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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 Becky Alexander and the anonymous reviewer for this thorough and careful reviews of this manuscript. All the changes requested by both reviewers have been made. Responses to the individual reviews have already been presented. Here all the changes made in response to both reviews are shown in the order in which they appear in the final manuscript. Page and line numbers refer to the discussion paper before changes were made.

Changes to the text

- 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...'

- P2941 L20-21 (Introduction): B. Alexander - *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...'

- P2942 L21-23: B. Alexander - *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).'

- P2493 L11: Reviewer 2 requests that more detail is added to the section referring to connected flow calculations, particularly regarding the coefficient of divergence. We have added more detail into the text (P2493 L9-17):

'...the local meteorological conditions were stable.

Connected flow between sites was investigated with ozone concentration profiles, ozone cross correlations, and hydrodynamic flow analysis, as ozone is quasi-chemically-inert and relatively insoluble in water with no significant primary sources (Tilgner et al., 2014). The coefficients of divergence (COD) for several aerosol particle bins and ozone concentrations were also calculated to characterise connected flow conditions. The COD is a statistical measure of temporal similarities between the concentrations measured at the different stations; lower COD values indicate very similar concentration profiles, and a COD of <0.1-0.2 can be used as an indication of homogeneity between sites (Tilgner et al., 2014; USEPA, 2004). In addition, connected flow between the sites was periodically measured with tracer experiments following the release of an inert gas (SF_6) at Goldlauter, with measurements at 5-minute intervals at nine sites including the in-cloud and downwind stations. The connected flow analyses are discussed in

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detail in a companion paper in this special issue of *Atmospheric Chemistry and Physics* (Tilgner et al., 2014).'

- P2950 L6-7: Reviewer 2 wonders how soot, coated soot and mixed OA/IA are differentiated without SEM analysis, based on the ratios in Figure 3. We have clarified now in the text that the combination of ratios is critical for distinction: in at least one ratio each particle used was able to be distinguished: '...it was possible to distinguish the different particle types from a NanoSIMS isotopic analysis without a corresponding SEM image. The distinction between OA/IA, soot and coated soot is challenging as there is a high degree of overlap in most ratios; however, when all the ratios are used in combination all the particles used for isotopic analysis were able to be definitively categorised. Ratios X_O, X_C and X_S are particularly useful to distinguish between mixed OA/IA and coated soot.'

- 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 $\delta^{34}S$ 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 $\delta^{34}S$ of SO_2 and H_2SO_4 for FCE 11.2 and 11.3.'

- P2955 L24: Reviewer 2 - *On how many particles in total is this analysis based? ...How representative is the particle collective of what is going on in these clouds?*

A total of 128 particles (54 for FCE 11.2 and 74 for FCE 11.3) were analysed, with at least five particles analysed on each of the 8 individual filters for each event (coarse and fine; upwind, downwind, cloud droplet residual and interstitial).

Particles with enough sulfate for isotopic analysis were chosen at random from the thousands of particles on each filter. We now mention this point in the text:

'A total of 128 particles, 54 from FCE 11.2 and 74 from FCE 11.3, were analysed to investigate the changes in isotopic composition between the measurement stations. At least five particles on each of the eight filters (up-wind/downwind/interstitial/cloud droplet residual; coarse/fine) were analysed. Particles were chosen at random from the thousands of particles present on the filter, therefore there is no apparent bias and despite the small sample size inherent in this technique, the results are expected to be representative.'

• 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...' (B. Alexander):

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

• P2962 L22-26 (Conclusions): Both reviewers requested substantial additions to the conclusions considering primarily the impact of these results for modelling studies.

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.

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Reviewer 2 mentions that it would be useful to give the modelling community a guide as to how wrong their answer may be if they do not account for the variation in particle composition when modelling sulfate production. *'For example, can you compared the estimated sulfate production within the cloud assuming an internal mixture for the particle population to the sulfate production based on different particle types'?*

A comparison as suggested by reviewer 2 would require a complex model treatment and is, as such, beyond the scope of this paper. There are a number of non-linear factors and feedbacks that complicate a quick assessment of how much this may affect a model; for example, particle lifetimes, CCN number concentration and the non-linear relationship to cloud droplet number concentration, the pre-existing particle population... We have therefore provided a few guideline examples of situations where a large effect may be expected and a hypothesis of what the effects may be.

Reviewer 2 also mentioned that a significant amount of organic matter is produced in clouds, and wonders if it may be possible to apply this technique to investigate this problem.

