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Interactive Comment

## Interactive comment on "Kinetics and mechanism of heterogeneous oxidation of sulfur dioxide by ozone on surface of calcium carbonate" by L. Li et al.

## Anonymous Referee #1

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This paper presents experiments designed to elucidate the rate and mechanism of interactions of SO2 and O3 on calcium carbonate particles with an emphasis on determining whether atmospheric mineral dust affects S(IV) to S(VI) conversion. This is an important aspect of atmospheric chemistry and of interest to ACP readers. The method is to monitor surface bound species on CaCO3 particles using DRIFTS which is not sensitive to gas-phase components. They focus on the appearance rate of sulfate absorption features as a function of SO2, O3, and H2O vapor concentrations to derive kinetic parameters (uptake coefficients) and to elucidate a mechanism. The DRIFT technique has been used by other investigators in a range of fields and is rel-



atively well established. The work appears to have been carefully performed and the paper is written fairly well but still does have some confusing statements which appear to be largely translation problems. The paper should be published in APC after the authors consider the following comments/questions with regard to experimental procedures and interpretation.

Major comments:

1) These are challenging experiments in the sense that to observe the process requires high concentrations. These high concentrations can push the chemistry into a different regime. For example, it is possible that with the high concentrations of O3 used, the rate is independent of O3 due to surface saturation, but that in the atmosphere where concentrations are  $\sim$  100X's lower, the rate may be linear in O3. The authors should add a bit more in terms of qualifying their conclusions with regard to the applicability of their mechanism to the atmosphere and whether this chemistry actually happens at an appreciable rate in the atmosphere.

2) Judging by Figure 8, which is largely what drives the mechanistic interpretation, the slight slope observed for steady-state measurements of the log of the rate vs. log of O3 concentration is probably being determined by the lowest O3 value. I would predict that if the authors used even lower [O3], a slope of 1 might be achieved. The reproducibility of that low O3 measurement becomes important. If it was always low, it may be an indication of transitioning from a saturated to unsaturated regime. But perhaps the authors have data to rule this out?

3) Along this line, it appears there's some inconsistency between the values of O3 used in the experiments as listed in the table and as shown in Figure 8. In the table it appears that experiments were performed with 1.2 - 12x10<sup>13</sup> molec/cm<sup>3</sup> where as the data in Figure 8 don't go below 1.0x10<sup>14</sup> molec/cm<sup>3</sup>.

4) The authors raise another common problem with these experiments related to available or accessible surface area. The authors' point out that the influence of the chemi6, S50–S53, 2006

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cal composition of the dust cannot be elucidated until this issue of which surface area to use in the derivation of the reaction probability is resolved. Moreover, meaningful comparison between results obtained with different techniques becomes difficult. There was a similar discussion on another ACPD manuscript recently. DRIFTS and Knudsen Cells operate on very different timescales and that in itself calls into question the comparison of initial uptake coefficients determined by each technique. This paper says that the best time resolution in there experiments was 40 seconds per measurement. That means 40 seconds have elapsed since the initial exposure whereas Knudsen Cell experiments typically obtain a point on the 1 second (or less) time scale. So wouldn't comparing steady-state uptake coefficients be more meaningful in this case?

5) A recent paper by Umann, et al JGR-Atmospheres vol 110, D22306 2005 showed measurements of SO2 during dust plumes from the MINATROC II campaign. The SO2 observations suggested that dust had no (negative) impact on SO2 concentrations. The authors might want to at least cite this paper and offer a reason (rates too slow, not CaCO3 rich dust, etc).

Minor Comments:

1) The authors refer to the "special chemical properties" of carbonates a few times (e.g. pg 581 line 7). What are they? Basic?

2) The range of concentrations used in the expts should appear in the abstract.

3) The authors refer to "different sulfates" or "different forms of sulfate" on pg 586. Are these forms known or just inferred from the different maxima in the spectral band?

4) What is meant by H2O being able to regenerate reactivity of CaCO3? Does the reactivity decrease after long exposure? I didn't notice this aspect from the description of the results.

5) On pgs 593-4 the authors write that Li and coworkers introduced the mass transfer rate coefficient subject to equations 11 - 13. I don't see how these are any different

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than the Fuchs-Sutugin approach to determining mass transfer in the transition regime. A minor point, obviously, but maybe I'm not seeing the difference.

6) On pg. 594-5 the authors compare the lifetime of SO2 by their mechanism to other gas-phase oxidation processes (OH and HO2). Shouldn't the authors mention that the actual average lifetime of SO2 in the absence of dust is more like 5 days due to cloud processing?

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