

## ***Interactive comment on “Sulfur isotope analysis of individual aerosol particles – a new tool for studying heterogeneous oxidation processes in the marine environment” by B. W. Sinha et al.***

### **Anonymous Referee #2**

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Ion Microprobe analysis of specific S aerosol particles is an ambitious and powerful new technique that the authors demonstrate can potentially be used to determine the S isotope characteristics of specific particles. Using a number of assumptions the authors use this technique to classify and characterize the source and the oxidation process for non-sea-salt-sulfate. Sinha et al., demonstrate the source of individual S aerosol particles can be identified using a combined elemental composition/isotope approach if a number of assumptions are made. There are, however, a number of issues with respect to the assumptions used in S isotope source and oxidation attribution that are not robust.

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The attribution of non-sea-salt-sulfate to heterogeneous versus homogeneous oxidation rests on knowledge of the sulfur isotope fractionation factors involved. The authors assume the fractionation factor (here I will refer to alpha as  $[\text{}^{34}\text{S}/\text{}^{32}\text{S}]_{\text{product}}/[\text{}^{34}\text{S}/\text{}^{32}\text{S}]_{\text{reactant}}$ ) 1.0165 applies for heterogeneous oxidation and that fine aerosols are solely formed by homogeneous processes with a fractionation of 0.991. As the authors clearly state, there is considerable disagreement in the literature regarding fractionation factors for  $\text{SO}_2$  oxidation and few relevant laboratory studies of fractionation exist. They present a reasonable summary of the literature on  $\text{SO}_2$  fractionation but chose the largest difference in fractionation in order to differentiate heterogeneous and homogeneous oxidation. These fractionation factors may not be appropriate for reasons outlined below.

### Laboratory Studies

Eriksen's work from 1972 on fractionation from heterogeneous oxidation is incorrectly cited: Eriksen published four companion papers (discussed below) but the two cited in the manuscript in fact do not show a fractionation of 1.0165 as stated. A summary and review of the four experiments by Eriksen in 1972 regarding heterogeneous oxidation of  $\text{SO}_2$  are described below. Fractionation factors range from 0.9999 to 1.0161 depending on whether equilibrium or kinetic reactions are considered. An important consideration is: what are the relevant analogous conditions in the atmosphere for these experiments?

The two Eriksen papers cited by Singha et al., show fractionations between 0.9999 and 1.0099 for steps involved in  $\text{SO}_{2\text{gas}}$  oxidation to  $\text{HSO}_3^-$ . It is Eriksen's paper (IV) on the S isotope effects with respect to anion exchange that shows a fractionation factor of 1.0161.

Which of the reactions discussed by Eriksen in his four 1972 publications are most relevant to the atmospheric oxidation of  $\text{SO}_2$ ? Eriksen I (1972a) describes factors affecting the fractionation during  $\text{SO}_{2\text{g}}$  oxidation to  $\text{HSO}_3^-$  as a three step process involving

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i. migration of  $\text{SO}_2$  into solution (row two in Table 1 below), ii. hydration (row three), and iii. equilibrium isotope exchange (row one). Isotope fractionation for processes i & ii are measured in Eriksen II (1972b), and III (1972c). Process iii is determined in Eriksen I (1972a). The fourth paper by Eriksen (1972d) considers fractionation of  $\text{SO}_2$  with absorption of  $\text{HSO}_3^-$  onto ion exchange resin.

Sulfur dioxide oxidation on or within aerosols can be related back to Eriksen's work. The first three Eriksen papers are relevant to mixtures of gaseous  $\text{SO}_2$  dissolved *into* liquid aerosols. The fourth can be compared to gaseous  $\text{SO}_2$  evolved *out from* suspended solids saturated with  $\text{HSO}_3^-$

The first paper deals with equilibrium fractionation but this is not relevant to atmospheric  $\text{SO}_2$  and liquid aerosols except under extremely polluted conditions. Migration of gaseous  $\text{SO}_2$  into liquids (Eriksen II) *is* relevant but the fractionation is much smaller than Singha has used. More relevant to gas and liquid mixtures in the atmosphere (where contact time between gaseous and liquid constituents is diminished by rapid vertical and horizontal mixing of air masses) are the results from Eriksen III where the fraction of reaction (fraction  $\text{SO}_{2g}$ ) approaches zero (row three of the table). In this experiment under these conditions the fractionation is less than 1.002. At very high humidity and during washout events, when the fraction of  $\text{SO}_2$  reacted could potentially approach 1, then the larger fractionation of 1.0091 to 1.0099 might apply. However, the atmosphere is not a simple mixture of gas and liquid constituents: particulate matter must be considered. The results from Eriksen IV are then relevant where a fractionation of 1.0161 is found for  $\text{SO}_2$  evolving from acidic aerosol surfaces.

