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Atmospheric
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Discussions

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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Final Response

We would like to thank J. Savarino and the anonymous referee for their constructive comments and suggestions.

We have individually responded to all comments and have implemented the following suggestions for improvement.

Section 2

We have added the following discussion of the isotopic fractionation during the ho-

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mogeneous oxidation and heterogeneous oxidation of SO_2 to explain why we use the fractionation factor calculated by Tanaka et al. (1994) and not the fractionation factor calculated by Leung et al. (2001) for the sulfur isotope fractionation occurring during gas-phase oxidation of SO_2 by OH. This discussion has been phrased as response to the concerns of both referee 1 and referee 2 and has been further refined following the discussion with J. Savarino. We have also revised Figure 1.

"Saltzman et al. (1983) and Tanaka et al. (1994) determined the isotopic fractionation (α_{hom}) for gas phase oxidation of SO_2 by OH as being kinetically driven. Tanaka et al. (1994) calculated a fractionation of $-9‰$ ($\alpha_{hom} = 0.991$, ${}^{34}S/{}^{32}S_{fractionation} = (\alpha - 1)$) using ab initio quantum mechanical calculations. In contrast, Leung et al. (2001), using RRKM (Rice, Ramsperger, Kassel, and Marcus) transition state theory, calculated the fractionation as an inverse kinetic isotope effect, with ${}^{34}SO_2$ reacting faster than ${}^{32}SO_2$ resulting in a $\delta^{34}S$ increase of $140‰$ ($\alpha_{hom} = 1.14$) under atmospheric conditions.

At first sight, the fractionation calculated by Leung et al. (2001) agrees well with measurements of stratospheric sulfate (Castleman et al., 1974). The data of Castleman et al. (1974) seemed to indicate that during the oxidation of SO_2 to sulfate in the stratosphere following the Mt. Agung eruption, Rayleigh fractionation occurred with ${}^{34}S$ being enriched in sulfate and SO_2 depleted in ${}^{34}S$. However, recent research has shown that following the volcanic eruption a separation of the sulfur into two reservoirs carrying a mass independent isotope fractionation with opposing signs took place (Baroni et al. 2007) and UV induced photooxidation has been suggested to explain the mass independent signature. Since the oxidation of SO_2 by OH is not responsible for the mass independent signature observed in the sulfate during the time period in question, this reaction is not the only reaction dominating the isotopic signature of the sulfate. Therefore, the simple Rayleigh fractionation during oxidation of SO_2 by OH proposed by Leung (2001) can no longer be used to interpret the dataset.

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 and to evaluate 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. The contribution of the gas phase oxidation (f_{hom}) 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. 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) (Saltzmann 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 increases, compared to the summer values at the same site (Caron et al. 1986; Niagru et al. 1987; Ohizumi et al. 1995; Alewell et al. 2000; Ohizumi et al. 2001). In contrast, the $\delta^{34}S$ of the 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. The seasonal trends support a positive fractionation for the aqueous oxidation pathway ($\alpha_{het} > 1$). 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 ($\alpha_{hom} < 1$).

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. The numbers associated with both processes are far from certain. For the heterogeneous oxidation pathway only the fractionation during the uptake of SO_2 into the aqueous phase and the dissociation to HSO_3^- has been determined, that too under equilibrium conditions ($\alpha_{het} = 1.0165$; Eriksen, 1972a; Eriksen 1972b). The effect of the terminating reactions such as oxidation by 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 and equilibrium is typically not reached under atmospheric conditions. The fractionation of the gas phase oxidation pathway (α_{hom}) has not been determined experimentally at all. The absence of laboratory 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. Based on current scientific understanding, we consider the kinetic fractionation during the gas phase oxidation of SO_2 by OH as suggested by Saltzman et al. (1983) and Tanaka et al. (1994) to be the most reasonable estimate for the isotope fractionation during gas phase oxidation of SO_2 (α_{hom} = 0.991) and the equilibrium fractionation for the uptake and dissociation measured by Eriksen (1972a) the best approximation for the fractionation during oxidation in the aqueous phase ($\alpha_{het} = 1.0165$)."

Section 3.1

We have added more details concerning the sampling conditions and revised Table 2.

"Samples were collected on gold coated 47-mm-diameter Nuclepore polycarbonate filters with 0.4 μm pore sizes. The filters were placed in a stacked filter unit operated with one stage only. The start and stop time of each individual sample are specified in Table 2."

Section 3.2

We have clarified the paragraph concerning the particle sizing:

“Filters were sampled at predefined equidistant spots. Whenever the predefined spots were located within a particle, the particle was counted and its size and chemical composition were measured. Typically more than 500 particles of each sample were examined at a magnification of 6000x. The 2D surface area of each particle was measured by counting the number of pixels it occupied in the digital secondary electron image and converted to μm^2 (pixel size at 6000x = 111 nm).Based on the 2D surface area of the particle, the particle equivalent diameter was calculated. The equivalent diameter is the diameter of a spherical particle occupying the same area as the analyzed particle.”

