The Cryosphere Discussions

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Comment on tc-2021-147

Anonymous Referee #1

Referee comment on "Fractionation of O_2/N_2 and Ar/N_2 in the Antarctic ice sheet during bubble formation and bubble–clathrate hydrate transition from precise gas measurements of the Dome Fuji ice core" by Ikumi Oyabu et al., The Cryosphere Discuss., https://doi.org/10.5194/tc-2021-147-RC1, 2021

This paper reviews all of the non climatic mechanisms responsible for dO2/N2 fractionation in ice cores, and includes a compilation of most existing measurements, in addition to a large dataset of new measurement from the Dome F ice core, with a variety of sampling strategies.

It is an extremely useful and valuable paper, that clearly identifies optimal strategies for sampling ice cores to retrieve a valuable dO2/N2 signal. In particular, the authors did a great effort in cutting the ice in various ways to identify where and how dO2/N2 fractionation was happening, both between outer and inner ice samples, and with high resolution vertical sampling. Their new datasets shed new light on processes affecting gas loss in ice cores. The paper is very well written, the scientific quality of the analyses is excellent, and the figures are also very clear. Although I have a few important comments on the presentation of the results, I recommend its rapid publication.

Major comments:

- Section 4, called “Discussion” actually has results in it, and I am missing a “discussion” section that would include perspectives. I think it would be valuable to add a small “perspective” section, devoted to next steps: Do you think that everything is known about the different mechanisms of fractionation? What could/should be done next to improve either our understanding and isolation of the various processes, or improve the corrections? In particular, a summary on how your data could be picked up by ice physicists to test hypotheses about the mechanisms that you talk about in the paper would be an important addition, to make sure that your results are re-used.
- Related to my first comment, I am missing a summary at the end of the paper of the

optimal sampling strategy. I think it would be great, either to add it to the conclusion, or to have a "sampling strategy" summary section, separated for each of the zones that you added. This section could summarize for each zone, the mechanisms controlling non gravitational d02/N2 signal, and how to mitigate these.

- For someone who is not close to the literature of O2/N2, it would be good to have, maybe in the introduction, or in your discussion section, a schematics of the fractionation mechanisms. You may have to have 3 or 4 of them, for each of your zones, and maybe one more for post-coring. Generally speaking, all of the mechanisms are discussed in a hand-wavy matter, and it's a bit difficult, through the reading of your paper, to understand what hypotheses about what mechanisms are actually testable or tested in your presentation.
- In the conclusion, in addition to specific recommendations for sample handling and storage to avoid fractionation in the first place, I am missing an optimal strategy for correcting for gas loss. You find different slopes of O2/N2 vs Ar/N2 and for d180 vs O2/N2. I wonder if you could separate out the different mechanisms involved in "gas loss" fractionation, and provide several sequential correction strategies that could account for these differences, valid across different zones and different cores, to make it less heuristic.

Detailed comments:

- You don't explain clearly what you mean in the figures by dO2/N2_grav. It's only explained in Figure 8, but you use it already in Fig 4. You should briefly explain in Section 2 how (and why) you correct for gravitational fractionation, and introduce your notation.
- The section on your diffusion model is a bit difficult to understand. In the main text, you should start by saying what you want to do with this model, what you want to test. Do you want to validate the effective diffusivity? Do you want to predict how much diffusion there will be in newly drilled deep ice cores, to inform the sampling strategy?

Then you might consider including the main equation, it does not take too much space, but helps the reader. It's maybe more useful than the Argon diffusivity (which is also described in the appendix), since O2 is the focus of your paper.

Finally, you need to describe better what you use for inputs, what you use for outputs, what are the tunable versus known parameters. In the main text, you need to have a sentence or 2 that have enough details that the reader understands what you are trying to do, and in the appendix, you need to add more details. As it is now, there is not enough information to reproduce your results. Can you describe more the model set up? How deep, the discretisation scheme you used, how long you ran it for, the input that you used, the outputs that came out.

- Regarding the input of the diffusion model, have you considered using a tuned version of the Ca record, since the O2/N2 seems well correlated with Ca, rather than reproducing a shallow segment of data? There is a funny offset in your figures, that I presume cannot be interpreted, but it would be interesting to see if we could use Ca + your diffusion model as a predictor (and then, maybe, as a correction factor).

- Raman spectroscopy is not described at all (line 186). You could add a sentence or 2 describing how this technique does, what it shows. I expect your readership will have a lot of ice core scientist who may not be too familiar with it. Just 1-2 sentences would help them understand (even if of course, they could read the cited paper).

Line 270 : precise before/after gravitational correction.

Line 310 : You say that highly fractionated bubbles and clathrates are stratified in mm scale samples. Then, if you average over a certain depth, do you retrieve a better signal? Later on, you say 50cm, but here, you could go into a bit more detail, and justify this number. I also wonder if averaging is enough, or if, in addition to this layering, you have selective fractionation (perhaps post coring, or diffusion) that creates a bias.

Line 325: lower dissociation pressure should produce a steeper Ar partial pressure of gradient from bubbles to clathrate. Why? Can you explain a bit more ? (it's maybe obvious to you, but not to me)

Paragraph near line 355 : Add that nucleation increases dO2/N2. If you average over two annual cycles of Ca, do you get back a good value or is it also biased? Is there a selective loss for some layers?

Could the correlation to Ca also be due to different bubble sizes for different densification rates in the firn, like in Freitag's papers?

Line 368: Here, it's difficult to understand the hypothesis, the inputs and the results. What mechanisms are you taking into account? Do you start with very high bubble/clathrate layered concentrations?

Line 389 : explain where the 50cm nb comes from, maybe above.

Figure 7: add some vertical bars to help the reader.

Figure 8 and 9 : it would be useful to put them on the same figure (except panel 1), to help the comparison.