, according to the latest Intergovernmental Panel on Climate Change (IPCC) report (5), they are receiving increased scrutiny by regional and international regulatory agencies because of their potential impact on air quality and human health in communities downwind from major shipping lanes and ports (6). Primary sulfate from ships is emitted predominantly as submicron-sized solid particles and comprises ≈2% of the total sulfur mass emitted (7). The fate of these gaseous (SO_2) and particulate sulfur emissions (SO_4) in the atmosphere are determined by the chemical transformation (oxidation) and removal (i.e., wet and dry deposition) processes that occur after they are emitted (8). The fate of sulfur emissions in the atmosphere is particularly important for global climate, because sulfate particles can directly affect the Earth's albedo via the reflection and/or absorption of sunlight (the direct effect) and can act as cloud condensation nuclei (CCNs), thereby affecting the radiative properties of the atmosphere in an indirect way as well (9). Sulfur emissions into the atmosphere can also have an adverse affect on human health, especially particulate matter <2.5 microns in size (PM2.5), because these have been linked to cardiopulmonary disease and death (10). Recent modeling work indicates that ship emissions may be responsible for as many as 60,000 deaths per year worldwide (6), and the economic cost of ship emissions are estimated to surpass 500 million dollars a year in the U.S. alone (11). These estimates have large uncertainties because the atmospheric transformation and transport processes governing gaseous and particulate sulfur emissions are not fully understood (6). Thus, understanding the strength and transport of particulate and gaseous sulfur emissions from the relatively unregulated shipping industry is desirable (3, 6).

Measurements of aerosol sulfate concentrations in the atmosphere are ambiguous indicators of source contributions in urban environments because of the variety of potential contributors of primary and secondary sulfate that exist. Determining the amount of particulate sulfate contributed by ships in urban areas is especially challenging, given that elevated levels of diesel truck engine traffic, a known source of primary sulfate, are also associated with major ports. Attempts at using isotopes of sulfur ($\delta^{34}S$) in aerosol sulfate yield ambiguous results because of the wide variation of $\delta^{34}S$ in potential sources such as coal and fossil fuels and a lack of a simple definitive isotope ratio for specific sources (1).

Recently, triple-isotope measurements of oxygen (^{16}O,^{17}O,^{18}O) in aerosol sulfate and nitrate have been used to address a variety of facets of atmospheric chemistry, from climate change (12) to the impact of biomass burning in preindustrial America on the oxidation of nitrogen and sulfur (13) and the variability of ozone concentrations in the Antarctic (14). Using size-segregated sampling and triple oxygen isotopic analysis of atmospheric as well as direct samples of primary sulfate from a ship, we demonstrate that triple-oxygen isotopic measurements of aerosol sulfate can also be used to estimate the concentration primary sulfate found in the atmosphere that is emitted from ships (15).

Results

A summary of the oxygen isotopic composition of the total and non-sea-salt (nss)-sulfate triple-oxygen isotopic compositions is found in Table 1. The triple isotopic composition of nss-sulfate was calculated by subtracting the triple-oxygen isotopic composition of sea-salt sulfate ($\delta^{18}O = 10‰$, $\delta^{17}O = 5.2‰$, $\Delta^{17}O = 0‰$) using Na^+ cation concentration measurements (ion chromatography,

ENVIRONMENTAL SCIENCES

www.manaraa.com

Table 1. Sample IDs, sampling periods, size fractions, sulfate and sodium ion concentrations, and triple-isotope values for aerosol total and nss-SO$_4$ portions

