Correction

EARTH, ATMOSPHERIC, AND PLANETARY SCIENCES

The authors wish to note the following: “We would like to draw attention to the work of Molinero and co-workers (1, 2), which is relevant for our article. Moore and Molinero (2) very recently conducted a large scale molecular dynamics study into the structure of ice that crystallizes at 180 K. They find that the ice that forms in their simulations contains both cubic and hexagonal sequences with a ratio of about 2:1, similar to their previous study on ice formation in a nanopore (1). This work supports our conclusion that the material referred to as cubic ice in the literature is actually stacking disordered ice, but our experiments and simulations indicate that the ratio of cubic to hexagonal sequences is not restricted to 2:1.”


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The freezing of water to ice is fundamentally important to fields as diverse as cloud formation to cryopreservation. At ambient conditions, ice is considered to exist in two crystalline forms: stable hexagonal ice and metastable cubic ice. Using X-ray diffraction data and Monte Carlo simulations, we show that ice that crystallizes homogeneously from supercooled water is neither of these phases. The resulting ice is disordered in one dimension and therefore possesses neither cubic nor hexagonal symmetry and is instead composed of randomly stacked layers of cubic and hexagonal sequences. We refer to this ice as stacking-disordered ice I. Stacking disorder and stacking faults have been reported earlier for metastable ice I, but only for ice crystallizing in mesopores and in samples recrystallized from high-pressure ice phases rather than in water droplets. Review of the literature reveals that almost all ice that has been identified as cubic ice in previous diffraction studies and generated in a variety of ways was most likely stacking-disordered ice I with varying degrees of stacking disorder. These findings highlight the need to reevaluate the physical and thermodynamic properties of this metastable ice as a function of the nature and extent of stacking disorder using well-characterized samples.

The freezing of water to ice is of fundamental importance in both nature and technology. Yet the structure of the phase of ice that initially crystallizes is poorly understood. Freezing is thought to follow Ostwald’s rule of stages, which states that a metastable phase crystallizes initially, which may later transform to the stable phase (1). In the case of ice crystallized from liquid water at ambient pressure, the metastable phase has been previously identified as cubic ice (ice Ic) (2–4). This metastable phase is thought to persist in the coldest regions of Earth’s atmosphere where temperatures fall below 200 K (2, 4–8). It is also observed in biological tissues during cryopreservation where it can have a lasting effect. For example, in the atmosphere, the transient presence of the metastable phase is thought to modify the shape of snowflakes (11) and lead to substantial changes in ice-particle concentrations in cold cirrus clouds (5).

In both modifications of ice I, ice Ih, and ice Ic, the water molecules form layers consisting of six-membered puckered rings. The difference between ice Ih and ice Ic lies in the stacking of these layers. In the case of ice Ih, each layer is a mirror image of the previous layer, which results in an overall structure with hexagonal symmetry. In ice Ic, on the other hand, each successive layer is shifted a distance equal to half the diameter of a six-membered ring. In the resulting structure, the oxygen atoms are arranged in the same way as carbon atoms in the cubic lattice of diamond (12, 13).

It has been noted in the past that the diffraction patterns of metastable ice crystallized from bulk water droplets are not in agreement with a perfect cubic crystal structure (e.g., refs. 3, 4, and 14). In fact, ice referred to as cubic ice, which was generated by recrystallization from high-pressure phases (15–17), by freezing of confined water in mesopores (18), and by warming amorphous ice (19), is also not perfect cubic ice.

It is well known that crystallites with periodic stacking sequences can contain stacking faults where, for example, a cubic sequence might “accidentally” appear in a predominantly hexagonal structure. This kind of disorder is common in clays, metals, and zeolites (20). The stacking faults interrupt the periodicity of the crystal in the direction of the stacking, although the crystal may remain well ordered in the other two dimensions. A number of authors have suggested that the noncubic features in metastable ice can be explained by stacking faults (3, 14, 17, 21). More recently, Hansen et al. (16, 22) quantified the stacking faults in what they referred to as cubic ice, which was recrystallized from ice V and IX. In contrast, Morishige et al. (18) refer to ice in mesopores as cubic ice, but suggest that it is in fact small crystallites of hexagonal ice with growth faults.

In this paper, we elucidate and characterize the structure of the metastable phase of ice I that crystallized from droplets of supercooled water and quantify the stacking disorder by means of stacking probabilities. We also use Monte Carlo simulations to probe crystallization of ice at a molecular level. Both the experimental and computational data support the thesis that stacking disorder is a general feature of ice formation from supercooled water.

