

# Small, soluble fractions are sufficient for fine mineral dust particles to serve as efficient CCN

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**Abstract:** Mineral dust particles include many different components, but are often treated by models as insoluble resulting in limited activation to cloud droplets. Experimental critical supersaturations of mineral dust particles 0.2  $\mu\text{m}$  in diameter from different sources indicate that their composition is partially soluble. Using a Köhler model, the soluble fraction of each dust sample was calculated from the measured critical supersaturation and used to predict the fraction of fine ( $< 1 \mu\text{m}$ ) particles that could activate using atmospherically relevant conditions (e.g. a supersaturation of 0.2%) and size distribution parameters representative of fine dust particles. Activated fractions ranged from 0.01-0.41 with the sensitivity of these results depending primarily on particle size. The results indicate that dust particles with as little as 3% soluble material can be up to ~80% as efficient at activating cloud droplets as pure ammonium sulfate particles with the same size distribution characteristics.

have indicated that clouds influenced by dust particles have smaller effective radii [Rosenfeld et al., 2001] and measurements of cloud droplet residues have shown that up to 58% contained unreacted mineral dust [Twohy et al., 2009]. These observations were attributed to minor components in dust such as salts [Koehler et al., 2007; Twohy et al., 2009], compounds rich in  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  [Kelly et al., 2007; Koehler et al., 2009], and sulfates [Rosenfeld et al., 2001]. These components have been predicted to contribute soluble material to dust particles enabling droplet activation to occur at smaller particle diameters and supersaturations [Kelly et al., 2007]. Although the importance of these constituents has been suggested, the extent to which these soluble components enhance cloud droplet formation is unknown. Using realistic representations of dust particles, this paper provides evidence of the importance of considering soluble, minor constituents when predicting the CCN activity of dust particles.

## 1. Introduction

Atmospheric particles can influence climate by acting as cloud condensation nuclei (CCN) [Poschl, 2005]. Mineral dust is a particle type that could become more important as a source of CCN with desertification due to climate change [Rosenfeld et al., 2001]. Mineral dust is primarily composed of carbonates, metal oxides, and silicates [Baker et al., 2006]. Observations have suggested that dust is insoluble yet wettable requiring either mixture with sea salt [Levin et al., 2005] or acquisition of nitrate due to heterogeneous reactions [Kaaden et al., 2009; Shi et al., 2008] in order to nucleate cloud droplets. Dust particles are, therefore, modeled as contributing to cloud droplet number as giant CCN primarily after heterogeneous reactions or cloud processing [Wurzler et al., 2000]. However, recent findings have suggested the importance of unreacted dust particles as CCN. Measurements

## 2. Methods

### A. Experimental

Eight mineral dust samples from different locations in the southwestern United States were collected for laboratory analysis. The samples were size selected using a differential mobility analyzer (DMA) to obtain monodisperse distributions. The particles were then introduced to a cloud condensation nuclei counter (CCNc) [Roberts and Nenes, 2005] that counted the number of activated particles at a particular supersaturation ( $S_v$ ). Total particle counts were monitored using a condensation particle counter (CPC, TSI model 3010). The  $S_v$  was scanned from 0.1-1% in the CCNc to obtain the activated number as a function of  $S_v$  for the selected size. Comparison of total particle counts to activated particle counts for each sample at a given size allowed for the generation of an

\*This work was completed by Cassandra Gaston as part of SIO217D term projects advised by Lynn Russell from experimental measurements by Cassandra Gaston and Kaitlyn Suski as part of a research project developed by Kimberly Prather, Kerri Pratt, and Cassandra Gaston. Models for this project were developed by Greg Roberts and technical and writing help was obtained by Doug Day, non-anonymous, and anonymous reviewers. However, the submitted work has not yet been reviewed and approved by all of the coauthors and is not suitable for citation at this stage. Please contact Cassandra Gaston at [cgaston@ucsd.edu](mailto:cgaston@ucsd.edu) to receive an update on these results.

activation curve. The experimental critical supersaturation ( $S_{c,exp}$ ) is defined as the  $S_v$  where half (0.5) the fraction of particles activated.

