Pore condensation and freezing is responsible for ice formation below water saturation for porous particles

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Edited by Dan Cziczo, Massachusetts Institute of Technology, and accepted by Editorial Board Member A. R. Ravishankara March 13, 2019 (received for review August 7, 2018)

Ice nucleation in the atmosphere influences cloud properties, altering precipitation and the radiative balance, ultimately regulating Earth’s climate. An accepted ice nucleation pathway, known as deposition nucleation, assumes a direct transition of water from the vapor to the ice phase, without an intermediate liquid phase. However, studies have shown that nucleation occurs through a liquid phase in porous particles with narrow cracks or surface imperfections where the condensation of liquid below water saturation can occur, questioning the validity of deposition nucleation. We show that deposition nucleation cannot explain the strongly enhanced ice nucleation efficiency of porous compared with nonporous particles at temperatures below −40 °C and the absence of ice nucleation below water saturation at −35 °C. Using classical nucleation theory (CNT) and molecular dynamics simulations (MDS), we show that a network of closely spaced pores is necessary to overcome the barrier for macroscopic ice-crystal growth from narrow cylindrical pores. In the absence of pores, CNT predicts that the nucleation barrier is insurmountable, consistent with the absence of ice formation in MDS. Our results confirm that pore condensation and freezing (PCF), i.e., a mechanism of ice formation that proceeds via liquid water condensation in pores, is a dominant pathway for atmospheric ice nucleation below water saturation. We conclude that the ice nucleation activity of particles in the cirrus regime is determined by the porosity and wettability of pores. PCF represents a mechanism by which porous particles like dust could impact cloud radiative forcing and, thus, the climate via ice cloud formation.

Significance

The formation of ice at relative humidity below 100% is assumed to proceed without the presence of liquid water. However, it has been shown that liquid water can exist well below water saturation in narrow cracks and pores. Here we show that the barrier for deposition nucleation of ice directly from the vapor is insurmountable in experiments; liquid water is involved in ice formation on porous particles, regardless of the ambient humidity. Thus, our results render deposition nucleation unlikely for the formation of ice clouds in the atmosphere.


The authors declare no conflict of interest.

This article is a PNAS Direct Submission. D.C. is a guest editor invited by the Editorial Board.

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Data deposition: The datasets generated and analyzed during the current study have been deposited in the ETH Library Research Collection (DOI: 10.3929/ethz-b-000330406).

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This article contains supporting information online at www.pnas.org/lookup/suppl;doi:10.1073/pnas.1813647116/-/DCSupplemental.

Published online April 4, 2019.
can form homogeneously in pores and subsequently trigger ice growth out of the porous material at warmer temperatures. Furthermore, recent studies have shown that organic (14, 15) and water (16) vapors crystallize via the liquid phase condensed in wedge-shaped pockets, suggesting a PCF mechanism being responsible. Regardless, the generally accepted mechanism for ice nucleation below water saturation is currently deposition nucleation. Here we provide further evidence of the PCF mechanism by comparing the ice nucleation ability of synthesized porous and nonporous particles composed of the same material, in combination with CNT and molecular dynamics simulations.

**Results**

Advances in material sciences have allowed for the synthesis of porous silica (significant component of atmospheric mineral dust) with well-defined pore diameters and morphologies (17). This allowed testing the so-called deposition nucleation with silica particles that have uniformly distributed 3.8-nm pores, as well as with nonporous silica particles (Methods). The ice nucleation ability of silica particles exposed to varying temperatures and ice supersaturations in the Zurich Ice Nucleation Chamber (ZINC) (18), shows a strong dependence on the presence of pores (Fig. 2). In Fig. 2A, the silica samples with monodispersed pore diameters of 3.8 nm (open symbols) show an increase in activated fraction at a much lower relative humidity with respect to water (RH<sub>w</sub>) than the nonporous samples (filled symbols) for −50 °C. Due to the inverse Kelvin effect, the 3.8-nm pores should be full at RH<sub>w</sub> = 67% (dashed line in Fig. 2A; see SI Appendix, section 2.1), which corresponds to the RH<sub>n</sub> at which the porous samples start to nucleate ice. It is important to note that this RH<sub>n</sub> is also close to the required RH for ice crystals to grow to a detectable size in ZINC (SI Appendix, section 3.1). The observation of ice crystals at this RH<sub>n</sub>, in combination with the ability of pores of this size to nucleate ice homogeneously (10, 19, 20), is strong evidence that the enhanced freezing ability of the porous samples is due to pore filling and subsequent homogeneous freezing of the pore water at or near the predicted RH<sub>n</sub> for pore filling.

