

Cite as: Bianchi *et al.*, *Science* 10.1126/science.aad5456 (2016).

New particle formation in the free troposphere: A question of chemistry and timing

F. Bianchi,^{1,2,3*} J. Tröstl,¹ H. Junninen,³ C. Frege,¹ S. Henne,⁴ C.R. Hoyle,^{1,5} U. Molteni,¹ E. Herrmann,¹ A. Adamov,³ N. Bukowiecki,¹ X. Chen,³ J. Duplissy,^{3,6} M. Gysel,¹ M. Hutterli,⁷ J. Kangasluoma,³ J. Kontkanen,³ A. Kürten,⁸ H. E. Manninen,³ S. Münch,⁸ O. Peräkylä,³ T. Petäjä,³ L. Rondo,⁸ C. Williamson,^{8,†} E. Weingartner,^{1,‡} J. Curtius,⁸ D. R. Worsnop,^{3,9} M. Kulmala,³ J. Dommen,¹ U. Baltensperger^{1,*}

¹Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, 5232 Villigen, Switzerland. ²Institute for Atmospheric and Climate Science, ETH Zurich, 8092 Zurich, Switzerland. ³Department of Physics, University of Helsinki, 00014 Helsinki, Finland. ⁴Empa, Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland. ⁵WSL (Swiss Federal Institute for Forest, Snow and Landscape Research) Institute for Snow and Avalanche Research SLF, 7260 Davos, Switzerland. ⁶Helsinki Institute of Physics, University of Helsinki, 00014 Helsinki, Finland. ⁷Tofwerk, 3600 Thun, Switzerland. ⁸Institute for Atmospheric and Environmental Sciences, Goethe University Frankfurt, 60438 Frankfurt am Main, Germany. ⁹Aerodyne Research, Billerica, MA 01821, USA.

*Corresponding author. Email: federico.bianchi@psi.ch (F.B.); urs.baltensperger@psi.ch (U.B.)

†Present address: Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309, USA.

‡Present address: Institute for Aerosol and Sensor Technology, University of Applied Sciences (FHNW), 5210 Windisch, Switzerland.

New particle formation (NPF) is the source of over half of the atmosphere's cloud condensation nuclei, thus influencing cloud properties and Earth's energy balance. Unlike in the planetary boundary layer, few observations of NPF in the free troposphere exist. We provide observational evidence that at high altitudes, NPF occurs mainly through condensation of highly oxygenated molecules (HOMs), in addition to taking place through sulfuric acid–ammonia nucleation. Neutral nucleation is more than 10 times faster than ion-induced nucleation, and growth rates are size-dependent. NPF is restricted to a time window of 1 to 2 days after contact of the air masses with the planetary boundary layer; this is related to the time needed for oxidation of organic compounds to form HOMs. These findings require improved NPF parameterization in atmospheric models.

Atmospheric aerosols influence climate through direct interaction with radiation and by acting as cloud condensation nuclei (1, 2). There is considerable uncertainty about what fraction of cloud condensation nuclei is attributable to new particle formation (NPF) (3–5). Studies of NPF in the free troposphere have used ground-based (6–9) and airborne (10) platforms but with limited instrumentation and/or over short time scales. Because of the lack of data at high altitudes, the vast majority of models use free-troposphere NPF schemes in which particle formation rates depend only on the concentration of sulfuric acid, relative humidity, and temperature (11). Recently, comprehensive NPF measurements performed as part of the CLOUD (Cosmics Leaving Outdoor Droplets) project detected ternary nucleation of sulfuric acid with water and oxidized organics (12). Implementation of this NPF scheme in GLOMAP (Global Model of Aerosol Processes) (13) yielded a photochemically and biologically driven seasonal cycle of particle concentrations in the continental boundary layer, comparable to observations (12). Further CLOUD experiments observed NPF without involvement of sulfuric acid, which is expected to be important especially in pristine regions and the preindustrial atmosphere (14). These laboratory and

modeling studies call for field verification.

To chemically and physically characterize the early stage of NPF in the free troposphere, we used a suite of state-of-the-art mass spectrometers and particle counters at the high-altitude research station Jungfraujoch (JFJ), Switzerland [3580 m above sea level (15)]. At this site, NPF occurs on 15 to 20% of days, without apparent seasonal dependence (fig. S9), as shown by long-term observations (16) and dedicated campaigns (17). We report measurements collected over the period of a year, including two intensive 1-month campaigns (table S1).

We identified three typical situations, represented by consecutive example days (days 1 to 3) (Fig. 1); in addition, we show a special case (day 4) where the sulfuric acid concentration was unusually high ($\sim 6 \times 10^6 \text{ cm}^{-3}$). Day 1 (25 February 2014) is an example of one of the many non-event days during sunny conditions. During the afternoon, there is a slight enhancement in the concentration of 5- to 10-nm particles, but the simultaneous increase in larger particles (up to 90 nm) suggests that this enhancement is related to vertical transport of particles formed elsewhere (15). Day 2 (26 February 2014) is typical of days when the JFJ is within clouds, when NPF is suppressed by reduced global radiation

and the high condensation sink of the cloud droplets. Days 3 and 4 (27 February and 2 March 2014) are two examples of NPF days, classified as 1A events (15), where the number concentration of particles larger than 3.2 nm increases strongly from a few hundred to 40,000 cm⁻³.

On most sunny days, the sulfuric acid concentration followed a consistent diurnal cycle, with concentrations <10 cm⁻³ during the night and $\leq 5 \times 10^5$ cm⁻³ during the day (except day 4, which had much higher concentrations). However, no link was found between sulfuric acid and NPF, suggesting that sulfuric acid at these concentrations does not explain NPF at the JFJ (Fig. 1D). Highly oxygenated molecules (HOMs), which we detected with a chemical ionization–atmospheric pressure interface–time of flight mass spectrometer (CI-APi-TOF), were formed on some sunny days (e.g., day 3) but not on others (e.g., day 1) (Fig. 1D). This variability is probably dependent on the presence of organic precursors in the free troposphere. Figure 1E shows the time evolution of several negative ions measured with an APi-TOF: HSO₄⁻, NO₃⁻, the family of clusters containing NH₃ and H₂SO₄, and ions with mass/charge ratios *m/z* > 400 thomsons (Th; 1 Th = 1 Da *e*⁻¹, where *e* is the elementary charge), which are likely to be mainly organic compounds (15). Nucleation nearly exclusively occurred on days when the concentration of organic compounds was high. The nucleation event on day 4 had a somewhat different ion cluster composition; the organic ions were present, but HSO₄⁻ and the H₂SO₄-NH₃ cluster family were of equal magnitude, probably because the H₂SO₄ concentration was very high (Fig. 1). However, throughout the year of APi-TOF measurements, we never observed pure H₂SO₄ clusters with more than four molecules (table S3), confirming the findings of previous studies, which showed that binary H₂SO₄-H₂O nucleation does not explain atmospheric NPF (18, 19).