Results and Discussion

X-Ray Diffraction Study of Frozen Water Droplets. In order to determine the crystal structure of ice that crystallized homogeneously from supercooled water, water droplets were suspended in an oil matrix by emulsification, and the phase of ice that formed was monitored with X-ray diffraction (see Methods).

Comparison of the diffraction pattern of frozen 0.9-μm droplets that froze around 232 K (Fig. 1A) with the calculated pattern for ice Ih (Fig. 1B) reveals that the characteristic hexagonal peaks at about 26°, 34°, and 61° 2θ, which are the 101, 102, and 203 peaks of ice Ih, are absent, whereas the remaining peak intensities are inconsistent with ice Ih. Our diffraction pattern is similar to numerous patterns published in the literature, which have been identified as ice Ic (e.g., refs. 3, 4, 19, and 23). However, comparison of the experimental pattern with the numerically calculated pattern for ice Ic (Fig. 1C) reveals obvious discrepancies. The experimental pattern has a strong peak at approximately 23° (corresponding to the 100 peak of ice Ih) and the region between approximately 23° and 26° is elevated above the baseline: both of these features are incompatible with cubic symmetry. Moreover, the relative peak intensities of the three primary peaks of ice Ih are a poor match to the experimental
pattern, and the high angle peaks (ca. 58° and 64° corresponding to the 400 and 331 peaks of ice I₃) are absent. In the past, it has been suggested that crystallization of amorphous ice on heating is incomplete, resulting in a mixture of crystalline and amorphous ice. It is also apparent from a Rietveld refinement (Fig. 1E) that the meta-stable material is not a simple phase mixture of crystallites of ice I₃ and ice Ih. In summary, it is clear from these diffraction patterns that the ice, which crystallizes from supercooled water, is neither ice I₃, ice Ih, nor a mixture of distinct phases.

The experimental diffraction pattern of ice from supercooled water is in fact consistent with ice that contains stacking disorder. For perfectly ordered crystals, diffraction intensity in reciprocal space, which means that streaks in the experimental diffraction pattern correspond to diffraction peaks from the sample support.

Monte Carlo Simulations of Water Freezing. Independent evidence for the ice I₃ structure comes from computer simulations that yield molecular resolution and bring direct insights into molecular processes of ice crystallization. Homogeneous nucleation of ice occurs on timescales that are generally not accessible by brute-force simulation, and here we employed advanced Monte Carlo (MC) simulations in which we efficiently direct and enhance ice growth from supercooled water at 220 K for a periodic system comprising 2,880 TIP4P model water molecules (note that the melting temperature for this model is 232 K). An essential issue with such simulations is that one must ensure that the methodology does not favor a particular structure or phase (27), and to this end, we used the order parameters previously developed and verified by Brukhno et al. (28).

The striking observation from our simulations is that, during crystallization of ice I, the emerging ice layers randomly switch between cubic and hexagonal sequences, which is confirmed by Brukhno et al. (28).
By definition, a crystalline solid is a material in which there is periodicity in all three dimensions. Ice $L_d$ is only ordered in two dimensions and is disordered in the direction of stacking of oxygen atom layers; hence it is unlikely to form macroscopic crystals of a distinct shape (habit). Ice $I_h$ is expected to form cubes or octahedra, and ice $I_0$ most often forms hexagonal plates and columns and underlie the familiar shape of snowflakes (32). The habit of single crystallites of ice $L_d$ is unknown, but they might be expected to have two smooth parallel faces corresponding to either the [0001] face of ice $I_h$ or the [111] face of ice $I_s$ (which are equivalent), but with the other sides poorly defined. Intriguingly, Lawson et al. (33) reported that more than 80% of the crystals they imaged in tropical cirrus were “quasi-spheroids” but with some flat edges. Recent results from 2D laser scattering probes also suggest that many ice crystals in cirrus and mixed-phase clouds are irregular and may have rough surfaces (34).

Ice generated in different ways appears to have different stacking fault densities. Our study has established that the ice formed from supercooled water under atmospherically relevant conditions is fully stacking disordered (50% : 50%), whereas ice recrystallized from the high-pressure phase ice V contains about 60% cubic sequences, and ice from ice IX contains about 42% cubic sequences at 175 K (16, 22). Also, Kuhs et al. (17) estimated that ice $L_d$ from ice II contained only a few percent of hexagonal sequences, although this should be reassessed with a quantitative model. The appearance of varying degrees of stacking disorder raises important questions about the validity and applicability of the physical data for so-called cubic ice in the literature, including thermodynamic quantities, such as heat capacity and vapor pressure as well as interfacial energies, optical constants, and spectroscopic properties. It is necessary to revisit many of these measurements using well-characterized ice in order to understand the relationship between stacking disorder and the physical properties of the ice I family. Such studies will underpin our understanding of ice formation and properties in a wide range of fields including the atmospheric sciences, cryobiology, glaciology, geophysics, engineering, and the planetary sciences (13).