The last paragraphs of the conclusions, from P2962 L22 onwards, now read:

'The results demonstrate the potential of sulfur isotope measurements for investigating SO_2 oxidation, particularly when single-particle isotope ratios are measured with NanoSIMS. The application of this technique to other systems, for example, the formation of nitrate and other nitrogen compounds in clouds, may show similar behaviour to the sulfate system and be an ideal topic for NanoSIMS investigation. Organic matter production in clouds accounts for a large amount of mass gain. A NanoSIMS study of OA formation could yield exciting results although it may be challenging compared to the simpler sulfate case. Investigatory studies looking at the variation in carbon isotopic composition between characteristic SOA types or important precursor compounds, as well as an study of the

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behaviour, matrix effects, and precision of ^{13}C measurements in aerosol particles with NanoSIMS, would provide an idea of the feasibility of a study of this type.

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 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. These effects will be most important in environments such as Asia, where SO_2 and dust concentrations may be very high, and in areas where water vapour concentrations are higher so that clouds are more sensitive to increases in CCN number concentration. Under these two cases, we would expect that models in which sulfate addition is not resolved for particle type may overestimate and underestimate the cooling effect and lifetime of sulfate aerosol respectively. Future model studies considering the potential role of these processes first on a smaller scale, as in the black carbon case, and then on a regional scale in sensitive areas, will help to parameterise these effects to improve modelling of SO_2 and sulfate in global-scale studies.'

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Changes to figures and tables

- Figure 3: We thanks the anonymous reviewer for pointing out that the abbreviation 'PBA' used in the figure was not defined. We have added to the figure caption: '...are shown on the right-hand axis. PBA = Primary Biological Aerosol, OA = Organic Aerosol, IA = Inorganic Aerosol.'

- Figure 4: B. Alexander - *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 = δ^{34}S$_{\text{downwind}}$ - δ^{34}S$_{\text{upwind}}$) and the 1σ error of the measurement.'

- 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. In addition, we have now added a reference to Table 3 (Table 4 in the revised manuscript) as requested by Reviewer 2. 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.'

  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

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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 added from the SO_2 removal (α_{cloud}) as discussed in Harris et al. (2013) (values given in Table 4). 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.'

- Table 1: Reviewer 2 mentions that some of the processes defined as occurring on solid particles can actually also occur on liquid particles, ie. CON, SCAV and COAG. The lines between various processes are blurry as particles are not simply 'liquid' or 'solid', but rather occur across a continuum from, for example, truly solid mineral dust through OA/IA which covers a range of viscosity states to cloud droplets which are true liquids. We have amended the table to reflect this more clearly:

  – COND refers to solid and semisolid (ie. OA) particles in this paper; once a particle crosses the bounday to liquid, the process become dissolution. This is of course a simplified distinction; for most particles which are semisolid, gases may first 'condense' on the surface and then be very slowly mixed through the particle in a delayed 'dissolution'.

  – SCAV and COAG could occur for both solid and liquid particles as mentioned by the reviewer.

  The revised version of Table 1 is attached to this comment.

- Table 2 (of the revised manuscript): B. Alexander - *It would be useful to have a table of alpha values for each reaction discussed in the introduction.*

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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.' Table 2 is attached to this response.

- Table 3 (Table 4 in the revised manuscript): B. Alexander - *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(4) 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}),...'

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Process	Abb.	Description	Effect on:	
			Number conc.	Mean diameter
Condensation	CON	Phase transfer of gaseous H$_2$SO$_4$ to the solid (particle) or semisolid phase	None	Increase
Uptake (dissolution)	DISS	Dissolution of H$_2$SO$_4$ into a cloud droplet or a liquid particle	None	Increase
Impaction scavenging	SCAV	Collision and combination of an interstitial particle with a cloud droplet	Decrease	Increase
Coagulation	COAG	Collision and combination of two smaller particles to form one larger particle	Decrease	Increase
Cloud droplet nucleation	NUC	Formation of a cloud droplet on a CCN, and dissolution of CCN components (eg. sulfate)	None	None
Aqueous oxidation	AQOX	Dissolution and oxidation of SO$_2$ in the aqueous phase (cloud droplet)	None	Increase

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Table 1 (revised): Definitions and abbrevations ('Abb.') for processes involving modification of particulate by sulfur species observed at HCCT-2010, after Seinfeld and Pandis (1998), p.933. For in-cloud processes, effects on number concentration and mean diameter refer to the effect on the particle population following evaporation after an air particle leaves the cloud, ie. downwind vs. upwind of a cloud. Processes CON, DISS, COAG and SCAV collectively involve direct transfer of sulfate from the gas-phase and ultrafine particle into a larger particle mode, and will be referred to as 'direct uptake', which can occur both in and out of a cloud.

Fig. 1. Table 1 (revised)

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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$_2$O$_2$	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

Table 2 (added): Sulfur isotope fractionation factors for the major known 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).

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Fig. 2. Table 2 (added)