

Thank you to Thomas Bauska for providing specific and valuable feedback on our manuscript. We have carefully reviewed and incorporated the recommendations into a revised manuscript and describe the changes in the following response. The reviewer's responses are written in black text, and **our answers are written in red text**. **Revised sentences in the manuscript are written in blue text**.

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Review of Sailer et al., Ice Core Site considerations from modelling CO<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> ratio diffusion in interior East Antarctica.

*Sailer et al.*, have performed a critical analysis of the potential preservation of gas signals at locations in Antarctica containing the world's oldest ice with implications for existing and future ice coring efforts. I really enjoyed reading this study and particularly appreciated that the authors provided their code (which I have tested and look forward to using in the future!). By and large, the authors employ a previously established methods (Bereiter et al., 2014) and existing data on gas diffusion (Ahn et al, 2008; Ikeda-Fukazawa et al., 2005, etc) but expand the scope of previous work to include new, unexplored regions of Antarctica. In this effort, they also expand the range of parameters tested by Bereiter et al., 2014 to investigate the sensitivity of their model to different temperatures, accumulation rates, geothermal heat flux, ice column thickness, etc. – effectively all the key parameters one would want to see varied when looking for old ice sites. I would support publication in the *Climate of the Past* after some revisions, mostly minor.

**We thank Dr. Bauska for his enthusiasm and helpful suggestions. We are particularly glad he went to the trouble to run our code and test its performance.**

First, I will raise a few bigger picture questions and then go line-by-line.

**Can this analysis be reconciled with the observations that there is O<sub>2</sub>/N<sub>2</sub> variability in 1.5-million-year-old ice at Allan Hills?** The major take-home from both Bereiter et al., 2014 and this study is that we should have lost all the 20-kyr and shorter variability. Yet Yan et al., 2021 report variations in O<sub>2</sub>/N<sub>2</sub> from very old ice at Allan Hills. I'll admit that you'll be comparing apples-to-oranges when jumping from a well-resolved deep ice core to a jumbled-up blue ice site where the ice (at least in the present) is colder than the ice buried

~3,000 meters below East Antarctica. None-the-less, I can't reconcile in my mind how O<sub>2</sub>/N<sub>2</sub> variations would remain if the diffusion rates are indeed so fast. In fact, I even tried a quick test with your model by making an isothermal ice column at -30C. The SDR of O<sub>2</sub>/N<sub>2</sub> @1.5 million years age (with about 10,000 years per meter) was coming out quite high at 0.86.

This is an interesting observation and one that we have pondered too. There are many unknowns of the Allan Hills ice, which make it difficult to assess how much diffusion should occur in Allan Hills ice.

First, we do not understand the ice flow history of the old ice parcels. Where and how thick was this ice in the past? When did it thin to its current thickness? We have few constraints on these questions.

Second, the Allan Hills ice cores are not continuous climate records. Mechanical mixing (as indicated by the age-scale reversals) could tend to homogenize the O<sub>2</sub>/N<sub>2</sub> ratios, but might also bring packets of ice that have been isolated from each other into contact more recently than the age of the ice. We note that emerging work, particularly improved dating, from COLDEX is suggesting that the dO<sub>2</sub>/N<sub>2</sub> trend in older ice could be related to age, rather than insolation.

Third, we don't know the starting conditions very well. The S27 core provides some reasonable estimates, but the firn densification processes in a 40ka world may be different. Further, the Allan Hills firn is challenging to understand because the accumulation rates are very low, and potentially switch from net accumulation to net ablation.

Because of the large uncertainties in the histories and processes, we do not want to include such speculation in this manuscript. This is a good topic for future work. One thought that occurs to us in response to this comment, is that we might be able to use high resolution dO<sub>2</sub>/N<sub>2</sub> measurements from the Allan Hills to better constrain the diffusivity, which is something we will discuss within the project at an upcoming meeting.