The ability of the nonporous silica particles to nucleate ice below water saturation (Fig. 2A) might suggest the concurrent presence of a deposition nucleation mechanism. However, applying CNT to the porous and nonporous particles we find that the barrier for deposition nucleation on nonporous silica is 8,000 times the thermal energy, rendering the barrier for deposition nucleation insurmountable on the timescales relevant to clouds or laboratory experiments (SI Appendix, section 3.4). Furthermore, high-resolution scanning electron and atomic force microscopy images (SI Appendix, Fig. S1) reveal the presence of imperfections and steps on the surface of the nonporous silica particles, which provide pore-like features for PCF to occur, albeit at higher RH<sub>w</sub> than the truly porous samples. Therefore, the observed freezing on the nonporous particles suggests a PCF mechanism occurring due to the presence of surface imperfections.

At −40 °C, freezing for both porous and nonporous samples shifts to water saturation (Fig. 2B). The absence of ice nucleation activity of the porous sample is explained by considering the nucleation rate for homogeneous freezing of water inside the
The freezing characteristics of the porous and nonporous silica particles at −50, −40, and −35 °C are in agreement with PCF. However, CNT predicts an energy barrier that limits the ability of ice to grow out of pores (SI Appendix) (11, 14). The homogeneous nucleation temperature of water in 3.8-nm pores is −43 °C (19). The contribution of freezing within the pore is, therefore, not the limiting barrier in our experiments at −45 and −50 °C. Rather, the second process of ice growing out of the pores into the unconfined vapor region is the step that limits PCF to yield bulk ice crystals. We therefore focus on investigating the ice growth out of ice-filled pores. To that end, we conducted grand canonical molecular dynamics simulations of vapor deposition with the monatomic water model (mW) (26, 27), which reproduces the structure and thermodynamics of melting and nucleation of ice in bulk, in pores, and on surfaces (20, 27–31). We expose three different models for silica surfaces to supersaturated mW water vapor: a nonporous slab, a porous slab with a single 3-nm ice-filled pore, and a model of the porous silica used in this study with a triangular array of 3-nm ice-filled pores separated by 1-nm-wide walls, similar to the porous silica particles used in the experiments (32–34; see Methods and SI Appendix, section 3.4). Ice was unable to form on the nonporous silica slab (Fig. 3A), and grew extremely slowly from the single ice-filled pore as a spherical cap that expands onto the silica surface with a constant contact angle until bulk ice forms (Fig. 3B and SI Appendix, section 3.4). However, ice grew rapidly out of the array of pores of the porous silica model surface, producing bulk ice (Fig. 3C). Using CNT with experimental properties of water, we calculated the effective contact angle between ice and the silica surface for nonporous silica, a single pore, and an array of pores as shown in Fig. 4A (SI Appendix, section 3.4). In the presence of an array of pores, bulk ice can either form through the merging of neighboring spherical ice caps (Fig. 4B) or from the bridging of growing ice caps due to capillary condensation of water and subsequent freezing of the water between them (Fig. 4B). The latter pathway has the lowest energy barrier (SI Appendix, Fig. 3) and thus a lower effective contact angle (Fig. 4A). We calculate the barriers (from which we derive the effective contact angle; see SI Appendix, section 3.4) along the minimum free-energy path for the nucleation and growth of ice out of the pore, accounting for the change in volume as the ice caps emerge from neighboring pores. We conclude that arrays of narrow, closely spaced pores are key for producing low ice nucleation barriers in porous silica. The narrow width of the pores is needed for capillary condensation and freezing, while the close spacing of the pores results in ice bridging that leads to fast nucleation out of the pores (Fig. 4 and SI Appendix, section 3.4). The area of the array of pores needs not be macroscopic, only larger than the size of the critical ice embryo with respect to the vapor. The molecular simulations and the theoretical analysis of nucleation pathways (SI Appendix, section 3.4) support that ice formation below water saturation proceeds through a PCF mechanism, which is boosted when pores are closely spaced. Furthermore, the lack of freezing in the molecular dynamics simulations on the nonporous silica slab, together with the insurmountable ice nucleation barriers determined from CNT (SI Appendix, section 3.4), indicates that ice nucleation cannot proceed via deposition nucleation. Instead, ice nucleation occurs via PCF below water saturation. We note that for pores with large openings, bridging ice growth out of narrowly spaced pores may not be necessary, as has been demonstrated for wedge-shaped pockets (16).
In view of these results, we investigated the susceptibility of atmospheric mineral dust to PCF. The contribution of various desert dusts to ice nucleation via the PCF mechanism depends on their transported airborne fraction together with their pore-size distribution (SI Appendix, section 1.1). To assess the relevance of PCF for irregular pore structures occurring in natural mineral dust particles, we chose the clay mineral illite due to its important contribution to airborne dust (35) (44%) and its established porosity in the range from 2 to 5 nm (36−38).

