

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.

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We thank Prof. Dr. Savarino for his interesting and helpful comments on our manuscript, but we do not agree with the points raised concerning the fractionation of the $SO_2 + OH$ reaction.

We strongly believe that the time period following a volcanic eruption is not a suitable time period for estimating the fractionation of the $SO_2 + OH$ reaction. The sulfate in the aftermath of the volcanic eruption does display a mass independent signature, which shows that the $SO_2 + OH$ reaction is not the only process governing the isotopic composition of the sulfate during that time period. Therefore, since part of the sulfate derives from a different process, and the rate coefficient of that process is controversial,

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we do not agree that this time period is suitable to estimate the isotopic fractionation of the $SO_2 + OH$ reaction. Such a calculation would require the rate coefficients of both reactions to be known.

The $SO_2 + OH$ reaction governs the formation of sulfate in between volcanic eruptions, and the isotope fractionation could be estimated based on simultaneous measurements of the isotopic signature of the stratospheric sulfur dioxide and sulfate. Unfortunately the isotopic signature of stratospheric SO_2 has never been measured.

We believe that currently the best way to estimate the fractionation of the gas phase and aqueous phase oxidation is to look at seasonal trends in the isotopic composition of simultaneously collected SO_2 and SO_4 . The contribution of the gas phase oxidation varies from 0% (nighttime, arctic winter) to roughly 60% (bright summer day) of the total sulfate formed. Therefore, during winter more sulfate should be formed through oxidation in the aqueous phase, while during summer the importance of gas phase oxidation by OH should increase. The seasonal trends of the isotopic composition of simultaneously collected SO_2 and sulfate allow an estimate of the direction of the isotopic fractionation involved in both pathways, by evaluating the equation $\delta^{34}S_{so_4} - \delta^{34}S_{so_2} = (1 - f_{hom}) \cdot \alpha_{het} + f_{hom} \cdot \alpha_{hom}$ for different seasons. It has been observed that during summer months (more gas phase oxidation) the difference in the $\delta^{34}S$ of SO_2 and sulfate ($\delta^{34}S_{SO_4} - \delta^{34}S_{SO_2}$) is generally lower than during winter months (more aqueous phase oxidation) (Saltzman et al. 1983; Mukai et al. 2001, Kawamura et al. 2001; Tichomirowa, unpublished data). Occasionally, the sulfate is depleted in ^{34}S compared to the SO_2 during summer months. The same holds for the comparison of the isotopic composition of throughfall (wet deposition of sulfate plus SO_2 from dry deposition on the leaves) and bulk precipitation (Groschekova et al. 1998; Novak et al. 2000, Zhang et al. 1998,) with the throughfall occasionally showing a higher $\delta^{34}S$ than the bulk precipitation at the same site during summer months. Even when only one of the species (SO_4 or SO_2) was collected the seasonality encountered is similar for most sites in the northern hemisphere. In winter the $\delta^{34}S$ of bulk sulfate

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increases, compared to the summer values at the same site (Caron et al. 1986; Nigru et al. 1987; Ohizumi et al. 1995; Alewell et al. 2000; Ohizumi et al. 2001). In contrast, the $\delta^{34}S$ of the remaining SO_2 during winter is typically lower than during summer (Novak et al. 2001). This is in line with an enrichment of the heavier isotope in the sulfate due to the increased importance of the aqueous phase oxidation in the winter months and depletion of the remaining SO_2 . These seasonal trends support a positive fractionation for the aqueous oxidation pathway. The fact that $\delta^{34}S_{SO_4} - \delta^{34}S_{SO_2}$ and $\delta^{34}S_{bulkprecipitation} - \delta^{34}S_{throughfall}$ is sometimes negative during summer months supports a negative fractionation for the gas phase oxidation.

The alpha calculated by Leung is extremely difficult to reconcile with our current knowledge of sulfur oxidation and numerous data sets of the sulfur isotopic composition of aerosol, sulfur dioxide and sulfate in precipitation. Such a huge alpha should lead to huge variations in the isotopic composition of sulfate between daytime and nighttime and summer and winter, but the amplitude of the seasonal cycles is typically only 1–4 permil. Even if the fractionation of the gas phase oxidation was not that large, but more positive than the fractionation during the oxidation in the aqueous phase, seasonal trends of the isotopic composition of SO_2 and sulfate should be inverse to what they are. In conclusion, the alpha of the $SO_2 + OH$ reaction should be lower than the alpha of aqueous phase oxidation. So far, data sets where sulfate is depleted in ^{34}S compared to the SO_2 have been collected during the summer months and on aircraft campaigns, under conditions where high OH and low humidity is expected, thus supporting a negative alpha of the gas phase oxidation pathway. Even though sampling details for the aircraft data is lacking and the sampling periods are generally too long to efficiently correlate the data with meteorological parameters we still believe there is strong circumstantial evidence for a negative alpha of the gas phase oxidation pathway. The alpha of 0.991 that we used for the $SO_2 + OH$ reaction is based on the quantum mechanical calculation of the fractionation constant by Tanaka et al. (1994). This alpha can be reconciled with our dataset and other datasets of simultaneously collected SO_2 and SO_4 .

We believe that in the absence of any conclusive laboratory experiments, the seasonality of the sulfur isotopic composition is the best way to estimate the direction of the isotopic fractionation during gas phase oxidation and aqueous phase oxidation. It is true that the numbers associated with both processes are far from certain. For the heterogeneous oxidation only the fractionation during uptake and dissociation to HSO_3^- has been determined, that too under equilibrium conditions. The effect of the terminating reactions with H_2O_2 , O_3 , and metal catalyzed oxidation by O_2 , to name just the three most important ones, has never been properly assessed. The fractionation of the gas phase oxidation pathway has not been determined experimentally at all. The absence of any lab experiments that include the net effect of the reaction for both the formation of sulfate in the gas phase as well as for the aqueous phase oxidation makes the data interpretation a challenging task. However, since there is clear evidence for a negative fractionation, we do not think it is useful to include a discussion of the influence of a positive fractionation during gas phase oxidation by OH on the interpretation of our results.

To account for the reviewers concerns and for the experimental evidence as outlined above, we propose to change the discussion into a more general tone speaking of two constants rather than of specific numbers in the general discussion and then proposing the alpha by Tanaka and Eriksen as currently the best estimates for both numbers and to discuss the uncertainties of both estimates. We propose to furthermore add a statement to the discussion that any change of these numbers that might come from new laboratory experiments will affect the fraction of the homogeneous and heterogeneous oxidation pathway calculated.

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