Disordering effect of the ammonium cation accounts for anomalous enhancement of heterogeneous ice nucleation

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ABSTRACT: Heterogeneous nucleation of ice from supercooled water is the process responsible for triggering nearly all ice formation in the natural environment. Understanding of heterogeneous ice nucleation is particularly key for understanding the formation of ice in clouds, which impacts weather and climate. While many effective ice nucleators are known the mechanisms of their actions remain poorly understood. Some inorganic nucleators have been found to nucleate ice at warmer temperatures in dilute ammonium solution than in pure water. This is surprising, analogous to salty water melting at a warmer temperature than pure water. Here, the magnitude of this effect is rationalized as being due to thermodynamically favorable ammonium-induced disordering of the hydrogen bond network of ice critical clusters formed on inorganic ice nucleators. Theoretical calculations are shown to be consistent with new experimental measurements aimed at finding the maximum magnitude of the effect. The implication of this study is that the ice-nucleating sites and surfaces of many inorganic ice nucleators are either polar or charged and therefore tend to induce formation of hydrogen ordered ice clusters. This work corroborates various literature reports indicating that some inorganic ice nucleators are most effective when nominally neutral and implies a commonality in mechanism between a wide range of inorganic ice nucleators.

Introduction

The freezing of liquid water into solid ice is one of the most familiar and important phase transitions in both everyday experience and the natural world.[1] At atmospheric pressure solid ice I_h is the stable phase at temperatures between 0°C and about -210°C.[2] However, pure liquid water can supercool to temperatures below -40°C before freezing.[3, 4] This is because homogeneous nucleation, where ice clusters large enough to grow spontaneously form in truly pure supercooled water, is a strikingly slow process.[5] In the natural world the majority of ice nucleation is heterogeneous in nature, meaning a surface in contact with supercooled water catalyzes the formation of ice crystals.[6]

Heterogeneous nucleation of ice has been extensively studied due to its role in the atmosphere, where cloud glaciation temperatures are often controlled by the ice nucleating ability of the aerosol in cloud water droplets[6, 7] with consequent impacts on weather and climate.[8, 9] Ice nucleation is also of great relevance to cryobiology, the study of life at low temperatures, where the location and nature of ice formation can often determine how well biological material copes with low temperatures, both in environmental contexts[10] and medically-relevant cryopreservation procedures.[11] As such, a great deal is known about what substances do and don't nucleate ice well. Examples of effective ice nucleators include AgI,[12, 13] proteins from bacterial plant pathogens[14] and the mineral feldspar.[15, 16] However, understanding of the microscopic mechanism of heterogeneous ice nucleation is lacking, and is an area of substantial recent interest with a great deal of both experimental[7] and computational[17] work produced in the last few years.

Ice nucleation very often occurs from aqueous solution rather than from pure water. As such, the impact of aqueous solutes on the freezing temperature of water has been of interest since the 18th century[18] and the interaction of different nucleators with solutes has been intensively studied over the last 50 years. Improved understanding of the impact of solutes on heterogeneous nucleation has the potential to shed light on mechanism of heterogenous ice nucleation.

The 'water activity criterion' (WAC) developed by Koop et al.[19] accounts for colligative effects on ice nucleation, analogous to the familiar melting point depression observed in salty water. It states that there is a constant offset between the water activity of a solution at the ice-water equilibrium and the water activity at the freezing temperature. The offset for homogeneous ice nucleation $\Delta a_{w,hom}$ was determined to be 0.311,[19] later updated to 0.314.[20] Subsequent work showed that solute induced changes in heterogeneous nucleation temperatures could also be described by the water activity criterion, with smaller values of Δa_w.[21] For instance, silica spheres used to induce freezing in picolitre scale emulsion droplets have been found to give $\Delta a_{w,het}$ of 0.173. The smaller Δa_w indicates that the heterogeneous nucleation process takes place at warmer temperatures than homogeneous nucleation, due to a smaller free energy barrier to nucleation. The WAC can only account for depressions in nucleation temperature.

Recently, Kumar et al.[22] and Whale et al.[23] reported that ice nucleation induced by the mineral feldspar, known to be a highly effective nucleator,[15] was enhanced by low concentrations of various ammonium salts. The finding of enhancement is striking and means non-colligative effects must be in action. It is thought possible that ammonium salts in the atmosphere could make significant differences to the freezing temperatures of droplets in clouds[22, 23] and atmospheric condensation mode ice nucleating particle concentrations have been observed to increase in the presence of ammonium sulfate rich aerosol.[24]

Deviations from the WAC have also been observed for other mineral nucleators. To briefly summarize, feldspar, kaolinite, mica and gibbsite have all recently been found to nucleate ice at higher temperatures in dilute (0.01 M to about 0.1 M) ammonium solutions than in pure water. [23, 25] A similar result has been found for quartz,[23] although deactivation has also been observed.[25, 26] Other electrolytes have been found to impair ice nucleation by feldspars more than predicted by the WAC.[27, 28] Two studies observed that potassium salts can increase the temperature at which feldspars nucleate ice,[27, 28] although other studies have found the reverse, a reduction in nucleation temperature greater than that predicted by the WAC.[23] Amorphous silica and humic acid-type substances have been found to follow the WAC with all tested solutes. [21, 23]

In 1974 Reischel and Vali[29] reported freezing of 12 µl droplets containing 'kaolin'. Their data are largely compatible with findings of more recent studies, although it should be noted that the nucleator used may have contained minerals besides kaolinite, so may not be directly comparable to studies using the mineral kaolinite. They reported beyond-colligative suppressions of ice nucleation activity by NaI, NaCl, CsCl, K_2SO_4 and KI. They also reported enhancements caused by 0.01 M and 0.1 M of NH_4Cl, NH_4Br, NH_4I and 0.01 M $(NH_4)_2SO_4$. 1 M concentrations of these salts started to inhibit ice nucleation activity. Reischel and Vali found a 12°C increase in freezing temperatures in 1 M LiI. A recent attempt to replicate this result with kaolinite did not see similar behavior.[30]

Several studies have looked at the impact of aqueous solutes on AgI, the archetypal and much studied ice nucleator whose activity was famously predicted by Bernard Vonnegut on the basis of its structural similarity to ice I_h.[12] Macromolecular 'anti-nucleators' such as proteins, polymers and surfactants have been found to strongly inhibit the nucleating effectiveness of AgI. It has been reported that ice nucleation temperature of AgI dispersions can be reduced by up to 15.8°C by the presence of 1.0 mg/ml of polyvinyl alcohol.[31] Many other polymers and surfactants[32] reduce nucleation temperatures of AgI by around 10°C.[33] Zobrist and Koop[21] froze emulsions of picoliter scale solution droplets of various concentrations containing AgI particles. In the presence of $(NH_4)_2SO_4$ an anomalous increase in freezing temperatures was observed. This was attributed to changes in crystal habit caused by crystallization of AgI in the presence of NH_4^+. The response to other salts including $LiCl_2$, $MgCl_2$, K_2CO_3 and $Ca(NO_3)_2$ followed the WAC.

Reischel and Vali[29] also froze droplets containing AgI particles together with varying concentrations of a range of electrolytes, including five ammonium salts. Complex and often large deactivations were observed with many non-ammonium salts. This was reasonably attributed to varying degrees of

solubilization of AgI in different salt solutions. Freezing temperatures were found to be raised in solutions of NH_4I, NH_4Br and NH_4CNS although not NH_4Cl.

Finally, recent work by Curland et al.[34] and Javitt et al.[35] found that ice nucleation on charged AgI and $LiTaO_3$ surfaces can be enhanced by nitrate, bicarbonate, guanidinium and biguanidinium[34, 35] ions. Guanidinium and biguanidinium were found to enhance negatively charged surfaces while nitrate and bicarbonate were found to enhance positively charged surfaces.

Overall, enhancement of heterogeneous nucleation on inorganic surfaces by solutes is almost unique to the NH_4^+ cation. Indeed, it has recently been proposed that enhancement in of ice nucleation on $(NH_4)_2(SO_4)$ solution might be used as an indicator for the presence of mineral dust ice nucleators in natural samples.[36] The only exceptions are enhancements to alkali feldspars caused by KCl and the contested enhancement to kaolin caused by LiI, as well as the recent findings of enhancement by various ions on charged surfaces. It is striking that the NH_4^+ induced enhancement been observed in AgI, various feldspars, kaolinite, muscovite mica, gibbsite and quartz. These materials all have quite different structures and presumably nucleate ice in different ways so the common response to the presence of NH_4^+ is, perhaps, surprising.

In this study I argue that polar and charged surfaces which tend to orient water molecules are likely responsible for the ice nucleation ability of many inorganic nucleators and that unexplained increases in heterogeneous nucleation temperatures caused by ammonium salts[22, 23] are likely due to the disruption of thermodynamically unfavorable hydrogen ordering of ice clusters induced by these water-orienting nucleating surfaces.

