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Isotopic constraints on non-photochemical sulfate production in the Arctic winter

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[1] The oxygen isotopic composition ($\Delta^{17}\text{O}$) of non-seasalt sulfate (NSS) aerosol was measured in samples from Alert, Canada over one year (July 1999–June 2000) and used to quantify the S(IV) oxidants. Measurements of $\Delta^{17}\text{O}$ in NSS are used to evaluate the relative contributions of O_3 , H_2O_2 , and OH oxidation leading to the formation of SO_4^{2-} compared to a model of Feichter et al. (1996). The isotopic values suggest that there is a twofold overestimate of ozone oxidation in the model during winter. The isotopic composition is consistent with 10 to 18% contribution from a non-photochemical oxidation pathway, likely $\text{Fe}^{3+}/\text{Mn}^{2+}$ -catalyzed O_2 oxidation, during the dark Arctic winter. Isotopic evidence also invokes a 3 to 10% contribution of a mass dependent oxidant during springtime Arctic ozone depletion events. **Citation:** McCabe, J. R., J. Savarino, B. Alexander, S. Gong, and M. H. Thiemens (2006), Isotopic constraints on non-photochemical sulfate production in the Arctic winter, *Geophys. Res. Lett.*, 33, L05810, doi:10.1029/2005GL025164.

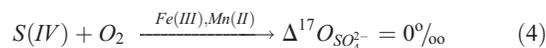
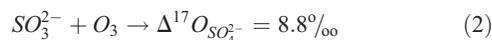
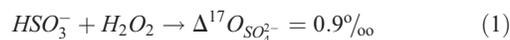
1. Introduction

[2] Alert, Canada (82.5°N, 62.3°W) provides a setting where unique meteorology and chemistry have been evoked to explain the annual presence of “Arctic Haze.” Arctic haze consists primarily of fine sulfate aerosol accumulating in the winter from distant pollution sources (primarily Eurasia and to a lesser extent North America) [Barrie et al., 1989; Sirois and Barrie, 1999] and manifests a mechanism for surface ozone destruction with the return of sunlight in the spring [Barrie et al., 1988; Bottenheim et al., 1990]. While the source of the haze is understood, questions remain regarding the chemical processes controlling sulfate formation. Most model studies overestimate (underestimate) SO_2 (SO_4^{2-}) by a factor of 1.5 to 2.5 compared with observations in the Arctic region [Berglen et al., 2004; Chin et al., 2000b; Feichter et al., 1996]. The possibility of a missing sink for S(IV) has been suggested and includes wet and dry deposition of SO_2 and/or an

overlooked oxidation pathway of SO_2 to sulfate. This study presents a methodology to quantify the oxidation pathways controlling the conversion of S(IV) to S(VI) based upon the multi-oxygen isotopic composition of sulfate.

[3] Chemical tracer studies [Akeredolu et al., 1994; Barrie et al., 1989] and sulfur isotope measurements ($\delta^{34}\text{S}$) have been utilized for studying the source of sulfate aerosol in the Arctic and have revealed high seasonal variability [Norman et al., 1999; Nriagu et al., 1991]. During the winter months, transport of anthropogenic sulfate from fossil fuel and coal burning are the primary sources while during summer, biogenic sources such as DMS oxidation dominate. No study, however, has investigated the chemical formation of Arctic sulfate aerosol using oxygen isotopes ($\delta^{18}\text{O}$, $\delta^{17}\text{O}$).

[4] Sulfate aerosols collected from a variety of environments have been observed to possess a mass-independent oxygen isotopic composition ($\Delta^{17}\text{O} \neq 0$) [Lee and Thiemens, 2001; Alexander et al., 2005]. Mass dependent fractionation is approximated by the linear relationship $\delta^{17}\text{O} = 0.52 \times \delta^{18}\text{O}$. Mass-independent fractionation (MIF) is any deviation from this relationship and is expressed by $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ [Thiemens, 1999], with $\Delta^{17}\text{O} = 0$ for a mass dependent process. Two of the main heterogeneous S(IV) oxidants, O_3 ($\Delta^{17}\text{O} = 35\text{‰}$) and H_2O_2 ($\Delta^{17}\text{O} = 1.8\text{‰}$), have distinct mass independent compositions in the atmosphere [Savarino and Thiemens, 1999; Johnston and Thiemens, 1997; Krankowsky et al., 1995]. In contrast, OH and O_2 in the atmosphere have $\Delta^{17}\text{O} \approx 0\text{‰}$ [Lyons, 2001; Luz et al., 1999]. In the laboratory, Savarino et al. [2000] demonstrated that the origin of mass independent sulfate is a result of oxygen atom transfer by H_2O_2 and O_3 during oxidation, while gas phase OH oxidation and aqueous-phase metal-catalyzed O_2 oxidation produce mass dependent sulfate ($\Delta^{17}\text{O} = 0$). The product sulfate has a different $\Delta^{17}\text{O}$ value depending on the oxidation pathway according to [Savarino et al., 2000]:



