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Date: May 27, 2017
To: "Christian Holme" christian.holme@nbi.ku.dk,chred123@hotmail.com
cc: frank.mcdermott@ucd.ie
From: "GCA Editorial Office" eesserver@eesmail.elsevier.com
Reply To: "GCA Editorial Office" gca@elsevier.com
Subject: Your submission GCA-D-17-00136 has received a decision

Manuscript Number: GCA-D-17-00136

Title: Molecular diffusion of stable water isotopes in polar firn as a proxy for past temperatures
Geochimica et Cosmochimica Acta

Dear Mr. Holme,

Our editorial evaluation of manuscript number GCA-D-17-00136 which you submitted to Geochimica et Cosmochimica Acta has been completed. In light of this evaluation, the manuscript will require substantive revision before it can be considered further for publication in GCA.

A report from the Associate Editor with the external reviews is appended below and available to you via EES. We invite you to address the issues raised by this report and the reviewers in a revised manuscript. A detailed reply should accompany the revised manuscript as a separate document titled "Response to Reviewers."

Please address each review comment, point by point, referencing page or line numbers of the manuscript file to facilitate the next round of editorial assessment.

Please submit your revision online by logging onto the Elsevier Editorial System as an Author:

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NOTE: Please contact the Editorial Office at GCA@ELSEVIER.COM if you require more than the 90 days to submit your revision.

Thank you and we look forward to receiving your revised manuscript.

Sincerely,

Dr. Marc Norman
Executive Editor
Geochimica et Cosmochimica Acta

Additional comments from the Editors and Reviewers (if any):

Dear Dr Holme,

I have now received three thorough reviews of your manuscript 'Molecular diffusion of stable water isotopes in polar firn as a proxy for past temperatures'. Having read your manuscript and having tried to evaluate the approach from the viewpoint of a non-specialist reader, I agree with the reviewers that the manuscript requires very substantial revision before it can be reconsidered by GCA. All three reviewers raise many points about how the clarity of the text could be improved, but I would especially draw your attention to the comments of Reviewer 2 concerning deficiencies in the model physics of the (oversimplified) forward diffusion model.

Please address the concerns of all reviewers. Your revised manuscript will be sent out for review again should you decide to resubmit. If you do, please attach a separate document explaining point-by-point and in detail how you have addressed every point raised by the three reviewers.

Thank you for submitting your work to GCA and I hope that you find the reviews helpful in taking your manuscript to the next stage.

Yours Sincerely,

Frank McDermott
Associate Editor

Reviewer #1: This manuscript examines a variety of methods for inferring temperature from diffusion of water stable isotopes. The authors use both synthetic and ice-core data to assess the reconstructions of temperature. They conclude that despite some theoretical advantages of using differential diffusion lengths, the single diffusion length methods are more robust. This is a strong paper and should be published after minor revisions. The science is sound and well described. This is a technical study and the conclusions are a little underwhelming, but I suppose the authors don't want to negatively bias methods while the field is still emerging. However, I would have liked at least a paragraph of forward looking discussion about how their testing of different methods should impact future measurements of ice cores.

[note from GCA Executive Editor: As the primary aim of GCA is to present studies of fundamental significance and broad relevance for understanding geochemical systems, mechanisms, and processes, this is a reasonable request and should be addressed specifically in the revised manuscript.]

While I understand choosing climate conditions applicable to Central Greenland and the East Antarctic Plateau because there is ice core data available, I was disappointed that the authors did not take advantage of being able to create synthetic data from warmer and wetter climates. Many ice cores are being drilled closer to the margins of the ice sheet and the work would have greater applicability if it focused on where ice coring was going rather on where it's been.