Experimental measurements of enhancement and suppression of ice nucleation

Fig. 1 shows heterogeneous nucleation data illustrating the unexplained deviations. To produce these measurements the freezing temperatures of 2 µl water droplets containing the known effective ice nucleators BCS 376 feldspar and pollen washing water (PWW) from *Betula pendula* the silver birch tree were measured. BCS376 was the alkali feldspar used in the first study[15] reporting feldspar's exceptional ice nucleating activity and has typical nucleation effectiveness for an alkali feldspar.[37, 38] PWW contains ice nucleating polysaccharides of unknown structure,[39] also thought to nucleate ice in the atmosphere.[40, 41]

Experiments were conducted on an apparatus essentially similar to that described by Whale et al.[42] Approximately 40 one microliter droplets of either filtered PWW or a suspension containing 0.1 wt% of BCS376 feldspar were placed onto a silanised glass slide using an electronic pipette. One microliter droplets containing various concentrations of a range ammonium salts, NaCl, KI and $MgCl_2$ were then pipetted on top of the nucleator-containing droplets and the freezing experiment started immediately, minimizing the possibility of solute-induced aging of nucleators. The concentrations reported are the final concentrations of the resulting two microliter droplets. It can be seen that in NH_4Cl solution freezing temperatures of feldspar droplets increases, while in NaCl droplets freezing temperatures are reduced to a greater extent than for PWW with similar salt concentrations.

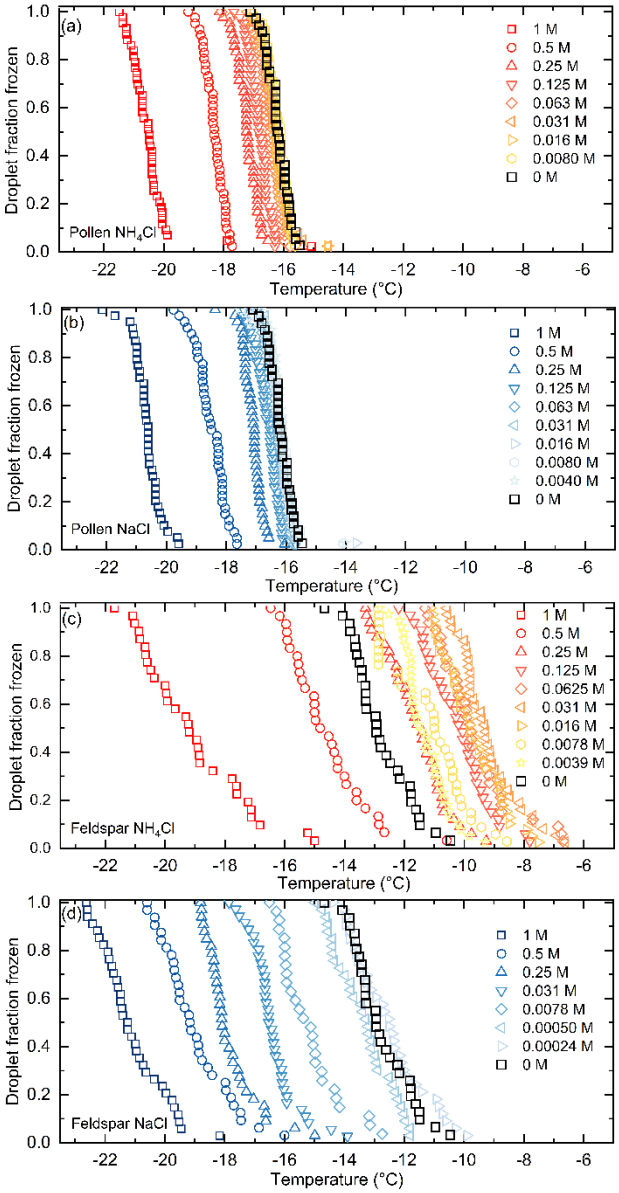

Figure 1: Fraction frozen curves for 2 µl droplets containing (a) Birch PWW in various concentrations of NH_4Cl (b) Birch PWW in various concentrations of NaCl (c) 0.05 wt% BCS376 feldspar in various concentrations of NH_4Cl and (d) 0.05 wt% BCS376 feldspar in various concentrations of NaCl.

In Fig. 2 the difference between observed average freezing temperatures for the nucleators and that predicted by the WAC is shown. In the case of nucleation induced by PWW both NH_4Cl and NaCl follow the water activity criterion at lower salt concentrations. There is a small negative deviation for 1 M and 0.5 M solutions. [43]

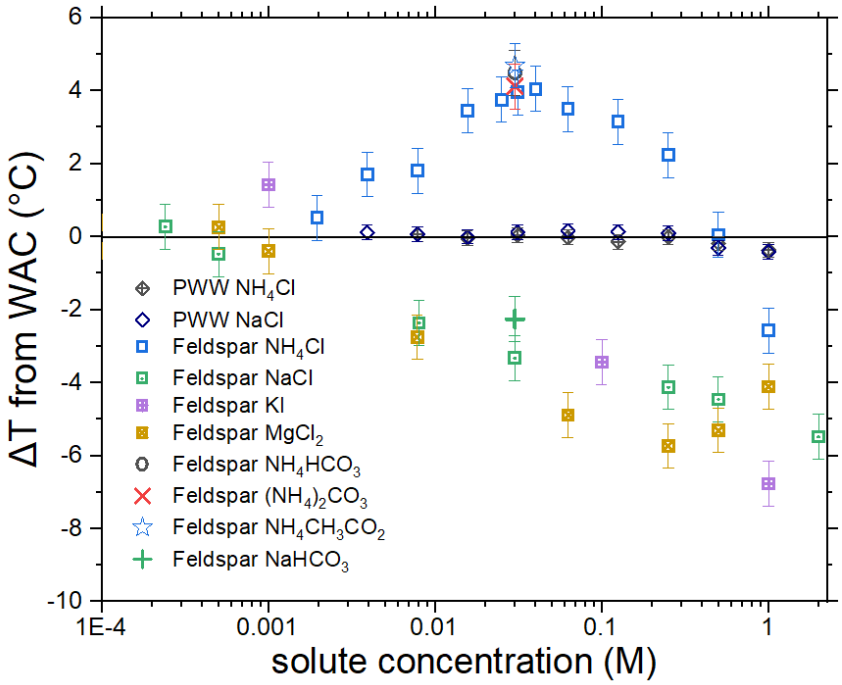

Figure 2: Deviation of nucleation temperature from that predicted by the WAC for the nucleators pollen washing water and BCS376 feldspar in a variety of electrolytes. $\Delta a_{w,het}$ was in both cases calculated from the pure water measurement for both nucleators giving $\Delta a_{w,het} = 0.117$ for BCS376 and $\Delta a_{w,het} = 0.146$ for PWW. Confidence intervals were calculated using a Monte-Carlo simulation described in section S2 of the supplementary information.

In contrast, Fig. 2 shows that heterogeneous ice nucleation induced by feldspar did not obey the WAC. As expected the measurements for BCS376 in pure water indicated essentially identical activity to that reported in Atkinson et al.[15] Figure S1 in the supplementary information shows a comparison of active site density demonstrating this. At solute concentrations below 5×10^{-4} M, all measurements were compatible with the WAC. At higher concentrations however, dissolved NaCl and $MgCl_2$ caused steadily decreasing negative deviations from the expected colligative freezing temperature, indicating an inhibition of heterogeneous nucleation. At 2 M this deviation is as much 6°C. Increasing concentration of NH_4Cl caused a steadily increasing positive deviation from the WAC up to 0.03 M, where a nucleation temperature 4°C higher than expected was found. Measurements conducted using 0.025 M and 0.04M NH_4Cl gave similar freezing temperatures, suggesting that the maximum enhancement due to ammonium occurs in this sort of concentration range. Other ammonium salts tested generated similar or slightly larger enhancements at 0.03M, up to 4.5°C, strongly suggesting that concentration of NH_4^+ is the critical factor defining enhancement ice nucleation. At still higher concentrations ice nucleation was anomalously suppressed by NH_4Cl. $MgCl_2$ and KI generate broadly similar degrees of non-colligative suppression to NaCl.

It seems obvious from these data to conclude that there are two competing effects; an enhancement associated with the presence of NH_4^+ ions and a deactivation associated with all electrolytes, including those containing NH_4^+ ion. The degree of suppression observed appears to depend to some extent on the nature of the electrolyte. Experiments using KI revealed a small enhancement at 1×10^{-3} M as reported by Yun et al.[28] for KNO_3. These enhancements are much smaller than those reported by Perkins et al.[27] in potassium salts. Higher concentrations of KI suppressed ice nucleation to a degree similar to other non-ammonium salts.

These data are essentially compatible with those reported by Whale et al.[23] and Kumar et al.[22] In particular, Figure 3 of Kumar et al.[22] reports very similar trends for ice nucleation by feldspar, both in

terms of enhancement by NH_4^+ and suppression by other salts. In Kumar et al.[22] the maximum observed nucleation temperature was about -21°C with a similar maximum enhancement of about 4°C observed. This occurred at the higher concentration of 0.103 M NH_4Cl solution, more concentrated than the concentration of maximum enhancement found here. The study of Whale et al.[23] found a smaller maximum increase in freezing temperature of around 3°C with identical freezing temperatures found in 0.15 M and 0.015 M solutions suggesting that Whale et al.[23] missed the concentration of peak effect, concluding incorrectly that observed maximum increase in freezing temperature was due to a saturation effect.