Sample ID	Start date	End date	Size cut	[SO$_4^{-2}$], μmol·m^{-3}	[Na] μmol·m^{-3}	[SO$_4^{-2}$] δ^{18}O, ‰	[SO$_4^{-2}$] δ^{17}O, ‰	[SO$_4^{-2}$] Δ^{17}O, ‰	[SO$_4^{-2}$] nss-δ^{18}O, ‰	[SO$_4^{-2}$] nss- δ^{17}O, ‰	[SO$_4^{-2}$] nss-Δ^{17}O, ‰
SIO060905-A	9/1/06	9/5/06	C	0.05	0.25	–	–	–	–	–	–
SIO060905-B	9/1/06	9/5/06	F	0.05	0.07	10.56	6.37	0.88	10.62	6.48	0.96
SIO060907-A	9/6/06	9/7/06	C	0.02	0.22	–	–	–	–	–	–
SIO060907-B	9/6/06	9/7/06	F	0.06	0.11	10.84	6.55	0.91	10.96	6.73	1.04
SIO060908-A	9/7/06	9/8/06	C	0.02	0.16	10.94	6.31	0.62	12.20	7.79	1.45
SIO060908-B	9/7/06	9/8/06	F	0.05	0.11	13.32	7.92	0.99	13.86	8.36	1.16
SIO060911-A	9/8/06	9/11/06	C	0.02	0.15	9.79	5.22	0.13	9.66	5.23	0.21
SIO060911-B	9/8/06	9/11/06	F	0.05	0.05	14.32	8.18	0.74	14.62	8.39	0.79
SIO060912-A	9/11/06	9/12/06	C	0.02	0.23	10.83	6.04	0.41	11.97	7.19	0.97
SIO060912-B	9/11/06	9/12/06	F	0.07	0.12	13.93	7.80	0.56	14.40	8.11	0.62
SIO060913-A	9/12/06	9/13/06	C	0.01	0.16	12.68	7.20	0.61	40.83	28.26	7.02
SIO060913-B	9/12/06	9/13/06	F	0.09	0.12	14.36	8.08	0.61	14.78	8.36	0.67
SIO060914-A	9/13/06	9/14/06	C	0.02	0.20	12.88	7.38	0.68	19.61	12.46	2.27
SIO060914-B	9/13/06	9/14/06	F	0.05	0.00	11.02	6.56	0.83	11.02	6.57	0.84

Samples with– have not been measured.

Dionex Ionac AS4A-SC column) and the molar ratio SO$_4$:Na$^+$ = 0.0604 for sea salt.

A plot of the mass-independent (or excess in ^{17}O as expected from the amount of ^{18}O) in the nss-sulfate (nss-SO$_4$) in fine and coarse particles vs. δ^{18}O is shown in Fig. 1 (For a review of mass-independent effects see ref. 15). Trend-lines for fine and coarse particles determined by using a χ^2 minimization algorithm (written in Matlab) are also shown. The trend lines for the coarse and fine aerosol sulfate fractions are distinct at a statistically significant level (>3 σ). For reference, we also plot the triple-isotope composition of oxygen in nss-SO$_4$ in the fine and coarse aerosols from a pristine coastal marine environment in Northern California (16). The distinct slopes observed in fine and coarse aerosol nss-SO$_4$ indicate that the sources and/or oxidative pathways of nss-SO$_4$ are isotopically distinct, with the mixing line of aerosol nss-SO$_4$ in coarse aerosols being consistent with varying

degrees of sulfate production via ozone (δ^{18}O = 81.6 ± 6‰, Δ^{17} = 26.7 ± 5‰) (17) oxidation of SO$_2$(aq) in sea-salt aerosols in this size fraction (18). The slope and intercept of the sulfate in fine aerosol particles differs significantly from those of the coarse particles.

The results of our measurements of the isotopic composition of oxygen in primary sulfate from a marine vessel are significant and are summarized in Table 2. It is interesting to note that the average isotopic ratios of oxygen in primary ship sulfate (δ^{18}O = 21.06‰, δ^{17}O = 0.07‰) are almost identical to those of oxygen in the atmosphere (δ^{18}O = 23.5‰, Δ^{17}O = 0‰).