On a somewhat related note, from Sailer et al. it's not as clear as in Berrieter et al., 2014 if we will have lost longer periods variation. One limitation of this study is they only consider CO<sub>2</sub> changes on the obliquity timescale and O<sub>2</sub>/N<sub>2</sub> on the precessional timescale. I understand why the authors have chosen to impose the two different timescales to illustrate potential gas preservation. On the other hand, it makes for a somewhat convoluted apples-to-oranges comparison for the reader during some later stages in the paper. I hesitate to call for major revision, so I will only loosely suggest to the authors that

they consider running experiments with the same timescale of forcings for both gases. One could then derive a parameter that describe the additional smoothing of O<sub>2</sub>/N<sub>2</sub> compared to CO<sub>2</sub>. From the gas world perspective, yes, we want to know the absolute smoothing. But we'd also want to know if the ratio of smoothing between gases changes with under different conditions.

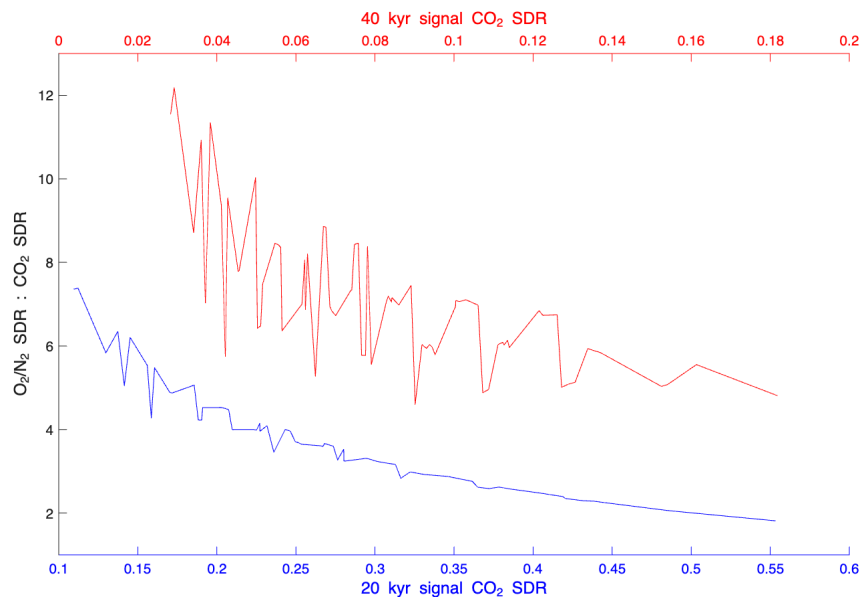
We have investigated the amount of diffusion for each gas given the same period of variation. We overall expect O<sub>2</sub>/N<sub>2</sub> to diffuse more than CO<sub>2</sub>, although at the warmest temperatures the permeability of O<sub>2</sub> increases above that of CO<sub>2</sub>, which may affect the relative diffusion. Because the permeabilities have different temperature sensitivities, we expect complexity in the relative diffusion of the two gases. To see to what extent the O<sub>2</sub>/N<sub>2</sub> SDR is fixed relative to the CO<sub>2</sub> SDR, we test a parameter space with variations in each of the four forcings: 2, 2.5, 3 cm/yr accumulation rate; -60, -57.5, -55 C surface temperature; 2500, 2750, 3000 m ice thickness; 45, 47.5, 50 mW/m<sup>2</sup> GHF. We then calculate the ratio of O<sub>2</sub>/N<sub>2</sub> 1.5 Ma SDR to CO<sub>2</sub> 1.5 Ma SDR. If the ratio is constant, then O<sub>2</sub>/N<sub>2</sub> always diffuses by the same amount more than CO<sub>2</sub>.

What we find, shown in the figure below, is that on average O<sub>2</sub>/N<sub>2</sub> diffuses 3.6 times more than CO<sub>2</sub> on 20 kyr period variations, and 7 times more on 40 kyr period variations. There is noticeable variation too. The ratio of O<sub>2</sub>/N<sub>2</sub> SDR to CO<sub>2</sub> SDR generally decreases as CO<sub>2</sub> SDR increases, but this is largely because O<sub>2</sub>/N<sub>2</sub> SDR reaches an upper limit of 1, although the higher O<sub>2</sub> permeability at warm temperatures may also be playing a role. For both period variations, the parameter combinations that lead to the smallest ratio between SDRs (i.e. where O<sub>2</sub>/N<sub>2</sub> has diffused relatively less compared to CO<sub>2</sub>) are where accumulation rate is high and ice thickness is low, which leads to more layer thinning. The opposite is also true; the SDR ratios are greatest where accumulation rate is low and ice thickness is high, which leads to less layer thinning. This makes sense since we find in Section 3.2 that O<sub>2</sub>/N<sub>2</sub> is more sensitive to the temperature changes in the thicker ice scenarios than CO<sub>2</sub>.