The role of HOMs is further illustrated in Fig. 2, which shows mass defect plots (20, 21) for negative ions for three of the days depicted in Fig. 1 (fig. S4 shows plots for corresponding neutral clusters). During the sunny day without NPF (day 1), most of the ions observed had *m/z* values <300 Th and were small acid clusters. These ions appear to be spectators (ions that are always present but unlikely to participate in cluster growth, such as nitrate, oxalate, and other organic acids that are too volatile to condense on such small particles). The smaller ions observed on day 3 (Fig. 2B) did not greatly differ from those observed on day 1; however, many ions with *m/z* values >300 Th were also present. The organic contribution is confirmed by the chemical composition of neutral clusters, shown in figs. S4 and S5 and table S2. The most intense organic peaks measured by the APi-TOF overlap with those measured by the CI-APi-TOF. In both cases, we attribute these peaks to HOMs clustered with nitrate (table S2). The difference is that in one case (in

which ions were detected by the APi-TOF), the HOMs were clustered with NO₃⁻ in the ambient atmosphere, whereas neutral HOMs were clustered with NO₃⁻ inside the CI-APi-TOF ion source. Even though the chemical formulae of these HOMs differ from those of HOMs generated by monoterpene oxidation (22–25), they are similar in mass range and O:C ratio. They are therefore expected to have similarly low volatility and nucleating properties. Chemical identification of the negative ions detected on day 3 (Fig. 2 and fig. S5) indicates that the HOMs cluster exclusively with NO₃⁻, except the three most abundant peaks, which also cluster to a minor extent with HSO₄⁻ (peaks 2a, 3a, and 4a in fig. S5). This confirms recent CLOUD findings that sulfuric acid is not important for NPF (14) at this concentration.

On day 4, we detected a distinctive sequence of ions, (H₂SO₄)_{*m*}(NH₃)_{*n*}HSO₄⁻ (where *m* and *n* are integers varying from 3 to 9 and from 1 to 9, respectively), which closely resembles the sequence identified in CLOUD experiments involving purely H₂SO₄-NH₃ nucleation (18, 20, 21). In addition to this sequence, we observed other similar clusters in which the charging ion was IO₃⁻ instead of HSO₄⁻ (pink dots, Fig. 2). However, because these ions were only a minor fraction of all the clusters, and only a single iodate was found, we do not consider iodate to be important for this nucleation event.

On day 3, the total particle formation rate *J* decreased as a result of the coagulation processes that occur with increasing size, with *J*_{1.6} = 51 cm⁻³ s⁻¹ and *J*₂ = 46 cm⁻³ s⁻¹ (where subscripts denote mobility diameter in nanometers) (Fig. 3A). The formation rates of positive and negative ions with a diameter of 1.6 nm, determined from neutral cluster air ion spectrometer (NAIS) ion-mode measurements, were much lower (<1 cm⁻³ s⁻¹) than those of the neutral particles of the same size, suggesting that the neutral process dominated (26) in this nucleation event. CLOUD results for pure sulfuric acid nucleation indicate a *J*_{1.7} below 10⁻⁵ cm⁻³ s⁻¹ (27) at a similar concentration and temperature. There is strong indication of the presence of HOMs in the nucleating clusters but not of ammonia or amines. Because the saturation concentration is expected to decrease substantially with decreasing temperature, we consider this to be in good agreement with the findings of Kirkby *et al.* (14), who reported *J*_{1.7} = 40 cm⁻³ s⁻¹ at [HOM] = 4 × 10⁸ cm⁻³ and temperature *T* = 5°C.

On day 4, the observed *J*_{3.2} of ~4.5 cm⁻³ s⁻¹ at temperatures between -12°C and -15°C was similar to that measured by CLOUD: *J*_{1.7} ~ 4 cm⁻³ s⁻¹ for [H₂SO₄] = 6 × 10⁶ cm⁻³ and [NH₃] = 1 part per billion by volume (ppbv) at *T* = -15°C (18). Because the ammonia concentration during this event at the JFJ is expected to have been lower than 1 ppbv, we hypothesize a synergistic effect of H₂SO₄, NH₃, and nonnegligible concentrations of HOMs. This event was a

special case where the sulfuric acid concentration was extremely high. However, API-TOF measurements show that HOMs were present in the initial clusters in 13 out of 19 nucleation events (type 1A or 1B; table S3). Nucleation thus appears to be influenced by the presence of organic compounds in the majority of cases. The importance of HOMs is further illustrated by the size-dependent growth rates observed during particle formation (Fig. 3), confirming that nano-Köhler growth (3) also applies in free troposphere conditions. On day 3, the growth rate was initially driven by HOMs and continued to increase after the HOM concentration began to decline, probably due to a reduced Kelvin effect at larger particle sizes, enabling the condensation of more volatile (unmeasured) molecules (fig. S8) (28) [as recently found in laboratory experiments (29)]. On day 4, a greater part of the initial growth rate can be explained by sulfuric acid and water under the assumption of condensation at the kinetic limit (fig. S7) (30). After that, the higher growth rate cannot be explained by sulfuric acid alone, which is again probably indicative of condensation of more volatile (unmeasured) molecules (29) on the newly formed particles, showing that this process is also not entirely inorganic.

An important question is where the condensable vapors or their precursors originate. We used the Lagrangian particle dispersion model FLEXPART in time-inverse mode and compared air mass origins of all the major events (type 1A and 1B) with those of typical non-event days during the same period (15). Increases in simulated carbon monoxide concentration and the strength of the source-receptor relationship, indicative of influence by the planetary boundary layer, were evident in individual backward simulations (Fig. 4 and fig. S10). This suggests an anthropogenic source of the HOM precursors but does not preclude a biogenic source. For all simulated cases, the small increase in CO within 6 hours before air mass arrival suggests no substantive influence from local emissions during this period. Air masses experienced enhanced uptake of CO and also an increase in the strength of the source-receptor relationship (fig. S11) 12 to 40 hours before type 1A events were detected at the JFJ, caused by contact with polluted boundary layer air. Similarly, air masses connected to type 1B events experienced increased CO uptake, though somewhat farther upwind, between 12 and 72 hours before arrival at the JFJ, with a maximum uptake at 48 hours. In contrast, for non-event days, CO uptake was considerably below that during nucleation events. This indicates that one requirement for observing NPF at the JFJ is nonlocal contact (fig. S12) with the planetary boundary layer and, hence, the uptake of emissions hours before arrival at the JFJ, allowing a sufficiently long processing time in the free troposphere. An optimal transport time from the planetary boundary layer to foster

nucleation appears to be around 1 day, whereas longer transport times result in less clear nucleation events, due to ongoing oxidation and dilution of the precursor gases.

Combining in situ observations and modeling results, we thus find that NPF in the free troposphere depends on the availability of highly oxidized organic species, providing confirmation for NPF pathways observed in recent laboratory experiments. The availability of these highly oxidized organic species in turn depends on previous surface contact of the air mass and appropriate time to process the precursors from the boundary layer on their way up. In short, chemistry and timing play the main roles. To properly represent nucleation in the free troposphere, future atmospheric models should take these factors into account.

