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## Toward Direct Measurement of Atmospheric Nucleation

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Atmospheric aerosol formation is known to occur almost all over the world, and the importance of these particles to climate and air quality has been recognized. Although almost all of the processes driving aerosol formation take place below a particle diameter of 3 nanometers, observations cover only larger particles. We introduce an instrumental setup to measure atmospheric concentrations of both neutral and charged nanometer-sized clusters. By applying the instruments in the field, we come to three important conclusions: (i) A pool of numerous neutral clusters in the sub-3-nanometer size range is continuously present; (ii) the processes initiating atmospheric aerosol formation start from particle sizes of ~1.5 nanometers; and (iii) neutral nucleation dominates over the ion-induced mechanism, at least in boreal forest conditions.

Formation of new atmospheric aerosol particles (diameter of 3 to 10 nm) by nucleation and subsequent growth has been observed in a wide variety of low- and high-altitude locations (1). Once the formed particles grow further in size, they may participate in cloud formation and influence the regional or even global radiation balance and ultimately climate. On more local scales, these particles may be deleterious to human health and impair visibility.

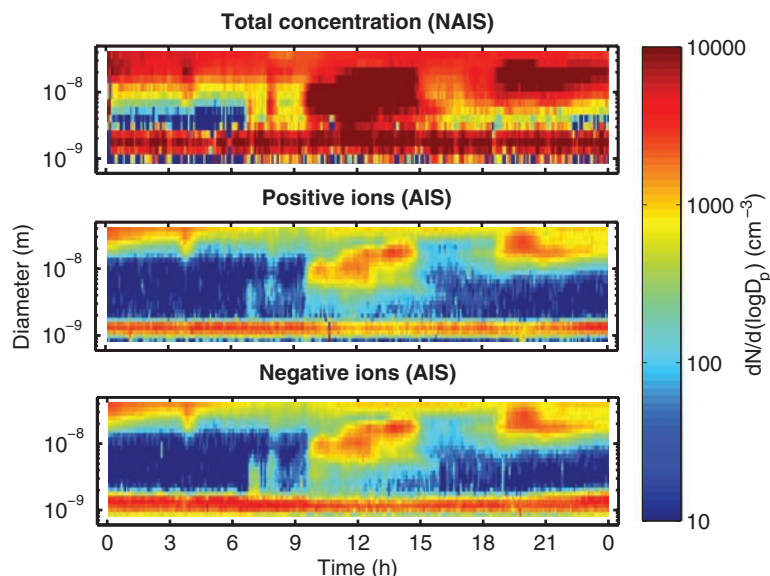
Despite the growing list of locations where frequent aerosol formation has been observed, the overall magnitude of this source is still very poorly understood compared with that of any other major source generating particles into the atmosphere. There are at least two reasons for this. First, atmospheric aerosol formation is driven by processes taking place below a 3-nm particle diameter, which is outside the range of most measuring devices in use. Second, the nu-

cleation mechanism initiating aerosol formation is likely to vary with location and atmospheric conditions. Proposed atmospheric nucleation mechanisms include kinetic (or barrierless), binary, ternary, and ion-induced (or ion-mediated) nucleation (1–3), some of which might further be affected by meteorological processes such as turbulent fluctuations, atmospheric waves, and

mixing (4, 5). Most nucleation mechanisms have been thought to involve gaseous sulfuric acid, even though nucleation taking place in association with clouds and in coastal areas could be induced by water-insoluble (6) and iodine compounds (7), respectively.

Recently it was suggested that the formation of new atmospheric aerosol particles is connected with the existence of thermodynamically stable 1- to 2-nm clusters (8), formed in the atmosphere by some nucleation mechanism. From a physical standpoint, two very different cluster types in the sub-3 nm size range can be distinguished: charged (air ions or ion clusters) and neutral species. The existence of atmospheric ion clusters as small as 0.5 to 1 nm in diameter has been known for decades, and measurements with ion spectrometers, such as the Air Ion Spectrometer (AIS) and Balanced Scanning Mobility Analyzer (BSMA), have demonstrated that such clusters are present almost all the time (9). The production rates of ion clusters are, however, generally too low to explain the observed aerosol-formation rates (10).

