

Recommendation and replies (marked by “→”)

Minor revisions. I would suggest that the paper is nearly ready for publication, and would ask the author to consider the comments below during revisions. There will be a lot of people reading this paper who will not be familiar with the author's previous work (especially Nelson and Baker, 1996) and will want to parameterize this effect approximately in their models. As a result, most of my suggestions ask for increased exposition (probably only a sentence or two in each case), so that these readers better understand the context of the mechanism proposed in the paper and how to approximate its effect in a model.

→I agree that this will be helpful, so I've added brief explanations, including the ones specifically requested under “Minor comments”.

Major comments:

1. The main weakness of the paper is that the surface impedance of the water isotopologues is unknown and can only be guessed at in the present manuscript. I think of the present manuscript as framing the issue of surface fractionation effects and leaving the determination of its sign and magnitude to future work. While this is a limitation of the present paper, I still believe that it is worthy of publication in ACP.

It would be useful if the author could give some intuition as to the sign of this effect and its likely magnitude, if this is possible. Could one make an argument that the surface impedance of the heavy water might be lower than that of standard water because the heavy molecules would be less likely to leave the face of the crystal before attaching to a surface step? Any such arguments/intuition would be appreciated, including a justification for thinking on p. 17438, line 5, that the heavy water migration distance curve would be similar to that of standard water but shifted in temperature from it.

Minor comments/suggestions (all page numbers start w/174):

- 1) A note on language: The word "isotope" refers to atoms, as in deuterium is an isotope of hydrogen. "Isotopologue" refers to a molecule which combine different isotopes, so that HDO or H<sub>2</sub>O<sup>18</sup> are properly spoken of as isotopologues of water. See, e.g., the

discussion at the beginning of section 2 of: Nassar et al. JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 112, D21305, C7120ACPD 11, C7119–C7123, 2011.

The adjective is "isotopic", so that the title should have "isotopic fractionation", rather than "isotope fractionation".

→ Thanks for correcting me on my use of terms. I've made these changes.

- 2) p. 25, line 7: Could a reference be given that states/shows that "surface processes ... are crucial to the growth of faceted crystals." Perhaps, this sentence could be reworded as: "But the KF coefficient ignores surface processes that have been shown to be crucial to the growth of faceted crystals by XXX."

→ The next section "Faceted growth implies regulation by surface processes" addresses this point, so I added "as shown below" to the sentence

"But the KF coefficient ignores surface processes that, as shown below, are crucial to the growth of faceted crystals."

- 3) p. 26, line 9: Could an explanatory/expository sentence or two about beta be added after "... or some other orientation." to give the reader some intuition for this parameter that is rather central to the paper? Perhaps, "While  $\beta \rightarrow 1$  for non-faceted crystals, beta can be much less than one for faceted crystals. In particular,  $\beta \rightarrow 0$  as  $\sigma_s \rightarrow 0$  for faceted crystals." or something of the sort.

→ To address this suggestion, I changed the description to

"...and  $\beta(\sigma_s, T_s)$  is the deposition coefficient function, a measure of the probability that an incident molecule to the surface reaches *and* attaches to a growth site on a surface step. In general,  $\beta$  is nearly 0 at the lowest  $\sigma_s$  because few steps are generated, but rises to nearly 1 (assuming an efficient attachment process) as step generation increases at high  $\sigma_s$ . The exact behavior will depend on whether the crystal face is basal, prism, or some other orientation."

- 4) p. 26-27, section 2: Some kind of cartoon or sketch, along the lines of figure 2 in Nelson and Baker (1996) might be helpful in illustrating to the reader where surface effects might be important and how they compare to the vapor impedance. One aspect that might

be emphasized (and isn't considered in NB96's figure 2) is that small ice particles – even at very cold temperatures – would not be subject to these effects as long as they remained roughly spherical. I am thinking of tropical tropopause layer cirrus as an example.

→ I haven't yet decided upon adding the sketch, but to the first paragraph of the discussion section, I addressed the case of the small, nearly spherical crystals:

“However, precipitating crystals in polar regions (e.g., Lawson et al. 2006), crystals in many cirrus and other high clouds (except the very small, roughly spherical, non-faceted crystals in some very high, cold cirrus), as well as surface hoar often consist of mainly faceted forms for which the new surface-kinetic model may be required.”

I've seen some descriptions of small, nearly spherical crystals in very high, cold cirrus, but was not convinced that they were growing when they were sampled. Crystals tend to become round when they sublime, and the process is faster for smaller and for nearly equiaxial crystals (though it will be slower for colder conditions). Thus, small faceted crystals may fairly quickly turn spherical when briefly exposed to sub-saturated conditions.