These studies show that typical heterogeneous oxidation of  $\text{SO}_2$  is likely attended by isotope fractionation lying somewhere between 0.9999 and 1.0161. Small fractionations for heterogeneous oxidation are more likely under reasonably clean, and/or dry atmospheric conditions whereas larger fractionations, up to about 1.0161 might occur in polluted air and/or very humid conditions. The problem with using the larger fractionation factor, is that even under extremely polluted conditions it has not been observed

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in numerous field applications (see Newman's papers from the 1980's). The potential for variation in fractionation factors has not been considered in Singha's manuscript. Furthermore the authors do not distinguish between aerosol  $\text{SO}_4^{2-}$  and MSA when measuring their aerosol isotope composition (line 26 pg 3322). Instead the bulk sulfur in aerosol is assumed to be mainly  $\text{SO}_4^{2-}$ . Since the MSA and sulfate will likely have different isotope compositions the picture is complicated by how much MSA is present – a difficult problem to solve since MSA was not measured.

**Table 1.** Summary of fractionation factors described in Eriksen's papers from 1972.

Paper	Analogy	Species	Eq/R/nonEq	alpha
Eriksen I	very polluted e.g. stack gas	$\text{SO}_{2g}$ $\text{HSO}_3^-_{aq}$	equilibrium	$^{34}\text{S}/^{32}\text{S}_{aq}/^{34}\text{S}/^{32}\text{S}_g$ 1.011 – 1.012
Eriksen II	gas/liquid normal atmos.	$\text{SO}_{2g}$ $\text{SO}_{2aq}$	Rayleigh	$^{34}\text{S}/^{32}\text{S}_{aq}/^{34}\text{S}/^{32}\text{S}_g$ 0.9999 – 1.0029
Eriksen III	gas/liquid	$\text{SO}_{2aq}$ $\text{HSO}_3^-_{aq}$ $\text{SO}_{2g}$ $\text{SO}_{2aq}$	kinetic fraction $\text{SO}_{2g} = 0$ fraction $\text{SO}_{2g} = 1$	$^{34}\text{S}/^{32}\text{S}_{aq}/^{34}\text{S}/^{32}\text{S}_g$ 1.0009-1.0016 1.0091-1.0099
Eriksen IV	liquid/solid Internal aerosol gas/solid external mixing	$\text{HSO}_3^-_{aq}$ $\text{HSO}_3^-_s$ $\text{SO}_{2g}$ $\text{HSO}_3^-_s$	equil Rayleigh	$^{34}\text{S}/^{32}\text{S}_s/^{34}\text{S}/^{32}\text{S}_{aq}$ 1.0044-1.0070 $^{34}\text{S}/^{32}\text{S}_s/^{34}\text{S}/^{32}\text{S}_g$ 1.0150-1.0161

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## Field Studies

Singha et al., attempt to determine the most appropriate fractionation values by invoking  $\text{SO}_2$  and sulfate  $\delta^{34}\text{S}$  values from field experiments. They discuss seasonal variability using  $\delta^{34}\text{S}$  values for  $\text{SO}_2$  and  $\text{SO}_4$  measured simultaneously as the best measure. Unfortunately, only a few studies contain appropriate data, including studies from two contrasting locations in Canada that were not cited. Neither Calgary, Alberta, where relative humidity is typically 35% or less, nor the greater Vancouver region with  $\text{RH} > 65\%$ , respectively (Norman *et al.* 2004a,b) display evidence of sulfur isotope fractionation on  $\text{SO}_2$  oxidation. At both locations, extensive measurements of the isotope composition of  $\text{SO}_2$ , and coincident measurements of aerosol and precipitation  $\text{SO}_4$  do not support isotope fractionation. Data for  $\delta^{18}\text{O}_{\text{SO}_4}$  from Alberta should be strongly correlated to  $\Delta\delta^{34}\text{S}$  if fractionation is the source of S isotope variations (less positive  $\delta^{18}\text{O}$  values indicate a larger proportion of secondary sulfate). These measurements are shown in Table 2 and Figure 1 below. It is very clear that there is little to no fractionation on oxidation. The difference in isotope composition between precipitation sulfate and  $\text{SO}_2$  should clearly show a fractionation but in two of three instances have the smallest  $\Delta\delta^{34}\text{S}$  values.

