**Atmospheric
Chemistry
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Discussions**

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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.

B. Winterholler et al.

Received and published: 12 July 2008

Authors comment, Reply to Referree #2

We thank the anonymous reviewer for his comments on this manuscript. Detailed below are the replies to specific concerns raised by the reviewer.

General comments:

Paragraph 4.2: We agree that mixing the group classification and sample description in the same paragraph (4.2.) may be confusing for the reader and will separate the two into different paragraphs in the revised version.

Table 6: Replacing table 6 with a figure, which will allow an easier comparison of the

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main chemical features with the results in Table 7 is a good suggestion. We will replace the table 6 by a figure in the revised version.

Table 8 We will move Table 8 to an electronic supplement.

Uncertainty of the isotope fractionation during the $SO_2 + OH$ reaction:

We appreciate the concern regarding the uncertainty of the isotope fractionation during the $SO_2 + OH$ reaction. We will add a discussion of this issue to Section 2 (please see reply to referee #1 for the text we intend to insert).

We agree with referee #2 that Leung et al. (2001) proposed a $^{34}S/^{32}S$-fractionation factor of $\alpha = 1.14$ for the SO_2 + OH reaction. We disagree with referee #2 regarding the interpretation of the positive $\delta^{34}SO_4$ in the aftermath of the Mt. Agung eruption. The research by Baroni et al. (2007) shows, that $SO_2 + OH$ is not the only reaction occurring in the stratosphere after the Mount Agung eruption. A major conclusion of their paper is that UV-induced photooxidation is responsible for the increase of $^{34}SO_4$ as well as a positive $\Delta^{33}S$ in the sulfate just after the injection of the volcanic aerosol. In the light of these new results, the data of Castelman et al. (1974), who reported only the $\delta^{34}S$ of sulfate no longer supports an positive $^{34}S/^{32}S$- fractionation of the $SO_2 + OH$ reaction. Therefore, there is no independent experimental data to support the fractionation factor calculated by Leung et al. (2001).

We strongly disagree with referee #2 that there is no experimental data to support the fractionation constant of $\alpha = 0.991$ calculated by Saltzman et al. (1983) and Tanaka et al. (1994). Newmann and Forrest (1991) presented more than 250 datasets of simultaneously collected SO_2 and SO_4 showing that SO_4 is on average only $3\%_0$ enriched in ^{34}S compared to simultaneously collected SO_2. Moreover they presented 50 datasets of flue gas from power plant stacks for simultaneously collected SO_2 and SO_3, where SO_3 is on average $1.5\%_0$ enriched in ^{34}S compared to simultaneously collected SO_2. Our discussion and interpretation is based on the following two points: firstly, heterogeneous oxidation in the aqueous phase and oxidation by OH in the gas phase are the

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two major mechanisms leading to sulfate formation. Secondly, the isotopic fractionation during uptake of SO_2 into the aqueous phase is well constrained by experimental data (Eriksen, 1972a; 1972b) with $\alpha = 0.0165$ at 25 °C and modeling results (Saltzman et al., 1983). From this it follows that the fractionation of the $SO_2 + OH$ reaction must have $\alpha < 1$. This is supported even stronger by the fact, that the only datasets of simultaneously collected SO_2 and SO_4 which show significant depletion of ^{34}S in the sulfate were collected on aircrafts (Newmann and Forrest, 1991). Therefore, the direction, not necessarily the magnitude of the fractionation proposed by Saltzman et al. (1983) and Tanaka et al. (1994) has strong experimental support. At the same time it is impossible to reconcile neither the direction nor the magnitude of the fractionation proposed by Leung with our current understanding of sulfate chemistry and the available sulfur isotope data ($\alpha = 1.14$ corresponds to $+140\%_0$ not to $+14\%_0$!). We agree that experimental work on this issue is highly desirable, however, considering the current lack of experimental data the ab initio quantum mechanical calculations by Saltzman et al. (1983) and Tanaka et al. (1994) provide a good estimate for the fractionation during gas phase oxidation.

Since the fractionation calculated by Leung et al. (2001) cannot be reconciled with the current knowledge of stable sulfur isotopes and the atmospheric sulfur cycle and since Baroni et al. (2007) demonstrate that the basic assumptions of Leung et al. (2001) are not applicable, the major modifications suggested by referee #2 are not necessary.

Referee # 2 states that the urban environment too complex to demonstrate the power of the new technique, however it has already been shown that the technique works on comparatively simple model systems. The first application of the NanoSIMS to aerosol samples was performed on a simple model system using two samples, one dominated by sea salt aerosol and the other dominated by Sahara dust (Winterholler at al., 2006). The current work demonstrates that the technique can be successfully applied to more complex aerosol as well.

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Paragraph 3.2: We will improve the readability of this paragraph.

