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Evidence for Transition of Metastable Ice to Hexagonal Ice in Bulk Solutions at Relatively High Temperatures

P. W. Wilson[1*], C. Marshall[2], M. Bayer-Giraldi[3], M. Agustin Mateo[4]

[1]School of Environment, Science and Engineering, Southern Cross University, Lismore, NSW, Australia
[2]Biochemistry Department, School of Medical Sciences, University of Otago, Dunedin, New Zealand
[3]Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research (AWI), Bremerhaven, Germany
[4]Physics Department, Interdisciplinary Sciences Building, University of South Florida, Tampa, FL, USA
Email: *peter.wilson@scu.edu.au

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Abstract

There have been many reports that a metastable form of ice can exist in the atmosphere and that it transitions rapidly to stable, hexagonal ice at temperatures above about 200 K. Although this often-called cubic ice has also been created in laboratories over the years, we present here a method for the simple formation of this metastable phase in the laboratory, at one atmosphere, in relatively large volumes and at higher temperatures than previously reported. Evidence for this phase is found during the monitoring of optical transmission through bulk samples of quenched aqueous solutions. In our experiments, frozen samples were created by quenching 0.2 ml aqueous volumes in glass tubes to 195 K which are then warmed to and held at 267 K. Results show an unusual drop in optical transmission occurring in the first few minutes. Such a change is best explained by the transition of a metastable phase to hexagonal ice, rather than by any freeze concentration effects. In the minutes following nucleation and freezing of the sample, the average size of the poly-crystals forming the frozen matrix would be typically expected to increase due to recrystallization, causing lower side and back-scatter of the traversing light and so a subsequent increased optical transmission. However, the drop in transmission we see with samples nucleated at such a low temperature cannot be explained by recrystallisation but rather by a re-ordering of the ice, the grain boundaries, and the interstitial water.

Keywords

Ice, Hexagonal, Cubic, Stacking Disorder, Metastable

1. Introduction

Ordinary water-ice formed under ambient conditions has traditionally been thought to have two polytypes, hexagonal ice (I_h) and cubic ice (I_c). Cubic ice is known to be metastable with respect to I_h and has not been studied to the same extent as hexagonal ice. Its existence in nature is increasingly the subject of debate, recent reports suggesting that a variation on the two forms, known as stacking disordered ice I (I_{sd}), may also exist or may in fact be ice I_c but with a variety of cubicity ratios manifesting under various conditions. This field of research is important because this metastable ice may be a dominant phase in our planet's coldest clouds. It has been argued that differences in the surface chemistry of cubic and hexagonal ice could influence perhaps both cloud formation and even ozone depletion [1]. We report here a simple method to produce, and monitor, a transition from a metastable form to hexagonal ice.

It has long been reported that at low temperatures water crystallizes into I_c and that it is metastable, transforming to ice I_h at around temperatures above 170 K and below 240 K [2] [3]. The actual temperature below which ice I_c preferentially forms is under debate, as is the general range of the transition temperature, the upper limit for that transition and its time frame. Below about 190 K, Ic is the dominant form of ice and no phase transformation has been reported, allowing for the possibility that at low temperatures I_c is energetically preferred [4]. It has been reported however that water droplets can homogeneously freeze to I_c at ambient pressure and temperatures between 160 K and about 240 K [5] [6], and with radii in the range of 5 nm to 5 mm [6] [7] [8]. Other studies concerning the transition from ice I_c to I_h reported that ice I_c is stable for several minutes and up to hours at temperatures around and below 240 K [9] [10]. A temperature dependency of the time of transformation from I_c to I_h has been observed, implying that it is possible that above 230 K water also nucleates to I_c but the transformation to I_h is so rapid that the nucleation of I_c is not observed [9].

The presence of a transient liquid layer has been suggested [11] [12] who proposed that cubic ice crystals will melt and transform to hexagonal at higher temperatures due to the Gibbs Thomson Effect, rather than the direct transformation at colder temperatures, often called grain boundary migration, resulting in a transient liquid layer. Murray [13] showed that aqueous organic acid added to the water droplets can shift the formation temperature to higher values. That is, I_c and I_h can exist in the same solution droplet and share a common aqueous phase through which water molecules must diffuse, the solutes becoming a limiting factor to the mass transfer from I_c. More recent work stresses the role of stacking faults/disorder in metastable ice [14] examining cubic ice in emulsions and monitoring the x-ray patterns showed stacking faults to be a significant factor in the nucleation and growth of any metastable phase.

