Author Response to Interactive Discussion Comments

Thank you very much to the four reviewers for the comments and reviews on our paper, “Mesoscopic surface roughness of ice crystals pervasive across a wide range of ice crystal conditions”. Your insights and suggestions regarding this manuscript have been carefully considered – we found the feedback very constructive and we believe the manuscript has been significantly strengthened as a result. The most significant change has been the addition of an appendix table and discussion of experimental thermodynamics, mainly in response to the comments from B. Murray and A. Kiselev suggesting that the experimental conditions were hard to derive from the small data bars in the figures, and that the values therein were not given sufficiently thorough consideration in the text. We have added references and short discussions on satellite polarimetric studies and formvar replicas of ice suggested by B. Baum and A. Kiselev, respectively. We have also added some additional discussion to the details of the chamber grown crystals and transport process. Finally, we have carefully incorporated all technical corrections and suggestions into the final manuscript. We particularly thank B. Baum for catching the spelling errors; we discovered that the spell-check language was set to German, and had resulted in not catching the multiple errors. Responses to specific questions and suggestions from each reviewer are addressed below:

Reply to Dr. Bryan Baum, short comment C2386

Q. 1 – *What percentage of ice particles demonstrate roughening? Were the transported crystals (section 3.3) the primary source of smooth faceted particles?*

Every crystal we observed demonstrated some evidence of roughening at the microscale or sub-microscale. The main differences were in scale, degree, and morphology of the roughness. In a qualitative sense, the actively sublimating crystals (e.g. fig. 4) showed the largest scale and most extensive roughness while the transported crystals at equilibrium showed the largest facets with small-scale or barely perceptible roughness. Actively growing crystals tended to show intermediate roughness, but the scale and morphology of roughness was highly varied. Some crystal facets clearly showed roughness features with heights >5 µm, while other growing facets appeared to be smooth until examination at high magnification revealed roughness on a scale below 100 nm.

Q. 2 – *Is there a way to discriminate conditions that lead to smoother versus more roughened particles? The reason for this question is that one often observes cirrus haloes and other optical phenomena, but more generally when updraft velocities are low. It would be useful if the authors could relate their observations to natural cirrus if possible.*

We agree that discriminating among conditions that lead to the various degrees and scales of roughness observed would be highly desirable. Unfortunately, in the experiments described here, we could not detect systematic variation in roughness scale, degree, or morphology beyond the description in the response to question 1. Resolving the causes of varied roughness will be a primary goal of our continuing work. We have also been intentionally reluctant to draw direct comparisons between natural cirrus and the crystals grown in ESEM because the lack of air pressure and the presence of the growth substrate could render such comparisons misleading (see Reviewer Comment C4758 and reply). The surface character of the transported crystals should be more directly relatable to natural cirrus; however, in this set of experiments we were not able to explore a range of growth conditions for the transported crystals – all observed transported crystals were grown at low supersaturation (rhi ~105% or less) and at a temperature near -50 C. The observation of larger facets with less roughness on the slowly grown transported crystals may be consistent with the observations of optical phenomena primarily in gentle-updraft, low supersaturation environments.

Q3. *page 8401, paragraph beginning on line 13: we find that ice particles in environments of high updraft velocities (e.g., convection) tend to demonstrate characteristics consistent with the most roughening (e.g., Cole et al. 2013; 2014) in passive remote sensing using polarization data. Perhaps the severe roughening is caused by the formation mechanism for aggregates (i.e., crystals colliding with ridges radiating outwards from point of impact). Please comment.f*

This is an interesting idea that we had not considered, and we have mentioned this possibility in the revised manuscript (section 3.1.1). One event that clearly does enhance roughness during active growth (e.g. Fig. 1, panel b.) is the disruption of the growing surface by another crystal. In natural environments with high ice particle collision rates and aggregating crystals, it does seem plausible that this could be a significant influence on the total roughness of the particles.

