

***Interactive comment on “Sulfur isotope analyses of individual aerosol particles in the urban aerosol at a central European site (Mainz, Germany)” by B. Winterholler et al.***

**Anonymous Referee #1**

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General comments

Winterholler et al. present novel measurements of the sulfur isotopic composition of individual sulfate-containing aerosol particles. The  $\delta^{34}\text{S}$  value reflects the source of sulfur to the atmosphere and the specific oxidation mechanism (gas-phase or heterogeneous) of S(IV) to S(VI). If one of the two is known (source or oxidation pathway), the other can be determined. This offers potential for source apportionment, important for regulatory control of SO<sub>2</sub> emissions, and for providing insights on the importance of different oxidation pathways in the atmosphere. The authors suggest that changes in the latter (increasing amounts of aqueous-phase S(IV) oxidation over time) may ac-

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count for the non-linear behavior in the response of atmospheric sulfate aerosol to decreasing industrial emissions of SO<sub>2</sub>.

This paper presents novel and interesting measurements and should be published. Interpretation of their results is complicated, but the authors generally do a good job of noting the uncertainties in their assumptions (except for one point which is detailed below). Large uncertainties still exist in our understanding of the sulfur budget. These uncertainties were highlighted during COSAM [Barrie et al., 2001] and other modeling studies, showing that models tend to overestimate surface SO<sub>2</sub> concentrations by factors of two or more, while predicting sulfate concentrations within 20% of observations. Studies such as those done by Winterholler et al. may help to resolve some of these discrepancies. I recommend publication after addressing some specific comments outlined below.

#### Specific comments

The authors do not appropriately address uncertainties in the fractionation due to homogeneous and heterogeneous oxidation of S(IV). Notably, there is also evidence that gas-phase oxidation may result in an enrichment of the product sulfate [Castleman et al., 1974; Loung et al., 2001]. If the authors are able to discount these studies, they should explain why. Their results may offer evidence to support depletion due to gas-phase oxidation, and enrichment due to heterogeneous chemistry; however, I'm not sure that this issue is solved. The authors should provide some discussion of this in Section 2. If there is enrichment due to gas-phase oxidation, how would this effect the interpretation of your results? Is this a realistic assumption? These measurements may shed light on this issue, but it is not clear how without appropriate discussion. This is important because in order to derive the isotopic composition of source SO<sub>2</sub>, they are using sulfate particles formed from the gas-phase, and assuming S-34 depletion from this process (e.g. some of their conclusions rest heavily upon this assumption).

The authors should provide more detail on how their samples were collected. What

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sort of aerosol sampler was used? What was the collection period (1 hour, 24 hours)?

I find the "Groups" used to be confusing. For example, it would be much better to put "aged sea-salt" in Table 7 in place of "Group 2". This would make it much easier for the reader to digest this information.

Technical corrections

In Figure 9, the color scale should have a label (d34S).

References

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[Interactive comment on Atmos. Chem. Phys. Discuss., 8, 9347, 2008.](#)

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