

Response to review comments of manuscript " Distinguishing between old and modern permafrost sources with compound-specific $\delta^2\text{H}$ analysis"

The Cryosphere Discussions doi:10.5194/tc-2017-17

We thank the three reviewers for their comments, and provide answers to these comments and suggestions below.

Black: review comment

Blue, italic: our response and edits in manuscript

Reviewer Trevor Porter

General comments:

Title should indicate the study region (e.g., Laptev Sea catchment, NE Siberia).

We have added "in the Northeast Siberian land-shelf system".

Abstract is one of the longest I've read in recent years. It includes a lot of useful information, but could (and probably should) be more concisely written. I leave this to authors and editor to decide.

We have shortened the abstract, as indeed it was rather long.

There is now a large body of literature on the isotopic composition of relict ice from ICD's in this very same region (see Opel et al. 2017 Climate of the Past; and references therein). These studies find that precipitation isotope composition recorded in these ICD's was highly variable during Pleistocene cold stages; for example, texture and pore ice 2H values range from roughly -250‰ to -160‰ between ca. 50-30 cal ka BP, while ice wedge values (winter precip) during the same interval range from roughly -260 to -230‰. If the fossil plants were using the same water that is preserved in the pore ice, then there may be a significant amount of variance not yet captured in the n-alkyl dataset from the (n = 9) ICDs sampled in this study. The spatial distributions of distinct ICD units in this region are not equal (see Opel et al., 2017) and, thus, have different potentials for erosion and contribution to the blend of n-alkyls deposited on the shelf. I would like the authors to acknowledge this potentially major source of uncertainty. I would also ask the authors disclose any information they have on the age of the sampled ICDs and, if possible, cross-reference to the regional stratigraphy scheme outlined in Opel et al. (2017).

Thank you for highlighting this point. We had not seen the article by Opel et al. While it is still not a peer-reviewed published paper (status listed as "in discussion"), it clearly provides additional insight to ICD from this region. We have now cited this paper, as well as a few others in the Introduction (and elsewhere) of our revised paper. We agree that the point brought up can be a source of uncertainty, and have acknowledged this fact in section 4.2 quite extensively.

We have also added the 14C information we have available on a few of the samples analyzed (Table 1). The new text reads as follows (line 492-510):

"Finally, we realize that the amount of soil and ICD samples analyzed in this study is limited, and want to point out that the results may change when more data are analyzed in the near future. Additionally, studies have shown that the $d^2\text{H}$ signature of ice within ICD permafrost deposits can range from roughly -150‰ to -260‰ depending on the type of ice (wedge ice vs. texture ice) as well as the period of formation (different Pleistocene cold stages) (Opel et al., 2017 and references therein). The source of water (i.e. type of ice) and age of the deposit will therefore influence the n-alkane or n-alkanoic acid $d^2\text{H}$ signal. However, regardless of the natural variability associated with the processes mentioned above, both ICD and texture-ice isotopic compositions appear to reflect long-term climate changes (Opel et al., 2017; Schwamborn et al., 2006; Dereviagin et al., 2013; Porter et al., 2016) which, likely, were also captured in the n-alkane or n-alkanoic acid $d^2\text{H}$ signal. Unfortunately, we do not have ^{14}C -ages available for all ICD samples, so cross-referencing to published stratigraphies in the region is not possible. Coastal sediments, however, will represent a

mixture of material released from different depths, outcrops, and stratigraphies within the catchment or coast. For source-apportionment applications, we reason that a growing body of leaf wax d^2H end-member data from the ICD region can overcome the variability issues highlighted above."

This paper would benefit from another figure that provides photographic examples of the ICDs and topsoil sections.

We do not have high-quality photographic material available from all the sites, unfortunately, but have added a figure as supplementary information with some examples.

