

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 paper outlines a series of carefully constructed experiments designed to determine sulfur isotope fractionation on heterogeneous oxidation of SO₂ on sea salt particles over a range in pH. The authors have taken care to examine and eliminate or account for biases due to the methodology used and have demonstrated a significant sulfur isotope fractionation exists. The paper is very well written, clearly defines the terminology applied (an unambiguous specification of what the authors refer to with respect to the fractionation factor α), and outlines succinctly the results and implications of their

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experiments. In particular, the oxidation of SO₂ by NaOCl aerosols was found to be highly efficient and attended by an inverse isotope fractionation, producing sulfate that was isotopically lighter than the reactant by $11.8 \pm 3.6\%$ at 19°C. Oxidation of SO₂ by O₃ on sea salt aerosols gave the opposite result: sulfate was enriched in ³⁴S by $12.4 \pm 1.7\%$ at 19°C and the opposing fractionations for alkalinity-limited and non-limited pathways can potentially explain why ambient samples downwind of polluted coastal airmasses show variable to no fractionation for SO₂ oxidation. This is a very important publication that is expected to contribute significantly to our understanding of SO₂ oxidation in the marine boundary layer through the isotope composition of atmospheric sulfur species.

There are a few issues the authors should address prior to publication. These are itemized below:

pg 2722 line 6. Explain where, when and why SO₂³⁻ is formed. I'm not familiar with it.

pg 2724 line 5: Spell out how the value of $17.3 \pm 3.6\%$ was derived. Adding up the various fractionation factors associated with equilibrium reactions shown in equations 6 through 10 gives +12 to +23% and the summation of the error is much higher than 3.6%.

pg 2724 line 17 versus line 24. Clarify what the difference (29% versus 40%) is due to - HOCl formed in the presence of photolysis?

pg 2727 line 1: lower appears twice in this sentence - once on the previous page and as the first word on this page.

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