Malkin *et al.* [15] have analyzed much of the available diffraction data on I_c and I_h and argue that metastable ice always contains features associated with stacking disorder (called here ice I_{sd}). They also argue that the crystal structure of

a macroscopic frozen droplet is independent of the structure of the initial critical cluster which nucleates. In the context of the current work, this concept relates to the time dependence of the I_{sd} to I_h transition. They show that ice initially formed at high temperatures also has I_{sd} features but that increased liquid water allows annealing at a faster rate. They determine that at about 237 K, ice is predominantly I_{sd}, and as high as 257 K there may still be one stacking fault in every 100 layers of I_h. Quigley [16] invokes a thermodynamic argument to show that hexagonal is preferred to stacking disordered as temperature increases but points out that the mechanism by which cubic stacking faults in low temperature nuclei persist to macroscopic size is yet to be well understood. Recently, Lupi *et al.* [17] modeled the nucleation of ice at 230K and showed the preference of critical embryos for I_{sd}, and indeed an excess of I_c over I_h.

We present here evidence for the transition of the metastable ice I_c to I_h. A simple method to produce this metastable form in the laboratory is described. Our result confirms directly the findings of Lupi *et al.* [17].

2. Experimental Methods

We describe here an optical recrystallometer instrument (http://www.otago-osmometers.com/), which is purpose built and which measures the change in light transmittance through a frozen sample of polycrystalline ice. Because of the Kelvin Effect, smaller ice crystals, with high curvature, have a lower melting point and melt at some pre-set annealing temperature. The liquid water released then migrates to nearby, larger crystals and refreezes, as these crystals have a higher melting point (above the ambient temperature in the matrix). The overall effect is that an ice crystal matrix held at a high subzero temperature develops fewer, but larger, crystals with time, an effect found commonly when ice cream is allowed to partially melt. Larger crystals tend to back-scatter and side-scatter light to a lesser extent than small crystals and the result is that during recrystallization, also known sometimes as Ostwald ripening, the levels of transmitted light increase with time when the sample is held at a constant annealing temperature.

Aqueous samples (200 μl) were placed in a shortened glass NMR tube (5 mm OD, length 100 mm) which resides snugly in a hollowed-out 10 mm thick aluminum block of cross sectional area 25 cm^2.

A K-type thermocouple rests close to the sample glass tube. The heat capacity of the block and the thin walls of the glass tube ensure that the temperature of the sample tracks very closely the temperature of the block, as recorded by the thermocouple. The block sample holder is sandwiched between two 65 Watt thermoelectric (Peltier) modules which are used to heat and cool the sample as desired. Excess heat is taken from the outsides of these modules by heat sinks cooled by flowing isopropanol. A schematic of the recrystallometer device is shown in **Figure 1**. The light source is white LED and this passes through a 1 mm diameter tube prior to meeting the sample, creating a 1 mm diameter beam

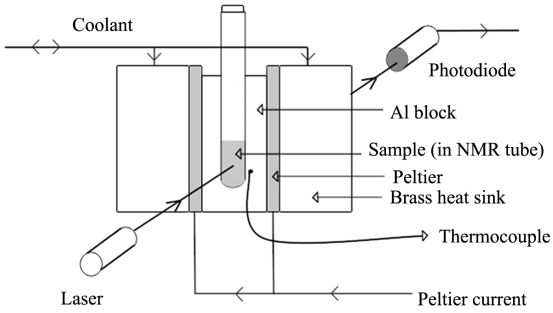

Figure 1. Schematic of the optical recrystallometer used to collect optical transmission data presented in this report. Reprint from Bayer-Giraldi *et al.* [18], with permission by Humana press.

traversing the sample. Having the light integrate over $3 * 10^{-9}$ m^3 gives ample opportunity for side and back scattering and so an averaging over many crystals. The temperature and optical transmittance, measured as current through the photodiode (in arbitrary units) of the sample are available as a digital readout on the instrument and also monitored continuously via an A/D converter and a computer.

We report here extracts of data sets created at both Otago University, New Zealand and at the Alfred Wegener Institute, Germany, on two, identical, optical recrystallometer instruments. Protocols for sample preparation are also very similar, making the remarkably coincident results from both laboratories even more interesting. This has led us to closely examine an anomaly we find in the first minutes of each run on a variety of samples of aqueous solutions. The anomaly is thought now to be caused by the transition of a metastable ice phase and is outlined further below.