In view of the insufficient numbers of ion clusters, the key to understanding atmospheric aerosol formation is clearly the presence of neutral clusters. Theoretical arguments predict the existence of such clusters (8, 11) and suggest that



**Fig. 1.** Evolution of particle number size distribution measured with the NAIS on a particle formation event day (23 April 2006) in Hyttälä, Finland.

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they should play an important role in aerosol formation processes via their activation (12). Proposed candidates for neutral clusters include ammonium bisulfate clusters (12, 13) and clusters formed by ion-ion recombination (14). The presence of neutral atmospheric clusters has not been experimentally verified so far, because the commercially available instruments cannot reliably detect neutral aerosol particles smaller than about 3 nm in diameter.

Here we provide experimental evidence for the existence of neutral clusters in the atmosphere and demonstrate that the processes initiating atmospheric aerosol formation include clusters with sizes close to 2 nm in diameter. The investigation is based on three very recently developed instruments: the Neutral Cluster–Air Ion Spectrometer (NAIS), the UF-02proto Condensation Particle Counter (UF-02proto CPC), and a Grimm nanoDMA and Faraday Cup Electrometer preceded by a unipolar charger (15, 16). Measured total (air ion plus neutral) cluster concentrations are compared with corresponding air ion concentrations obtained from BSMA and AIS measurements, as well as with cluster concentrations calculated theoretically (16, 17).

The data collected in this work were measured in Hyttiälä, southern Finland, during 10 weeks and during 3 weeks in Birmingham, UK, in spring 2006 (16). The most compelling evidence for the existence of neutral clusters is given by the NAIS measurements. Figure 1 shows the evolution of the cluster size distribution, both neutral and charged clusters, on one particle-formation event day in Hyttiälä. Similarly to ion measurements (see also figs. S7 to S9), there seems to be a cluster mode present all the time, with a median size of ~1.5 to 1.8 nm and extending to slightly below 1 nm at the lower end and to ~2.5 nm at the upper end. The total number concentration of this cluster mode is on the order of  $1000 \text{ cm}^{-3}$ . Owing to continuous scavenging of the clusters by coagulation, the presence of a continuous cluster mode suggests also continuous nucleation. If the particles do not grow above 3 nm before they are scavenged, they cannot be detected with traditional aerosol sizing instruments (such as Differential Mobility Particle Sizer, DMPS; fig. S6). This is the case for our example day before ~9 a.m.

At ~10 a.m. a fraction of the clusters activate, i.e., start growing to larger sizes. This can be caused by a sudden lowering of the coagulation sink and/or an increase of condensable vapor concentrations. The particle formation is also observable with DMPS (fig. S6).

The air ion and total cluster concentrations in Hyttiälä, in the size range of 1.8 to 3.0 nm, are shown in Fig. 2 for a period of 70 days. Typical concentrations of air ions were between about 10 and  $100 \text{ cm}^{-3}$  in the daytime and  $<10 \text{ cm}^{-3}$  during the night. The total cluster concentrations were much higher, on the order of  $1000 \text{ cm}^{-3}$ . Therefore, there must have been a large number (~1000 to  $10000 \text{ cm}^{-3}$ ) of neutral clusters present almost all the time. The observed order of magnitude can

