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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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We thank Ann-Lise Norman, Shuhei Ono and the anonymous reviewer for their helpful comments on the paper. We will discuss below the changes that have been made in response to the reviewer's comments. The changes will be presented in the order they appear in the manuscript.

- P2708 L19: two arrows with an empty space in between is used to indicate that the steps in the middle have been skipped one arrow would indicate a direct for-

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mation of SO₃²⁻ from SO₂(g) without any intermediate step. To make this more clear we have written "multiple steps" in between the two arrows.

- P2710 L12-23: The reviewer requested that this paragraph be restructured for clarity. Two sentences from the end of the previous paragraph were shifted to this paragraph, and the paragraph itself was reordered and expanded. The text now reads:

“Field measurements and laboratory studies commonly find that sulfate production is larger than would be expected from the neutralisation capacity of sea salt aerosol estimated from the alkalinity of bulk sea water (Sievering et al., 1999; Caffrey et al., 2001). Two explanations have been proposed: (i) oxidants other than O₃ play a more important role than currently known, and (ii) the alkalinity of sea salt aerosol is larger than the alkalinity of bulk sea water. As sea salt aerosol form from bursting bubbles, they efficiently skim the surface microlayer which can have high alkalinity due to cations associated with organic molecules and biogenic skeletal fragments. This could provide up to 2.5 times additional alkalinity at typical marine sites, and >200 times more at especially favourable sites (Sievering et al., 1999, 2004). Following sea salt aerosol production, shifting of the carbonate equilibrium with evaporation causes the alkalinity of sea salt aerosol to be somewhat higher than bulk sea water, however this is insufficient to explain observed excess sulfate concentrations (Sievering et al., 1999). Laskin et al. (2003) proposed that interface reactions between OH (g) and surface chloride ions could also generate excess alkalinity in sea salt aerosol, however observations and models show that this pathway will account for <1 % extra sulfate production in the ambient environment (Sander et al., 2004; Keene and Pszenny, 2004; Alexander et al., 2005; von Glasow, 2006). As none of these mechanisms can adequately explain observations of sulfate production compared to alkalinity, it is likely an oxidant other than O₃ is playing a significant role in the MBL.”

- P2710 L24: The sentence was expanded to: “Several reactions have been identified
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- tified that may be as or more important than oxidation by O_3 for sulfate production on sea salt aerosols in the marine boundary layer.”
- P2710 L27 (and others): The IUPAC convention in the position of the dot signifying a radical. The conventional representation of radicals puts the dot next to the atom which has the unpaired electron (the O atom in an $\cdot OH$ radical). The symbol could also be written $HO\cdot$ to show the dot after the chemical name as suggested by the reviewer, however the hydroxyl radical is most commonly written OH and not HO. For other radicals in the paper have changed the position of the dot as suggested by the reviewer.
 - P2711 L1: The reaction is second order in S(IV); SO_2 has been changed to S(IV) in the text (Paragraph 4, Hoppe and Caffrey, 2005).
 - P2711 L10-12: The following sentence was added to the end of this paragraph to better express the level of uncertainty in the rate of halogen-sulfur chemistry: “However, the pH-dependent rate of halogen oxidation (eg. the rate of oxidation by HOCl compared to OCl^-) is not well-constrained, although results suggest the oxidation rate will increase at lower pH (Yiin and Margerum, 1988; Shaka et al., 2007).”
 - P2711 L19: ‘a standard ratio’ has been changed to ‘V-CDT’.
 - P2711 L25: Reference to ^{36}S has been removed from the sentence discussing V-CDT: “ ^{36}S is one of the heavy isotopes (^{33}S or ^{34}S) and V-CDT is the international sulfur isotope standard, ...”
 - P2712 L6: ‘are’ has been changed to ‘can be’.
 - P2712, paragraph starting L8: Shuhei Ono pointed out that Section 2: Sulfur Isotopes in the Marine Environment is part of the introduction. Therefore the

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previous introduction section (P2709 L5 - P2711 L12) has been given the sub-heading '1.1 The sulfur cycle in the marine boundary layer', and the previous Section 2 is now '1.2 Sulfur isotopes in the marine boundary layer'.