Reply to Dr. Benjamin Murray, reviewer comment C3386

Q1. *Section 3.3. It is stated that the transported crystals may have changed during transport, if so, how useful are these results. They don't seem to add anything greatly to the paper. Either justify their inclusion and make the conclusion clear or remove the section.*

The primary motivation for including the discussion and images of the transported crystals lies in showing the nature of roughness on ice crystals grown in a cirrus-analog environment and without full substrate contact. Pointing to the absence of ambient air pressure in the actively growing and sublimating crystals, other readers and reviewers of this manuscript and other recent ESEM studies have questioned whether the observed mesoscopic roughness may be entirely absent for crystals grown in natural cirrus conditions (see C4758 by A. Kiselev, below). We acknowledge that precise measurements of the growth and transport environment of the transported crystals have not been yet accomplished, but the images still convey valuable information – they demonstrate that crystals grown in cirrus-analog environments (not just in the pure vapor ESEM environment) do still show mesoscopic roughness. We have tried to clarify this conclusion in the manuscript and add more careful discussion around the significance of the images in figure 5. Our next experimental goals are to 1) ensure and demonstrate maintenance of equilibrium conditions during transport and 2) to make careful roughness measurements on crystals subject to conditions spanning the range of natural cirrus environment. These goals will require significant additional engineering of the experiment design, but should be feasible.

2. *Section 3.3, 8405 'Tabular'. Is this the correct name. Do you mean shorter columns. The name tabular refers to a special class of crystal. There is an illustration on p 42 of Tape (1994, Atmospheric Halos, vol 64, Antarctic research series). A tabular crystal is one in which a hexagonal column has two prismatic faces much wider than the other two.*

Yes, thank your for the correction. We intended to describe short columns, with dimensions along the a-axis and c-axis nearly isometric. The improper usage of 'tabular' has been removed.

3. *P8404. The section on 'ice Ic/ice Ih combinations' not quite correct. The references* are fully *relevant, but are rather technical in nature. Revise this section to something closer to: 'Several recent studies have also suggested that ice up to 243 K does not have a well ordered hexagonal crystal structure. Instead ice can contain a mixture of cubic and hexagonal sequences which can give rise to roughness on the prismatic faces (Malkin et al., 2012; Kuhs et al. 2012). It has also been shown that the proportion of cubic sequences decreases as ice is heated and the ice tends towards perfect hexagonal ice (Murray and Bertram, 2006; Kuhs et al., 2012). Both of these..*

Thank you for the suggested rewording, we have adopted your suggestion. These sentences were also awkward to J. Harrington, and the rephrasing is a significant improvement. In future work, we hope to make progress on quantitative analysis of ice microscopic crystallographic phases and alignments using in-situ Electron Backscatter Diffraction (EBSD) mapping.

4. & 5. Fig 1-6. I encourage ACP to print these images as large as possible – i.e. full two column width. The details are central to the paper. The scale bar and conditions is hard to read in many cases. Either include this information clearly in the figures or put in a table. Put scale bars on figures

Thank you for this suggestion – we agree that the images are of central importance to value of the manuscript and anything that can be done by ACP to maximize image size would be greatly appreciated. The nine-panel figure 1 is particularly affected, with the full size .pdf image still resulting in significant resolution loss; if nothing can be done to increase size or resolution on the viewable .pdf, the original full-size images will be included in the supplemental data. The scale bar conditions are hard to read without viewing the images at full size --since trying to write this data directly into the figure could interfere with maximum space for the images themselves, we have included this data (as well as calibrated surface temperature and calculated saturation ratio) in an appendix table.

6. & 7. *Fig. 5 caption: Add more detail of what this image is. Figure 6 caption. More detail. What magnification. Are we looking at the prismatic or basal face. What does this look like on a lower magnification (include second inset image?)*

For figure 5, we agree that more information should have been provided in the caption. The following details have been added: the images show portions of 4 different crystals grown slowly at -50 ºC in a static diffusion chamber between 100 and 105% rhi. The crystals were maintained in cryogenic equilibrium during transport into the ESEM for imaging under matched equilibrium conditions. We acknowledge that figure 6. also needs more context – this is a close-up of a portion of a prismatic face near the location where the basal face of an adjacent crystal had intersected an adjacent prism face of this crystal. An inset image at lower magnification is a good idea – we've used an inset from a lower magnification (1903x) image and highlighted the region of close-up. The inset frame was taken 115 s prior to the high-magnification view.

Reply to reviewer Dr. Jerry Harrington, reviewer comment C4311

All technical corrections and suggestions (notes 1, 2, and 6) have been adopted.