In all measurements, the temperature of the aluminum block was first set to the annealing test temperature. In all cases reported here this was 267 K, controlled to ±0.2 K, but at both institutions 265 K was also used on occasion and the results are qualitatively the same. A dry sample tube was placed in an ethanol/dry ice slush at 195 K and allowed to cool. Then 200 μl of the test sample liquid, which had been precooled to 273 K, was rapidly transferred by pipette to the bottom of the tube. This technique causes multiple nucleation sites and many, small ice crystals to form. The frozen sample was then held at 195 K for between 60 s and 150 s to ensure full freezing of the solution and the tube then quickly dried and transferred to the cold block of the recrystallometer. For comparison, a sample was also frozen at 253 K and kept at this temperature until transfer to the recrystallometer. The entire recrystallometer is housed in an enclosure flushed with dry nitrogen gas at slight positive pressure to preclude condensation on the cold tube.

Levels of light transmittance were measured while the frozen sample was held at the subzero annealing test temperature. The levels of transmitted light do not change with time if the tube is empty, or contains ethanol, which will not freeze, ruling out condensation effects on the outside of the tube as being an issue. The

device is designed to test aqueous frozen solutions for the presence of inhibition of recrystallization (RI), as is found in many substances containing ice active proteins, such as rye grass extract, or polar fish blood supernatant. In a sample without RI, the transmittance level tends to increase with time as the crystals increase in size and cause less side- and back-scattering of the light. Figure 2 demonstrates what we typically see if there is inhibition of recrystallization (RI) and if recrystallization does exist.

The optical transmittance of samples nucleated at 195 K was measured continuously for up to 30 minutes after the transfer of the specimen to the cold block. Samples tested and reported below included ultrapure water with a resistivity of 18 MΩ·cm, 25 - 200 mM NaCl and 10 mM Tris buffer solutions in ultrapure water.

3. Results

Both Tris buffer and NaCl samples created by the freezing protocol described above showed an initial rapid decrease in transmittance within the first minute or so, followed by an increase over the next 30 minutes. Figure 3 shows exemplarily typical data sets portraying this anomaly.

As seen in Figure 3, when a protocol is used to form the initial ice, *i.e.* initially frozen at 253 K and we see recrystallization then the anomaly is not seen, suggesting the absence of metastable ice transitioning to hexagonal. The only difference in protocol being the freezing temperature, too high for nucleation of ice I_c. Our results fit nicely onto the spread outlined recently by Stan *et al.* who recently plotted cubicity as a function of freezing temperature for known historical experiments (see Figure 4) and our results for nucleation at 190 K and at 253 K are added to his spreads.

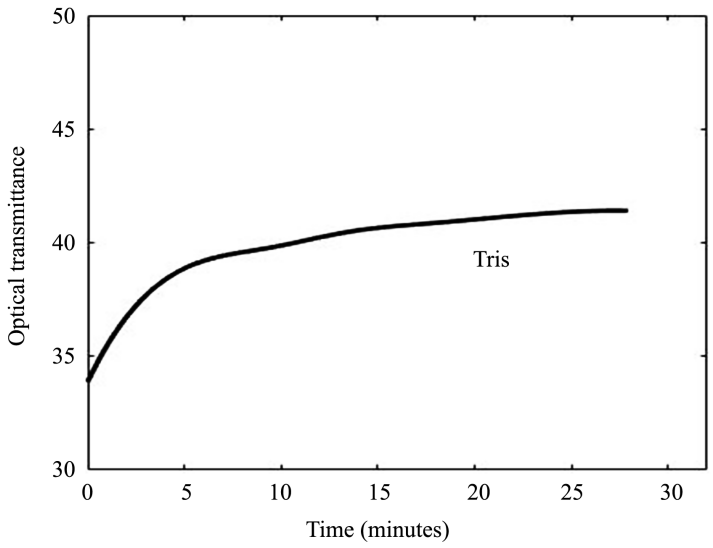

Figure 2. Plot of optical transmission from samples which demonstrate recrystallization and are nucleated at 253 K. This plot is very typical of such scans of all aqueous solutions we have measured to date. Optical transmission scale is arbitrary.