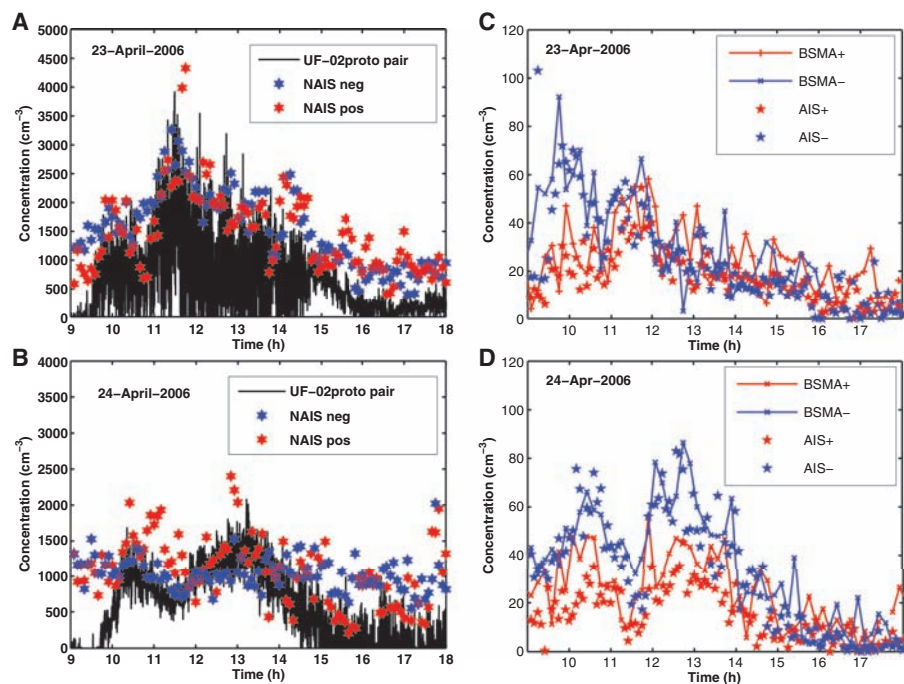
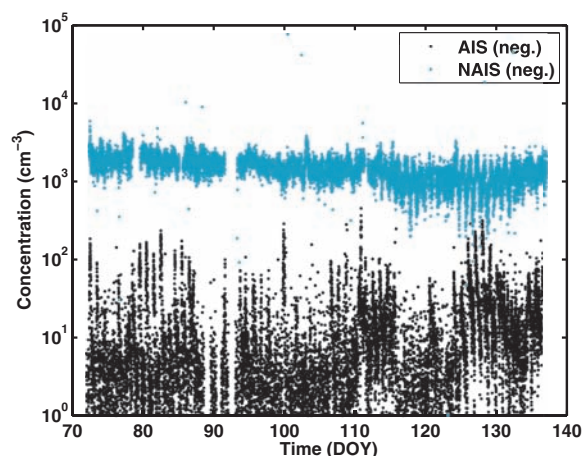
be predicted by using simple balance equations for neutral and charged particle concentrations (16), but only if a substantial neutral nucleation rate is assumed. Consequently, ion-induced nucleation, activation of ion clusters, or ion-ion recombination cannot produce sufficient number of neutral clusters, and thus the majority of nucleation (at least in Hyttiälä) has to be neutral.

For a more detailed analysis, we selected two aerosol formation event days in Hyttiälä, during which simultaneous data from the NAIS, UF-02proto CPCs, AIS, BSMA, and DMPS were available. On the first day (23 April), we observed an aerosol formation event between about 09:00 and 15:00 (16). The time evolution of the total cluster concentration in the size range of 1.8 to 3.0 nm, as measured by the UF-02proto CPC

pair, followed closely that measured by the NAIS (Fig. 3A). On the next day (24 April) there was less agreement between these two measurement systems, yet both showed similar overall cluster concentrations (Fig. 3B). Compared with the total cluster numbers, which reached concentrations of up to  $1500 \text{ to } 3000 \text{ cm}^{-3}$ , the concentrations of air ions in the same range were much lower, on the order of  $10 \text{ to } 100 \text{ cm}^{-3}$  (Fig. 3, C and D).

Figure 4 compares theoretically calculated cluster concentrations with those measured by the NAIS on 23 April during the active period of 3-nm particle formation. Outside the actual particle formation and growth time frame, our calculation procedure is not valid (16). Excluding the few short periods when momentary decreases in particle formation rate drive down calculated

**Fig. 2.** Time series of cluster concentrations. Number concentrations of 1.8- to 3-nm aerosol particles and negative air ions measured with the NAIS (blue) and AIS (black) between 13 March and 16 May 2006.