Note that while the figure is ordered by increasing CO<sub>2</sub> SDR, the O<sub>2</sub>/N<sub>2</sub> SDR for each parameter combination does not have the same order. The high frequency variations in the ratio are an indication of this. For instance, the CO<sub>2</sub> SDR can remain unchanged, while the O<sub>2</sub>/N<sub>2</sub> SDR increases. The conditions for such an occurrence can be complicated, with the CO<sub>2</sub> SDR is remaining unchanged due to offsetting impacts, such as thicker ice creating both less layer thinning and also warmer temperatures. These impacts can then affect O<sub>2</sub>/N<sub>2</sub> differently, in this case the warmer temperatures having a larger impact than the thicker layers. In the manuscript, we have explored related ideas with the sensitivity

analysis (Section 3.2). Although this does not directly compare the two gases with the same period of variation, the sensitivity to various forcings is independent of the period.

After this analysis, we chose not to include this in the paper because we did not find a clear message and believe that adding a discussion of this in the manuscript would distract from the main focus. The most consistent trend we find in this experiment is driven by O<sub>2</sub>/N<sub>2</sub> fully diffusing; otherwise, the relationship of diffusion of O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub> is complex. We hope that the code provided will allow readers interested in technical questions, such as this one, the ability to explore them.



**How does this study differ from Bereiter et al., 2014 (if it all) in approach?** From my reading, I believe the temperature-depth-age models are virtually indistinguishable. However, this would be nice to be spelled out exactly. Particularly if there are a few differences.

The age model is identical to the one in Bereiter et al. (2014). The temperature model differs in that we use temperature dependent thermal conductivity and specific heat capacity instead of ice column averages. We have edited the text to reflect this:

We use a one-dimensional, steady state ice and heat flow model to calculate the temperature and age of ice with respect to depth. The age model is identical to that in Bereiter et al. (2014). The temperature model differs in that we utilize a temperature dependent thermal conductivity and specific heat capacity, rather than an ice column average.

**A few more tests to confirm performance of the model would be useful.** I recommend showing at least two examples of how the model performs for both a low-accumulation site with little melting (Dome Fuji?) and a high-accumulation site with high melting (WAIS Divide)? In both cases, I believe the borehole temperature and melt-rates (possibly inferred not measured directly) data should be available. It would be sufficient to this only for the review documents or in a supplemental figure. I don't think it would be necessary for the main body. That said, the introductory material is somewhat lacking in a real-world grounding that could be better illustrated for non-ice core specialist. For example, around lines 55-60, it's taken for granted that reader has a good grasp how thinning and temperature evolve with depths. This could benefit from an illustrative figure that shows some real-world examples. For example, the way Berietter et al., 2014 introduces the problem with real and modelled examples in Figure 1 is quite useful.

To better assist the reader in understanding temperature and thinning, we have included additional panels in Figure 3 to show what temperatures ice packets of different ages are experiencing and how thin the layers have become. Additionally, modeling locations with high accumulation rates, such as WAIS, is not feasible with the steady-state model. We discuss this further in a later response.

Also, on the subject of model testing, I took my best crack at an apples-to-apples comparison with a similar model we use in-house at BAS and found very good agreement in the modelled temperature and age with depth. Suffice it to say, the version of the model I used is mostly educational purposes such as teaching "where to find old ice?" exercises so a full model inter-comparison isn't needed and well beyond the scope of this review. However, I noticed one discrepancy could call for a little bit more description of your model. In the scenario with -60C surface temperature,  $2 \text{ cm a}^{-1}$  accumulation and 3,000-meter thick ice column, I didn't see any basal melting until the geothermal heat flux tipped over  $55 \text{ mW a}^{-1}$ .

