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Distinct CCN activation kinetics above the marine boundary layer along the California coast

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[1] The influence of aerosols on cloud properties remains one of the largest sources of uncertainty in estimates of the anthropogenic component of climate change. Here we report the rate of cloud droplet formation on particles sampled at a site near the California coast that is typically above the marine boundary layer. We observed persistent bimodal diameter spectra which are better explained by kinetic limitations than by differences in equilibrium properties. The slowly-growing mode contained 10–25% of the total cloud condensation nuclei (CCN) and had apparent mass accommodation coefficients (α) 10–30 times smaller than that measured for ammonium sulfate. Cloud parcel modeling suggests that most of these slowly-growing CCN will not form cloud droplets. The relatively small and narrow size distribution of the low-α droplets suggest that a condensed film is a more likely cause of these limitations than slow dissolution. **Citation:** Ruehl, C. R., P. Y. Chuang, and A. Nenes (2009), Distinct CCN activation kinetics above the marine boundary layer along the California coast, *Geophys. Res. Lett.*, *36*, L15814, doi:10.1029/2009GL038839.

1. Introduction

[2] All cloud droplets in the atmosphere form on preexisting aerosol particles. The ability of a particle to act as a cloud condensation nuclei (CCN) depends on both its dry mass and chemical composition; if these are known, Köhler theory [*Köhler*, 1936] can be used to predict the critical (minimum) water vapor supersaturation (S_c) required to activate a CCN (i.e., nucleate a cloud droplet) assuming the droplet is in equilibrium with the surrounding water vapor. It is possible, however, that limitations on droplet growth rate ("kinetic limitations") prevent some droplets from achieving their equilibrium size. It is not known to what extent kinetic limitations might prevent CCN from activating on atmospherically-relevant time scales, largely because of the difficulty in distinguishing between equilibrium and kinetic effects for particles with unknown or only partially known compositions, but they could have an non-negligible effect on atmospheric radiative forcing, at least locally [*Chuang et al.*, 1997; *Nenes et al.*, 2001].

[3] Evidence for kinetic limitations has been previously presented for both lab-generated and ambient CCN. Delayed growth relative to ammonium sulfate (AS) has been observed for lab-generated carboxylic acid particles [*Shantz et al.*, 2003], as well as for particles formed via ozonolysis of gaseous precursors [*Hegg et al.*, 2001; *Asa-Awuku et al.*, 2009]. Evidence for kinetic limitations has also been found in several field experiments [*Shantz et al.*, 2008; *Murphy et al.*, 2009]. These limitations could be due to solubility effects or inhibited mass transfer of water, possibly due to a compressed (insoluble) organic film at the droplet-air interface. Such a film has been suggested for droplets under subsaturated conditions, both in field [*Chuang*, 2003] and laboratory studies [e.g., *Chan and Chan*, 2005, and references therein]. This inhibition can be quantified with the mass accommodation coefficient (α). Although strictly speaking, use of α implies a mass transfer inhibition, anything limiting droplet growth (e.g., slow dissolution) can be quantified with an "apparent" value of α.

[4] In the summer of 2006, we made measurements at four field sites across the continental United States [*Ruehl et al.*, 2008], and found that while most CCN did not have limited growth relative to lab-generated AS (i.e., $\alpha \sim 10^{-1}$), on some days up to 50% of ambient CCN had $\alpha < 10^{-2}$, and some had α as low as $\sim 10^{-3}$. In this paper, we report CCN measurements from a high-elevation (800 m), coastal California site with air characteristic of the free troposphere during the summer. We also use observed α in a cloud parcel model to predict the ability of these CCN to nucleate cloud droplets under normal atmospheric conditions. Our goal is to determine the extent to which potential CCN are prevented from nucleating cloud droplets in the atmosphere, and to understand the mechanism preventing such nucleation.

2. Experimental

2.1. Field Site

[5] We measured α of ambient CCN at the Ben Lomond Youth Conservation Camp (elevation 805 m) approximately 10 km from the central California coast, from 23 July to 2 August, 2007, when the site was above the marine stratocumulus cloud top (Figure 1a). Low condensation nuclei concentrations ([CN$_{D>10\ \mathrm{nm}}$] < 1000 cm^{-3}) and dew point temperatures ($T_d < 0°\mathrm{C}$) demonstrate that air at the site was often typical of free tropospheric conditions (Figures 1b and 1c), particularly at night. Rapid increases in T_d and [CN] at the site during the day (particularly towards the end of the campaign) suggest that mixing of particles from the boundary layer also influences air at the site. A total of 980 differential mobility analyzer (DMA) scans of particle diameters ranging from 10–300 nm made throughout the campaign indicate a peak in the number distribution around 40 nm, and relatively low concentrations ($\sim$300 cm^{-1}) in

