

Interactive comment on “Interactions of meteoric smoke particles with sulphuric acid in the Earth’s stratosphere” by R. W. Saunders et al.

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We thank the referee for their prompt and considered reading of our paper. Our responses to the points raised in this review are as follows;

Major points

- UV spectra; standards

The referee states that “the experiments seem incomplete...there are no standards shown for calibration of the UV spectra”. In fact, there are no such ‘standards’ for the complexed ion species. We felt that the inclusion of any available reference spectra with Figure 2 would unnecessarily complicate the plot and thus detract from our own

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experimental data. All the general and specific absorption features of the relevant solution species are described in detail with reference to the cited works at the start of section 2.2.

- Literature spectra; temperature/acidity range

The referee is then unclear whether “the literature spectra cover the range of acidity and temperature studied in this manuscript”. Even though the cited literature for the spectra of relevant iron species in solution does not cover the exact acidity and temperature range of our experiments, the observed peak positions in our spectra and their variation with increasing acidity are entirely consistent with the literature data. There is, to the best of our knowledge, no reported temperature dependence for the peak positions.

- Solubility measurement

The calculation which the referee describes as “rough” in fact used well- and long-established molar absorbance values for bare and complexed ferric ions from the literature which provided for a highly accurate molarity/mass balance of iron as detailed in the text (page 1560). In all cases, to within experimental error, this balance showed full dissolution of Fe from the initial powder. We would argue that this is a rigorous method for accurately determining the degree of solubility.

The stated error associated with the reported rate constant (k) reflects the range of values obtained from a number of experiments in which different masses of a specific powder were added to acid-water solutions. We feel it is not necessary to determine a ‘saturation’ limit for these powders in light of the large (orders of magnitude) disparity between the size/mass of MSPs compared with SSA and the very low reported Wt% Fe in sampled SSA.

- Fate of Mg and Si in SSA

Mg from the amorphous silicates will form hydrated $MgSO_4$ species upon dissolution in the acid-water solutions, whilst Si will be converted into silicic acid form. Crystalline

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magnesium sulphates are highly soluble in aqueous solvents – amorphous forms are likely to be even more soluble in light of our observations of the iron sulphate solubility.

Mg ion peaks are evident in the PALMS stratospheric aerosol spectra shown in the cited studies of Murphy et al (1998) and Cziczo et al (2001). There are also peaks at mass number 28 which, although not assigned in the spectra, would be consistent with the presence of Si.

Neither of the stated Mg and Si solution species display any significant UV-vis absorption features and so are not amenable to the technique we used to monitor the iron species in solution.

The points above will be added to the revised text.

- Sedimentation of MSPs

Firstly, with regard to our 3-D modelling approach, we accurately quote the conclusion regarding the relative importance of sedimentation and vertical advection made in Bardeen et al., and therefore disagree with the referee that this statement is misleading. Figure 10 of Bardeen's paper shows that the % difference with and without sedimentation treated (top and bottom right hand panels) is less than 30% at altitudes below 80 km (as also stated in section 3.2 of their paper) which is the top level of our 3-D model. Throughout the lower mesosphere/upper stratosphere, their data (stippled regions) shows no significant effect of sedimentation, particularly in the mass density plot. The 'roughly factor of 2' as stated by the referee is only evident in their Figure 10 (and stated in section 3.2) above 90 km. The 1-D model, which we used to provide the MSP input for the 3-D model at 80 km, includes treatment of sedimentation at all levels, including above 90 km. We will clarify this point in the revised text.

Secondly, our model approach only set out to treat the transport of 'bare' MSPs to the stratosphere and not of acid-coated particles resulting from condensation of H_2SO_4 . Any uptake of acid vapour onto MSPs is highly unlikely to grow the particles signif-

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icantly above the 1.5 nm tracer radius to sizes at which sedimentation would then become more important than transport by turbulent diffusion and the residual flow. The dissolution of MSPs in sulphate aerosol in the stratosphere would result purely from a Brownian collision-assimilation process rather than acid uptake-condensation.

Finally, the referee's assertion that our model 'detracts' from mass flux estimates is clearly erroneous. The meteoric mass flux is the critical input to the 1-D model which determines the MSP number concentration set at the top level of the 3-D model in order to match the cited measurements of particle numbers in the mesosphere. This in turn, determines the transport of MSP mass (flux) as treated within the 3-D model.

- Mie theory validity

Mie theory was only used to calculate the extinction by larger MSP aggregates (for which the relevant extended size dimension is the fractal radius) composed of a number of the 'tracer' size particles. This appeared in the discussion of possible reasons for the differences between calculated and SOFIE data. With regard to single, spherical MSPs, as treated in the 3-D model, Rayleigh theory was used as stated to compare with the Hergiv et al data (i.e. Figure 6).

Such size increases due to aggregation (as discussed on p. 1567) do result in a change in optical properties as the refractive indices require re-calculation upon the assumption of a porous nature for such aggregates. We therefore do not agree that there are 'misleading statements' in this section of the paper.

- 'Iron:sulphur ratio'

Strictly speaking, we do not make an 'iron to sulphur ratio' calculation but an iron to SSA mass ratio calculation, as this is equivalent to the data reported for the in-situ sampled SSA. For this we simply took a typical (mean) SSA size with assumed Wt% acid composition – such an approach does not require a 'sulphur flux'. The MSP number required for determination of iron mass is dependent upon *both* the assumed

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meteoric flux and transport of the tracer particles as treated within the model. The referee states that our approach was too complicated but then suggests a number of other factors which should be added (i.e. sedimentation, sulphur flux). We do not see how this would simplify the treatment – in any case, for the reasons given above, we consider the treatment of these factors to be unnecessary in our approach.

Minor points

- Figure 2

If the referee is referring to the top panel of this plot, it is common practice to display absorption spectra as continuous profiles rather than discrete data points. We clearly stated the resolution level used for spectra acquisition on p. 1559 (line 7). The bottom panel of this figure shows the individual data points for each time at which spectra were acquired.

- Figure 6

There is not 'a factor of 10 relative discrepancy' between the calculated and SOFIE data points at any altitude in the plot. As stated in the text, the maximum difference is a factor of 4 at 75 km (p. 1566, line 24). We subsequently discussed at length, the likely reasons for the differences shown.

- HNO_3 relevance

With no experimental data being available for sulphuric acid uptake onto particles of any form (size, morphology or structure), it seems appropriate to indicate the massive uncertainty in the range of measured uptake coefficients for another mineral acid which is also present at some level in the gas phase throughout the atmosphere. The reference to HNO_3 data also clearly indicates the need (as stated) to replicate particle form and ambient conditions as closely as possible to avoid significant errors in the choice

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of uptake coefficient value for a specific gas-particle system within a model treatment.

- Lower limit for gamma validity

We take issue with the referee's statement that the determination of a lower limit for the uptake coefficient (not accommodation coefficient) from our modelling work is 'not especially interesting'. We would argue that such a lower limit is of interest because there have been no measurements of this quantity to date. Furthermore, a lower limit will be useful for designing future laboratory experiments to measure the uptake coefficient on realistic particle analogues and under ambient stratospheric conditions. In light of the huge range of measured values for HNO_3 , establishing a lower limit is vital for narrowing down, potentially by many orders of magnitude, this important quantity which is fundamental to an assessment of the loss of sulphuric acid to meteoric smoke particles in the atmosphere.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 1553, 2012.

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