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**Table 2.**  $\delta^{34}\text{S}$  values (‰) for  $\text{SO}_2$ , aerosol sulfate and sulfate in precipitation from Calgary, Alberta, Canada. Sulfate  $\delta^{18}\text{O}$  values in aerosol sulfate and sulfate in precipitation should be strongly correlated with  $\Delta\delta^{34}\text{S}$  ( $\text{SO}_4\text{-SO}_2$ ) if isotope fractionation were the source of the difference in isotope composition but this is not observed.

$\delta^{34}\text{S}_{\text{SO}_2}$	$\delta^{34}\text{S}_{\text{SO}_4\text{a}}$	$\delta^{18}\text{O}_{\text{SO}_4\text{a}}$	$\delta^{34}\text{S}_{\text{SO}_4\text{p}}$	$\delta^{18}\text{O}_{\text{SO}_4\text{p}}$	$\Delta\delta^{34}\text{S}_{\text{SO}_4\text{-SO}_2}$
+17.5	+11.7	+7.7			-5.8
+20.4			+20.3	+6.2	-0.1 (precip)
+20.2	+21.0	+12.8	+15.7	+14.3	0.8 (aerosol)
					-4.5 (precip)
+20.7	+22.4	+13.8			+1.7
+18.2	+17.4	+13.9			-0.8
+20.2	+19.0	+6.9			-1.2
+19.8	+16.1	+10.5			-3.7
+14.6	+19.5	+13.5			4.9
+17.4	+15.6		+17.6	+14.0	-1.8 (aerosol)
					0.2 (precip)
+19.1	+18.8	+12.8			0.3
+19.1	+15.8	+13.7			-3.3

Figure 1. Plot of the  $\delta^{18}\text{O}$  in aerosol and precipitation sulfate versus the difference in isotope composition between sulfate and  $\text{SO}_2$ .

Singha's arguments suggest the isotope composition and the difference in isotope composition between  $\text{SO}_2$  and  $\text{SO}_4$  reflect fractionation processes and use a number of field data reported in the literature to do this. Before such a comparison is valid, a number of assumptions need to be met. The first assumption is that  $\text{SO}_2$  and  $\text{SO}_4$  in air are well-mixed. Singha uses the difference in sulfur isotope composition seasonally to argue that the fractionations he has chosen are reasonable. This assumes that  $\text{SO}_2$  and/or  $\text{SO}_4$  emissions are isotopically uniform through time in each of the studies he

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cites; that no seasonality in sulfur emissions and/or transport exists. Uniformity has not been demonstrated in many cases. A third is that the isotope composition of sulfate reflects non-sea-salt sources, which unfortunately, has not been the case in many studies cited. Since sea-salt has a  $\delta^{34}\text{S}$  value near +21 ‰ and all sources of  $\text{SO}_2$  described have lower  $\delta^{34}\text{S}$  values, it is not surprising that  $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$  is positive (note that seasonality in  $\Delta\delta^{34}\text{S}$  wasn't observed in the Alberta study). Seasonal variations in the proportion of sea-salt could result in the patterns observed for  $\Delta\delta$  and  $\delta^{34}\text{S}_{\text{SO}_4^{2-}}$ . Seasonal changes in sulfur emission sources, such as increased oil or coal combustion for heating in winter months will affect the isotope composition of both  $\text{SO}_2$  and  $\text{SO}_4^{2-}$ .

### Comments & Suggestions

This paper contains considerable valuable information but sections should be revised for resubmission prior to publication. Attribution of sulfur dioxide to heterogeneous and homogeneous oxidation should be either removed or altered (section 4.3). One approach would be to include the results from sensitivity tests where a range of reasonable fractionation values is explored.

A second major issue with the results presented lies in the blank correction. Blank corrections are typically done on aerosol filter extracts – measured in ug/L or ppm *before* considering the volume of air through the filters. Blank measurements for single particle analysis should be scaled to represent the material on the each filter before dividing by the volume of air. There is no air flow through the blanks so dividing by the average volume will simply introduce error into the analysis. Since the air volume varied from 5.4 to 42 cubic meters, the error introduced is quite considerable. Using the method described too much blank correction would have been applied to sample 3 and too little to sample 11. Since the isotope values in Table 6 are calculated using data from Table 5, I have little assurance the results or interpretation from this point forward in the paper are representative of actual conditions. The data should be recalculated after 'filter blank' correction has been applied.

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