Tellus (2002), 54B, 193–200
Printed in UK. All rights reserved

Copyright © Blackwell Munksgaard, 2002

TELLUS
ISSN 0280–6509

Sulfur (^{32}S, ^{33}S, ^{34}S, ^{36}S) and oxygen (^{16}O, ^{17}O, ^{18}O) isotopic ratios of primary sulfate produced from combustion processes

By C. C.-W. LEE[1], J. SAVARINO[1,2]*, H. CACHIER[3] and M. H. THIEMENS[1], [1]*Department of Chemistry and Biochemistry, University of California — San Diego, La Jolla, 92093-0356 CA, USA;* [2]*Laboratoire de Glaciologie et Géophysique de l'Environnement, CNRS, BP 96, 38402 St Martin d'Hères, France;* [3]*Laboratoire des Sciences du Climat et de l'Environnement, CEA/CNRS, 91190 Gif sur Yvette, France*

(Manuscript received 4 October 2001; in final form 28 January 2002)

ABSTRACT

The recent discovery of an anomalous enrichment in ^{17}O isotope in atmospheric sulfate has opened a new way to investigate the oxidation pathways of sulfur in the atmosphere. From laboratory investigations, it has been suggested that the wet oxidation of sulfur in rain droplets was responsible for the excess ^{17}O. In order to confirm this theory, sulfur and oxygen isotope ratios of different primary sulfates produced during fossil fuel combustion have been investigated and are reported. None of these samples exhibits any anomalous oxygen or sulfur isotopic content, as compared to urban sulfate aerosols. These results, in agreement with the laboratory investigations, reinforce the idea of an aqueous origin for the oxygen-17 anomaly found in tropospheric sulfates.

1. Introduction

Among natural biogeochemical cycles, the sulfur cycle is one of those most heavily perturbed by human activities. Today, it is estimated that around 70–80% of the atmospheric sulfur species present in the northern hemisphere are anthropogenic (Rasch et al., 2000; Rodhe, 1999). Anthropogenic sulfur emissions are dominated by SO_2. In the atmosphere, sulfur dioxide is predominantly oxidized by OH in the gas phase and by H_2O_2 and O_3 in the aqueous phase to produce sulfate particles. An important impact of sulfate aerosols is their effect on the Earth's global radiative budget. In recent years, intensive studies have been devoted to the issue of the radiative forcing of atmospheric sulfate (Chuang et al., 1997; Feichter et al., 1996; Kiehl et al., 2000; Koch et al., 1999; Pan et al., 1998; van Dorland et al., 1997). Despite significant advances in our understanding of the sulfur cycle, there are still processes that are not well understood and/or quantified. The oxidation of SO_2 to sulfate is one of the processes that has gaps in our understanding (Kasibhatla et al., 1997; Koch et al., 1999). Models based upon current oxidation pathways reveal a systematic trend towards an overestimate of SO_2 and subsequent underestimate for sulfate concentrations, particularly at northern latitudes (Kasibhatla et al., 1997; Lelieveld et al., 1997). Thus a heterogeneous oxidation pathway to convert SO_2 into sulfate is often invoked to reconcile observations and model outputs (Kasibhatla et al., 1997).

Recent oxygen isotopic studies of sulfate have revealed a potentially new tool to investigate SO_2