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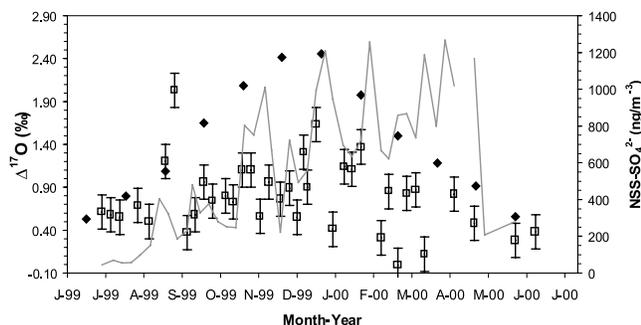


Figure 1. Non seasalt- SO_4^{2-} concentrations at Alert, Canada (82.5°N , 62.3°W) from July 1999– June 2000 in ng m^{-3} are plotted on the right axis (grey line). $\Delta^{17}\text{O}$ -NSS from measurements (open squares) at Alert, Canada and from monthly estimates of sulfur chemistry in a model (solid diamonds) [Feichter *et al.*, 1996] are plotted on the left axis.

The $\Delta^{17}\text{O}$ value of sulfate in the atmosphere ranges from 0 – 8.8‰ and is dependent upon the relative importance of each oxidant controlling its formation.

2. Experimental

[5] Samples were collected from July 1999 – June 2000 at Alert, Canada (82.5°N , 62.3°W) on $20\text{ cm} \times 25\text{ cm}$ Whatman 41 cellulose fiber filters using a high-volume sampler according to the methods of Sirois and Barrie [1999]. Ion concentrations measurements were conducted at the University of Ontario, Canada, via ion chromatography. ICP-MS measurements of elemental iron and manganese were also conducted at the University of Ontario. One quarter of the filter was sent to UC San Diego for isotopic analysis. Oxygen isotope measurements ($\delta^{17}\text{O}$, $\delta^{18}\text{O}$) were carried out at weekly resolution according to the methods of Savarino *et al.* [2001]. Chemical separation was conducted on a Dionex AS9-HC column to isolate the sulfate ion. Conversion to silver sulfate (Ag_2SO_4) was performed with a Dionex AMMS-III suppressor column using 2.5 mM Ag_2SO_4 as the regenerant. Oxygen produced via combustion of Ag_2SO_4 salts at 1050°C was analyzed for isotopic ratios using a Finnigan MAT 251 multiple-collector isotope-ratio mass spectrometer. Corrections for primary seasalt sulfate were made using Na^+ concentrations provided by the University of Ontario according to the relationship $\text{NSS} = \text{SO}_4^{2-} - 0.25 \times \text{Na}^+$ [Calhoun *et al.*, 1991]. The average sea salt contribution in our samples was $\sim 8\%$ in accordance with the results of Sirois and Barrie [1999]. The precision of the $\Delta^{17}\text{O}$ measurements is $\pm 0.3\%$.

3. Results and Discussion

[6] The rise in sulfate concentrations characteristic of “Arctic Haze” from Alert, Canada [Sirois and Barrie, 1999] is present in our record from 1999–2000 and shown in Figure 1. Summer/fall (June to September) concentrations ranged between 35 to 207 ng m^{-3} while winter/spring (October to May) concentrations reached up to 1267 ng m^{-3} . Figure 1 also shows the oxygen isotopic composition from this year-long record of sulfate. The overall variability of $\Delta^{17}\text{O}$ -NSS is -0.1 to 2.1% throughout

the year. From April to August, the $\Delta^{17}\text{O}$ of NSS aerosol varies between 0.3 and 0.9% . During winter, a larger range in $\Delta^{17}\text{O}$ is present with values as high as 1.7% in December and as low as 0.4% in January.

