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Atmospheric
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Discussions

# *Interactive comment on* "A comprehensive evaluation of water uptake on atmospherically relevant mineral surfaces: DRIFT spectroscopy, thermogravimetric analysis and aerosol growth measurements" *by* R. J. Gustafsson et al.

**R. J. Gustafsson et al.**

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## Comment 1

These latter measurements are the weakest link in the story, as will be detailed below, and are therefore only of limited use for the understanding of H2O uptake by CaCO3 and ATD aerosol. It is a bit surprising that the authors present this work as a stand-alone contribution to the scientific literature in view of the limited albeit admittedly useful information they provide. It would have been more appropriate as a separate section on the reactivity of mineral dust aerosol. In spite of this I recommend publication of this work in Atmospheric Chemistry and Physics once the authors have had a chance to respond to the criticism outline below in a satisfactory manner.

**Response to comment 1**

We would like to thank the referees for their insightful comments. We can assure referee 1 that we do not overestimate the impact of this publication and do consider it as a modest (albeit useful) contribution to the existing literature on water interaction with mineral surfaces.

**Comment 2**

- pg. 7194: Conditioning of CaCO3 at 120oC in He will not remove strongly-bound water that desorbs beginning at approximately 300oC. Polycrystalline CaCO3 has approximately 1-2 percent of a formal monolayer of strongly-bound H2O which is a small but measurable fraction of the total quantity of water adsorbed at 80 percent RH according to Figure 2.

**Response to comment 2**

We acknowledge the presence of a small amount of chemisorbed water remaining on the carbonate surface after conditioning. However, 1-2 percent of a formal monolayer coverage is 0.25 percent of the highest coverage observed. We therefore consider this to have a negligible effect on the data and the conclusions derived from them.

**Comment 3**

-pg. 7196: The Kubelka-Munk transformation will affect the IR absorption spectrum ofadsorbed H2O displayed in the insert of Figure 1 to a certain extent. How important is the (red) shift of the band positions displayed in Figure 1? In addition, it would be helpful to briefly summarize the procedure and present the involved parameters.

**Response to comment 3**

The referee has correctly pointed out that there is a small shift in absorption frequencies as the amount of adsorbed water increases (as observed by Finlayson-Pitts et. Al. J. Phys. Chem. A. 2001, 105, 10339-10346). However, given the broadness of the peak we do not specify an exact value for the shift, in view of the associated uncertainties. The Kubelka-Munk function (as well as limitations/advantages related to the transformation) is discussed in the reference we cited in our paper. (Armaroli, T., Becue, T., and Gautier, S.: Diffuse reflection infrared spectroscopy (DRIFTS): Application to the in situ analysis of catalysts, Oil Gas Science and Technology-Revue De L Institut Francais Du Petrole, 59, 215-237, 2004). Even so, to accommodate the reviewer, we shall add the requested information. **Manuscript to be amended.**

### Comment 4

pg. 7197: The authors do not provide a convincing argument in favor of considering just one aerosol mode at the expense of the larger diameter mode. They advance uncertainties in particle morphology to remove the larger mode from consideration. Is the particle morphology of the smaller mode better known or better defined compared to the one for the larger mode?

### Response to comment 4

Our reasons for considering only the small mode are largely practical. The growth of the small aerosol mode could be measured much more precisely using our current DMA set-up than the larger mode. The low hygroscopicity of the dust particles means that there is only a very small change in diameter of the large mode with increasing RH of less than 2 percent, which is within the uncertainty of our measurements. Nevertheless, this low observable growth is consistent with that of the smaller mode and the DRIFTS/TGA measurements. While the morphology of neither mode may be defined at present, we feel it may be instructive to present the growth of both modes in our revised manuscript and to show that growth of the two modes is consistent and this will be done. **Manuscript to be amended.**

### Comment 5

It may be appropriate to graphically present typical particle size distributions for both substrates for inspection by the readers in view of the disparate widths of both components.

**Response to comment 5**

The revised manuscript will include both the CaCO3 and ATD size distributions. **Manuscript to be amended.**

**Comment 6**

It is both interesting and unusual that the ratio of widths (standard geometric deviation) is reversed in going from CaCO3 to ATD: sigma (55nm) = 10, sigma (260nm) = 4 for CaCO3, sigma (61nm) = 10 and sigma (270nm) = 31 for ATD. What could be the reason for this?

