

***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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I thank the authors for their throughout reply to my comments and questions. I'm satisfied with their answer except for the major issue of this paper: the  $\text{SO}_2 + \text{OH}$  reaction. I strongly disagree with the reply given by the authors on this point. All their conclusions are based on Baroni manuscript, which it uses advantageously to dismiss Castelman data. The authors on this particular point are clearly over interpreting Baroni's data. Quoted from Baroni paper 'In today's atmosphere, OH radicals remain the main sink of  $\text{SO}_2$  emitted after a volcanic eruption, and the  $\text{SO}_2^* + \text{SO}_2$  reaction is a minor reaction when compared to the  $\text{SO}_2 + \text{OH}$  reaction. The sulfur MIF measured in volcanic sul-

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phate recorded in snow is a diluted signal and may actually reach the extreme values recorded in Archean rocks. To estimate the upper limit of the sulphur isotopic anomaly generated by the photooxidation process, researchers should compare the kinetics of the  $\text{SO}_2 + \text{OH}$  and  $\text{SO}_2^* + \text{SO}_2$  reactions. Unfortunately, the rate of  $\text{SO}_2^* + \text{SO}_2$  is controversial (25) and is needed for such quantification. Moreover, the photo oxidation process is simply an assumption not a fact. The reality is when this reaction is injected in a stratospheric chemistry/transport model, it barely produces more than few % of the sulphate everything else is formed by  $\text{SO}_2 + \text{OH}$  (Bekki, personal communication) and this explain why Baroni et al clearly stated that photo oxidation should be a minor oxidation pathway. The correlation they observed btw  $\delta^{34}$  and  $\Delta^{33}$  doesn't eliminate the  $\text{SO}_2 + \text{OH}$  sink. It just says that part of the 34 enrichment found in sulphate comes from the reaction generating the sulphur anomaly, not all since both mechanism are running at the same time. Same is true for the lab experiments done by Farquhar et al. (2001). The photochemistry of sulphur is so complex that in none of Farquhar's experiments one can pinpoint exactly the step at the source of the sulphur anomaly.

Eriksen's experiments are done at isotopic equilibrium which takes more than few days to reach it (Eriksen et al, 1972a, 1972b) with concentrations of sulphur species are well above atmospheric conditions. As correctly mentioned by Saltzman et al., isotopic equilibrium is not attained in the atmosphere because of the oxidation sinks. Unfortunately Saltzman never considered  $\text{H}_2\text{O}_2$  as a possible oxidant for the aqueous phase. So the fact that sulphate is not enriched in 34 relative to  $\text{SO}_2$  in a proportion expected from isotopic equilibrium doesn't mean that  $\text{SO}_2 + \text{OH}$  should possess an alpha lower than one, simply because isotopic equilibrium is not reached. Leung's (Leung et al. 2001) alpha of 140 permil (sorry to have missed a 0 in my review) seems effectively too high but direction is in agreement with Castleman and Baroni data. Furthermore, there is no reason why the addition of OH to  $\text{SO}_2$  should be the most predominate step for the fractionation factor instead of the unimolecular dissociation of the adduct  $\text{OHSO}_2$ . Actually this metastable product, being in steady state with reactants and products may well be the step to consider for isotopic studies, as

in the case of CO+OH (Conny, 1998). Regarding Newmann data, the comparison btw SO<sub>2</sub> and SO<sub>3</sub> is irrelevant because SO<sub>3</sub> in power plant stack is formed by SO<sub>2</sub>+O, a very different mechanism than SO<sub>2</sub>+OH (eg. Flagan and Friedlander, 1978; Burdett et al., 1983). For the aircraft measurements, the authors themselves recognized that the lower atmosphere data were not significantly different than ground-level data (p337, L24). See also figure 8.15, where only 4 sulphate samples out of 13 show a slightly depletion compared to SO<sub>2</sub>. I note that no details of the atmospheric conditions are given for the aircraft collections. The true is that there is conflicting results, outdated experiments and missing lab experiments, and as today nobody knows what the sulphur fractionation factors for SO<sub>2</sub> is for heterogeneous and homogeneous sinks. The best data in our hands to estimate at least the direction of the sulphur fractionation of SO<sub>2</sub>+OH is still today the Castleman and Baroni, which both indicate an alpha greater than 1 for SO<sub>2</sub>+OH.

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