---

* Corresponding author.
e-mail: jsavarino@chem.ucsd.edu

oxidation pathways (Lee and Thiemens, 2001; Lee et al., 2001). Sulfates formed in the atmosphere are mass-independently fractionated (Lee et al., 2001). In most conventional processes (e.g. diffusion, kinetic reactions, and phase changes), for oxygen-bearing species, the three stable oxygen isotopes (^{16}O, ^{17}O, ^{18}O) are generally strictly correlated in a predictable manner. Using the conventional delta notation, mass-dependent compositions obey the relation $\delta^{17}\mathrm{O} \approx 0.52\delta^{18}\mathrm{O}$ (Thiemens, 1999), while mass-independent compositions do not do so. The deviation from a mass-dependent fractionation relationship (i.e. mass-independent anomaly or oxygen-17 excess or deficiency) is represented by $\Delta^{17}\mathrm{O} = \delta^{17}\mathrm{O} - 0.520\delta^{18}\mathrm{O}$, where the coefficient (here 0.520 has been determined from a replicate analysis of samples and standards) depends upon the atomic weight of the isotopes. Savarino et al. (2000) have shown that the oxygen-17 excess measured in atmospheric sulfate was the result of its aqueous oxidation chemistry. Ozone and hydrogen peroxide are two atmospheric oxidants known to present an oxygen-17 excess ($\Delta^{17}\mathrm{O} > 0$). During the oxidation of S^{IV} in the aqueous phase by these two oxidants, the Δ^{17}O of the oxidant is transferred to the produced sulfate. The oxidation of sulfur by OH radicals in the gas phase does not generate any oxygen-17 excess. The quantification of Δ^{17}O in atmospheric sulfate is therefore a means to explore the relative contributions of wet and dry chemistry in the sulfate budget. In view of the inherent problems attached to global sulfur cycle models in reproducing atmospheric sulfate concentrations, this new analytical tool has the potential to test the chemical codes of these models. As is the case for oxygen isotopes, sulfur isotopes also have the potential to resolve the origin of sulfate aerosols (Calhoun et al., 1991; Patris et al., 2000; Saltzman et al., 1983; Tanaka et al., 1994; Thode, 1991; Wadleigh et al., 1996). Sulfur has four stable isotopes (^{32}S, ^{33}S, ^{34}S, ^{36}S) which are also (in atmospheric species) strongly correlated to each other in a mass-dependent way, i.e. $\delta^{33}\mathrm{S} \approx 0.52\delta^{34}\mathrm{S}$ and $\delta^{36}\mathrm{S} \approx 1.9\delta^{34}\mathrm{S}$. Recently, laboratory experiments have shown that deviation from these correlations can be obtained in the UV photolysis of $\mathrm{SO_2}$ (Farquhar et al., 2001), with the mass-independent isotopic composition for sulfur defined as $\Delta^{33}\mathrm{S} = \delta^{33}\mathrm{S} - 0.515\delta^{34}\mathrm{S}$, and $\Delta^{36}\mathrm{S} = \delta^{36}\mathrm{S} - 1.91\delta^{34}\mathrm{S}$.

In an attempt to better understand the sulfur and oxygen isotope anomalies observed in atmospheric species, we investigated the isotopic composition of primary sulfates produced by biomass and car combustions during controlled field experiments. On a global scale, primary sulfate produced by combustion sources (i.e. fossil-fuel combustion and biomass burning) is only a minor source of sulfate in the atmosphere: ~3% of the global sulfur emissions (Seinfeld and Pandis, 1998). However, close to these sources, primary sulfate from combustion can locally contribute to a significant portion of atmospheric sulfate (20–30%) (Holt et al., 1982). Therefore, the isotopic composition of this primary sulfate and a knowledge of its role with respect to the mass-independent anomaly observed in atmospheric aerosol/rain sulfate could provide an important insight for an understanding of the sulfur atmospheric cycle.

2. Experimental

Field experiments were conducted at the Centre de Recherches Atmosphériques in Lannemezan (France) in a dark chamber specially designed to study aerosol and gas emissions from fuel combustion (Van Dinh et al., 1996). This chamber has a volume of $\sim 160\ \mathrm{m}^3$ ($10 \times 4 \times 4\ \mathrm{m}^3$) and has ventilation for smoke homogenization. Measurements of $\mathrm{CO_2}$ or total suspended particulates (TSP) showed that the chamber was homogenized within 1 min, and leaks were negligible for a time period beyond 30 min. A few holes present in the walls of the chamber allow probes to be fed inside. Collections are done in the dark. Various types of vegetation (savanna grass, hay, and rice straw) were combusted in a fireplace which had a vent connected to an adjacent chamber where total aerosols were collected on glass filters using a high-volume aerosol sampler. Controlled amounts of vegetation were burned in the fireplace. The control of oxygen supply allows smoldering and flaming combustions. In addition to vegetation burning, we also sampled diesel smoke out of the exhaust pipe of an automobile engine directly connected to the aerosol chamber.

An experiment of charcoal burning open to the outside air was also conducted at the University of California — San Diego (UCSD). Commercial charcoal was used as a non-flaming biomass source. About 8–10 charcoal briquettes were ignited in a portable grill without the use of igniting fluid, but using a fan blowing air. The burning temperature of the charcoal was raised to ~870 °C. A high-volume air sampler was placed at the downwind position adjacent (~0.3 m) to the grill, and TSP from smoke-filled air generated by charcoal combustion was collected for about an hour. Interference from atmospheric sulfate aerosols from other sources is virtually negligible considering the short total time of collection.

To study the isotopic composition of primary sulfate emitted by vehicles engines, the TSP were also collected on the roof of a five-story apartment building in Paris 13th, France. Another aerosol collection was performed close to the ring highway surrounding Paris. The former actually represents an urban environment (mostly influenced by traffic) whereas the latter portrays primary traffic emission environment. Details of the samples analyzed are display in Table 1.