We get melt initiating  $55 \text{ mW m}^{-2}$  with these forcings, assuming  $p=4$  for the vertical velocity profile. We aren't sure how to further investigate this. In terms of differences between the BAS model and ours, there could be a variety of differences such as temperature-dependent thermal properties and a constant firn column based on South Pole values.

\*Important aside, is that water or ice equivalent accumulation?

Accumulation is in ice equivalent. This has been addressed in the following change:

The accumulation rates across the study area are inferred from an englacial layer dated to 4.7 ka (Singh et al., in prep) and given in ice equivalent.

Upon further investigating and the running the code for your model I saw that the temperature of the bedrock (possibly down to a few kilometers is modelled). This is more sophisticated than the model I used and probably the main reason for the difference. **It would be nice to know a little bit more about this portion of the model, particularly as the areas you eventually rule out for old ice exploration appear sensitive to the presence or absence of melting.**

This steady-state ice-and-heat flow model is actually what was used to initialize the transient model which has been used to infer the magnitude of LGM-Holocene temperature change at Dome C and Dome Fuji (Buizert et al., 2021) and in other work like tracking ice parcel temperatures at WAIS Divide (Aydin et al., 2014) or calculating geothermal flux constraints at ice rises (Fudge et al., 2019). Modeling the bedrock is important for transient applications but isn't critical for steady-state applications. We have added more description to the text, as detailed in our next response.

Also, I struggled a bit to understand the iterative approach to solve the basal melt rate. I believe a bit more detail is warranted along with a brief review of the implications of this approach. For examples, could you calculate how much heat is “lost” via conduction up into the ice and how much is “lost” via latent heat? Also, I assume the implication is that the latent heat is indeed “lost” from the system? As in, it is implied that a thin layer of water is flowing away from the site?

The basal melt needs to be calculated iteratively because applying a basal melt rate affects the vertical velocity (equation 2) and hence the englacial temperature profile. We revise our description of the basal melt to:

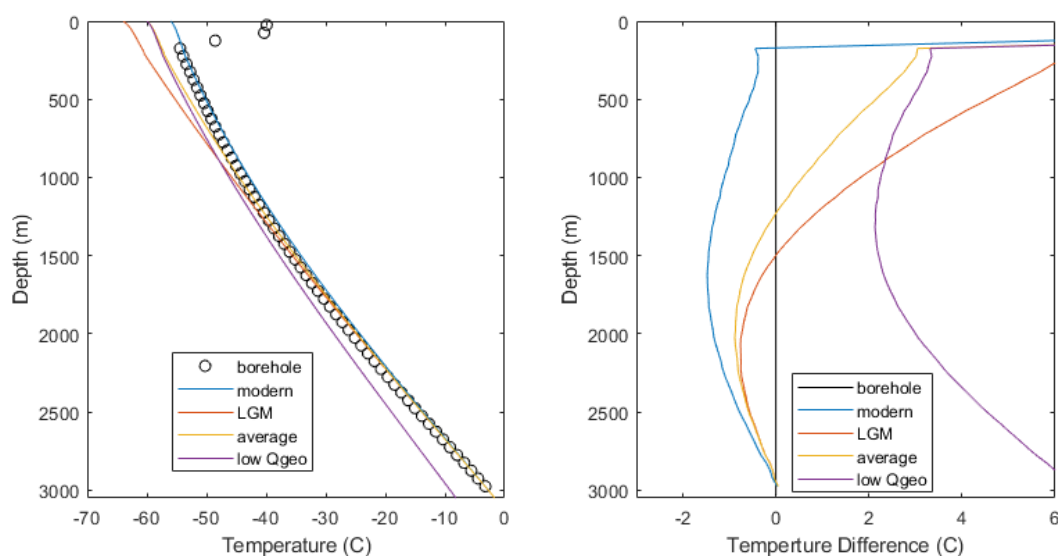
The deformation parameter is assumed to be  $p = 4$  in all scenarios, unless otherwise stated. We include bedrock in the thermal calculation and set the GHF at 7 km below the ice surface. The melt rate,  $m$ , is first set at 0 for calculating the temperature profile. Equation (1) is solved similarly to Firestone et al. (1990) with an integration factor ...