REFERENCES AND NOTES

1. T. L. Anderson, R. J. Charlson, N. Bellouin, O. Boucher, M. Chin, S. A. Christopher, J. Haywood, Y. J. Kaufman, S. Kinne, J. A. Ogren, L. A. Remer, T. Takemura, D. Tanré, O. Torres, C. R. Trepte, B. A. Wielicki, D. M. Winker, H. Yu, An "A-Train" strategy for quantifying direct climate forcing by anthropogenic aerosols. *Bull. Am. Meteorol. Soc.* **86**, 1795–1809 (2005). doi:10.1175/BAMS-86-12-1795
2. R. J. Charlson, S. E. Schwartz, J. M. Hales, R. D. Cess, J. A. Coakley Jr., J. E. Hansen, D. J. Hofmann, Climate forcing by anthropogenic aerosols. *Science* **255**, 423–430 (1992). Medline doi:10.1126/science.255.5043.423
3. M. Kulmala, H. Vehkamäki, T. Petäjä, M. Dal Maso, A. Lauri, V.-M. Kerminen, W. Birmili, P. H. McMurry, Formation and growth rates of ultrafine atmospheric particles: A review of observations. *J. Aerosol Sci.* **35**, 143–176 (2004). doi:10.1016/j.jaerosci.2003.10.003
4. J. Merikanto, D. V. Spracklen, G. W. Mann, S. J. Pickering, K. S. Carslaw, Impact of nucleation on global CCN. *Atmos. Chem. Phys.* **9**, 8601–8616 (2009). doi:10.5194/acp-9-8601-2009
5. R. Zhang, A. Khalizov, L. Wang, M. Hu, W. Xu, Nucleation and growth of nanoparticles in the atmosphere. *Chem. Rev.* **112**, 1957–2011 (2012). Medline doi:10.1021/cr2001756
6. S. Rodríguez, Y. González, E. Cuevas, R. Ramos, P. M. Romero, J. Abreu-Afonso, A. Redondas, Atmospheric nanoparticle observations in the low free troposphere during upward orographic flows at Izaña Mountain Observatory. *Atmos. Chem. Phys.* **9**, 6319–6335 (2009). doi:10.5194/acp-9-6319-2009
7. C. Rose, K. Sellegrí, F. Velarde, I. Moreno, M. Ramonet, K. Weinhold, R. Krejci, P. Ginot, M. Andrade, A. Wiedensohler, P. Laj, Frequent nucleation events at the high altitude station of Chacaltaya (5240 m a.s.l.), Bolivia. *Atmos. Environ.* **102**, 18–29 (2015). doi:10.1016/j.atmosenv.2014.11.015
8. H. Venzac, K. Sellegrí, P. Laj, P. Villani, P. Bonasoni, A. Marinoni, P. Cristofanelli, F. Calzolari, S. Fuzzi, S. Decesari, M. C. Facchini, E. Vuillermoz, G. P. Verza, High frequency new particle formation in the Himalayas. *Proc. Natl. Acad. Sci. U.S.A.* **105**, 15666–15671 (2008). Medline doi:10.1073/pnas.0801355105
9. F. Q. Yu, A. G. Hallar, Difference in particle formation at a mountaintop location during spring and summer: Implications for the role of sulfuric acid and organics in nucleation. *J. Geophys. Res. Atmos.* **119**, 12246–12255 (2014). doi:10.1002/2014JD022136
10. S. Mirme, A. Mirme, A. Minikin, A. Petzold, U. Hörrak, V.-M. Kerminen, M. Kulmala, Atmospheric sub-3 nm particles at high altitudes. *Atmos. Chem. Phys.* **10**, 437–451 (2010). doi:10.5194/acp-10-437-2010
11. M. Kulmala, A. Laaksonen, L. Pirjola, Parameterizations for sulfuric acid/water nucleation rates. *J. Geophys. Res. Atmos.* **103**, 8301–8307 (1998). doi:10.1029/97JD03718
12. F. Riccobono, S. Schobesberger, C. E. Scott, J. Dommen, I. K. Ortega, L. Rondo, J. Almeida, A. Amorim, F. Bianchi, M. Breitenlechner, A. David, A. Downard, E. M. Dunne, J. Duplissy, S. Ehrhart, R. C. Flagan, A. Franchin, A. Hansel, H. Junninen, M. Kajos, H. Keskinen, A. Kupc, A. Kürten, A. N. Kvashin, A. Laaksonen, K. Lehtipalo, V. Makhmutov, S. Mathot, T. Nieminen, A. Onnela, T. Petäjä, A. P. Praplan, F. D. Santos, S. Schallhart, J. H. Seinfeld, M. Sipilä, D. V. Spracklen, Y.