Correction of IMF Referee #2 has raised concerns that the instrumental mass fractionation (IMF), in particular the influence of the chemical composition of the particles is not accurately corrected for.

As detailed in Winterholler et al. (2008) IMF correction depends on two factors, firstly, the size of the particles and, secondly, the chemical composition of the particles.

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. This correction is relevant mainly for coarse mode particles.

Referee #2 is right to point out that the chemical composition of particles influences the instrumental mass fractionation. 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. Since the instrumental mass fractionation of most sulfates relevant for atmospheric research has been established (ammonium sulfate, gypsum, anhydrite, sodium sulfate, potassium sulfate, magnesium sulfate), correction of pure sulfate particles and ʽinternally mixed ʼ 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 ʽinternally mixed ʼ from an aerosol point of view, but ʽexternally mixed ʼ, i.e., separated into distinct components on the spatial scale relevant for IMF correction in the NanoSIMS. Referee #2 is mostly concerned about the correction of ʽinternally mixed ʼ particles. Most ʽinternally mixed ʼ particles, as pointed out above can be easily corrected. Other

particles contain several cations in the same sulfate (e.g. glauberite, $Na_2Ca(SO_4)_2$) and IMF correction for such particles (part of the particles in group 6, mixed sulfates) is difficult indeed. For such particles ($< 5\%$ 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. Since complex sulfate mixtures with known isotopic composition are not readily available the IMF of such particles is not easy to establish experimentally.

We will add a few more details concerning the treatment of `internally mixed ´particles during correction of the matrix specific IMF to paragraph 3.3.

Page 9361 line 2 Referee #2 criticized that the comparison with the state agency measurements are not clear. PM 10 and PM 2.5 data is only available at Mainz Zitadelle east of our sampling site. The PM 2.5-10 of our measurements and the state agency measurements typically agree within $\pm 30\%$. Table 3 compares daily averages of the state agency measurements with 24 h samples that were typically changed in the afternoon, and the mismatch in the sampling time explains part of the discrepancies. We meanwhile acquired hourly averages of the state agency measurements. We would like to update table 3 to compare the exact sampling times in the final revised version. The major conclusions however will not change. PM 2.5 is typically underestimated by 80%, while the difference PM 2.5-10 agrees within $\pm 10\%$ for those samples where Mainz Zitadelle is upwind of our sampling site and within $\pm 30\%$ for other wind directions.

Page 9361 line 21-23 and Page 9362 line 3 Referee #2 is correct that group 4b should be included in line 22 and also in line 28. Referee #2 is concerned that sample 5 should not be grouped with the other filters because the $\delta^{34}S$ of group 5 and 6 in this sample is lower than that of group 5 and 6 in other samples. We do not intend to compare the $\delta^{34}S$ of individual groups, e.g., Group 5 in between different samples in this paragraph. Our sole intent is to compare the isotopic composition of the individual groups within the same sample with each other. This also explains why sample 4

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is different and sample 5 is not. The weighted average for all secondary sulfates is $\delta^{34}S = (4 \pm 3)\%_0$ and $\delta^{34}S=(4\pm2)\%_0$ for sample 4 and 5, respectively. In terms of their isotopic composition the samples are similar. However, focusing on how the individual groups in each sample compare with each other, in sample 5 the isotopic composition of Groups 3a, 4b, 5 and 6 overlaps with the average and with each other within the analytical uncertainties. For sample 4 this is not the case. The isotopic composition of Group 5 overlaps neither with the average nor with that of Groups 3a and 4b of the same sample within the analytical uncertainty.

We will clarify page 9361 line 21 to page 9362 line 3 accordingly: `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 incloud 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. ´

Page 9362 line 22 We clearly stated, that $+18\%_0$ is the average difference between the isotopic composition of fresh ammonium sulfate from gas to particle conversion (Group 4a) and processed/coarse mode ammonium sulfate (Group 4b). See page 9362, line 11 and Page 9362 line 22. This is not the difference between the homogeneous and heterogeneous oxidation pathway.

Page 9371 line 3-10 Referee #2 rightly points out, that O_3 oxidation only dominates aqueous phase oxidation at pH 5.5 and that at pH 4.4 and pH 4.9 the oxidation by

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H_2O_2 is the dominant pathway of aqueous phase oxidation. It is correct that 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, as stated in line 6 that same change of pH increases the oxidation rate by O3 by one order of magnitude from $10^{-10}Ms^{-1}$ to $10-9Ms^{-1}$ for 0.2 ppb = $[SO_2(g)]$, 46 ppb = $[O_3 \text{ (g)}]$ and 0.6 ppb = $[H_2O_2]$ (Lee and Thiemens, 2001). If we 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 will increase. We will phrase this paragraph more clearly in the revised version.

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

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