Discussion

The isotopic composition of oxygen in nss-SO$_4$ found in the remote marine boundary layer (MBL) is determined by the relative strengths of OH (δ^{18}O ≈ 0‰, (δ^{17}O = 0‰), H$_2$O$_2$ (δ^{18}O = 21.9–52.6‰, (Δ^{17}O = 1.4–2.4‰) (19), and ozone (δ^{18}O = 81.6 ± 6‰, (Δ^{17}O = 26.7 ± 5‰) [here, we are quoting the average and standard deviation of the triple-oxygen isotopic composition of ozone at La Jolla as measured by Johnston and Thiemens (17)] oxidation of SO$_2$ (Δ^{17}O = 0‰) (20) and the associated δ^{18}O fractionations (equilibrium and/or kinetic) and Δ^{17}O compositions of these oxidants (21). Given the possible natural explanations for the trend lines seen in our data, it is interesting that the Δ^{17}O of sulfate in fine aerosols decreases for higher δ^{18}O values, indicating the influence of a distinct mass-dependent source of $_{SO4}$ in the atmosphere of Southern California. This trend is in marked contrast to the nss-SO$_4$ found in our coarse particles.

Given the location of the sampling site and the measured isotopic composition of primary sulfate from the ship stack (Table 2), it is plausible that the fine aerosol trend line represents a mixing line between a background with a marine nss-SO$_4$-like composition and that of primary particulate sulfate from ship emissions in coastal San Diego and/or the greater Los Angeles
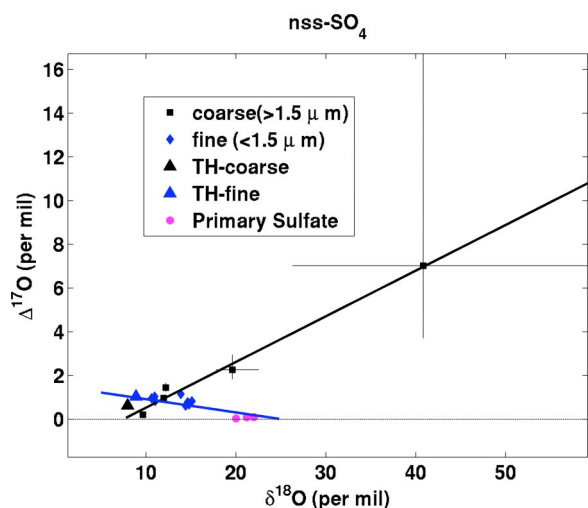
Fig. 1. Oxygen isotopes of nss- SO$_4$ in fine and coarse aerosol size fractions. For reference, the measurements of size-segregated aerosol sulfate from Trinidad Head (TH), California by Patris *et al.* (16) as well as measurements of primary sulfate sampled directly from a ship (see Table 2) are also shown. The solid lines indicate the best fit to the coarse (black) and fine (blue) aerosol size bin data. Uncertainty in isotopic composition of nss-SO$_4$ is dominated by the uncertainty ($\approx$10%) of the ion-chromatographic data. The uncertainty estimates are smaller than the marker size for the sulfate found in the fine aerosols.

Table 2. Results of triple-isotope measurements of primary particulate sulfate from the large container ship Sine Maersk, Post-Panamax Series S

Sample ID	δ^{18}O, ‰	δ^{17}O, ‰	Δ^{17}O, ‰
Denmark-AB65	20.01	10.41	0.04 ± 0.1
Denmark-AB68	21.99	11.53	0.10 ± 0.1
Denmark-AB81	21.20	11.12	0.09 ± 0.1

Dominguez *et al.*

www.manaraa.com

Table 3. Lower and upper limits to the amount of primary particulate ship sulfate in coastal San Diego's air, assuming that ships contribute 39% and 100% of the mass-dependent nss-SO₄ in the air

