Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Direct Observation of Ice Nucleation Events on Individual Atmospheric Particles

Bingbing Wang[1*†], Daniel A. Knopf[2], Swarup China[1], Bruce W. Arey[1], Tristan H. Harder[3,4], Mary K. Gilles[3], Alexander Laskin[1]

[1]William. R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352, USA

[2]Institute for Terrestrial and Planetary Atmospheres, School of Marine and Atmospheric Sciences, Stony Brook University, Stony Brook, NY 11794, USA

[3]Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

[4]Department of Chemistry, University of California, Berkeley, California 94720, USA

[†]Present address: State Key Laboratory of Marine Environmental Science (Xiamen University); College of Ocean and Earth Science, Xiamen University, Xiamen 361102, China

*Corresponding author:

Bingbing Wang

Email: Bingbing.Wang@xmu.edu.cn

Phone: +86-592-2880816

Address: A1-413, Zhoulongquan Building, Xiang'an Campus, Xiamen University, Xiamen 362100, China

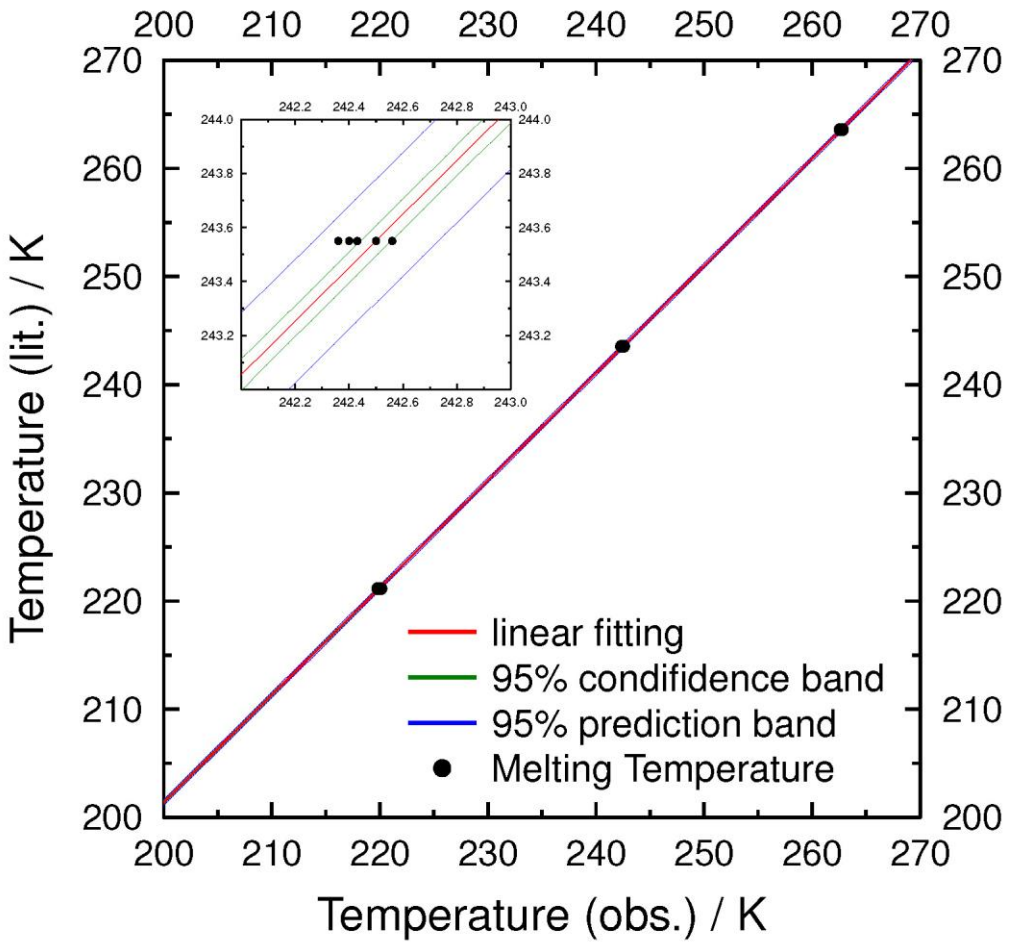


Figure S1. Temperature calibration of the sample holder using melting points of organic compounds including decane (243.55 K), dodecane (263.58 K), and 1-hexanol (221.15 K). The inset plot shows exemplary a magnified view of the measured melting points of decane at 243.55 K.