Specific comments:

L44, The n-alkane sum and interquartile range given (210 ± 350 ug/gOC) implies negative concentrations are possible, and is not consistent with Figure 2a. This also occurs on L299. *Since we shortened the abstract, we have removed the n-alkane concentrations from the abstract (L44) but have changed the notation in (the previous) L299 as this was perhaps confusing. The interquartile range was 350 (Q1-Q3), so we have chosen to now report this as 210_{148}^{494} to make it more clear that IQR1 is 148 and IQR3 is 494. (lines 344-349 and lines 364-369). We have also adjusted Table 4.*

L149, instead of citing the IAEA website, better to cite a peer-reviewed article that supports your statement. Dansgaard (1964, Tellus) is appropriate. *OK, good suggestion, we have done this (line 160).*

L158, it might be worth stating the underlying assumption, that colder air temperatures during the Pleistocene generally correlate with $2H$ -depleted precipitation; therefore, long-chain n-alkyl $2H$ during Pleistocene cold-stages should also be depleted compared to present. Also note that 'colder' and 'drier' could have opposing effects. All other factors equal (e.g., biochemical fractionation), a drier atmosphere during Pleistocene cold-stages could result in a larger leaf water enrichment and $2H$ n-alkyls (if RH is lower, despite lower air temps), which would lessen the overall offset between modern and Pleistocene n-alkyl $2H$.

Thanks, this is a good suggestion. We have edited this sentence to now read "Despite the plant fractionation associated with kinetic and plant physiology (Sachse et al., 2012), we hypothesize that δ^2H signatures of leaf wax n-alkanoic acids and n-alkanes are more depleted in OC from permafrost deposits formed during the colder Pleistocene (generally correlating with 2H -depleted precipitation), compared to more enriched values in OC from active layer or surface permafrost formed during the warmer Holocene. " (lines 178-183)

L199-201, if species information is available for the grasses and birch, please indicate.

Both samples were grass samples, but one of them was collected in the tundra, and one of them further south in a birch forest. We have clarified this (line 227-229). Unfortunately, we do not have species information available.

L308, the sphagnum index could also include C23 (see Bush and McInerney, 2013, GCA). For modern sphagnum samples I've collected in NW Canada (>65N), C23 is usually abundant (unpublished data). This suggestion isn't critical, but might be a more accurate metric for sphagnum vs. woody plants. *We are aware that either C23 or C25 can be abundant, but meant to illustrate the general differences (very small) between the two sample types. But, for comparison we have now replaced the $C25/(C25+C29)$ ratio with $C23/(C23+C29)$ in Figure 2 and added the C23 ratio to Table 4. Also, we have added a sentence to the text (line 357-360). Here, the average values for topsoil vs. ICD samples are further apart, yet still not statistically significant.*

L345, please delete 'it seems'. If there is uncertainty, this can be described in a more quantitative way.

We have deleted it (line 407).

L519-521, unclear if you are talking about potential overprinting of the fossil 2H in situ (e.g., with water in the frozen ICD), or following transport and deposition on the shelf. Please clarify. Also, give a citation that supports the statement that overprinting is enhanced in low pH environments.

We have clarified this by stating that the environmental water can be coming from various sources (e.g. in situ or during transport after thaw). Also, we have removed the statement on low pH environments as we could not support this with a proper reference, and it is less relevant to our study (lines 603-607).

Anonymous reviewer #1

If a positive decision is made I have no other detailed comments than the references need to be looked over. Some of them even lack publication year.

We have carefully read through the references list and edited/corrected where needed.

Anonymous reviewer #2

General comments:

I think the abstract is too long, and that it goes into too much specific detail. I think that it could and should be made more succinct.

We agree. This point was also brought up by Reviewer Trevor Porter. We have shortened the abstract.

The phrase "molecular-bulk upscaling challenge" is used without enough introduction/ definition. I understand what you mean by it, but I think that it would be better to explain what this is exactly in a bit more detail.

We have added a bit more specific description the first time we use this definition, in the introduction: " This $\delta^{13}\text{C}-\Delta^{14}\text{C}$ dual-carbon isotope approach carries the strong advantage that it operates on the bulk OC level, thereby circumventing the "molecular-bulk upscaling challenge". This challenge relates to issues associated with upscaling from the molecular isotope level to the bulk level. These issues relate to the relative concentration (n-alkanes and n-alkanoic acids represent only a fraction of the total OC) but also to processes such as selective degradation, differences in physical association, or dispersion differences. " (lines 132-138).

A general comment about the structure of the discussion is the separation of the 13C-14C data from the bulk geochemistry. Why are these measurements not included in this grouping? If you measure 13C or 14C on a bulk sample, isn't that "bulk geochemistry"?

