

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 the anonymous reviewer for his suggestions to improve the manuscript. Detailed below are the replies to the specific comments raised by the reviewer.

We will add the following discussion to Section 2, in order to explain why we disregarded the theoretical work of Leung et al. (2001) on the sulfur isotope fractionation occurring during gas-phase oxidation of SO_2 by OH.

Saltzman et al. (1983) and Tanaka et al. (1994) determined the isotopic fractionation (α) for gas phase oxidation of SO_2 by OH as being kinetically driven. Tanaka et al. (1994) calculated a fractionation of -9‰ ($\alpha = 0.991$, $^{34}S/^{32}S_{fractionation} = (\alpha - 1)$) using ab initio quantum mechanical calculations. In contrast, Leung et al. (2001), using

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RRKM (Rice, Ramsperger, Kassel, and Marcus) transition state theory, calculated the fractionation as an inverse kinetic isotope effect, with $^{34}\text{SO}_2$ reacting faster than $^{32}\text{SO}_2$ resulting in a $\delta^{34}\text{S}$ increase of 140‰ ($\alpha = 1.14$) 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). 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. Studies of the mass-independent sulfur isotope fractionation of sulfate deposited in the Antarctic after the Mt. Agung eruption suggest that UV induced photooxidation ($\text{SO}_2^* + \text{SO}_2 \rightarrow \text{SO}_3 + \text{SO}$ followed by the reaction of $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$) contributes significantly to sulfate formation in the initial weeks after the eruption. This reaction leads to an enrichment of ^{34}S and a positive $\Delta^{33}\text{S}$ in the sulfate and a negative $\Delta^{33}\text{S}$ and a depletion of ^{34}S in the remaining SO_2 . After the initial weeks the importance of the normal oxidation mechanism ($\text{SO}_2 + \text{OH}$) increases leading to a depletion of ^{34}S and a negative $\Delta^{33}\text{S}$ in the sulfate.

An isotopic fractionation of +140‰ for gas phase oxidation of SO_2 is inconsistent with numerous observations in the troposphere. Typically, the isotopic composition of sulfate samples is on average only 3‰ more positive than simultaneously collected SO_2 (for a summary of data collected until 1990 see Krouse and Grinenko, 1991; for more recent datasets, e.g., Mayer et al., 1995; Querol et al., 2000; Novak et al., 2001; Tichomirowa et al. 2007). Considering the fractionation by heterogeneous oxidation, which has been calculated as +20‰ ($\alpha = 1.02$) (Saltzman et al., 1983) and measured as +16.5‰ ($\alpha = 1.0165$) (Eriksen, 1972a; 1972b), an average difference of +3‰ can only be explained

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by a significant contribution of kinetic fractionation to sulfate formation ($3\text{‰} \neq f_{het} \cdot 16.5\text{‰} + f_{hom} \cdot 140\text{‰}$; $3\text{‰} = f_{het} \cdot 16.5\text{‰} + f_{hom} \cdot x < 3\text{‰}$). 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 .

Samples were collected on gold-coated 47-mm-diameter Nuclepore polycarbonate filters with $0.4 \mu\text{m}$ pore sizes. The filters were placed in a stacked filter unit operated with one stage only. We will add a column specifying the start and stop time of each individual sample in Table 2. The sampling time of samples 1-6 and 8 was roughly 24 h (between 1280 minutes and 1550 minutes). The sampling time for sample 7 was 43 h.

We will replace the group number in Table 7 by the group name and add a label to the color scale in Figure 9.

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