

Estimation and calibration of the water isotope differential diffusion length in ice core records
tc-2014-208

Author response to the review of Eric Steig, Referee #2

We'd like to thank Eric Steig for his comments and suggestions for improvement of our manuscript. Below we restate his report in bold and answer each comment directly below it.

This paper makes valuable progress on the use of diffusion of water isotopologues as a paleothermometer. The paper is very good, and certainly deserving of publication in The Cryosphere. I have some concerns, however. There are a number of statements made in the paper that are not well-supported. The paper should be re-reviewed after revision.

1) I concur with the first comment that the equations should be more fully developed in the paper.

See comments to referee #1 and respective changes in the manuscript.

2) On page '930', it states that "these common factors cancel out to a large extent . . .".

I think this is incorrect. The point of Johnsen et al.'s (2000) work is that the various factors such as tortuosity will cancel out completely in the differential diffusion. If this is incorrect, the authors should clarify: what does not cancel out?

The squared diffusion length is proportional to the integral of diffusivity over time:

$$\sigma^2 = \int 2 \Omega_{fi} dt$$

where Ω_{fi} is a function of various parameters (see eq 2, p 931). The differential diffusion length calculated in ice equivalents is then given by:

$$\Delta\sigma^2 = 2 \int (\Omega_{f18} - \Omega_{f2}) \left(\frac{\rho}{\rho_{ice}}\right)^2 dt$$

Which, using eq 2, is equal to:

$$\Delta\sigma^2 = 2 \frac{m}{R} \int \frac{p_{sat}}{T\tau} \left(\frac{\Omega_{a18}}{\alpha_{18}} - \frac{\Omega_{a2}}{\alpha_2}\right) \left(\frac{1}{\rho} - \frac{1}{\rho_{ice}}\right) \left(\frac{\rho}{\rho_{ice}}\right)^2 dt$$

From this it is clear that although the tortuosity is a common factor to both isotopic diffusivities, it does not cancel out completely in the calculation of $\Delta\sigma^2$. The advantage of using the differential diffusion length is that with the PSD method the variations of the PSD of the initial (undiffused) signal with frequency are very similar for both isotopes. As a result, when taking the ratio of the two PSD spectra these common variations cancel to a large extent, which is why the first term on the right hand side of eq 10 can be assumed to be independent of frequency (or wavenumber k). This is what we meant by "common factors cancel

to a large extent". We agree that this is not clear from the current text and will modify it.

To have factors such as tortuosity completely cancel out one should take the ratio of diffusivities, which is done in van der Wel et. al. (2011). However, this is only possible in a laboratory set up where these factors are approximately constant.

3) Also on page '930', it is said that the correlation of the two isotopes decreases with diffusion. This is only true for some timescales. Johnsen et al. 2000 showed that for seasonal timescales, the correlation increases, because the initially out-of-phase deuterium excess signal becomes in phase. This should be clarified.

In our synthetic data we also observe this effect in deuterium excess, which illustrates that most of the d-excess signal in high resolution ice cores is diffusion induced and not atmospheric. However, this does not imply that the correlation increases. This is also clear from our test where we start off with a synthetic data set with initial correlation equal to 1. The initial constant d-excess changes into a signal in phase with the isotopes when diffusion is applied. At the same time the correlation decreases to a value of 0.9947 (see page 942 and Fig 5).

4) A general comment regarding impurity content: The work of Freitag et al is cited, and assumed to be correct. Yet other studies have shown no such relationship (see Buizert et al. 2015, in CP). This suggests that the apparent affect of Ca on densification is an artifact. The authors need to acknowledge that the question of impurity affecting densification is not settled, and to discuss the implications for their diffusion results. My impression is that this is a correction to the H-L model that is really not very important.

It is correct that the Ca effect on densification is still under debate. We will acknowledge this in the updated version of the manuscript. We disagree, however, with the referee that this correction is not very important. In Fig.7 it is clearly illustrated that the traditional H-L model is unable to reliably reproduce the density profile. We agree, however, that the improved density profile, when including Ca as a parameter to change the densification rate, could be fortuitous and that Ca may not be the driving factor for the changed densification rate. We will acknowledge that in the revised manuscript. Here, we use the different density models as a sensitivity experiment. In Fig. 7 calculated diffusion lengths with and without this effect for part of the EDML Holocene record are shown. This shows that including the effect leads to an approximately 1 °C change in the reconstructed temperature. The Ca concentration varies in this interval between 1 and 3 ppb. For glacial periods the Ca concentration is at least 1 order of magnitude higher and the effect on the temperature reconstructions is several °C. We will make the latter statement in the manuscript to alert the reader of the problems of our insufficient understanding of densification for past temperature reconstructions using isotope diffusion thermometry.