- Stozhkov, F. Stratmann, A. Tomé, G. Tsagkogeorgas, P. Vaattovaara, Y. Viisanen, A. Vrtala, P. E. Wagner, E. Weingartner, H. Wex, D. Wimmer, K. S. Carslaw, J. Curtius, N. M. Donahue, J. Kirkby, M. Kulmala, D. R. Worsnop, U. Baltensperger, Oxidation products of biogenic emissions contribute to nucleation of atmospheric particles. *Science* **344**, 717–721 (2014). [Medline doi:10.1126/science.1243527](https://doi.org/10.1126/science.1243527)
13. G. W. Mann, K. S. Carslaw, D. V. Spracklen, D. A. Ridley, P. T. Manktelow, M. P. Chipperfield, S. J. Pickering, C. E. Johnson, Description and evaluation of GLOMAP-mode: A modal global aerosol microphysics model for the UKCA composition-climate model. *Geosci. Model Dev.* **3**, 519–551 (2010). [doi:10.5194/gmd-3-519-2010](https://doi.org/10.5194/gmd-3-519-2010)
14. J. Kirkby, J. Duplissy, K. Sengupta, C. Frege, H. Gordon, C. Williamson, M. Heinritzi, M. Simon, C. Yan, J. Almeida, J. Tröstl, T. Nieminen, I. K. Ortega, R. Wagner, A. Adamov, A. Amorim, A.-K. Bernhammer, F. Bianchi, M. Breitenlechner, S. Brilke, X. Chen, J. Craven, A. Dias, S. Ehrhart, R. C. Flagan, A. Franchin, C. Fuchs, R. Guida, J. Hakala, C. R. Hoyle, T. Jokinen, H. Junninen, J. Kangasluoma, J. Kim, M. Krapf, A. Kürten, A. Laaksonen, K. Lehtipalo, V. Makhmutov, S. Mathot, U. Molteni, A. Onnela, O. Peräkylä, F. Piel, T. Petäjä, A. P. Praplan, K. Pringle, A. Rap, N. A. D. Richards, I. Riipinen, M. P. Rissanen, L. Rondo, N. Sarnela, S. Schobesberger, C. E. Scott, J. H. Seinfeld, M. Sipilä, G. Steiner, Y. Stozhkov, F. Stratmann, A. Tomé, A. Virtanen, A. L. Vogel, A. Wagner, P. E. Wagner, E. Weingartner, D. Wimmer, P. M. Winkler, P. Ye, X. Zhang, A. Hansel, J. Dommen, N. M. Donahue, D. R. Worsnop, U. Baltensperger, M. Kulmala, K. S. Carslaw, J. Curtius, Ion-induced nucleation of pure biogenic particles. *Nature* **10.1038/nature17953** (2016).
15. Materials and methods are available as supplementary materials on *Science* Online.
16. E. Herrmann, E. Weingartner, S. Henne, L. Vuilleumier, N. Bukowiecki, M. Steinbacher, F. Conen, M. Collaud Coen, E. Hammer, Z. Jurányi, U. Baltensperger, M. Gysel, Analysis of long-term aerosol size distribution data from Jungfraujoch with emphasis on free tropospheric conditions, cloud influence, and air mass transport. *J. Geophys. Res. Atmos.* **120**, 9459–9480 (2015). [doi:10.1002/2015JD023660](https://doi.org/10.1002/2015JD023660)
17. J. Boulon, K. Sellegri, H. Venzac, D. Picard, E. Weingartner, G. Wehrle, M. Collaud Coen, R. Bütkofer, E. Flückiger, U. Baltensperger, P. Laj, New particle formation and ultrafine charged aerosol climatology at a high altitude site in the Alps (Jungfraujoch, 3580 m a.s.l., Switzerland). *Atmos. Chem. Phys.* **10**, 9333–9349 (2010). [doi:10.5194/acp-10-9333-2010](https://doi.org/10.5194/acp-10-9333-2010)
18. J. Kirkby, J. Curtius, J. Almeida, E. Dunne, J. Duplissy, S. Ehrhart, A. Franchin, S. Gagné, L. Ickes, A. Kürten, A. Kupc, A. Metzger, F. Riccobono, L. Rondo, S. Schobesberger, G. Tsagkogeorgas, D. Wimmer, A. Amorim, F. Bianchi, M. Breitenlechner, A. David, J. Dommen, A. Downard, M. Ehn, R. C. Flagan, S. Haider, A. Hansel, D. Hauser, W. Jud, H. Junninen, F. Kreissl, A. Kvashin, A. Laaksonen, K. Lehtipalo, J. Lima, E. R. Lovejoy, V. Makhmutov, S. Mathot, J. Mikkila, P. Minginette, S. Mogo, T. Nieminen, A. Onnela, P. Pereira, T. Petäjä, R. Schnitzhofer, J. H. Seinfeld, M. Sipilä, Y. Stozhkov, F. Stratmann, A. Tomé, J. Vanhanen, Y. Viisanen, A. Vrtala, P. E. Wagner, H. Walther, E. Weingartner, H. Wex, P. M. Winkler, K. S. Carslaw, D. R. Worsnop, U. Baltensperger, M. Kulmala, Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation. *Nature* **476**, 429–433 (2011). [Medline doi:10.1038/nature10343](https://doi.org/10.1038/nature10343)
19. F. L. Eisele, E. R. Lovejoy, E. Kosciuch, K. F. Moore, R. L. Mauldin III, J. N. Smith, P. H. McMurry, K. Iida, Negative atmospheric ions and their potential role in ion-induced nucleation. *J. Geophys. Res. Atmos.* **111**, D04305 (2006). [doi:10.1029/2005JD006568](https://doi.org/10.1029/2005JD006568)
20. F. Bianchi, A. P. Praplan, N. Sarnela, J. Dommen, A. Kürten, I. K. Ortega, S. Schobesberger, H. Junninen, M. Simon, J. Tröstl, T. Jokinen, M. Sipilä, A. Adamov, A. Amorim, J. Almeida, M. Breitenlechner, J. Duplissy, S. Ehrhart, R. C. Flagan, A. Franchin, J. Hakala, A. Hansel, M. Heinritzi, J. Kangasluoma, H. Keskinen, J. Kim, J. Kirkby, A. Laaksonen, M. J. Lawler, K. Lehtipalo, M. Leiminger, V. Makhmutov, S. Mathot, A. Onnela, T. Petäjä, F. Riccobono, M. P. Rissanen, L. Rondo, A. Tomé, A. Virtanen, Y. Viisanen, C. Williamson, D. Wimmer, P. M. Winkler, P. Ye, J. Curtius, M. Kulmala, D. R. Worsnop, N. M. Donahue, U. Baltensperger, Insight into acid-base nucleation experiments by comparison of the chemical composition of positive, negative, and neutral clusters. *Environ. Sci. Technol.* **48**, 13675–13684 (2014). [Medline doi:10.1021/es502380b](https://doi.org/10.1021/es502380b)
21. S. Schobesberger, H. Junninen, F. Bianchi, G. Lönn, M. Ehn, K. Lehtipalo, J. Dommen, S. Ehrhart, I. K. Ortega, A. Franchin, T. Nieminen, F. Riccobono, M. Hutterli, J. Duplissy, J. Almeida, A. Amorim, M. Breitenlechner, A. J. Downard, E. M. Dunne, R. C. Flagan, M. Kajos, H. Keskinen, J. Kirkby, A. Kupc, A. Kürten, T. Kurtén, A. Laaksonen, S. Mathot, A. Onnela, A. P. Praplan, L. Rondo, F. D. Santos, S. Schallhart, R. Schnitzhofer, M. Sipilä, A. Tomé, G. Tsagkogeorgas, H. Vehkämäki, D. Wimmer, U. Baltensperger, K. S. Carslaw, J. Curtius, A. Hansel, T. Petäjä, M. Kulmala, N. M. Donahue, D. R. Worsnop, Molecular understanding of atmospheric particle formation from sulfuric acid and large oxidized organic molecules. *Proc. Natl. Acad. Sci. U.S.A.* **110**, 17223–17228 (2013). [Medline doi:10.1073/pnas.1306973110](https://doi.org/10.1073/pnas.1306973110)
22. M. Ehn, J. A. Thornton, E. Kleist, M. Sipilä, H. Junninen, I. Pullinen, M. Springer, F. Rubach, R. Tillmann, B. Lee, F. Lopez-Hilfiker, S. Andres, I. H. Acir, M. Rissanen, T. Jokinen, S. Schobesberger, J. Kangasluoma, J. Kontkanen, T. Nieminen, T. Kurtén, L. B. Nielsen, S. Jørgensen, H. G. Kjaergaard, M. Canagaratna, M. D. Maso, T. Berndt, T. Petäjä, A. Wahner, V. M. Kerminen, M. Kulmala, D. R. Worsnop, J. Wildt, T. F. Mentel, A large source of low-volatility secondary organic aerosol. *Nature* **506**, 476–479 (2014). [Medline doi:10.1038/nature13032](https://doi.org/10.1038/nature13032)
23. T. Jokinen, T. Berndt, R. Makkonen, V. M. Kerminen, H. Junninen, P. Paasonen, F. Stratmann, H. Herrmann, A. B. Guenther, D. R. Worsnop, M. Kulmala, M. Ehn, M. Sipilä, Production of extremely low volatile organic compounds from biogenic emissions: Measured yields and atmospheric implications. *Proc. Natl. Acad. Sci. U.S.A.* **112**, 7123–7128 (2015). [Medline doi:10.1073/pnas.1423977112](https://doi.org/10.1073/pnas.1423977112)
24. T. F. Mentel, M. Springer, M. Ehn, E. Kleist, I. Pullinen, T. Kurtén, M. Rissanen, A. Wahner, J. Wildt, Formation of highly oxidized multifunctional compounds: Autoxidation of peroxy radicals formed in the ozonolysis of alkenes – deduced from structure–product relationships. *Atmos. Chem. Phys.* **15**, 6745–6765 (2015). [doi:10.5194/acp-15-6745-2015](https://doi.org/10.5194/acp-15-6745-2015)
25. M. P. Rissanen, T. Kurtén, M. Sipilä, J. A. Thornton, J. Kangasluoma, N. Sarnela, H. Junninen, S. Jørgensen, S. Schallhart, M. K. Kajos, R. Taipale, M. Springer, T. F. Mentel, T. Ruuskanen, T. Petäjä, D. R. Worsnop, H. G. Kjaergaard, M. Ehn, The formation of highly oxidized multifunctional products in the ozonolysis of cyclohexene. *J. Am. Chem. Soc.* **136**, 15596–15606 (2014). [Medline doi:10.1021/ja507146s](https://doi.org/10.1021/ja507146s)
26. C. Rose, K. Sellegri, E. Asmi, M. Hervo, E. Freney, A. Colomb, H. Junninen, J. Duplissy, M. Sipilä, J. Kontkanen, K. Lehtipalo, M. Kulmala, Major contribution of neutral clusters to new particle formation at the interface between the boundary layer and the free troposphere. *Atmos. Chem. Phys.* **15**, 3413–3428 (2015). [doi:10.5194/acp-15-3413-2015](https://doi.org/10.5194/acp-15-3413-2015)
27. J. Duplissy, J. Merikanto, A. Franchin, G. Tsagkogeorgas, J. Kangasluoma, D. Wimmer, H. Vuollekoski, S. Schobesberger, K. Lehtipalo, R. C. Flagan, D. Brus, N. M. Donahue, H. Vehkämäki, J. Almeida, A. Amorim, P. Barmet, F. Bianchi, M. Breitenlechner, E. M. Dunne, R. Guida, H. Henschel, H. Junninen, J. Kirkby, A. Kürten, A. Kupc, A. Määttänen, V. Makhmutov, S. Mathot, T. Nieminen, A. Onnela, A. P. Praplan, F. Riccobono, L. Rondo, G. Steiner, A. Tome, H. Walther, U. Baltensperger, K. S. Carslaw, J. Dommen, A. Hansel, T. Petäjä, M. Sipilä, F. Stratmann, A. Vrtala, P. E. Wagner, D. R. Worsnop, J. Curtius, M. Kulmala, Effect of ions on sulfuric acid–water binary particle formation: 2. Experimental data and comparison with QC-normalized classical nucleation theory. *J. Geophys. Res. Atmos.* **121**, 1752–1775 (2016). [doi:10.1002/2015JD023539](https://doi.org/10.1002/2015JD023539)
28. M. Kulmala, J. Kontkanen, H. Junninen, K. Lehtipalo, H. E. Manninen, T. Nieminen, T. Petäjä, M. Sipilä, S. Schobesberger, P. Rantala, A. Franchin, T. Jokinen, E. Järvinen, M. Äijälä, J. Kangasluoma, J. Hakala, P. P. Aalto, P. Paasonen, J. Mikkila, J. Vanhanen, J. Aalto, H. Hakola, U. Makkonen, T. Ruuskanen, R. L. Mauldin III, J. Duplissy, H. Vehkämäki, J. Bäck, A. Kortelainen, I. Riipinen, T. Kurtén, M. V. Johnston, J. N. Smith, M. Ehn, T. F. Mentel, K. E. Lehtinen, A. Laaksonen, V. M. Kerminen, D. R. Worsnop, Direct observations of atmospheric aerosol nucleation. *Science* **339**, 943–946 (2013). [Medline doi:10.1126/science.1227385](https://doi.org/10.1126/science.1227385)
29. J. Tröstl, W. K. Chuang, H. Gordon, M. Heinritzi, C. Yan, U. Molteni, L. Ahlm, C. Frege, F. Bianchi, R. Wagner, M. Simon, K. Lehtipalo, C. Williamson, J. S. Craven, J. Duplissy, A. Adamov, J. Almeida, A.-K. Bernhammer, M. Breitenlechner, S. Brilke, A. Dias, S. Ehrhart, R. C. Flagan, A. Franchin, C. Fuchs, R. Guida, M. Gysel, A. Hansel, C. R. Hoyle, T. Jokinen, H. Junninen, J. Kangasluoma, H. Keskinen, J. Kim, M. Krapf, A. Kürten, A. Laaksonen, M. Lawler, M. Leiminger, S. Mathot, O.

