

RC1 Comments and Responses

“The manuscript submitted by Kopec and others deals with the relationship between d_{18O} and dD in Greenland with new data from the Owen ice core drilled at Summit and covering the period 1977 to 2010. The main message conveyed by this manuscript is a discussion of the slope between dD and d_{18O} with difference in summer and winter that is attributed to an important contribution of surface sublimation in Greenland to the precipitation at Summit in summer. The authors also propose a way to link the slope to a budget of sublimation vs precipitation amount.

I can not support the publication of such manuscript for many reasons given below:

-The authors can not ignore all the recent literature on the d_{18O} – d -excess in surface snow and shallow firn cores showing different results than those presented here. As an example, Steen-Larsen et al. (2011) did a very detailed analysis of d_{18O} – d -excess variations on a shallow ice core at NEEM. This study was followed by the manuscript of Masson-Delmotte, Steen-Larsen et al. (2015) with much more data. In these two manuscripts, the link between d_{18O} and d -excess is clearly different from what is presented in the present paper. The interpretation is thus different as well, with an important contribution of marine source evaporation in the whole d -excess signal. I don't challenge the measurements performed in the present study since the water isotopic measurements are routine work but it is not correct to present new data contradicting previous recent ones in ignoring this work. This is particularly problematic since the authors propose an interpretation by using the global sublimation flux over Greenland and not any regional estimate (or calculated using backtrajectories for example) so that there is no reason why the explanation proposed in the present study should not be valid for another Greenland site.”

- We apologize for not citing some of the work related to our study and will do so in subsequent versions of this manuscript. However, we discuss the work presented here in context of Kopec et al (2019), which does describe in great detail how the precipitation d -excess measurements at Summit differ from those at NEEM and other sites around the Arctic, and why we invoke a new mechanism - sublimation. In a revised version of the manuscript, we will ensure the language makes this point clear, and we will include discussion and citations of these studies as needed.
- The proposed explanation is certainly valid elsewhere on the ice sheet. Our SPI calculation takes into account the water vapor flux off the ice sheet and the total precipitable water at a given site. In most other locations, the precipitable water is a larger amount (since most locations are meteorologically closer to marine moisture sources than Summit), and thus this effect is minimized.
 - o While sublimation contribution might be minimal elsewhere, this phenomenon does not have to be limited only to Summit. As Steen-Larsen et al. (2011) state, on average, the diffusion corrected d -excess appears to lag $\delta^{18}O$ by 4-5 months at NEEM, and thus δD - $\delta^{18}O$ slopes are less than 8. However, it can be seen in their Figure 7 that, at times, the d -excess is close to being in-phase with $\delta^{18}O$, and thus annual δD - $\delta^{18}O$ slopes are likely greater than 8 for those years. It is possible that sublimation contribution to precipitation at NEEM is significant under certain conditions. While detailed analysis of NEEM data is beyond the scope of this work, we point out that sublimation is only one potential source of moisture for all Greenland sites. Whether this signature can be singled out at each site depends on the relative importance of all potential sources.

Even in our work at Summit, the SPI and PDI only explain 61% of the total variance in slope variations. We only argue here that the signature of sublimation is sufficiently prominent to be identified.

- We would like to make an additional point regarding SPI. As presently discussed in the manuscript, SPI is described as a quantitative estimate of how much sublimation sourced moisture is contributing to Summit precipitation. We recognize that we should present the concept of SPI as more of a proxy rather than a rigorous quantitative measure of the sublimation contribution, and plan to alter the discussion in the revised version of the manuscript.

“In the same line, Steen-Larsen, Bonne and others (see some references at the end of the review) have largely studied the imprint of evaporation over the ocean and sublimation over the snow in Greenland on the d_{18O} , dD and hence d -excess signals both with monitoring of the water vapor isotopic composition and with modelling approaches including water isotopes. Again, the authors does not quote any of these studies and only quote for sublimation some older papers that are even not listed in the reference list (Moser and Stichler, 1974; Stichler et al., 2001).”

- The study by Steen-Larsen et al. (2014), which is discussed in Kopec et al. (2019), presents evidence that sublimation caused isotopic change to the remaining snow, but the changes were not systematic (due to a variety of other factors, including the surface water vapor isotopic composition, rate of wind pumping, and the temperature gradient in the snow) and thus did not reach any conclusion on how snow fractionates during sublimation. In fact, they discuss the need for “controlled laboratory experiments and isotopic modeling” to better constrain these mechanisms. In a constrained laboratory study like the one presented by Moser and Stichler (1974), which we cited, they can more readily isolate isotopic changes due to fractionation during mass loss by sublimation, in which they show a reduction of d -excess of the snow (and thus an addition of relatively high d -excess water vapor to the atmosphere). We also cited a study containing isotopic modeling of sublimation, the study by Stichler et al. (2001), which was able to effectively calculate the changes observed in the snowpack.
- Two of the studies that were mentioned by the Reviewer just came out a few months ago – Bonne et al. (2019) and Madsen et al. (2019), which we did not address in the previous version of the manuscript but will do so in the revised version. Both studies show that significant isotopic change occurs during sublimation. Bonne et al. show that the sublimation of snow over sea ice produces water vapor with relatively high d -excess, especially compared to that which would be sourced from the cold ocean surface below. A straightforward assumption can be made that sublimation of snow on the ice sheet would also produce high d -excess. Madsen et al. show that significant sublimation and deposition take place over eight diurnal cycles, which alters the isotopic composition significantly. Although not stated explicitly in this manuscript, it appears that from their Figure 2, when the latent heat flux is positive (sublimation is taking place), the water vapor d -excess is higher than that when the latent heat flux is negative (deposition). This is consistent with the findings of Bonne et al. and what we inferred from Moser and Stichler. We will describe these findings in the revised manuscript.