5) p. 28, line 7: Even if using the values for alpha from Jouzel (1986), it seems worthwhile to cite the original sources:

M. Majoube (1970). Fractionation factor of  $^{18}\text{O}$  between water vapor and ice. *Nature*, vol. 226, 27 June 1970, p. 1242. <http://dx.doi.org/10.1038/2261242a0>

L. Merlivat and G. Nief (1967). Fractionnement isotopique lors des changement d'état solide-vapeur et liquide-vapeur de l'eau a des temperatures inferieures a 0 degC. *Tellus*, 1. XIX, p. 122-127. <http://dx.doi.org/10.1111/j.2153-3490.1967.tb01465.x> C7121ACPD 11, C7119–C7123, 2011.

Note that the Merlivat-Nief paper has slightly different coefficients in the HDO formula.

I'm not sure why this would differ from Jouzel (1986), but I suppose the latter reference may be more reliable.

→ Thanks. I added the original references.

- 6) p. 30, line 4: Could some motivation or a reference be provided for the power law approximation for  $\beta$ ? In particular, it seems worth noting explicitly that  $\beta=0$  for the case of no surface supersaturation and so that the vapor flux onto the surface increases rather slowly for small surface supersaturations.

→ I added the reference. Also, I mention the physical significance of the various cases:

“When  $n$  equals 1 or 2 (which represent the case of defect-generated steps), one can solve for  $\beta$  analytically and deduce  $\sigma_s$ , but cases with larger  $n$  (e.g., layer-nucleated steps) requires a numerical method.”

- 7) p. 30, lines 13-14: Part of this sentence confused me. Specifically: " ... the former [surface impedance ratio,  $z$ ] ... decreases with increasing crystal size, as shown in figure 1." When I look at figure 1, I see crystal size increasing to the right, marked along the top of the figure. Each of the curves show  $z$  increasing to the right, which suggest to me that  $z$  increases with crystal size. Am I missing something here? The " $z$ " label on the left axis is partly cut off, but the caption does suggest that this is " $z$ " and not " $Z_S$ " or something else.

→ The description and caption are correct, but I had mistakenly used an old plot that showed  $1/z$ , not  $z$ . The revised manuscript has the correct plot.

- 8) p. 30, line 16: Should this be re-worded as: "Deviations from the KF prediction \_can\_occur at large  $z$  \_or\_ when  $x$  differs from the KF limit of  $d'$ ."?

→ Because no reason exists for  $x$  to equal  $d'$ , I simply deleted the last half of the sentence:

“Deviations from the KF prediction occur at large  $z$ .”

- 9) p. 32, line 13: Perhaps, the word "Results" could be replaced here by "The resulting analysis" or "This analysis", so that it is more clear where the results are coming from.

→ Thanks. I chose “This analysis”.

- 10) p. 35, line 22-24: This is a nice idea and is similar in some respects to the estimation of source region humidity as in, for example: S. J. Johnsen, W. Dansgaard and J. W. C.

White (1989). The origin of Arctic precipitation under present and glacial conditions. Tellus B, Vol. 41B, p. 391-486. <http://dx.doi.org/10.1111/j.1600-0889.1989.tb00321.x>

→ Thank you for the useful reference.

11) p. 38, appendix C: Why is everything here in terms of  $\sigma_\infty$ , while equation 5 is written in terms of  $\sigma_S$ ? I can understand that there is a probably a good reason for the switch, but it is a bit confusing to the reader.

→ I now explain the reason at the start of the appendix:

“According to eqs. 3 and 10,  $Z_S$  depends directly on  $\sigma_S$ , a quantity we can know only indirectly. To estimate  $\sigma_S$ , and thus  $Z_S$ , we can apply root-finding methods to eq. 2. The result will depend on the other variables in the equation, namely  $\sigma_\infty$ ,  $T$ , and crystal parameters  $n$ ,  $\sigma_1$ , and  $r$ . By using such a method, I found an approximate formula for  $Z_S/Z_V$  in terms of these other variables.”

12) It would also be useful to have a bit more detail in this appendix, specifically:

- a reference for computing the correct value of  $z$  (or, equivalently,  $Z_S$  or  $\beta$ ),
- explicit mention of the assumptions about crystal habit/size, and
- a range of values that  $\sigma_1$  could take on.

→ The first two suggestions are now addressed in the appendix, whereas the last one is addressed below eq. 10:

“For example, in a study of critical supersaturations for growth,  $\sigma_1$  varied between 0.0015 and 0.025 for the basal face as the temperature decreased between -1 and -16 °C (Nelson and Knight, 1998). The value may be higher at lower temperatures. “