You might be able to circumvent this issue just by renaming the bulk section to "bulk elemental geochemistry" or something like that.

We do not really follow the reviewer here. In the first section of the discussion we talk about %C, C/N values, as well as $d^{13}\text{C}$ on bulk samples. As such, we named this section " ... bulk geochemistry ... as it includes both elemental and isotopic measurements on bulk samples. The same is the case for the first section of the Results.

One thing that I think is also missing from the discussion is some mention of the possibility that the terrestrial sampling density may have missed some of the possible heterogeneity in permafrost chemistry. I realize that it's not easy to sample in this part of the world, but is there any reason to think that the results might look different if you had soil samples from 50 more sites? Why or why not? This would apply to the 2H data, as well as the other data.

This is a valid point. We have added the following text to the manuscript, at the end of section 4.2: "Finally, we realize that the amount of soil and ICD samples analyzed in this study is limited, and want to point out that the results may change when more data are analyzed in the near future." (line 492-494)

Regarding the second point/suggestion of this review comment, we think it would be too speculative to give more detail regarding the possible differences in results if more data were to be obtained.

Specific comments:

Line 78 – change “into” to “in”

Changed.

Line 99 – Personally, I’m not a fan of non-standard acronyms like this (ICD in this case). They require an elevated level of buy in from the reader, which I think takes away from the accessibility of the manuscript. That’s just my opinion, there’s plenty of precedent for this kind of thing of course.

We realize there are different opinions with respect to acronym usage, but prefer to continue using it as this shorter version is commonly used and it also improves readability.

Line 137 – At the introduction of the 2H discussion, it might help to frame the study better if you begin by saying that you propose the new tool, as well as evaluate the performance using a suite of other geochemical data including the aforementioned ^{13}C -radiocarbon method.

This is a good suggestion. We have now in the revised ms better introduced our tools in the introduction: " We will evaluate the performance of this complementary tool using additional geochemical data as well as the bulk $\delta^{13}\text{C}$ - $\Delta^{14}\text{C}$ mixing approach." (lines 148-150).

Line 142-143 - These are nice papers, but they aren’t really the best references to support the assertion that “the isotopic value of local precipitation is a function of local climate”

Yes, we agree. We have added: Craig H. 1961. Isotopic variations in meteoric waters. Science 133: 1702–1703. (line 154)

Line 149 - If you mean to give the maximum range you could point out that precip in east africa can be upwards of +50 per mil, while the SLAP2 (Standard Light Antarctic Precipitation 2) standard is - 427.5 per mil.

We have edited this to now present the maximum range, using the values/locations that this reviewer provides (lines 160-163).

Line 162-168 – The end of the introduction falls a little flat in my opinion. At the moment you say what you do in your study, followed by a general statement about why it’s important to study these types of questions. What’s missing to me is a statement that directly comments on how what you do with this study will help with these important questions. As it is currently written it doesn’t setup the next section so effectively.

We see the point, and have therefore now added one more sentence that specifically mentions the use of our proposed tool, at the very end of the introduction: "Our proposed tool may be used to trace these temporal and spatial differences in OC release from permafrost thaw, as well as the extent of burial of OC in sedimentary reservoirs."(lines 191-193).

Line 195 - I think it is better to replace your internal lab sample codes with something more straightforward when reporting the results (things like “CH DY-3A” are meaningless to the reader and hard to remember). Include them in a data file or something if you want to be able to cross-reference with Vonk et al., 2013, but for presentation purposes I would simplify.

We have renamed the samples with TS-1, TS-2, ICD-1, ICD-2 etc, and include the original sampling ID in Table 1.

Line 232 – Remember to define acronyms at first use.
This acronym was defined in the previous paragraph.

Line 243 – Check super/subscripting for H₃⁺.
We have edited this into H₃⁺ (line 276).

Line 244 – Give units for H₃⁺.
We have added units (% per V) and have also added a reference for the use of H₃⁺ (Sessions et al., 2011) (line 277).

Line 248 - The “methylation effect” language is odd to me, since it makes it sound like what was quantified was the difference in 2H values between the derivatized and non derivatized standard, rather than the 2H value of the hydrogen in the added methyl group. Since the magnitude of the “methylation effect” will be different depending on what the 2H value of the covalently bonded hydrogen in the methylated fatty acid is in addition to the chain length, you want to do the correction by mass balance. Probably that is what you did, but the language doesn’t make it sound that way.