Ice nucleation experiments in ZINC with submicrometer illite NX particles are very similar to that of the porous silica with 3.8-nm pores (SI Appendix, Fig. S2) and yield similar ice nucleation results (SI Appendix, Fig. S2). This is true even over a wide range of particle sizes (SI Appendix, Fig. S3), suggesting that even the smallest illite particles exhibit narrow pore structures and confirming the suitability of PCF to predict ice nucleation on atmospherically relevant dust types. Other clay minerals have typical pore sizes that are narrower (montmorillonite) or wider (kaolinite) than illite (36, 38), also making them susceptible to PCF. Indeed, ice nucleation on kaolinite particles has been found to occur at the particle edges with a high density of trenches (25).

Based on the fraction of transported clay mineral particles and their porosity, we present a parameterization (SI Appendix, section 1.1 and Fig. S2) for climate models that can utilize an AF as a function of humidity (6, 39, 40), by incorporating experimental results from ZINC on illite NX and nonporous silica (SI Appendix, Fig. S2). This parameterization discriminates between accumulation and coarse-mode particles. The parameterization of accumulation mode particles is based on the AFs observed for illite NX, assuming that 60% of the transported accumulation mode particles are clays (35, 41), containing pore-size distributions similar to the sample used in this study and 40% of the particles are nonporous. All coarse-mode particles are assumed to exhibit pores and, therefore, nucleate ice below water saturation. Unlike conventional deposition nucleation parameterizations, which are temperature dependent (6, 42), the PCF-based parameterization applies to all temperatures below −38 °C. This is consistent with results from previous experiments on natural dusts that have shown little dependence of the onset RH_{w} required for ice nucleation at temperatures below −38 °C (8, 9, 43), supporting the occurrence of PCF rather than deposition nucleation. In the atmosphere, airborne dust particles may acquire a coating with atmospheric aging, potentially leading to a deactivation of pores when they are completely filled (13). However, in our parameterization we assume PCF does not depend on aging time, since single-particle mass spectrometry of ice crystal residuals from cirrus clouds found dust particles to be predominantly uncoated (5, 44, 45).

Our findings suggest that at conditions subsaturated with respect to liquid water, the ice nucleating ability of the most common components of airborne mineral dust is determined by their porosity. This, in combination with experiments with synthetic particles, molecular dynamics simulations, and nucleation theory, confirms that PCF should be considered as an important mechanism for ice formation below water saturation. Due to the large radiative impact of cirrus clouds on climate (3, 4), conventional ice formation parameterizations, which rely on deposition nucleation, should be replaced with schemes that incorporate PCF in cirrus cloud models (6, 7). In the presence of heterogeneous ice-nucleating pore surfaces, the PCF mechanism should remain active above the HNT for humidity conditions subsaturated with respect to water, making deposition nucleation less likely at warmer temperatures as well. We anticipate that other atmospherically relevant porous particles nucleate ice via the PCF mechanism (46), potentially further increasing the contribution of PCF to anthropogenic climate change.

