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Interactive comment on "In-cloud sulfate addition to single particles resolved with sulfur isotope analysis during HCCT-2010" *by* E. Harris et al.

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We thank the reviewer, Becky Alexander, for agreeing to review the manuscript and for providing a helpful and constructive review. We will incorporate all her suggestions into the final paper. The comments are addressed pointwise below in the order they appear in the review. Page and line numbers refer to the discussion paper before changes were made.

- P2939 L18-19: Dr. Alexander points out that the pH-dependence of oxidation catalysed by transition metal ions (TMI catalysis) is not strictly pH-independent, as the concentration of S(IV), on which the rate depends, is not pH-independent.

We have addressed this in the manuscript with a more detailed discussion of the state of knowledge regarding pH-dependence of the TMI-catalysed pathway: ‘Oxidation by transition metal catalysis is less strongly pH-dependent than oxidation by O_3. The concentration of S(IV) available for oxidation is pH-dependent and studies suggest reaction of SO_3^{2-} may be favoured over HSO_3^- (Rani et al., 1992; Cohen et al., 1981), however the availability of metal ions is higher at lower pHs, and the rate constants for oxidation may peak around pH 4-6, leading to a complex pH dependence which is not fully understood (Cohen et al., 1981; Ibusuki and Takeuchi, 1987). The oxidant (O_2) for TMI-catalysed oxidation is not limiting, however the concentration of transition metals present...’

- Introduction: *You need to mention Criegee chemistry [...] Some discussions about its potential impacts on sulfate formation in this location during this time poeriod is warranted.*

  We have added information and discussion about Criegee radicals:

  - P2941 L20-21: The fractionation factor for the recently identified gas-phase oxidation pathway involving Criegee radicals (Mauldin et al., 2012; Boy et al., 2013) has not yet been measured.
  - Table 1 (new table) - see next comment.
  - P2955 L3: ‘...reaching the sample site. Criegee radical oxidation is not expected to play an important role in sulfuric acid production during late autumn in temperature regions (<1%; Pierce et al. (2013); Sarwar et al. (2013))) and it is therefore very unlikely the pathway played a significant role in the sulfur cycle during HCCT-2010. Air parcels in FCE 11.2 and 11.3 had recently...’

Table 1. Sulfur isotope fractionation factors for the major knwon continental atmospheric SO_2 oxidation pathways. $\epsilon_{34} = (\alpha_{34} - 1) \times 1000$; ie. ϵ_{34} is an expression of α_{34} in permil. Reaction types: Gas = gas-phase, AQ = aqueous, SURF = surface oxidation on mineral dusts, possibly with O_3 as an oxidant, as described in Harris et al. (2012a). References: 1) Harris et al. (2014), 2) Harris et al. (2012b), 3) Harris et al. (2012a).

Oxidant	**Type**	**ϵ_{34} at ~20°C** permil	**T dependence** permil $°C^{-1}$	**Ref.**
OH	Gas	10.5±0.7	-0.004±0.015	1
Criegee	Gas	*Unknown*		
H_2O_2	AQ	14.8±0.2	-0.085±0.004	1
O_3	AQ	17.4±2.8	*Unknown*	2
O_2 (TMI-catalysis)	AQ	-9.8±0.04	-0.237±0.004	1
Unknown	SURF	9.6±3.6	*Unknown*	3

- Section 2: *It would be useful to have a table of alpha values for each reaction discussed in the introduction.*

  A table (Table 2 in the revised manuscript) has been added, as well as a cross-reference to the table at P2941 L20-21: 'Values of α_{34} for the major oxidation pathways - such as oxidation by OH, H_2O_2, O_3 and transition metals - have been measured, as shown in Table 2.', and a cross-reference at P2955 L25-26: 'The δ^{34}S of the sulfate that could be added from each potential source was calculated from the upwind isotopic composition of SO_2 or H_2SO_4 and the fractionation factors shown in Table 2.'

- P2942 L21-23: *It's not clear why isotopic analysis is particularly useful for distinguishing between these two reactions.*

  The addition of the table under the previous comment makes this point clearer; in addition, the following text was added (P2941 L21 to P2942 L2): 'Isotopic analyses are particularly useful to quantify the importance of transition-metal catalysed oxidation of SO_2 compared to oxidation by H_2O_2 in clouds, as TMI-catalysed oxidation is the only known pathway that produces negative isotope fractionation in continental environments, as shown in Table 2 (Harris et al. 2013).'

- P2954 L24: Dr. Alexander mentioned that it is necessary to clarify *what* has a smaller magnitude than for FCE 11.2 and 11.3 - the observed isotopic composition, the fractionation factor, or something else?

  We have now clarified this in the text (P2954 L21-24): 'The fractionation factor for gas-phase production of sulfuric acid from oxidation of SO_2 by OH radicals is 10.6±0.7 permil at 0°C (Harris et al. 2014), which agrees with the observed difference between δ^{34}S of SO_2 and H_2SO_4 for FCE 7.1. However, the known fractionation factor has a much smaller magnitude than the observed difference between δ^{34}S of SO_2 and H_2SO_4 for FCE 11.2 and 11.3.'