(3) Enough information is provided for me to understand how the ESEM substrate measurements were conducted, but little information is provide on how the diffusion chamber studies were done. Was the chamber similar in design to Bailey and Hallett? How were the grown crystals from the chamber transferred into the containment cell? It also was not clear to me how long the containment cell was exposed to ambient conditions (and what those conditions were) prior to being transferred to the ESEM cold stage.

The design is indeed based on Bailey and Hallett, though the current version is a static diffusion chamber held within a 25 ft^3 low-temperature freezer (So-Low Inc.), with top and bottom diffusion chamber-plate temperatures driven by thermoelectric modules. The full freezer volume is held at -55 ºC and near 100% RH_i, which is accomplished by coating all freezer walls in a thin layer of ice. The transfer of the chamber-grown crystal to the pre-chilled cryo-containment cell occurs within the saturation-balanced freezer air, and transfer is complete in about 5 s. The containment cell thereafter remains sealed and held in dry ice until equilibrium temperature is matched within the ESEM chamber. At no time are the crystals exposed to warm ambient room conditions nor to under-saturated air. At the time of collection, the diffusion chamber used to produce the crystals shown in figure 5 was only capable of producing approximately 5% supersaturation relative to ice at -50 ºC. These details have been added to the manuscript. It is certainly true that the full relevance of ice surface roughness in atmospheric clouds won't be manifest until it is possible to report careful imaging of crystals transferred from well controlled laboratory conditions and from natural clouds. Improvements to our chamber are underway to enable automated collection and capabilities for ice saturation ratios from 0.7 to 2.0 through temperatures between -40 and -70 ºC. We are also attempting to directly gather natural snowflakes and cirrus crystals and to equip the ESEM and crystal-transfer process with continuous liquid nitrogen immersion, to guard against unintentional growth or sublimation during transfer.

(4) I think the discussion regarding ice-Ic and ice-Ih in relation to the presented results is a little confusing. First, you may wish to define what ice-Ih and ice-Ic are for readers. Most of your readers will (or should) know, but some will not. You may need to provide a couple sentences on the combined existence ice-Ic and Ih, and why that could lead to stacking faults and hence roughening features. I think you need that to then make a connection to the steady-state and inhibited growth you observe. (Are you suggesting that in your case it was annealing towards Ih that caused the inhibited growth? This wasn't clear, at least to me, from what is written.)

B. Murray also commented on this discussion, which was partly inspired by some of his recent work. With his suggestions, these sentences have been rephrased. As we noted in our response to his comment, we are also hopeful that Electron Backscatter Diffraction (EBSD) analysis may prove conclusive regarding the confirmation or absence of a potential role of cubic ice sequences.

(5) With respect to the inhibited growth: Is it possible that competition for vapor was important here?

It appears that vapor competition is not likely to play a significant role in any of the experiments conducted. The inhibited growth was observed for both isolated crystals and in the vicinity of multiple crystals within closer proximity. We never observed growth rates to vary as a function of crystal proximities – indeed, with the exception of the inhibited growth cases, all crystals within the field of view could always be seen to grow at the same rate. You might refer to the supplemental video: Basal_Roughness_Layers.mp4, where multiple crystals with variable spacings nucleate and then grow at the same rates. Because total vapor supply was unlimited and diffusive resistance was so low, we are convinced that our observations are consistent with all crystals receiving essentially equal and direct access to the full measured vapor concentration.

(7) I think it is very interesting that sublimation leads to scalloping, and that this seems to start at the roughness locations. Is it possible to provide more information here on how the scallops develop over time? Do the scallops originate at the tips of ridges and corners, or in the crevasse regions? How do they propagate?

The process is fascinating to watch, but not easy to describe. The recent ESEM images from Ulanowski et al. (2014) show sublimated crystals with similar scalloped roughness. The scale of the scalloping can become fairly large, so it is somewhat hard to believe that these structures couldn't be seen by optical microscopy if they were indeed characteristic of sublimation in diffusion-limited regimes—perhaps this mode of sublimation is unique to the kinetic attachment regime. Probably the best view of this process can be seen in the supplemental video "GrowandSublime.mp4". It appears that sublimation occurs radially outward from various centers, often at the side of a ridge or roughened feature. In fact, on the basal plane, the sublimation can even be seen to produce hexagonal pits (watch the above video carefully at ~14s) and the scalloping develops partly from the intersection of multiple spreading pits. We've tried to enhance this description in the text discussion in section 3.2.