Methods

Particle Synthesis. The porous silica particles (MCM-41) were synthesized adapting the procedure in ref. 47 by dissolving 1.74 g cetyltrimethylammonium bromide (C_{16}TMABr; 99%, Acros Organics) in a mixture of 122 mL aqueous ammonia (28%, Aldrich), 300 mL distilled water, and 500 mL ethanol (99.8%, Aldrich). The mixture was stirred for 15 min before 4.5 mL of tetraethyl orthosilicate (TEOS, 99%; Aldrich) were added within 3 s. After 2 h of reaction time, the silica particles were extracted from the solution using a filter (Grade 939, Sarostak) and subsequently dried at 80 °C. The particles were then ground in methanol (99.9%, Aldrich) and dried again before being calcined at 550 °C (4.5-h ramp to 550 °C) for 12 h. Pores larger than 3.0 nm were obtained by aging the suspended silica particles in distilled water for 24 h at 120 °C before grinding in methanol. Verification of pore size was obtained using nitrogen adsorption and desorption isotherms combined with nonlinear density-functional theory (SI Appendix, Fig. S5).

Nonporous silica particles were synthesized applying the procedure described in ref. 48 with adjusted ratios of ammonia, distilled water, and ethanol in the initial solution to achieve the desired particle diameters. Namely, 44 mL of TEOS were added to a vigorously stirred solution composed of 66 mL ammonia (28%, Aldrich), 133 mL distilled water, and 217 mL ethanol (99.8%, Aldrich). After a 4-h reaction time, the particles were extracted and washed twice with water by centrifugation (1,864 × g, Hettich Rotofix 32). The drying and calcination procedure was the same as for the porous particles.

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Particle-size distributions were created by measuring at least 100 particle diameters with ImageJ on SEM (Quanta, FEG 250; see SI Appendix, Fig. S1) images. The nitrogen adsorption and desorption isotherms at −196 °C (77 K) were measured using a Quantachrome Nova 3000e system. The sample was pretreated at 80 °C overnight in air and the pore-size distributions were obtained by nonlinear density-functional (NLDFT) calculations. NLDFT provides an accurate method to determine pore-size distributions (49) using theoretical isotherms to predict the pore-size distribution through a comparison with previous experimental data (50). As can be seen in SI Appendix, Fig. S5, a very narrow pore-size distribution is achieved with the synthesis method used in this study. The total surface area was obtained using the standard Brunauer–Emmett–Teller (BET) method to determine the surface area of the samples tested in this study, particles were exposed to increasing RH, at a rate of 2% per minute for a selected temperature. The RH, where ice begins to form is determined by distinguishing larger ice crystals (1 μm) from the smaller (400 nm) unactivated particles by an optical particle counter (OPC, Lighthouse, Remote 5104) at the bottom of the chamber. The activated fraction of the aerosol was calculated as the ratio of ice crystals (i.e., particles larger than 1 μm) detected by the OPC at the bottom of the chamber to the total number of aerosols entering the chamber determined by a water-based condensation particle counter (model 3787, TSI Inc.).

**Particle Characterization.** Particle-size distributions were created by measuring at least 100 particle diameters with ImageJ on SEM (Quanta, FEG 250; see SI Appendix, Fig. S1) images. The nitrogen adsorption and desorption isotherms at −196 °C (77 K) were measured using a Quantachrome Nova 3000e system. The sample was pretreated at 80 °C overnight in air and the pore-size distributions were obtained by nonlinear density-functional (NLDFT) calculations. NLDFT provides an accurate method to determine pore-size distributions (49) using theoretical isotherms to predict the pore-size distribution through a comparison with previous experimental data (50). As can be seen in SI Appendix, Fig. S5, a very narrow pore-size distribution is achieved with the synthesis method used in this study. The total surface area was obtained using the standard Brunauer–Emmett–Teller (BET) method to determine the surface area of the samples tested in this study, particles were exposed to increasing RH, at a rate of 2% per minute for a selected temperature. The RH, where ice begins to form is determined by distinguishing larger ice crystals (1 μm) from the smaller (400 nm) unactivated particles by an optical particle counter (OPC, Lighthouse, Remote 5104) at the bottom of the chamber. The activated fraction of the aerosol was calculated as the ratio of ice crystals (i.e., particles larger than 1 μm) detected by the OPC at the bottom of the chamber to the total number of aerosols entering the chamber determined by a water-based condensation particle counter (model 3787, TSI Inc.).