[7] In order to evaluate the significance of our isotope results, we calculate the expected $\Delta^{17}\text{O}$ -NSS from a chemical model. Feichter *et al.* [1996] present a model of the global sulfur burden using on-line calculations of transport, dry and wet deposition and chemistry based on the ECHAM3 global 3D chemical transport model. DMS, SO_2 , and SO_4^{2-} are treated as prognostic variables. Removal processes include dry and wet deposition, including in-cloud and below-cloud processing. Gas-phase oxidant concentrations necessary for SO_2 and DMS oxidation are those proposed by Dentener and Crutzen [1993] for H_2O_2 and Roelofs and Lelieveld [1995] for OH, NO_2 , and O_3 . Aqueous-phase oxidation of SO_2 depends on temperature and pH, which influence the uptake of SO_2 by clouds and the oxidation rate of O_3 . In the model, pH is calculated and ranges between 3 to 5 according to $[\text{H}^+] = 2[\text{SO}_4^{2-}] + [\text{HSO}_3^-] + [\text{NH}_4^+]$. The oxidation rate of sulfur is simplified to consider only $[\text{S(IV)}] = [\text{HSO}_3^-]$. They present the monthly mean estimates of O_3 , H_2O_2 , and OH oxidation of S(VI) to S(VI) in Tg S over the course of one year for the northern hemisphere above 40°N .

[8] Based on their results, we calculate the monthly average $\Delta^{17}\text{O}$ -NSS using a simple mass balance approach according to the following equation:

$$\Delta^{17}\text{NSS}_{\text{model}} = \Delta^{17}\text{NSS}_{\text{OH}} * f_{\text{OH}} + \Delta^{17}\text{NSS}_{\text{O}_3} * f_{\text{O}_3} + \Delta^{17}\text{NSS}_{\text{H}_2\text{O}_2} * f_{\text{H}_2\text{O}_2} \quad (5)$$

where $\Delta^{17}\text{NSS}_{\text{OH}} = 0\%$, $\Delta^{17}\text{NSS}_{\text{O}_3} = 8.8\%$, and $\Delta^{17}\text{NSS}_{\text{H}_2\text{O}_2} = 0.9\%$ and f represents the fraction of S(IV) oxidation by OH, O_3 , and H_2O_2 . The results are presented in Figure 1 and Table 1. Solving equation 5 results in $\Delta^{17}\text{NSS}_{\text{model}}$ values of 0.4% in mid summer and 2.5% in mid-winter, as a result of a shift in the oxidation pathway from OH in summer to O_3 in winter.

[9] During summer months (June through September), the model accurately approximates (within 2%) the $\Delta^{17}\text{O}$ -NSS. From October through May, the model over-predicts $\Delta^{17}\text{O}$ by a factor of 1.5 to 2.5, suggesting an overestimate of the contribution of mass independent oxidants (O_3 and H_2O_2) by the model during winter (Figure 1). A maximum of 5% primary sulfate ($\Delta^{17}\text{O} = 0$) [Lee *et al.*, 2002] associated with smelters and coal combustion coming from long-range transport [Chin *et al.*, 2000a], is insufficient to reconcile differences between the modeled and observed isotope values and demands consideration of a mass dependent oxidant ($\Delta^{17}\text{O} = 0$) during winter. Based on the assumption that the model correctly accounts for H_2O_2 and OH oxidation, we use the following mass balance equations to recalculate the fraction of ozone oxidation (f_{O_3}) and the previously unaccounted for mass dependent fraction (f_{MD}) based on $\Delta^{17}\text{O}$ -NSS obtained from monthly averages of our measurements:

$$\Delta^{17}\text{NSS}_{\text{model}} = \Delta^{17}\text{NSS}_{\text{OH}} * f_{\text{OH}} + \Delta^{17}\text{NSS}_{\text{O}_3} * f_{\text{O}_3} + \Delta^{17}\text{NSS}_{\text{H}_2\text{O}_2} * f_{\text{H}_2\text{O}_2} + \Delta^{17}\text{NSS}_{\text{MD}} * f_{\text{MD}} \quad (6)$$

$$f_{\text{O}_3} + f_{\text{OH}} + f_{\text{H}_2\text{O}_2} + f_{\text{MD}} = 1 \quad (7)$$