We also clarified the paragraph describing how to avoid multiple sampling of the same particle:

“Sampling regular spots is an established method to quantify the phase composition of samples with randomly distributed particles (Amelinckx et al., 1998). To avoid multiple sampling of the same particle, the distance between the spots has to be greater than the feret diameter of the largest particle. Whenever this criteria is fulfilled, the probability of acquiring an EDX spectrum of a particle of particular size and chemical composition is directly proportional to the total filter area covered with particles of that size and chemical composition and, therefore, to the number of the particles. This method allows fast quantification of the abundance of different particle types in the samples. To ensure that the distance between the spots is larger than the feret diameter of the particles the grid chosen for EDX data acquisition and image analysis was varied according to the particle size range investigated. The grid chosen for data analysis was 10 μm for particles with a feret diameter <10 μm, 20 μm for particles with a feret diameter between 10 μm and 19 μm and 50 μm for particles 8805;20 μm in diameter. ”

Section 3.3

We added a paragraph with a few more details concerning IMF correction to paragraph

3.3.

“The grain size and matrix dependence of the instrumental mass fractionation (IMF) were corrected based on the equivalent diameter and chemical composition measured for the respective particle in the SEM according to the method described in Winterholler et al. (2008). The necessity to correct for the size of the particles is caused by charging. Since the size determination of particles in the SEM is very accurate, this is a simple and straightforward correction, which is relevant mainly for coarse mode particles. Matrix dependent instrumental mass fractionation occurs during sputtering and ionization. Winterholler et al. (2008) found a linear relationship between the ionic radius of the cation (i.e., the chemistry) and the matrix specific instrumental mass fractionation for different sulfate salts. Riciputi et al. (1998) showed that the IMF of fine grained mixed samples, which contain two phases on a spatial scale smaller than the primary ion beam, can be accurately corrected using coarse grained standards of the individual phases. The instrumental mass fractionation relative to $BaSO_4$ has been established for most sulfates relevant for atmospheric research (Winterholler et al. 2008). Correction of pure sulfate particles and “internally mixed” particles in which the sulfate containing phases are clearly separated such as the aged sea salt particle in Figure 5 containing sodium chloride, gypsum and sodium sulfate as separate phases, is straightforward. This particle is a classical example of a particle that is “internally mixed” from an aerosol point of view, but “externally mixed”, i.e., separated into distinct components on the spatial scale relevant for IMF correction in the NanoSIMS. IMF correction of particles contain several cations in the same sulfate (e.g. glauberite, $Na_2Ca(SO_4)_2$) is difficult. For such particles (part of the particles in group 6, mixed sulfates, <5% of the total particles) we calculated the IMF of the mixture based on the chemical composition of the respective particle as a linear mixture of the IMF of the pure salts of the major cations. ”

Section 4.2

We have separated the group classification and sample description in Section 4.1

“Chemical analysis of aerosol particles” into two different sections in the revised version. Section 4.1 “Chemical classification of aerosol particles” contains the group classification and Section 4.2 “Chemical composition of aerosol sample” the sample description We shifted group classification of ammoniums sulfate from Section 4.2. “Isotopic composition of different types of sulfate aerosol particles and bulk samples” (Section 4.3 of the revised version) to Section 4.1 “Chemical classification of aerosol particles”.

Page 9361, line 2

We revised the text to be more specific concerning the comparison with the state agency measurements at Mainz Zitadelle and updated Table 3 using hourly data for the exact sampling times rather than 24 h averages.

“ The difference PM2.5-10 estimated from our data agreed within $\pm 10\%$ with PM2.5-10 reported for the monitoring station Mainz Zitadelle for those samples where Mainz Zitadelle is located upwind of our sampling site (Sample 4 and 5) and within $\pm 30\%$ for other wind directions (Table 3).”

Section 4.3

Page 9361, line 21-23, Page 9362 line 3, line 5 and line 7

We included group 4b in line 22, 28 and page 9362 line 5 and 7 and clarified the comparison the different groups within the same sample:

“When comparing the isotopic composition of chemically different groups of secondary sulfates within the same sample, a sticking feature is, that for five out of six samples, the isotopic composition of secondary gypsum (Group 5), mixed sulfate particles (Group 6), sulfur coatings on silicates (Group 3a) and ammonium sulfate (Group 4b) agree with each other within the analytical uncertainty. Thus, irrespective of the chemical composition, precursor SO_2 and oxidation process that might have lead to the formation of different secondary aerosol particles, all secondary particles in the same sample show a uniform isotopic signature. This is only possible if all of these particles were formed from droplets that had been isotopically homogenized by frequent in-cloud processing. The weighted averages of particles from Groups 2, 3a, 4b, 5 and 6 are $\delta^{34}S = (19 \pm 3)‰_0$, $\delta^{34}S = (19 \pm 3)‰_0$, $\delta^{34}S = (4 \pm 2)‰_0$, $\delta^{34}S = (15 \pm 1)‰_0$, and $\delta^{34}S = (8 \pm 3)‰_0$ for Samples 1, 2, 5, 7 and 8, respectively."