**Ice Nucleation Experiments.** The particles used in this study were aerosolized using a rotating brush generator (Palas, RBG 1000) and then passed through a cyclone with a 1-μm cut size (URG-2000-30EHB) before entering a 2.7-m cubic stainless-steel tank (53). The particles were then size selected to produce a quasi-monodisperse aerosol of 400 nm using a polonium source neutralizer and a differential mobility analyzer (Long DMA, model 3081; TSI Inc.) column before entering the continuous flow diffusion chamber, ZINC (18). However, due to multiple charging in the neutralizer, aggregates of particles larger than 1 μm can pass through the DMA and enter ZINC where they are misidentified as ice (Fig. 2). The porous particles were observed to have a higher fraction of aggregates than the nonporous particles and this explains the difference in the AF curves in Fig. 2 B and C before an increase in AF is observed. The size distribution of size-selected aerosols is presented in SI Appendix, Fig. S5. The secondary peaks at 200 and 300 nm are due to 400-nm particles being multiply charged. Further evidence that the peaks at these sizes are artifacts and not representative of the samples can be seen in SI Appendix, Fig. S1D, displaying an SEM image presenting the uniform size of the silica particles. In ZINC, the aerosol particles are layered between two-particle free-sheath flows of 4.5 L min⁻¹ each on either side of the 1 L min⁻¹ aerosol layer for a total flow rate of 10 L min⁻¹ (ref. 18). With a flow rate of 10 L min⁻¹, the residence time in ZINC is ~10 s but varies with increasing ice supersaturation and temperature due to buoyancy effects in the chamber (18). To determine the ice nucleating ability of the samples tested in this study, particles were exposed to increasing RH, at a rate of 2% per minute for a selected temperature. The RH, where ice begins to form is determined by distinguishing larger ice crystals (1 μm) from the smaller (400 nm) unactivated particles by an optical particle counter (OPC, Lighthouse, Remote 5104) at the bottom of the chamber. The activated fraction of the aerosol was calculated as the ratio of ice crystals (i.e., particles larger than 1 μm) detected by the OPC at the bottom of the chamber to the total number of aerosols entering the chamber determined by a water-based condensation particle counter (model 3787, TSI Inc.).

**Molecular Simulations of Ice Growth out of Nanopores Under Controlled Supersaturation.** To study the growth of ice on nonporous amorphous silica and porous silica we run molecular dynamics simulations in the grand canonical (µVT) ensemble (GCMD) (54), coded into the MDS software LAMMPS (55). The dimensions of the periodic simulation cells are 8 nm × 8 nm × 10 nm, containing a 5-nm-wide silica-like slab with either (i) no pores, (ii) a single pore of 3-nm diameter, or (iii) a triangular array of 3-nm-diameter pores separated by 1-nm silica walls. The latter corresponds to the arrangement of pores in the porous silica used in this work (32–34). The pores in (i) and (ii) are filled with hexagonal ice exposing the primary prismatic face to vapor. Water is represented with the mW model (26). We consider two sets of parameters from ref. (54) for the interaction between the silica-like (s) walls and water (w): (i) a more hydrophilic silica (contact angle with water θ = 0°), with a characteristic interaction energy of εws = 6.19 kcal mol⁻¹, a characteristic interaction size is


48. Perez Sirkin YA, Factorovich MH, Molinero V, Scherlis DA (2016) Vapor pressure of water (S) for about 200 ns. Ice is identified with the CHILL+ algorithm (S8).

ACKNOWLEDGMENTS. The authors are grateful to H. Wydler for laboratory and technical support. R.O.D. acknowledges A. Laaksonen for fruitful discussions about theoretical aspects of this work. We thank the Center of High Performance Computing at The University of Utah for technical support and a grant of computing time. Z.A.K., R.O.D., D.B., and J.F. acknowledge funding from Swiss National Science Foundation Project 200011_156581. Z.A.K. and F.M. acknowledge funding support from Swiss Federal Institute of Technology (ETH) Zurich Grant application ETH 25-15.1. Y.Q. and V.M. acknowledge support by the United States National Science Foundation through Award CHE-1305427 “Center for Aerosols Impacts on Climate and the Environment.” Y.A.P.S. acknowledges support by the Fulbright Foundation.