Sample ID	Start date	End date	Fine-[SO₄] mg m⁻³	Fine-[nss-SO₄] mg m⁻³	Fine-[SO₄(ships)] mg m⁻³	nss-SO₄ (fine) from ships, %	All (fine plus coarse) SO₄, %	Back-trajectory origin of aerosols
SIO060901-B	8/29/06	9/1/06	8.53	8.18	2.89–3.64	35–44	34–42	1, 2, 3
SIO060905-B	9/2/06	9/6/06	4.61	4.20	0.43–0.53	10–13	4–11	1, 3, 2
SIO060907-B	9/6/06	9/7/06	5.34	4.69	0.50–0.63	11–13	7–9	1, 2, 3
SIO060908-B	9/7/06	9/8/06	4.56	3.93	0.92–1.16	23–29	15–18	1, 2
SIO060911-B	9/8/06	9/11/06	4.56	4.27	1.44–1.80	33–42	21–26	1, 2
SIO060912-B	9/11/06	9/12/06	6.54	5.84	2.06–2.59	25–44	23–29	1, 3
SIO060913-B	9/12/06	9/13/06	8.19	7.48	2.71–3.41	36–46	29–37	1, 3
SIO060914-B	9/13/06	9/14/06	4.33	4.31	0.61–0.77	14–18	10–13	1, 2

The origin of air sampled at the Scripps Pier was determined by using the National Oceanic and Atmospheric Administration's HYSPLIT Backtrajectory program. All sampled air masses were predominantly ''oceanic'' (1), but smaller portions of their air originated from the Port of San Diego (2) and the Port of Los Angeles (3).

area. The trend line in the coarse particles also indicates that oxidation of SO₂ by ozone in supramicrometer-sized sea-salt aerosols is a significant, but not exclusive, source of nss-SO₄ in the polluted MBL. We examine the relative role of the various oxidation pathways in the fine-size fraction using a simple mixing model and mass balance. For simplicity, we assume that the measured triple-isotopic composition of aerosol sulfate is represented as a linear combination of fractions of sulfate that was formed similarly to the "background" nss-SO₄ in a remote marine environment (f_B), mass-dependent primary particulate sulfate (f_P), and sulfate made from the oxidation of SO₂(aq) by O₃ (f_{O_3}) This general model can be expressed as follows:

$$\Delta^{17}O(nss-SO_4) = \Delta^{17}O(B)f_B + \Delta^{17}O(P)f_P + \Delta^{17}O(O_3)f_{O_3}$$

[1]

$$\delta^{18}O(nss-SO_4) = \delta^{18}O(B)f_B + \delta^{18}O(P)f_P + \delta^{18}O(O_3)f_{O_3}$$

[2]

$$1 = f_B + f_P + f_{O_3},$$

[3]

where f_B, f_P, and f_{O_3} are the fractions of nss-SO₄ with isotopic compositions matching the "background," primary sulfate, and ozone oxidation, respectively. These relationships can be written in matrix form and solved for f_B, f_P, and f_{O_3}, yielding the relative contributions by each for each sample.

We can now estimate the upper and lower limits to the amount of particulate primary sulfate found in coastal San Diego. To obtain an upper limit, we assume that ships contribute 100% of the mass-dependent primary sulfate, and therefore the primary sulfate end-member in this case is found at $\delta^{18}O(P) = 21‰$, $\Delta^{17}O(P) = 0‰$. There is the possibility that the observed influence of a mass-dependent source originates either wholly or partly from land-based diesel engine exhaust. An examination of the triple-isotopic composition of oxygen in primary sulfate from diesel engines (22) found that the $\delta^{18}O$ ranged from 5‰ to 7‰ and $\Delta^{17}O$ from −0.2‰ to 0.2‰. The $\delta^{18}O$ values of diesel engine primary sulfate are too low to satisfy the isotopic constraints of our data. If we treat the mass-dependent primary sulfate as a generic end-member, it can be easily shown that physically meaningful values of f_P ($0 \leq f_P \leq 1$) are obtained when the mass-dependent $\Delta^{17}O = 0‰$) source of primary sulfate has a $\delta^{18}O > 13‰$. This end-member ($\delta^{18}O(P) = 13‰$, $\Delta^{17}O(P) = 0‰$) is equivalent to a mixture of diesel primary sulfate (61%) and ship primary sulfate (39%), and the results for f_P derived from this end-member composition constitute a lower limit to the amount of ship sulfate needed to explain the triple-oxygen isotopic data. A summary of the lower and upper limits to the concentration of primary particulate sulfate from ships in coastal San Diego are shown in Table 3, and Fig. 2 graphically illustrates

the necessity of having a mass-dependent sulfate end member with relatively high $\delta^{18}O$ values to explain our triple-oxygen isotope data in fine-particle sulfate. It is interesting to note that f_{O_3} in the fine aerosols is typically <0.02, with $f_B + f_P \approx 1$, making the results relatively insensitive to the isotopic composition of ozone in the atmosphere.