The melt rate is calculated from the excess geothermal heat that the ice cannot conduct away from the bed. This is calculated iteratively because the melt rate affects the vertical velocity (equation 2) and thus the englacial temperature profile. The GHF is equal to the

heat conduction through the basal ice and the latent heat lost in melting, which we assume is lost as the water flows away at the bed.

Finally, to circle back to my original suggestion of doing some model-data comparison, the “proof would be in the pudding”. So if the model does well at simulating the temperature and melt-rates at Dome Fuji and WAIS Divide (or any other sites of your choosing) then the reader will be more confident in the approach.

Because the model is steady-state, a model-data comparison is a bit harder than it might seem. For a site like WAIS Divide, whose mid-depth temperatures are colder than the surface temperature, the ice sheet temperatures clearly retain the thermal signature of the LGM (Cuffey et al., 2016). A steady-state model cannot capture the temperature profile. For sites like Dome C and Dome Fuji, a steady-state model does a better job, but even then we’ve shown that the borehole temperature retains information that can be used to estimate the LGM cooling (Buizert et al., 2021). The transient temperature influence is largest at the surface and minimal near the bed, which is why our assumption of steady-state temperature is appropriate for this study – the temperature of the old ice does not vary much. But the change in temperature near the surface makes a model-data comparison difficult. We illustrate this with the following figure for Dome Fuji where we run the steady-state model under four forcing scenarios. The first three have either a modern, LGM, or glacial-interglacial-average surface forcings and a geothermal flux of  $50 \text{ mWm}^{-2}$  which puts the base at the pressure melting point without inducing much melt. The fourth scenario uses the glacial-interglacial average surface forcings, but a lower geothermal flux.



We want to highlight two take-aways from this figure

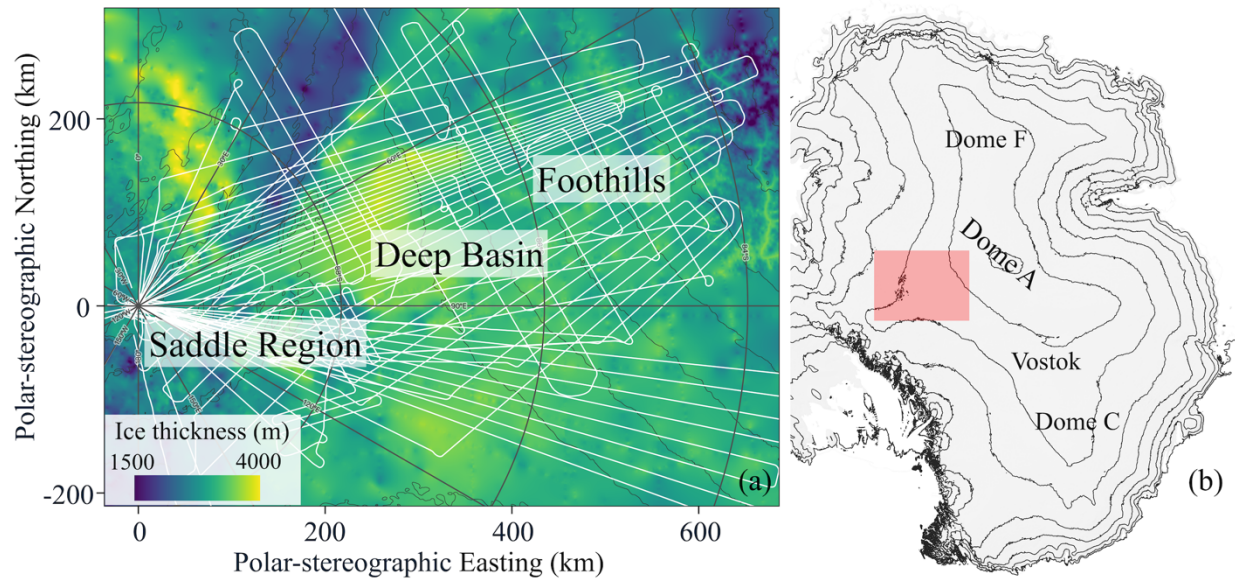
1 The borehole temperature profile is fit decently (i.e. within a couple of degrees) by the modern surface forcing but the mid-depths are too warm, which is because the colder glacial temperatures are not part of the history. The LGM and glacial-interglacial average surface forcings yield too cold of temperatures in the upper third of the ice sheet, but improve the fit in the lower two thirds. The temperature variations in upper ice sheet are not particularly important for our analysis for two reasons: a) the layers are thick so little diffusion occurs, and b) the temperatures are cold so little of the overall diffusion occurs.