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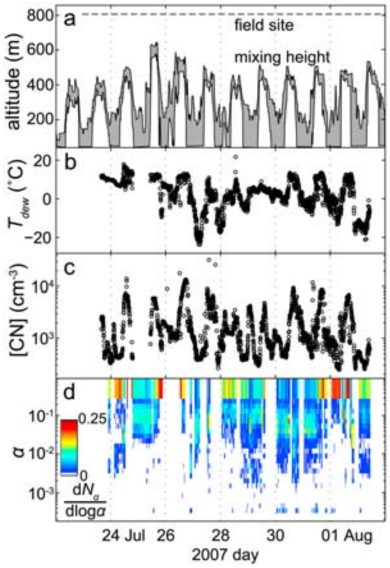

Figure 1. Overview of field campaign. (a) Mixing height, from Ft. Ord Profiler, (b) dew point temperature, (c) particle concentration, and (d) normalized CCN α distributions.

the larger size range expected for most CCN (100–300 nm) (see auxiliary material).[1]

2.2. Instrumentation

[6] We sampled ambient particles and exposed them to a water vapor supersaturation (S) in a continuous-flow thermal gradient chamber (CF-TGC) [*Roberts and Nenes*, 2005] without any RH conditioning. The ambient RH at the site was 26 ± 12%, suggesting that the particles contained little, if any, water. The duration of particle exposure to S (t_s) was varied from 10 to 30 s. We measured the velocity and diameter of the resulting droplets (D_{wet}) with a phase-Doppler interferometer (PDI, manufactured by Artium Technologies), before the droplets exited the CF-TGC. The accuracy of the D_{wet} measurements is 0.3 to 0.5 μm [*Bachalo*, 1980; *Bachalo and Houser*, 1984].

[7] We calculated the mass accommodation coefficient (α) corresponding to each observed D_{wet} using a fully-coupled fluid model [*Roberts and Nenes*, 2005], which calculates the final D_{wet} given initial particle composition and size, α, ΔT and flow rate. When this method is applied to droplets formed on lab-generated ammonium sulfate (AS) particles, $\alpha = 10^{-0.82\pm0.52}$, or 0.15 (0.045–0.51) [*Ruehl et al.*, 2008]. To distinguish between kinetic and equilibrium effects in the field, S was repeatedly stepped from ~0.2 to ~0.6%. At a single value of S, inhibited growth (i.e., D_{wet} lower than that of AS particles) could be due to kinetic limitations (low α), or to ambient CCN with S_c only slightly below the value of S in the CF-TGC. If the latter is true, smaller values of D_{wet} will result from purely equilibrium properties of the CCN, because the difference in water activity driving droplet growth prior to activation ($S - S_c$) will be small. However, if S in the CF-TGC is more than ~0.1% (absolute) greater than S_c, this effect will be negligible [*Ruehl et al.*, 2008, Figure 3], because the CCN will be activated relatively quickly, and after activation the water activity of the droplet drops from S_c to ~1. Therefore, if inhibited growth is seen over an S range of several tenths of a percent, we conclude that kinetic limitations must be the cause.

2.3. One-Dimensional Cloud Parcel Model

[8] The CFTGC-PDI measures D_{wet} of individual droplets at a given S, from which α can be inferred; however, in the atmosphere, feedbacks exist between characteristics of the CCN spectrum and the maximum S in a cloud. To determine under what conditions low-α particles will activate in the atmosphere, we modified a 1-D cloud parcel model similar to the one used by *Feingold and Chuang* [2002] to include low-α CCN. We initialized the model with a log normal particle size distribution, with a geometric mean of 0.04 μm and standard deviation of 2.0. The total number of particles was varied from 100 to 10,000 cm^{-3}, the updraft velocity from 10 to 1000 cm s^{-1}, and the fraction of low-α particles from 0.1 to 0.5. Two low-α values were considered: 0.01 and 0.003.

3. Results and Discussion

3.1. Field Observations

[9] Throughout the campaign, we observed both droplet growth rates similar to 100-nm AS particles ($\alpha \sim 0.1$), and slightly larger growth rates ($\alpha \sim 1$). These larger-α droplets could have either formed on dry particles larger than 100 nm, or alternatively made up of a more CCN-active substance (i.e., NaCl). A distinct slowly-growing (low-α) mode of CCN was observed early (24 July and 27 July) and late (29 July–2 Aug) in the campaign, during roughly 50% of ~200 total hours (Figure 1d). This mode was evident from bimodal D_{wet} spectra, which persisted even when S was varied from ~0.2 to 0.6% (Figures 2a and 2b). While differences in S_c can explain bimodal spectra observed at a single S (Figure 2a), distinct kinetics (i.e., some CCN with $\alpha \sim 0.003$–0.01) are required to explain the bimodal spectra at a range of S (Figure 2b). This is because CCN with high values of S_c will only grow to smaller D_{wet} over a very narrow range of S (the black lines on Figures 2a and 2b), but low-α CCN (red lines) will have smaller D_{wet} at all values of S. Furthermore, the number of CCN does not increase significantly as S increases from ~0.3% to ~0.6%, indicating that the same CCN comprise the low-α mode throughout this range.

