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Atmospheric
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Interactive comment on “The uptake of SO_2 on Saharan dust: a flow tube study” *by* J. W. Adams et al.

J. W. Adams et al.

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The following are replies to the **Comments of referee 2**

General Comments

Comment 1: To my knowledge, this is the first application of a coated-wall flow tube technique to mineral dust studies of this type. Also, this is the first study of the impact of elevated relative humidity on the kinetics of SO_2 uptake on dust, because Knudsen cells cannot operate at high RH. These points should be emphasized, in part because it is another example of the (somewhat surprising) evidence that water does not affect the kinetics of oxidation reactions involving dust materials; see also Sullivan *et al.* (ACP, 2004).

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Reply: Judeikis *et al.* (1978) used a flow reactor very similar to that used in this work. They also studied the impact of elevated relative humidity on the kinetics of SO_2 uptake on dust. More recently, Ullerstam *et al.* (2002) have also investigated the effect of elevated humidity on the uptake of SO_2 on Saharan mineral dust samples.

Comment 2: The observation that the integrated amounts of SO_2 taken up by the surface do not scale linearly with the partial pressure of SO_2 is very interesting. There might be a tendency to interpret such behavior in terms of a two-site adsorption isotherm or surface saturation. The nice agreement between the kinetic model simulation of this behavior and the experiments should be emphasized more strongly as an illustration that kinetic factors can lead to this observation as this is the first illustration of this effect that I have seen. In this regard, I would add a couple more sentences to qualitatively explain the processes that make this relationship non-linear.

Reply: Two site adsorption was considered as a possible uptake mechanism, but the experimental data could not be represented, either by a two site Langmuir isotherm, or by a kinetic model, based around a two site reaction scheme.

The relationship is non-linear because the mechanism depends on 2 reactions. At low surface coverages reaction R2 dominates over diffusion into the pores. As the surface concentration increases reactant/site R_1 is depleted and the diffusion into the pores drives the continued uptake. The switch between the regimes will occur after different times depending upon the initial SO_2 concentration. Hence the non-linearity of figure 6. The text has been modified to include this explanation of the non-linearity.

Comment 3: The paper would benefit from more discussion of what the irreversible chemistry might be on the surface. I know that this will be speculation to a large degree without other (e.g. spectroscopic) evidence but I think this would be valuable nevertheless.

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Reply: As the referee points out, discussion of the irreversible chemistry, beyond what is already mentioned in the text, would be largely speculation. As such, we do not feel it would add significantly to the paper.

Minor points:

Comment 1: In the Introduction, it should also be mentioned that sulfate might arise on a mineral dust particle surface by deposition of sulfuric acid vapour. It does not need to arise via heterogeneous reaction alone.

Reply: Comment added to paper.

Comment 2: In the last paragraph of the Introduction, I am not sure what is meant by the phrase "allows better time resolution of uptake rates". Surely a Knudsen cell offers better time resolution than a flow tube?

Reply: This comment was directed at the DRIFTS technique used in some previous studies of the uptake of SO_2 onto Mineral dust. The text has been clarified.

Comment 3: Experimental, Section 2.2. How has the dust been collected and prepared? Has it been size filtered, washed, etc.?

Reply: The sample comes from deposits on the Cape Verde islands. It was used as supplied, without size filtering or washing. A comment has been added to the text

Comment 4: Page 2650. It would be valuable to compare the values of dust mass/geometric surface area in this work to the same ratio in the work of Underwood *et al.* (2000) to show that the films were of comparable (or lesser) thickness, thus giving justification to using the BET surface area to scale the uptake coefficients in a linear

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manner.

Reply: The dust mass/geometric surface area in this work varied between 0.02 and 0.5 mg cm^{-2}. For experiments with low dust loadings Underwood et al used between 0.2 and 8 mg cm^{-2}. The text now contains this information.

Comment 5: Page 2651. Was a control experiment done on a tube prepared in an identical manner to one prepared in a dust experiment, i.e. with the ethanol and parafilm plug, but without the dust? I wonder whether the ethanol may have extracted organics from the parafilm and formed a reactive surface coating of them.

Reply: No such experiment was performed.

Comment 6: Last paragraph in section 3.2. "Obtain" should be "obtained".

Reply: This error has been corrected.

Comment 7: What is the line in Figure 7?

Reply: A single site Langmuir isotherm fit to the data. The legend to figure 7 has been amended.

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