The manuscript could also use a quick edit from a native English speaker as some of the idioms and transitions are slightly off (e.g. "wavelengths in the order of 50cm" should be "wavelengths on the order of 50cm" or the use of "nowadays"). I've noted some of these at the beginning, but there are many I didn't note. A few other general points:

- 1) There was little if any discussion of the initial power spectrum at deposition. This became particularly apparent in the removal of the annual cycle, which struck me as odd - the one signal that you know the frequency of just gets thrown away. Is there no way to use the annual signal in a constructive way?
- 2) The use of warm and humid to describe a site with an annual average temperature of -30C and an annual average accumulation of 22cm per year is very confusing. Not even among ice core sites would this be considered warm and humid. Why not just use CG - central Greenland and EAP - East Antarctic Plateau since this is what you really mean. In addition, CD is not representative of much of Antarctica, just the East Antarctic Plateau.
- 3) The ability of the single diffusion length methods to reconstruct synthetic data to within 0.5C seems quite good. But as I think about it more, I wonder if this is really something to be excited about. Given that the amount of temperature change within the Holocene is about 0.5C, does this imply that water stable isotope cannot be used to infer anything about temperature in the Holocene? The synthetic tests don't really address the question of what amount of temperature change can be confidently identified. For instance, what percentage of the time can a synthetic data set created with a surface temperature of -31C be distinguished from a data set create with -30C?

Specific comments:

- Line 30 - add "of the water isotope diffusion methods" so as not to imply that the water isotope diffusion methods are better than other methods, i.e. borehole temperature reconstructions
- Line 36 - change "invaluable". Maybe use unique or some other qualifier, but something with less subjectivity.
- L43 - delete "however"
- L45 - reword this sentence. Don't start with "However"; I'm not sure what "more physical principles" means, should it read "such as"?
- L51 - seminal seems strong for a paper read only by the very small community into water isotope diffusion
- L57 - "More specifically" does not seem like the correct transition
- L59 - "Nowadays" is a bit archaic and informal, no?
- L62 - A reference to the Univ. of Colorado system is noticeably absent here. Jones et al., 2017, JGR.
- L76 - define what you mean by flavors. I think you can make this word choice work, but not without explaining how "flavor" applies to water isotope diffusion
- L83 - Sentence beginning "For some cases" does not make sense to me. Also, the Holocene Climate Optimum is a bit nebulous, so you should define what you mean.
- L85 - don't call your own work "interesting". Let the reader decide that.
- L 92-93 - If you use "can" then "possibly" is redundant
- L94 - delete "that have dealt with the matter". This is implied
- L97 - I like this approach and feel you have struck a good balance with what information is included in the main, what's in the appendix, and what is referenced
- L117 - use different word than "sensor"

L137 - I wonder why the authors only considered such cold sites. Given that much of the paper focuses on synthetic data, why not include coastal sites with warmer temperature and higher accumulation rates. This would make the work more broadly applicable, particularly since the vast majority of ice cores (not necessarily deep ice cores) are being drilled in locations warmer and wetter than either of the CG or EAP situations.

Figure 2.1 - I favor more detailed figure captions so that a reader can scan the manuscript and know what's going on in a figure without needing to find lots of details in the text. In this case, provide the accumulation rates and temperatures for WH and CD. I'd also like a sentence describing the main takeaway from the figure; something like: The increase in diffusion length with depth from vapor transport is partially offset by compaction of the firn which moves the ice closer together.

Figure 2.1 - why is there a kink at ~20m depth. Does this have to do with the transition from Zone 1 to Zone 2 densification?

Figure 2.1 - make the legend lines bigger

L150 - "borehole temperature profiles" is the more common description

L150 - This sentence confuses me. Do you just mean that the temperatures you use in your model are based on borehole temperature profiles? The sentence implies that you are obtaining the diffusivities from the high precision borehole temperature profiles. But really you just need a number to plug into the Ramseier equation.

L166 - "in" should be "on"

L178 - this notation comes out of nowhere

L232 - add comma after f_{λ}

L232 - is there really nothing useful to be gained from the annual signal? This raises the question of why the power spectral density is the way it is.

L270 - is the ice diffusion the same for all isotopologues? What is the evidence for this?

L284 - delete the comma and change "can be" to "is"

L285 - define dxs . This is the first usage

Reviewer #2: Review of "Molecular diffusion of stable water isotopes in polar firn as a proxy for past temperatures" by Holme et al.

