

Review of « Precipitation and ice core δD - $\delta^{18}O$ line slopes and their climatological significance» by Ben G. Kopec, et al.

This paper presents new measurements of water isotopic composition from the site of Summit in Greenland where several ice cores have been drilled. The results compare precipitation isotopic composition to an ice core record and highlight a peculiar relationship between $\delta^{18}O$ and δD (greater than 8), leading to values of d-excess singularly lower to what is usually found in Greenland. They interpret this different behaviour to the impact of sublimation on the snow isotopic composition, and thus suggest that a large part of the d-excess signal represent the sublimation over the ice sheet, and not the evaporation conditions as commonly interpreted.

I read the manuscript with great interests, it rises an interesting and plausible alternative explanation of the slope between $\delta^{18}O$ and δD affecting the interpretation of the isotopic paleothermometer. However, I have several concerns of major and minor nature, which address a few methodological aspects as well as the description of the relevant processes.

General comments:

1. In this manuscript, the authors suggest that the slope between $\delta^{18}O$ and δD found at summit is an anomaly basing their studies on the results of Feng et al, 2009. The new results from summit seems to present positively correlated variations of d-excess against $\delta^{18}O$ while GNIP data (Feng et al, 2009) indicate that the normal behaviour is negatively correlated at the seasonal scale.

The negatively correlated relation between d-excess and $\delta^{18}O$ is normal for low isotopic composition areas due to the Rayleigh distillation. Typically, for a Rayleigh distillation process, the local variations of $\delta^{18}O$ and δD can be calculated by:

$$\frac{d\delta D}{d\delta^{18}O} = \frac{\alpha_D - 1}{\alpha_{18} - 1} \frac{1 + \delta D}{1 + \delta^{18}O}$$

where α_D and α_{18} are the respective equilibrium fractionation coefficients (or effective if you include kinetic fractionation). For very low temperature conditions, $\frac{\alpha_D - 1}{\alpha_{18} - 1} \approx 10$ (typically for -30°C , you would have 9.65). Yet, for low isotopic composition such as found at summit ($\delta D \approx -300\text{‰}$, $\delta^{18}O \approx -35\text{‰}$), This means the expected slope between $\delta^{18}O$ and δD would be $7\text{‰}/\text{‰}$. This effect has been described in multiple papers such as (Touzeau et al., 2016; Casado et al., 2016).

This generalise to any time scales the results of Feng et al (2009), and thus is key for your manuscript where you compare precipitation isotopic composition at the seasonal scale to an ice core records spanning more than 30 years. It also shows that in both winter and summer, the slopes you obtained are larger than expected by the Rayleigh distillation.

2. There are previous observations of positively correlated d-excess and $\delta^{18}O$ (or δD) in Greenland. For instance, Barlow et al. (1993) present data from Summit where δD and d-excess are correlated at the seasonal scale in an ice core. This seesaw variation was later attributed before to variations of SST in the north atlantic (Hoffmann et al., 2001) using a Rayleigh distillation model. In depth discussion on the difference between your results and their results are necessary.

3. Section 4.1 is essentially a second introduction. I recommend that you to consider integrating it into the introduction and removing it from here.

Oppositely, what is missing from the discussion is the comparison of your results with time series and slopes from other study at summit and in other neighbouring sites in Greenland.

4. Section 4.2 is essentially a method sub-section, except for the first two paragraphs which are introduction material. Consider integrate it into the methods and removing it from here.
5. The arguments in section 4.3, which are central to the arguments of this manuscript, are developed with unsatisfactory level of details.

First, it is not clear what data are used to calibrate the multi-linear regression problem in section 4.3.3. and in Fig. 5. Only 16 diffusion corrected slope data points appear on the plots while you initially have 32 years obtained from the owen ice core. Were the data selected to cover the period observed in Box et al, 2006 ? If yes, is this period representative of the entire period ?