Taking these new data with previous measurements we can conclude that a) the maximum degree of ammonium-induced enhancement of ice nucleation by feldspar is around 4°C or a little more, irrespective of the nucleation temperature of the feldspar in pure water b) all ammonium salts tested to date enhance ice nucleation by feldspar. The list of ammonium salts which have been tested now stretches to NH_4Cl, NH_4NO_3, $(NH_4)_2SO_4$, NH_4HSO_4, NH_3OH, NH_4HCO_3, $(NH_4)_2CO_3$ and $NH_4CH_3CO_2$ c) the concentration NH_4^+ is likely a key factor for enhancement of ice nucleation by feldspar and d) that ice nucleation by feldspar is suppressed by all salts, including ammonium salts, more than would be anticipated by the WAC. In the case of the ammonium salts this inhibition is overcome by the enhancing effect of ammonium at lower concentrations.

The interaction of the NH_4^+ ion with ice

As discussed in the introduction, enhancements to heterogeneous ice nucleation are observed across multiple inorganic nucleators, not just feldspar, when ammonium is present. What then is special about the ammonium cation and why does it enhance heterogeneous ice nucleation? Kumar et al.[22] argued that NH_3 formed from excess NH_4^+ adsorbs to the surface of feldspar, providing multiple hydrogen bonding opportunities directed into the water on the surface, enhancing ice nucleation effectiveness while Whale et al.[23] mentioned that ion adsorption, ion exchange with the substrate or an unknown aqueous phase effect could all potentially explain the observations. Molecular dynamics simulations aimed at resolving the question looking at both kaolinite[30] and feldspar[43] substrates found no enhancements to nucleation in the presence of NH_4^+. In total, there is no clear picture of why NH_4^+ can enhance ice nucleation, or why other salts have non-colligative impacts on some nucleators.

It has long been known that NH_4^+ has an unusual relationship with water and ice, being isostructural with the H_2O molecule.[44] Indeed, NH_4F is thought capable of forming co-crystals with water ice,[45, 46] meaning that individual NH_4^+ cations can take the place of water molecules in the ice lattice. Other ammonium salts do not form co-crystals with ice, presumably because other anions do not fit into the ice lattice as F^- is apparently able to. The difference between NH_4^+ and the water molecule is the number of hydrogen bonds donated and accepted. H_2O donates two bonds and accepts two bonds while NH_4^+ donates four bonds.

Recently, it has been found that NH_4F can act as a hydrogen disordering agent for ice.[47-49] The most profound impact of this is that water doped with small quantities of NH_4F cannot be frozen into ice II, the phase of ice stable at pressures above 0.2 GPa and below -40°C. The structure of ice II relies on an ordered hydrogen bond network[47] and small amounts of NH_4F prevent its formation because the differences in number of bonds accepted and received when NH_4^+ and F^- replace water molecules disrupts this order.

Hydrogen ordering in ice I_h

To understand the possible role of NH_4^+ in heterogeneous ice nucleation we must consider the structure of ice which nucleates at atmospheric pressure. The third law of thermodynamics dictates that the ice I_h structure, which is stable at atmospheric pressure and temperatures below 0°C, cannot be the ground state of the ice crystal because it is hydrogen disordered and its configurational entropy will therefore always be greater than zero. Linus Pauling calculated the residual entropy of a disordered ice I crystal

to be $R\ln(3/2)$.[50] Due to the slow kinetics of the phase transition to the ordered phase pure water ice does not order on cooling to low temperatures.

It was eventually found that an ordered form of ice I, named ice XI, could be produced by doping the ice with KOH.[51] At this point, it was determined that ice I_h is the stable phase above about -201°C while below that temperature ice XI is stable.[51] Structurally, they differ only in that ice XI, shown in Fig. 3(a), is hydrogen ordered, meaning protons adopt the same locations throughout the crystal, while ice I_h is hydrogen disordered, meaning that the orientation of individual water molecules is random, although constrained by the Bernal-Fowler ice rules, essentially meaning that only one hydrogen can sit between each pair of oxygen atoms.[52]

It is possible to calculate the Gibbs free energy of ice XI as a function of temperature from the equation of state of ice Ih[53] if it assumed that the enthalpy of the ice I-ice XI phase transition doesn't change with temperature. In this way it can be shown that a hypothetical bulk ice XI would melt into liquid water at about -29°C demonstrating substantially lower stability than ice I_h at the temperatures of interest for heterogeneous ice nucleation. Details of this calculation can be found in section S3 of the supplementary information, where Fig. S3 shows the stabilities of ice I_h, ice XI and supercooled water. Clearly, ordered, low entropy ice is less stable than completely disordered, high-entropy ice at the temperatures (>-35°C or so) generally of interest in the study of heterogeneous ice nucleation. While we should not expect ice XI to nucleate at temperatures relevant for heterogeneous ice nucleation if a nucleator tends to induce formation of partially hydrogen-ordered ice clusters we might expect that ice to be less thermodynamically stable than completely disordered ice.

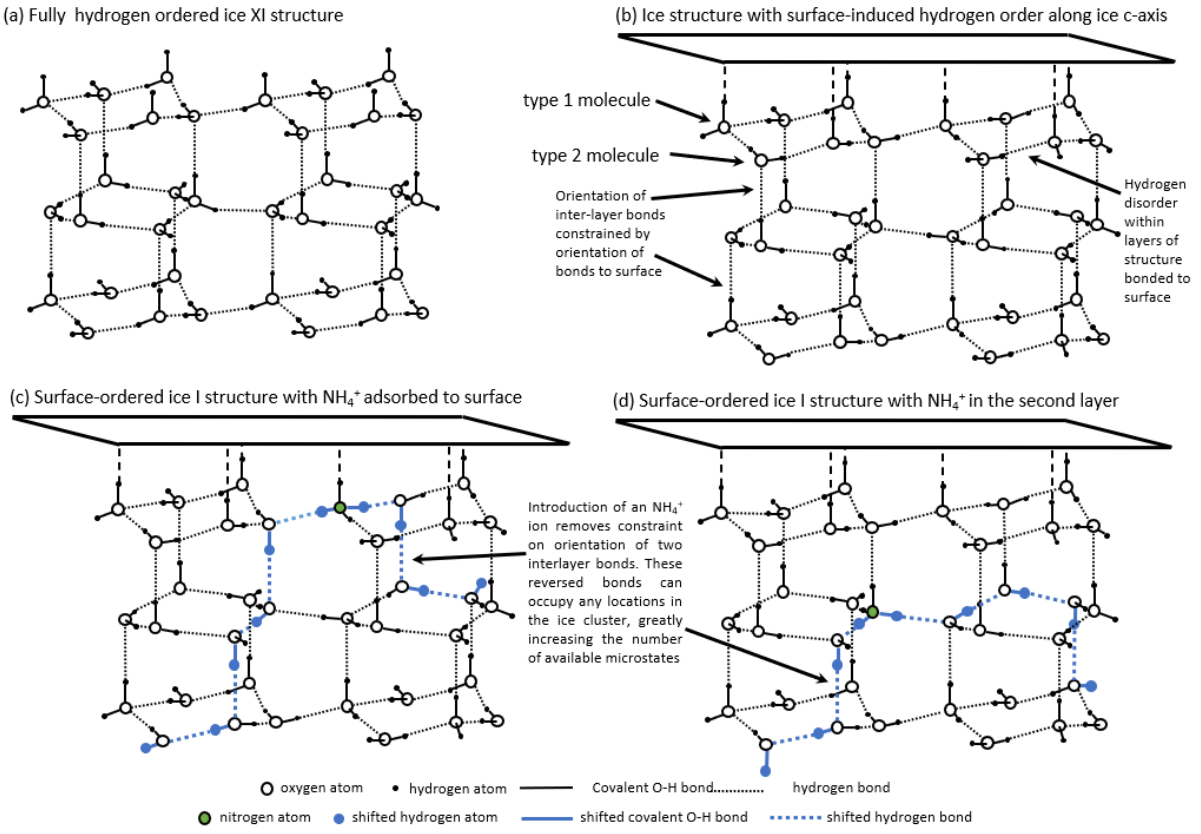

Figure 3: Schematic showing (a) the structure of fully hydrogen-ordered ice XI (b) a possible structure of ice bound to a nucleating substrate which induces orientation of hydrogen atoms in the contact layer towards itself (c) a possible structure of a similar ice crystal with one water molecule in the contact layer replaced by an NH_4^+ ion (d) a possible structure of a similar ice crystal with one water molecule in the second bilayer replaced by an NH_4^+ ion. In structures (c) and (d) two interlayer bonds can reverse

their orientation compared to structure (b). As there is no constraint on which bonds in a bilayer are reversed this offers the structure many more possible microstates, increasing its entropy.

