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Atmospheric
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Discussions

Interactive comment on "Inhibition of ice crystallisation in highly viscous aqueous organic acid droplets" *by* B. J. Murray

B. J. Murray

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The author thanks referee 1 (H. Grothe) for his helpful and constructive comments.

The referee's comments are italicised and the author's response is in normal type.

The author's laboratory is within only few others, who investigate atmospheric relevant cryogenic particles by X-ray diffraction. Diffraction techniques have the inherent advantage of monitoring the long-range order of solid particles and therefore are indispensable for exact phase analysis. It is state-of-the-art that the diffractograms of a phase mixture are finally quantitatively analysed concerning their composition, e.g. by Rietveld refinement (Young 2003). The author has chosen a different way applying a semi-quantitative analysis, which requires a model calibration and is often used for systems where one or more phases are unknown. However, in this study all ice structures *(hexagonal, P63/mmc and cubic, Fd3m) are well-known, and therefore a more detailed analysis would enhance the significance of the paper. I would recommend using a fundamental parameter method like TOPAS or BGMN, since these methods supply not only the fraction of the different phases but also monitor texture effects and crystallite sizes. The need for such an analysis becomes very obvious when discussing figure 1:*

Unfortunately Rietveld refinements are not appropriate for much of the diffraction data presented in this paper. The referee correctly points out that the quantities of different components can be determined using this technique only if the phases are known and well characterised. As was discussed in a previous manuscript (Murray and Bertram, PCCP, 2008) cubic ice contains significant stacking faults and the diffraction pattern of the cubic component is therefore not the perfect cubic ice pattern. I am currently quantitatively modelling the diffraction patterns of cubic ice, but this is a separate study and beyond the scope of the present paper. In addition, the main point of the present paper is to investigate the lack of crystallisation in the most concentrated solution droplets and not to quantify the relative proportions of cubic verses hexagonal ice.

Also, I disagree that the technique of quantifying fraction of water crystallised used here is 'semi-quantitative'. I quantitatively integrated the intensity of Bragg peaks in order to quantify the fraction of water that froze to ice in these droplets. Hence, this is a quantitative approach. The only assumptions that need to be made are that there is no preferred crystallographic orientation in the sample and that there is no dependence of water activity with temperature. As is argued below and shown in a published paper (Murray and Bertram, PCCP, 2008), the use of emulsions results in negligible preferred orientation and water activity is known to vary weakly with temperature.

For trace 1a the author proposes a mixture of hexagonal and cubic ice, but the accurate mixing ratio is unknown. Due to my own experiments I may assume that the cubic ice fraction is very small. Please, comment on this and assign the individual peaks.

The relative proportion of cubic versus hexagonal ice in citric acid solution droplets

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is the topic of a recent published paper (Murray, Env. Res. Lett., 2008). This has been emphasised by modifying an existing sentence which now reads: 'The issue of ice phase in organic solution droplets has been addressed in a separate manuscript Murray, 2008 377 and will not be discussed further here.'

I have also inserted an extra section in the introduction (p8746, end of 1st para) in order to emphasise that this paper is focused on the inhibition of crystallisation and glass formation. It also serves to define the term glassy solid and glass transition temperature. This reads:

'It is well known in the food industry and the field of biological tissue preservation that the addition of oxygenated organic compounds, such as sugars, to aqueous solution can lead to the formation of glassy solids Angell, 2002. These glassy solids form at temperatures which are relevant for the Earth's atmosphere. A glassy solid is a solid in which the arrangement of its constituent molecules lacks long range order, i.e. they are amorphous rather than crystalline. Glassy solids form if a liquid is cooled to a sufficiently low temperature so that the molecules effectively cease to diffuse and become locked in a 'liquid-like' amorphous state. The threshold temperature where an ultra-viscous liquid becomes glassy is known as the glass transition temperature (Tg). The viscosity of a liquid at glass transition is on the order of 1014 cP, some 14 orders of magnitude larger than that of water at room temperature. The impact of highly viscous and glassy solution droplets on the Earth's atmosphere and cloud formation is at present unknown and this paper seeks to begin addressing this area.'

Peak labels have also been included in Figure 1.

In trace 1b the reflexes of hexagonal ice disappeared and the remaining (?) reflexes of cubic ice appear much broader, which can not be explained by stacking faults only. The Debye-Scherrer formula describes the correlation between the half-width of the peaks in the diffractogram and the crystallite size, D [Å]..... k geometry parameter for the morphology of the investigated crystals, which is about 0.9 assuming nearly *spherical crystals wavelength of the X-ray radiation in Angström, i.e. 1.54051 Å for Cu-K1 radiation. peak position in rad.2 half-width at half height of the reflex in rad, which has to be corrected by an instrument parameter.*

This formula is based upon the assumption that micro distortions, voids and stacking faults are negligible, which of course is not always true. Unless we assume a remarkable error for those calculations, up to 20%, the method would be still valid in order to show rough trends for the changes of crystallite sizes in concentration and temperature dependence (see Tizek 2004). This might be very interesting for the present study since it would show the crystallite sizes decreasing with increasing concentration. This would indeed support the conclusion of the author that increasing viscosity and hindered diffusibility have an important impact on crystal growth.

