

## ATMOSPHERIC SCIENCE

## Ion-induced sulfuric acid–ammonia nucleation drives particle formation in coastal Antarctica

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Formation of new aerosol particles from trace gases is a major source of cloud condensation nuclei (CCN) in the global atmosphere, with potentially large effects on cloud optical properties and Earth's radiative balance. Controlled laboratory experiments have resolved, in detail, the different nucleation pathways likely responsible for atmospheric new particle formation, yet very little is known from field studies about the molecular steps and compounds involved in different regions of the atmosphere. The scarcity of primary particle sources makes secondary aerosol formation particularly important in the Antarctic atmosphere. Here, we report on the observation of ion-induced nucleation of sulfuric acid and ammonia—a process experimentally investigated by the CERN CLOUD experiment—as a major source of secondary aerosol particles over coastal Antarctica. We further show that measured high sulfuric acid concentrations, exceeding  $10^7$  molecules  $\text{cm}^{-3}$ , are sufficient to explain the observed new particle growth rates. Our findings show that ion-induced nucleation is the dominant particle formation mechanism, implying that galactic cosmic radiation plays a key role in new particle formation in the pristine Antarctic atmosphere.

## INTRODUCTION

Antarctic air is virtually free of anthropogenic air pollution, and primary particle sources only weakly contribute to the number of aerosol particles (1, 2). Consequently, surface-air cloud condensation nuclei (CCN) concentrations are extremely low, and most of the CCN are due to secondary aerosol formation resulting from oxidation of biogenic volatile vapors in the atmosphere. While Antarctica is a desert, the surrounding Southern Ocean is biogenically highly active and a source of numerous aerosol precursor vapors, including dimethyl sulfide (DMS), volatile organic compounds, molecular iodine, and iodine hydrocarbons (3).

Elevated concentrations of nucleation mode particles indicative of formation of new aerosol particles have been reported over the Antarctic ocean (4), at various sites near the Antarctic coast (3, 5), as well as deep inland on the Antarctic plateau (6, 7). The formation of secondary aerosols in the Antarctic regions has been correlated with oceanic emissions of DMS and its subsequent atmospheric oxidation, producing low-volatility gas-phase compounds, such as sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and methane sulfonic acid (MSA) (8, 9). Organic oxidation products have also been suggested (5). However, a molecular understanding of new particle formation (NPF) in Antarctica remains unresolved. This is a consequence of the inaccessibility of the Antarctic continent and the lack of previously deployed field instruments to measure the ultrafine particles, precursor vapors, and chemical composition of nucleating clusters during particle formation events.

Here, we report measurements we made in Antarctica during the austral summer, November 2014 to February 2015, using an unprecedented suite of instruments to reveal the molecular mechanisms responsible for NPF (see Materials and methods and the Supple-

mentary Materials for details). We performed the measurements at the Finnish Antarctic Research Station (Aboa) ~130 km inland from the Southern Ocean coast.