- Möhler, T. Nieminen, A. Onnela, T. Petäjä, F. M. Piel, P. Miettinen, M. P. Rissanen, L. Rondo, N. Sarnela, S. Schobesberger, K. Sengupta, M. Sipilä, J. N. Smith, G. Steiner, A. Torné, A. Virtanen, A. C. Wagner, E. Weingartner, D. Wimmer, P. M. Winkler, P. Ye, K. S. Carslaw, J. Curtius, J. Dommen, J. Kirkby, M. Kulmala, I. Riipinen, D. R. Worsnop, N. M. Donahue, U. Baltensperger, The role of low-volatility organic compounds in initial particle growth in the atmosphere. *Nature* 10.1038/nature18271 (2016).
30. T. Nieminen, K. E. J. Lehtinen, M. Kulmala, Sub-10 nm particle growth by vapor condensation – effects of vapor molecule size and particle thermal speed. *Atmos. Chem. Phys.* **10**, 9773–9779 (2010). doi:10.5194/acp-10-9773-2010
31. U. Baltensperger, H. W. Gäggeler, D. T. Jost, M. Lugauer, M. Schwikowski, E. Weingartner, P. Seibert, Aerosol climatology at the high-alpine site Jungfraujoch, Switzerland. *J. Geophys. Res. Atmos.* **102**, 19707–19715 (1997). doi:10.1029/97JD00928
32. E. Weingartner, S. Nyeki, U. Baltensperger, Seasonal and diurnal variation of aerosol size distributions ($10 < D < 750$ nm) at a high-alpine site (Jungfraujoch 3580 m asl). *J. Geophys. Res. Atmos.* **104**, 26809–26820 (1999). doi:10.1029/1999JD900170
33. N. Bukowiecki, E. Weingartner, M. Gysel, M. C. Coen, P. Zieger, E. Herrmann, M. Steinbacher, H. W. Gäggeler, U. Baltensperger, A review of more than 20 years of aerosol observation at the high altitude research station Jungfraujoch, Switzerland (3580 m asl). *Aerosol Air Qual. Res.* **16**, 764–788 (2016). doi:10.4209/aaqr.2015.05.0305
34. J. Vanhanen, J. Mikkilä, K. Lehtipalo, M. Sipilä, H. E. Manninen, E. Siivola, T. Petäjä, M. Kulmala, Particle size magnifier for nano-CN detection. *Aerosol Sci. Technol.* **45**, 533–542 (2011). doi:10.1080/02786826.2010.547889
35. K. Lehtipalo, M. Kulmala, M. Sipilä, T. Petäjä, M. Vana, D. Ceburnis, R. Dupuy, C. O'Dowd, Nanoparticles in boreal forest and coastal environment: A comparison of observations and implications of the nucleation mechanism. *Boreal Environ. Res.* **19**, 215–236 (2014).
36. S. C. Wang, R. C. Flagan, Scanning electrical mobility spectrometer. *Aerosol Sci. Technol.* **13**, 230–240 (1990). doi:10.1080/02786829008959441
37. E. O. Knutson, K. T. Whibey, Aerosol classification by electric mobility: Apparatus, theory, and applications. *J. Aerosol Sci.* **6**, 443–451 (1975). doi:10.1016/0021-8502(75)90060-9
38. S. Mirme, A. Mirme, The mathematical principles and design of the NAIS – a spectrometer for the measurement of cluster ion and nanometer aerosol size distributions. *Atmos. Meas. Tech.* **6**, 1061–1071 (2013). doi:10.5194/amt-6-1061-2013
39. N. Hyttinen, O. Kupiainen-Määttä, M. P. Rissanen, M. Muuronen, M. Ehn, T. Kurtén, Modeling the charging of highly oxidized cyclohexene ozonolysis products using nitrate-based chemical ionization. *J. Phys. Chem. A* **119**, 6339–6345 (2015). Medline doi:10.1021/acs.jpca.5b01818
40. T. Berndt, S. Richters, R. Kaethner, J. Voigtländer, F. Stratmann, M. Sipilä, M. Kulmala, H. Herrmann, Gas-phase ozonolysis of cycloalkenes: Formation of highly oxidized RO₂ radicals and their reactions with NO, NO₂, SO₂, and other RO₂ radicals. *J. Phys. Chem. A* **119**, 10336–10348 (2015). Medline doi:10.1021/acs.jpca.5b07295
41. A. Kürten, L. Rondo, S. Ehrhart, J. Curtius, Calibration of a chemical ionization mass spectrometer for the measurement of gaseous sulfuric acid. *J. Phys. Chem. A* **116**, 6375–6386 (2012). Medline doi:10.1021/jp212123n
42. R. Fröhlich, M. J. Cubison, J. G. Slowik, N. Bukowiecki, F. Canonaco, P. L. Croteau, M. Gysel, S. Henne, E. Herrmann, J. T. Jayne, M. Steinbacher, D. R. Worsnop, U. Baltensperger, A. S. H. Prévôt, Fourteen months of on-line measurements of the non-refractory submicron aerosol at the Jungfraujoch (3580 m a.s.l.) – chemical composition, origins and organic aerosol sources. *Atmos. Chem. Phys.* **15**, 11373–11398 (2015). doi:10.5194/acp-15-11373-2015
43. M. Kulmala, T. Petäjä, T. Nieminen, M. Sipilä, H. E. Manninen, K. Lehtipalo, M. Dal Maso, P. P. Aalto, H. Junninen, P. Paasonen, I. Riipinen, K. E. Lehtinen, A. Laaksonen, V. M. Kerminen, Measurement of the nucleation of atmospheric aerosol particles. *Nat. Protoc.* **7**, 1651–1667 (2012). Medline doi:10.1038/nprot.2012.091
44. J. H. Seinfeld, S. N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change* (Wiley, ed. 2, 2006).
45. H. E. Manninen, T. Petäjä, E. Asmi, I. Riipinen, T. Nieminen, J. Mikkilä, U. Hörark, A. Mirme, S. Mirme, L. Laakso, V.-M. Kerminen, M. Kulmala, Long-term field measurements of charged and neutral clusters using Neutral cluster and Air Ion Spectrometer (NAIS). *Boreal Environ. Res.* **14**, 591–605 (2009).
46. A. Hirsikko, T. Nieminen, S. Gagné, K. Lehtipalo, H. E. Manninen, M. Ehn, U. Hörark, V.-M. Kerminen, L. Laakso, P. H. McMurry, A. Mirme, S. Mirme, T. Petäjä, H. Tammet, V. Vakkari, M. Vana, M. Kulmala, Atmospheric ions and nucleation: A review of observations. *Atmos. Chem. Phys.* **11**, 767–798 (2011). doi:10.5194/acp-11-767-2011
47. K. E. J. Lehtinen, M. Kulmala, A model for particle formation and growth in the atmosphere with molecular resolution in size. *Atmos. Chem. Phys.* **3**, 251–257 (2003). doi:10.5194/acp-3-251-2003
48. N. A. Fuchs, A. G. Sutugin, *Highly Dispersed Aerosols* (Ann Arbor Science Publishers, 1970).
49. P. A. Baron, K. Willeke, *Aerosol Measurement: Principles, Techniques, and Applications* (Wiley-Interscience, 2001).
50. A. Stohl, C. Forster, A. Frank, P. Seibert, G. Wotawa, Technical note: The Lagrangian particle dispersion model FLEXPART version 6.2. *Atmos. Chem. Phys.* **5**, 2461–2474 (2005). doi:10.5194/acp-5-2461-2005
51. P. Seibert, A. Frank, Source-receptor matrix calculation with a Lagrangian particle dispersion model in backward mode. *Atmos. Chem. Phys.* **4**, 51–63 (2004). doi:10.5194/acp-4-51-2004
52. D. Brunner, S. Henne, C. A. Keller, M. K. Vollmer, S. Reimann, B. Buchmann, in *Lagrangian Modeling of the Atmosphere*, J. Lin, D. Brunner, C. Gerbig, A. Stohl, A. Luhar, P. Webley, Eds. (Geophysical Monograph Series vol. 200, American Geophysical Union, 2012), pp. 207–221.
53. C. A. Keller, D. Brunner, S. Henne, M. K. Vollmer, S. O'Doherty, S. Reimann, Evidence for under-reported western European emissions of the potent greenhouse gas HFC-23. *Geophys. Res. Lett.* **38**, L15808 (2011).
54. M. I. García, S. Rodriguez, Y. Gonzalez, R. D. Garcia, Climatology of new particle formation at Izaña mountain GAW observatory in the subtropical North Atlantic. *Atmos. Chem. Phys.* **14**, 3865–3881 (2014). doi:10.5194/acp-14-3865-2014
55. E. Järvinen, A. Virkkula, T. Nieminen, P. P. Aalto, E. Asmi, C. Lanconelli, M. Busetto, A. Lupi, R. Schioppo, V. Vitale, M. Mazzola, T. Petäjä, V.-M. Kerminen, M. Kulmala, Seasonal cycle and modal structure of particle number size distribution at Dome C, Antarctica. *Atmos. Chem. Phys.* **13**, 7473–7487 (2013). doi:10.5194/acp-13-7473-2013
56. K. Neitola, E. Asmi, M. Komppula, A.-P. Hyvärinen, T. Raatikainen, T. S. Panwar, V. P. Sharma, H. Lihavainen, New particle formation infrequently observed in Himalayan foothills – why? *Atmos. Chem. Phys.* **11**, 8447–8458 (2011). doi:10.5194/acp-11-8447-2011
57. J. Boulon, K. Sellegrí, M. Hervo, D. Picard, J.-M. Pichon, P. Fréville, P. Laj, Investigation of nucleation events vertical extent: A long term study at two different altitude sites. *Atmos. Chem. Phys.* **11**, 5625–5639 (2011). doi:10.5194/acp-11-5625-2011
58. A. G. Hallar, D. H. Lowenthal, G. Chirokova, R. D. Borys, C. Wiedinmyer, Persistent daily new particle formation at a mountain-top location. *Atmos. Environ.* **45**, 4111–4115 (2011). doi:10.1016/j.atmosenv.2011.04.044