Second, is the SPI over the entire surface of Greenland representative of the SPI across the area where moisture travels from the North Atlantic to Summit ? As there is a significant surface north of Summit where one does not expect any summer precipitation travel path to go to, it would be important to evaluate how this impacts the data. Are the precipitation also coming more generally from trajectories from the Davis Straight of the Denmark Straight ? Considering that the patterns observed are very different for the South East, the South West, and the North, one would expect this to impact the results. In general, changes of origin of the air masses from the west or the east of Greenland would be expected to impact the results, and is not discussed here relatively to the impact of sublimation.

Third, how good is ERA-interim precipitable water amount ? In general, the amount of precipitation over the ice sheets is quite biased.

There is no interpretation of the various regressions in Fig. 5. For instance, earlier in the manuscript, you describe the temporal slope of the diffusion corrected slopes as not significant. So how are the trends compared to the original trend ?

It seems also that the vertical axes of the three different sub-figures of figure 5 are different as the horizontal levels of the larger and smaller vertical values do not match (I can't judge for the other points).

How crucial is the diffusion correction for these results ?

How good would be a prediction from the multi-linear regression using the best fit to actually predict your slope time serie ?

6. It is not clear to me how you discard the change of trajectory of the air masses between summer and winter, which could also explain the offset between summer and winter values.

For instance, have you performed any back-trajectory analysis that shows that for the period from 1979 to today, the air masses originates and travel roughly across the same areas and are under the same level of distillation ?

7. As you mention the large impact of sublimation across the Greenland ice sheet to the moisture that leads to the formation of precipitation, I think you need to mention the impact on the surface snow (see the comments of the other reviewers).
8. Alternatively, there are measurements of vapour isotopic composition at Summit (Berkelhammer et al., 2016) which would provide an estimation of the vapour d-excess value which can be of interest to validate the hypothesis that sublimation from the ice sheet provides a significant amount of moisture into the precipitation. The impact of the exchanges between the snow and the vapour could also affect the surface d-excess.
9. The study presented here focuses mainly on seasonal and interannual time scales. The previous study of the authors (Kopec et al, 2019) focuses on the synoptic time scale. In general, I do not believe it is possible to generalise the results from these time scales to large time scale without further studies and recommend caution to the authors to really assess at which time scales they results can be applied.
10. In general, the authors need to include a greater representation of the relevant literature. There are a lot of papers that would be relevant for this study that have been overlooked, which as a result weaken the manuscript.

Specific comments:

Page 2 - Line 17: "Over the past half century, variations of hydrogen (δD) and oxygen ($\delta^{18}O$) isotopic ratios of precipitation have served as increasingly powerful tools in a wide range of disciplines of research, including paleoclimate, hydrology, and atmospheric sciences."

While this is generally true, there is a large body of literature, including review papers that you can cite here to your point...

Page 2 - Line 19: "One of the most striking features of these two paired isotope ratios is that they are remarkably well correlated over time and space, and this relationship is defined as the meteoric water line (MWL)."

At this stage, one of the early reference could also be used, for instance: (Dansgaard, 1964). You could also add one of the GNIP paper (Schotterer et al., 1996).

Page 2 - line 26: "In the field of paleoclimate studies, for example, δD or $\delta^{18}O$ variations in ice cores have been used to infer temperature changes at ice core drilling sites (e.g. Jouzel et al., 1987; Dansgaard et al., 1989; Johnsen et al., 1995, 2001; Blunier et al., 2001; Petit et al., 1999) and deuterium-excess variations in ice cores have been used to infer

changing marine moisture source conditions over a range of time scales (e.g. Johnsen et al., 1989; Barlow, et al., 1993; Vimeux et al., 1999, 2001; Uemura et al., 2004, 2012; Masson-Delmotte, et al., 2005; Jouzel et al., 2007).”

For temperature reconstruction, there are a large number of recent reference that could be included, including from Greenland: (NEEM, 2013;NorthGRIP, 2004)...