All TSP samples from combustion were collected on a quartz fiber filter (20 × 25 cm) for ~30 min at 1.2 $m^3\,min^{-1}$, and sent to the isotope laboratory in California. Filters were soaked in ~50 mL of Millipore water (double deionized). After shaking, centrifugation, filtration on a bed of activated carbon, evaporation and acidification, water-soluble sulfate was precipitated as barite ($BaSO_4$) by adding saturated $BaCl_2$ solution. Blank filters collected in the dark chamber in the absence of combustion exhibited no quantifiable amounts of barite. $BaSO_4$ samples were subsequently converted into CO_2 and BaS following the procedure described by (Mizutani, 1971). CO_2 was ultimately converted into O_2 (Bhattacharya and Thiemens, 1989). Sulfur was quantitatively recovered as barium sulfide (BaS) from the reduction of barite by graphite (Rafter, 1957a; Rafter, 1957b). Sulfur was then converted into Ag_2S at the end of chemical separation and finally to SF_6 for isotopic measurements (Gao and Thiemens, 1991). $\delta^{17}O$, $\delta^{18}O$, $\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$ were measured on O_2 and SF_6, respectively. Analytical precision as determined from replica standard analysis was ±0.5‰, ±0.2‰ and 0.1‰ for, respectively, $\delta^{18}O$, $\delta^{17}O$ and $\Delta^{17}O$, and ±0.02‰, ±0.05‰, ±0.1‰, ±0.01‰ and ±0.5‰ for, respectively, $\delta^{33}S$, $\delta^{34}S$, $\delta^{36}S$, $\Delta^{33}S$ and $\Delta^{36}S$. All isotopic data are reported in standard δ notation with respect to SMOW for oxygen isotopes and to CDT (Canyon Diablo Troilite) for sulfur isotopes.

3. Results

3.1. Oxygen isotopes

Figure 1 displays the isotopic composition of primary sulfates generated from biomass and fuel burning on a three-oxygen isotope diagram. $\delta^{18}O$ values of combustion sulfate range from 5.5 to 10.5‰. Despite the large variation in $\delta^{18}O$, the multiple oxygen isotopic measurements indicate

Table 1. *Experimental parameters and oxygen and sulfur isotopic ratios obtained for different kinds of fuel and combustion processes*

Materials	Burning stage	Amount of sulfate (μmol)	$\delta^{18}O$ (‰) SMOW	$\delta^{17}O$ (‰) SMOW	$\Delta^{17}O$ (‰)	$\delta^{33}S$ (‰) CDT	$\delta^{34}S$ (‰) CDT	$\delta^{36}S$ (‰) CDT	$\Delta^{33}S$ (‰)	$\Delta^{36}S$[a] (‰)
Mixture savanna grass	Flaming	4.9	9.8	5.0	−0.1	5.90	11.84	22.2	−0.13	0.4
Savanna grass	Flaming	6.3	9.9	5.3	0.1	7.60	14.75	27.6	0.08	0.4
Savanna grass	Smoldering	12.5	6.3	3.2	−0.1	8.07	15.99	28.7	−0.09	−0.8
Lamto grass	Flaming	6.5	6.9	3.6	0.0	7.99	15.70	30.1	−0.02	1.2
Rice straw	Flaming	10.7	10.5	5.5	0.0	4.68	9.55	17.0	−0.19	−0.5
Hay france	Flaming	23.1	7.6	3.8	−0.1	7.86	15.48	28.5	−0.04	0.0
Diesel fuel	Idle	4.6	7.3	4.0	0.2	6.83	13.28	24.7	0.06	0.3
Diesel fuel	Acceleration	16.5	5.5	2.7	−0.2	8.42	16.42	29.9	0.04	−0.3
Charcoal	n.a.	11.4	9.0	4.6	−0.0					
Paris 13th zone	n.a.	22.5	13.2	7.7	0.8					
Paris Ring Highway	n.a.	6.2	8.7	4.8	0.2					

[a] A slope of 1.84 has been used to calculate $\Delta^{36}S$.

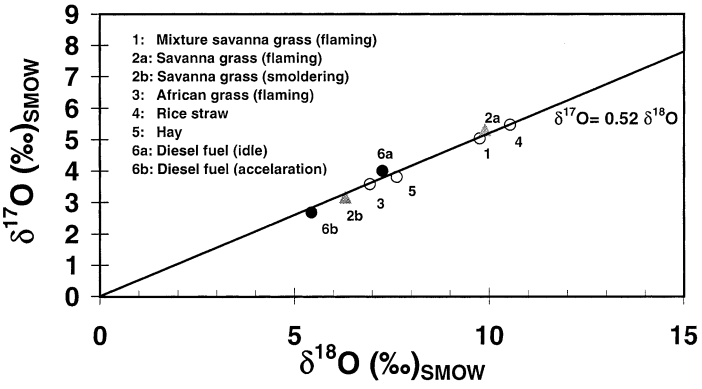

Fig. 1. Three-oxygen isotope diagram of aerosol sulfate from the biomass and diesel fuel combustion experiments. Savanna grasses are from Lamto (Ivory Coast, 5°02′W, 6°13′N), and were collected at sites distant from major anthropogenic activity. Experiments were conducted in Lannemezan, Pyrenees, France in a closed dark combustion chamber ($\sim 160\,m^3$). Analytical uncertainty are approximately the size of datum marks.