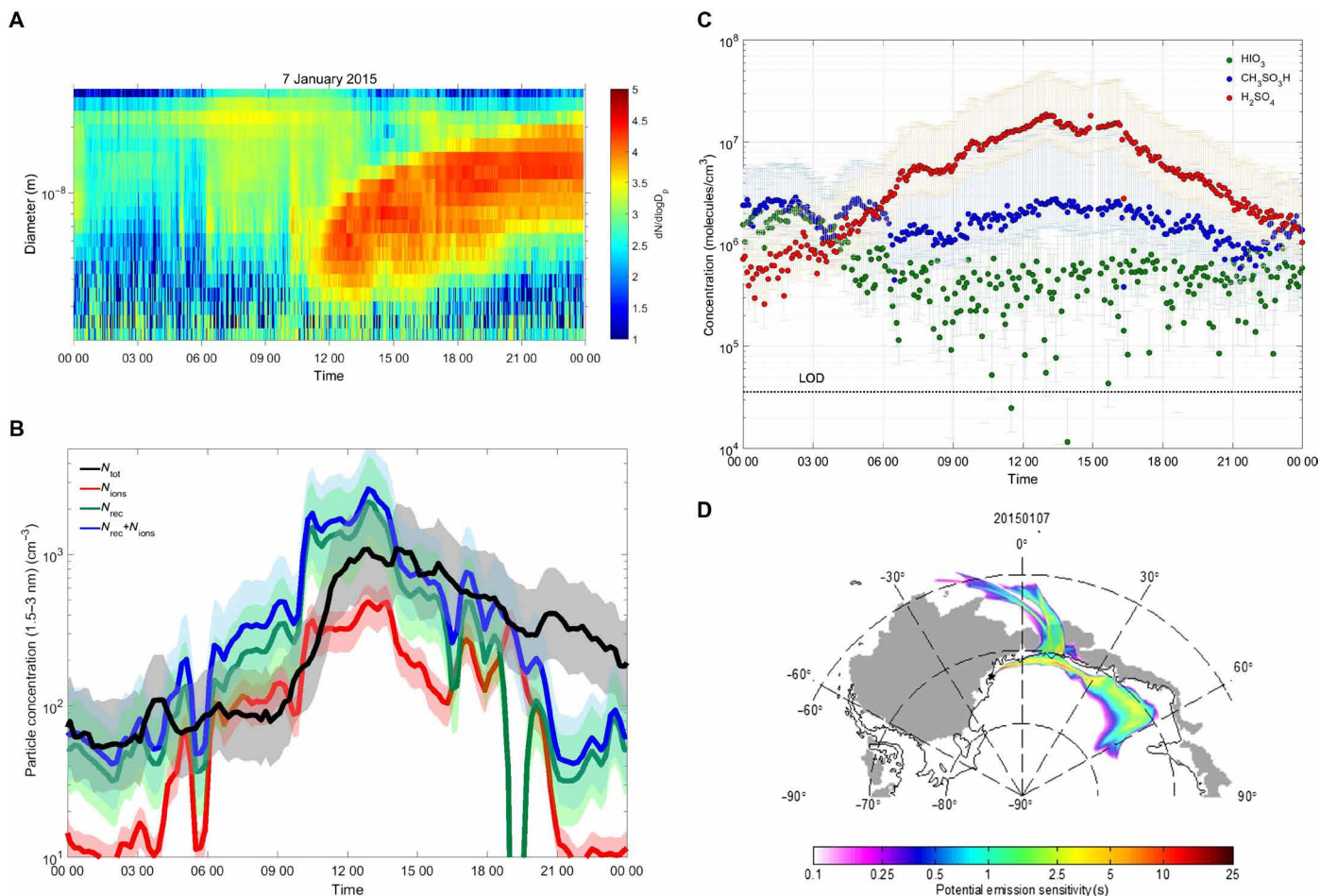
## RESULTS

We observed NPF events with subsequent growth of newly formed particles into larger sizes on 9 days out of a total of 54 days of operation (fig. S1). In addition, there were several days with some indication of either local or regional NPF. All events were associated with high solar radiation conditions and air masses arriving from the ice-free region of the Southern Ocean (fig. S2). No NPF events were observed in air masses arriving from continental or ice-covered ocean regions (fig. S3). An example of an NPF event, observed on 7 January 2015, is shown in Fig. 1, together with observed gas-phase concentrations of sulfuric acid, MSA, and iodic acid, as well as the nanoparticle (diameter range, 1.5 to 3 nm) number concentrations. During this NPF event, the sulfuric acid concentration was remarkably high with a maximum concentration of  $(2 \pm 1) \times 10^7$  molecules  $\text{cm}^{-3}$ —substantially higher than the rare studies have reported from Antarctica (10–12). MSA concentrations were lower, reaching a maximum of  $(3 \pm 1) \times 10^6$  molecules  $\text{cm}^{-3}$ . Very low levels, fewer than  $10^5$  molecules  $\text{cm}^{-3}$ , of iodic acid were recorded, and they showed no association with the NPF. Other NPF events observed during the campaign showed similar characteristics (see figs. S1 to S4).