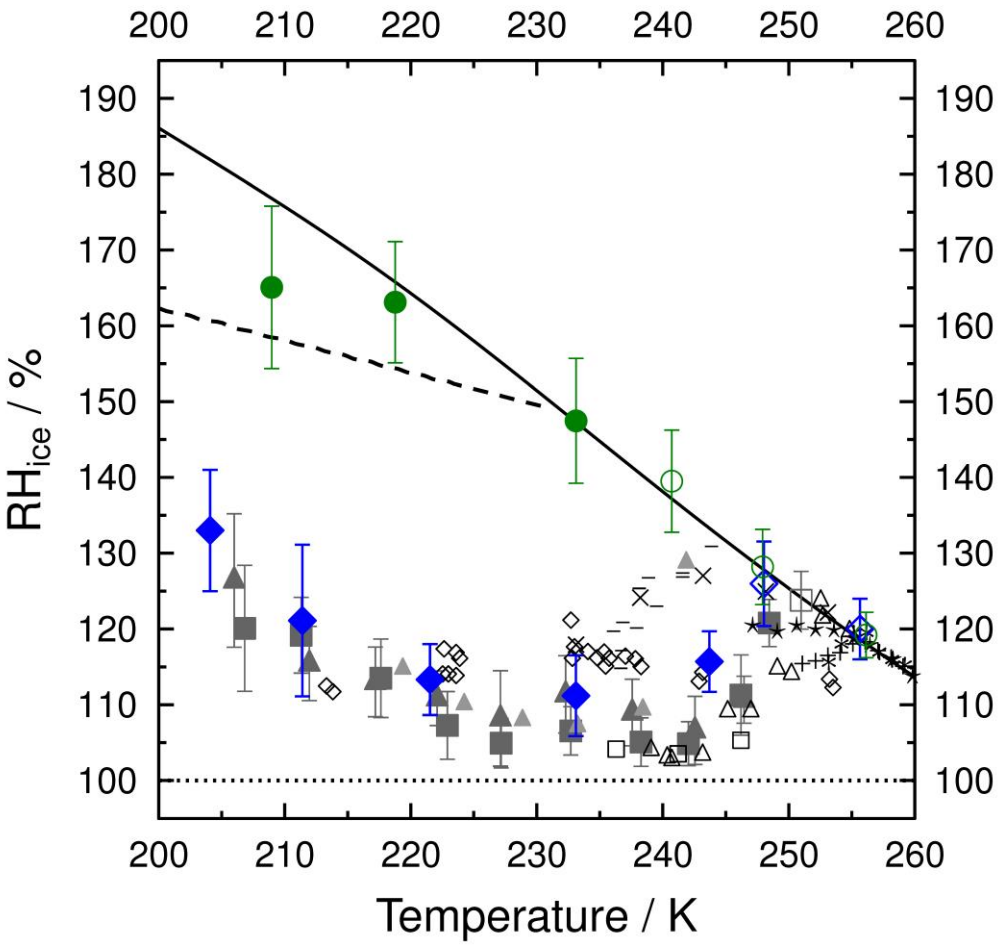


Figure S2. Comparison of ice nucleation onsets of kaolinite particles using IN-ESEM system (blue diamonds) with previous studies.[1-10] Figure is adapted from Wang and Knopf (2011).[1] Previous ice nucleation data on kaolinite are shown as solid square (Wang and Knopf, 2011),[1] solid triangles (Knopf et al., 2010),[3] open triangles (Dymarska et al., 2006),[4] open squares (Eastwood et al., 2008),[5] open diamonds (Bailey and Hallett, 2002),[6] pluses (Schaller and Fukuta 1979),[8] stars (Roberts and Hallett, 1968),[7] gray solid triangles (Welti et al., 2009),[9] and crosses (Salam et al., 2006)[10]. Green solid and open circles indicate the onsets of ice nucleation and water condensation on a blank substrate, respectively. The solid, dotted, and dashed lines represent water (RH_w = 100%), ice saturation (RH_{ice} = 100%), and homogeneous freezing limit, respectively.[11]