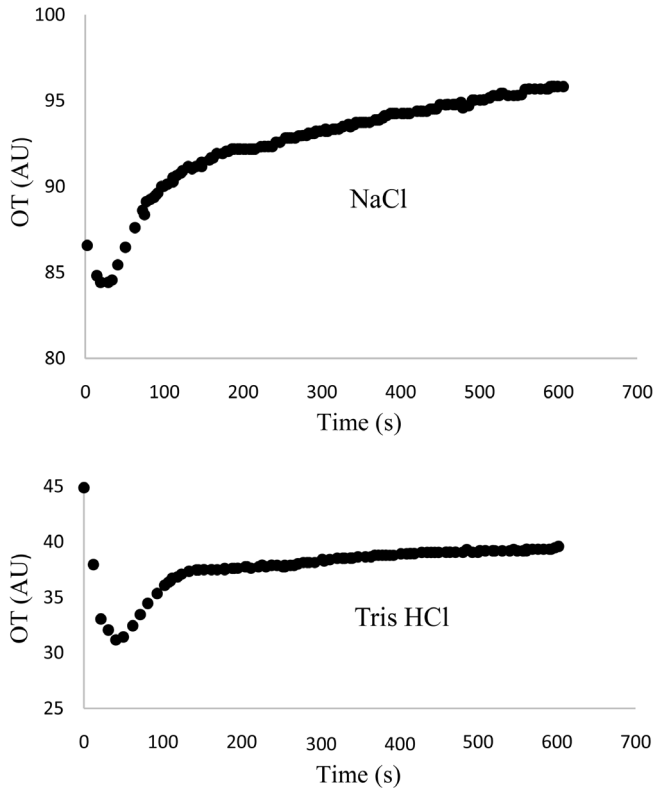

Figure 3. Variations of the optical transmittance over time, measured in frozen solutions of NaCl solution and Tris HCl buffer nucleated at 195 K. The first 10 minutes of the measurements are shown here. The increase in transmittance after the first 2 - 3 minutes indicates ongoing recrystallization processes. An anomaly with a rapid decrease in OT signal intensity within the first minutes of the measurements was consistently detected.

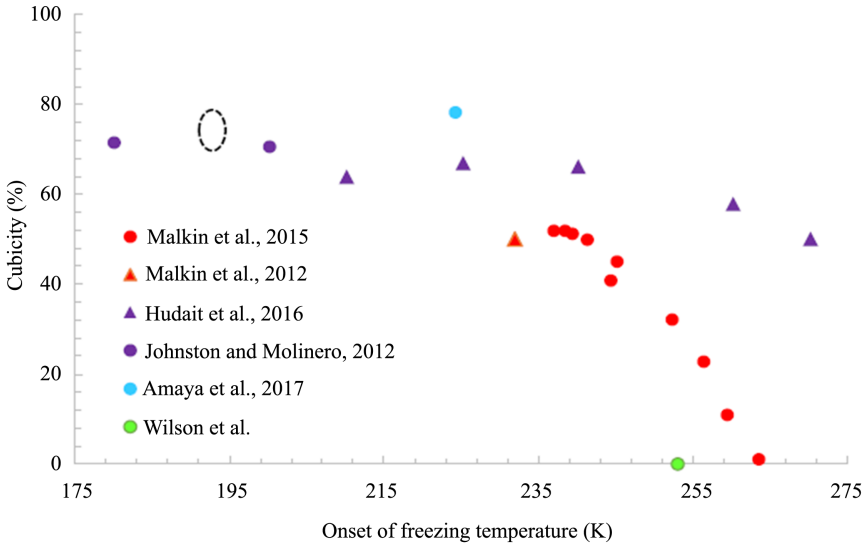

Figure 4. Cubicity as a function of freezing temperature for known historical experiments (replotted from Stan *et al.*) with our results for nucleation at 190 K (dotted ellipse) and at 253 K (green dot) added to his data analysis. The larger ellipse indicates where our cold nucleated data points fell, since the exact cubicity is unknown. Our ellipse may indeed be much further enlarged vertically, but the concept remains the same.

4. Conclusion

We have identified and measured an unusual behavior for small polycrystals of water-ice nucleated in the deeply supercooled region. The metastable transition which follows in the subsequent few minutes cannot be explained by simple re-crystallisation of smaller grain sizes to larger and all evidence suggests we are seeing the cubic ice to hexagonal ice transition which is hypothesized to occur at these temperatures and in this time frame. This is the first, albeit indirect, evidence for this transition to be seen in bulk samples in the laboratory.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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