

## ***Interactive comment on “Estimation of gas record alteration in very low accumulation ice cores” by Kévin Fourteau et al.***

### **Anonymous Referee #1**

Received and published: 19 September 2019

#### General Comments:

The authors present a study of the alteration of atmospheric records preserved in ice cores at Antarctic sites where ice accumulates very slowly. The main point of the paper is to understand how well a measured signal from a low-accumulation ice core reflects the true atmospheric history. The findings are then applied to a hypothetical 1.5 million-year-old ice core record. The topic of this paper is quite specific, but it will be of great interest to those in the ice coring community studying trapped gases and firn processes (particularly using high-resolution instrumentation). The paper will also be of interest to those who seek to develop gas records in ice cores retrieved as part of the oldest ice effort. The authors present a sound study with important conclusions, though the various methods of analysis, data handling, and analytics need to be explained and/

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or justified somewhat more clearly in the text to convince readers of their validity (see comments below).

Specifically, the authors investigate the degree of alteration of gas records due to (1) artifacts resulting from early/ late bubble close-off in the firn, and (2) smoothing due to dispersive mixing in the firn column and gradual bubble close-off. The authors present new high-resolution measurements of methane concentration as recorded in five different ice core sections from low-accumulation sites in East Antarctica. To address process (1) the authors identify layer-trapping artifacts in the new datasets including testing a previously published algorithm for artifact identification. The authors also make fundamental observations about the frequency and magnitude of layer-trapping features in the new datasets, and finally they simulate the occurrence of artifacts in a hypothetical 1.5 million-year-old ice core record.

In order to investigate process (2), the authors derive gas age distributions for the new ice core records that reproduce the magnitude of the features resolved in the new data when convolved with an atmospheric reference record. The gas age distributions are explored by applying the smoothing to different datasets, from which the authors come to the conclusion that the gas age distributions of glacial East Antarctic ice cores are very similar. The glacial gas age distribution is then applied to a hypothetical 1.5 million-year-old and highly thinned ice core record to understand the magnitude of smoothing that might be anticipated from such an old ice core.

The data and analyses represent important contributions to the field and are suited for publication in *Climate of the Past*. However, the article needs significant improvements in clarity and organization for readers to be convinced of the arguments presented therein. Despite the fact that the methods are explained in Fourteau 2017, the derivations of the gas age distributions, the modeling of layer-trapping artifacts, and details about the analytics need more explanation for this article to be standalone. Generally speaking, there are also a number of details related to the analyses that require more justification and/or explanation (see specific comments below).

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I recommend the paper is published after major revisions. Please refer to the specific comments below, which I separated into Major Specific Comments, Minor Specific Comments, and Technical Comments (the latter are numerous but very minor, only concerning writing style and typos).

#### Major Specific Comments:

Introduction – The authors may consider adding a brief description of work that has been done previously to estimate gas record alterations, including information about gas age distributions (what do we expect the distributions to look like? what magnitude of smoothing of gas records has been observed previously?).

Methods – I understand the analytical methods are further described in the Fourteau 2017 paper, but I suggest the authors state at least briefly the analytical precision on the CH<sub>4</sub> measurements and any other processing of raw data that occurred. E.g., How are the raw data calibrated? To what standard scale? Are there any corrections besides solubility in the melt stream? I notice that the data are quite noisy (see further comments about the results section), even after cleaning for layer trapping effects – please address this. I also notice there are gaps where data are missing, but the removal of raw data is not explained in the paper. More information about the datasets will help to convince readers that the layer trapping artifacts are real features, not instrumental noise.

Results and Discussion – Readers may be more convinced of the conclusions if the authors (1) explain what they see in the data more exactly and how they judge the results to be “better” or “worse” - here I am referring to the authors’ estimations of the gas alteration (see specific comments), (2) explain the limitations of the data more clearly (see specific comments about data noise, data gaps, and analytical noise), (3) more clearly explain how the GADs are derived, and why they behave differently when applied to different ice cores and intervals, and (4) emphasize the main conclusions of the paper more overtly.

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A final point that seems missing from this paper would be some discussion about to what extent preexisting, published records may be affected by layer-trapping artifacts or smoothing. It would also be fitting to describe how discrete records might be affected by these processes relative to CFA, given that discrete measurements integrate over multiple annual layers.

#### Minor Specific Comments:

P2L25 – Can the authors describe these anomalous strata in more detail? How large are they? What is the horizontal/ vertical scale? How/ why do they form?

P3L12 – Please define a closed porosity profile.

P3L13 – Please explain briefly why the closed porosity profiles are associated with larger uncertainties.

P3L29 – In case the reader is less familiar with the topic (and perhaps is not following your rationale), specify that the higher accumulation ice cores have significantly less alteration of the gas records, thus approximating more closely the true atmospheric history.