## B. Modeling

$$S_v^{eq} = \exp\left(\frac{4\sigma' M_w}{kT\rho_w D_p} - \frac{\Phi M_w}{\frac{\pi\rho' D_p^3}{6} - \sum_i m_i} \left[\sum_i \frac{v_i m_i}{M_i}\right]\right) \quad (1)$$

Köhler theory as modeled by Roberts *et al.* [2002] from equation (1) was applied to the dust samples where  $S_v^{eq}$  is the equilibrium saturation ratio for a given droplet diameter ( $D_p$ ) and temperature ( $T$ );  $M_w$  and  $M_i$  are the molecular weights of water and solute, respectively;  $\rho_w$  and  $\rho'$  are the densities of water and the solution, respectively;  $\sigma'$  is the surface tension of the solution;  $\Phi$  is the osmotic coefficient;  $v_i$  is the van't Hoff factor; and  $m_i$  is the dissolved solute mass. Equation (1) describes the saturation ratio required for droplet activation at a given set of physical and chemical properties associated with the Kelvin term (first term on the RHS), which increases the required saturation ratio due to curvature, and the Raoult term (second term on the RHS), which lowers the required saturation ratio due to the presence of a solute. The maximum value of  $S_v^{eq}$  for a given diameter, composition, etc., is the critical supersaturation ( $S_c$ ).

The dust samples were treated as two component particles using an insoluble dust composition and ammonium sulfate (AS) for 0.2  $\mu\text{m}$  particles, which was chosen because the values of  $S_{c,exp}$  were obtained for all samples at this size. The fractions of both components were varied for each dust sample until the modeled  $S_c$  matched the experimentally obtained  $S_{c,exp}$  for a given dry diameter. AS is a good proxy for soluble material that has been used in previous studies [Koehler *et al.*, 2009; Twohy *et al.*, 2009] and is used in this case to represent soluble components in the unreacted dust samples. Once the soluble fraction was predicted, the fraction of particles that could potentially activate under typical  $S_v$  conditions of 0.2% [Roberts *et al.*, 2002; Twohy *et al.*, 2009] was then modeled. The parameters for the size distribution were taken from Twohy *et al.* [2009] and Levin *et al.* [2005]. Sensitivity studies were

conducted to determine the influence of the choice of the size distribution and the chemical component assumed to be the soluble fraction on the activated fraction (Table 1).

Component	$\rho$ (g/mL)	Sol (g/mL H <sub>2</sub> O)	$v_i$	$M_w$ (g/mol)	Case
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	1.768	0.764	3	132.4	1
K <sub>2</sub> SO <sub>4</sub>	2.66	0.12	3	174.24	2
NaCl	2.165	0.36	2	58.44	3
CaSO <sub>4</sub> ·2H <sub>2</sub> O	2.32	0.0026	2	172.2	4

Reference	$N$ (cm <sup>-3</sup> )	$D_g$ ( $\mu\text{m}$ )	$\sigma_g$	Case
Twohy et al 2009	225	0.1	1.6	1-4
Levin et al 2005	200	0.2	2	5

**Table 1:** Chemical components and size distributions used for model calculations where  $\rho$  is the density, Sol is the solubility,  $v_i$  is the Van't Hoff factor,  $M_i$  is the molecular weight,  $N$  is the number concentration,  $D_g$  is the median diameter,  $\sigma_g$  is the geometric standard deviation, and case corresponds to the cases in Figure 1.

## 3. Results

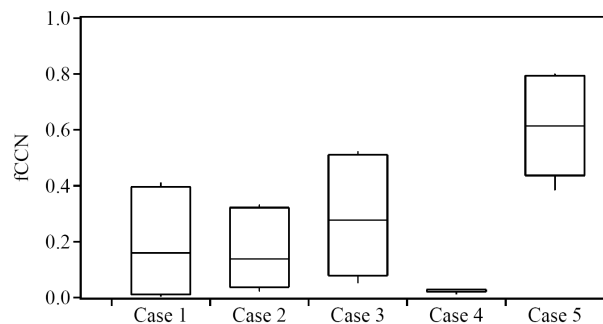
As seen in Table 2, soluble fractions ( $\epsilon$ ) for the dust samples ranged from 0.002-0.03 with a median of 0.012.