**Fig. 3.** Cluster concentrations on 2 days with new particle formation. (A and B) Total cluster-number concentrations between 1.8 and 3.0 nm observed by the NAIS (blue and red) and UF-02proto CPC pair (black) during 23 and 24 April 2006. (C and D) Negative (blue) and positive (red) air ion number concentrations measured with the AIS and BSMA during 23 and 24 April 2006.

cluster concentrations, a close agreement between calculated and measured cluster concentrations is seen. The data measured in Birmingham (16) show also a strong diurnal cycle in particles of 1.8- to 3-nm diameter (fig. S10)

Thus, the three different approaches applied here give total cluster concentrations that are usually within a factor of 2 of each other and roughly two orders of magnitude larger than air ion concentrations of similar size. These findings demonstrate unambiguously that sub-3 nm neutral clusters exist in the atmosphere and that they dominate over corresponding charged clusters at least down to 1.8 nm in size.

Hints about the existence of neutral clusters can be found in the scientific literature. In their laboratory measurements of prenucleation molecular clusters in a ternary  $\text{NH}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  system, Hanson and Eisele (18) observed large amounts of neutral clusters, using a transverse chemical ionization apparatus. The composition of their clusters might be comparable to that of atmospheric clusters observed in the present study. In another laboratory study, Kim *et al.* (19) analyzed homogeneous and ion-induced nucleation in the ternary  $\text{NH}_3/\text{SO}_2/\text{H}_2\text{O}/\text{air}$  mixture. They proposed homogeneous nucleation of  $(\text{NH}_4)_2\text{SO}_4$  molecules produced by the  $\text{H}_2\text{SO}_4\text{-NH}_3$  reaction as the main nucleation mechanism.

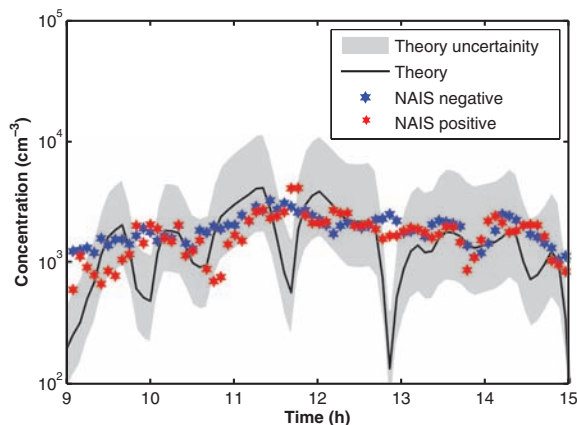
Regardless of the details of the nucleation mechanism, e.g., ammonium bisulfate clusters can be considered proper candidates for neutral clusters in the atmosphere. Our CPC is probably not the only such instrument capable of observing the neutral clusters: Gamero-Castaño and de la Mora (20) proposed clusters as “impurities in the gas phase.” However, their study focused on the activation of ions and charged nanoclusters under laboratory conditions.

Our observations can be used to test different hypotheses related to atmospheric nucleation and initial growth of nucleated clusters. For example, we have calculated the formation rate of 1.8-nm clusters in Hyytiälä, denoted here as  $J_2$  (16). On 23 April, the value of  $J_2$  for all clusters together was in the range of 1.5 to 1.6  $\text{cm}^{-3} \text{s}^{-1}$ , as calculated from the NAIS data, and 1.1  $\text{cm}^{-3} \text{s}^{-1}$ , as calculated from the UF-02proto CPC pair data. For negative and positive ions, values of  $J_2$  calculated from the AIS data were 0.02 and 0.04  $\text{cm}^{-3} \text{s}^{-1}$ , respectively. On the basis of our ion-DMPS method (21), no appreciable ion-nucleation was observed on this day. On 24 April, the values of  $J_2$  for total clusters and positive ions were similar to those observed on the previous day, whereas the average  $J_2$  for negative ions was roughly three times as high. These features are reflected in the ratio between total cluster and air

