

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

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9 The influence of aerosols on cloud properties remains one of the largest sources
10 of uncertainty in estimates of the anthropogenic component of climate change.
11 Here we report the rate of cloud droplet formation on particles sampled at
12 a site near the California coast that is typically above the marine boundary
13 layer. We observed persistent bimodal diameter spectra which are better ex-
14 plained by kinetic limitations than by differences in equilibrium properties.
15 The slowly-growing mode contained 10–25% of the total cloud condensa-
16 tion nuclei (CCN) and had apparent mass accommodation coefficients (α)
17 10–30 times smaller than that measured for ammonium sulfate. Cloud par-
18 cel modeling suggests that most of these slowly-growing CCN will not form
19 cloud droplets. The relatively small and narrow size distribution of the low-
20 α droplets suggest that a condensed film is a more likely cause of these lim-
21 itations than slow dissolution.

1. Introduction

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

34 Evidence for kinetic limitations has been previously presented for both lab-generated
35 and ambient CCN. Delayed growth relative to ammonium sulfate (AS) has been observed
36 for lab-generated carboxylic acid particles [*Shantz et al.*, 2003], as well as for particles
37 formed via ozonolysis of gaseous precursors [*Hegg et al.*, 2001; *Asa-Awuku et al.*, 2009].
38 Evidence for kinetic limitations has also been found in several field experiments [*Shantz*
39 *et al.*, 2008; *Murphy et al.*, 2009]. These limitations could be due to solubility effects or
40 inhibited mass transfer of water, possibly due to a compressed (insoluble) organic film
41 at the droplet-air interface. Such a film has been suggested for droplets under subsat-
42 urated conditions, both in field [*Chuang*, 2003] and laboratory studies [e.g., *Chan and*

43 *Chan, 2005*, and references therein]. This inhibition can be quantified with the mass ac-
44 commodation coefficient (α). Although strictly speaking, use of α implies a mass transfer
45 inhibition, anything limiting droplet growth (e.g., slow dissolution) can be quantified with
46 an “apparent” value of α .

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

2. Experimental

2.1. Field site

57 We measured α of ambient CCN at the Ben Lomond Youth Conservation Camp (ele-
58 vation 805 m) approximately 10 km from the central California coast, from 23 July to 2
59 August, 2007, when the site was above the marine stratocumulus cloud top (Fig. 1a). Low
60 condensation nuclei concentrations ($[\text{CN}_{D>10\text{nm}}] < 1000 \text{ cm}^{-3}$) and dew point tempera-
61 tures ($T_d < 0^\circ\text{C}$) demonstrate that air at the site was often typical of free tropospheric
62 conditions (Fig. 1b,c), particularly at night. Rapid increases in T_d and $[\text{CN}]$ at the site

63 during the day (particularly towards the end of the campaign) suggest that mixing of
64 particles from the boundary layer also influences air at the site. A total of 980 differen-
65 tial mobility analyzer (DMA) scans of particle diameters ranging from 10–300 nm made
66 throughout the campaign indicate a peak in the number distribution around 40 nm, and
67 relatively low concentrations ($\sim 300 \text{ cm}^{-3}$) in the larger size range expected for most CCN
68 (100–300 nm) (see supplemental material).

2.2. Instrumentation

69 We sampled ambient particles and exposed them to a water vapor supersaturation
70 (S) in a continuous-flow thermal gradient chamber (CF-TGC) [Roberts and Nenes, 2005]
71 without any RH conditioning. The ambient RH at the site was $26 \pm 12\%$, suggesting that
72 the particles contained little, if any, water. The duration of particle exposure to S (t_s) was
73 varied from 10 to 30 s. We measured the velocity and diameter of the resulting droplets
74 (D_{wet}) with a phase-Doppler interferometer (PDI, manufactured by Artium Technologies),
75 before the droplets exited the CF-TGC. The accuracy of the D_{wet} measurements is 0.3 to
76 0.5 μm [Bachalo, 1980; Bachalo and Houser, 1984].