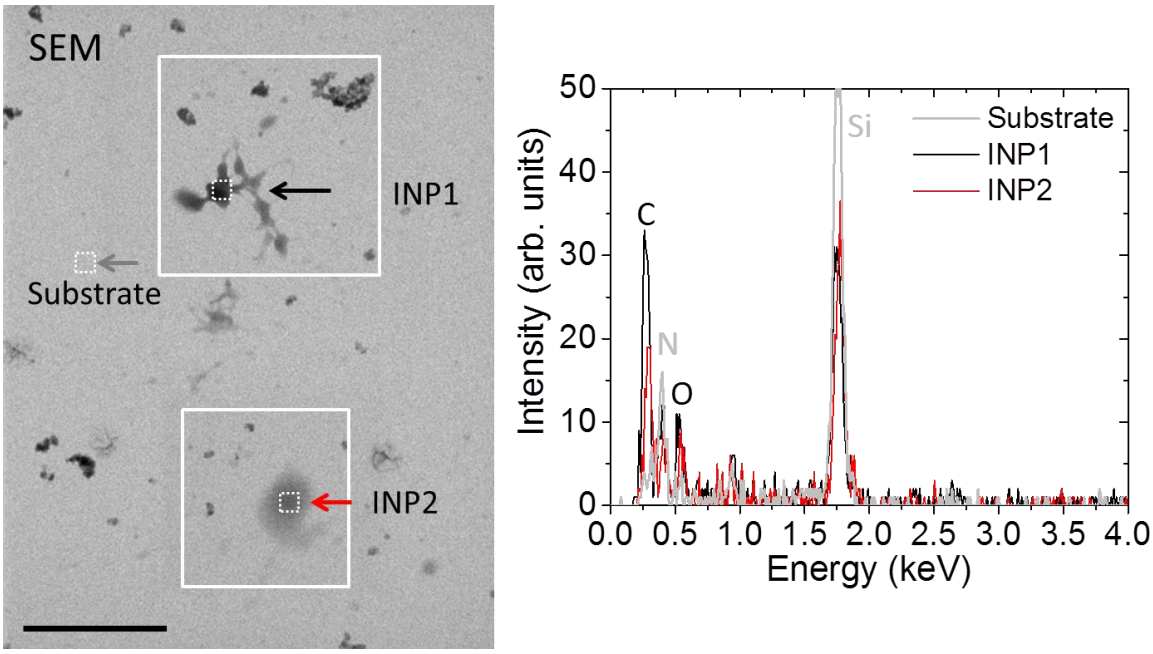


Figure S3. An example of chemical imaging by SEM/EDX showing particles in the field collected sample. The SEM image is shown in the left panel. The squares indicate the selected areas analyzed using STXM/NEXAFS as shown in Fig. 9. The arrows indicate the ice nucleating particle INP1 and INP2. Scale bars are 3 µm. The EDX spectra (right panel) acquired over the INP and substrate (small dashed boxes) indicate that these two INPs mainly consist of C and O, with N as a minor component. The silicon nitride substrate contains Si and N elements.

