

Review for Harris Stuart et al. 2023: *Towards an understanding of the controls on $\delta O_2/N_2$ variability in ice core records* by Jochen Schmitt, Bern

The paper, led by Romilly Harris Stuart, aims to improve our process understanding of a key ice core parameter - the O_2/N_2 ratio - that is used to orbitally date Antarctic ice core records. Decades ago it was discovered that the O_2/N_2 ratio resembles the orbitally-controlled solar insolation at the drill site. Already at that time, it was speculated how the upper firn layer is modulated by the amount of sunlight during summer. To affect the archived O_2/N_2 ratio in the bubbles, firn surface properties need to travel through the firn column to influence gas-specific (size-dependent) gas loss processes during the pore closure at the bottom of the firn. Over the years, a large number of studies suggested ideas to explain the observed O_2/N_2 variations, but we still lack an overall process understanding. While insolation apparently contributes a large fraction of the measured O_2/N_2 ratio, local temperature and accumulation rate modulate the orbital signal and lead to noise and uncertainty in the orbital tuning. At this target, Harris Stuart et al. place their study, which consists two approaches. Their study contributes to an important question relevant to the readers of *The Cryosphere*. Mostly, the paper is written clearly and provides the right depth of information and the figures are well-crafted and provide a visual support for the text. Overall, I support the publication of this study after minor revisions.

Their first approach is to apply an existing snowpack model to see if and to what extent differences in the solar radiation lead to changes in firn properties that might explain the observed O_2/N_2 ratios. Since the snowpack model was originally designed for alpine firn, applying it to low accumulation sites in Antarctica sets limitations. The authors became well aware of several limitations of their model (1-dimension, no wind compaction, merging box design) and thus interpreted their results with care. I got the impression that they used the model as much as it was possible for this study and then realized that no further insight could be obtained with this setup and that the model would need a significant improvement to capture the situation of low accumulation sites.

Their second approach is data-based and it was certainly a large effort to collect and screen all available O_2/N_2 records. The screening and data evaluation of the different cores and measurement campaigns is an important step and it would be crucial to provide a figure or two to allow the reader to see and understand the underlying problems of that step. Since it likely took a long time to collect all the records it would be helpful for others and the next generations of scientists to have easy access to these data sets and their meta information. So please spend some hours (perhaps more realistically days) of your time to bring all these data sets to a public database (both the already published and the new data). The analyses done on these 14 selected ice core sites conclude that factors other than insolation (accumulation rate and local temperature) have a sizable effect on the observed O_2/N_2 records and set limits to the precision and accurate of orbital tuning. This is a valuable outcome, but I feel that - in an ideal world with more time and resources - more can be done to disentangle the interplay between accumulation rate and temperature. As for the length of the diffusive firn column (i.e. d_{15N-N_2}), it might be the location on an accumulation vs temperature plot that determines if the firn column gets longer or shorter, or if the grain size within the first meter of firn increases or decreases. Since the temperature and accumulation rates are either known from present-day conditions or are output parameters of models (e.g. can be derived from delta age etc.), the team of this study might want to look a bit deeper into the interplay of temperature and accumulation rate in modulating O_2/N_2 ratios.

I also wondered if more process understanding can be gained from analyzing the O_2/N_2 data from firn air studies. At least there should be some O_2/N_2 data from some drill sites available. The authors mention several times that one modulating factor of the O_2/N_2 imprint in the archived air bubbles is the degree by which the O_2 -enriched air that was expelled by the closing pores is advected upwards or diluted in firn. In other words, the O_2/N_2 fractionation during pore closure is only seen if it happens in an open system, i.e. if the O_2 -rich air is removed from that layer. See e.g. lines 433 – 438. Perhaps using a full firn model that allows the simulation of permeability in the deep firn could help here?

Further suggestions and technical comments:

Line 3: “trapped bubbles”. I guess you want to say that the air in the bubble is sealed off from the open pore space; you can just say bubble since bubbles are closed anyway.

Line 4: write “... N₂ molecules in extracted ice core air relative to the **modern** atmosphere - ”

Line 6: write “...and show a new additional link...” delete: “, in addition to the influence of the summer solstice insolation”

Line 8: “... forcings modulate snow physical properties near the surface ”

Line 10: “**a** mechanisms..”

Line 16: firm...unconsolidated snow? Firm is the consolidated snow

Line 18: rewrite “become sealed off from the firm air to form bubbles within the ice.

Line 18: “lock-in depth (LID)” actually you never use LID throughout the paper while you often use lock-in zone.

Line 22: komma after sites?

Line 21 to 28: perhaps restructure this a bit. Essentially you describe two different kinds of dating approaches. O₂/N₂ and TAC are due to local effects of the firm column, thus these parameters are highly site-specific. On the other hand, d₁₈O of O₂ is a globally mixed atmospheric gas parameter that is not site-specific, and all ice cores yield the same record. Thus it can be used to wiggle-match different records but also relate the record to a certain orbital parameter.

Would be good to mention these two different approaches

Ideally, you could mention that d₁₈O₂ is used to date the gas phase of the ice core while O₂N₂ is an ice age parameter

Line 28: delete “trapped within the ice” so it gets a bit more general

Line 30/31: delete “vice versa”

Line 31: you could delete “numerous” as you already name quite a few sites...