77 We calculated the mass accommodation coefficient (α) corresponding to each observed
78 D_{wet} using a fully-coupled fluid model [Roberts and Nenes, 2005]. This model calculates
79 the final D_{wet} given initial particle composition and size, α , ΔT and flow rate. When this
80 method is applied to droplets formed on lab-generated ammonium sulfate (AS) particles,
81 $\alpha = 10^{-0.82 \pm 0.52}$, or 0.15 (0.045–0.51) [Ruehl et al., 2008]. To distinguish between kinetic
82 and equilibrium effects in the field, S was repeatedly stepped from ~ 0.2 to $\sim 0.6\%$. At
83 a single value of S , inhibited growth (i.e., D_{wet} lower than that of AS particles) could be

84 due to kinetic limitations (low α), or to ambient CCN with S_c only slightly below the
85 value of S in the CF-TGC. If the latter is true, smaller values of D_{wet} will result from
86 purely equilibrium properties of the CCN, because the difference in water activity driving
87 droplet growth prior to activation ($S - S_c$) will be small. However, if S in the CF-TGC
88 is more than $\sim 0.1\%$ (absolute) greater than S_c , this effect will be negligible [Ruehl *et al.*,
89 2008, Fig. 3], because the CCN will be activated relatively quickly, and after activation
90 the water activity of the droplet drops from S_c to ~ 1 . Therefore, if inhibited growth is
91 seen over an S range of several tenths of a percent, we conclude that kinetic limitations
92 must be the cause.

2.3. 1-D cloud parcel model

93 The CFTGC-PDI measures D_{wet} of individual droplets at a given S , from which α can
94 be inferred; however, in the atmosphere, feedbacks exist between characteristics of the
95 CCN spectrum and value of S that the CCN experience in a cloud. To determine under
96 what conditions low- α particles will activate in the atmosphere, we modified a standard
97 1-D cloud parcel model similar to the one used by *Feingold and Chuang* [2002] to include
98 low- α CCN. We initialized the model with a log normal CCN size distribution, with a
99 geometric mean of $0.04\ \mu\text{m}$ and standard deviation of 2.0. The total number of aerosol
100 particles was varied from 100 to $10,000\ \text{cm}^{-3}$, the updraft velocity was varied from 10 to
101 $1000\ \text{cm s}^{-1}$, and the fraction of particles with the lower value of α was varied from 0.1
102 to 0.5. Two low- α values were considered: 0.01 and 0.003. The model was run until the
103 maximum value of S was obtained, and any droplets with $D_{wet} > 2\ \mu\text{m}$ at that point were
104 considered activated.

3. Results & Discussion

3.1. Field observations

105 Throughout the campaign, we observed both droplet growth rates similar to 100-nm
106 AS particles ($\alpha \sim 0.1$), and slightly larger growth rates ($\alpha \sim 1$). These larger- α droplets
107 could have either formed on dry particles larger than 100 nm, or alternatively made up
108 of a more CCN-active substance (i.e., NaCl). A distinct slowly-growing (low- α) mode of
109 CCN was observed early (24 July and 27 July) and late (29 July–2 Aug) in the campaign,
110 during roughly 50% of ~ 200 total hours (Fig. 1d). This mode was evident from bimodal
111 D_{wet} spectra, which persisted even when S was varied from ~ 0.2 to 0.6% (Figs. 2a,
112 b). While differences in S_c can explain bimodal spectra observed at a single S (Fig. 2a),
113 distinct kinetics (i.e., some CCN with $\alpha \sim 0.003$ –0.01) are required to explain the bimodal
114 spectra at a range of S (Fig. 2b). This is because CCN with high values of S_c will only
115 grow to smaller D_{wet} over a very narrow range of S (the black lines on Figs. 2a, b), but
116 CCN with low values of α (red lines) will have smaller D_{wet} at all values of S .

