Dear Dr. Christenson,

Thanks for your interest and comments on our work. Please find our response to your comments (in blue).

Referee Comment (RC):

There is one puzzling aspect of the results. I understand that the authors have identified the muscovite mica surface as the origin of the nucleation using a video camera.

However, I am surprised that the basal plane of muscovite mica nucleates ice heterogeneously in the immersion mode at a temperature as high as -13°C (Figure 4). In a recent study of water droplets on mica, glass and silicon we found no experimentally significant difference in the freezing temperature of 50 µm diameter (approximately hemispherical) water droplets between the three surfaces (Campbell et al., 2015). For all three substrates the freezing temperature was – 35 °C, close to but slightly above the homogeneous freezing temperature of water. These results hence suggested that the mica basal plane is not a good ice nucleator in the immersion mode.

Authors Comment (AC):

We agree with the Referee that -13 °C is high and cannot be the heterogeneous freezing point of any of our selected surfaces. In the text we wrote that "The video recording could determine that the ice phase was nucleated at the interface between the crystal surface and the cell opening and subsequently propagated through our optically probed region." So we believe that the ice nucleation was not started at the sample basal planes neither for mica nor for sapphire. This was the conclusion after having installed the camera. This also confirmed our concerns about the results from (Anim-Danso et al., 2013) on water freezing at sapphire surface. They concluded that 1) even though the structure of water and ice are affected with pH the freezing point is independent of pH and 2) the heterogeneous freezing point was "constant" and about -6°C which is very high value for sapphire which is considered as a poor ice nucleator. We believe that even in their case ice nucleation started somewhere else but not the sapphire surface especially since they were cooling the whole cell while we were cooling the sample directly. Anyway, avoiding ice nucleation at the joint point between the cell and the surface in our work or anywhere else in the work of (Anim-Danso et al., 2013) is impossible with the cell designs presently available. Note also that what we wanted to communicate by our paper that the water molecules on each surfaces develop in different ways during cooling and to show that the SHG set-up can be used to detect such details. We did not address the onset temperature. To pursue the work as indicated above, we will try to overcome the extrinsic ice nucleation, and we are currently designing a pioneer cell which allows us to freeze a single water droplet on the surface while measuring the SHG (SFG is also planned) at the interface. We expect another level of results and interpretations on mica and sapphire using the new cell and the SFG.

Probably the manuscript text should have addressed this point in more detail along with the results of the previous studies of the ice nucleating ability of muscovite mica (as the Referee suggested). Please see text in next AC.

RC:

Moreover, in our experience ice nucleation on the basal plane of mica from vapour (deposition mode) almost always occurs in surface defects such as cracks or pockets under cleavage steps, as has also been found with many organic vapours nucleating on mica (Campbell et al., 2013).

As far as I am aware, most studies that show that mica is an efficient ice nucleator, whether in the deposition mode or in the immersion mode, such as the ones cited by the authors (Eastwood et. al., 2008, and Glaccum and Prospero, 1980), have been conducted with ground mica or naturally occurring small flakes (e.g. in aerosols). It may be that other crystal planes exposed in the ground samples and flakes are the efficient nucleating agents, or that chemical effects arising from the leaching of ions via edges contribute. It should be noted, however, that in the study referred to above we did not find any noticeable enhancement of nucleation on scratching the basal plane of mica with diamond powder, which leads to the production of small flakes of mica. By contrast, such a procedure has proven very effective at enhancing nucleation from vapour with some organic substances (Holbrough et al. 2012). I think that it would be useful if the authors were to discuss in more detail the results of previous studies of the ice nucleating ability of muscovite mica.

AC:

In the revised version of the manuscript, we will write:

"Mica (a layered clay mineral: $KAl_2[AlSi_3O_{10}(OH)_2]$) is believed to be among the most effective ice nucleating minerals in the deposition mode, at least as natural particles, (Eastwood et al., 2008;Mason and Maybank, 1958). However, it could be different for the basal plane of mica. It was shown by (Holbrough et al., 2012;Campbell et al., 2013) that nucleation of some organic substances from vapor on mica surface (deposition mode) is enhanced only when producing a high density of nanoscale features of the surface topography. This was not the case when studied ice nucleation from supercooled water droplet on the surface of mica (immersion mode) where they reported that freezing occurred close to the expected homogeneous freezing temperature and surface roughening has no significant effect (Campbell et al., 2015). (Atkinson et al., 2013) showed that mica particles are not good ice nucleators in the immersion mode. On the other hand, (Steinke, 2013) using cold stage setup showed that muscovite initiated heterogeneous ice nucleation at approximately -23°C which is far above the homogenous freezing but much less than those of other ice-active mineral dusts."

RC:

I would also like some more technical detail on the contact angle measurements, particularly how the value of zero degrees for mica was obtained (AC: The contact angle was determined on the freshly cleaved surface by depositing a drop. The drop spread immediately, which we interpret as a contact angle of zero. On the sapphire prism the drop retained a finite size and we could measure the contact angle). What was the volume of liquid in the cell (AC: 7.5mL)?

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