

## ***Interactive comment on “The effects of nitrate on the heterogeneous uptake of sulfur dioxide on hematite” by L. D. Kong et al.***

### **Anonymous Referee #1**

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This laboratory study demonstrates the positive effect that nitrate has on the heterogeneous oxidation of sulfur dioxide on hematite. The resulting acidification of the surface and formation of sulfate is monitored by DRIFTS, while release of nitrous acid and nitrous oxide has been observed by FTIR. Sulfur (IV) oxidation on mineral dust has been the target of many studies in the past, but the novel aspect here is that the authors uncover the linked redox cycles of iron, nitrogen and sulfur, where iron (III) acts as an oxidant for sulfur dioxide and iron (II) as a reductant for nitrate.

By themselves, the experiments seem to be well performed and analyzed; however, some concerns remain with respect to the way samples were prepared and exposed in the DRIFTS experiments. These will not affect the general conclusion about the convoluted redox chemistry but will affect the extrapolation to atmospheric conditions.

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While the samples are prepared by equilibrating the hematite powder with the nitrate salt at 68% relative humidity, once the samples are introduced to the DRIFTS cell, they are not exposed to humidity anymore (correct?) and will therefore dry out during the actual sulfur oxidation experiments. Therefore, significant changes in the physical properties are induced (over what time scale?), which likely suppress the efficiency of the redox cycles, which would require some aqueous phase to allow exchange of ions by diffusion. This aspect needs to be considered in the experimental and results/discussion sections.

The manuscript is unnecessary long, even though it is in general reasonably well written. Most of the discussions are too detailed and repetitive and distract from the main line of the paper. This could be solved for instance by placing the detailed spectral IR assignments into a supporting online part and only integrate the result of that into the main paper. Several other sections could be shortened in the same way, such that an overall much more concise paper with the main aspects would result.

Detailed comments:

P4, top paragraph: To what degree has the work by Harris et al. (2013) on the role of transition metals in cloud oxidation resolved the issue of missing sulfate sources?

P5, lower paragraph: this should be shortened substantially. The involvement of HNO<sub>3</sub> and HONO is not introduced before and thus should not appear here.

Line 130: ‘desiccator’ is probably not the right word, since the vessel has been used to expose the sample to high humidity and not to dry it. This word is causing confusion here.

Line 132: ‘saturation’ should be replaced by ‘equilibration’ Section 2.2: Here, it should be explicitly stated and explained what happens with the water, once the sample is in the DRIFTS cell.

Section 2.4: Again, the final amount of water in the bottle after introducing the gases

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should be estimated to get an idea of the water activity within the sample.

Line 216: The preparation of the pure nitrate samples is not described in the experimental section. At high humidity it deliquesces and will form a solution?

P12/13: Also this part discussing the pure hematite case should be exported to the supporting online material. This is known from previous studies and serves more as a reference for the other experiments.

P13: the discussion of FN samples in terms of adsorption configurations should be cautioned, since the system here is likely an amorphous nitrate film in contact with hematite. What is the average thickness of the film if the nitrate is evenly distributed over the particles?

Line 364: The surface complexes of  $N_2O_4$  likely only exist at relatively high  $NO_2/N_2O_4$  concentrations in the gas phase. Since the surface concentrations are low here, wouldn't  $N_2O_4$  immediately decay into  $NO_2$  and desorb under the conditions of the present experiments?

#### Reference

Harris, E., Sinha, B. r., van Pinxteren, D., Tilgner, A., Fomba, K. W., Schneider, J., Roth, A., Gnauk, T., Fahlbusch, B., Mertes, S., Lee, T., Collett, J., Foley, S., Borrmann, S., Hoppe, P., and Herrmann, H.: Enhanced Role of Transition Metal Ion Catalysis During In-Cloud Oxidation of  $SO_2$ , *Science*, 340, 727-730, 2013.

Line 464: what was the estimated partial pressure of HONO? Related to that, line 474: the self-reaction of HONO is probably not relevant at these HONO pressures?

Page 25: The suggestion of the formation of  $N_2O$  as a product of secondary HONO chemistry is likely correct. However, in terms of atmospheric implications, the high surface to volume ratio of the experiments leads to relatively more  $N_2O$  than in the atmosphere. There, the lifetime of HONO is probably limited by photolysis. This should be discussed in the atmospheric implications section.

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Page 28/29: in the discussion of the mechanism, the authors should come back to the fate of water during the experiments and the relevance of the fact of 'drying out' on the mechanism interpretation.

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 14, 11577, 2014.

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