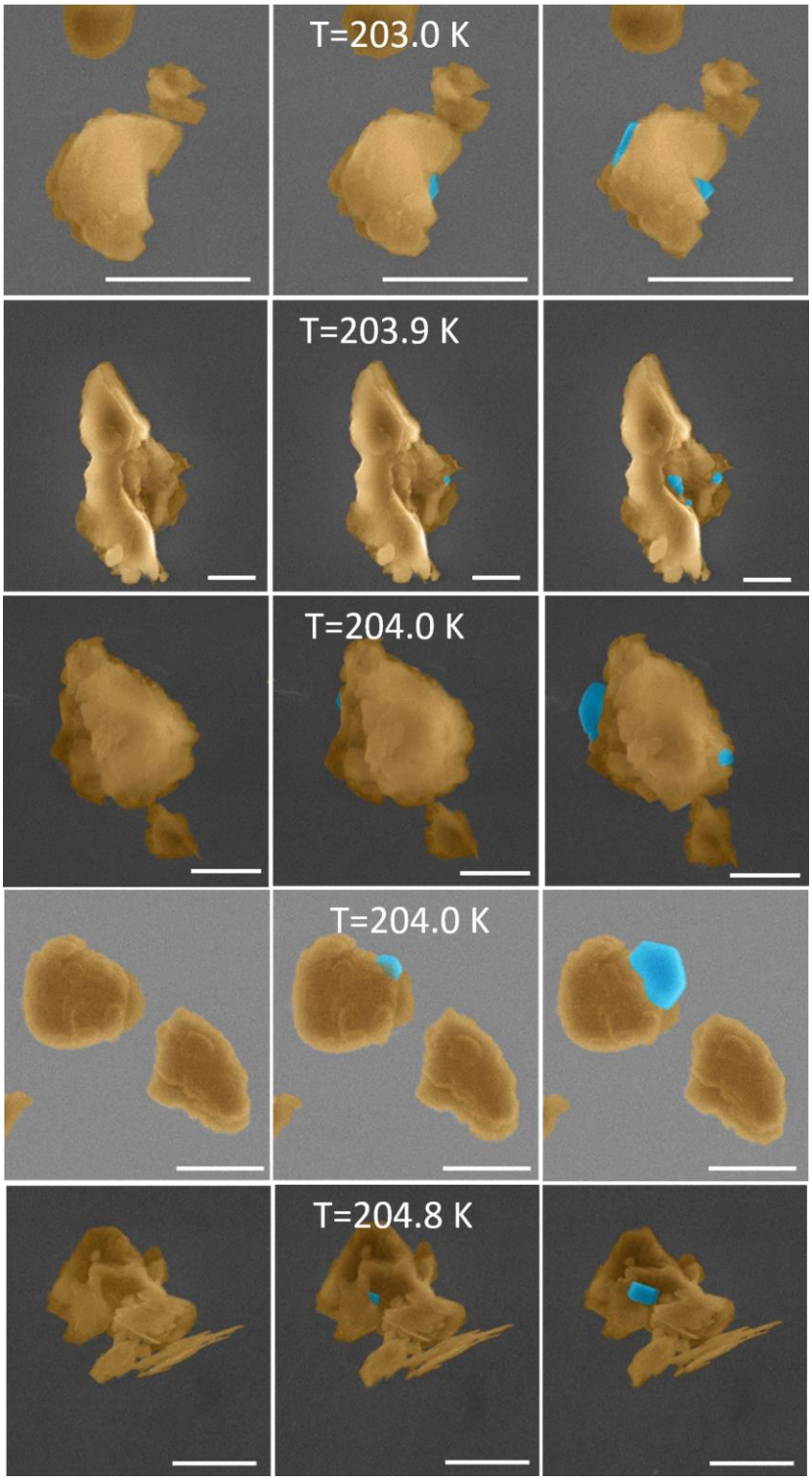


Figure S4. Five isothermal ice nucleation experiments on kaolinite particles showing the formation of ice on investigated particles. Each row shows one experiment proceeding in time from left to right with corresponding increase in RH_{ice}. False-colored images of kaolinite particles (brown) and ice crystals (blue) are shown for clarity. Scale bars are 5 µm.