I suspect the referee is correct in his suspicion that the crystallite size decreases the lower the freezing temperature and with ordered well formed crystals the Debye-Scherrer formula can be used to quantify the crystallite size. However, as I discussed above, cubic ice contains significant stacking faults and modelling I have performed for stacking faults in ice (not yet published) shows that stacking faults have a significant impact on peak shape and also peak width. In the past people have published crystallite size of cubic ice, however I think that this data might be erroneous and am therefore very reluctant to publish crystal sizes based on this approach without first quantifying the impact of stacking faults.

In response to the referee's comments I have added more diffraction patterns to Figure 1 which show the progression from crystalline material to X-ray amorphous material. In addition I have added the following text and adjusted text where necessary:

'The hexagonal peak at 23 remains in these cubic ice patterns, whereas it is clear from the absence of other hexagonal peaks that no bulk hexagonal ice crystallised. This feature is thought to be related to stacking faults in the cubic structure Murray, 2005 164. All of the peaks can be attributed to ice and it is concluded that no citric acid phases crystallised. Stacking faults are also known to cause some broadening of Bragg peaks and also asymmetry in Bragg peaks. In the absence of a method to quantify the impact of stacking faults an analysis of the size of ice crystallites based on peak widths should not be attempted.'

On the other hand, it put the statement into question that the remaining brine is really amorphous. Another explanation is that the crystallites are too small to be recorded and that the broad reflexes merge and contribute to an amorphous-like signal.

This is absolutely correct. The lack of an X-ray signal shows that bulk ice crystal did not form, but crystals in the nanometer size range may have formed. In fact, critical ice clusters of nanometer sized crystals obviously did form in solutions of concentration less then 59 wt%, but the further growth of these crystals was inhibited. This was evident on warming when bulk ice crystals grew. In solutions of higher concentration critical clusters most likely did not form since bulk ice did not crystallise on warming.

The following has been added: 'X-ray diffraction is insensitive to nanometer sized crystals, and therefore insensitive to critical clusters, hence the lack of Bragg diffraction peaks only indicates that bulk ice crystals did not form. These droplets formed what is referred to as X-ray amorphous materials, i.e material lacking bulk ice crystals and therefore with diffraction patterns that lack distinct Bragg diffraction peaks, but in which nanocrystalline ice may exist.'

And the following paragraph has been modified to: 'Droplets with concentrations of 59.6 and 61.2 wt% did not crystallise on cooling to 173 K or on subsequent warming indicating that nucleation of ice did not occur at all in these very concentrated solution droplets. These droplets most likely formed true glassy solids (i.e. an amorphous solid with the absence of any crystalline components, even nanocrystalline ice) before they became sufficiently supersaturated for nucleation, hence nucleation was inhibited and they therefore did not crystallise on cooling or warming. This will be discussed in more detail in section 3.3.'

Here, low-frequency Raman spectroscopy could help, since it can differentiate lattice vibrations of nanostructured crystallites, i.e. 60 cm-1 and 215 cm-1 for cubic and hexagonal ice.

I agree that a Raman spectroscopic study would be an interesting future study.

Finally, trace 1c exhibits only one signal at 24, which belongs neither to hexagonal ice nor to cubic ice, since the other peaks are missing. A possible explanation might be orthorhombic citric acid monohydrate or monoclinic citric acid, a mixture of which might be expected at higher concentrations. The author should control for such a possible assignment.

This peak is common to all cubic ice diffraction patterns in the literature and is related to hexagonal-like stacking faults. The sentence has been added: 'All of the peaks can be attributed to ice and it is concluded that no citric acid phases crystallised.'

Specific Comments:

The author claims that the oil matrix preparation method will avoid crystal orientations. I may put this into question since the frozen oil matrix is finally placed on a sample support, which induces a temperature gradient from below into the whole sample. This might be a source of texture effects.

The lack of preferred orientation in previous studies employing emulsions strongly suggests that this is not a significant problem. A few lines have been added to the experimental section to clarify this:

'A number of advantages of employing emulsified samples were listed by Murray (2008); one advantage is that there is no significant preferred crystallographic orientation when ice crystallises in emulsified samples. Orientation of crystals results in changes in the relative intensities of the diffraction peaks and can complicate interpretation of the resulting diffraction data. Rietveld refinements of frozen emulsified solution droplets (which crystallised to hexagonal ice, letovicite and sulphuric acid tetrahydrate)

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conclusively demonstrate that the crystallographic orientation of each frozen droplet is random and that there is no overall preferred orientation Murray, 2008 370.'

Obviously, a phase separation into a crystalline and a brine fraction has been recorded. I may propose to investigate this process also by environmental scanning electron microscopy (cryo-ESEM). The sample could be prepared the same way as described in the paper, but will be freeze-fractured horizontally in a cryo-transfer chamber and the upper section will be removed. Thus, a virgin surface will be available showing cross-sections of individual particles (see Grothe 2006).

This would be a very interesting experiment that should be done in the future.

Fig. 2, 4, and 5: The arrows are confusing. A real legend would be more helpful. However, arrows could be used in order to show the direction of annealing or cooling processes in the state diagrams for the respective data series.

Legends have been included and arrows removed from these figures.

Concentrations should be given not only in wt.% but also in mol% as well.

A mol% scale has been added to Fig 2 and 5.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 8743, 2008.

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