Table 1. Monthly $\Delta^{17}\text{O}$ -NSS Measured in Aerosol Collected at Alert, Canada, Between July 1999 and June 2000 ($\Delta^{17}\text{O}$ -data) and Calculated Based on the Model by Feichter *et al.* [1996] ($\Delta^{17}\text{O}$ -model)^a

Month	$\Delta^{17}\text{O}$ -Data	$\Delta^{17}\text{O}$ -Model	$f\text{-O}_3$ -Data	$f\text{-O}_3$ -Model	$f\text{-H}_2\text{O}_2$	$f\text{-OH}$	$f\text{-MD}$
January	1.1	2.6	0.06	0.23	0.74	0.03	0.17
February	1.3	2.0	0.08	0.16	0.79	0.05	0.08
March	0.6	1.5	-0.01	0.09	0.82	0.09	0.10
April	0.5	1.0	-0.02	0.04	0.82	0.13	0.06
May	0.5	0.8	-0.01	0.02	0.73	0.24	0.03
June	0.4	0.4	-0.01	0.00	0.56	0.44	0.01
July	0.6	0.4	0.02	0.00	0.53	0.47	-0.02
August	0.6	0.7	0.02	0.03	0.56	0.41	0.01
September	1.1	1.0	0.07	0.06	0.65	0.29	-0.01
October	0.8	1.6	0.02	0.12	0.76	0.12	0.10
November	1.1	2.1	0.05	0.17	0.80	0.03	0.12
December	1.0	2.5	0.05	0.22	0.75	0.03	0.18

^aThe fractions of H_2O_2 ($f\text{-H}_2\text{O}_2$), OH ($f\text{-OH}$), and O_3 ($f\text{-O}_3$ -model) oxidation responsible for sulfate formation are taken from the model. Using the modeled amount of H_2O_2 and OH oxidation, the contribution of O_3 ($f\text{-O}_3$ -data) and mass dependent ($f\text{-MD}$) oxidation are calculated from the isotopic composition of the NSS aerosol. See text for further details.

where $\Delta^{17}\text{NSS}_{\text{OH}}$ and $\Delta^{17}\text{NSS}_{\text{MD}} = 0$ [Savarino *et al.*, 2000]. Solving these two equations for f_{O_3} and f_{MD} yields $f_{\text{O}_3} = 5\text{--}8\%$ and $f_{\text{MD}} = 10\text{--}18\%$ during winter (Table 1.). In the Feichter *et al.* [1996] model, ozone oxidation of S(IV) increases in winter due to low OH and H_2O_2 concentrations. Hydrogen peroxide concentrations are an order of magnitude lower during winter (10–40 ppt) compared to summer (100–400 ppt) [de Serves, 1994], and OH production is limited in the Arctic winter due to the lack of sunlight. Modeled concentrations of OH above 40°N during winter are $<2.5 \times 10^5$ molecule cm^{-3} compared to $>5 \times 10^5$ molecules cm^{-3} during summer months [Berglen *et al.*, 2004]. Isotopic contributions from H_2O_2 and OH alone appear insufficient due to their extremely low concentrations in the Arctic winter, and another mass dependent oxidant is required.

[10] Given the isotopic requirement for a mass dependent oxidant of S(IV) in the polar winter, Fe/Mn oxidation is a likely candidate for two reasons. First, there is no other oxidation pathway that occurs at appreciable rates in the dark Arctic winter. Second, the large intrusion of Eurasian air masses in winter contributes high concentrations of trace metals [Akeredolu *et al.*, 1994]. Iron and manganese in the liquid phase are known to catalyze oxidation of S(IV) to S(VI) via O_2 [Ibusuki and Takeuchi, 1987; Martin and Good, 1991]. Despite cold temperatures, this reaction may proceed on ice surfaces based on solute freeze-concentration effects [Gross *et al.*, 1975] and evidence of efficient adsorption and aqueous oxidation of SO_2 on ice surfaces down to -60°C [Conklin *et al.*, 1993]. During the winter of 1999–2000, Fe concentrations averaged 79 ng m^{-3} while Mn concentrations averaged 1.6 ng m^{-3} , more than double the summer averages of 33 ng m^{-3} and 0.7 ng m^{-3} , respectively. Assuming that a significant fraction of these metals are available as dissolved Fe(III) and Mn(II) to catalyze O_2 oxidation of S(IV), this is the most likely sulfate production pathway that could proceed in the northern hemisphere winter without photochemistry, and can account for the observed $\Delta^{17}\text{O}$ values.