P4Fig1 – Consider including a second map panel showing the Greenland core mentioned in this paper (NEEM). Also consider adding markers on the map of Antarctica to indicate other ice cores used in the paper (e.g., DE08 and Fletcher).

Methods – A table describing each coring site with local accumulation rate, elevation, coordinates, etc. would be helpful.

P5L4-L21 – Please include the uncertainty on the accumulation rates at each site if available.

P5L18 – Strictly speaking, the CH<sub>4</sub> excursions are associated with DO events. I suggest rewording this sentence accordingly.

P6L5 – Perhaps say why the solubility correction might change between ice cores.

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P6L23 – It would be helpful to see a supplementary figure showing the agreement between the raw data and the records used for correction (WD and EDC). Earlier the authors stated that the solubility correction could be different between cores, but now they state the data are all corrected by about +13%. So there are no differences in solubility between the different cores? Could the solubility change due to changes in the dust or ion content in the ice, i.e. during an interstadial versus a stadial? Could this affect the estimation of the smoothing?

P6L23 – 1.13 is a rather high solubility correction. Can the authors say why, or perhaps compare to corrections used by other groups?

P7L5 – Is it problematic that the atmospheric reference dataset changes below 330 m? It seems like this point deserves another sentence of explanation or justification.

P7L8 – Is the gas age scale for Fletcher Promontory also consistent with AICC 2012? Please address how the age scale uncertainties affect your results, given that the records used in your analysis are sometimes on different age scales.

P7L13 – Have the authors considered using EDML, Taylor Dome, or Talos Dome data to estimate or confirm the gradient you determined? These cores may not necessarily fit the criteria of “weakly smoothed” and “high-resolution,” but they could still be useful. If not, at least mention them and state why the authors didn’t use them.

P7L14 – What spline version of the NEEM data do the authors refer to? The data I have seen from NEEM have many gaps due to instrumentation problems, including the CH<sub>4</sub> peak associated with DO 21. Did the authors fit the splines themselves? If so, please explain.

P7L14-L15 - It seems like this statement about the gas age distribution comes too early. The reader does not yet know how the authors determine the gas age distributions, so they cannot (at least at this point) easily see for themselves how the authors have come to this conclusion. In any case, doesn't the need to deconvolve the NEEM dataset imply

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that NEEM firm has smoothed the true atmospheric signal? Is the implied smoothing at NEEM reasonable?

P7L18 – How much does the deconvolution increase the amplitude of the DO21 methane event in NEEM?

P7L20 – Can the authors estimate the extra bias/ uncertainty introduced by the deconvolution of the NEEM record, including using the NEEM gas age distributions as input? Or at least justify that it does not significantly affect the conclusions.

Section 3.2 – A table showing which atmospheric reference is paired with which new dataset would be helpful. Additional information such as the age scale of the atmospheric reference dataset, the time interval, the measurement technique used, the resolution of the data, the accumulation rate at the core site, and any treatments to the reference dataset (e.g., spline fit, deconvolution) could also be listed.

Section 3.2 - A few more thoughts: (1) Could NGRIP be used instead of NEEM? Would the NGRIP record also need to be deconvolved to be consistent with Vostok at DO21? (2) Can the authors say more about why there is a need to deconvolve the NEEM signal while other reference datasets appear to work without the deconvolution? (3) I can't help but notice there are actually not any new CFA data at 1260 m in Vostok. There is a large data gap between 1260-1261 m or so. So the authors are assuming the height of the CH<sub>4</sub> feature there? How did they do this?

P8Fig2 – Legends on this figure and others would be very helpful. Please label the events in the figures (e.g., DO6, DO7, DO8, etc.). Why are there data gaps in the new CFA records? For this figure and others that follow, plotting the atmospheric reference on depth is very confusing. The depths are obviously not the same in the reference core as for the new data – they are from different cores.

P8Fig3 – See comments about Figure 2 with respect to plotting the reference records on depth.

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P9Fig5 – For this figure and for others, the reader must follow multiple cross-references to different captions in order to understand what is being plotted. Consider adding legends to the figures for clarity, or writing full captions for each figure rather than cross-referencing.

P9Fig5 - Please explain how one can measure a layer-trapping artifact that is higher in CH<sub>4</sub> concentration than any measured value during DO8? I'm referring to the highest light blue value in Figure 5 near 740 m.

P9L2 – This is the first mention of the analytical noise. Consider putting this in the methods section where the authors discuss the analytical technique.

P10L5-8 - This is a very fundamental and robust conclusion – that late close-off artifacts are rare relative to early close-off artifacts. What does that mean for the GADs? Is there a connection?

P11L3 – What about Na<sup>+</sup> or other ions? How good is the assumption that Ca<sup>2+</sup> is a predictor of total ion content?

P11L6 – How many volcanic markers are there common to both cores in the depth intervals relevant here?