that they are all mass-dependently fractionated, $\Delta^{17}O = 0 \pm 0.1$‰. The good agreement of biomass combustion data with the previously determined mass-dependent fractionation line (Lee and Thiemens, 2001; Lee et al., 2001) demonstrates that during that type of combustion, no oxygen-17 excess is generated. Sulfate produced from smoldering (2b in Fig. 1) appears to be ~3.5‰ lighter in $\delta^{18}O$ than for flaming conditions (point 2a). Automobile combustion of diesel fuel also produced sulfate that has a mass-dependent isotopic composition, as illustrated by points 6a and 6b in Fig. 1. Similarly to the smoldering and flaming regimes, acceleration and idle regimes influence the oxygen isotopic composition of the primary sulfate, with the former depleted by ~2‰. Outdoor samples depict a distinctly different pattern (Fig. 2). The charcoal and highway samples are mass-dependent in isotopic composition, with $\delta^{18}O$ values identical to each other (9‰), and they are within the range of the chamber experiments. In contrast, the sulfate collected at the 'Paris 13th zone' possesses a significant oxygen-17 excess composition, in addition to a heavier $\delta^{18}O$ composition (13.2‰) than the previous samples.

3.2. *Sulfur isotopes*

In most studies, $\delta^{34}S$ alone is used to serve as a 'fingerprint' to identify sources of sulfur and trace its fate in the environment. However, the primary interest of this work is to determine whether the mass-independent signature is present in sulfur-stable isotopes or not. Sulfur-isotope ratio measurements of aerosol sulfate from the biomass combustion experiment demonstrates that they spread from 9.5 to 16.4‰ in $\delta^{34}S$ and possess mass-dependent isotopic compositions, regardless of material type. Figure 3 depicts a three-sulfur isotope diagram that correlates $\delta^{33}S$ and $\delta^{36}S$ against the common $\delta^{34}S$. The slope of the mass-dependent fractionation line for $\delta^{33}S/\delta^{34}S$ should be approximately 0.515 and for $\delta^{36}S/\delta^{34}S$, approximately 1.91 (Hulston and Thode, 1965; Xu, 1998). As shown, $\delta^{33}S/\delta^{34}S$ data of biomass combustion sulfate fit on the mass-dependent fractionation line, whereas $\delta^{36}S/\delta^{34}S$ data fit on a fractionation line with a slope of 1.84 and not 1.91 as recommended by Hulston and Thode (1965) on the basis of statistical-thermodynamic theory. This discrepancy between the experimental and theoretical slopes was also mentioned in a technical comment (Ohmoto et al., 2001). Our experimental slope is in perfect agreement with the slope found by Farquhar based on repetitive measurements of present-day geological samples (Ohmoto et al., 2001). We therefore assume no ^{36}S anomaly in our samples.

4. Discussion

The exact sulfate formation mechanism cannot be identified from this specific isotopic analysis.

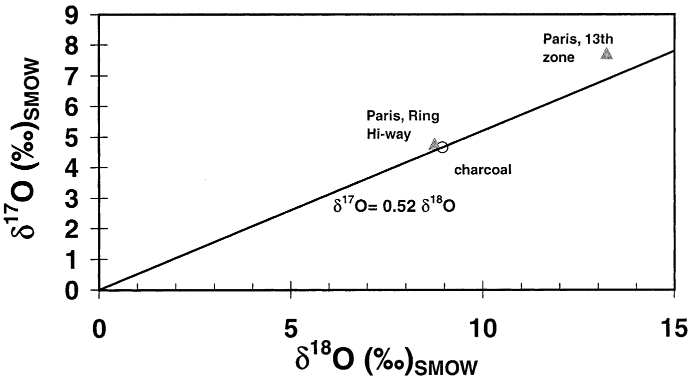

Fig. 2. Three-oxygen isotope diagram of aerosol sulfate from charcoal combustion experiments and urban city environment (Paris, France). The sample 'Paris 13th zone' has been collected on the roof of five-story apartment building and is the only sample showing significant ^{17}O excess. Analytical uncertainties are approximately the size of the datum marks.