5) Page 938: The biggest problem with the paper is the attempt to examine whether the initial signal is independent of frequency. The authors use precipitation data from the GNIP database, look at the spectra, and note that it is not white. From there, they argue that one cannot assume that the initial spectrum of the isotope ratios is white. This is probably correct, but only in a very strict sense, and I think it is misleading. In fact, Johnsen argued that the spectrum of the isotope ratios in polar firn was essentially white, in spite of the spectra of temperature and other relevant meteorological variables not being white. He proposed that this was due deposition noise, which tends to whiten the signal. Furthermore, the question of "redness" depends very much on the timescale being considered. The relevant climate variables are red on an multiannual to decadal and longer timescale, but rather white on shorter timescales. The diffusion affects the signal – at moderate and high snow-accumulation sites – mostly at the high frequencies, where the initial signal is white. Gkinis et al. (2015) did an extensive set of tests in which they examine the degree to which the redness of the climate signal actually matters, and concluded that it does not significantly affect the results. Having suggested these tests to them, I am familiar with what they did, and I believe that they are correct, for all but the lowest accumulation-rate locations (e.g. perhaps Vostok). Another point is that it does not actually matter if the initial spectrum is white, if one is interested in relative temperature change through time, as long as temperature changes are calculated relative to the initial spectrum at the surface. In short, I believe it is incorrect to say (as the authors do) that "the assumption of an initially white spectrum of water isotopes in precipitation should not be made."

We have looked at precipitation data from the GNIP database as we realized that when the initial spectrum is not white (when P_0 varies with k), this would influence the result obtained with the single isotope diffusion method. Unfortunately, there is no way of obtaining this initial spectrum as the isotope signal just below the surface is already being influenced by diffusion, so an ultimate proof of the whiteness of the initial spectrum is missing. Therefore, we regard the GNIP data to be the best approximation. However, we will discuss this issue in the revised version of the manuscript. Note that with using the differential diffusion length, the issue of the color of the spectrum is not important anymore and therefore we still prefer to use both isotopes for diffusion thermometry. Moreover, using our new forward diffusion method (instead of the power spectral estimates) only $\Delta\sigma^2$ can be obtained anyway.

The fact that at least for high frequencies, where diffusion effects are strongest, the initial spectrum is white does not help as in the determination of the diffusion length the low frequency part is also included. An annual peak in this low frequency part may significantly offset the calculated diffusion length.

As far as we can work out from the supplementary material provided in Gkinis et al (2014), they did not quantify the color of the initial spectrum before diffusion. Instead they assume a red spectrum for the noise P_n which may include both

white measurement noise as well as red noise from other sources. While this is certainly an improvement over assuming only a white noise spectrum, it is still no proof of the true color of the noise in the signal before diffusion. That is why in a stringent sense we prefer to use $\Delta\sigma^2$, where this issue is not relevant. We will change our wording accordingly.

We do not support the referee's suggestion to calculate the temperature changes relative to the initial spectrum at the surface. This would mean that we assume that the initial spectrum has not changed in time. We doubt this is a valid assumption as deposition regimes may have changed. Also, the thinning of the ice leads to the whole spectrum being stretched towards higher frequencies, which means the initial spectrum (if one would have it) would need to be stretched as well.

In short, we think it is justified to raise a warning flag regarding the single isotope method for this reason. We will change the wording in the abstract, main text and conclusion such that we no longer state that this method should not be used, but rather state that the uncertainty in the result is larger as a consequence of this as long as the whiteness of the initial spectrum cannot be proven.

6) A major conclusion of this paper seems to be that "the estimation of the differential diffusion length is much more reliable than the estimation of the individual diffusion lengths is". This must be true, in principle, as Johnsen showed. But I am not convinced that the authors have demonstrated that it is true in practice. Much attention is paid to the absolute accuracy of the temperature reconstruction, but in general we are not interested in absolute accuracy, but relative temperature change (e.g., working out the size of the glacial-interglacial temperature change). In that case, it appears to me that the differential diffusion calculation does not do better than the single-isotope diffusion. At least, I do not think that the authors have demonstrated this. There are more assumptions that need to be made with the single-isotope diffusion, but there are problems with differential diffusion as well. In particular, the fractionation factors at cold temperatures are not yet well enough known, particularly for deuterium. In summary, I think the authors are too quick to dismiss the "single diffusion" calculation. I would like to see a calculation of the *relative* temperature change, based on 1) d18O, 2) dD, and 3) both. Is the answer actually meaningfully different between these? If so, why?

This conclusion follows from the dependence of P_0 on k as discussed extensively in point 5. We believe this will also influence the relative temperature change. The initial spectrum P_0 may not be the same for glacial and interglacial periods. Especially the effect of thinning which stretches the PSD to higher frequencies will have an influence.

Using the differential diffusion technique this problem is avoided, as it is likely that the initial spectra of the two isotopes have the same characteristics. It therefore becomes unimportant whether the initial spectrum is white, red or has a large annual peak. These features will cancel when the ratio of the two PSD's is taken. This is how we come to our conclusion that the differential diffusion method is

more reliable than the single isotope diffusion method. With the new correlation method described in this manuscript, this conclusion is even more justified, as there is now a second independent method for determining $\Delta\sigma^2$.

In Fig. 11 we already show temperature reconstructions based on both isotopes (psd method and correlation method) and based on d18O only for part of the EDML ice core record. We will add the reconstruction based on d2H in this figure. From the figure it is clear that within the uncertainty the methods agree. We will acknowledge this in the revised manuscript. However, we believe that this is not a guarantee that this is also the case in general.

References:

Gkinis, V., Simonsen, S. B., Buchardt, S. L., White, J. W. C., and Vinther, B. M.: Water isotope diffusion rates from the NorthGRIP ice core for the last 16,000 years – glaciological and paleoclimatic implications, *Earth Planet. Sc. Lett.*, 405, 132–141, 2014.

van der Wel, L. G., Gkinis, V., Pohjola, V. A., and Meijer, H. A. J.: Snow isotope diffusion rates measured in a laboratory experiment, *J. Glaciol.*, 57, 30–38, 2011