The fraction of all nss-SO₄ attributable to ships (See Table 3) is somewhat surprising considering that it is generally believed that only 2–7% of the total sulfur emissions from combustion sources is partitioned into primary sulfur (7, 23). Chemical modeling of ship S emissions typically focus on the chemistry and transport of the gaseous component (3, 4), but our results support the argument that the submicron particulate sulfate component, because of its long atmospheric residence time, should be considered in these models. Our results also beg the question: What happened to the much larger fraction of S from ships that was emitted as SO₂? A qualitative analysis of back trajectories (see Table 3) indicates that the origin of the air sampled at the Scripps Pier have both oceanic and urban origins, including the Ports of San Diego and Los Angeles/Long Beach (strong SO₂ and SO₄ source regions). And, although detailed modeling of the interaction between SO₂-NOx plumes and sea-salt aerosols is beyond the scope of this work, it is instructive to look at a plot of the $\Delta^{17}O(nss-SO_4)$ vs. the concentration of nss-SO₄ in our coarse-aerosol samples (See Fig. 3). Here, we see
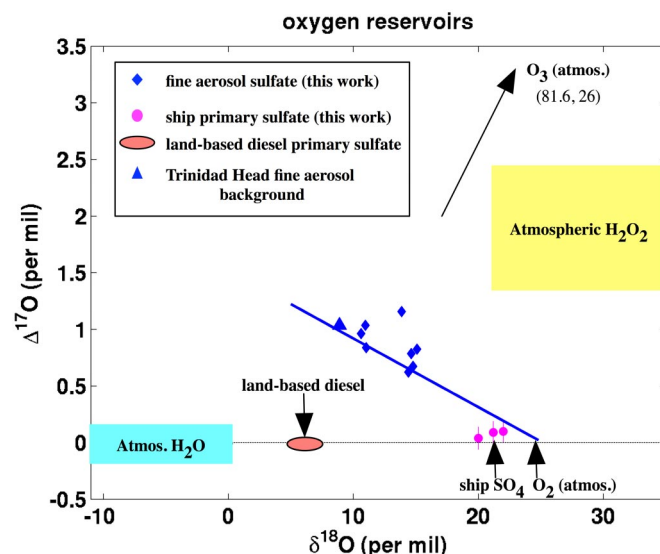
Fig. 2. A summary of potential sources of oxygen in aerosol sulfate found in the atmosphere.

Dominguez *et al.*

ENVIRONMENTAL SCIENCES

nss-SO$_4$ in coarse particles
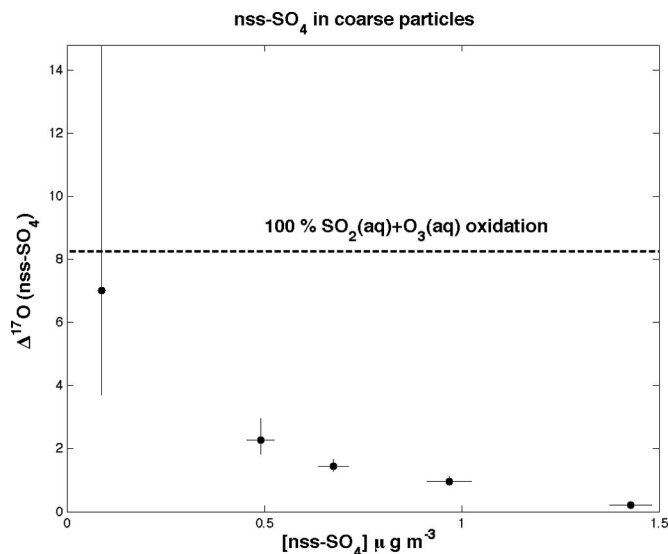
Fig. 3. Δ^{17}O vs. [nss-SO$_4$(coarse)] at La Jolla. The decreasing slope demonstrate that SO$_2$(aq) + O$_3$(aq) oxidation does not continue indefinitely. The decrease in Δ^{17}O of nss-sulfate as a function of the concentration of nss-SO$_4$ suggests that other sulfate production mechanism become important as aerosols become acidified in polluted marine environments.