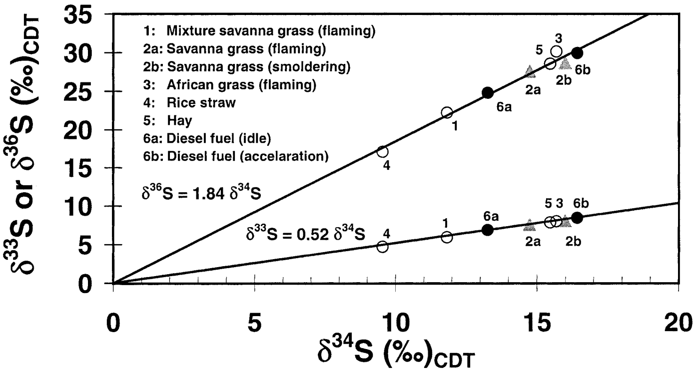

Fig. 3. Three-sulfur isotope diagram for aerosol sulfate from biomass and diesel fuel combustion experiments. Analytical uncertainties are approximately the size of the datum marks.

However, there is an abundant literature on sulfur-containing species oxidation in combustion reactions (Burdett et al., 1983; Flagan and Friedlander, 1978; Hulden and Astrom, 1973; Hunter, 1982; Squires, 1982; Tschinkel, 1972). These works were devoted principally to a study of the formation of SO_3 and salt sulfates in gas turbines and coal boilers in relation to their corrosive properties. Sulfur in the form of organic and inorganic compounds is inexorably converted into SO_2 in combustion processes, which is the predominant sulfur species in stack gases (Hunter, 1982). Formation occurs in the flame as part of the overall combustion reactions, and SO_2 forms at rates comparable to H_2O and faster than CO_2. The fast rate ensures nearly complete conversion of fuel sulfur into SO_2, even in fuel-rich conditions (e.g. smoldering). Radicals such as SO, S_2O, CS and S_2 have been identified as intermediates during this process (Cullis and Mulcahy, 1972). Sulfate is not directly formed in flames, due to its instability at high temperature. Rather, sulfate is produced downstream when the gas cools sufficiently. The initial step involves the formation of sulfur trioxide (SO_3). SO_3 may be formed by several reactions, but reactions involving direct O_2 attack on SO_2 have been shown to be very slow (Cullis and Mulcahy, 1972). The primary reaction leading to SO_3 production appears to be:

$$SO_2 + O + M \leftrightarrow SO_3 + M \qquad (1)$$

Since the concentration of oxygen atoms is much higher than its equilibrium value within the flame, SO_3 can reach few percent of the total sulfur species, well above thermodynamic equilibrium conditions (Flagan and Friedlander, 1978). It has also been suggested that catalytic oxidation of SO_2 on the surfaces of fly ash particles may enhance SO_3 production outside the flame zone (Flagan and Friedlander, 1978). When the combustion products are cooled below ~ 430 K, SO_3 co-condenses with water to form sulfuric acid droplets via (Lovejoy et al., 1996):

$$SO_3 + (H_2O)_2 \rightarrow H_2SO_4 + H_2O \qquad (2)$$

Alternatively, sulfur oxides may also react with alkaline or metal oxides to form sulfates (Krause et al., 1969). The mass-dependent characteristic of our combustion samples is consistent with the reaction scheme described above and the conclusions previously drawn (Savarino et al., 2000). Primary sulfate from combustion sources (vegetation, engine fuel and charcoals) thus does not contribute to the mass-independent anomaly observed in the oxygen isotopes of atmospheric aerosol sulfate. Methods of combustion may cause some fractionation in $\delta^{18}O$ depending on the temperature, but they do not produce a mass-independent isotope effect: they all produce strictly mass-dependent compositions. Although the types of vegetation and fuel used for this experiment do not include all possibilities, it is reasonable to state that they generally represent the emission sources of primary sulfate in the atmosphere. There is no obvious explanation of the wide spread of $\delta^{18}O$ values. It is possibly a consequence of dynamic conditions of the combustion, as suggested by smoldering/flaming and idle/acceleration experiments, which yield different $\delta^{18}O$ values for the same fuel type. Our relatively low $\delta^{18}O$ values (5.5–10.5‰) are somewhat surprising, as Holt and Kumar (1984) found that high-temperature air oxidation of SO_2 via SO_3 to sulfate in the presence of water vapor induces ^{18}O enrichment ($\sim$40‰) in the sulfate product. However, the relevance of their experiments, set up for the simulation of primary sulfate formation in combustion processes, is questionable. Indeed, the accumulation of SO_3 in their reaction vessel was obtained after many hours of reaction and only via metal catalysis (Pt, V_2O_5, Fe_2O_3). The difference in isotopic signature suggests that biomass combustion sulfate is formed via various mechanisms, probably different from those simulated by Holt and Kumar (1984).