2. The temperature misfit is much larger if the basal temperature is incorrect. The transient temperature variations are small compared to not getting the basal forcing correct. This is additionally important because most of the diffusion occurs in the warm, highly strained, basal ice which does not vary temperature much due to the time-varying surface temperature.

**All the maps could be made more accessible.** I suggest you provide some more geographic context as I was a little bit lost as to the extent of the “COLDEX Search Region”. I suggest adding an Antarctic-wide map inset to Figure with the region currently covered in Figure 1 highlighted. Dome A and Dome C play important roles in the paper. Please show their location and also an arrow pointing in their direction (also Vostok?). The subplots in Figure 8 (as long as they are same extent as Figure 1) are okay but seem to be missing lines of latitude and longitude. I would also appreciate some more points of reference here.

We have added a map to Figure 2 to better present the geographic context:





### Line-by-line comments:

Abstract: “foothills” is not yet precisely defined and comes across as quite a colloquial term to use in the abstract. I recommend using a more precise term, or using the spatial information you provide about location between Dome A and South Pole, or add on a line like “...roughly equidistant between Dome A and South Pole, a region we call the “Foot Hills” of the Gamburstev Mountains”

We have revised the sentence as follows:

The most promising region for recovering 1.5 Ma ice is approximately 400 km from both South Pole and Dome A, a region we call the “Foothills,” due to low accumulation rates and moderate ice thickness.

Line 35: “However, this method is limited, providing different results based on the species and location and requiring several assumptions. Köhler (2023) suggests that some of these assumptions may be incorrect by comparing reconstructions to a carbon cycle model.” It would be helpful for a reader unfamiliar with Kohler et al to mention some of these key assumptions. Otherwise, it sounds like a quite a broad, unsupported swipe at the boron method.

We have added some of the assumptions Köhler (2023) discusses:

However, this method is limited, providing different results based on the species and location and requiring several assumptions. Köhler (2023) suggests that some of these assumptions, such as equilibrium between atmospheric and equatorial sea surface  $p\text{CO}_2$ , lower estimated surface ocean pH in the Pacific than the Atlantic, and assumptions on total alkalinity and dissolved inorganic carbon, may be incorrect by comparing reconstructions to a carbon cycle model.

Lines 55-65. There are some very short, two-sentence, paragraphs here. I think it could be restructured into one, possible with some bullet points.

We have condensed these points into one paragraph by removing some line breaks.

Line 74: *“This is the most reliable method for dating ice cores of this age.”* A fairer statement would be that  $\text{O}_2/\text{N}_2$  is one of the key pillars of dating as in practice all available information is used (e.g. Bouchet et al., 2023)

Agree, we have reworded the sentence as follows:

This is a key method in dating gases in the oldest ice cores.

Line 150. *“Bubbly ice resides in the upper ~1000 m where diffusive smoothing is unimportant due to thicker annual layers and colder temperatures.”* I would rephrase. As shown by experimental evidence that underlies these results (Ahn et al., 2008) diffusion does occur in bubble ice. In fact, one could argue that those rates derived in Ahn and most subsequent work don’t apply for clathrate ice in question here. I would say something like “although diffusion occurs within bubbly ice, the time spent within the bubble phase is relatively short (e.g. 25,000 years at a site like EDC) compared to the timescales of interest here (e.g 1,500,000).”