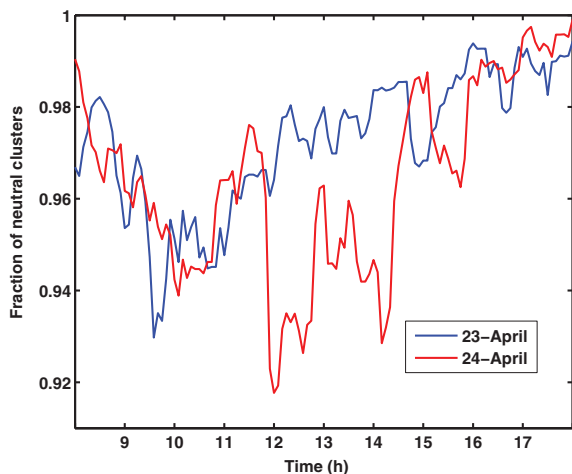
ion concentrations in the 1.8- to 3-nm size range (Fig. 5). On both days, the relative fractions of neutral clusters tracked each other, except during the new particle formation from 12:00 to 15:00 on 24 April. In this time period, the fraction of neutral clusters decreased from 0.97 to 0.93, indicating a larger (but less than 10%) contribution of ion-induced nucleation to  $J_2$ . The dominance of neutral over ion-induced nucleation is consistent with the findings of Eisele *et al.* (22) at another continental location.

Cluster size distributions (16) measured by the NAIS revealed that, similar to cluster ions, there appears to be a large pool of neutral clusters in the atmosphere all the time. These clusters have a larger mean size than ion clusters, and their distribution has a tail extending slightly above 2 nm. The presence of such a tail even in the absence of 3-nm aerosol formation, and the ~2-nm upper size of the continuous ion cluster and neutral cluster band, indicate strongly that dynamic processes initiating atmospheric aerosol formation take place at a particle diameter of ~2 nm, not 1 nm as previously thought. If true, this finding is important for at least two reasons. First, it suggests that with the latest instrumental developments, we can probe the size range in which atmospheric aerosol formation begins. Second, it makes atmospheric aerosol formation much less sensitive to nucleating vapor concentrations than if the aerosol formation were driven by traditional thermodynamic nucleation. The second point is consistent with the reported interdependencies of the atmospheric aerosol formation rate and gaseous sulfuric acid concentration (23, 24). The obtained values of  $J_2$  are in agreement with the nucleation rates predicted by the recent cluster activation theory (12), which further supports our experimental findings.

The observed nearly global occurrence of atmospheric aerosol formation provides compelling justification to include this phenomenon in large-scale atmospheric models, such as regional air-quality models and global climate models. Attempts to realize this objective have already been made (25–29). These pilot studies have demonstrated the need for more reliable nucleation parameterizations than are currently available. The instrumental developments described here, by observing neutral clusters about a nanometer smaller than previously measured, offer the opportunity to test existing nucleation theories against real atmospheric data. By conducting measurements similar to those reported here in a few carefully selected locations, it should be possible to develop simple yet sufficiently accurate nucleation parameterizations for large-scale modeling.



**Fig. 4.** Comparison with theory. Theoretically calculated total cluster concentrations (black) during the aerosol formation event on 23 April, along with the corresponding concentrations measured by the NAIS (blue and red). The shaded area gives an uncertainty range for theoretically calculated values (16, 17), obtained by assuming that the real growth rate of 1.8- to 3.0-nm clusters might be a factor of 2 lower or higher than the growth rate estimated from the BSMA data (2.1 nm/hour).



**Fig. 5.** Neutral cluster fraction. The neutral fraction of the total cluster concentration (1.8 to 3.0 nm) during 23 April 2006 (blue curve) and 24 April 2006 (red curve). During the latter day, the formed particles are negatively overcharged compared to the steady-state charge distribution based on observations obtained with the ion-DMPS (21).

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### Supporting Online Material

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## A Cretaceous Scleractinian Coral with a Calcitic Skeleton