We agree, we have changed this into "methylation correction" (lines 281-282).

Line 251 – This call to table 5 is out of order since you haven’t called tables 2-4 yet.
This sentence is a general remark on how we report the d2H values, so we decided to not call table 5 at this particular place.

Line 259 – Not sure what you mean exactly by “with mean and standard deviations obtained from the literature values”.
This was meant to refer to the end-member values for the d13C-D14C source apportionment, but is perhaps confusing. We have now specified this to "with mean and standard deviations obtained from our analysis (d2H on TS and ICD samples) and from literature (13C and 14C on end-members)" (lines 298-299).

Line 296 – I might add a few words to the start of the sentence that begins on this line to make it clear that you are discussing distributions within individual samples, and that you are still talking about topsoil samples only.
We have done this by adding " for Topsoil-PF samples" to this sentence (line 343).

Line 318 – This call to table 3 is out of order.
Indeed, this should be table 2. In the previous sentence, however, we have changed a call to table 2 into table 3. As all tables have already been called before, we did not change the order of the tables.

Line 354 – spell check.
Thanks, we have corrected this.

Line 417 – change “proxies” to “proxy”
We have changed this.

Line 452 – This is the first mention of results from the shelf-slope samples. In the methods you point out a reference for more information on the sampling procedures, but what about the laboratory analyses and results? This should be included in the earlier sections.
Yes, good point. We have added a brief paragraph at the end of section 2.2 (lines 286-290).

Line 454 - I like how you use the individual n-alkanes rather than arbitrarily averaging them together.
Thanks.

Lines 481 – 500 – Somewhere in this section, or somewhere else in the manuscript if it fits better, it would be good to discuss how variability within an end member might impact the results. This is important for both the 2H and the 13C-radiocarbon approaches, but it seems like it would be especially important for the radiocarbon. In addition to the acknowledged aging along the transect won't there be different ages within a topsoil permafrost? How might this impact the results if melting/erosion occurs at different depths/ages within a site?

We agree that variability within the end-members plays an important role and should be taken into account. For the 13C and 14C approaches, the amount of end-member data available is fairly good (and growing) with 30-40 data points for 13C and >300 data points for 14C. This is described in the second paragraph of section 4.3. Our Markov Chain Monte Carlo mass-balance model actually accounts for the end-member variability (described and referenced in section 3.2). When thawing and erosion occurs at different depths or ages, at various locations throughout a watershed or coastline, the signal will be averaged when measured in coastal sediments. We have now acknowledged this important point (lines 505-507) (reviewer Trevor Porter also posted a related comment). Regarding the amount of d2H end-member data available: we are aware that our sample set only exists of n=9 data points for each source. Variability in the mean end-member values may therefore change (or, perhaps, decrease) when more data become available. We have now also briefly mentioned this point at the end of section 4.2 (lines 492-494).

Line 568 – As with the end of the introduction, I think that the end of the conclusion could go a little further to bring this study back together with the big picture goals. Remind us how “increasing our understanding of the fate of thawing permafrost in the coastal environment” will help us and why we should care about it.

We have added a bit more "big picture" text to place the results of our study into context with the general goals outlined in the introduction. The final paragraph of the conclusions now reads: "This study shows that $\delta^2\text{H}$ of leaf wax molecules has the potential to be used in quantitative source-apportionment studies of thawing permafrost in coastal or marine settings. It can serve as an alternative or complementary approach to the commonly applied bulk $\delta^{13}\text{C}$ - $\Delta^{14}\text{C}$ method. We recommend continuing data collection and optimization of end-member definition and calibration. Refining the molecular $d^2\text{H}$ proxy presented here will be beneficial in pinpointing the location and extent of OC release from thawing permafrost in the coastal or fluvial environment. With enhanced Arctic warming and associated intensification of permafrost thaw, constraining the amount and fate of permafrost OC release will help to assess the magnitude of the permafrost carbon feedback to climate warming." (lines 658-663).

Figure 2 – I would add the color legend to this figure that you already use on the other figures. I would also list n values in the caption or on the figure.

Yes, this has been changed.

Figure 5 - I would list the modern/ICD labels as headers rather than within the data.

OK, we have done this.