The formation of negative ion clusters was observed concurrent with elevated sulfuric acid concentrations. These clusters were composed mainly of sulfuric acid, ammonia, and a bisulfate ion, indicative of a negative ion–induced nucleation mechanism. Figure 2 shows the mass defect versus mass/charge ratio (Th) observed (A) before and (B) during a nucleation event. The mass defect is the difference of the molecular/cluster mass from integer mass; each point in the mass defect plot corresponds to a unique atomic composition. Data emphasize that the cluster formation proceeds initially with the addition of sulfuric acid molecules on a bisulfate core ion up to a “tetramer” (i.e., bisulfate ion plus three molecules of neutral sulfuric

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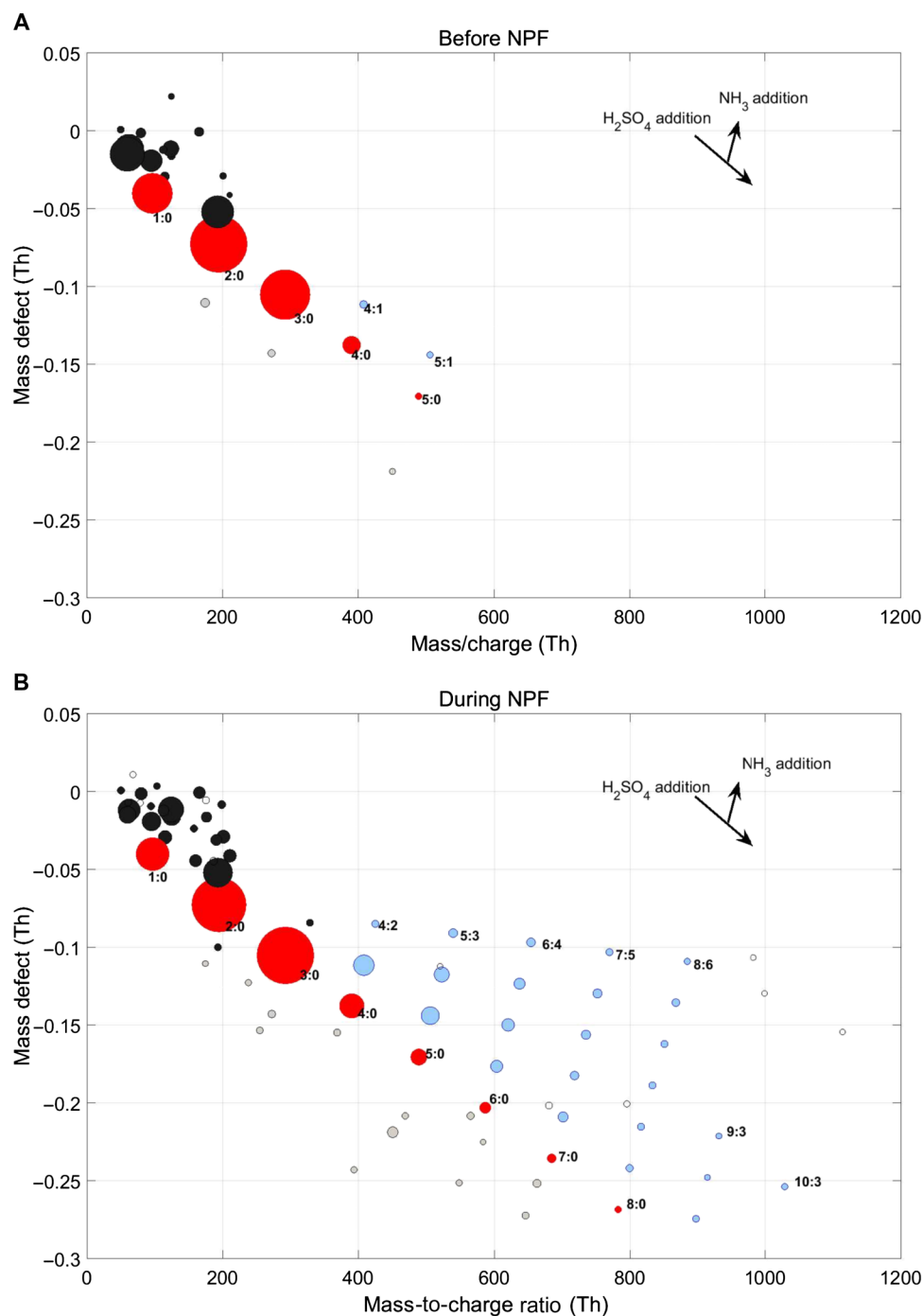
**Fig. 1. Example of an NPF event at Aboa, Antarctica, 7 January 2015, ~130 km inland.** (A) Size distribution of 2.25- to 40-nm aerosol particles measured with the Neutral cluster and Air Ion Spectrometer (NAIS). NPF starts around noon (UTC time) and continues for around 7 hours. The particles continue to grow beyond midnight, in 24-hour daylight. (B) Number concentrations of 1.5- to 3-nm ( $\pm 0.2$ -nm) particles:  $N_{\text{tot}}$  is the total number concentration ( $\pm 50\%$ ) in the size range of 1.5 to 3 nm, measured with the particle size magnifier (PSM);  $N_{\text{ions}}$  is the small ion concentration ( $\pm 30\%$ ) measured with the NAIS; and  $N_{\text{rec}}$  is the calculated neutral cluster concentration from ion-ion recombination. The sum of  $N_{\text{ions}} + N_{\text{rec}}$  shows that ion-induced nucleation accounts for all particles measured with the PSM during this event. (C) Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), MSA ( $\text{CH}_3\text{SO}_3\text{H}$ ), and iodic acid ( $\text{HIO}_3$ ) concentrations measured by a nitrate chemical ionization atmospheric pressure interface time-of-flight (CI-API-TOF) mass spectrometer. Remarkably high sulfuric acid concentrations,  $\sim 2 (\pm 1) \times 10^7$  molecules/ $\text{cm}^3$ , were recorded during the peak of the NPF event. The uncertainty limits for sulfuric acid indicate the collision limit of sulfuric acid with charger ions (lower error bar) and overestimation of the losses in the inlet tube by a factor of 2 (upper error bar). The mean concentrations were calculated using a calibration factor of  $1.195 \times 10^{10}$  that was obtained with the same 60-cm inlet tube. Very low levels of iodic acid were recorded, and they showed no association with the NPF. The LOD line depicts the limit of detection ( $3.6 \times 10^4$  molecules  $\text{cm}^{-3}$ ) recorded for sulfuric acid. (D) Emission sensitivity for the air masses traveling to Aboa (72-hour back trajectory) in the estimated boundary layer (<600 m). Gray areas depict the sea ice cover, and we see that the air masses originate from the open Southern Ocean. No NPF events were observed from continental air masses or from areas completely covered by sea ice (figs. S2 and S3).

