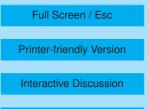**Atmospheric
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Interactive
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Interactive comment on "Fractionation of sulfur isotopes during heterogeneous oxidation of SO$_2$ on sea salt aerosol: a new tool to investigate non-sea salt sulfate production in the marine boundary layer" *by* E. Harris et al.

Anonymous Referee #2

Received and published: 22 March 2012

Harris et al., 2012 present the sulfur isotope fractionation factors associated with SO$_2$ oxidation on sea salt and NaOCl aerosols. This work is appropriate for publication in ACP because it contributes a potentially powerful new tool for the investigation of atmospheric sulfur chemistry, particularly in the marine boundary layer. The manuscript is well written. I have a couple structural suggestions as well as some sections that require clarification. Assuming these comments are addressed, I recommend the manuscript for publication in ACP.

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Interactive Discussion

Discussion Paper

1 Scientific comments:

p. 2711, l. 10-12: von Glasow et al., 2002 uses rate constants for HOCl/HOBr $+$ HSO_3^- that are assumed to be identical to those based on experiments conducted at high pH with SO_3^{2-}. I have been able to find little justification for this assumption. For sulfate production in alkaline sea salt aerosols (in clear-sky conditions), this is fine, but on more acidic aerosols or in cloud droplets, most S(IV) will be HSO_3^-, so if the rate constant is too high, the role of halogens in in-cloud sulfate production will be overestimated (such as in Table 3 of von Glasow). Some of the papers that you cite later on in Section 4.4 suggest that the HOCl reaction is also fast at low pH, but do not go so far as to provide rate constants. I'd suggest that the introduction might express a little more of the uncertainty of our knowledge of the role of halogens in sulfur chemistry.

p. 2721 l. 9: The lack of a significant difference between the experiments with and without O_3 is in part due to the large error bars on the ssaltirr experiment. What is the source of the large uncertainty on this experiment?

p. 2726 l 10-15: Regarding the $\Delta^{17}O$ associated with HOX. The $\Delta^{17}O$ of sulfate is determined by both the isotopic composition of the oxidant and how oxygen is transferred to that sulfate during the oxidation process. In addition to needing to know the oxygen isotopic composition of HOX, the the source of the oxygen transferred to the sulfate also need to be known. If the oxidation process is terminated through hydrolysis, the O-atom comes from a water molecule making the composition of HOX is irrelevant, as the sulfate will take on the D17O of the water (roughly 0 per mil). In contrast, if the oxygen comes directly from the HOX, the isotopic composition of that HOX becomes important. Based on the work of Yiin and Margerum [1988], which points to hydrolysis, it is likely that HOX leads to a sulfate $\Delta^{17}O=0$. See McCabe et al. [2006] for some discussion of this.

2 Structural comments:

A paragraph should be added to the beginning of Section 3 to outline the experimental method before going into the details of the different steps. The introduction lacks a discussion of pH, so you should at least introduce the issue of S(IV) speciation at the beginning of Section 3 before jumping into 3.1.1 to explain its relevance in the context of the sea salt aerosol experiments that follow.

p. 2710, l. 12-23: This paragraph is awkward. I expect the values of sea salt aerosol and bulk sea water alkalinity to be included in the first sentence, but they are not presented until the third sentence.

p. 2710, l. 24: Change first sentence to "...as or more important than oxidation by O_3 in marine boundary layer production *of sulfate on sea salt aerosols*" or "clear-sky marine boundary layer production" to specify that the following discussion of oxidation pathways is specific to heterogeneous oxidation. The 4% figure from Gurciullo, 1999 is specific to their sea salt aerosol model. Hydrogen peroxide will represent a larger fraction of total MBL sulfate formation when in-cloud processing is included.

p. 2722: Keep a consistent order in describing the experiments. In the text, the order is generally water, NaOCl, sea salt, but there are some inconsistencies (e.g. waterAO3 is discussed last in Section 4.3). The tables are organized water, sea salt, NaOCl.

3 Technical comments:

p. 2710, l. 27 (and others): my understanding is that the convention for radical symbols puts the "dot" after the chemical name, not before.

p. 2711, l. 25: While I'm not familiar with all the details of sulfur isotope standards, as far as I can tell, VCDT is not strictly an international stan-

dard for ^{36}S (see http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/ Stable_Isotopes/34S32S/IAEA-S-1.htm; the IAEA report encourages future establishment of ^{36}S values for the international sulfur standards)

p. 2713, l. 7: add "by H_2O_2" after "during sulfate production".

p. 2718, l. 24: too many significant digits. Change "0.65$\pm$0.74 nmol h^{-1}" to "0.6$\pm$0.7 nmol h^{-1}"

p. 2722, l. 5: comma before "respectively"

p. 2722, l. 28: change "different to ssalt O_3" to "different from ssalt O_3"

p. 2724 l. 2: change "different to oxidation" to "different from oxiation"

p. 2725 l 8: change "isotopic observations" to "sulfur isotope observations"

p. 2727 l 1: remove duplicate "lower"

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