(8) Theoretically, faceted growth requires a constant vapor flux over the facet. Could you perhaps comment on this in relation to the roughening shown by your observations?

As we indicated in response to (5) above, we don't think that vapor competition is likely to be playing a role in our roughening observations – as such, the impingement flux should be evenly distributed. We believe that some combination of island nucleation and the presence of crystallographic defects are the most likely sources of the observed roughening, given that each of these provide mechanisms for preferential, non-symmetric incorporation of adjoined molecules. We think that both mechanisms are likely to be playing significant roles – the challenge will be to discriminate between the regimes where each mechanism is dominant and how that interplay becomes manifest in the morphology of natural cirrus particles.

Reply to reviewer Dr. Alexei Kiselev, reviewer comment C4758

1. My main concern is about the role of the substrate and the absence of the background pressure in the mechanism of the ice crystal growth. Both issues are very briefly mentioned in the manuscript (as in page 8400 lines 8-11: "These images do show mesoscopic surface roughness, but suggest that the presence of air or different modes of internal heat transfer may significantly affect the character of surface texture development") but not discussed further with respect to the surface morphology of the growing regime of ice crystals. However, they can be very important for comparing the ice morphology observed in ESEM with ice growing under atmospheric conditions. For example, it is known that the diffusion coefficient Dw of water vapor in air-vapor mixture is inversely proportional to the background pressure. Using approximation *given by Marrero and Mason in "Gaseous diffusion coefficients" in J. Phys. Chem. Ref. Data, v1. no1(1972) for near-vacuum conditions of ESEM (-20_C, 1 Torr) the value of Dw would be 120 cm2/s, which is 600 times larger than the diffusivity of water in air at atmospheric pressure (_0.2 cm2/s). At the same time, diffusivity of water is the important factor influencing, together with the supersaturation, the crystal growth mechanis (diffusion limited vs. attachment kinetics limited, see, for example K. G. Libbrecht, The physics of snow crystals, Rep. Prog. Phys. 68, 2005). Since no background pressure was provided in the specimen chamber of the ESEM, all crystals images reported in the manuscript have been obtained with crystals grown in the attachment kinetics limited regime, meaning that the growth of crystals is controlled by the rate of the incorporation and redistribution of water molecules within the surface of the ice crystal, and not by the rate of diffusion of water molecules towards the crystal surface. The influence of enhanced diffusivity on the sublimation morphology of ice can be even more pronounced. The role of the substrate is not so evident for the surface morphology of the growing ice crystals. In case of freely levitated crystals, the latent heat of solidification is removed only by thermal diffusion (0.025Wmˆ-1Kˆ-1 for air at standard pressure). Because this heat removal is slow, the heating of the ice crystal may slow down the growth, driving the growth into the heating-limited regime. This effect should be more pronounced for lower pressure, because of the much stronger flux of water vapor towards the surface (see, again, K.G.Libbrecht, 2005). In case of the crystal having thermal contact to a substrate, this heating limitation will be removed because of the much higher thermal conductivity of a substrate (from appr. 2 Wm-1K-1 (mica) to 400 Wm-1K-1 for copper) and ice (2.5 Wm-1K-1). Therefore, ice crystals having thermal contact with any substrate in pure water vapor environment would be growing in the kinetic limited regime already at low supersaturation, as opposed to the atmospheric ice crystals mostly growing in diffusion limited or heating limited regime under realistic atmospheric conditions. To my understanding, the specific thermodynamic conditions in ESEM (absence of the background pressure and thermal contact to a substrate) is also the reason why no systematic dependence of the surface morphology was observed on the degree of supersaturation and growth rate. In fact, the authors correctly recognize the growth mechanism dominant in the experiments as a 2D nucleation, which is specific for the attachment kinetics limited growth regime (see, for example, the textbook “Crystals: Growth, Morphology and Perfection” by Ichiro Sunagawa, Cambridge University Press, 2007). This conclusion does not reduce the need to understand und quantify this mechanism of ice crystal growth nor it diminishes the value of the presented observations. My main point is that one must be very careful extrapolating the observation results obtained in the ESEM towards the atmospheric conditions. Please consider including some more careful discussion of this issues in the revised version of the manuscript. However, I fully support the suggestion made by authors, that “. . .the next steps should focus on efforts to examine and quantify roughness in crystals transported from cirrus-analog environments and development of a mixed air/vapor capability for ice crystal growth in ESEM”, but the thermodynamics underlying this conclusion should be elaborated more carefully.*