acid), after which ammonia can stick to the clusters as well. Thus, the  $\text{H}_2\text{SO}_4$  tetramer was detected with zero to one molecule of  $\text{NH}_3$  and the corresponding pentamer was detected with zero to two molecules of  $\text{NH}_3$ . Larger sulfuric acid clusters contain progressively between zero and six  $\text{NH}_3$  molecules. These observations are consistent with CLOUD (13–15) and indicate that the dominant particle formation mechanism is ion-induced nucleation of sulfuric acid and ammonia under ammonia-limited conditions, where full neutralization to ammonium sulfate is not reached. Note that if amines were present, they would substitute ammonia in the clusters (16). The sulfuric acid concentrations are sufficiently high and the temperatures are sufficiently low that ion-induced binary nucleation ( $\text{HSO}_4^- - \text{H}_2\text{SO}_4 - \text{H}_2\text{O}$ ) also takes place (extending up to eight sulfu-

ric acid molecules; Fig. 2B, red points), accounting for ca. 10 to 15% of the total rate.

Our observations of negative ion clusters containing up to 10  $\text{H}_2\text{SO}_4$  molecules and 6  $\text{NH}_3$  molecules demonstrate that negative ion-induced nucleation took place at the immediate vicinity of the Aboa measurement site. During 1 day with strong NPF, positive ion clusters were measured. Contrary to expectations (15), no clusters consisting of sulfuric acid, ammonia, and an ammonium ion were detected. Instead of ammonia, strong signals of a higher proton affinity compound, dimethyl sulfoxide, were observed (fig. S5). This likely prevented a positive ion-induced nucleation pathway (fig. S6).

