

Interactive comment on “Sulfur isotope fractionation during heterogeneous oxidation of SO₂ on mineral dust” by E. Harris et al.

Anonymous Referee #1

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Harris et al. measure the fractionation factors for the oxidation of SO₂ in aqueous solutions of mineral dust leachate and on the surface of mineral dust particles. They found that oxidation of SO₂ in an aqueous solution of mineral dust leachate is fast, faster than that of solutions of Fe, suggesting synergistic enhancement by multiple transition metal species. The fractionation factor for oxidation of SO₂ in aqueous solutions of mineral dust leachate and of Fe are similar ($\alpha \approx 0.99$), suggesting similar mechanisms. The oxidation of SO₂ on the surface of mineral dust particles was much slower, and was enhanced by the simultaneous presence of light, humidity and ozone. The rate of this reaction is controlled by uptake of SO₂ to the surface of the particle, and not subsequent oxidation. The fractionation factor $\alpha \approx 1.01$ is similar to that of SO₂ oxidation in the aqueous-phase by H₂O₂ and O₃. They use PMF analysis to determine the impact of dust mineralogy on their results, and demonstrate that this fractionation

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factor will be dependent upon the mineralogy, as well as the degree of chemical ageing.

This manuscript is very well written and represents a significant contribution towards our understanding of the influence of dust on tropospheric sulfate formation, and the isotopic fractionation that occurs during chemical processing. I highly recommend publication. I have only a few minor corrections/clarifications that are detailed below.

2nd paragraph of Introduction: change “on to” to “onto”

Section 3.1: Change the title of section 3.1 to reflect what is actually discussed in that section.

Figure 4: Does this mean that sulfate formation on dust is only significant in the presence of ozone, light and RH?

Section 5.1: You estimate the concentration at exactly 8 hours, but not all of your experiments last this long. Do you extrapolate linearly?

Section 5.1: Define MDRHO_{3hv}, etc

Figure 4: Should y-axis read x-axis?

Figure 4 and earlier: Specifically define “untreated”.

Section 5.3: Can you use a different word than “factor”? All the factors in this paragraph are confusing.

Section 5.3.1: Factor 1 contributes to what % of total sulfate production?

Section 5.3.2: I would rather read “depleted in ³⁴S” instead of “enriched in ³²S”, but I realize it means the same thing.

Section 5.5 last sentence: Remove “is” between “rate” and “of”

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 2303, 2012.