It is certainly true that the absence of background air pressure and the role of the substrate are the two most significant impediments to drawing atmospheric conclusions from these and other observations about the mesoscale topography of ice crystals. As you point out, the diffusive resistance is greatly reduced in the absence of N_2 and O_2, and the thermal transport is also organized much differently than would be found for an isolated particle in air. The growth observed in figs. 1-5, and in the supplemental videos, is indeed well within the attachment kinetics regime, and should therefore demand circumspection before making conclusions about the likely results of diffusion-limited growth. Nevertheless, real atmospheric conditions do include the kinetic attachment regime for very small crystals (typically under ~10 μm diameter and further enhanced at particularly low pressures) and this regime could be expected to be even more important if atmospheric crystals are subject to low deposition coefficients, as suggested by some measurements. We definitely don't mean to imply that these substrate or pressure factors are unlikely to affect the morphology of ice crystals and their surfaces; we have added additional caveats to the discussion and conclusion, cautioning against over-interpretation. We have also added several sentences of additional motivation to the section on transported crystals (figure 6), the inclusion of which is intended to provide some qualitative evidence that mesoscale roughness is still present in crystals grown in diffusion limited regimes, though not identical in morphology to what is observed in the pure-vapor environments (figs. 1-5). As indicated in our response to comment 3. from J. Harrington, we agree that the full relevance of ice surface roughness in atmospheric clouds won't be manifest until it is possible to report careful imaging of crystals transferred from well-controlled laboratory conditions and from natural clouds. The quantitative analysis of roughness in pristinely-preserved crystals, grown at precisely defined humidity and temperature, and without substrate, and at realistic pressures, is beyond the technical capability we currently possess, but it is our hope that our group and others will be able to accomplish this within the next few years.

2. *In contradiction to your statement (page 8398, lines 15-16), "We are confident that vapor pressure values were precisely and accurately controlled and reported;. . .", there seems to be an inconsistency between the ESEM conditions reported in the text and the pressure and temperatures values shown on the ESEM images. For example, the crystal shown in Figure 2 is claimed to be held at equilibrium at -23_C, and the pressure of water vapor that can be read on the ESEM image is 7.02e-1 Torr. However, the saturation value of water vapor with respect to ice at this temperature is 0.58 Torr (I'm using parameterization from Buck, A. L., New equations for computing vapor pressure and enhancement factor, J. Appl. Meteorol., 20, 1527-1532, 1981). That would mean supersaturation of 1.21, instead of 1 as would be required by the equilibrium condition. Same story with Figure 4, panel C: pressure reads 0.19 Torr and reported temperature 39_C, but even if I assume the maximum possible temperature offset of 2.5K, the saturation vapor pressure for 36.5_C would be 0.143 Torr, not 0.19!. At the same time the crystal in the panel is clearly evaporating. Was some other independent pressure measurement employed or the temperature offset is stronger than you admit? A temperature and humidity calibration with e.g. deliquescence of NaCl would be highly recommendable, as well as placing additional temperature sensor on the surface of substrate.*

Thank you for your careful attention to the details of the temperature and vapor pressure values shown in the figure data bars. We agree that more space should have been taken to explain how surface temperatures were calibrated and used to arrive at the calculated saturation ratios. In response to this comment and that of B. Murray we have added an appendix that describes the calibration procedure and includes a table displaying the figure databar measurements, along with derived values of surface temperature and saturation ratio and their estimated uncertainties. Based on substrate-free experiments and freezing studies (not shown in the paper), we are still confident in the vapor pressure readings, however, you are correct that the sub-stage temperature offset was understated for the figure 2 crystals and for the lower temperature experiments. Because the ESEM is a shared-use instrument, we have thus far been unable to customize instrumentation, but finding a way to directly measure surface temperature would greatly enhance precision of the humidity measurement, and permit quantitative modeling of the observed deposition and sublimation processes.