But was the negative ion-induced mechanism the dominant pathway for NPF? The CI-API-TOF has insufficient sensitivity to



**Fig. 2. Molecular composition of the negative ion clusters measured by the API-TOF.** Negative ion clusters detected (A) before and (B) during an NPF event on 3 January 2015. Both mass spectra are integrated for 180 min. Other event days show similar distributions (fig. S4). Colors indicate negative molecular clusters of nitric acid and other identified compounds with no role in particle formation (black), pure sulfuric acid (red), sulfuric acid–ammonia (blue), and iodic acid–sulfuric acid–ammonia (gray). Open dots depict clusters known to be associated to system-originating impurities or with unknown composition. The largest detected negative cluster contains 10 molecules of sulfuric acid and 3 molecules of ammonia (labeled “10:3”). The area of the circles is proportional to the signal rate (counts  $s^{-1}$ ).

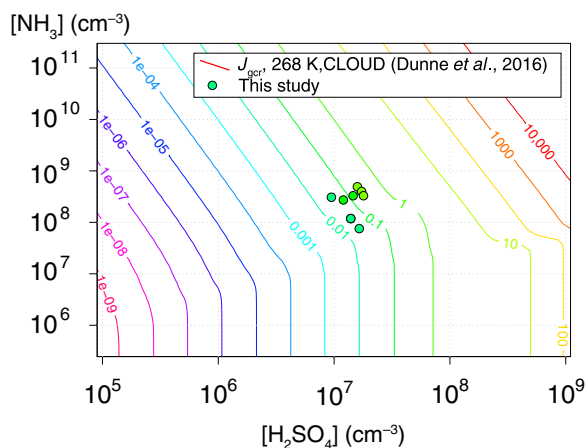
detect the extremely low concentrations of new particles involved (around  $1000 \text{ cm}^{-3}$  or below). However, particle number concentrations measured in the 1.5- to 3-nm size range by the PSM were low, usually exceeding the ion cluster concentrations measured by the NAIS by only a factor of about 2 (Fig. 1B and figs. S7 and S8). After

accounting for ion-induced clusters that were expected to be neutralized by ion-ion recombination before detection by the PSM, we find that ion-induced ternary inorganic and binary nucleation can account for all of the observed new particles (Fig. 1B). This is consistent with CLOUD observations (14, 15). Last, we comment that

no highly oxidized multifunctional organic molecules (HOMs) (17), which seem to play a major role in nucleation over vegetated continents (17, 18), were detected throughout the entire campaign—by either the CI-API-TOF or the API-TOF—corresponding to HOM concentrations below the detection limit ( $\sim 10^4$  molecules  $\text{cm}^{-3}$ ), which indicates that HOMs contributed neither to the nucleation nor to the growth of new particles.

We have quantitatively compared our nucleation rates with those measured in the CERN CLOUD chamber for the  $\text{H}_2\text{SO}_4\text{-NH}_3$  system in the presence of ions from galactic cosmic rays (13). The nucleation rates we measured at Aboa, Antarctica, at temperatures between  $-7^\circ$  and  $-3^\circ\text{C}$ , are well described by CLOUD data at  $-5^\circ\text{C}$  with 3 to 30 parts per trillion by volume (pptv) of ammonia (Fig. 3) (19). We have no direct information on concentrations or sources of ammonia in our measured air masses, but it has been shown that both the Southern Ocean and penguin and seabird colonies commonly present in coastal Antarctica emit ammonia with local atmospheric mixing ratios of 10 to 1000 pptv (20, 21). The bulk aerosol measurements made previously at the Neumayer III site, 300 km upwind from Aboa, showed an average particulate ammonium-to-sulfate mass ratio of 3% (molar ratio  $\approx 0.16$ ) during the NPF days (3). In our case, 1 to 7% of the mass of the clusters containing at least four sulfuric acid molecules was due to ammonia depending on the NPF day. Together with the CLOUD observations, we conclude that NPF in this region occurs under conditions where the nucleation rate is sensitive to both sulfuric acid and ammonia concentrations in the gas phase (see Fig. 3).