P11L10 – Exactly how are the layer trapping artifacts identified? This should be explained more clearly, possibly in the methods section. How can the authors be sure these are not analytical artifacts?

P11L20 – Do the DO17 data also show a high number of layer artifacts?

P11L26 – What do the authors mean by the “bulk behavior?” How is that defined?

P12L14 – How sensitive is the model to the assumed densification rate?

P13L6 – I don't see a “clear underestimation” of the layering artifacts for DO events 7 and 8 in Figure S4. Please clarify what the authors see in the data.

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It would be helpful to also plot the reference records in the upper panels of these plots so readers can compare how the data look relative to the better record of atmospheric history.

P13L9 – I don't understand which visual results the authors are judging to be correct here, so the 1.5 factor seems arbitrary.

P14L3 – How is the analytical noise estimated?

P14L5 – Here (in the Holocene data) I can't help but question if the authors have actually identified real layer trapping artifacts or just the outlier analytical noise. Can they really distinguish? Please provide some justification.

P14L11 – Please justify why providing a manually specified artifact-free signal is not circular. If the authors can visually identify the artifacts so straightforwardly, why then is it necessary to run the algorithm at all?

P17L6-10 – This seems like the main point of this paragraph and possibly one of the more important conclusions of the paper. Consider starting the paragraph with this sentence and filling in the details thereafter.

P17Fig10 – I'm still having trouble understanding how the atmospheric references can be plotted on the depth scale of a different ice core. Also consider plotting the atmospheric reference in dashed orange lines to be consistent with previous figures.

P17Fig10 - I would like to see more discussion of why the various GADs estimate the smoothing of DO6-9 similarly well, but they have larger discrepancies for DO21.

P18Fig11 – Again the reference is plotted on depth, which is very confusing without further explanation. Consider plotting in dashed orange to be consistent, similar to previous comment.

P19L2 – How does the skew relate to the firn? What's the physical reason for the skew?

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P19L8 – Can the authors explain this conclusion further? Readers may think synchronizing to a high-accumulation record would increase the accuracy of the gas chronology.

P21Fig12 – The artificial depth scale is confusing, can you explain where it comes from?

PS1Fig1 - Again the NEEM reference data are plotted on the same depth scale as the Vostok DO21 data, which is confusing.

PS1Fig1 - I think a problem with the point the authors are trying to make here is that there is a large data gap at the onset of DO 21. The full magnitude of the CH4 rise in the Vostok DO21 record is not technically resolved.

Technical Corrections:

The following are suggestions to improve the writing and readability of the paper. They are mainly word changes, clarifications, and minor grammar mistakes.

P1L1 – “East Antarctic Plateau” rather than “East Antarctic plateau” This is throughout the paper.

P1L2 – Change “affect” to “influence” or a word that is not so similar to the preceding word “effects”. P1L6 – “Concentration measurements. . ., which removes. . .” Do the authors want to say the concentration measurements themselves alias the fast variability? Or that the fast variability is removed because of smoothing in the firn, as a consequence of layers containing gas with a distribution of ages? Reword.

P1L15 – Change “estimate” to a word that is less similar to the preceding word “estimation.”

P1L15 – Change to “. . .their potential impacts on a hypothetical million-and-a-half years old ice core. . .”

P1L18 – Change to “. . .in the case of methane and carbon dioxide, respectively.”

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P2L2 – I prefer “accumulation” rather than “precipitation” because accumulation is the net sum of precipitation and removal by sublimation and wind scouring. Also “precipitations” should be singular.

P2L4 – Remove “back” so it reads “dated to 800,000 years. . .”

P2L6 – Change to “. . .the reconstruction of Earth’s past temperatures. . .”

P2L14 – Change to “. . .in low accumulation ice cores cannot be interpreted as a perfect record of the atmospheric history.”

P2L15 – Remove “might.”

P2L16 – Add “. . .imprint in the ice.”

P2L26 – Remove the comma.

P3L4 – Change to “. . .degree of alteration between the actual atmospheric history and the signal recorded in ice cores is strongly dependent. . .”

P3L10 – Change to “Gas age distributions can be calculated for the purpose of estimating firn smoothing, and in the case of modern ice cores this may be accomplished by using gas trapping models parameterized by firn air and pore closure data (refs).”

P3L15 – Reword “. . .temperatures that have no known equivalent nowadays” to be more specific about what the authors mean. Also “nowadays” sounds like slang, even though it is technically a real word.

P3L16 – Change to “Thus it is not possible to sufficiently constrain gas trapping models, prohibiting robust estimation of the gas age distributions that were responsible for smoothing during glacial periods.”

P3L17 – Consider starting a new paragraph at “Concerning. . .” Also change the wording to “Layered gas trapping, on the other hand, originates from firn heterogeneities and is a stochastic process.”