3. *I suggest that more details should be provided for the diffusion chamber experiment. How did you control the water vapor pressure at this temperature (it is below 4 Pa at -50_C)? How did you manage to nucleate ice at supersaturation below RHi of 110%? Have you been measuring the pressure and temperature inside the containment cell? How many ice crystals were collected into the cell for transport? Would that be possible to observe the crystal growth in the diffusion chamber visually (by means of a microscope) – that would provide necessary information on the growth regime!*

This is a similar comment to that of reviewer comment 3.-3 by J. Harrington. In response to these comments (and that of B. Murray questioning the relevance of this section), we have added more motivation for this section and more detail to the description of the diffusion chamber and the transfer environment. Ice crystals were nucleated by extra pre-chilling of fiber supports; subsequent growth proceeded at ambient room pressure (~1000 mb) and low (~5%) supersaturation, and typically with many crystals growing in close proximity. The full crystal dimensions were generally quite large (>200 μm) by the time they were captured and transferred, and their growth should be well within the diffusion-limited growth regime. Our continuing efforts to image transferred crystals will include fuller characterization of diffusion chamber-grown crystals, including in-chamber optical microscopy, complete thermometry, minimization of substrate effects, and imaging of crystals grown across a broad range of temperature and humidity conditions.

Minor comments:

1. You might want to mention the method of formvar (polyvinil acetal resin) replication of ice crystals to study its surface morphology (introduced by Vincent J. Schaefer, Science, New Series, Vol. 93, 1941). This method, combined with scanning electron microscopy, offers quite a detailed insight into the surface morphology and habit variability of atmospheric ice crystals. Some works involving SEM date back already to 1950th, first visualization of different roughness of basal and prismatic facets by (Kuroiwa, J. of Glaciology v.8 no. 54, 1969). At that time the link between etched pits and defects in ice has been suggested. A short review of this method would be a valuable addition to the manuscript (introduction and literature survey).

Thank you for this suggestion. We were unfamiliar with the early literature associated with SEM analysis of formvar ice crystal replicas and the related study of etching and lattice defects. We have added a short discussion of this literature to the introduction section.

2. "Wide range of ice crystal conditions" (in the title and elsewhere) is not very precise statement. In view of discussion of the different growth regimes (see general remarks) would it not be better to reduce it to "wide temperature range"?

The "wide range of conditions" is rather ambiguous and we agree it isn't a great title, though it was intended to refer to more than just temperature range. We mean to refer to the observations that mesoscale roughness was observed across a wide range of temperatures, irrespective of substrate, on both basal and prism facets, and also in crystals transferred from the diffusion-limited regime.

3. You have mentioned many different substrates in section 2.1, but never discussed any of them afterwards. At the same time nucleation of ice on natural mineral substrates is highly interesting, especially as a potential source of induced crystallographic defects in the nucleus at the early stage of growth. Could you report any substrate dependence?

We found (somewhat surprisingly to us) that we did not observe any dependence of nucleation or growth character on the substrate composition, other than the effect of substrate thickness and thermal conductivity on the sub-stage vs. surface temperature offset. All substrates used were bulk samples (>1 mm wide), and generally freshly cleaved or polished specimens; nucleation generally occurred just above equilibrium values. We anticipate that the introduction of a roughened or micro-particulate substrate, along with presence of background atmosphere is likely to reveal significant substrate dependence.

4. I wonder if there is any sense in reporting the roughness measure obtained for such small areas of the crystal (section 3.1.2). To my understanding, the main idea of defining roughness is to provide a measure for the whole population of crystals grown under similar conditions. This measure could be used then for correctly predicting their optical properties. How representative is the shown value for the single crystal and for the ensemble?

The indicated location were chosen at sites we determined to be fairly representative of individual crystals and for the whole ensemble. However, the main purpose of calculating and reporting the roughness measure was to demonstrate that previously described roughness measures are scale-dependent and therefore inadequate to describe roughness that may be smaller than the scale of an observer’s resolution.