Sample Number	$S_{c,exp}$ (%)	$\epsilon$	$S_c$ (insol)/ $S_{c,exp}$
1	0.24	0.03	3.29
2	0.25	0.03	3.21
3	0.26	0.025	3.07
4	0.30	0.02	2.66
5	0.56	0.004	1.43
6	0.59	0.003	1.35
7	0.60	0.003	1.33
8	0.68	0.002	1.18

**Table 2:** Modeled characteristics of each dust sample.  $S_{c,exp}$  denotes the measured  $S_c$ ,  $\epsilon$  is the modeled soluble mass fraction where  $\epsilon = 1 - (m_{insoluble}/m_{total})$ , and  $S_c$ (insol)/ $S_{c,exp}$  denotes the ratio between the experimental  $S_c$  and the  $S_c$  predicted for an insoluble, dust composition.

The values of  $S_{c,exp}$  shown in Table 2 are significantly lower than that predicted for dust particles containing no soluble material ( $S_{c(insol)}$ ), which is 0.8% for particles 0.2  $\mu\text{m}$  in diameter. As seen in Table 2, the values of  $S_c$ (insol)/ $S_{c,exp}$  were all greater than unity showing that assuming an insoluble dust composition over-predicts the actual  $S_{c,exp}$  by an average factor of 2. At an atmospherically relevant  $S_v$  (0.2%), the smallest diameter that will activate assuming a completely insoluble chemical composition is  $\sim 0.7$   $\mu\text{m}$ . Due to the presence of soluble components, calculations of CCN spectra were made using the soluble fractions

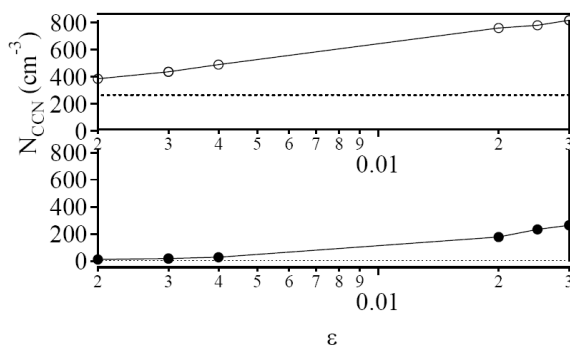
for all 8 samples and the size distribution parameters denoted by Twohy *et al.* [2009] to assess if smaller dust particles could activate (see Figure 1, Case 1). The fraction of activated particles (fCCN) ranged from 0.01-0.41 with a median of 0.16.



**Figure 1:** Plot of fCCN for different assumptions of chemical composition and size distribution for  $S_v=0.2\%$ . The top of the box represents 75<sup>th</sup> percentile, middle represents median, bottom of the box represents 25<sup>th</sup> percentile and whiskers represent 10<sup>th</sup> and 90<sup>th</sup> percentiles of predicted fCCN. Case 1=AS, Twohy; Case 2= $K_2SO_4$ , Twohy; Case 3=NaCl, Twohy; Case 4=gypsum, Twohy; Case 5=AS, Levin.

This outcome, however, is sensitive to both the proxy chosen for the soluble fraction of the particles as well as the characteristics of the assumed size distribution of the dust particles. Using the same size distribution,  $K_2SO_4$ , NaCl, and gypsum ( $CaSO_4 \cdot 2H_2O$ ) were assumed to be the soluble components (Figure 1, Case 2, 3, and 4 respectively).  $K_2SO_4$  and gypsum were chosen because they are common constituents of mineral dust that contain sulfate yet have very different solubilities from AS [Kelly *et al.*, 2007]. NaCl is also a common constituent. The total ranges of the activated fractions were 0.02-0.33, 0.05-0.52, and 0.01-0.03 with medians of 0.14, 0.28, and 0.03 for  $K_2SO_4$ , NaCl, and gypsum (cases 2-4), respectively. The sensitivity of the activated fraction to the size distribution was determined using AS and the parameters given in Kelly *et al.* [2007] and Levin *et al.* [2005] (Table 1). The activated fraction ranged from 0.38-0.8 with a median of 0.61 (Figure 1, Case 5). To assess the impact that these particles might have on CCN concentrations during dust storm conditions ( $N \sim 1000 \text{ cm}^{-3}$ ) [Levin *et al.*, 2005], the number of CCN ( $N_{CCN}$ ) was predicted for both size distributions assuming AS at 0.2%  $S_v$ .  $N_{CCN}$  ranged from 11-264  $\text{cm}^{-3}$  for Twohy's parameters and from 385-817  $\text{cm}^{-3}$  for Levin's parameters. The dashed lines in Figure 2 show

cases for  $\epsilon=0$  (e.g. completely insoluble composition) for comparison. As seen in Figure 2, dust could contribute significantly to cloud droplet number concentrations when the soluble fraction is considered.