that SO$_2$ plus O$_3$ oxidation as a fraction of all nss-SO$_4$ (corresponding to the highest Δ^{17}O values) is highest on sampling dates with the lowest nss-SO$_4$ concentrations, with a systematic decrease at higher nss-SO$_4$ concentrations. This pattern strongly suggests that the additional SO$_4$ found in coarse aerosols must have come from either the uptake of H$_2$SO$_4$ (g) (Δ^{17}O = 0‰) on existing aerosols in the coarse size, although the isotopic data alone cannot be used to quantify the contribution that halogenic compounds like HOCl and HOBr may have had because these would also produce sulfate with the same triple-isotopic composition (24). Our results can, however, be used to constrain the relative ratio of SO$_2$(aq) + O$_3$(aq) vs. all other oxidative pathways that produce mass-dependent SO$_4$ with low δ^{18}O values in coarse particles. These results and their interpretation are consistent with the results of previous modeling work indicating the importance of sea-salt aerosol acidification in controlling the production of sulfate via the SO$_2$(aq) plus O$_3$(aq) oxidative pathway (25). Although it is not the main focus of this paper, our data indicate that triple-oxygen isotope measurements of samples from pristine and polluted marine environments, when combined with other field measurements and with chemical modeling of sea-salt aerosol and associated halogen chemistry (26), could be used to provide tight constraints on the oxidative pathways of secondary sulfate in the atmosphere and, as a consequence, provide insights into the global S cycle. For example, if significant amounts of S from ship emissions are taken up by coarse sea-salt particles as SO$_2$(g) and H$_2$SO$_4$(g), as our results suggest, then this has important implications for the distribution and deposition of sulfur in the atmosphere because sea-salt particles have limited residence times ($\approx$1–6 h) and may therefore act as efficient removal agents in the MBL (18, 21). This interpretation is consistent with the isotopic composition of nss-SO$_4$ found in coarse (sea-salt-dominated) particles in coastal La Jolla that are presented in Figs. 1 and 3.

Elevated levels of certain metal ions (Mn^{2+}, Fe^{3+}) are known to catalyze the oxidation of aqueous SO$_2$ by O$_2$. This oxidation pathway could also produce a mixing line (in our fine-aerosol sulfate) with a very similar slope (23, 27). In fact, given that the isotopic composition of primary sulfate from the ship samples we analyzed is so similar to that of atmospheric oxygen and differs

significantly from that of particulate sulfate from land-based diesel engines, we suggest that primary particulate sulfate made in marine diesel engines may be the end product of the catalytic oxidation of S by atmospheric oxygen within ship engines. Studies of ship plumes indicate that most of their particulate emissions are submicron in size and have elevated levels of trace metals such as Ni, Zn, V, and Pb (28, 29). At this time it is unclear whether these metals are capable of acting as catalysts in ship engines or the atmosphere, but this possibility should be explored in future work by using the combination of triple-oxygen isotope and trace-metal analysis. The work we have presented demonstrates that triple-isotope determinations of oxygen in size-segregated sulfate in the environment can be used to greatly clarify our understanding of the local, regional, and global sulfur budgets and associated impacts on human health and climate.