Holme et al. compare several methods of reconstructing paleotemperatures from water isotope diffusion lengths. Based on synthetic and real ice core data, they argue that single diffusion length estimates are more reliable than differential methods, both in terms of their precision and their accuracy. The comparison of these different methods is a good and timely contribution to the literature, and should be performed. However, due to the strong reliance on synthetic data, it is unclear to me whether these conclusions will actually hold for real-world studies. I think additional work is needed to provide realistic estimates of the accuracy of the method when applied to real-world problems.

I personally have not worked on the problem of water isotope diffusion, but I've been following the field out of interest. In principle the method is very original and powerful, but I've always had the feeling that several key uncertainties are being ignored, which means that the cited uncertainties are much too optimistic. The 0.5 degree accuracy claimed for the single profile method seems unrealistic to me. The method shows up to 3-4 degrees offset for modern sites (Fig. 5.2), which seems like a much more realistic and meaningful estimate of the accuracy to me.

My main concern is that there is likely a lot of missing physics in the forward diffusion model, which is not accounted for. This is particularly problematic when using synthetic data, as I will argue below.

Some missing physics includes:

1) The work assumes that the initial deposited isotope record has a more or less white noise spectrum. This assumption is made implicitly in the work of Holme et al., and never really addressed. This assumption is baked into Eq. 4.2. We know for certain that the annual cycle has a big imprint, which is briefly addressed (but not included in the synthetic data, as far as I can tell). Besides that, Greenland ice cores are strongly affected by the NAO, and the WAIS core by ENSO/PDO variability as well as the SAM. We know that all these modes of variability have considerable power in the sub-annual bands. Also, snow is deposited in finite events (up to several cm of precip each), which leads to considerable autocorrelation. How does this influence the accuracy of the methods?

There have been studies of isotopes in surface snow and vapor. Can the assumption of whiteness be proven or disproven?

2) There is considerable uncertainty in the densification model and tortuosity parameterization. There is a large literature from gas studies that looks into tortuosity (in models, measurements, and firn pumping experiments). These suggest that tortuosity is highly site-specific, as well as scale dependent (for example, cm-scale tortuosity is different from m-scale). This will skew the reconstructions (it's not clear in which direction...). This bias will not show up in synthetic data tests, because both the forward and inverse model assume the same firn properties.

3) Does the seasonal temperature cycle matter? This drives both intense grain metamorphism (depth hoar) and influences vapor pressure and diffusivity (exponentially!). Density layering in general is probably important, because the diffusion length is not a single value, but presumably varies within each annual layer. This means that the final PSD is not Gaussian, but a superposition of Gaussians with different sigma values.

4) Recently, it was shown that at WAIS the diffusion length changes through time in a very unpredictable way (doi: 10.1002/2016JF003938). Also, field tests suggest large differences between modeled and observed diffusion (doi:10.5194/tc-9-1089-2015). All these observations argue for missing physics. I do

not pretend to know what such physics would be; I just think that these observations should caution us that the physics is not as simple as Johnsen et al. (2000) would have us believe.

The use of synthetic data is interesting in principle, because it allows testing in a controlled environment. But it can also be very misleading, because it assumes that the forward model (i.e., how the diffused isotope records are created) is exactly known - which I think is a fallacy, see above. Perhaps I misunderstood, but it seems that in the synthetic tests the exact same firn properties (density, tortuosity) are used in the forward model, as in the "inverse" model (with the inverse model I mean the calculations used to go from sigma to temperature). I think this artificially improves the accuracy, and favors the single diffusion length methods (perhaps explaining why they look so good in the synthetic comparison). The differential diffusion methods should be less sensitive to these errors, because both isotopes diffuse through the same firn (tortuosity, density), canceling out some of these uncertainties.

What I would advise the authors to do is to build some of this missing physics into their forward model that generates the synthetic data series. For example, they could use random number generators to control annual accumulation rates, temperatures, precip events, firn density layering and densification rates, tortuosity parameterizations, fractionation factors, etc. The isotope input spectrum should have an annual cycle, as well as a "redness" that is randomly selected. These random perturbations are not known to the part of the model that interprets the synthetic data. Then when the authors use the synthetic data to reconstruct T, there are unknown "biases" in their data, which is a much more realistic test than currently performed.

The authors use an AR(1) process currently, but it is clear that the model does not introduce any meaningful level of redness (See Figure C.2). Where do the auto-correlation parameters come from?