ACKNOWLEDGMENTS

We thank the International Foundation High Altitude Research Stations Jungfraujoch and Gornergrat for the opportunity to perform experiments at the Jungfraujoch and especially the research station's custodians J. and M. Fischer and M. and U. Otz for their support and hospitality. This work was supported by the Swiss National Science Foundation (grant nos. 200020_135307, 20020_152907, 206021_144947, and 200021_140663), MeteoSwiss in the framework of the Global Atmosphere Watch program, and the EC FP7 (European Commission Seventh Framework Programme for Research and Technological Development) project ACTRIS (Aerosols, Clouds, and Trace Gases Research Infrastructure Network) (grant agreement no. 262254). Funding was also received from the Academy of Finland Centre of Excellence (grant nos. 272041 and 1118615), the EC FP7 Marie Curie Initial Training Network (CLOUD-TRAIN, grant no. 316662), the German Federal Ministry of Education and Research (project no. 01LK1222A), the EC FP7 project BACCHUS (Impact of Biogenic Versus Anthropogenic Emissions on Clouds and Climate: Towards a Holistic Understanding; grant agreement no. 603445), and the European Research

Council (grant no. 615922-BLACARAT). We thank the tofTools team for providing tools for mass spectrometry analysis. The authors declare no competing financial interests.