The combined use of simple sample collection using high-volume size-segregated aerosol samplers followed by the triple-oxygen isotopic analysis of these samples in the laboratory should be widely applicable to other regions with major ports (e.g., New York City, San Francisco, Hong Kong, Houston, Singapore, etc.). With global shipping expected to continue to increase in the years and decades to come, the quantitative assessment and monitoring of ship emissions and their transport should allow policy makers to make more informed decisions aimed at minimizing their negative impacts on human health and the environment.

Materials and Methods

To collect our aerosol samples, a standard high-volume (Thermo-Electron), five-stage slotted impact collector with glass-fiber filter papers was deployed at the end of the Scripps Pier (32.87 °N, 117.25 °W) in La Jolla, CA. This site is particularly interesting because it is just north ($\approx$10 miles) of a major urban area and port (San Diego, CA), west ($\approx$30 miles) of a major shipping lane with heavy traffic ($\approx$7–14 per day),[†] and is also downstream from a large metropolitan city (Los Angeles, CA) with the third largest port in the world.[‡] In general, the meteorology of this site produces periods of onshore and offshore winds as well as periods of time when pollutants from Los Angeles are sampled. Thus, in many ways, the sampling site is ideally situated to address issues of marine vessel emissions and their identification in a complex urban environment.

During late August 2006 through early October 2006, aerosol samples with time resolutions between 1 and 3 days were collected. During this time, the sampling site experienced various degrees of pure marine and urban air. A subset of these samples was prepared for determination of the oxygen isotopic composition in aerosol sulfate. Because of the analytical requirement of sample size, sulfate from the first three stages, which will be referred to hereafter as coarse (D > 1.5 μm), and the last two stages, referred to as fine (D < 1.5 μm), were aggregated and prepared by using standard techniques for the isolation of SO$_4^{-2}$ anions and subsequent conversion to Ag$_2$SO$_4$ and liberation of O$_2$ using a standard combustion technique.[§] The product of combustion, O$_2$, was isolated by using a gas chromatograph, and a MAT 251 mass-spectrometer was used to determine the isotopic ratios δ^{17}O, δ^{18}O, and Δ^{17}O (30).[¶] These same techniques were also used to measure the oxygen-isotopic ratios of primary particulate sulfate from the exhaust of a large container ship

---

$$\delta^{17,18}O = \left[\left(\frac{\left(\frac{^{17,18}O}{^{16}O}\right)_{sample}}{\left(\frac{^{17,18}O}{^{16}O}\right)_{standard}} \right) - 1 \right] \times 1000.$$

Dominguez *et al.*

(Sine Maersk, Post-Panamax Series S), operating at various loads, using PM filters that were provided to us by the California Air Resources Board (CARB).