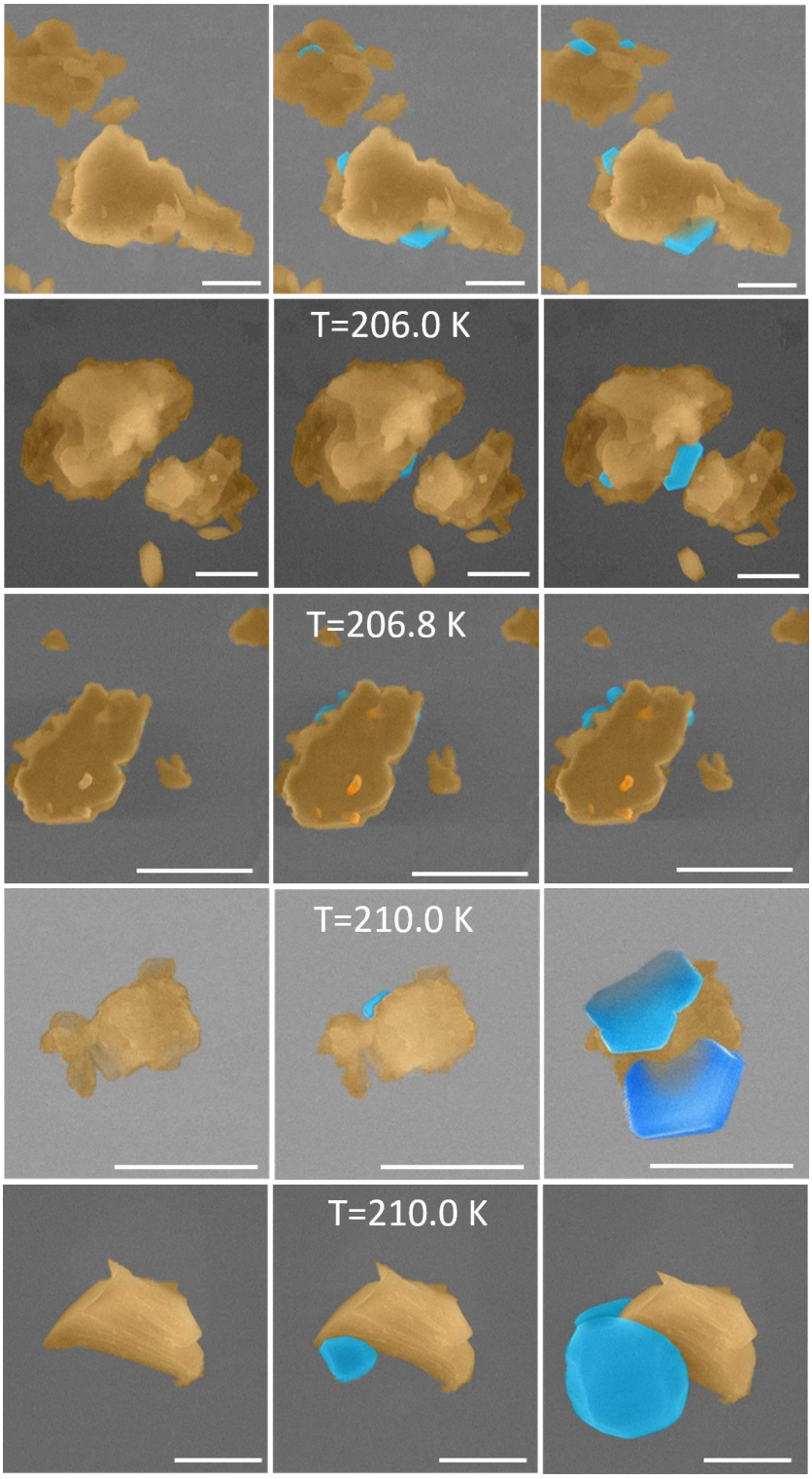
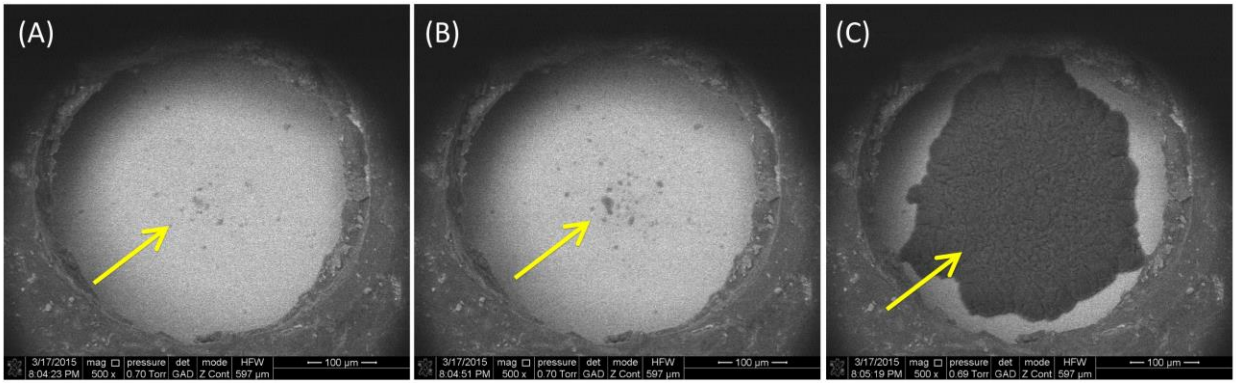
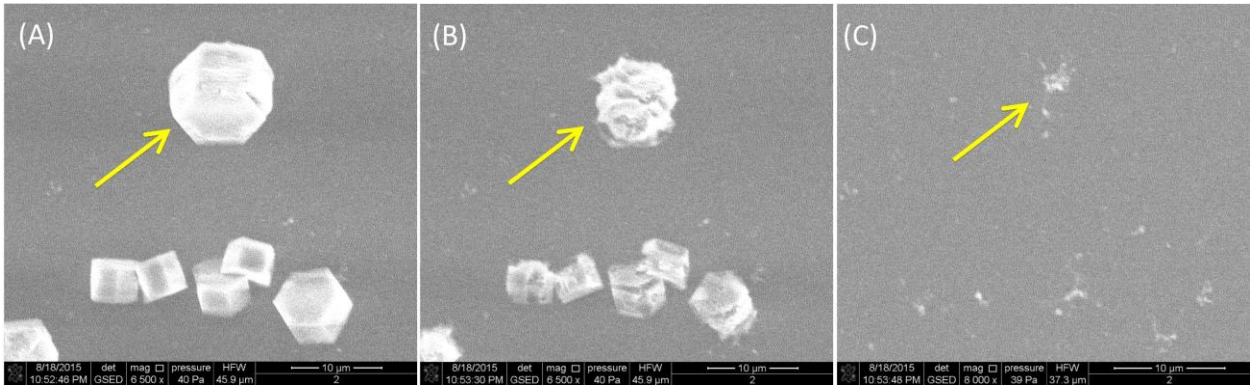