- Figure 5: It appears that Figure 5 did not appear properly in the published discussion, and in addition the correct figure requires some alterations for clarity. The new version of Figure 5 addresses the points raised by Dr. Alexander and is much easier to understand. The caption of the new version of Figure 5 reads:

  'Isotopic composition of particles measured during HCCT-2010 for cloud events 11.2 and 11.3: *a)* fine mixed particles (= OA + salt), *b)* coarse mixed particles, *c)* fine mineral dust, *d)* coarse mineral dust. Mixed particles are shown in red and mineral dust in orange. Size-resolved mixed particles could only be measured in cloud droplet residual; upwind and downwind results are therefore equal for fine and coarse particles. In '*b)* Coarse mixed particles' for FCE 11.3 sulfur was also measured in coated soot particles, and these are shown as grey crosses. Straight thick lines (blue, green and brown) show the isotopic composition of sulfate that could be added to particles in the cloud from different sources according to the legend, and the dashed dark blue line shows the sulfate that would have been

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added from the SO_2 removal (α_{cloud}) as discussed in Harris et al. (2013). Pale circles show measurements for individual grains and larger, dark circles with error bars show the mean and the 1σ error. Dotted lines follow from upwind to in-cloud to downwind particles and show the change in δ^{34}S due to cloud processing.'

- P2956 L25-28: The term 'cloud droplet residual particles' is now defined, and a cross-reference was added to the part of the experimental section where the collection of these particles is described: 'Mixed particles and coated soot particles >1 μm in diameter were present only on the cloud droplet residual filters (ie. those particles that were activated in the cloud, see Section 3.2); in the interstitial and at the valley sites these two types of particles were always <1 μm in size.'

- P2957 L14: We have clarified what is referred to by 'during FCE 11.3 the increase in δ^{34}S could be due to...':

  'During FCE 11.3 the increase in δ^{34}S of fine mixed particles could be due to either...'

- Conclusion: As stated by Dr. Alexander, large-scale models will never be able to capture the details of these single particle processes; she therefore requests that we mention i) ideas for parameterization, and ii) the most important thing models may be missing in light of these results.

  We have added on P2962 L22-26: 'The results demonstrate the potential of sulfur isotope measurements for investigating SO_2 oxidation, particularly when single-particle isotope ratios are measured with NanoSIMS. Incorporating the findings of this study into models will result in a much more accurate depiction of the continental sulfur cycle and the effect of cloud processing on the environmental effect of SO_2 and sulfate. However, it is not currently feasible to mechanistically capture extremely detailed single-particle results, such as those obtained in this study, into full-scale global climate models - although a number of recent studies have successfully applied particle-resolved models to investigate black carbon on

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a local and regional scale (Riemer et al., 2009; Kajino and Kondo, 2011; Ching et al., 2012). The findings of this study which are most likely to have a large impact on modelled sulfate distributions and associated radiative forcing are i) the importance of the TMI catalysis pathway, particularly in creating sulfate that may be quickly removed from the atmosphere on large particles, and ii) the large impact direct sulfate uptake may have on the smallest particles, even when it is not the most important process on a total mass basis. Future model studies investigating the potential role of these processes first on a smaller scale, as in the black carbon case, will help to parameterise these effects to improve modelling of SO_2 and sulfate in global-scale studies.'

- Table 3: *Is the oxidation of SO_2 on the surface of aerosols (surf) via O_3?*

  The exact mechanism(s) and oxidation pathway(s) on dust surfaces are unknown, although results suggest a role for O_3. This is now clarified in the Table 3 caption: '...SO_2 oxidation on the surface of Sahara dust with no aqueous phase (ie. on interstitial particles, possibly involving O_3 as described in Harris et al. (2012a); α_{surf}),...'

- Figure 4: *The label 'change' is not descriptive enough [...] Please show an equation instead.*

  An equation for 'change' has been added to the caption of Figure 4 to clarify this point: 'Points show the upwind and downwind values of δ^{34}S while columns show the change (change = $\delta^{34}S_{\text{downwind}}$ - $\delta^{34}S_{\text{upwind}}$) and the 1$\sigma$ error of the measurement.'

- Figure 5 caption: A mistake was corrected in the caption: 'Straight lines show the isotopic composition of sulfate that could **be** added to particles in the cloud from different sources according to the legend.'

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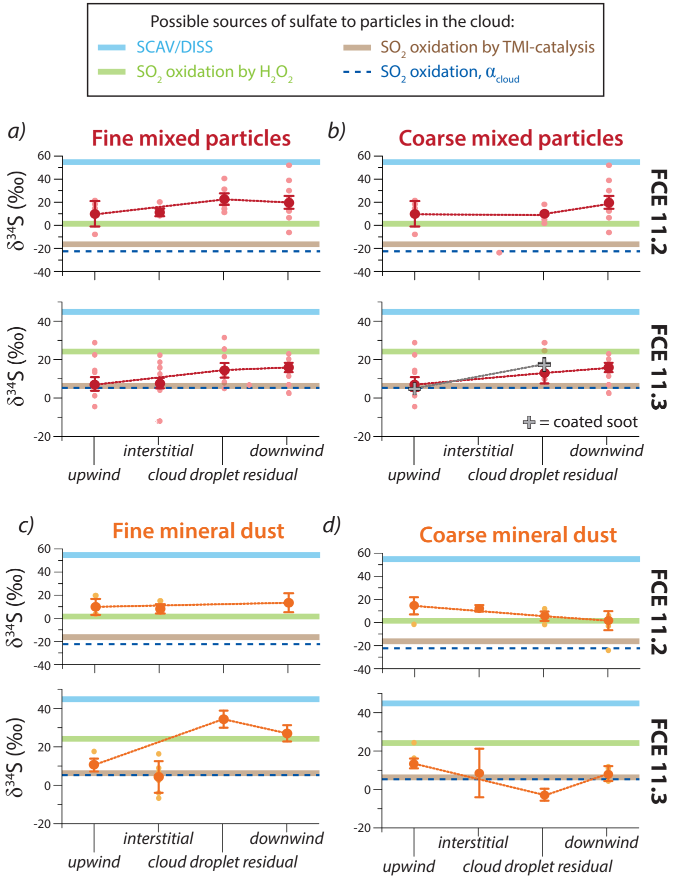

Fig. 1. Updated Figure 5