1. Schlesinger WH (1997) Biogeochemistry: An Analysis of Global Change (Academic, New York).
2. Streets DG, Waldhoff ST (2000) Present and future emissions of air pollutants in China: SO2, NOx, and CO. *Atmos Environ* 34:363–374.
3. Capaldo K, Corbett JJ, Kasibhatla P, Fischbeck P, Pandis SN (1999) Effects of ship emissions on sulphur cycling and radiative climate forcing over the ocean. *Nature* 400:743–746.
4. Corbett JJ, Fischbeck P (1997) Emissions from ships. *Science* 278:823–824.
5. Ribeiro K, *et al.* (2007) in *Contribution of Working Group III Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, eds Metz B, Davidson OR, Bosch PR, Dave R, Meyer LA (Cambridge Univ Press, Cambridge, UK).
6. Corbett JJ, *et al.* (2007) Mortality from ship emissions: a global assessment. *Environ Sci Technol* 41:8512–8518.
7. Fleischer F, Ulrich EJ, Krapp R, Grundmann W (1998) in *Proceedings of the 22nd CIMAC International Congress on Combustion Engines, Copenhagen, Denmark* (Int Council on Combustion Engines, Frankfurt, Germany).
8. Schwartz SE (1989) Acid deposition: Unraveling a regional phenomenon. *Science* 243:753–763.
9. Charlson RJ, *et al.* (1992) Climate forcing by anthropogenic aerosols. *Science* 255:423–430.
10. Pope CA (2000) Review: epidemiological basis for particulate air pollution health standards. *Aerosol Sci Technol* 32:4–14.
11. Gallagher KP, Taylor R (2003) *International Trade and Air Pollution: The Economic Cost of Air Emissions from Waterborne Commerce Vessels in the United States* http://ase.tufts.edu/gdae.
12. Alexander B, Savarino J, Barkov NI, Delmas RJ, Thiemens MH (2002) Climate driven changes in the oxidation pathways of atmospheric sulfur. *Geophys Res Lett* 29:30–31.
13. Alexander B, Savarino J, Kreutz KJ, Thiemens MH (2004) Impact of preindustrial biomass-burning emissions on the oxidation pathways of tropospheric sulfur and nitrogen. *J Geophys Res* 109:D08303.
14. McCabe JR, Thiemens MH, Savarino J (2007) A record of ozone variability in South Pole Antarctic snow: Role of nitrate oxygen isotopes. *J Geophys Res Atmos* 112:D12303.
15. Thiemens MH (2006) History and applications of mass-independent isotope effects. *Annu Rev Earth Planet Sci* 34:217–262.
16. Patris N, Cliff SS, Quinn PK, Kasem M, Thiemens MH (2007) Isotopic analysis of aerosol sulfate and nitrate during ITCT-2k2: Determination of different formation pathways as a function of particle size. *J Geophys Res Atmos* 112:D23301.
17. Johnston JC, Thiemens MH (1997) The isotopic composition of tropospheric ozone in three environments. *J Geophys Res* 102:25395–25404. *0*
18. Krischke U, et al. *0 (2000) Removal of SO2 from the marine boundary layer over the Atlantic Ocean: A case study on the kinetics of the heterogeneous S(IV) oxidation on marine aerosols.* J Geophys Res *0* 105:14413–14422.
19. Savarino J, Thiemens MH (1999) Analytical procedure to determine both d18O and d17O of H2O2 in natural water and first measurements. *Atmos Environ* 33:3683–3690.
20. Holt BD, Kumar R, Cunningham PT (1981) Oxygen-18 study of the aqueous-phase oxidation of sulfur dioxide. *Atmos Environ* 15:557–566.
21. Alexander B, *et al.* (2005) Sulfate formation in sea-salt aerosols: Constraints from oxygen isotopes. *J Geophys Res Atmos*) 110:D10307.
22. Lee CC-W, Savarino JH, Cachier H, Thiemens MH (2002) Sulfur (32S, 33S, 34S, 36S) and oxygen (16O,17O,18O) isotopic ratios of primary sulfate produced from combustion processes. *Tellus B* 54:193–200.
23. Seinfeld JH, Pandis SN (2006) *Atmospheric Chemistry and Physics* (Wiley—Interscience, New York).
24. Vogt R, Crutzen PJ, Sander R (1996) A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer. *Nature* 383:327–330.
25. Keene WC, *et al.* (1998) Aerosol pH in the marine boundary layer: A review and model evaluation. *J Aerosol Sci* 29:339–354.
26. Dickerson RR, *et al.* (1999) Ozone in the remote marine boundary layer: A possible role for halogens. *J Geophys Res* 104:21385–21395.
27. McCabe JR, Savarino J, Alexander B, Gong S, Thiemens MH (2006) Isotopic constraints on non-photochemical sulfate production in the Arctic winter. *Geophys Res Lett* 33:L05810.
28. Isakson J, Persson TA, Selin Lindgren E (2001) Identification and assessment of ship emissions and their effects in the harbour of Goteborg, Sweden. *Atmos Environ* 35:3659–3666.
29. Lu G, *et al.* (2006) Identification and characterization of inland ship plumes over Vancouver, BC. *Atmos Environ* 40:2767–2782.
30. Savarino J, Alexander B, Thiemens MH (2001) Sulfur and oxygen isotope analysis of sulfate at micromole levels using a pyrolysis technique in a continuous flow system. *Anal Chem* 73:4457–4462.

ENVIRONMENTAL SCIENCES

Dominguez *et al.*