We measured particle growth rates of 0.3 to 1.3 nm/hour during the NPF events, in agreement with previous observations in Antarctica (table S2) (3, 5). The measured sulfuric acid concentration can explain the particle growth rates during the days when this growth rate could be determined from measurements, although the mea-



**Fig. 3. Comparison to nucleation rates measured in CLOUD.** Comparison of nucleation rates (unit  $\text{cm}^{-3} \text{s}^{-1}$ , shown by different colors) with the CLOUD (19).  $J_{\text{ger}}$  parameterization contours at 268 K ( $-5^\circ\text{C}$ ). The CLOUD parameterization assumes a ground-level galactic cosmic ray ionization rate of 1.8 ion pairs  $\text{cm}^{-3}$  and no contribution from terrestrial radioactivity, which gives an equilibrium ion pair concentration of about 1100  $\text{cm}^{-3}$  under pristine Antarctic conditions. An agreement between our  $J_{1.5}$  measurements and CLOUD results is obtained for ambient  $\text{NH}_3$  concentrations between 3 and 30 pptv. On the other hand, without  $\text{NH}_3$ , the CLOUD measurements predict a factor of 10 to 30 lower nucleation rates than we observed. These  $\text{NH}_3$  levels are consistent with the  $\text{NH}_3$  fraction measured by the API-TOF (16).

surement uncertainties on both quantities leave open the possibility that MSA and iodic acid, together with ammonia, may also contribute to particle growth.

In addition to sulfuric acid and ammonia, we found that some ion clusters contained iodic acid (Fig. 2), which is an important precursor for small clusters in mid-latitude coasts and in the immediate vicinity of Arctic sea ice (22). However, the measured contribution of iodic acid to the cluster production at Aboa was very small, and no pure iodic acid or iodine oxide clusters were detected. Because Aboa is far from potential iodine emission sites, it may be that most of the iodine compounds had been oxidized to  $\text{HIO}_3$  and other condensable compounds and removed by deposition to the background aerosol before the air mass reached Aboa.

## DISCUSSION

In summary, our measurements show that ion-induced nucleation of sulfuric acid and ammonia, followed by sulfuric acid-driven growth, is the predominant mechanism for NPF and growth in eastern Antarctica a few hundred kilometers from the coast, and probably throughout the lower-troposphere coastal Antarctic region during the summertime. The nucleation rates are likely to be highly sensitive to both sulfuric acid and ammonia. Therefore, any change in marine phytoplankton DMS production (23), volcanic activity, or biological ammonia sources may be rapidly reflected in new particle and eventually CCN concentrations over the Southern Hemisphere. For the precursor gas and environmental conditions representative of our site, ion-induced ternary nucleation rate is sensitive also to ion production rate and cosmic radiation intensity (13). Because galactic cosmic rays are the sole source of ions in the Antarctic lower atmosphere (see the Supplementary Materials), they play a key role in NPF in this region. Our observations on ion-induced nucleation in Antarctica are therefore relevant to the long-standing question of a physical mechanism for solar-climate variability in the pristine preindustrial climate (24). Our study provides a rare insight into aerosol formation in a pristine environment with negligible anthropogenic influence and organic precursor vapors. These measurements are important because they help to reveal the poorly known baseline preindustrial aerosol state from which anthropogenic aerosol radiative forcing is determined (25).

## MATERIALS AND METHODS

Aerosol size distribution was measured using several particle-counting methods. A PSM coupled with a condensation nuclei counter measured 1- to 3-nm ( $\pm 0.2$ -nm) nanoparticles and was calibrated using ammonium sulfate to represent low organic compound conditions in Antarctica. Size distributions of larger ( $\sim 2$ - to 40-nm and 6- to 820-nm) particles were measured by the NAIS and a differential mobility particle sizer (DMPS), respectively. The NAIS was also operated in negative and positive ion modes simultaneously to neutral size distribution measurements. The chemical composition of naturally charged air ions and ion clusters was measured with an API-TOF mass spectrometer, mostly in the negative ion mode. A CI-API-TOF mass spectrometer using nitrate ions for charging was used to measure low-volatile aerosol precursor gases such as sulfuric acid, MSA, iodic acid, and HOMs. Data coverage is presented in table S1, and all instruments and their measurement uncertainties are described, in detail, in the Supplementary Materials.

## SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/4/11/eaat9744/DC1>

Section S1. Field site and instrumentation

Section S2. Methods

Table S1. Data coverage of individual instruments during the FINNARP 2014 campaign.

Table S2. Sulfuric acid concentration, condensation sink, particle growth rates, and particle formation rates for 3-nm ( $J_3$ ) and 1.5-nm ( $J_{1.5}$ ) particles determined for NPF events using different methods.

Fig. S1. Overview of the FINNARP 2014 campaign at Aboa, Antarctica (no flagged data).

Fig. S2. NPF days.

Fig. S3. No NPF days.

Fig. S4. Negative ion composition measured by the API-TOF.

Fig. S5. API-TOF (positive ions) mass defect plot during the observed NPF event on 18 January at Aboa.

Fig. S6. NAIS size distribution of negative (top) and positive (bottom) ions during the NPF event day when chemical composition of ion was measured in the positive polarity (fig. S5).

Fig. S7. Number concentrations of 1.5- to 3-nm particles during 1 week of the measurement period (4 to 10 January 2015).

Fig. S8. The size distribution of 2- to 42-nm particles (top), 0.8- to 42-nm negative (second) and positive (third) ions measured with the NAIS, and the sum of particle concentration measured with the PSM [1.5 to 3 ( $\pm 0.2$ ) nm; bottom] during the measurement campaign.

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**Acknowledgments:** We thank P. P. Aalto, F. Korhonen, E. Siivola, R. D. Kouznetsov, N. Sarnela, V. Hemmälä, and C. Yan for technical assistance; the tofTools team for providing tools for mass spectrometry analysis; and the Finnish Antarctic Research Program (FINNARP) for logistics services. We thank H. Gordon for providing the CLOUD nucleation rate parameterization contours in Fig. 3. **Funding:** This work was partly funded by the Academy of Finland (Centre of Excellence 1118615, projects nos. 251427, 264375, 264390, 272041, 296628, and 306853), the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (GASPARCON grant agreement nos. 714621 and 689443 via project iCUPE, Integrative and Comprehensive Understanding on Polar Environments), and the NordForsk funded Nordic Centre of Excellence CRAICC (Cryosphere-atmosphere interactions in a changing Arctic climate, project no. 26060). V.V. is beneficiary of an AXA Research Fund postdoctoral grant. This work was supported by European Regional Development Fund, project MOBTT42, under Mobilitas Plus programme. **Author contributions:** T.J., M.S., and P.T. collected the data from Aboa. T.J., J.Ko., E.-M.D., H.J., J.Ka., H.E.M., and V.V. analyzed the data and drew the supplementary figures. T.J. drew Figs. 1B and 2. J.Ko. drew Fig. 1 (A and B). V.V. calculated emission sensitivities for air masses arriving to Aboa and is responsible for drawing Fig. 2D. J.Ki. made comparisons to CLOUD experimental data and drew Fig. 3. T.J., M.S., T.P., A.V., D.R.W., and M.K. designed measurements. M.S., T.J., and V.-M.K. wrote the manuscript. All authors commented on the manuscript during the writing process. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** Aboa weather data can be uploaded directly from [www.antarctica.fi/aboa-weather-observations](http://www.antarctica.fi/aboa-weather-observations). Link to the meteorological data files: <http://cdn.fmi.fi/legacy-fmi-fi-content/products/aboa-weather/data>. All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 11 May 2018  
 Accepted 26 October 2018  
 Published 28 November 2018  
 10.1126/sciadv.aat9744

**Citation:** T. Jokinen, M. Sipilä, J. Kontkanen, V. Vakkari, P. Tisler, E.-M. Duplissy, H. Junninen, J. Kangasluoma, H. E. Manninen, T. Petäjä, M. Kulmala, D. R. Worsnop, J. Kirkby, A. Virkkula, V.-M. Kerminen, Ion-induced sulfuric acid–ammonia nucleation drives particle formation in coastal Antarctica. *Sci. Adv.* **4**, eaat9744 (2018).

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*Sci Adv* 4 (11), eaat9744.  
DOI: 10.1126/sciadv.aat9744

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