117 When present, this slowly-growing mode contained approximately 10–25% of all CCN,
118 and had α 10–30 times lower than the high- α mode (Figs. 2c, d). While the absolute
119 value of α is sensitive to the assumption made concerning the size and composition of
120 the CCN, both the difference (in log space) between the higher and lower value of α ,
121 as well as the proportion of CCN with low- α , are roughly equal for 100 nm AS and
122 200 nm NaCl particles. Although no compositional analysis was done of these low- α
123 CCN, upper or lower limits for some of their properties can be inferred from CCN and
124 other measurements. Known mechanisms for kinetic limitations to condensational growth
125 (e.g., film formation at the air-water interface, slow dissolution) are expected to occur in

126 organic-rich particles. Previous work has suggested that only particles with a large organic
127 component ($\gtrsim 75\%$) will exhibit lower CCN activity relative to particles that are primarily
128 inorganic [*Chang et al.*, 2007]. It therefore seems likely that the growth inhibition was
129 observed for particles that were primarily, if not overwhelmingly, organic. The low- α
130 CCN typically activated at relatively low S (0.2–0.3%). If we assume a hygroscopicity
131 for these particles, their minimum diameters can be estimated from this range of S . Most
132 CCN-active organic compounds have a hygroscopicity of ~ 0.1 , using the κ formulation
133 of *Petters and Kreidenweis* [2007]. (In contrast, κ of ammonium sulfate is ~ 0.6 .) If
134 $\kappa = 0.1$, which assumes the contribution of inorganics to hygroscopicity is negligible, then
135 only particles with $D_{dry} > 150$ nm will activate at $S = 0.2\%$.

136 We did not observe low- α CCN at all times during the campaign when $[\text{CN}]$ and T_{dew}
137 were low, which suggests that they are not ubiquitous in the free troposphere. Low- α
138 CCN were observed at an elevation roughly corresponding to the organic-rich aerosol
139 layers observed by aircraft above the MBL roughly 30 km to the west [*Sorooshian et al.*,
140 2007] at the same time of year in 2005. Because these particles were up to 90% organic
141 and had $D_p > 100$ nm [*Wang et al.*, 2008], they seem likely candidates for the low- α CCN
142 observed in this study.

3.2. Cloud parcel modeling

143 The results of our 1-D cloud parcel modeling suggest that under most relevant val-
144 ues of updraft velocity and aerosol number concentration (i.e., 10–1000 cm s^{-1} and 100–
145 10,000 cm^{-3}), activation of such low- α CCN will be inhibited relative to particles with high
146 α (Fig. 3). Only at either low $[\text{CN}]$ and strong updrafts (in which $S_{max} \gtrsim 1\%$) or high

147 [CN] and weak updrafts (in which $S_{max} < 0.1\%$), do low- α CCN activate with comparable
148 efficiency to high- α CCN. This is because the maximum S reached at low [CN]/strong
149 updraft is high enough to activate low- α CCN, while in the opposite situation, S_{max} is so
150 low that it (rather than α) limits CCN activation (see supplemental material).

