

## ***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.***

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### General comments

Sinha et al present novel measurements of the chemical and sulfur isotopic composition of single particles collected in a coastal, North Atlantic region (Mace Head). Their findings are significant and should be published, but I thought the paper could be better organized, and the major findings emphasized more. As I see it, the major findings are: 1) Isotopic results are consistent with  $\alpha(\text{hom}) = 0.991$  and  $\alpha(\text{het}) = 1.0165$  2) Homogenous oxidation pathway is more important than previous estimates based solely on the  $\text{SO}_2 + \text{OH}$  source, suggesting an additional (or missing) gas-phase ox-

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idation pathway in coastal regions. There should be numbers (estimates) attached to this.

In addition, a couple of important issues need to be addressed:

1) Is the second conclusion based on having a similar  $\alpha(\text{hom})$  as the  $\text{SO}_2+\text{OH}$  reaction? What if it doesn't?

2) Also, I think there is a distinction to be made between reactions on an aerosol surface (heterogeneous) and in cloud water (aqueous). It seems you are grouping these two together. If one is an equilibrium process (dissolved concentrations of  $\text{SO}_2$  and oxidants are usually assumed to be at their equilibrium concentrations in cloud liquid water) and one is a kinetic process (such as heterogeneous oxidation of  $\text{SO}_2$  by  $\text{O}_3$  on sea-salt particles, which as you say is a factor of  $10^5$  times faster than oxidation by  $\text{H}_2\text{O}_2$  in clouds), might the fractionation factor ( $\alpha$ ) be different? In other words, could  $\alpha(\text{het})$  be less than 1 if the reaction is dependent upon the gas-to-particle transfer of  $\text{SO}_2$  to the surface of aerosols (a kinetic process like the  $\text{SO}_2+\text{OH}$  reaction)?  $\alpha(\text{het}) > 1$  is based on an equilibrium assumption, so what if it's not an equilibrium process, would  $\alpha(\text{het})$  still be  $>1$ ? Could this be your "missing" homogenous oxidation pathway?

Specific comments

Abstract: - Shorten abstract and make major findings more obvious. - Organize better throughout the paper. For example, you have this sentence: "The fractionation with respect to the source  $\text{SO}_2$  is poorly characterized." Then you go on to discuss the fractionation factors during oxidation of  $\text{SO}_2$ , then come back to the source signature. The above sentence should be moved down to just before "Particles with known oxidation pathway" - State what the main sources of  $\text{SO}_2$  are based on your analysis in the abstract. - The discussion of the fractionation factors could be shortened and begin something like: "Our results are consistent with  $\alpha(\text{hom}) = 0.991$ , etc" - Sea-salt sulfate is 10-60%, sulfate/sulfuric acid particles are 15-65%, why not attach a similar

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range to nss-sulfate?

1. Introduction - Page 3311. Shouldn't "oxidation of sulfuric acid" read "oxidation of SO<sub>2</sub>" - Page 3311. The Alexander et al. [2005] reference decreased (not increased) gas-phase H<sub>2</sub>SO<sub>4</sub> production rates by 10-30%.

2. Isotope chemistry of sulfur in the marine atmosphere - Page 3314. There should be a reference for the contribution of gas phase oxidation (0-60%). - Page 3316. Somewhere it should be considered that different homogeneous oxidation pathways may have different values of  $\alpha(\text{hom})$ . How would this influence your interpretation if the value was different from 0.991?

4. Results - Page 3323. Can some of the N be in the form of NH<sub>4</sub><sup>+</sup>? - Page 3327. "comprised a significant (X-Y%) portion of the fine mode aerosol" Fill in X and Y. - Page 3331. In your list 1, 2, 3, I don't understand what you mean in #2. - Page 3334. "Tanaka et al. provide an accurate estimate" Does accurate apply to both the magnitude and direction of the fractionation, or just the direction? It seems that the magnitude could differ significantly and still be consistent with your results. How sensitive are your conclusions to the magnitude of the fractionation factor? - Page 3335. It is confusing that for "clean" samples the anthropogenic source of S dominates.

5. Discussion - Page 3341. Alexander et al. [2005] estimate that ozone oxidation accounts for 16% of total sulfate production, 9% of which is in sea-salt aerosol (not 10-30%). - Page 3341. Alexander et al. [2009] estimate heterogeneous (aerosol + cloud) chemistry accounts for 79-80% (not 84%).

Technical corrections

Table 2. Na should be defined here. Also, what are the units for the semi-quantitative composition of different particle groups - mass %?

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 3307, 2009.

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