The role of NH_4^+ in heterogeneous ice nucleation

Neville Fletcher suggested in 1959[54] that pristine basal faces of AgI and PbI_2, which are polar[55] would nucleate a partially hydrogen-ordered, low entropy form of ice. These nucleators are thought to be effective because their ionic surfaces can bond to water molecules and their structural similarity to ice means that interfacial water molecules adopt ice-like spatial locations, reducing the free energy barrier to nucleation, an epitaxial mechanism.

As discussed by Fletcher,[54] on such a surface, the energy of the interface with water will be minimized when the O-H dipole of a water molecule is parallel to the local electric field. The oxygen atoms of ice I_h can be thought of as forming a layered structure, with each bilayer consisting of puckered 6-member rings of water molecules. In the bilayer next to the nucleating surface (hereafter the 'contact bilayer') there are two types of molecule. 1) Those with a bond to the surface and 2) those with a bond to the second layer of water molecules. Fig. 3 (b) shows a schematic of an ice I_h crystal adhered to a surface with water molecules next to the nucleating surface oriented in this manner. The orientation of the interlayer bonds of the first class of water molecules constrains the orientation of the second class of water molecules as both hydrogen atoms of these molecules must remain associated with in-layer bonds if there are to be enough in-layer hydrogens to satisfy the Bernal-Fowler ice rules. This means only lone pairs will be available to bond to the next ice bilayer. As such, orientational order will be transmitted through the entire ice-like structure. It is important to note that the structuring does not imply an ice XI structure of the type shown in Fig. 3 (a) as the in-layer bonds will still be disordered, as shown in Fig. 3 (b). The same idea holds with the direction of all bonds reversed, in the case of a surface with positive charge or polarity. The entropy of polar ice I of the type shown in Fig. 3 (b) is thought to be close to $R \ln 20^{\frac{1}{24}}$, 1.04 J K^{-1} mol^{-1} as calculated by Lipscomb[56] meaning it is substantially is more ordered than Ice I, whose entropy is approximately $R \ln \frac{3}{2}$, 3.37 J K^{-1} mol^{-1}.

Fletcher[54] concluded that the polar basal face of AgI would mostly likely not nucleate ice well because it presents only either Ag^+ or I^- ions to water and would therefore template formation of partially hydrogen ordered ice-like clusters, which would, due to their low entropy, have a low thermodynamic stability and therefore a low nucleation rate. Instead, he proposed that the prism faces of AgI most likely nucleate ice. These present alternating Ag^+ and I^- ions and would be capable of nucleating a cluster with a fully disordered ice I_h structure, except in the first bilayer, which would be constrained to a single arrangement possessing hydrogen bonds of alternating direction.

The proposed role of NH_4^+ in enhancing heterogeneous ice nucleation is shown schematically in Fig. 3(c) and (d). In Fig. 3 the polarity of the nucleating surface requires a proton to sit on all bonds between the surface and the first ice bilayer. If an NH_4^+ ion replaces a water molecule in the first ice bilayer it can both bond to the nucleator surface and donate three protons to the in-layer hydrogen bond network. In this way the obligation to donate a bond out-of-layer enforced on half the molecules in the structure is broken. Similarly, the obligation to bond in-layer forced on the other half of the molecules is broken. For each NH_4^+ ion in the contact bilayer, two of the hydrogens bonds to the next layer can be reversed. This will offer an ice germ more possible microstates and increase its entropy. In effect, the critical cluster will be able to adopt a more disordered, stabler structure, while still forming an energetically favorable interface with the nucleator surface. This will increase the thermodynamic driving force to nucleation, raising nucleation temperature.

If an NH_4^+ ion enters the second bilayer, as shown in Fig. 3(c) only this bilayer and those further from the surface are disordered; the entropy of bilayers closer to the nucleator surface will remain unchanged. If the polarity or charge of the nucleating surface is such that the lone pairs rather than the protons of

contacting water molecules are directed into the surface then NH_4^+ induced disorder will propagate from higher bilayers towards the nucleating surfaces.

In the picture presented so far it has been assumed that surfaces induce orientation of all water molecules in the contact layer between critical cluster and nucleator. This need not be the case for NH_4^+ to have an effect, as any partial induced orientation will necessarily result in a lower entropy, less stable structure which might be then disordered by the presence of NH_4^+ although, clearly, the magnitude of the effect will be lessened. Further, the arguments put forward in this paper are based upon nucleation of ice I_h but apply also to nucleation of cubic ice I_c and stacking disordered ice I_{sd}, which are similarly layered structures. All water ices have very nearly the same configurational entropy due to hydrogen disorder[57] and it is not expected that the disordering mechanism should apply differently to different ice phases. A related point is that the arguments above apply equally well to ice I_h bound to a surface by the basal face and by the primary prism plane.

It is also worth discussing the nature of the phase nucleated by nucleators which tend to form polar ice clusters in the absence of NH_4^+. As mentioned, Fletcher[54] envisioned that in pure water the basal plan of AgI doesn't nucleate ice as the low-entropy phase templated is less stable than the disordered phase templated by the prism faces of AgI, despite the inferior lattice match of the prism faces. For the other nucleators enhanced by NH_4^+, feldspar, Gibbsite, kaolinite and mica, there is no obvious second crystal face which might reasonably be expected to nucleate ice. As such, it seems more likely that either a somewhat ordered crystal is nucleated from pure water, or that the energy cost of having some bonds in the contact layer oriented unfavorably contributes to the energy barrier to nucleation of a disordered critical cluster. In either case the change in entropy calculated next will have the same impact on nucleation rate and measured nucleation temperatures.

The entropy of a heterogeneously nucleated critical cluster containing NH_4^+

While a thorough assessment of the impact of the introduction NH_4^+ on the entropy of an ice critical cluster will likely require molecular simulations an estimate of the magnitude of the change can be made. The entropy of a system is related to its multiplicity, Ω, by Boltzmann's equation:

$$S = k \ln \Omega \qquad (1)$$

Where k is the Boltzmann constant. As such, we must calculate the number of energetically equivalent microstates available to the ice critical cluster, with and without ammonium present. The assumption of energetic equivalence implicit in Eq. 1 will not be strictly correct for the smaller clusters discussed here, and calculation of the degree to which it is incorrect is a subject for simulation. As such, subsequent calculations neglect this complication. A second, related, assumption underpinning this work is that the presence of NH_4^+ in the critical cluster doesn't change the energetics of the heterogenous ice nucleation process. Again, it is difficult to assess the impact of this assumption quantitatively however given only a small proportion of water molecules will be replaced by NH_4^+ it seems likely the effect can be neglected. Finally, for most nucleating surfaces, the assumption of total order in the absence of NH_4^+ is most likely incorrect. The implications of this are discussed later.

We shall first consider an ice critical cluster that is attached to the nucleator surface by its basal face and consists of a stack of bilayers each containing an equal number of water molecules. If the nucleating surface has a sufficient negative polarity or charge, as shown in Fig. 3, all protons in the contact and subsequent ice bilayers will point towards the nucleator surface, meaning Ω for these protons equals 1. As mentioned, the entropy of the structure, taking into account this order, is approximately 1.04 J K^{-1} mol^{-1}.[56] Half of the water molecules in each bilayer have a bond to the next bilayer away from the nucleating surface. This number of bonds will be designated n_b meaning each bilayer contains $2n_b$ water molecules. As discussed, and shown in Fig. 3, addition of an NH_4^+ ion to the bilayer in contact with a water-orienting nucleating surface will allow two of the interlayer bonds to the next layer to instead orient with a proton pointing away from the nucleating surface allowing us to calculate that, to

a first approximation, $\Omega = \binom{n_b}{2}$ for that first bilayer, if it contains a single NH_4^+ ion. This is because we have n_b interlayer bonds of which any two can be oriented in the opposite direction to the rest of the bonds. Because the same degree of disorder will be transmitted to each subsequent layer we can estimate that the difference in total configurational entropy between an ice critical cluster containing a single NH_4^+ in the bilayer adjacent to the nucleating surface and one lacking the NH_4^+ ion as

$$\Delta S_{NH_4^+,cluster} = k \ln \left(\frac{n_b!}{2!\,(n_b-2)!} \right)^l \tag{2}$$

Where l is the number of ice bilayers in the critical cluster. The power l occurs because any of the possible arrangements of the first bilayer can be paired with any possible arrangement of the second bilayer, and vice versa, and so on for subsequent layers. For the broader case of $n_{NH_4^+}$ ions in the first bilayer of a critical cluster this can be generalised to

$$\Delta S_{NH_4^+,cluster} = lk \ln \left(\frac{n_b!}{\left(2n_{NH_4^+}\right)!\left(n_b-2n_{NH_4^+}\right)!} \right). \tag{3}$$

We can see that according to Eq. 3 $\Delta S_{n_{NH_4^+},cluster}$ depends on both the lateral extent and depth of the cluster.