[10] When present, this slowly-growing mode contained approximately 10–25% of all CCN, and had α 10–30 times lower than the high-α mode (Figures 2c and 2d). While the absolute value of α is sensitive to the assumption made concerning the size and composition of the CCN, both the difference (in log space) between the higher and lower value of α, as well as the proportion of CCN with low-α, are roughly equal for 100 nm AS and 200 nm NaCl particles. Although no compositional analysis was done of these low-α CCN, upper or lower limits for some of their properties can be inferred from CCN and other measurements. Known mechanisms for kinetic limitations to condensational growth (e.g., film formation at the air-water interface, slow dissolution) are expected to occur in organic-rich particles. Previous work has suggested that only particles with a large organic component ($\gtrsim$75%) will exhibit lower CCN activity

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[1] Auxiliary materials are available in the HTML. doi:10.1029/2009GL038839.

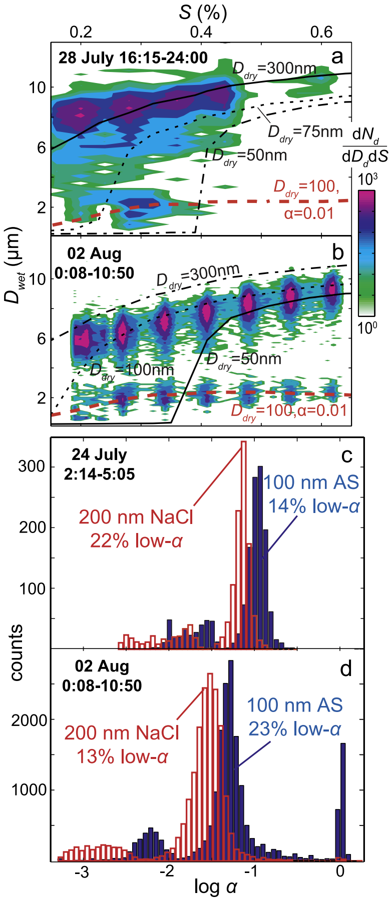

Figure 2. (a and b) D_{wet} histograms as a function of S, along with modeled D_{wet} on AS particles with various D_{dry} (given in nm) and $\alpha = 0.1$ (black) or lower (red). Color represents number of droplets per cm^3 normalized by D and S bin width (0.1 µm and 0.01%, respectively), in units of cm^{-3} μm^{-1} $\%^{-1}$. (c and d) α histograms corresponding to D_{wet} distributions, assuming dry CCN are (red) 200 nm NaCl particles and (blue) 100 nm AS particles.

relative to particles that are primarily inorganic [*Chang et al.*, 2007]. It therefore seems likely that the growth inhibition was observed for particles that were primarily, if not overwhelmingly, organic. The low-α CCN typically activated at relatively low S (0.2–0.3%). If we assume a hygroscopicity for these particles, their minimum diameters can be estimated from this range of S. Most CCN-active organic compounds have a hygroscopicity of ~0.1, using the κ formulation of *Petters and Kreidenweis* [2007]. (κ of ammonium sulfate is ~0.6.) If $\kappa = 0.1$, which assumes the contribution of inorganics to hygroscopicity is negligible, then only particles with $D_{dry} > 150$ nm will activate at $S = 0.2\%$.

[11] We did not observe low-α CCN at all times during the campaign when [CN] and T_{dew} were low, which suggests that they are not ubiquitous in the free troposphere. Low-α CCN were observed at an elevation roughly corresponding to the organic-rich aerosol layers observed by aircraft above the MBL roughly 30 km to the west [*Sorooshian et al.*, 2007] at the same time of year in 2005. Because these particles were up to 90% organic and had $D_p > 100$ nm [*Wang et al.*, 2008], they seem likely candidates for the low-α CCN observed in this study.

3.2. Cloud Parcel Modeling

[12] The results of our 1-D cloud parcel modeling suggest that under most relevant values of updraft velocity and aerosol number concentration (i.e., 10–1000 cm s^{-1} and 100–10,000 cm^{-3}), activation of such low-α CCN will be inhibited relative to particles with high α (Figure 3). Only at either low [CN] and strong updrafts (in which $S_{max} \gtrsim 1\%$) or high [CN] and weak updrafts (in which $S_{max} < 0.1\%$), do low-α CCN activate with comparable efficiency to high-α CCN. This is because the maximum S reached at low [CN]/strong updraft is high enough to activate low-α CCN, while in the opposite situation, S_{max} is so low that it (rather than α) limits CCN activation (see auxiliary material).