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P3L26 – The authors spell “parameterize” differently here. Pick one spelling to be consistent throughout the paper.

P3L26 – “gas layered trapping” or “layered gas trapping?”

P3L26 – Combine the two sentences to read “. . .proposed by Fourteau et al. (2017), with the goal of rendering the model applicable. . .”

P4L4 – Add to the end “. . .the deterioration of atmospheric information due to firn smoothing and layered gas trapping.”

P4L13 – Change to “The local accumulation is 3.9cm.ice.yr-1 (Yeung et al. 2019).”

P4L15 – Change to “Firn air sampling during. . .”

P5L1 – 1950 CE or AD 1950.

P6L2 – 3.6cm.ice.yr-1 can't be the right unit, you would melt a meter of ice in 28 years.

P6L2 – Change wording to “. . ., which resolves centimeter scale variations in the methane record.”

P6L3 – I don't think the authors mean to say “preferential” here. CH4 is less soluble in water than other greenhouse gases measured in ice cores. This term is used in other parts of the paper, too.

P6L4 – Change to “It is therefore necessary to apply a correction factor to account for the solubility effect.”

P6L5 – Change to “and potentially differs between ice cores.”

P6L5 – Change to “. . .methane dissolution is addressed in Section 3.1 below.”

P6L21 – Change to “The construction of the gas age chronologies indicated in the figures is described in Section 3.4.1.”

P6L26 – Change wording to “For the atmospheric references we used methane gas

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records from higher-accumulation ice cores where higher frequency variations are preserved relative to the low accumulation ice cores.”

P7L4 – “Fletcher Promontory” rather than “Fletcher promontory”

P7L12 – Change to “. . .possible that the inter-hemispheric gradient was not constant. . .”

P7L15 – Change “all” to “full” or “complete.”

P8Fig2 – Change the caption to read, “The blue and yellow spikes are randomly distributed early and late closure artifacts, respectively.”

P9L2 – Change to “during periods when the atmospheric CH4 concentration was varying.”

P9L4 – Add a comma after “respectively.”

P10L7-8 – Change “long distance gas transport” to “gas transport to greater depths.” Change “. . .late closer layers from enclosing young air (ref).”

P11L13 – Change “in advance” to “relatively shallower in the firn.”

P11L22 – Change “quantifying” and “predicting” to “quantify” and “predict.”

P11L26 – Change to “. . .its density difference relative to the bulk behavior.”

P12L5 – “The Fourteau et al. (2017) model. . .”

P12L12 – The authors might consider writing “2.2kg.m-4” as “2.2kg.m-3m-1.”

P13L8 – Change to “. . .during periods of high calcium. . .”

P13L11 – Change to “. . .displays calcium variability similar to. . .”

P14L7 – Add commas between core names.

P14L9 – Use a different word besides “concentration” to describe the number of arti-

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facts. One might confuse it with CH<sub>4</sub> concentration.

P15L4 – Use a different word besides “important.” Perhaps “significant” or “potentially significant.”

P15L13 – Consider using the word “function” instead of “law.”

P15L14 – Change “in the mathematical sense” to “in a mathematical sense.”

P15L14 – “independent” instead of “independents.”

P15L17 – “new gas age chronologies” instead of “a new gas age chronologies.”

P16L2 – Change to “Low-temperature ice deforms less easily, slowing the densification process such that bubble closure spans a larger time period.”

P16L2 – Remove “a” so it reads, “Moreover, low accumulation is also. . .”

P17L7 – Change “exhibits” to “exhibit” and “degree” to “degrees.”

P18L2 – “Latter” instead of “later.” Also add “is” to “This is illustrated with. . .”

P18L4 – Use different wording than “more important.” Perhaps “more significant” or simply “greater.”

P18L12 - Needs a figure reference.

P18L13 – Instead of “less variability” consider using “smaller magnitude.” Readers may confuse the term variability to mean noise or variation around a mean value.

P19L23 - I think the authors mean “depth resolution” instead of “spatial resolution.”

P20L6 – Change to “apply a thinning factor of 200.”

P20L23 – This is not easy to see on Figure 13. Consider labeling more of the axis tick marks and increasing the font size.

PS1L2 – Change the word order to “In the main article, we used the deconvolved

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methane CFA data of Chappellaz et al. (2013) as atmospheric reference for the Do21 period.

PS1L3 – Change to “This was done because using the data. . .”

PS2L2 – “Figure 1 of Fourteau et al. (2017).”

PS2Fig2 – State briefly how the data are cleaned for layering artifacts in the caption.

PS2L7 – Change to “. . .pointed out that one of the data points of Loulergue et al. (2008) might correspond to an early closure artifact and may not be climatically relevant.”

PS5FigS7-FigS10 – Same as Figure “S6”

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Interactive comment on Clim. Past Discuss., <https://doi.org/10.5194/cp-2019-94>, 2019.

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