Equation 3 can be generalised to account for situations where bilayers are of unequal size, as would be the case for any likely ice cluster geometry except a hexagonal prism, if it is assumed that all hydrogen bonds reversed by the presence of NH_4^+ bond to the next ice bilayer. If a reversed hydrogen bond forms part of the interface of the critical cluster with liquid water, rather than a bond to next ice bilayer, it would not be able to affect the orientation of bonds in that next ice bilayer. This would reduce the number of configurations available to the cluster. The probability of this occurring will increase as the difference in size between successive layers increases. Assuming that the effect is negligible (essentially that there is a small difference in the extent of the top and bottom layers of the cluster) we can write

$$\Delta S_{NH_4^+,cluster} = lk \ln \left(\frac{\tilde{n}_b!}{\left(2n_{NH_4^+}\right)!\left(\tilde{n}_b-2n_{NH_4^+}\right)!} \right) \tag{4}$$

where $\tilde{n}_b$ is the mean number of water molecules in the l ice bilayers forming the critical cluster. Clearly, these calculations neglect the reduction in entropy due to NH_4^+ ions replacing water molecules, meaning the replaced site will have fewer possible orientations, however it is reasonable to treat this effect as minor as the number of orientations allowed to the replaced water molecule is already severely constrained in the polar ice structure. Eqs. 2, 3 and 4 calculate the total entropy of an ice cluster. To find the molar entropy we must divide by the number of water molecules in the cluster and multiply by Avogadro's number. The number of molecules in the critical cluster is given by $2n_b l$. As such we can write:

$$\Delta S_{NH_4^+} = \frac{R}{2\tilde{n}_b} \ln \left(\frac{\tilde{n}_b!}{\left(2n_{NH_4^+}\right)!\left(\tilde{n}_b-2n_{NH_4^+}\right)!} \right) \tag{5}$$

Where $\Delta S_{NH_4^+}$ is the molar difference in entropy between molecules in an ice cluster ordered by a surface and a cluster with $n_{NH_4^+}$ NH_4^+ ions in the contact bilayer, and R is the gas constant.

Fig. 4 (a) shows the variation in $\Delta S_{n_{NH_4^+}}$ for one, two and three NH_4^+ ions in the contact layer for various values of $\tilde{n}_b$ according to Eq. 5. It is clear that inclusion of more NH_4^+ ions leads to a greater increase in cluster entropy, and will therefore give a greater increase in nucleation temperature, consistent with the experimental data in Fig. 2 where higher concentrations of NH_4^+ lead to larger increases in freezing temperature. It is also clear that differently shaped clusters will see different changes in entropy with addition of ammonium ion as entropy difference per molecule is larger for clusters with a smaller lateral extent.

According to classical nucleation theory (CNT) the size of heterogeneously nucleated ice critical clusters varies relatively little with large changes in nucleation rate, falling in a range from a few hundred to a few thousand water molecules at most.[58] As such, the range of water molecules per bilayer shown in Fig. 4 (a) (50-1000) covers the likely range of cluster sizes and geometries for heterogeneous ice nucleation in the temperature range of interest for this study. All things being equal, larger clusters will tend to have more molecules per bilayer, hence smaller clusters will be impacted more the presence of an NH_4^+ ion, as might be expected.

Fig. 4 (b) shows the variation in $\Delta S_{NH_4^+,cluster}$ with cluster size for a cluster three bilayers deep, according to Eq. 4. Clearly, taller, narrower clusters containing an equivalent number of water molecules would gain more entropy, shifting the curves up. The reverse would also be true.

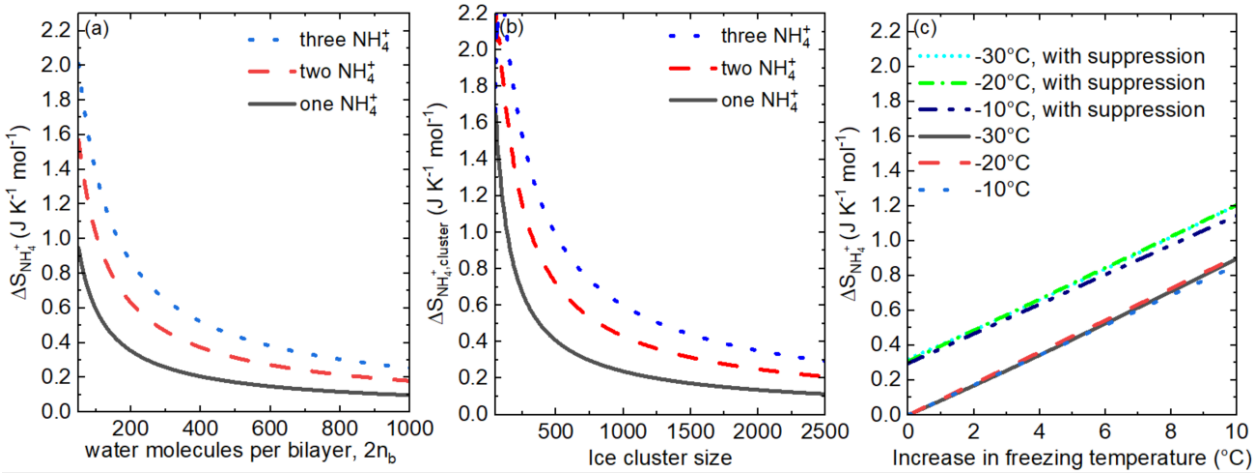

Figure 4: (a) Difference in molar configurational entropy due to presence of one, two or three NH_4^+ ions in in the contact layer of a polar ice cluster as a function the number of water molecules in each ice bilayer, according to Eq. 5. (b) Difference in molar configurational entropy as a function of cluster size for a cluster containing three ice bilayers, according to Eq. 4. (c) Difference in molar configurational entropy required to generate a given increase in heterogeneous freezing temperature according to Eq. 6. In all cases, a value of f_{het} which gave nucleation rate of 10^{10} cm^{-2} s^{-1} at the indicated starting temperatures was found. The entropy change is that required to give the same nucleation rate at the warmer temperature. For the -10°C line f_{het} = 0.0259, for the -20°C line f_{het} = 0.117 and for -30°C line f_{het} = 0.281. To generate the 'with suppression' lines the experimental $\Delta\mu_s$ due to 0.03M of NaCl, 82 J mol^{-1} was subtracted, to account for the anomalous suppression to heterogeneous ice nucleation by feldspar that appears to be common to all salts.

It will be apparent that this analysis contains a several simplifying assumptions. Due to the logarithmic nature of the Boltzmann equation the assumption of complete transmission of disorder between layers makes a fairly small difference to the entropy change due to NH_4^+. The section S7 of the supplementary

information details calculations of $\Delta S_{NH_4^+,cluster}$ for ice clusters of 470 molecules of approximately spherical cap geometry showing that these more tapered shapes retain over 75% of the entropy change of a cluster with equal numbers of molecules in each bilayer, as calculated by Eq. 4. This cluster size was chosen as it is the size of the critical cluster for nucleated by feldspar in the CNT formulation used later in this paper. Larger clusters of similar geometry will retain more of the entropy change calculated by Eq. 4 while smaller cap-shaped clusters containing only 200 water molecules still retain more than 70% of the entropy of equivalently sized cluster with equally sized layers.

All of the above assumes the nucleator tends to induce formation of ice clusters which are completely ordered orthogonal to the nucleating surface and completely disordered parallel to it, and so have the polar ice entropy calculated by Lipscomb.[56] It is possible to adapt the calculations above for cases where ice is partially disordered along its c-axis, meaning more than half but less than all of the inter-layer protons point towards the nucleator surface. This is discussed in section S8 of the supplementary information. As might be expected, larger numbers of NH_4^+ ions are required to generate a given $\Delta S_{NH_4^+,cluster}$ when the fraction of bonds oriented by the surface is lower. As shown in Fig. S6, replacement of small numbers of water molecules with NH_4^+ ions can still cause significant entropy changes to partially ordered clusters. For instance, the introduction of five NH_4^+ molecules into the contact bilayer of a cluster containing 200 molecules in the contact bilayer ($\tilde{n}_b = 100$) where 85% of bonds along the c-axis are oriented generates a $\Delta S_{NH_4^+}$ of 0.65 J K^{-1} mol^{-1}. Two NH_4^+ ions are required to give a similar entropy change in a completely oriented cluster.

It is important to note that Eqs. 4 and 5 hold best for cases where there are relatively few NH_4^+ ions in the critical cluster as they assume that the entropy of each bilayer is unaffected by the presence of the ions, which, as mentioned above, is a good approximation, rather than being strictly true. More complex calculations would need to be made for structures where NH_4^+ ions are present in layers above the contact layer. Similarly, for the case where water lone pairs are oriented into the surface in the contact layer NH_4^+ above the contact layer would induce disorder, and a different calculation would have to be made. In total, the complexity of the problem is difficult to approach thoroughly with calculations of the type conducted here and simulations will likely be required for a thorough analysis of all possible permutations of the mechanism. Nevertheless, it seems likely that the order of entropy change calculated and shown in Fig. 4 is reasonable.