“In addition to the recent literature, older papers are also fully ignored such as the study of Hoffmann et al. (2001) presenting a fully different interpretation of the recent d-excess signal at GRIP, i.e. at Summit, and a different signal too.”

- The study by Hoffmann et al. (2001) will be cited and discussed in the revised version of the manuscript. However, this study is not a relevant comparison to our analysis for two main reasons. 1) It only discusses longer term variations and not annual/seasonal variations, the timescales we focus on. 2) Their discussion focuses on marine source variations in the North Atlantic that cause the changes of d-excess observed in the core and bases the analysis on the classic Merlivat and Jouzel evaporation models. As discussed at length by Kopec et al. (2019), the type of explanation in Hoffman et al. cannot account for the precipitation d-excess annual cycle at Summit in their study.

“The dating of the Owen ice core is not described sufficiently while the whole analysis is dependent on this dating. A whole section should be devoted to this aspect showing the chemical concentrations, how they are used to date the ice. In the present manuscript, this section is not robust enough to support the conclusion.”

- As we write in the manuscript, the dating is done using $\delta^{18}\text{O}$. It is reaffirmed with chemical concentration measurements, but we strictly use the isotopic measurements to delineate each year. The dating analysis we employ here is quite standard and is how it is done in manuscripts cited by the reviewer, including Steen-Larsen et al. (2011) and Masson-Delmotte et al. (2015). As can be seen in the data presented in our Figure 2, the annual cycle of $\delta^{18}\text{O}$ is extremely clear (with the exception of two years, in which we gave a more detailed description in the original version of the manuscript), and thus the dating is quite straightforward. In the revised version of the manuscript, we will expand upon this section to more fully describe how we delineate different years to ensure greater clarity on this process.

“I am very concerned about the way diffusion is treated in this paper. Even if we consider the simple diffusion model of Johnsen correct, it is not used in the right way here. Indeed, in the initial paper by Johnsen et al. (2000), it is stated on section 2.2.3 (p. 171) that an artificial signal of d-excess is created by diffusion and this is observed in the figure 4 of this paper. In other words, the diffusion does not only play a role in the amplitude of the d-excess signal as mentioned and calculated in this study but also on the phasing between the d18O and d-excess signals. Steen-Larsen et al. (2013) used the Johnsen model and corrected then for a phasing between d-excess and d18O on the NEEM shallow ice core. I am very surprised that the authors do fully ignore this effect which probably fully biases their analysis and interpretation. I am also very surprised that the authors only show the raw series of d18O and d-excess and never the diffusion corrected series.”

- We disagree with the premise of this comment; we correctly account for the phase shift of d-excess in our analysis. The phase change of d-excess is a result of the change in the amplitude ratio of δD over $\delta^{18}\text{O}$. The d-excess value is calculated from δD and $\delta^{18}\text{O}$, and thus the effect of diffusion on d-excess is dealt with by calculating the diffusion effect on the amplitude of the δD and $\delta^{18}\text{O}$ annual cycles, and thus is presented as the change of slope. In the original version of

the manuscript, we account for this change. Our Eqn 3 skips the step of showing the calculated diffusion effect for each variable, and instead combines them to directly calculate the slope change. Steen-Larsen et al. (2011) also use this same correction model determined by Johnsen et al. (2000) and thus ultimately correct the d-excess phase in a similar manner.

- The changes to the d-excess phase by diffusion, and thus to the slope, can be seen in the results of the original manuscript. If diffusion over time caused d-excess to be in phase with $\delta^{18}\text{O}$, the slope of the $\delta\text{D}-\delta^{18}\text{O}$ line would be artificially increased, and thus removing the diffusion effect should reduce the slope. The time series of annual $\delta\text{D}-\delta^{18}\text{O}$ slopes in Figure 3 show that the diffusion correction reduces the slope the greatest for the oldest measurements, reducing raw slope values over 9 to slopes below 8. This slope change is equivalent to shifting d-excess from being in-phase with $\delta^{18}\text{O}$ to 180 degrees out-of-phase with $\delta^{18}\text{O}$.
- While the reviewer does not point this out, we realized that we did not state an implicit assumption in our discussion of the diffusion correction in the manuscript, which we will add to the revised version. The assumption we make in the calculation of the diffusion effect on the slope (our equation 2) is that δD and $\delta^{18}\text{O}$ are in phase. In other words, when δD and $\delta^{18}\text{O}$ are in phase, and this in-phase relationship does not change with diffusion, then the slope of δD vs. $\delta^{18}\text{O}$ ($d\delta\text{D}/d\delta^{18}\text{O}$) for a sinusoidal cycle is the amplitude ratio of δD over $\delta^{18}\text{O}$. We had observationally confirmed that this was true for both precipitation data and the ice core data.