Section 4.5 We have added a statement concerning the uncertainty of the fractionation occurring during the oxidation of SO_2 to the paragraph following equation 5

"The fraction of heterogeneous and homogeneous oxidation pathway calculated by this formula is very sensitive to the isotope fractionation assumed for both pathways. Any change of these numbers due to new experimental evidence will affect the fraction of the homogeneous and heterogeneous oxidation pathway calculated. "

Page 9367 line 23-30

Referee #2 is concerned that using Cl to calculate nss sulfate in aged sea salt is only justified if dechlorination is a minor process. We are aware that using Cl to calculate nss-sulfate in aged sea salt particles that have gone through a 2-3 day transport through a polluted continental atmosphere is problematic and loss of chlorine does occur. This would lead to an overestimation of the nss-sulfate in the sample and in consequence to a $\delta^{34}S_{nss}$ that is too high. However, using Na for urban samples is even more problematic since there are numerous sodium sources in the urban environment (e.g. soil minerals, refuse incineration, coal combustion, car exhaust and other industrial processes). The K/Na-ratio helps to evaluate sources of sodium (Ooki et al., 2002) and the K/Na-ratio even of those particles termed aged sea salt is clearly higher than marine values, while e.g. for mixed sulfates the K/Na-ratio is similar to the K/Na-ratio produced by refuse incineration and car exhaust (Ooki et al., 2002). Not only the chlorine concentration but also the K/Na-ratio of our samples indicates, that the contribution of sea salt to our samples is very minor compared to the aerosol contributed by urban sources. Since the number of aged sea salt particles in our samples

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Discussion Paper

is small (Table 6) and they do not contribute significantly to the conclusions of our paper we removed page 9367 line 23-30 and focused on the discussion and interpretation of other particles groups.

“The K/Na-ratio helps to evaluate sources of sodium in the urban atmosphere and the K/Na-ratio even of those particles termed aged sea salt is clearly higher than marine values, while for mixed sulfates the K/Na-ratio is similar to the K/Na-ratio produced by refuse incineration and car exhaust (Ooki et al., 2002). This and the low chlorine concentration of the samples indicate that the contribution of sea salt to our samples is very minor. Therefore, correction for sea salt sulfate is not necessary for particles of group 3a, 4a, 4b, 5 and 6.”

Page 9371 line 3-10

We have clarified this paragraph.

“Oxidation by H_2O_2 with an oxidation rate of $10^{-8}Ms^{-1}$ dominates aqueous phase oxidation both at pH 4.4 and pH 4.9. However, the oxidation rate by O_3 increases by one order of magnitude from $10^{-10}Ms^{-1}$ to $10^{-9}Ms^{-1}$ when the pH changes from 4.4 to 4.9 for 0.2 ppb = [SO_2(g)], 46 ppb = [O_3 (g)] and 0.6 ppb = [H_2O_2] (Lee and Thiemens, 2001). Consider the competitive rates of gas phase oxidation by OH and aqueous phase oxidation as a whole (i.e. oxidation by H_2O_2, O_3 and metal catalyzed oxidation by O_2) the overall importance of aqueous phase oxidation increases. ”

Table 2 We added the exact sampling times and revised the columns wind speed, T, RH_{min}, RH_{max} and precipitation to account for the exact sampling times rather than using daily averages.

Table 3 We updated this table using hourly data for the exact sampling times instead of 24h averages for the days on which samples were collected.

Table 6 We have replaced Table 6 by a figure (Figure 7) in the revised version and renumbered the subsequent Figures and Tables accordingly

Table 7 (Table 6 of revised version) Unfortunately, some of the group names (e.g., “ammonium sulfate/sulfuric acid particles from gas to particle conversion” group 4a) are too long to fit in the table. We have, therefore, kept the numbers in the table and added a list of the full names in the figure caption.

Table 8 (Table 7 of the revised version) We have moved Table 8 to an electronic supplement.

Figure 1 We changed Figure 1 to a general form using α_{hom} and α_{het} instead of specific numbers.

Figure 9 (Figure 10 of the revised version) We added a label to the color scale

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