Figure S5. Five isothermal ice nucleation experiments on kaolinite particles, conducted at higher temperatures compared to Fig. S4, showing the formation of ice on investigated particles. Each row shows one experiment proceeding in time from left to right with corresponding increase in RH_{ice}. False-

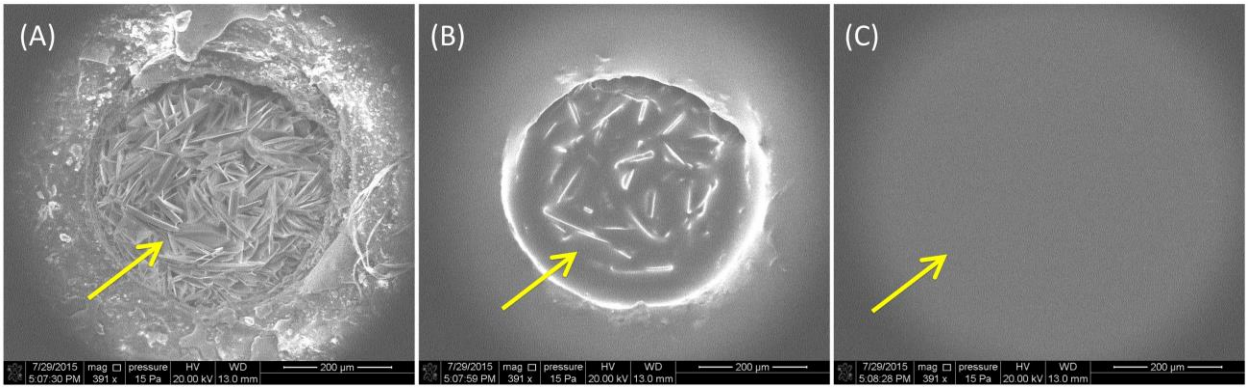
colored images of kaolinite particles (brown) and ice crystals (blue) are shown for clarity. Scale bars are 5 µm.