Sulfate collected in Paris in two different environments supports the experimental results, as shown in Fig. 2. The 'Paris Ring Highway' sample represents sulfate collected on the highway surrounding Paris, where primary sulfate from combustion sources should dominate. The similar isotopic composition to the charcoal experiment and the mass-dependent characteristics of the Highway sample agree very well with the notion of a strong source strength of primary sulfate at this location. The 'Paris 13th zone' sample, on the contrary, possesses a significant mass-independent isotopic composition. This result suggests that a secondary source already dominates $\sim$20 m above the ground, as already postulated for secondary organic particles (Ruellan and Cachier, 2000). The mass-independent characteristics of this sample imply that some of the sulfate collected on the roof of the building has been produced by atmospheric aqueous phase oxidation, which is an expected result. In urban environments, where oxidants are not limited, oxidation rates of SO_2 of up to 30% h^{-1} have been reported (Hewitt, 2001). Greater contributions of mass-independent sulfate sources above Paris are therefore not surprising. It is noteworthy to underscore that the main characteristics of the air mass have been captured by the three-oxygen isotope measurements, thus further demonstrating the power of such isotopic measurements.

Sulfur isotopic analysis of biomass combustion sources does not reveal any isotopically anomalous results. This result is expected. Indeed, at present, only photolysis of SO_2 (Farquhar et al., 2001), photopolymerization of CS_2 (Colman et al., 1996), and non-thermal formation of S_2F_{10} (Bains-Sahota and Thiemens, 1989) have been shown to produce mass-independent composition in sulfur isotopes. All of these processes are irrelevant to our present study and in general atmospheric conditions. All $\delta^{34}S$ values fall in the range observed in tropospheric aerosol sulfates (Newman et al., 1991) and the range observed is probably due to sulfur fractionation associated with a combination of plant sulfur fixation and burning dynamics.

5. Conclusions

Burning of savanna grass, hay and rice straw, which represent a major combustion source on a global scale, indicates that primary sulfate aerosols generated from combustion are strictly mass-dependent in oxygen and sulfur isotopes. In addition, sulfate aerosols derived from combustion of fossil fuels (diesel) and charcoals were isotopically analyzed, and the results show that they also display mass-dependent oxygen isotopic compositions. Ambient sulfate aerosols collected close to potentially strong primary sulfate sources (Paris, Highway) have no oxygen isotopic anomalies, as opposed to those collected above an urban city (Paris). These observations support the experimental results that fossil-fuel combustion generated primary sulfate is mass-dependently fractionated in oxygen isotopes, as the strength of fossil-fuel combustion dominates near the Paris Highway as opposed to central Paris. Sulfur isotopic analysis of sulfate aerosols produced from these experiments was also performed. Although a limited number of material types are burned, the results of these experiments suggest that primary sulfate aerosols generated from biomass-burning activities are strictly mass-dependent in oxygen isotopes, and thus do not contribute to the mass-independent oxygen anomaly found in ambient atmospheric sulfate.

6. Acknowledgements

NATO is gratefully acknowledged for financial support (grant no. CRG 961154). The Atmospheric Chemistry Division of the National Science Foundation also supported a portion of the research. We also thank the CRA (Lannemezan) staff and particularly Dr. Pham Van Dinh for the aerosol collections and for access to the combustion chamber facility. We thank the two reviewers for their constructive criticisms.

REFERENCES

Bains-Sahota, S. K. and Thiemens, M. H. 1989. A mass-independent sulfur isotope effect in the nonthermal formation of sulfur fluoride (S_2F_{10}). *J. Chem. Phys.* **90**, 6099–6109.

Bhattacharya, S. K. and Thiemens, M. H. 1989. New evidence for symmetry dependent isotope effect: $O + CO$ Reaction. *Z. Naturforcsh., Teil A* **44A**, 435–444.

Burdett, N. A., Gliddon, B. J., Hotchkiss, R. C. and Squires, R. T. 1983. Sulfur trioxide in coal-fired fluidized-bed combustors. *J. Inst. Energy* **56**, 119–124.

Calhoun, J. A., Bates, T. S. and Charlson, R. J. 1991. Sulfur isotope measurements of submicrometer sulfate aerosol particles over the Pacific ocean. *Geophys. Res. Lett.* **18**, 1877–1880.

Chuang, C. C., Penner, J. E., Taylor, K. E., Grossman, A. S. and Walton, J. J. 1997. An assessment of the radiative effects of anthropogenic sulfate. *J. Geophys. Res.* **102**, D3, 3761–3778.