SUPPLEMENTARY MATERIALS

www.sciencemag.org/cgi/content/full/science.aad5456/DC1

Materials and Methods

Figs. S1 to S12

Tables S1 to S4

References (31–58)

4 October 2015; accepted 29 March 2016

Published online 25 May 2016

10.1126/science.aad5456

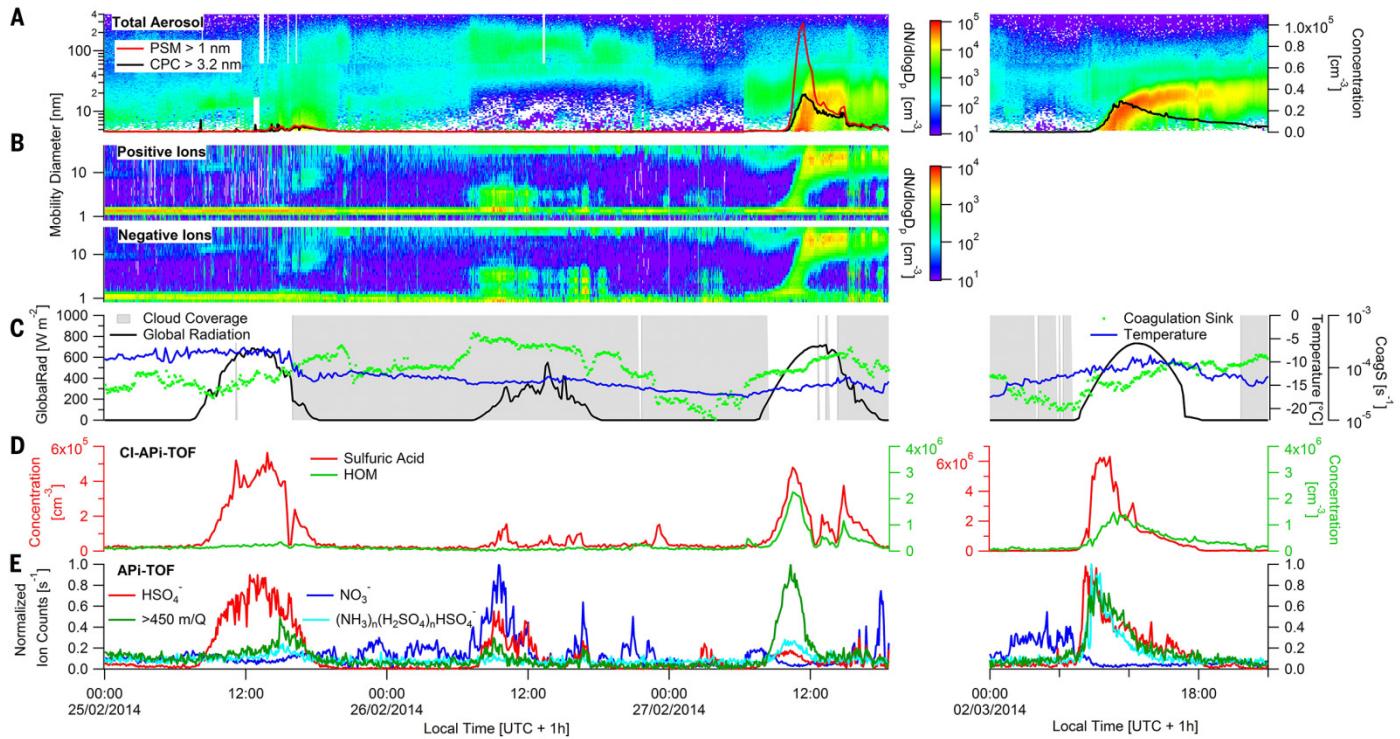


Fig. 1. Four representative situations observed at the JFJ. Shown are data from a sunny day with no nucleation (25 February, day 1), a cloudy day (26 February, day 2), a nucleation day with HOMs (27 February, day 3); and a nucleation day with H_2SO_4 , NH_3 , and HOMs (2 March, day 4) (h, hours). (A) Particle size distribution ($dN/d\log D_p$), measured with a nano-SMPS (scanning mobility particle sizer), and particle number concentration above 1 and 3.2 nm, measured with a particle size magnifier (PSM) and a condensation particle counter (CPC), respectively. (B) Size distributions of the positive and negative ions measured by the NAIS. (C) Global radiation, temperature, coagulation sink, and cloud coverage. (D) Concentrations of sulfuric acid (red) and HOMs (green) measured with the CI-API-TOF. A different axis is used for sulfuric acid in the right panel. (E) Measurements of specific ions with the API-TOF (HSO_4^- in red, NO_3^- in blue, and the sum of ions with $m/z > 400$ Th in green). The clusters containing sulfuric acid and ammonia are shown by the light blue line.

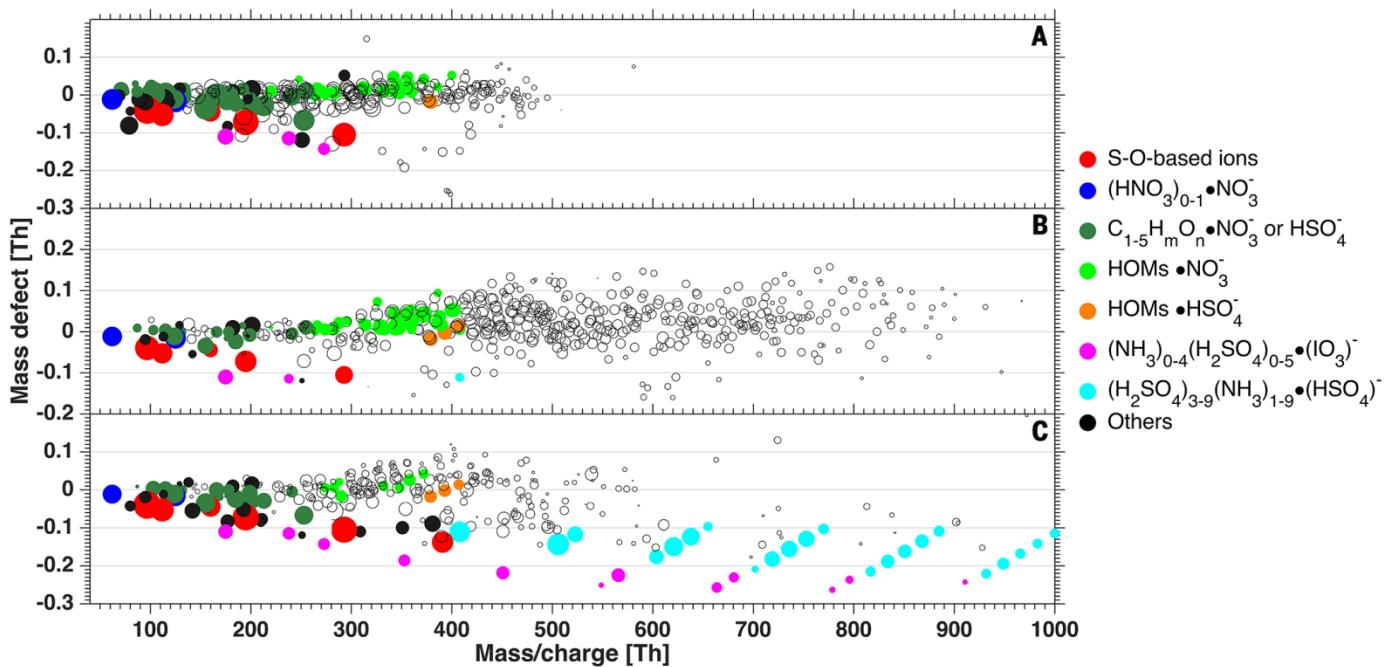


Fig. 2. Mass defect plots (negative ions). (A) Measurements from day 1, (B) day 3, and (C) day 4. The abscissa shows the mass/charge ratio and the ordinate shows the mass defect, which is the difference between the nominal (integer) mass and the exact mass. Colors relate to pure sulfuric acid clusters (red), nitrate (blue), small organic compounds alone or clustered with NO_3^- or HSO_4^- (dark green), HOMs clustered with NO_3^- (light green), HOMs clustered with HSO_4^- (orange), $\text{H}_2\text{SO}_4\text{-NH}_3\text{-HIO}_3$ (violet), and $\text{H}_2\text{SO}_4\text{-NH}_3$ clusters (light blue). Open circles represent unidentified peaks. The marker size is proportional to the logarithm of the count rate. The mass spectra for the same events are shown in fig. S3.