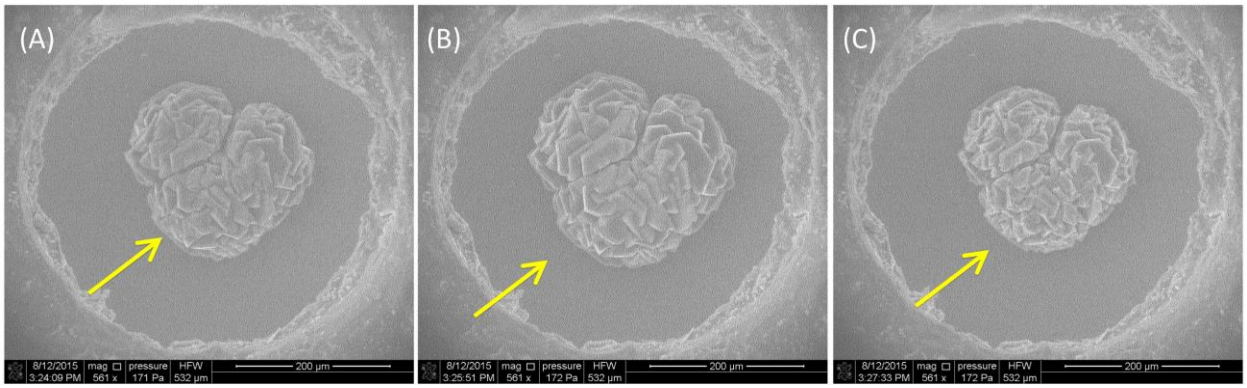
Movie S1. An example of immersion freezing on kaolinite particles. Panels A, B, and C are images for the before water uptake at 248.0 K and 116.1% RH_{ice} (A), water uptake by particles at 247.9 K and 117.2% RH_{ice} (B) and ice crystal formation by immersion freezing at 247.8 K and 118.4% RH_{ice} (C). Immersion freezing followed the condensation of liquid water on the particles. The entire experiment is also provided as a separate movie file (Movie S1).



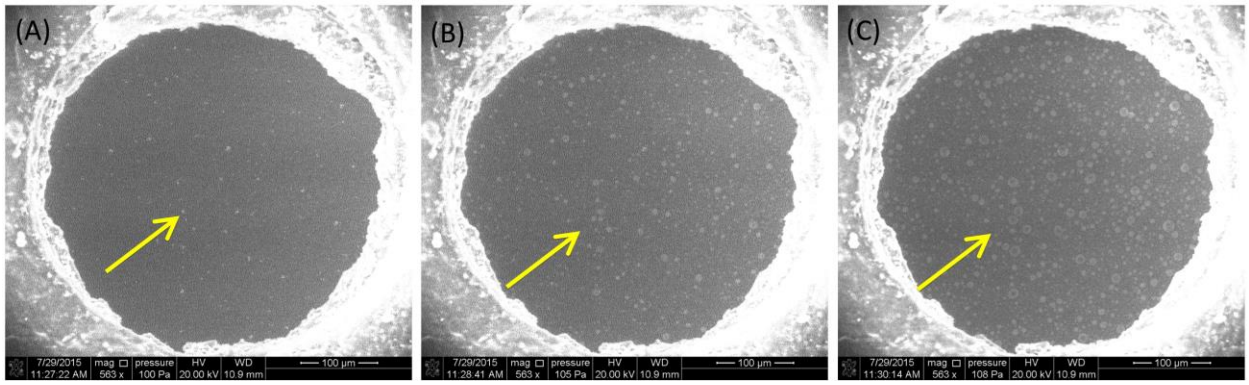
Movie S2. An example of the identification of the individual ice nucleating particles (INPs) from the field collected particle sample. Panels A, B, and C show three images recorded during the experiment. The arrows indicate one of the ice crystals at the beginning of experiment at 206.0 K and 94.4% RH_{ice} (A), during sublimation at 206.1 K and 93.0% RH_{ice} (B), and after complete sublimation at 206.1 K and 93.0% RH_{ice} (C). The entire experiment is available as a separate movie file (Movie S2).