**Figure 2:** Plots of the number of CCN ( $N_{CCN}$ ) using dust storm conditions ( $N=1000\text{cm}^{-3}$ ) and size distributions from Levin (line with open circles, upper graph) and Twohy (line with closed circles, lower graph).  $N_{CCN}$  for a completely insoluble dust composition is also shown for comparison for both size parameters (dashed lines).  $\epsilon$  denotes the soluble fraction.

#### 4. Discussion

Our results show the importance of including a soluble component when predicting the CCN properties of fine ( $< 1 \mu\text{m}$ ) dust particles. This is due to small amounts of soluble material (0.2-3%) present in the dust that contribute to the Raoult term enabling activation at lower values of  $S_v$ . Specifically, dust particles with a soluble mass of 3% are up to ~80% as efficient at activating cloud droplets as pure AS using the size distribution parameters of Levin *et al.* [2005]. This is consistent with the findings of Koehler *et al.* [2009], who found that particles with diameters of  $\sim 0.2 \mu\text{m}$  could activate at 0.2%  $S_v$  with only a few percent (~1-8%) soluble mass. This is also in agreement with Roberts *et al.* [2002] who found that  $N_{CCN}$  was most sensitive to changes in the amount of soluble material at low soluble fractions. The sensitivity of this result to the chemical composition of the soluble fraction was not found to vary significantly between  $K_2SO_4$  and AS because even though their solubilities are different, both species are still considered to be highly soluble [Kelly *et al.*, 2007]. Although gypsum has a similar molecular weight to  $K_2SO_4$ , fCCN was low for all soluble fractions when gypsum was considered. This is due to the limited solubility of

gypsum, and its inability to contribute significantly to the Raoult effect. Activated fractions were higher when NaCl was the proxy by a factor of 1.5 due to the smaller molecular weight. This means that more moles of solute will be present to enhance the Raoult effect for a given soluble mass fraction. This highlights some sensitivity to the chemistry of the soluble component assuming constant mass. A threshold in the soluble fraction was apparent for the different samples. Above a soluble fraction of 2%, the sensitivity to the chemical component used as the soluble fraction becomes less pronounced, which is consistent with the non-linear increase in  $N_{\text{CCN}}$  observed for different soluble fractions described by Roberts *et al.* [2002]. However, the factor that the activated fraction was most sensitive to was the size distribution. When dust storm conditions are present, the number concentration of dust particles that could activate is as high as  $\sim 800 \text{ cm}^{-3}$ , meaning that dust with even a low soluble fraction could contribute significantly to environments with low background concentrations of CCN.

Several potential sources of error may influence the accuracy of these results. Due to the irregular shape of dust particles, the size-selected particles would be smaller than predicted by the DMA causing the values of the soluble fractions calculated to be under-predicted. This error is typically 5% with the net effect being an under-prediction in the CCN activity of the dust particles. There is also an average error of 6.5% calculated for the values of  $S_{\text{c,exp}}$ . This error would propagate to calculations of  $\epsilon$  as well as to the predicted values of  $f\text{CCN}$  and  $N_{\text{CCN}}$ . Since changes at the lowest values of  $\epsilon$  have the most pronounced effect on predicted values of  $f\text{CCN}$  and  $N_{\text{CCN}}$ , the smallest values of  $\epsilon$  would be the most affected by this error.

## 5. Conclusions

The results show that a small, soluble fraction contributes significantly to the CCN activity of unreacted, fine dust particles at atmospherically relevant values of  $S_v$ . Once soluble material is present, the characteristics of the size distribution play the most important role in determining the

number of dust particles that can activate at a given  $S_v$ . This process could be especially important for environments that have low background concentrations of CCN.

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