[11] The Feichter *et al.* [1996] model also overestimates sulfate $\Delta^{17}\text{O}$ -NSS during the spring, when additional photochemical reactions cannot be discounted. The low sulfate $\Delta^{17}\text{O}$ values in spring could be the result of decreased ozone concentrations, increased OH production, and/or another mass dependent heterogeneous S(IV) oxidant. Surface

ozone depletions from February to May 2000 obtained from the Environmental Services of Canada coincide with the lowest measured $\Delta^{17}\text{O}$ -NSS values ($-0.1\text{--}0.2\text{‰}$) (Figure 2). In the Feichter *et al.* model, ozone oxidation accounts for 2–9% of sulfate production during spring and does not consider ozone depletion events during the Arctic sunrise. Increased OH production during spring resulting from HONO production during snowpack photolysis contributes to OH concentrations as high as 1.1×10^6 molecules cm^{-3} over Alert, Canada [Zhou *et al.*, 2001]. Elevated levels of photo-available halogens (up to 100 pptv Cl_2 and 38 pptv Br_2) also occur during the springtime polar sunrise [Impey *et al.*, 1997] with levels of BrO reaching 20 to 30 pptv during ozone depletion events [Honninger and Platt, 2002]. Vogt *et al.* [1996] suggest that HOBr and HOCl respectively contribute 20–40% of S(IV) oxidation in spring. Halogen S(IV) oxidation does not transfer the oxygen from the halogen compound, but rather promotes the hydrolysis of aqueous sulfite [Fogelman *et al.*, 1989], leading to an expected sulfate $\Delta^{17}\text{O} = 0\text{‰}$. The above three processes are not accounted for in the Feichter *et al.* model, and are all consistent with sulfate oxygen isotope measurements presented here.

4. Conclusions

[12] Oxygen isotope measurements reveal the importance of a mass dependent oxidant in the Arctic winter. It is

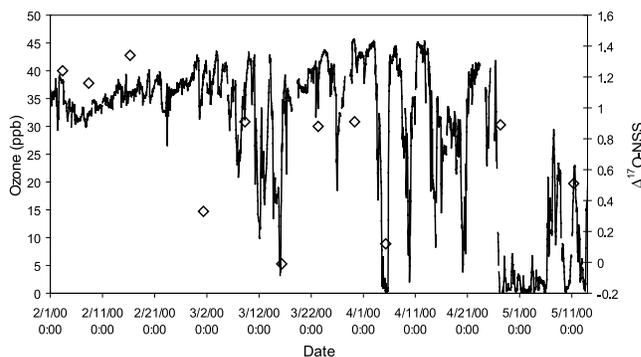


Figure 2. Coincidence of low $\Delta^{17}\text{O}$ -NSS on the right-hand axis (open diamonds) and decreased surface ozone on the left-hand axis at Alert, Canada. Ozone measurements were provided by the Environmental Services of Canada.

proposed that this oxidant is Fe(III) and Mn(II)-catalyzed O₂ oxidation for the following reasons: (1) this pathway is known to produce mass dependent sulfate and explains the isotope results, (2) the lack of sunlight during the Arctic winter shuts off photochemistry, and (3) concentrations of elemental iron and manganese in polluted air masses approximately double in the Arctic winter. Using the results of a chemical model [Feichter et al., 1996] and isotopic mass balance calculations, our measurements reveal a range of 10–18% sulfate production from metal catalyzed O₂ oxidation of S(IV) in winter. In contrast, the agreement between isotope measurements and model calculations agree within 2% during summer. Laboratory investigations of metal-catalyzed S(IV) oxidation on ice surfaces are necessary to provide further support for this possibility. The lowest observed Δ¹⁷O-NSS values occurred during spring ozone depletion events. Possible reasons for this include ozone depletion, an enhanced source of OH due to snowpack photolysis, and/or the influence of halogen (HOBr and HOCl) chemistry.

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