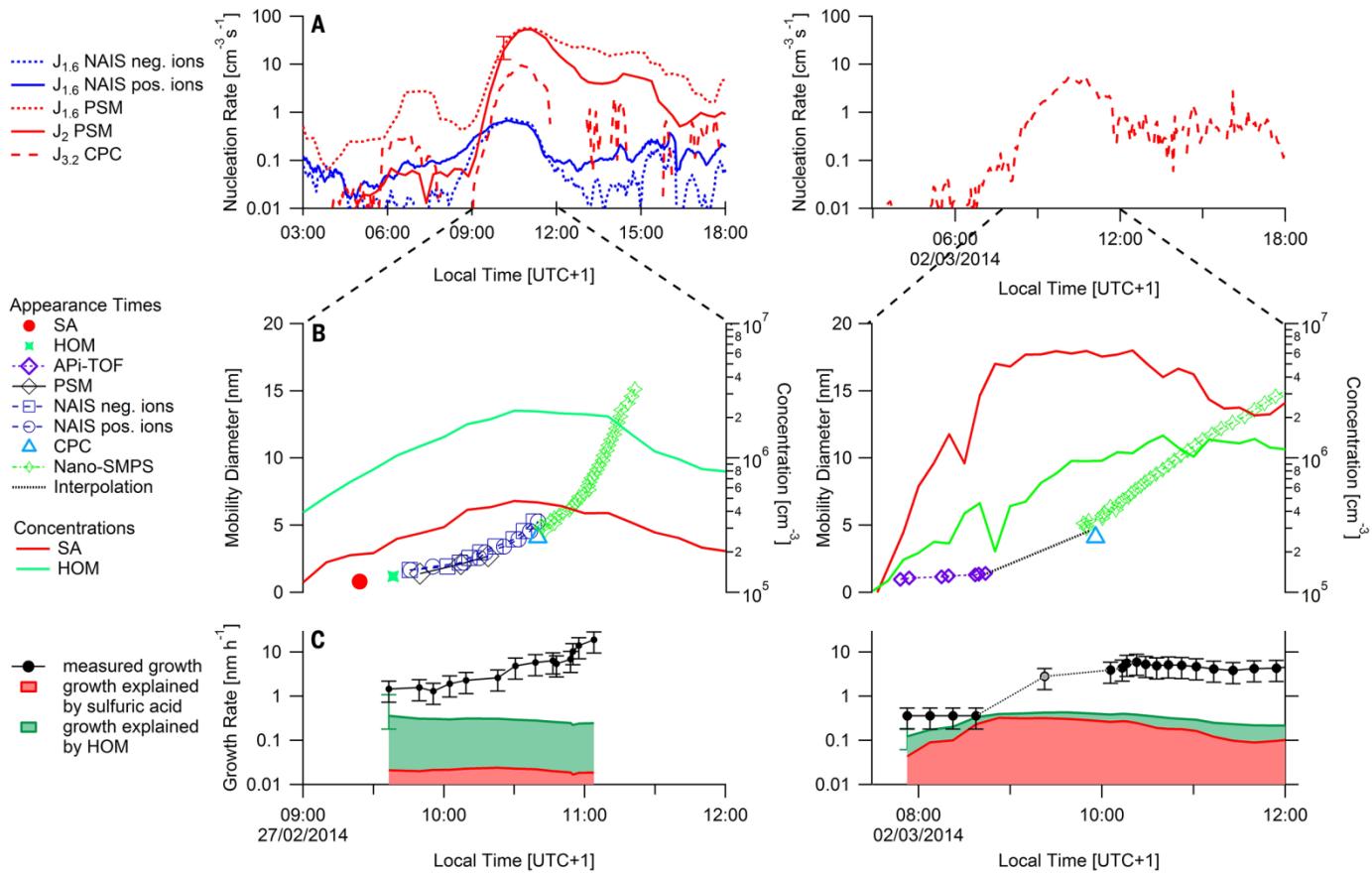


Fig. 3. Particle evolution during the nucleation events observed on days 3 and 4. Throughout, data for day 3 are shown on the left, and data from day 4 are shown on the right. (A) Formation rates (J) of the particles and ions at different sizes. (B) Evolution of particle diameter during the nucleation events. The two solid lines (red and green) show the concentrations of sulfuric acid (SA) and HOMs. (C) Comparison of the measured growth rates (black; error bars indicate systematic scale uncertainty) with growth rates calculated by assuming that solely sulfuric acid contributes to the growth (red) (30) or by also assuming a contribution from HOMs (green) (29). In addition to a much higher sulfuric acid concentration, the data for day 4 show a $J_{3.2}$ and growth rate that are slightly lower than those of day 3. On day 4, not all of the instruments required to measure particles across the full range from 1 to 15 nm were functioning. Therefore, the growth rate was interpolated between about 08:40 and 10:00.

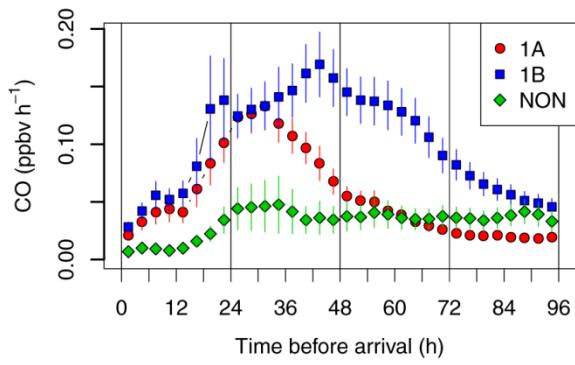


Fig. 4. Uptake of anthropogenic carbon monoxide versus time before arrival at the JFJ, for air masses sampled under different nucleation conditions. Shown are simulated means (symbols) and standard uncertainties of the means (error bars). Type 1A events (red) include pronounced and clearly identifiable events, type 1B events (blue) include less well-defined nucleation events, and NON (green) indicates no nucleation events.



New particle formation in the free troposphere: A question of chemistry and timing

F. Bianchi, J. Tröstl, H. Junninen, C. Frege, S. Henne, C.R. Hoyle, U. Molteni, E. Herrmann, A. Adamov, N. Bukowiecki, X. Chen, J. Duplissy, M. Gysel, M. Hutterli, J. Kangasluoma, J. Kontkanen, A. Kurten, H. E. Manninen, S. Münch, O. Peräkylä, T. Petäjä, L. Rondo, C. Williamson, E. Weingartner, J. Curtius, D. R. Worsnop, M. Kulmala, J. Dommen and U. Baltensperger (May 25, 2016)
published online May 25, 2016

Editor's Summary

This copy is for your personal, non-commercial use only.

Article Tools

Visit the online version of this article to access the personalization and article tools:

<http://science.scienmag.org/content/early/2016/05/24/science.aad5456>

Permissions

Obtain information about reproducing this article:

<http://www.scienmag.org/about/permissions.dtl>

Science (print ISSN 0036-8075; online ISSN 1095-9203) is published weekly, except the last week in December, by the American Association for the Advancement of Science, 1200 New York Avenue NW, Washington, DC 20005. Copyright 2016 by the American Association for the Advancement of Science; all rights reserved. The title *Science* is a registered trademark of AAAS.