- P2713 L4: The reviewer requested that "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." The following paragraph was added to the beginning of Section 3:

"The fractionation factors relevant to non-sea salt sulfate production in the MBL were considered with a series of experiments, in which SO₂ with a known isotopic composition was oxidised to sulfate under various conditions. The sulfur isotopic composition of the residual SO₂ and the product sulfate was measured with NanoSIMS to determine fractionation factors for SO₂ oxidation during the major MBL oxidation pathways. Due to the relatively high pH of sea water and sea salt aerosol, compared to, for example, polluted cloud water, the first experiments presented consider fractionation during uptake of SO₂ to the aqueous phase and the subsequent acid-base equilibria (Equations 7 to 10). Following this, fractionation factors specific to the various MBL oxidants are measured."

- P2713 L7: 'by H₂O₂' was added after during sulfate production'.
- P2715 L10: 'N₂ 6.0 (Westfalen AG)' has been changed to 'N₂ (Grade 6.0, Westfalen AG)'.
- P2715 L22: '102 ppm ± 2%' has been changed to '102±2 ppm'.
- P2718 L24: The number of significant figures was corrected: "The SEM measurements showed that 0.7±0.7 nmol h⁻¹ of sulfate was generated, ..."

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- P2720 L12: now reads ‘...to each step of SO₂ hydrolysis and deprotonation...’ The reference Eriksen, 1972 has been moved to L21 to better reflect its contents.
- P2720 L17: ‘Equation’ has been changed to ‘Reaction’: “Reaction (9) has a pK_a of 1.77 and Reaction (10) has a pK_a of 7.19...”
- P2720, paragraph beginning L19: Shuhei Ono stated that “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 an isotope effect during the oxidation of each species to SO₄²⁻.” Thus the sentence “Previous results have shown that the terminating oxidation reaction is unimportant for isotopic fractionation at this level of uncertainty (Harris et al., 2012b)” (P2721 L2-4) has been changed to “This analysis assumes fractionation is due to equilibration between the different S(IV) species and not due to fractionation during the oxidation of each S(IV) species to sulfate; this is a reasonable assumption has previous results suggest the terminating oxidation has a minimal isotopic effect (Harris et al., 2012b)”.
- P2721 L9: The following sentences were added to clarify the source of the large uncertainty in quantification for ssaltirr, and to show that this error does not significantly effect the conclusions: “The amount of sulfate generated in sea salt aerosol in the presence and absence of O₃ is not significantly different. Quantification for ssaltirr has a larger error than the other ssalt experiments due to tearing during mounting of the filter for SEM analysis, which could obscure differences in production rate. However, there is also no significant different between sulfate production rates for ssalt, ssaltO3 and ssaltirrO3, which have smaller errors. Sulfate generation from oxidation...”
- P2722 L5: A comma was added before ‘respectively’.
- P2722 L6: SO₂³⁻ was a typing error and was changed to SO₃²⁻. A reference

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to Equation 10, which describes formation of SO_3^{2-} , has been added to clarify the origin of this species: “Oxidation of sulfite by HOCl proceeds via nucleophilic attack of SO_3^{2-} (formed via Equation 10) on HOCl, which results in Cl^+ transfer to form ClSO_3^- .”