Colman, J. J., Xu, X. P., Thiemens, M. H. and Trogler, W. C. 1996. Photopolymerization and mass-independent sulfur isotope fractionations in carbon disulfide. *Science* **273**, 774–776.

Cullis, C. F. and Mulcahy, M. F. R. 1972. Kinetics of combustion of gaseous sulfur compounds. *Combust. Flame* **18**, 225–292.

Farquhar, J., Savarino, J., Airieau, S. and Thiemens, M. H. 2002. Observation of wavwlength-sensitive mass-independent sulfur isotope effects during SO_2 photolysis: application to the early atmosphere. *J. Geophys. Res.*, 106 E12, 32829–32840.

Feichter, J., Kjellström, E., Rodhe, H., Dentener, F., Lelieveld, J. and Roelofs, G. J. 1996. Simulation of the tropospheric sulfur cycle in a global climate model. *Atmos. Environ.* **30**, 1693–1707.

Flagan, R. C. and Friedlander, S. K. 1978. Particle formation in pulverized coal combustion — a review. In: *Recent developments in aerosol science* (ed. D. T. Shaw). Wiley & Sons, New York, 25–59.

Gao, X. and Thiemens, M. H. 1991. Systematic study of sulfur isotopic composition in iron meteorites and the occurence of excess ^{33}S and ^{36}S. *Geochim. Cosmochim. Acta* **55**, 2671–2679.

Hewitt, C. N. 2001. The atmospheric chemistry of sulphur and nitrogen in power station plumes. *Atmos. Environ.* **35**, 1155–1170.

Holt, B. D. and Kumar, R. 1984. Oxygen-18 study of high-temperature air oxidation of SO_2. *Atmos. Environ.* **18**, 2089–2094.

Holt, B. D., Kumar, R. and Cunningham, P. T. 1982. Primary sulfates in atmospheric sulfates: estimation by oxygen isotope ratio measurements. *Science* **217**, 51–53.

Hulden, B. and Astrom, L. 1973. Sulfate formation in magnesium sulfite-spent liquor fired boilers. *Tappi* **56**, 84–86.

Hulston, J. R. and Thode, H. G. 1965. Variations in the ^{33}S, ^{34}S, and ^{36}S contents of meteorites and their relations to chemical and nuclear effects. *J. Geophys. Res.* **70**, 3475–3484.

Hunter, S. C. 1982. Formation of sulfur trioxide in gas turbines. *J. Eng. Power* **104**, 44–51.

Kasibhatla, P., Chameides, W. L. and St. John, J. 1997. A three-dimensional global model investigation of seasonal variations in the atmospheric burden of anthropogenic sulfate aerosols. *J. Geophys. Res.* **102**, D3, 3737–3759.

Kiehl, J. T., Schneider, T. L., Rasch, P. J., Barth, M. C. and Wong, J. 2000. Radiative forcing due to sulfate aerosols from simulations with the National Center for Atmospheric Research Community Climate Model, Version 3. *J. Geophys. Res.* **105**, D1, 1441–1457.

Koch, D., Jacob, D., Tegen, I., Rind, D. and Mian, C. 1999. Tropospheric sulfur simulation and sulfate direct radiative forcing in the Goddard Institute for Space Studies general circulation model. *J. Geophys. Res.* **104**, D19, 23,799–23,822.

Krause, H. H., Levy, A. and Reid, W. T. 1969. Radioactive sulfur oxide studies of external corrosion reactions on surfaces. *J. Eng. Power* **91**, 216–222.

Lee, C. C.-W. and Thiemens, M. H. 2001. δ^{17}O and δ^{18}O measurement of atmospheric sulfate from a coastal and high alpine region: a mass independent isotopic anomaly. *J. Geophys. Res.* **106**, D15, 17,359–17,374.

Lee, C. C.-W., Savarino, J. and Thiemens, M. H. 2001. Mass independent isotopic composition of atmospheric sulfate: origin and implications for the present and past atmosphere of Earth and Mars. *Geophys. Res. Lett.* **28**, 1783–1786.

Lelieveld, J., Roelofs, G. J., Ganzeveld, L., Feichter, J. and Rodhe, H. 1997. Terrestrial sources and distribution of atmospheric sulfur. *Philos. Trans. R. Soc. London, Ser. B* **352**, 149–158.

Lovejoy, E. R., Hanson, D. R. and Huey, L. G. 1996. Kinetics and products of the gas-phase reaction of SO_3 with water. *J. Phys. Chem.* **100**, 19,911–19,916.

Mizutani, Y. 1971. An improvement in the carbon-reduction method for the oxygen isotopic analysis of sulphates. *Geochem. J.* **5**, 69–77.