For the d-excess variations and the link with marine moisture source conditions, I would also recommend including more recent references

Page 3 - Line 1: “There are relatively fewer studies focusing on how the slope of the MWL changes over space and time, and determining how such variations may contain climate information.”

This sentence needs to be more precise:

1. the slope of the MWL in the isotopic composition of precipitation is what you’re focusing on, as the MWL slope can change in the snow for instance due to diffusion, and thus is not containing any climatic information
2. Fewer than what ?
3. I’m not convinced that there are few studies which have looked at the spatial variations of the slope δD vs $\delta^{18}O$, for instance (Masson-Delmotte et al., 2008;Touzeau et al., 2016;Landais et al., 2017;Werner et al., 2018;Jouzel et al., 2000), for the temporal variations (Oyabu et al., 2016;Masson-Delmotte et al., 2015;Werner et al., 2001;Steen-Larsen et al., 2011;Persson et al., 2011) and for the space-time (Hendricks et al., 2000;Risi et al., 2013;Sodemann et al., 2008;Ekaykin et al., 2002)

Page 3 - Line 3: “For example, if the slope of a LMWL with seasonally resolved observations is less than 8, then d-excess and δD (or $\delta^{18}O$) would have an anti-phase relationship, and the opposite is also true “

I believe this is generally true, regardless of the seasonal resolution.

Page 3 - Line 6: “This out-of-phase relationship between the two is equivalent to the fact that, in these locations, the LMWL (with a monthly or higher resolution) has a slope less than 8. “

Here, the relationship is in “phase opposition”, not out of phase. Out of phase could mean everything as completely random, to in phase opposition.

Page 3 - Line 10: “To our knowledge, this is the only work that described the slope distribution of LMWLs on a hemispheric scale and discussed the climatological significance of these slopes.”

This is a very strong statement. For instance, this study (Pfahl and Sodemann, 2014) seems to do something quite similar using d-excess, which is equivalent to the slope δD - $\delta^{18}O$.

Page 3 - Line 11: "Temporal changes, e.g., seasonal or inter-annual, in the δD - $\delta^{18}O$ relationship for a given location have not been explored and can potentially provide information and understanding of seasonal or interannual variations in the planet's climate system."

There is body of research exploring for a given location the δD - $\delta^{18}O$ relationship. In Antarctica: (Touzeau et al., 2016; Dittmann et al., 2016; Stenni et al., 2016). In Greenland: (Landais et al., 2012; Steen-Larsen et al., 2011)

Page 3 - Line 14: "Summit, Greenland is one of the most important sources of deep ice cores that provide valuable paleoclimate records, particularly through the measurement of water isotopes. "

I think the term "most important source of deep ice cores" is not very precise. Please reformulate.

Page 3 - Line 17: "While Feng et al. (2009) demonstrated that almost all sites in the mid-to high-latitudes of the Northern (and Southern) hemisphere exhibit an out-of-phase relationship between δD and d-excess, and the mechanisms controlling this pattern are relatively well understood, Kopec et al. (2019) recently reported a nearly in phase relationship between δD and d-excess of event-based precipitation measurements at Summit, Greenland."

The demonstration from Feng et al (2009) is at the seasonal scale from GNIP data. δD and d-excess are there anticorrelated.

Your previous study (Kopec et al, 2019) presents results across the synoptic scale and the seasonal scale.

Both results are not necessarily opposed considering the different time scales.

Page 6 - Line 22: "This result is consistent with the observations of Kopec et al. (2019), where they reported d-excess measurements in phase with δD or $\delta^{18}O$ values."

Why don't you present the slope and the correlation ? "In phase" is vague to describe the link between d-excess and δD .

Page 7 - section 3.2: As you are comparing results obtain from precipitation samples and from an ice core, it would be important to transpose the diagnosis made in section 3.1 to section 3.2. In particular, I think presenting the equivalent of figure 1.b) for the Owen ice core would be beneficial. In the precipitation, you show that the slopes are actually smaller than 8 if you look at winter and summer separately, but there is a shift between the cloud of winter points and the cloud of summer points. Is the same shift visible in the Owen ice core if you do the slope on all the summer points (high $\delta^{18}O$ points) and all the winter points ?