- P2722 L18: “different to ssalt O3” was changed to “different from ssaltO3”.
- P2723 L5: “can be directly taken as the α_{34} without considering Rayleigh fractionation effects due to depletion of the reservoir” was changed to “can be directly taken as the α_{34} as Rayleigh fractionation effects due to depletion of the reservoir are insignificant” to emphasise that Rayleigh fractionation effects are always occurring but are too small to have any effect on results in this case.
- P2723 L14: ‘the low pH value’ was changed to ‘the value for H_2O_2 oxidation under $\text{pH} = 2$ ’.
- P2724 L2: “different to oxidation” was changed to “different from oxidation”.
- P2724 L4 and L7: the permil (ϵ) value is used here to better express the changes for each reaction; the alpha values have now been added in brackets for consistency ($\alpha_{34} = 1.0173 \pm 0.0037$ and $\alpha_{34} = 0.972$).
- P2724 L5: The value of 17.3 ± 3.7 was taken directly from the pH experiments. The error is smaller than the sum of the errors of the individual reactions 7 - 10, as the experiments considered the fractionation produced by the accumulated reaction steps; these were then plotted to determine the fractionation of the individual steps. A cross-reference has been added in the text for clarity: “This suggests that following the equilibrium fractionation of $17.3 \pm 3.7\text{‰}$ (from pH-dependent experiments, as shown in Figure 3) for $\text{SO}_2(\text{g}) \rightleftharpoons \text{HSO}_3^-$ at 19°C , kinetic effects related to...”

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- P2724 L17: The value of $29\pm 9\%$ was obtained from isotopic mass balance of the two fractionation factors and the resulting measured fractionation. This is now reflected in the text: “Isotopic mass balance shows that HOCl contributes $29\pm 9\%$ of oxidation...”
- P2724 L17 versus L24: Lines 18-24 have been altered to clarify the source of the extra HOCl oxidation: “The ssaltirrO3 sample would be expected to have the highest concentration of hypochlorous acid from interface reactions whereby photolysis of O_3 leads to formation of $\cdot OH$ radicals and subsequently HOCl (see Oum et al. (1998); Knipping et al. (2000) for details). The measured α_{34} for ssaltirrO3 shows HOCl contributed $40\pm 16\%$ of oxidation in this experiment: an increase of 11% due to photolytic production of HOCl via O_3 .”
- P2725 L8: “isotopic observations” was changed to “sulfur isotope observations”.
- P2725 L9: ‘heavy’ has been changed to ‘ ^{34}S -enriched’.
- P2725 L23 “by the influence of oxidation pathway”, S. Ono requested to calculate what would be expected for the isotope ratios if 70 % of SO_2 was oxidized in MBL (page 2709)?

In the absence of simultaneous measurements of the isotopic composition of SO_2 (g) in the studies discussed here, using their data for, quantitative isotope balance calculations would be purely speculative. The isotopic composition of the nss-sulfate depends on the source dependent isotopic composition of the SO_2 as well as on the oxidation pathway of the SO_2 . Only simultaneous measurements of the isotopic composition of both allow quantitative estimates of the contribution of individual oxidation pathways.

- P2726 L10-15: The reviewers pointed out that the discussion of the $\Delta^{17}O$ of sulfate produced from HOX oxidation was incomplete, as it considered only the

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$\Delta^{17}\text{O}$ of the oxidant and not the transfer of the O atom. This following sentences have therefore been added to L11:

“...if the HOX oxygen atom comes from atmospheric water. The $\Delta^{17}\text{O}$ of HOX is only relevant if the O atom is transferred to sulfate during oxidation. The results of Yiin and Margerum (1988) suggest that the O atom is added to sulfate from atmospheric water during hydrolysis of chlorosulfuric acid, thus the sulfate formed would have a $\Delta^{17}\text{O}$ of 0‰. However this has not been conclusively shown, for example, with an experiment involving isotopically-labelled HOX. If the $\Delta^{17}\text{O}$ of sulfate produced from hypohalite oxidation was reliably known, it would be possible to distinguish...”

- P2727 L1: The extra ‘lower’ has been removed.
- Tables 1 and 4 and Figures 2 and 4 were altered to keep consistency in the order in which the three types of experiments are presented (water, OCl, seasalt).
- ‘Fractionation’ in Figure 3 was defined: “Fractionation of $^{34}\text{S}/^{32}\text{S}$ at the different stages of $\text{SO}_2(\text{g}) \rightarrow \text{SO}_3^{2-}(\text{aq})$ expressed as $((\alpha_{34} - 1) \times 1000)$ ”.

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