My gut feeling is that the single diffusion methods are much more sensitive to such "unknown physics", because they will cancel out to some degree in the differential methods.

How does the inverse model deal with accumulation rates? Are these assumed to be known exactly? Here some noise should be added too, since these are never known precisely. The same is true for the thinning function.

There are different types of uncertainties: unknown firn physics, fractionation factors, accumulation rates, ice thinning, etc. In general, it would be interesting to know how sensitive these methods are for each of the sources of uncertainty. That could help decide which method is most suitable under which condition.

More detailed comments:

Line 44: assuming a linear relationship is of course not the same as using the spatial slope. The temporal slope is also a linear one.

Line 47: Schwander 1988 is not the correct reference here. Thermal fractionation wasn't discovered until a decade later.

Line 51: While Johnsen 2000 is undoubtedly a good paper, there were many others that made just as seminal contributions, like Whillans and Grootes 1985, and Johnsen 1977.

Line 85: HCO is poorly defined, give the age!

Eq 2.1: Technically D is a function of depth also, particularly in the presence of layering. Also, this equation is an approximation, because delta is not a mass-conserving quantity.

Equation 2.2: is this an exact solution, or an approximation?

Line 117 and elsewhere: This is confusing. How can sigma be used to reconstruct both T and A? It has to be either one. You cannot reconstruct two independent parameters from a single number.

Line 126-127. This is conceptually sloppy. Both ρ_{ice}/dt and D do not care about accumulation rate, of course. ρ_{ice}/dt cares about T and overburden pressure (not A), and D cares about temperature and firn connectivity.

Line 128: again, I don't think you could do both T and A, unless you have some other source of info.

Line 129: what are the typical measurement precisions for these various isotopes?

Line 139: above the close-off depth ice diffusion also happens of course, within the grains.

Figure 2.1: Why Fig 2.1? please change to Fig. 1

Eq. 4.2: Shouldn't P_0 be a function of (k) also? It seems to be a constant here.

Line 171: I am confused by the use of AR(1) processes. In Eq. 4.2, the noise term represents the instrumental noise floor, correct? Shouldn't this be white noise? That's what's assumed elsewhere on Line 561. Also, this AR(1) is distinct from the AR(1) used in appendix C to estimate the input time series, correct?

Line 174/Fig 4.2: Could you show us some more real data PSDs, instead of synthetic ones? Ideally at least one PSD per core site (can be an appendix). Of course the fit to the synthetic data is good, because the synthetic data has the assumption of being Gaussian baked into it. I'm curious to see how well your method fits the actual data-based spectrum at various sites. Also, do the spectra at Greenland and Antarctic sites look very different?

Line 179: This is a little unclear. What is the difference between regular P and fancy P? Is regular P the model, and fancy P the observations?

Line 179: It appears that the background noise level is used as a fitting parameter. Isn't the noise level known from the instrument used?. Do the fitted noise levels agree with the known analytical precision of the instrument?

Line 196: I assume integrating Eq. 2.7 includes all the parameterizations used for tortuosity, density, thinning, etc? Please be more clear about this.

Line 205-213: is the single diffusion method more sensitive to this than the differential one?

Line 218: the annual peak is clearest when there is little diffusion, this is obvious. But the enhanced power in the annual band (in the input spectrum) should be preserved under all circumstances, correct? It may just be

smear out at high diffusion sites, but the power is there. It seems to me that at all sites the annual band should be disregarded from the spectral fitting. Please confirm how this is done. Also, is the annual band avoided in all analyses done here?

Why was there no annual peak added to the synthetic series?

Equation 4.7: What value of df_{λ} do you use?

Figure 4.2: please use real data here, synthetic ones are not as interesting.

Figure 4.5: are these real or synthetic data? I guess you know my preference by now :-)

Section 4.3: since this method performs so poorly, perhaps it can be left out to shorten the MS?

Eq. 4.12: Define α

Line 321: Here I was confused. Is the noise white or AR(1), as claimed earlier?

Is the noise

Line 324: As mentioned above, I think each time you generate synthetic data you should also perturb the firn physics, because this is an unknown in any real-world problem.

