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Interactive comment on "No anomalous supersaturation in ultracold cirrus laboratory experiments" *by* Benjamin W. Clouser et al.

Anonymous Referee #1

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First of all, my apologies for my late review and delaying the process.

This paper describes an experimental study focused on addressing the hypothesis that a metastable form of ice might form in cold cirrus clouds and that this ice has a larger vapour pressure. The paper is well written and well presented. Overall, the conclusions are well supported and the caveats are discussed. I recommend that this paper is published once the following points are addressed.

Abstract: 'If metastable ice forms in ultracold cirrus clouds, it appears to lack the defects and interfaces that are assumed to produce differences in vapor pressure from hexagonal ice.' I agree with the sentiment of this statement, but the vapour pressure of metastable ice is not necesserily defined by defects and interfaces. The vapour pressure is defined by the material's chemical potential, which is related to crystal structure

and in the case of ice, the degree of disorder as well as defects. Ice I is a material with two end members – hexagonal ice and in theory at least cubic ice. A more correct statement would be 'If metastable ice forms in ultracold cirrus clouds, it appears to have a vapour pressure indistinguishable from hexagonal ice to within xx%.' I think the quantification is important. The uncertainty is around 5%, but the authors stress that a vapour pressure of 20% larger would have a substantial impact on water transport into the stratosphere. The measurements constrain this value, but it could be 5% given the uncertainty which is perhaps not insignificant. Using words like 'negligible', as is done in the conclusions, is inappropriate.

Nomenclature: Ih should be ice Ih (i.e. ice one h; and similarly for ice Isd and ice Ic). I realise that this paper is only referring to ice, but it I think it is better to use the correct nomenclature.

Top of page 4. Murphy [2003] should be cited in the discussion of the transformation timescales.

P4, ln 5-8. This discussion on shape needs to be revised. I don't think (Murray and Bertram, 2006) and (Lowe and MacKenzie, 2008) say anything to support the statement made. Also, Furukawa (1982) doesn't suggest crystals with three fold symmetry will form. Furukawa suggest that cubic ice may form octahedral crystals of cubic ice and the subsequent growth may be off the faces of the octahedral. These early references do not refer to stacking disorder and therefore could not have identified the space group for ice Isd. Some older literature does refer to cubic ice and there is three-fold symmetry in cubic ice (look at a cube from a corner), but this is an example of getting the right answer for the wrong reasons. I think the first mention of the trigonal symmetry of stacking disordered ice was in Hansen et al. [2008] (first para of section 6). Also, in reference to Murray et al. (2015), they show that large proportion of small crystals had trigonal symmetry in the TTL in the one campaign (or one of very few) where they were sampled [Heymsfield, 1986]. Imaging probes tend to only have the resolution to look at larger particles, hence there are only very few measurements of small ice crystal shape in TTL conditions.

P2, ln 23. Bogdan has also proposed some mechanisms for the elevated S in TTL cirrus e.g.[Bogdan and Molina, 2010].

Results and fig 5. I think there is an error in Fig 5. S for stacking disordered ice should be T dependent. Murphy and Koop discuss this: 'Cubic ice can be estimated to have a vapour pressure 3 to 11% higher than hexagonal ice at 200 K (Fig. 5). The vapour pressure ratio is just exp(ΔG/RT), where ΔG=ΔH-TΔS is the Gibbs energy difference between hexagonal and cubic ice, and ΔH and ΔS are the corresponding enthalpy and entropy differences. Calculations by Tanaka (1998) indicate that the entropy is nearly identical for cubic and hexagonal ice. If so, then the Gibbs energy difference is equal to the latent heat of transformation between cubic and hexagonal ice, and that is what is shown in Fig. 5. The wide variation in measured ΔH can be attributed to its small magnitude as well as the difficulty in preparing samples of cubic ice that are not contaminated with either amorphous or hexagonal ice.'

Results: Some discussion of what the Shilling et al. value for S means and some context is required. Metastable ice I will not have a single value. It is a disordered state and its vapour pressure will depend on the way the sample was made. Shilling made their ice by first making amorphous ice and then annealing, which was a pragmatic way of making it in a reproducible manner. Ice made through the direct deposition of ice from vapour may well have a different degree of disorder and therefore a different vapour pressure. Murphy reviewed the available data and came up with a range of possible values, these could be shown in Figure 5.

P18, ln 19. 'its effect on vapor pressure and on transfer of water to the stratosphere would be negligible.'. Be quantitative. The effect of the presence of stacking disordered ice is less than 5% (I've estimated this based on the error bars in fig 5).

Conclusions, 1st line: Amend to reflect the uncertainty in the experiments: 'We see no evidence of an anomalous supersaturation in ultracold cirrus formation, of greater than

$\sim$5%, that field measurements had suggested.

Minor corrections:

P15, ln 6. Shilling should be Shilling et al. (xxx).

P17. Ln 1. 'depresses implied', insert 'the'.

P2 ln 24. Add Murray [2008] to the refs stating that aerosol in a glassy state might inhibit ice nucleation.

P2 ln 29. Murray et al. [2010] also showed how small ice concentrations resulting from heterogeneous nucleation can yield elevated S in clouds.

Citations

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