Atmospheric SO_2 oxidation by NO_2 in the urban atmosphere: a view through sulfur multi-isotope compositions

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Modern anthropogenic aerosols usually exhibit a low but significant $\Delta^{33}S$ signature (-0.1 to 0.5‰). While the main oxidation pathways (O_2+TMI, H_2O_2, OH) would explain most of this $\Delta^{33}S$ range they cannot explain the highest $\Delta^{33}S$-values (close to 0.5‰). We investigated the possibility that an additional oxidation pathway is involved in urban areas, focusing in particular on the one involving NO_2, a major species in urban atmospheres.

We are reporting $^{34}\alpha$, $^{33}\beta$ and $^{36}\beta$–values specific to the NO_2 oxidation pathway at different temperatures (3 to 52°C). The NO_2 oxidation pathway (excluding the datum at 3°C) is characterized by a higher $^{34}\alpha$ (-0.349T+11.632) than the O_2+TMI oxidation pathway (-5.039-0.237T), H_2O_2 (16.51-0.085T), OH (10.60-0.004T) reported by Harris *et al.* (2013). The NO_2 oxidation pathway is also characterized by $^{33}\beta$-value = 0.514 and $^{36}\beta$-value = 1.921 that are closer to the mass dependent values (0.515 and 1.889, respectively) than the others oxidation pathways (Harris *et al*., 2013). This leads to the conclusion that the NO_2 oxidation pathway cannot explain the high $\Delta^{33}S$-values measured among the urban aerosols.

Those new parameters were then added to an oxidation model apparented to a Rayleigh distillation where both SO_2 oxidized into sulfate (SO_4) and SO_2 deposition are removed. Our results shows that the NO_2 oxydation pathway may be overprinted by a mixing of O_2 +TMI and OH as both fractionate the ^{33}S and ^{36}S isotopes similarly. We thus conclude that both O_2+TMI and OH oxydation pathways could be overestimated in urban areas. Another yet undiscovered process should be involved to explain the highest $\Delta^{33}S$-values that we observed in our urban aerosol samples, possibly the Criegee intermediate complex.

Harris, E., Sinha, B., Hoppe, P. et Ono, S. (2013). High-precision measurements of ^{33}S and ^{34}S fractionation during SO_2 oxidation reveal causes of seasonality in SO_2 and sulfate isotopic composition. *Environmental science & technology, 47*(21), 12174-12183.