Figure 5.1: Do you have any idea where the clear $17\Delta^2$ bias comes from?

Lines 368-371: I couldn't agree more! This makes all the methods look too good, and as I argued above, particularly the single diffusion case.

Table 5.2: The selection of depth ranges seems somewhat arbitrary. Why were these depths chosen?

Line 389: 0.5deg C seems too good to be true. Many uncertainties were not really considered, so this number is not all that meaningful. The way of things is that this number will be cited by others in future work without all the caveats needed to understand that this value holds only under very narrow conditions of synthetic data in a perfect world where all physics is understood. I think this should be revised upward by including all the relevant uncertainties, in order for this number to be a meaningful reflection on the accuracy of the method in real-world applications.

Table 5.1 It's not precisely clear how you go from σ to T. What assumptions were made regarding the accumulation rates, for example? Were they precisely known?

Line 417: Why not just compare the reconstructed temperature with the modern day temperature? I understand there can be differences, but comparing to present day is the only meaningful way to test the accuracy of the method. The synthetic data are artificially unbiased because you assume you understand all the physics. Comparing the reconstructed temp from real isotope data to observed temps is the only meaningful metric to my mind. The abstract claims that the single isotope methods are the most accurate, but this doesn't always seem true when I look at Fig. 5.2, 5.3 and 5.4.

Line 485: I don't believe you have proved that the method is unbiased, because in the synthetic world you know all the physics and parameterizations, which is not true in the real world.

Line 502: Again, I don't think accuracy has been proven given that you didn't compare the temperatures reconstructed from the real data to real site temperatures.

Eq. A7: Note that there have been multiple different parameterizations. This is a very old study. A more recent result to use would be doi:10.5194/tc-8-319-2014, or doi:10.3189/172756402781816582.

Line 556: what are these parameters for the AR(1) input based on? Actual data? The input spectrum of the synthetic data is very white, and does not have an annual cycle.

Reviewer #3: This manuscript is well written and convincing for the material it chooses to cover.

My main reaction, however, is that it leaves the problem only half analyzed and this leads to the final conclusion being a logical fallacy.

The Abstract and the Conclusion sections finish (lines 29-30, 501-502) by claiming "this study has demonstrated that methods based on the single isotope diffusion length result in the most accurate and precise estimates of past temperatures."

But the authors have chosen not to analyze the factors that can make the single isotope methods problematic, in particular uncertainties in (1) firn densification and density-depth profiles as a function of climate, and (2) uncertainties in how vapor diffusivity varies as a function of density. These must be addressed!

The potential value of the multiple isotope analyses is to find methods independent of these uncertainties. The present analysis does a good job of revealing the inherent weakness of the multiple isotope methods, in turn. This is an original and useful contribution.

But ignoring the other side of the problem means that no conclusion can be reached about the relative or absolute merits of the different methods.

Another disappointment of the submitted paper is that the authors do not take advantage of the ice core data to quantify the accuracy of the thermometry methods. The reason, apparently, is that temperature varies (with depth and/or time) in the firn column, whereas Eq. 2.7 is for a steady-state (although this is never stated explicitly. I might be misinterpreting this.) Why don't the authors use Eq. 2.5 itself and time-dependent calculations of temperature and density to overcome this limitation??

The terrain covered by this analysis is already a narrow one for GCA. The authors can probably have this manuscript accepted almost "as is" at a good journal focusing on ice core or glacial studies. It would be much more useful to the readership, and to the authors' scientific reputations, if GCA returns this manuscript to them with instructions to expand the analysis to enable a useful and cogent conclusion. Then it will make a fine GCA paper.

A few minor points:

1. the authors neglect to cite the Whillans and Grootes JGR 1985 analysis, which is the source of most of our understanding of isotopic diffusivity
2. looking at Figure 5.2, is it just a coincidence that the $\Delta \sigma^2$ I method (the green circles) does a good job of matching the modern temperatures? A better job than any of the other methods?
3. there is a recent paper by T.R. Jones et al. in JGR Earth Surface (2017) that looks at isotope diffusion in the WAIS Divide core. It is a case in which the relationship between diffusion length and climate does not seem to work as expected.

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