**Response to comment 6**

This is an error and will corrected in the revised text. The widths of the two distributions are approximately the same for CaCO3, with sigma = 1.5. For ATD, typical values are between 1.4 and 1.6 for the two modes. **Manuscript to be amended.**

**Comment 7**

-pg. 7197: Without proof the authors offer an explanation for the presence of the accumulation mode: they attribute it to aggregation of particles taking place in the mother suspension BEFORE atomization. A simple study of the dependence of the PSDF (particle size distribution function) as a function of mass loading of the suspension might have revealed the real reason for the importance of the larger mode. If anything I find it more plausible that aggregation/accumulation of mineral dust particles occurs after atomization as these particles are most probably stabilized in solution.

**Response to comment 7**

We did indeed perform such experiments, but they did not conclusively reveal the origin of the second mode. We began with a very dilute suspension of ATD in water, of around 30 mg per liter, at which point only a single, small mode was observed. The concentration was increased to 100 mg per liter, at which point the second, larger mode was observed and further to 300 mg per liter. Over the range of concentrations studied, the number density of the second mode scaled linearly with that of the smaller mode. Thus, second order effects, such as the nucleation in the gas phase of fine particles may be excluded. We will incorporate this information into the revised paper. **Manuscript to be amended.**

**Comment 8**

-pg. 7198, line 1 and line 22: The numbers seem to have been interchanged according to the results displayed in Figures 4 and 6.

**Response to comment 8**

We thank the referee 1 for spotting the inconsistency in labeling the Figure 4 and Figure 6. We will change the labeling in the final version of the paper. **Manuscript to be amended.**

**Comment 9**

Figures 1, 2, 3 and 5: No uncertainty limits are given for any of these Figures. The “convergence” (pg. 7198, line 8) of the water adsorption isotherms displayed in Figure 2 at high relative humidity has to be discussed within the uncertainty limits of the last two individual data points. On pg. 7198, line 4 it must be Figure 2 rather than Figure 3.

**Response to comment 9**

This was an oversight. The associated error was 15 percent and error bars will be added in the revised paper and the discussion amplified accordingly. **Manuscript to be amended.**

**Comment 10**

pg. 7199, lines 7 and 8: It is true that flow reactors (laminar flow, fast flow and Knudsen reactors) do not address atmospherically relevant partial pressures of water vapor. However, I take exception to the statement that they are “unlikely to be of substantial relevance for atmospheric studies” because the amount of water vapor adsorbed on mineral dust is rarely the limiting factor for heterogeneous reactivity, even in the case of hydrolysis reactions. On line 15 the monolayer coverage on CaCO3 is reached at 45 rather than 55 percent according to Figure 2.

**Response to comment 10**

We appreciate the referee’s concern that the statement regarding the relevance of Knudsen cell studies. It will be reworded accordingly. **Manuscript to be amended.**

**Comment 11**

pg. 7200, lines 14 to 18: The Ca-(OH) bond is ionic whereas the Si-(OH) bond is covalent in nature. I do not understand the argument of the authors in terms of the electronegativity difference between Ca and Si and the related explanation of the strength of the hydrogen bonds. The strength of hydrogen bonding depends on many factors, one of which is the electronegativity. Can you really compare the two bonding situations in terms of such extreme simplification?

**Response to comment 11**

We consider the discussion regarding the dependence of hydrogen bonding strength upon the electronegativity difference between silicon and calcium to be reasonable. However, we accept that the interpretation offered is simplified and we shall moderate our statement accordingly. **Manuscript to be amended.**

**Comment 12**

- pg. 7201, line 8ff: The fits to the growth curves displayed in Figures 4 and 6 are grossly unsatisfactory. The analytical formula presented in relation (2) does not capture the change of the hygroscopic growth factor from low to high values of rh in both cases.

In addition, the measurement of the growth curves may involve an unusually large uncertainty because of the sequential nature of the experiment. Usually, growth curves are best measured using two DMA's in a tandem configuration.

**Response to comment 12**

While not satisfactory, the use of the power law is common to other observations of hygroscopic growth measurements and is provided for comparison with other studies. In any case, the manuscript provides sufficient data to reproduce the hygroscopic growth of mineral surfaces using the thermodynamic parameters derived from the BET functional fit.

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Interactive comment on Atmos. Chem. Phys. Discuss., 5, 7191, 2005.