However, this reviewer's comment challenged us to consider this assumption with more rigor. We have analyzed the annual phase relationship between δD and $\delta^{18}\text{O}$ for both precipitation data and the ice core data. For precipitation, the phase difference between δD and $\delta^{18}\text{O}$ ranges from -2.20 to +6.05 days, with the mean of 2.94 and standard deviation 3.57 days. The phase difference for any given year or for the average is not significantly different from zero ($p = 0.20$ for the average). For the ice core the phase difference ranges from -10.1 to +8.2 days, with the mean of 1.15 and standard deviation of 4.76 days. The phase difference of individual years and the average is again not significantly different from zero ($p = 0.18$ for the average). While it is difficult to theoretically establish that the phase difference between δD and $\delta^{18}\text{O}$ does not change by diffusion, we consider it adequate to assume that the phase difference is sufficiently close to zero both before and after diffusion, given the above analysis and many published observations for precipitation and ice cores where δD and $\delta^{18}\text{O}$ linearly covary.

To be further cautious, we assessed the error of the calculated slope when the phase difference is not zero. For the actual best fit phase differences, the error introduced to the slope calculations ranges from 0.00 (<1 day) to 0.38% (10 days). In addition, we conducted a correction of the annual slope estimates for the ice core using the best fit annual phase differences between δD and $\delta^{18}\text{O}$, and reconducted the analyses in Figures 3 and 5. The results remain the same. Therefore, we consider our results robust. Since none of the phase differences are significantly different from zero, we feel that it is better not to do any correction (keep the analysis as is in the original manuscript) because statistically it does not yield significantly different results. However, we would be pleased to incorporate this information in a Supplementary material, if so requested.

“Summarizing, I have serious doubts on the robustness of the dating and diffusion correction of the series presented here to follow the interpretation proposed. Moreover, the ignorance of a rich and documented literature on the subject limits the scientific interest of the present study for a large community working on water isotopes in the high latitudes of the northern hemisphere.”

- We hope that our explanation above adequately addresses the issues raised by the reviewer. While we believe many of the criticisms raised by the reviewer based on the suggested lack of acknowledgment of previous work are dealt with in the discussion of the precipitation d-excess data in Kopec et al. (2019), which provides the basis of much of the new work presented here, we do acknowledge that these earlier studies should be included in this manuscript to provide a clearer context for this work.

“References cited by Reviewer 1:

Bonne, J. L., Behrens, M., Meyer, H., Kipfstuhl, S., Rabe, B., Schöncke, L., ... & Werner, M. (2019). Resolving the controls of water vapour isotopes in the Atlantic sector. Nature communications, 10(1), 1632.

Hoffmann, G., Jouzel, J., & Johnsen, S. (2001). Deuterium excess record from central Greenland over the last millennium: Hints of a North Atlantic signal during the Little Ice Age. Journal of Geophysical Research: Atmospheres, 106(D13), 14265-14274

Johnsen, S. J., Clausen, H. B., Cuffey, K. M., Hoffmann, G., Schwander, J., & Creyts, T. (2000). Diffusion of stable isotopes in polar firn and ice: the isotope effect in firn diffusion. In Physics of ice core records (pp. 121-140). Hokkaido University Press.

Madsen, M. V., Steen-Larsen, H. C., Hörhold, M., Box, J., Berben, S. M. P., Capron, E., ... & Kipfstuhl, S. (2019). Evidence of isotopic fractionation during vapor exchange between the atmosphere and the snow surface in Greenland. Journal of Geophysical Research: Atmospheres, 124(6), 2932-2945.

Masson-Delmotte, V., Steen-Larsen, H. C., Ortega, P., Swingedouw, D., Popp, T., Vinther, B. M., ... & Falourd, S. (2015). Recent changes in north-west Greenland climate documented by NEEM shallow ice core data and simulations, and implications for past-temperature reconstructions.

Steen-Larsen, H. C., Masson-Delmotte, V., Sjolte, J., Johnsen, S. J., Vinther, B. M., Bréon, F. M., ... & Gallée, H. (2011). Understanding the climatic signal in the water stable isotope records from the NEEM shallow firn/ice cores in northwest Greenland. Journal of Geophysical Research: Atmospheres, 116(D6)

Steen-Larsen, H. C., Masson-Delmotte, V., Hirabayashi, M., Winkler, R., Satow, K., Prié, F., ... & Dumont, M. (2014). What controls the isotopic composition of Greenland surface snow?. Climate of the Past, 10(1), 377-392

Steen-Larsen, H. C., Risi, C., Werner, M., Yoshimura, K., & Masson-Delmotte, V. (2017). Evaluating the skills of isotope-enabled general circulation models against in situ atmospheric water vapor isotope observations. Journal of Geophysical Research: Atmospheres, 122(1), 246-263."