The impact of NH_4^+ ions on heterogeneous ice nucleation temperature

Having estimated the potential increase in entropy of partially ordered ice clusters due to the presence of NH_4^+ we now assess the increase in critical cluster stability needed to generate the experimentally observed changes in the temperature of ice nucleation induced by feldspar, assuming that feldspar tends to form polar ice-like clusters of the type shown in Fig. 3(b).

The underlying assumption behind the following approach is that all the anomalous differences between the observed freezing temperatures and those predicted by the WAC are due to solute-induced changes in the chemical potential of the ice cluster nucleated by a water-orienting surface caused by the presence of solutes. Fig. 2 clearly shows that in the case of ice nucleation by PWW dissolved NaCl and NH_4Cl have exactly the same impact on nucleation temperatures. We can therefore confidently state that any impacts that NaCl and NH_4Cl have on diffusion activation free energy or the interfacial tension between ice and water are identical when the nucleator is PWW. It is possible that this is untrue when a nucleated ice cluster is polar, as is hypothesized to be the case for ice nucleation by feldspar. However, in the absence of suitable theory to account for any such effects, or even to predict whether they would help or hinder nucleation, we must assume that they are negligible for the purposes of these calculations.

According to classical nucleation theory (CNT), the stationary rate of heterogeneous nucleation, measured in nucleation events per surface area per unit time, can be found as[59]

$$J_{het}(T) = \frac{kT}{h} n_l \exp\left(\frac{-\Delta G_{diff}}{kT}\right) \exp\left(\frac{-f_{het}\Delta G_{crit}}{kT}\right) \quad (6)$$

Where k is the Boltzmann constant, T is absolute temperature, h is the Planck constant, n_l is the number density of water molecules at the ice nucleus/water interface ($\approx 10^{15}$ cm^{-2}), ΔG_{crit} is the height of the free energy barrier to forming a critical cluster of ice molecules and ΔG_{diff} is the diffusion activation free energy, calculated here using equation S5 derived by Koop and Murray.[3] It is assumed here that $\Delta G_{diff}(T)$ is unaffected by the presence of dilute salts, as mentioned above, is an assumption but is qualitatively supported by simulations.[60] f_{het} is a parameter taking values between zero and one. When $f_{het} = 1$ the expression is equivalent to that for homogeneous nucleation[3] while for $f_{het} = 0$ the barrier to nucleation disappears. It is usual to relate f_{het} to a contact angle between a nucleating substrate and a spherical cap shaped ice cluster in the manner described by Eq. S8. How close this description is to the geometry of real ice critical clusters is not presently known.

The height of the free energy barrier to nucleation is given by

$$\Delta G_{crit}(T) = \frac{16\pi v_i^2 \sigma_{iw}^3}{3(\Delta\mu)^2} \quad (7)$$

where v_i is the molecular volume of a water molecule in ice, σ_{iw} is the ice-liquid interfacial energy and $\Delta\mu$ is the driving force for ice nucleation, the difference in chemical potential between liquid water and ice, $\Delta\mu = \mu_{water} - \mu_{ice}$.

It is generally accepted that homogeneous ice nucleation leads to the formation of stacking disordered ice, ice I_{sd}, which has a mixture of hexagonal and cubic sequences.[61-64] Ice I_{sd} is metastable with respect to normal ice I_h so its vapour pressure is higher. For heterogeneous ice nucleation it is not clear what phase will nucleate as direct observation of the critical cluster is not presently possible.[65] Hence, while the enthalpy difference between the ice I_{sd} and ice I_h can be estimated reasonably[3] here it is assumed that the hexagonal phase forms. This allows use of an existing water activity dependent parameterization for σ_{iw} in the presence of solutes, developed by Barahona[66], which is given in equation S6. The parameterisation predicts an increase in σ_{iw} with both increasing a_w and increasing T which is qualitatively consistent with the result of molecular simulations of homogeneous ice nucleation.[60, 67]

In the current formulation of CNT, considering both colligative impacts on ice nucleation and the anomalous effects reported here and elsewhere the driving force to nucleation, $\Delta\mu$, is given by

$$\Delta\mu(T, a_w) = kT \ln\left(a_w \left(\frac{p_w(T)}{p_i(T)}\right)\right) + \Delta\mu_s \quad (8)$$

where $p_w(T)$ is the vapor pressures of supercooled water and $p_i(T)$ is the vapour pressure of ice, both parameterised by Murphy and Koop.[68] a_w is the water activity of the solution, calculated using the AIM model[69] and assumed to change little with temperature.[20] $\Delta\mu_s$ is the anomalous change in chemical potential due to the presence of a solute.

We wish to compare $J_{het}(T)$ calculated using Eq. 6 to experimental results. Ice nucleation by feldspar is known to be site-specific, meaning that small patches of the surface are responsible for experimentally observed ice nucleation activity.[70, 71] For the PWW we do not know the quantity or surface area of the ice-active substance present in each droplet. As such, we cannot straightforwardly work out J_{het} for feldspar or PWW for the data reported in Fig. 1 and Fig. 2. Happily, we are interested in changes in nucleation temperature between experiments that detect essentially identical nucleation rates so we can simply choose an 'observable' J_{het} then calculate the change in driving force required to generate the experimentally observed change in average nucleation temperature.

Here, observable J_{het} for feldspar is taken to be 10^{10} cm^{-2} s^{-1}. The reasons for this are discussed in the SI in some depth. Briefly, it is possible to estimate the number of ice nucleation active sites per feldspar surface area per droplet at the temperatures used in thus study due to the work of Holden et al.[70] and possible to estimate the size of an ice nucleation active site using CNT, if the critical cluster is assumed to be spherical cap. Combining these two things a likely order of nucleating surface area per droplet can be determined. It is important to note that subsequent arguments do not depend strongly on the specific value of J_{het} used. The value of $\Delta\mu_s$ determined varies by less than 10% between a chosen rate of 1 cm^{-2} s^{-1} and 10^{20} cm^{-2} s^{-1}.

In this formulation of CNT the change in nucleation rate due to the WAC can be calculated using equations 6, 7, 8, S5 (to determine $\Delta G_{diff}(T)$) and S6 (to determine $\sigma_{iw}(T, a_w)$) if $\Delta\mu_s$ is taken to be zero. Fig. S4 shows that for ice nucleation induced by PWW in NaCl and NH_4Cl experimentally measured reductions in nucleation temperature shown in Fig. 2 can be accounted for using a single value of f_{het}. This demonstrates that CNT, appropriately adapted to account for changes in a_w, can account for variation in ice nucleation temperature in PWW in the presence of solutes.

Clearly, the anomalous changes in nucleation temperature observed for feldspar can't be accounted for in this way so we must consider $\Delta\mu_s$.We can solve Eq. 6 to find the value of f_{het} required to give a nucleation rate of $J_{het} = 10^{10}$ cm^{-2} s^{-1} at -12.8°C, the average nucleation temperature observed for the feldspar suspension used in pure water. In this way f_{het} = 0.0438 was determined as characteristic for the feldspar in the experimental system used. Note that this value is entirely specific to the system, and the somewhat arbitrary choice of J_{het}, and should not be taken as being characteristic for feldspar as an ice nucleator generally. We can then find the $\Delta\mu_s$ required to shift nucleation temperature from -12.8°C, as observed in pure water, to -16.4°C, as observed in 0.03M NaCl by using Eq. 6 and Eq. 8 at the lower temperature and a_w. In this way $\Delta\mu_s$ was found to be 78.0 J mol^{-1}. We can then solve Eq. 6 again to find the $\Delta\mu_s$ required to induce nucleation at -9.2°C, the average nucleation temperature for feldspar in 0.03M NH_4Cl, giving -86.3 J mol^{-1}. These values take into account the colligative effects predicted by the WAC, although these are so small as to be effectively negligible, due to the low solute concentration used. It can be seen in Fig. 1 (a) and (b) that 0.03M NH_4Cl and NaCl cause no measurable change in freezing temperatures of droplets containing PWW.

To facilitate estimation of the amount of stabilisation of the critical ice cluster formed by feldspar that would need to be provided by its NH_4^+ induced disordering to account for the observed changes in nucleation temperature we shall assume $\Delta\mu_s$ is composed of the enhancing and inhibitory influence due to solutes giving

$$\Delta\mu_s = \Delta\mu_{electrolyte} - \Delta\mu_{NH_4^+,experiemnt} \quad (9)$$

where $\Delta\mu_{electrolyte}$ is the anomalous reduction in driving force due to the presence of all salts, hypothesised later to be related to increased effective solute concentration in the vicinity of a charged or polar nucleating surface, and $\Delta\mu_{NH_4^+,experiment}$ is the increase in driving force due to favourable disordering of the ice germ allowed by the presence of NH_4^+. Using Eq. 9 implies that all anomalous

changes in nucleation rate, both enhancement and suppression, are due to change in the stability of ice rather than changes in the interfacial tension, changes in f_{het} caused by the solutes, or changes in the activation energy, which may not be physically accurate. However, the magnitude of $\Delta\mu_{NH_4^+,experiment}$ determined would not be changed if the magnitude of the anomalous suppression were accounted for differently.