We have made the following changes to reflect this suggestion:

While diffusion does occur within bubbly ice, the time gases spend in the bubble phase is relatively short compared to the timescales of interest here (e.g. ice 1000 m below the surface at EDC is ~65 ka, roughly the extent of bubbly ice; Bazin et al., 2013; Veres et al., 2013).

Please provide some more introduction to “fast” and “slow” datasets. Why the large discrepancy? I wouldn’t expect the authors to solve the problem but a figure like presented in Bereiter et al, 2014 would be helpful. I found myself going back and forth between Bereiter et al., and this study quite a lot.

We have added additional context for the fast and slow sets and a supplemental figure based on Figure 2 in Bereiter et al. (2014):

Bereiter et al. (2014) modeled  $O_2/N_2$  diffusion under two sets of gas parameters, a “fast set” and “slow set.” The “slow set” parameters are derived from empirical fits to ice core data (Salamatin et al, 2001). The “fast set” parameters are based purely on molecular dynamics simulations of gas diffusion in ice (Ikeda-Fukuzawa et al., 2004).

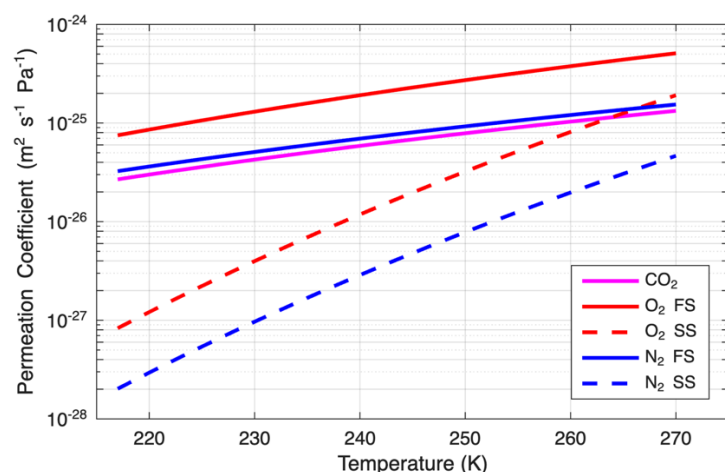


Table 1: I know it is mentioned somewhere the text, but it should be reiterated that you appear to be using some sort of glacial-interglacial average for the sites. Otherwise, -60C at EDC jumps out as the reader as strangely cold.

We have changed the caption to the following:

Forcing values used for each model scenario. EDC surface temperatures approximate a glacial-cycle average. The SDR from 0 to 1.5 Ma of each scenario is shown in Fig. 4.

Figure 4. “Current ice core measurements cannot be used to estimate diffusion in older ice.” I would disagree with such an unequivocal statement. One take home (I had) from Bereiter et al., 2014 is that millennial-scale and faster variability can be used to estimate diffusion. A narrower statement, like “current orbital-scale variations in gases cannot be used to estimate diffusion” would be more apt.

This text has been removed from the figure caption and additional explanation has been added to the main text:

It is important to consider gas diffusion in older ice because the preservation of orbital-scale variations in current ice cores does not imply that orbital-scale variations will persist in ice nearly twice as old.

Line 405: Does TAC diffuse? This is an interesting point. Actually, I believe it could be easily tested with your model as *Uchida et al., 2011* provide an estimate of whole air diffusion. They are shown in a figure in Bereiter et al., 2014.

TAC diffusion is an interesting topic for the future, but ultimately beyond the scope of this paper. Additionally, we are unsure about the values presented in Uchida et al. (2011), particularly at low temperatures.

Overall, very nice work. I'm looking forward to seeing the revision and then the paper published. Also, I'm excited to use this model!

All the best,

Thomas Bauska

Uchida T, Miyamoto A, Shin'yama A, Hondoh T. Crystal growth of air hydrates over 720 ka in Dome Fuji (Antarctica) ice cores: microscopic observations of morphological changes below 2000 m depth. *Journal of Glaciology*. 2011;57(206):1017-1026.  
doi:10.3189/002214311798843296

Yuzhen Yan *et al.* Ice core evidence for atmospheric oxygen decline since the Mid-Pleistocene transition. *Sci. Adv.* 7,eabj9341(2021).DOI:10.1126/sciadv.abj9341