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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Fractionation of sulfur isotopes during heterogeneous oxidation of SO₂ on sea salt aerosol: a new tool to investigate non-sea salt sulfate production in the marine boundary layer" *by* E. Harris et al.

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This is a well written manuscript, and authors carried out very careful experiments and data analysis. The manuscript present results of a series of experiments to characterize sulfur isotope effects during aqueous oxidation by H2O2, O3 and NaOCl, and potential application of this new data is discussed. This is an interesting and important study towards better constraining the SO2 oxidation pathway and aerosol formation process in MBL. Fig. 6 presents a very nice summary of the result.It nicely illustrates what are found, and also shows the potential limitation (e.g., knowing X, reservoir effect

after oxidizing most SO2), which might lead to further studies.

My comments are mostly technical and listed below.

Page 2708, Line 19, "SO2(g) -> -> SO32-", Is there something missing between two arrows?

page 2711, line 1, "second order in [SO2]," second order with respect to SO2, or first order with respect to Cl and SO2?

page 2711 line 19, and 2712, line 1, equation (2) says V-CDT so that the line 19 should be "V-CDT" in stead of "a standard ratio". The absolute ratios by Ding et al., 2001 are not used for calculating delta values for previous studies so that it may not be relevant here.

page 2712, line 6, "are" -> "can be"

page 2712, paragraph starting from line 8, This paragraph is technically an introduction for the paper. Can the whole section 2 be joined with 1?

page 2715, line 10, "N2 6.0" is this grade 6.0?

page 2715, line 22, ±2 %, this should be ±2 % of 102 ppm but it might be straight forward to say, 102 ± 2 ppm.

page 2720, line 12, each step of "SO2 hydrolysis and deprotonation"

page 2720, line 12, Eriksen, 1972 studied isotope exchange between SO2(g) and HSO3-. I wouldn't put this reference here but put it in line 19, perhaps.

line 17, equation (9) -> reaction (9)

line 19, It is difficult to follow here. It appears it was assumed that the observed isotope effect is due to equilibrium isotope effect among different sulfite species. This is somewhat reasonable. However, there might be be an isotope effect during the oxidation of each species to SO42-.

page 2722, line 6, SO23- -> SO32-

page 2723, line 5, "without considering" -> "Rayleigh fractionation effect is insignificant" the effect is there although it's small.

line 14, the low pH value from Sect. 4.2 -> "H2O2 oxidation under pH=2"

2724, line 4. Throughout the manuscript, isotope effect is described by fractionation factor (alpha). Here, so called epsilon value is used (i.e., 1-alpha, in per mil).

Line 17, I am not entirely certain how this 29±9 % is derived.

page 2725, line 9, heavy -> 34S-enriched

line 23, "by the influence of oxidation pathway", If 70 % of SO2 is oxidized in MBL (page 2709), what would be expected for the isotope ratios?

page 2726, "if the D17O of hypohalites was reliably known". According to the suggested reaction mechanism in this manuscript, oxygen in sulfate comes from water not from HOCl.

Fig.3, "Fractionation" is not defined although it appears alpha-1 in this case.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 2707, 2012.