As there is no NH_4^+ present in the 0.03M NaCl experiment we can use Eq. 9 to calculate that $\Delta\mu_{electrolyte}$ is 78.0 J mol^{-1} for 0.03M NaCl. Using Eq. 9 and assuming that $\Delta\mu_{electrolyte}$ is similar for NaCl and NH_4Cl at similar concentration we can calculate that $\Delta\mu_{NH_4^+}$ is 164.3 J mol^{-1}. If it is assumed that this change is entirely entropic in origin, we can divide this by the absolute nucleation temperature to find that the configurational entropy difference between the structure nucleated in the absence of NH_4^+ and that nucleated in the presence of NH_4^+, $\Delta S_{NH_4^+,experiment}$, is 0.62 J K^{-1} mol^{-1}.

As discussed, the entropy change of polar ice clusters expected due to addition of ammonium ions depends on the shape and size of the cluster. The geometry of heterogeneously nucleated ice clusters is discussed in section S6 of the supplementary information. Assuming spherical cap critical cluster geometry, a nucleation rate of 10^{10} cm^{-2} s^{-1} requires f_{het} = 0.0438 which can be shown to correspond to spherical cap shaped critical cluster containing 470 water molecules, using Eq. S7. This spherical cap is the height of ice 3 bilayers, as shown in Table S1. If we look at Fig. 4 (b) we can see that two NH_4^+ ions in the contact bilayer of such a cluster would increase its entropy by 0.75 J K^{-1} mol^{-1}. As mentioned, $\Delta S_{NH_4^+}$ will only be around 75% of that of a cluster with evenly sized layers as calculated by Eq. 5, giving a value of 0.57 J K^{-1} mol^{-1}, as detailed in Table S2, close to the value determined for $\Delta S_{NH_4^+,experiment}$.

In a 0.03M solution of NH_4Cl there will be only 1 NH_4^+ ion per approximately 1850 water molecules suggesting that on average the critical cluster may contain less than one NH_4^+ ion. However, it is likely that there will be a higher than bulk concentration of ions near a charged or polar nucleating surface capable of orienting water molecules than in bulk solution. As such having two or more NH_4^+ ions in a critical cluster does not seem implausible.

More generally, it is possible to calculate the $\Delta S_{NH_4^+}$ required to generate a given increase in nucleation temperature using the method described above. Fig. 4 (c) shows the outcome of these calculations for heterogeneous nucleation of ice, starting from various temperatures, and both accounting for the general ice nucleation suppressing effect of ions demonstrated in Fig. 2 and not accounting for it. It can be seen that the required entropy differences are in the range accounted for by the proposed disordering mechanism.

While these calculations make various assumptions of uncertain veracity it seems reasonable to conclude that the amount of stability provided to an otherwise-polar ice cluster by the presence of NH_4^+ ions is of the order to drive the increases in nucleation temperature observed experimentally. Depending on interfacial concentration of NH_4^+, the geometry of the critical cluster and the degree of order imposed by the nucleator quite a large range of enhancements are conceivable, as shown in Fig. 4. Experimental results presented here suggest that the maximum increase in nucleation temperature on feldspar due to the presence of NH_4^+ ions is around 4.5°C. The proposed disordering mechanism is easily capable of providing the enough stability to a critical cluster to account for this change. An upper limit to the entropy change due to disordering of is the difference in entropy between polar ice and completely disordered ice, 2.33 J K^{-1} mol^{-1}. In reality the upper limit is likely somewhat lower as incorporation of larger number of NH_4^+ ions into an ice cluster will at some point become energetically unfavourable. However, Fig. 4 shows that even the 9°C enhancement observed by Worthy et al.[36] for kaolinite requires only around 1.1 J K^{-1} mol^{-1} of disordering which can be accounted for by including only 3 NH_4^+ ions in a cluster of the order of size anticipated by CNT.

The role of anions

The experimental data presented in Fig. 2 and elsewhere[22, 23] suggests that the ammonium effect on ice nucleation caused by feldspar is anion-independent. The data of Reischel and Vali[29] suggests that the identity of the anion does matter for ice nucleation by AgI, however this is likely influenced by the variable solubility of AgI in the presence of different anions.

It is well known that freezing ice excludes most solute molecules, with progressive concentration of liquid surrounding growing ice occurring until the eutectic composition is reached. It seems likely that a critical ice germ would be free of solute molecules as they would presumably substantially raise the free energy of any ice-like cluster they were part of, favoring a return to a liquid-like arrangement. Indeed, the so-called 'unmixing' energy required to create a solute free ice germ has been suggested as the origin of the WAC.[66, 72] It is known that NH_4F incorporates readily into ice[45, 46] and also that NH_4Cl is around five times more soluble in ice than HCl, LiCl, NaCl, KCl, RbCl and CsCl.[73] It therefore seems quite possible that NH_4^+ can incorporate into the ice hydrogen bond network without significantly raising the structure's free energy, in contrast to other ions. Given the ice germ likely consists of at most 1000 molecules or so while a 0.03M solution contains, as mentioned, only 1 solute molecule for every 1850 water molecules it seems reasonable to suggest that clusters containing only NH_4^+ and no counter ions could come into existence.

The origin of anomalous suppression of ice nucleation by electrolytes

The necessary proximity of ions to polar surfaces raises a second intriguing possibility; that the non-colligative inhibiting impact of most non-ammonium salts on ice nucleation by feldspar and AgI is due to the energy cost of incorporating the charge balancing adsorbed ions, the effective concentration of which would be increased by the polar surface, into the ice germ anchored to the ice surface. It could also be that the energy penalty of moving these ions away from the surface accounts for the anomalously reduced nucleation rates observed. One or both of these effects may well be the origin of the $\Delta\mu_{electrolyte}$ term introduced above.

Interplay between the enhancing and inhibitory effects on ice nucleation by feldspar must lead to the observed peak in ice nucleation temperatures at an NH_4^+ concentration of 0.03M. The experimental data suggests that the disordering mechanism can work low NH_4^+ concentrations, which is consistent with the framework presented here, and that higher ion concentrations are required before the suppressing effect overwhelms it. Calculation or measurement of ion concentrations near charged and polar surfaces is complex and remains challenging however emerging methods may allow calculations of the likely impact of such effects to be made soon,[74, 75] facilitating comparison with experimental data of the type produced here.

It is perhaps surprising that Zobrist et al.[21] did not see anomalous suppression of ice nucleation activity of AgI by non-ammonium salts. One explanation of this is that, according to Fletcher[54] ice nucleates on the non-polar prism faces of AgI. These would not attract an excess of ions and may not be impeded by the suggested mechanism. However, in the presence of NH_4^+ ions the entropy penalty of ice clusters on the basal face of AgI, which has a better lattice match to ice than the prism face, may be relieved allowing it to take over as the ice-nucleating face.

Suppression of ice nucleation by macromolecules

The anomalous suppression of ice nucleation by AgI by various organics macromolecules[33] is potentially consistent with the idea that the nucleating surface of AgI is polar, contrary to the analysis of Fletcher[54] as such molecules would be likely to bond to polar surfaces. It seems possible that feldspar, mica, kaolinite and Gibbsite will also experience anomalous suppression to their ice nucleation temperatures in the presence of many organic macromolecules. This may plausibly have implications

for ice nucleation in mixed-phase clouds droplets which often contain organic compounds and mineral dusts.

The nature of ice-nucleating surfaces

An important implication of the proposed mechanism is that, if it is correct, ice nucleators whose activities are enhanced in NH_4^+ solution must induce nucleation through the action of polar or charged surfaces capable of orientating water. The nucleators known to respond anomalously to NH_4^+ are AgI, mica, Gibbsite and kaolinite. AgI is one of the examples given by Fletcher[54] and its (100) face is known to be polar.[55] The basal plane of kaolinite, which is thought to be responsible for kaolinite's ice nucleation activity,[76] is also polar.[77] The (001) surface of gibbsite is charged at pH below about 7[78] as it would be in NH_4^+ solutions of the type used for ice nucleation experiments.[25] Mica surfaces are charged at various pHs so are likely also be capable of imposing order on forming ice clusters as discussed later. The (100) face of microcline feldspar, thought to responsible for its activity[16, 79] is, by inspection, also likely to be polar.

It is very important to note that polar surfaces are intrinsically unstable.[80] Polarity compensation can occur either in a manner intrinsic to the crystal (e.g. surface reconstruction), or by the adsorption of ions. The latter scenario was investigated by Sayer and Cox, [55] who found that ions from solution stabilized unreconstructed polar surfaces of AgI on timescales relevant to ice nucleation. Sayer and Cox[55] also provided tentative evidence for ion specificity of the heterogeneous nucleation rate, which would be inconsistent with the WAC. The common observation of site-specificity of ice nucleation[81] may be due, at least in part, to the rarity and instability of polar or charged patches of lattice-matching surface on ice nucleators.