3.3. Potential mechanisms of kinetic limitations

151 Two commonly considered mechanisms for inhibited growth are condensed organic films
152 at the droplet interface and slow dissolution. Insoluble organic compounds have long been
153 known to form compressed films that reduce mass transfer rates across flat interfaces in
154 macroscopic solutions [Barnes, 1986], and inhibition of mass transfer across a curved
155 interface has been caused by insoluble organic material (1-hexadecanol) in droplets as
156 small as $\sim 1 \mu\text{m}$ [Otani and Wang, 1984]. The inhibition associated with a film can only
157 act until a complete monolayer of film-forming compounds exists at the droplet interface;
158 any further increase in D_{wet} will cause the film to break, resulting in much more rapid
159 growth [Feingold and Chuang, 2002; Podzimek and Saad, 1975]. Alcohol monolayers,
160 which can inhibit mass transfer to small droplets [e.g., Otani and Wang, 1984], have film
161 thicknesses $\sim 1.5\text{--}2 \text{ nm}$ [Berge and Renault, 1993], and reduced mass transfer to small
162 droplets has been observed through fatty acid monolayers with thicknesses $\geq 2.2 \text{ nm}$ [e.g.,
163 Xiong et al., 1998]. If all the material in a 300 nm particle formed a monolayer 2 nm thick,
164 it would break once the droplet had grown to $D_{wet} = 1.5 \mu\text{m}$. Most of the low- α droplets
165 were larger than this when they were observed, so it seems likely that their putative films
166 had already been broken. However, during the evening hours of both 30 July and 01 Aug,
167 the low- α droplets had $D_{wet} \sim 1.5 \mu\text{m}$. Thus if films were responsible for the inhibitions

168 to growth, then most of the low- α CCN were observed after they had been broken, but
169 the smallest observed droplets could potentially have still been completely covered (and
170 therefore would have been still growing slowly).

171 Another potential cause of kinetic limitations is slow dissolution, which can limit growth
172 only until the droplet is activated. Slow diffusion to the droplet-air interface can cause
173 delayed growth, but this effect is minor when $S = 0.2\text{--}0.3\%$ [Asa-Awuku and Nenes,
174 2007] and therefore cannot by itself account for these kinetic limitations. In addition
175 to diffusion the rate of dissolution may be limited to surface processes (at the solvent-
176 solute interface). The low- α droplets in this study could only be observed when they were
177 $\gtrsim 1\ \mu\text{m}$ in diameter, at which size the droplet curvature only raises S in equilibrium with
178 the droplet (S_{eq}) by $\sim 0.2\%$ (absolute). Because S was typically stepped from 0.2 to
179 0.6%, these droplets had almost certainly been activated before they were observed. Once
180 a particle activates, its rapid volumetric growth rate is proportional to its surface area,
181 meaning that its diameter increases rapidly at first, but this increase slows as the particle
182 grows. For example, if the ambient S is 0.4%, a 100 nm AS particle will grow to 1 μm
183 within $\sim 0.1\ \text{s}$ of activation and 2 μm within $\sim 0.5\ \text{s}$, but will not reach 5 μm for $\sim 3\ \text{s}$
184 and 8 μm for $\sim 6\ \text{s}$. It follows that the smallest droplets ($D_{wet} \simeq 1.5\ \mu\text{m}$) must all have
185 activated nearly instantaneously within the last fraction of a second, which is exceedingly
186 unlikely.

187 Although we varied t_s from 10 to 30 s, we never observed kinetic limitations when
188 $t_s = 10\ \text{s}$. Low- α droplets were observed most frequently after 20 s, suggesting that the
189 delays associated with the observed inhibitions were 10–20 s in duration. This range of

190 times would be required for a 300 nm organic particle to grow to $D_{wet} = 1.5 \mu\text{m}$ if its
191 accommodation coefficient ranged from $0.5 - 1 \times 10^{-3}$, which is broadly consistent with
192 previous observations [*Barnes, 1986; Chuang, 2003*]. Based on this evidence, as well as
193 the size distributions of the slowly-growing droplets, we conclude that an initial delay
194 caused by a compressed film, is more likely than a slow dissolution to have caused the
195 observed kinetic limitations, particularly the ones observed on 30 July and 01 August (see
196 supplemental material).

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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 (lower).

Figure 2. (a,b) D_{wet} histograms as a function of S (color), along with modeled D_{wet} on AS particles with various D_{dry} (given in nm) and $\alpha = 0.1$ (black) or lower (red). (c,d) α histograms corresponding to D_{wet} distributions, assuming dry CCN are (red) 200 nm NaCl particles and (blue) 100 nm AS particles.

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.

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