An obvious question is whether well-ordered ice $I_h$ can ever form. Although evidence from diffraction measurements is absent, crystals grown from water vapor at approximately 200 K can have a cubic habit (35) and 25% of crystals in the Antarctic stratosphere were solid cubes during one campaign (36). In addition, a halo at 28° from the sun has been photographed and is consistent with the rare presence of octahedral crystals of ice $I_h$ in the atmosphere (37). Perhaps the dearth of hard evidence for the existence of well-ordered ice $I_h$ indicates that it is rare and only forms under very specific conditions, which diffraction experiments have not yet accessed.

Methods

Sample Preparation. The experimental technique has been described previously (2, 3) and will only be briefly summarized here. For these experiments, pure water (18.2 MΩ) droplets were suspended in an oil matrix (10 wt % lanolin in mineral oil) and were agitated to make droplets of the desired size. The lanolin served as a surfactant and stabilized the emulsion. Droplets $>5 \, \mu m$ heated up during crystallization and partly anneal to the stable hexagonal phase (3). In contrast, very small droplets do not anneal to the stable phase. A diffraction pattern of 0.9-μm droplets cooled at 30 K min$^{-1}$ is shown in Fig. 1A. These droplets froze with a median freezing temperature of 231.7 ± 1.0 K, consistent with the temperature of 232.2 K expected for homogeneous freezing under these conditions (38), showing that the presence of the oil and surfactant did not alter the nucleation kinetics.

Experimental Procedure. The X-ray diffractometer (Bruker D8 Advance) used in these experiments was configured in a standard reflection geometry and...
was equipped with a Cu Kα X-ray source (λ = 1.5418 Å), a Vantec detector, and an Anton Paar TTK450 temperature-controlled stage. The sample holder was cooled by liquid nitrogen to 173 K at a rate of 30 K min⁻¹. The diffraction patterns were recorded with the sample under vacuum to prevent frost and reduce heat transfer. In order to measure the temperature at which the water droplets homogeneously froze to ice, the diffraction angle of a strong reflection associated with both ice Ic and ice Ih (diffraction angle, 2θ = 24°) was continually monitored as the cell was cooled. Once at 173 K, the diffraction pattern of the sample between 2θ = 20 and 70° was recorded. This range covered all of the strong ice Ic and ice Ih reflections, and selected examples of powder patterns were recorded with the sample under vacuum to prevent frosting.

We used in this study. The DIFFaX v1.812 software was used to simulate X-ray powder diffraction patterns of stacking-disordered ice structures (19). Structural information required by DIFFaX includes the cell dimensions, details of the atoms, and a coverage all of the strong ice Ic and ice Ih reflections, and selected examples of patterns were recorded with the sample under vacuum to prevent frosting. In a last step, the calculated intensities and widths and diffuse scattering contributions in powder diffraction. In this study, the DIFFaX calculations were carried out in the isothermal-isobaric (pressure = 1 bar) ensemble for a system of 2,880 water molecules with the use of the TIP4P model. We employed the well-known umbrella sampling method coupled with an order parameter based on the recently developed maximum projection method (28) in order to enhance ice crystal growth. The maximum projection order parameter is capable of efficiently directing the growth of both ice forms, Ic and Ih, without an undesirable preference of either symmetry. As a result, this scheme allows the two ice sequences to emerge and grow competitively at the same time, which in all our simulations yields structures consisting of approximately randomly stacked cubic and hexagonal layers.

A strong biasing potential with respect to a quality-weighted ice cluster size, q, was imposed with an incline toward its higher values. At a given temperature, parallel simulations were performed for a number of system replicas restricted to parameter “windows” spanning a range of q = [0, 0.1], which corresponded to the overall ice fraction of up to approximately 10%. In comparison to the results reported by Brukhno et al. (28), a significantly larger system (N = 2,880 vs. 768 and 360 water molecules) has been simulated.

Several simulations for the system of 2,880 water molecules have been performed at T = 220 K and the MC trajectories comprised up to 10⁶ sweeps (a sweep corresponds to one translation or rotation attempt for every molecule in the system). The size of the ice cluster reached up to 200–300 water molecules.

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