Newman, L., Krouse, H. R. and Grinenko, V. A. 1991. *Sulphur isotope variation in the atmosphere, in stable isotopes: natural and anthropogenic sulphur in the environment* (eds. H. R. Krouse and V. A. Grinenko). John Wiley & Sons, New York, 131–176.

Ohmoto, H., Yamaguchi, K. E., Ono, S., Farquhar, J., Bao, H., Thiemens, M. H., Hu, G. and Rumble III, D. 2001. Questions regarding precambrian sulfur isotope fractionation. *Science* **292**, 1959.

Pan, W., Tatang, M. A., McRae, G. J. and Prinn, R. G. 1998. Uncertainty analysis of indirect radiative forcing by anthropogenic sulfate aerosols. *J. Geophys. Res.* **103**, D4, 3815–3823.

Patris, N., Mihalopoulos, N., Baboukas, E. D. and Jouzel, J. 2000. Isotopic composition of sulfur in size-resolved marine aerosols above the Atlantic Ocean. *J. Geophys. Res.* **105**, D11, 14,449–14,457.

Rafter, T. A. 1957a. Sulphur isotopic variations in nature. Part 1 — the preparation of sulphur dioxide for mass spectrometer examination. *N. Z. J. Sci. Technol.* **B38**, 849–857.

Rafter, T. A. 1957b. Sulphur isotopic variations in nature. Part 2 — a quantitaive study of the reduction of barium sulphate by graphite for recovery of sulphide-sulphur for sulphur isotopic measurement. *N. Z. J. Sci. Technol.* **B38**, 955–968.

Rasch, P. J., Barth, M. C., Kiehl, J. T., Schwartz, S. E. and Benkovitz, C. M. 2000. A description of the global sulfur cycle and its controlling processes in the National Center for Atmospheric Research Community Climate Model, Version 3. *J. Geophys. Res.* **105**, D1, 1367–1385.

Rodhe, H. 1999. Human impact on the atmospheric sulfur balance. *Tellus* **51B**, 110–122.

Ruellan, S. and Cachier, H. 2000. Characterisation of fresh particulate vehicular exhausts near a Paris high flow road. *Atmos. Environ.* **35**, 453–468.

Saltzman, E. S., Brass, G. W. and Price, D. A. 1983. The mechanism of sulfate aerosol formation: chemical and sulfur isotopic evidence. *Geophys. Res. Lett.* **10**, 513–516.

Savarino, J., Lee, C. C.-W. and Thiemens, M. H. 2000. Laboratory oxygen isotopic study of sulfur(IV) oxidation: origin of the mass independent oxygen isotopic anomaly in atmospheric sulfates and other sulfate mineral deposits. *J. Geophys. Res.* **15**, D23, 29,079–29,089.

Seinfeld, J. H. and Pandis, S. N. 1998. *Atmospheric chemistry and physics.* John Wiley & Sons, New York, 1326 pp.

Squires, R. T. 1982. The kinetics of sulfur trioxide formation in oil-fired boilers. *J. Inst. Energy* **55**, 41–46.

Tanaka, N., Rye, D. M., Xiao, Y. and Lasaga, A. C. 1994. Use of stable sulfur isotope systematics for evaluating oxidation reaction pathways and in-cloud scavenging of sulfur dioxide in the atmosphere. *Geophys. Res. Lett.* **21**, 1519–1522.

Thiemens, M. H. 1999. Mass-independent isotope effects in planetary atmospheres and the solar system. *Science* **283**, 341–345.

Thode, H. G. 1991. Sulphur isotopes in nature and the environment: an overview. In: *Stable isotopes: natural and anthropogenic sulphur in the environment* (eds. H. R. Krouse and V. A. Grimenko). John Wiley & Sons, New York, 1–21.

Tschinkel, J. G. 1972. Formation of sodium sulfate in gas turbine combustors. *Corrosion* **28**, 161–169.

Van Dinh, P., Serpolay, R. and Lacaux, J. P. 1996. Laboratory investigations on aerosols from the combustion of savanna grass and cereal straw. In: *Biomass burning and global change* (ed. J. L. Levine). MIT Press, Cambridge, MA, 472–484.

van Dorland, R., Dentener, F. J. and Lelieveld, J. 1997. Radiative forcing due to tropospheric ozone and sulfate aerosols. *J. Geophys. Res.* **102**, D23, 28,079–28,100.

Wadleigh, M. A., Schwarcz, H. P. and Kramer, J. R. 1996. Isotopic evidence for the origin of sulphate in coastal rain. *Tellus* **48B**, 44–59.

Xu, X. 1998. *Mass independent isotopic fractionation in solid phase.* Ph.D. Dissertation, University of California, San Diego.