Ice nucleation by feldspar

Considering the case of ice nucleation by feldspar, the calculations performed here to establish the amount of entropy needed to account for the observed maximum enhancement in nucleation temperature were also applied to the data of Kumar et al.[22] which were conducted with much smaller amounts of feldspar in each droplet. This lead to a freezing temperature in pure water of around -26°C against -12.8°C in the present study. They observed a maximum increase in nucleation temperature of 4.5°C. By using the suppression observed for a Na_2SO_4 with equivalent water activity to calculate $\Delta\mu_{electrolyte}$ a maximum $\Delta\mu_{NH_4^+}$ of 156.6 J mol^{-1} was determined, equivalent to $\Delta S_{NH_4^+,experiment}$ of 0.61 J K^{-1} mol^{-1}, very similar to that determined for the experiments presented here, and similarly consistent with the proposed disordering mechanism.

Whale et al.[82] and Kiselev et al.[83] have shown that microtextural features on feldspars are responsible for their ice nucleation activities and argued that the exposure of different amounts of the (100) face hypothesised to be responsible for the nucleation activity of feldspars[16] may account for the different activities of different feldspars. That roughly the same magnitude of enhancement is observed irrespective of the ice-nucleating effectiveness and quantity of the feldspar used strongly suggests that a similar ice nucleation mechanism is in action in both active and inactive feldspars ice nucleation sites. The disordering mechanism predicts quite small changes in $\Delta S_{NH_4^+,cluster}$ as cluster size varies, as can be seen in Fig. S4(b). As such, different sized patches of (100) face would experience broadly similar enhancements in ice nucleation temperature via the disordering mechanism as be seen in so the idea that more ice nucleation-active feldspars possess larger patches of exposed (100) face seems qualitatively consistent.

Ice nucleation by mica and other water-orienting surfaces

Recently, two studies[84, 85] have found that the ice nucleation ability of natural potassium mica can be substantially increased by ion exchange with H^+, Na^+, Rb^+, Cs^+, Sr^{2+},[85] Ca^{2+}, Mg^{2+} and Al^{3+}.[84] Jin et al.[85] used sum frequency generation spectroscopy (SFG) to show that the mica surfaces which nucleated ice

well oriented water to a lesser extent than those which nucleated ice poorly. This agrees entirely with the mechanism proposed in the present study. Similarly, Abdelmonem et al.[86] found that a sapphire surface nucleated ice best in lower pH conditions and used SFG to show that these conditions led to disordered interfacial water. Again, this agrees with the proposed ammonium-disordering mechanism. We might predict that introduction of NH_4^+ would enhance ice nucleation by sapphire at higher pHs where interfacial water is ordered but not in pH conditions where interfacial water is disordered. Looking forward, SFG might be used to generate a greater insight into the nature of ammonium-induced disordering of ice clusters.

Enhancement of ice nucleation by gaunidinium and biguanidinium

As briefly mentioned in the introduction, it has recently been found that ice nucleation on the positively charged face of $LiTaO_3$ and AgI can be enhanced by addition of HCO_3 and NO_3^- while ice nucleation on the negatively charged face of $LiTaO_3$ can be enhanced by the guanidinium and biguanidinium ions.[34, 35] These papers suggest that the ions tend to encourage the formation of hexagonal ice clusters, thereby favouring ice nucleation. Work by the same authors found that ice nucleation on $LiTaO_3$ and pyroelectric amino acids varied with pH also.[87] It is worth noting that guanidinium and biguanidinium bear a strong structural resemblance to the ammonium ion. Guanidinium consists of three amino group bonded to a central carbon atom for instance. These ions would, if dissolved in an ice structure, offer only hydrogens and no lone pairs to the hydrogen bond network and might therefore be capable of inducing hydrogen disorder in ice. Given that HCO_3 and NO_3^- enhance ice nucleation on the positively charged surfaces it seems possible that these ions, which would donate lone pairs into a hydrogen-bond network, also have a disordering effect when ice is nucleated by a positively charged surface.

Future work should certainly be directed at establishing whether guanidinium and biguanidinium enhance the same range of nucleators as the ammonium ion and at establishing whether the two proposed mechanisms of ice nucleation enhancement, entropically favourable hydrogen-disordering proposed here and enhanced cluster formation as proposed by and Curland et al[34] Javitt et al[35] are compatible and whether they might interact.

Atmospheric implications

As well as being of substantial fundamental interest, the mechanism of ice nucleation enhancement proposed here has important consequences for understanding of heterogeneous ice nucleation in the environment. Kumar et al.[22] and Whale et al.[23] both argued that enhancement of the ice nucleation ability of feldspar could influence cloud properties. If the ice-nucleating sites of most mineral dusts are indeed charged or polar this could also have important implications for their interactions with the soluble organic molecules known to be present in many cloud droplets,[88, 89] particularly organic acids. In general, prediction of the interaction of the interaction of atmospheric ice nucleating particles with solutes, and their aging pathways, may be facilitated by this finding.

Conclusions

To summarize, it is proposed here that the anomalous enhancement of heterogeneous ice nucleation in NH_4^+ containing solutions is due to the relief of unfavorable configurational entropy caused by nucleator-surface-induced ordering of the hydrogen bond networks of ice clusters. The magnitude of the effect is estimated on the basis of statistical mechanical arguments and demonstrated to be capable of accounting for experimentally observed changes in nucleation temperature, in both the present study and previous studies.

If this picture is correct those nucleators which do not respond anomalously to NH_4^+ ions, which includes all biological nucleators that have been tested, amorphous silica and alcohol monolayers, must tend to induce formation of hydrogen-disordered ice clusters while nucleators that are anomalously enhanced by NH_4^+, namely feldspar, mica, kaolinite, Gibbsite and AgI, possess either polar or charged

sites or surfaces responsible for their observed ice nucleation activity. This work is consistent with previous findings of enhancement of ice nucleation in conditions of greater interfacial disorder of water, and ties together the ice nucleation mechanisms of a wide range of inorganic ice nucleators. This has important implications for ongoing work, both experimental and computational, aimed at understanding the mechanism of heterogenous ice nucleation, with further implications for understanding of the role of ice nucleation in the environment.

Experimental Methods

The data shown in Fig. 1 and Fig.2 were produced using a droplet freezing assay essentially similar to that described by Whale et al.[42] The apparatus employs a small (40 mm by 40 mm) aluminium cold stage thermally bonded to a TEC1-12704 Peltier thermoelectric cooler with Arctic Cooling MX-4 thermal compound. A Meerstetter TEC-1091-PT100 Precision Peltier Controller drives the Peltier and allows for precise control of temperature of the coldstage. Temperature is monitored using two Netshushin PT100 platinum resistance thermometers (NR-141-100S-2-1.0-10-2000PLi-A-3) read by a PicoTech PT-104 data logger. The use of redundant PRTs allows detection of any significant temperature gradients or other issues in temperature measurement. The PRTs are embedded directly under the part of the cold stage used for ice nucleation measurements, meaning temperatures are recorded from a point as close to freezing droplets as possible. Quoted measurement uncertainty for the PT100s is ±0.15°C although in practice both PRTs give the same reading to within a much smaller margin, typically 0.05°C. To prevent frost growth from interfering with experiments dry nitrogen gas is flowed over the droplets at a rate of 0.2 l/min. A video camera is used to monitor droplet freezing and custom LabView program used to link temperature measurements to video frames, allowing determination of freezing temperatures of individual droplets and therefore droplet faction frozen and average freezing temperatures.

To conduct the experiments performed in this study arrays of 30 to 40 one µl droplets of the nucleator suspensions were pipetted onto a 22 mm diameter silanized slide (Hampton Research HR3-231) using a Sartorius Picus® electronic micropipette. One µl droplets of appropriate concentrations of salt solutions were then pipetted onto the nucleator-containing droplets to produce 2 µl droplets containing known amounts of the nucleators and known concentrations of salts. The cold stage was then used to cool the droplets at a rate of 2°C per minute while droplet freezing was monitored as mentioned above. The error bars in Fig. 2 were calculated using a simple Monte-Carlo simulation based on that described by Vali.[90] A full description of the process is given in section S2 of the supplementary information.

The BCS376 feldspar sample used was the same powder used in the ice nucleation instrument intercomparison of DeMott et al.[91] and has a BET surface area of 2.6 $m^2 g^{-1}$. The sample was originally obtained from the UK Bureau of Analysed samples and was ground to achieve the measured surface area. Figure S1 shows that the activity of this sample is similar to that of the BCS376 tested by Atkinson et al.[15] The *Betula pendula* pollen sample was purchased from Pharmallerga. The various salts were of reagent grade and purchased from Sigma Aldrich.

Supplementary Material

The online supplementary material contains discussion of the ice nucleation activity of the feldspar used in this study, details of the uncertainty analysis used, a discussion of the stabilities of ice Ih and ice XI, the literature fits used for the diffusion activation energy and ice-liquid interfacial tension, calculation of the heterogeneous ice nucleation rate of pollen washing water, discussion of the relationship between heterogeneous ice nucleation rate and the size of the ice critical cluster, calculations of the entropy change of spherical cap shaped ice clusters with addition of ammonium and calculation of the entropy change due to addition of ammonium ions to partially ordered ice cluster.

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