3.3. Potential Mechanisms of Kinetic Limitations

[13] Two commonly considered mechanisms for inhibited growth are condensed organic films at the droplet interface and slow dissolution. Insoluble organic compounds have long been known to form compressed films that reduce mass transfer rates across flat interfaces in macroscopic solutions [*Barnes*, 1986], and inhibition of mass transfer across a curved interface has been caused by insoluble organic material (1-hexadecanol) in droplets as small as ~1 µm [*Otani and Wang*, 1984]. The inhibition associated with a film can only act until a complete monolayer of film-forming compounds exists at the droplet interface; any further increase in D_{wet} will cause the film to break, resulting in much more rapid growth [*Feingold and Chuang*, 2002; *Podzimek and Saad*, 1975]. Alcohol monolayers, which can inhibit mass transfer to small droplets [e.g., *Otani and Wang*, 1984], have film thicknesses ~1.5–2 nm [*Berge and Renault*, 1993], and reduced mass transfer to small droplets has been observed through fatty acid monolayers with thicknesses ≥2.2 nm [e.g., *Xiong et al.*, 1998]. If all the material in a 300 nm particle formed a monolayer 2 nm thick, it would break once the droplet had grown to D_{wet} = 1.5 µm. Most of the low-α droplets were larger than this when they were observed, so it seems likely that their

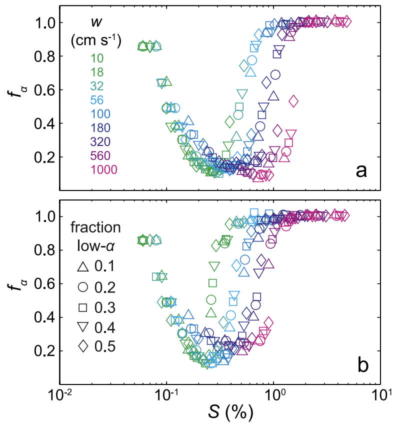

Figure 3. Ratio of the fraction of low-α CCN activated to the fraction of high-α CCN activated (f_α) as a function of maximum S, with low-α equal to (a) 0.01 and (b) 0.003. Color indicates the updraft (w), and symbols indicate the overall fraction of low-α CCN.

putative films had already been broken. However, during the evening hours of both 30 July and 01 Aug, the low-α droplets had $D_{wet} \sim 1.5\ \mu$m. Thus if films were responsible for the inhibitions to growth, then most of the low-α CCN were observed after they had been broken, but the smallest observed droplets could potentially have still been completely covered (and therefore would have been still growing slowly).

[14] Another potential cause of kinetic limitations is slow dissolution, which can limit growth only until the droplet is activated. Slow diffusion to the droplet-air interface can cause delayed growth, but this effect is minor when S = 0.2–0.3% [*Asa-Awuku and Nenes*, 2007] and therefore cannot by itself account for these kinetic limitations. In addition to diffusion the rate of dissolution may be limited to surface processes (at the solvent-solute interface). The low-α droplets in this study could only be observed when they were $\gtrsim 1\ \mu$m in diameter, at which size the droplet curvature only raises S in equilibrium with the droplet (S_{eq}) by ~0.2% (absolute). Because S was typically stepped from 0.2 to 0.6%, these droplets had almost certainly been activated before they were observed. Once a particle activates, its rapid volumetric growth rate is proportional to its surface area, meaning that its diameter increases rapidly at first, but this increase slows as the particle grows. For example, if the ambient S is 0.4%, a 100 nm AS particle will grow to 1 μm within ~0.1 s of activation and 2 μm within ~0.5 s, but will not reach 5 μm for ~3 s and 8 μm for ~6 s. It follows that the smallest droplets ($D_{wet} \simeq 1.5\ \mu$m) must all have activated nearly instantaneously within the last fraction of a second, which is exceedingly unlikely.

[15] Although we varied t_s from 10 to 30 s, we never observed kinetic limitations when t_s = 10 s. Low-α droplets were observed most frequently after 20 s, suggesting that the delays associated with the observed inhibitions were 10–20 s in duration. This range of times would be required for a 300 nm organic particle to grow to $D_{wet} = 1.5\ \mu$m if its accommodation coefficient ranged from $0.5 - 1 \times 10^{-3}$, which is broadly consistent with previous observations [*Barnes*, 1986; *Chuang*, 2003]. Based on this evidence, as well as the size distributions of the slowly-growing droplets, we conclude that an initial delay caused by a compressed film, is more likely than a slow dissolution to have caused the observed kinetic limitations, particularly the ones observed on 30 July and 01 August (see auxiliary material).

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