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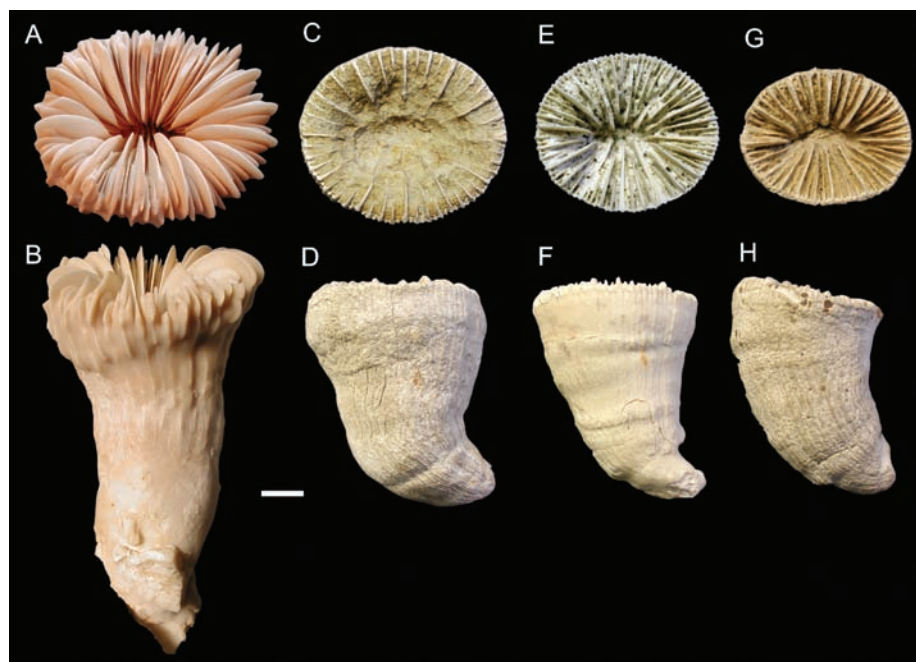
It has been generally thought that scleractinian corals form purely aragonitic skeletons. We show that a well-preserved fossil coral, *Coelosmilia* sp. from the Upper Cretaceous (about 70 million years ago), has preserved skeletal structural features identical to those observed in present-day scleractinians. However, the skeleton of *Coelosmilia* sp. is entirely calcitic. Its fine-scale structure and chemistry indicate that the calcite is primary and did not form from the diagenetic alteration of aragonite. This result implies that corals, like other groups of marine, calcium carbonate-producing organisms, can form skeletons of different carbonate polymorphs.

Scleractinian corals belong to the taxonomic class of anthozoans and are among the most prolific biomineralizing organisms in nature (1). Their calcium carbonate skeletons form shallow- and deep-water reefs and are prominent in the fossil record as far back as 240 million years ago (Ma) (2). Living scleractinians produce entirely aragonitic skeletons (3, 4). An identification of calcite in calcification centers of the shallow-water scleractinian *Mussa* sp. (5) was not confirmed by subsequent analysis (6). Aragonite is metastable at ambient temperatures and pressures and is susceptible to diagenetic transformation to calcite, the stable form of calcium carbonate under ambient conditions. Most fossil scleractinians have therefore been dissolved or transformed to calcite, preserving only their macroscopic morphology. In these cases, the original mineralogy can be inferred on the basis of their Sr content and by analogy with living scleractinians (7). Although some studies have left open the possibility that the original

mineralogy of some fossil Scleractinia was calcitic (8–10), it has been generally accepted that the aragonitic skeletal mineralogy of scleractinians

was highly conserved throughout their evolution (11).

Here we show that a fossil scleractinian coral formed a calcitic skeleton. We studied a suite of fossil corals attributed to the caryophylliid genus *Coelosmilia*. Our specimens are from the Upper Cretaceous (Maastrichtian) deposits of Poland (fig. S1) and are similar, but not identical, to the fossils studied in (12) in which the calcite in the corals was inferred to have formed diagenetically. We have now used a variety of micro-analytical methods to show that the calcite is instead primary. The overall skeletal architecture of *Coelosmilia* is similar to that of modern deep-sea corals, such as *Desmophyllum* (Fig. 1) and *Javania* (fig. S2). *Coelosmilia* sp. has a conical calice with septa arranged into five full cycles forming a hexameral pattern. Our specimens are complete skeletons and well preserved. External



**Fig. 1.** Morphology of the modern aragonite *Desmophyllum* sp. and the Late Cretaceous calcitic *Coelosmilia* sp. (A and B) *Desmophyllum* sp. Relatively smooth septa, a thick septothecal wall, and a lack of pali are typical features of this solitary, azooxanthellate scleractinian coral. (C to H) *Coelosmilia* sp. resembles *Desmophyllum* sp. in all morphological aspects. Distal [(A), (C), (E), and (G)] and lateral [(B), (D), (F), and (H)] views are shown. Scale bar, 10 mm.

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