Geophysical Research Abstracts,
Vol. 10, EGU2008-A-09447, 2008
SRef-ID: 1607-7962/gra/EGU2008-A-09447
EGU General Assembly 2008

High resolution sulfur isotope depth profiling of aged sea salt particles - Understanding the importance of reactions at interfaces as a source of sulfate formation in sea-salt particles

B. Winterholler (1), J. Huth (1), M.O. Andreae (2), P. Hoppe (1)

(1) MPI for Chemistry, Dep. Particle Chemistry, J.-J.-Becher-Weg 27, D-55128 Mainz, Germany, (2) MPI for Chemistry, Dep. Biogeochemistry, J.-J.-Becher-Weg 27, D-55128 Mainz, Germany (winterho@mpch-mainz.mpg.de / Phone: +49 (0)6131 305 358)

Sources of atmospheric sulfur and its oxidation pathways are studied by isotope analyses of sulfate particles. The new Cameca NanoSIMS 50 ion microprobe technique permits isotope analyses of individual aerosol particles down to 0.5 μm diameter (Winterholler *et al.*, 2008). During this analysis particles are gradually sputtered away permitting to construct a depth profile of the sulfur isotopic composition across the particles.

The sulfur isotopic composition of aged sea salt is controlled by the isotopic composition of the CCN (sea salt), condensation of gaseous sulfuric acid onto the particle and the heterogeneous oxidation of sulfur dioxide within the particle. Whenever condensation/heterogeneous oxidation on the surface dominates while the mixing within the particle is limited, particles show a gradient of the isotopic composition from the outside to the inside of the particles. Well mixed particles on the other hand show no such gradient. Heterogeneous oxidation of SO_2 and condensation of gaseous sulfuric acid can be differentiated, as oxidation of sulfur dioxide in the aqueous phase shows a fractionation for $^{34}S/^{32}S$ of +16.5 per mill (Eriksen, 1972) with respect to the source SO_2 while homogeneous oxidation in the gas phase shows an isotopic fractionation of -9 per mill (Tanaka *et al.*, 1994).

Combining the information about the chemical composition of particles with the spatially resolved isotopic signature enables source apportionment of non-sea-salt (nss) sulfate and elucidating mixing processes between nss sulfate and sea-salt sulfate for each sample as well as understanding oxidation and mixing processes within the particles. This method is a new tool to quantify the contribution of different processes to the formation of nss-sulfate in sea salt particles.

Results from aerosol samples collected in Mace Head (Western Ireland) are presented. These samples represent different airmass types, such as clean marine boundary layer air, moderately polluted air and strongly polluted air transported from the continent.

Eriksen, T. E. (1972): Sulfur Isotope-Effects 3. Enrichment of S-34 by Chemical Exchange between SO_2g and Aqueous-Solutions of SO_2. *Acta Chemica Scandinavica*, **26**:975.

Tanaka, N., Rye, D. M., Xiao, Y. & Lasaga, A. C. (1994): Use of Stable Sulfur Isotope Systematics for Evaluating Oxidation Reaction Pathways and in-Cloud Scavenging of Sulfur-Dioxide in the Atmosphere. *Geophysical Research Letters*, **21**:1519-1522.

Winterholler, B., Hoppe, P., Foley, S. & Andreae, M. O. (2008): Isotope ratio measurements of individual sulfate particles by NanoSIMS. *International Journal of Mass Spectrometry* **accepted**.