Line 34/35: you might rewrite this to convey that the modification due to insolation happens at the snow surface but the process that effectively alters the archived O₂N₂ ratio happens at the depth where the pores close off

Line 37: (COD) is just used twice ...just write it out in both cases

Line 40: replace ; with :

Line 41: Why cite also her first name Tomoko?

Line 48: Why “They”? you refer to Bender (2002) so technically just Michael Bender although he acknowledges at the end of his paper that he profited a lot from the discussion with many giants in this field

Line 85: WAISD would be a new abbreviation, commonly used is WD or WAIS

Line 102 Table 1 (and other tables): for better visibility please align numbers in columns on the right side, e.g. Table 3 in Petrenko et al. 2016 <http://dx.doi.org/10.1016/j.gca.2016.01.004>

Line Table 1: If possible and available please also add other site characteristics to this table, e.g. close-off depth or ice age at close-off depth (delta age) they might be useful as well

Line 157: “gas loss during coring”, can you explain a bit more here?

Line 163: Note that the brittle zone does not always correspond to the BCTZ, while for most of the ice cores, this is the case. I guess some ice cores have a technically defined brittle zone while they do not have the conditions to form clathrates at a certain set of depth or temperature; thus, without this coexistence of clathrate and bubbles, there shouldn't be a strong fractionation. Perhaps elaborate shortly on that.

Line 165: O₂/N₂ measurements within the brittle (or BCTZ) ice are not per se unreliable; it requires a post-coring gas loss, so the fractionated air in the bubbles escapes and thus induces scattered results. Also, small sample sizes resolve individual layers of bubbles vs clathrates

Line 167: see above, does Berkner have a clathrate zone? Perhaps this explains good data within the brittle zone.

Line 176: post-coring gas loss to differentiate between the gas loss happening during pore closure in the ice sheet

Line 214: you mention the black carbon content. How sensitive is the model to the black carbon? What about a similar effect of mineral dust during glacial times (OK, mineral dust is mostly light quartz but there are also darker particles...)

Line 277: are the dots after the permil and the m2 correct?

Line 282: “integrated summer insolation”: can say a few words on the difference between integrated summer insolation and SSI and why you use SSI?

Line 290: Figure 2 caption: you don't need to say that Dome C is plotted in dark-blue and Dome F in mid-blue because you can identify each panel with their name already. Please add a), b), c) as you do in Fig. 3

Line 290: Figure 2 caption: why do you use r² here, while in Fig. 3a, you use r for the same type of plot? perhaps always use r (as r² can be calculated from that)

Line 312: Figure 3: I very much like your colour scheme, but here, it would also help to provide more visual hints to distinguish between some sites, e.g. LD and BI have quite similar colours (same for NEEM and WAIS). You could additionally use squares and diamonds.

Line 328: Table 3: The 5 EDML samples (596 – 860) are from the brittle zone. Are there no other samples measured at EDML, why just in the brittle zone?

Line 331: Fig. 4: Would the residuals look different if it would be plotted on the AICC2023?

Line Figure. 4 caption: the respective structure always requires the reader to go to the end of the sentence while the classical way "Panel d shows the correlation" is often quicker to access

Line 354 Figure 5d: since there is no overlap between Jan and Jul, you could put both distributions into a single panel

Line 381 Figure 7: it is not easy to see the difference between the faded line and the max line, perhaps increase the thickness of the line or use dashed lines etc

Line 399: the long list of references affects a bit the readabilitynot sure if you need all the references here in the discussion section, perhaps write e.g. and two refs

Line 406: Fig. 3c, I guess you mean Fig. 3a showing as well O₂/N₂ vs SSI while Fig. 3c shows temperature. Where is the slope for Fig. 3a to compare it with the slopes of Fig. 2?

Line 438-440: I am not so sure if this argument holds that the O₂/N₂ signal would then be on the gas age scale. Still it happens in the lock-in zone due to a process that was imprinted originally at the surface.

Line 490: I am puzzled a bit about the term bulk ice...

Line 490: "The opposite – a decrease" not sure if this sentence describing the opposite effect is necessary I guess the sensitivity of grain size for a given density works in both directions

Line 493: yes, temperature and accumulation rate do generally covary, but they are not super tightly correlated, and there are sites that are above or below the expected line for the temperature–accumulation relationship. Perhaps you can derive some useful information from the deviations from this temperature-accumulation relation, i.e. a site that has too little accumulation rate for a given temperature. A scatter plot showing all sites with their accumulation vs temperature might help to identify sites that deviate from others in Figure 3. This requires O₂/N₂ data for the present-day conditions for accumulation and surface temperature that are likely more accurate than the reconstructed values based on modelling via water isotopes.

Line 500: this sentence is a bit unclear to me

Line 545: could you spend a few words on how the local SSI at EDC is linked to local accumulation rates since this is a larger-scale weather phenomenon and involves low-pressure systems entering the continent, etc.? Perhaps elaborate a bit on that?

Line 575: "local climate (accumulation rate)" I understand what you mean but accumulation rate might be largely determined by the circulation patterns in the Southern Ocean region.

Line 576: I guess this statement also holds for AICC2023 (although there seems to be a small circularity hidden into that because the age scale is constructed using the O₂/N₂ orbital tuning)

Line 582: this sentence misses some words...support the idea...