Movie S3. An example of the temperature calibration of the sample holder using organic compounds. Panels A, B, and C show three images taken during the melting experiment of decane. The organic solid was heated with 0.2 K min^{-1} under dry conditions. The arrows indicate the organic crystals at the beginning of experiment at 242.1 K (A), during the melting process at 242.2 K (B), and complete melting at 242.3 K (C). The entire experiment is available as a separate movie file (Movie S3). Temperature shown here are the readings from the sensor, uncalibrated.



Movie S4. An example of the dew point calibration against the calibrated sample holder temperature. Panels A, B, and C show three images taken during the experiment. The arrows indicate the ice crystal either growing at 218.5 K and 105.3% RH_{ice} (A), being in equilibrium at 218.9 K and 100% RH_{ice} (B), or sublimating at 219.3 K and 95.0% RH_{ice} (C) as the water partial pressure is varied. The entire experiment is available as a separate movie file (Movie S4).



Movie S5. An example of the deliquescence of NaCl particles indicating that water uptake proceeds uniformly across the substrate. Panels A, B, and C show three images taken during the experiment. The arrows indicate crystalline NaCl particles at 261.6 K and 47.7% RH (A) and aqueous NaCl droplets at 255.8 K and 76.8% RH (B) and 255.4 K and 79.5% RH(C). The entire experiment is available as a separate movie file (Movie S5).

References:

1 Wang, B. & Knopf, D. A. Heterogeneous ice nucleation on particles composed of humic-like substances impacted by O3. *J. Geophys. Res. Atmos.* **116**, D03205, doi:10.1029/2010jd014964 (2011).

2 Wang, B. B. *et al.* Heterogeneous ice nucleation and water uptake by field-collected atmospheric particles below 273 K. *J. Geophys. Res.-Atmos.* **117**, D00v19, doi:10.1029/2012jd017446 (2012).

3 Knopf, D. A., Wang, B., Laskin, A., Moffet, R. C. & Gilles, M. K. Heterogeneous nucleation of ice on anthropogenic organic particles collected in Mexico City. *Geophys. Res. Lett.* **37**, doi:10.1029/2010gl043362 (2010).

4 Dymarska, M. *et al.* Deposition ice nucleation on soot at temperatures relevant for the lower troposphere. *J. Geophys. Res.-Atmos.* **111**, doi:10.1029/2005jd006627 (2006).

5 Eastwood, M. L., Cremel, S., Gehrke, C., Girard, E. & Bertram, A. K. Ice nucleation on mineral dust particles: Onset conditions, nucleation rates and contact angles. *J. Geophys. Res. Atmos.* **113**, doi:10.1029/2008jd010639 (2008).

6 Bailey, M. & Hallett, J. Nucleation effects on the habit of vapour grown ice crystals from-18 to-42 degrees C. *Q. J. R. Meteorol. Soc.* **128**, 1461-1483, doi:10.1256/00359000260247318 (2002).

7 Roberts, P. & Hallett, J. A laboratory study of the ice nucleating properties of some mineral particulates. *Q. J. R. Meteorol. Soc.* **94**, 25-34, doi:10.1002/qj.49709439904 (1968).

8 Schaller, R. & Fukuta, N. Ice nucleation by aerosol particles: Experimental studies using a wedge-shaped ice thermal diffusion chamber. *J. Atmos. Sci.* **36**, 1788-1802 (1979).

9 Welti, A., Lueoend, F., Stetzer, O. & Lohmann, U. Influence of particle size on the ice nucleating ability of mineral dusts. *Atmos. Chem. Phys.* **9**, 6705-6715 (2009).

10 Salam, A. *et al.* Ice nucleation studies of mineral dust particles with a new continuous flow diffusion chamber. *Aerosol Sci. Technol.* **40**, 134-143, doi:10.1080/02786820500444853 (2006).

11 Koop, T., Luo, B. P., Tsias, A. & Peter, T. Water activity as the determinant for homogeneous ice nucleation in aqueous solutions. *Nature* **406**, 611-614, doi:10.1038/35020537 (2000).