Page 7 - Line 23: "Correction for the diffusion effect on the isotopic record produces some significant differences, most prominently, the elimination of the temporal trend in the δD - $\delta^{18}O$ slope"

Did you realise any sensitivity tests for this ? Considering this is widely used after, it would make sense to make sure that this is pertinent.

Also, considering other ice core have been drilled at summit in the 90's, can you compare the values with these ice cores ? It would be interesting as then, the values at the top of these old ice core would not have had time to be diffused, and thus, you can validate how much the back diffusion is not creating any artefacts.

Page 10 - Line 5: "Sublimation from the snow surface has been shown to reduce the d-excess of the remaining snow, while the vapor removed by sublimation has a high d-excess (Moser and Stichler, 1974; Stichler et al., 2001)."

There are more recent studies studying these processes (Sokratov and Golubev, 2009; Steen-Larsen et al., 2013; Steen-Larsen et al., 2014; Casado et al., 2016; Ritter et al., 2016)

Page 13 - Line 15: As figure 6 does not have a colour scale for the δD - $\delta 18O$ slope, it is very difficult to understand this paragraph. In general, I would recommend a more detail explanation.

Page 13 - Line 31: "First and foremost, we show that the slopes of δD - $\delta 18O$ lines observed over different timescales and from various records (i.e. precipitation or ice cores) can be valuable tools to explore hydrological processes through the climatological controls of the isotopic composition of precipitation."

In your study, you present results covering the seasonal and interannual scale. The generalisation to larger time scale is not shown, but hypothesised.

Also, in your manuscript, I was under the belief that you considered ice cores as precipitation (and diffusion which you are correcting). A discussion on the differences between precipitation and ice core would be interesting, but I don't believe it is central to your manuscript.

Page 14 - Line 2: "Using the slope of this line adds a new method of inquiry as it holds more information, or at least different information, than simply taking the average δD , $\delta 18O$, or d-excess over a given time window."

d-excess and the slope δD vs $\delta 18O$ is the same climatic information.

Page 14 - Line 11: "In order to use δD - $\delta 18O$ slope measurements in ice cores, it is critical to account for the effects of diffusion, which we show to have significant impacts on the slope. If done properly, the method we developed can be applied to deeper cores and/or at other locations."

I also believe this is very important. I suggest you include tests that evaluate what impact the correction of effects of diffusion has on the slopes.

Page 14 - Line 33: "Second, while the precise mass balance computations are beyond the scope of this study, the fact that this moisture source significantly

contributes to summer precipitation shows that moisture recycling is potentially an important component to consider for the mass balance of the Greenland Ice Sheet.”

This is indeed out of the scope of the study and brings a lot of questions:

- How much moles of water does your result suggest this represent?
- What is the relative proportion that this represent compared to the summer accumulation ?
- How do you distinguish surface sublimation from sublimation of the snow flakes by katabatic winds in coastal areas (Grazioli et al., 2017) ? Indeed, the sublimation of the later will not contribute to the SMB.

I suggest to remove this sentence or to go in more details.

Page 15 - Line 30: “Over the measurement period of the Owen ice core, the reduction of sea ice has caused an increase of Arctic sourced moisture at Arctic coastal sites (Kopec et al., 2016). If this sea ice effect has also reached Summit, Greenland, we would expect to see the δD - $\delta 18O$ slope decrease over time. However, after correcting for diffusion, there is no significant temporal trend in the δD - $\delta 18O$ slope (Fig. 3).”

At this stage, I don't think you can reach such conclusion without evaluating the impact of the diffusion correction on your data and by using a single ice core while multiple previous studies have proposed alternative explanations which fit several ice core, and even sometimes ^{17}O - excess.

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