

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.

Anonymous Referee #1

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Report on “ A comprehensive evaluation of water uptake on atmospherically relevant mineral surfaces : DRIFT spectroscopy, thermogravimetric analysis and aerosol growth measurements ” by R. J. Gustafsson, A. Orlov, C. L. Badger, P. T. Griffiths, R. A. Cox and R. M. Lambert Submitted to Atmospheric Chemistry and Physics

This work reports on important ancillary information needed to gauge the importance of heterogeneous reactions taking place on mineral dust surfaces. Although the relationship between cloud nucleation abilities of crustal aerosol particles, hydrophilic

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properties of aerosol particles and multilayer water adsorption is only briefly mentioned in the text, the intercomparison between three independent measurement techniques should garner the interest of the readership of Atmospheric Chemistry and Physics. Among the three chosen methods the TGA technique delivers the most useful results in terms of absolute amounts of adsorbed water on CaCO₃ and Arizona Test Dust (ATD) as a function of relative humidity. The DRIFT spectra provide spectroscopic data and the DMA measurements hint at the relative aerosol growth rate as a function of relative humidity. 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.

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

-pg. 7196: The Kubelka-Munk transformation will affect the IR absorption spectrum of adsorbed 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.

-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

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to the one for the larger mode? 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. It is both interesting and unusual that the ratio of widths (standard geometric deviation) is reversed in going from CaCO_3 to ATD: $\sigma(55\text{nm}) = 10$, $\sigma(260\text{nm}) = 4$ for CaCO_3 , $\sigma(61\text{nm}) = 10$ and $\sigma(270\text{nm}) = 31$ for ATD. What could be the reason for this?

-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.

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

- 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.

- 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 CaCO_3 is reached at 45 rather than 55% according to Figure 2.

- pg. 7200, lines 14 to 18: The $\text{Ca}(\text{OH})$ bond is ionic whereas the $\text{Si}(\text{OH})$ bond

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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?

- 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 r_h 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.

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