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Comment

Interactive comment on “Post bubble-closeoff fractionation of gases in polar firn and ice cores: effects of accumulation rate on permeation through overloading pressure” by T. Kobashi et al.

Anonymous Referee #2

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General comments :

The loss of small air molecule in ice cores is still a poorly known phenomenon. Ice core air samples have low dAr/N_2 and dO_2/N_2 due to the preferential loss of Ar and O_2 . This loss happens in the firn, in solid ice and during core storage. The principal mechanism is the permeation of small molecules through the ice lattice (Ikeda Fukasawa et al 2005), and this mechanism has been used to quantify gas loss at different temperatures, and to explain the enrichment in dAr/N_2 and dO_2/N_2 in steady state. Here, the authors go one step further and try to identify a link between the amount of Ar loss and climate, such that dAr/N_2 could be used as a climate (temperature and

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accumulation) proxy, rather than an indicator of the quality of the core storage. This subject is particularly interesting because of the observed correlation between dO_2/N_2 and insolation, which is so far unexplained.

The authors observe that there is a significant correlation between dAr/N_2 and temperature and accumulation, and explore the potential mechanisms for such a relationship. They build on existing ideas about permeation through the ice, and find that 1) micro-bubbles likely play an important role, and 2) firn thickness (controlled by temperature and accumulation) impacts the bubble pressure, and will lead to different amounts of post-coring fractionation.

Although the motivation of the study is well justified, and the methods used appropriate, the logical links between the observations and models, and between different mechanistic hypotheses are not well articulated, and the conclusions are not well supported by the data and models presented here. I offer here a few suggestions to rewrite the paper in order to better highlight the actual conclusions, and make a stronger relationship between hypotheses, models, and observations.

1. Are the dAr/N_2 time series the best tool to test your hypotheses ?

It is interesting that you find a correlation between dAr/N_2 and temperature or accumulation, but this relationship is not consistent between the two cores, and even the raw data has little common variability, which leaves me to wonder whether the correlations you find are actually significant. I realize that it's a difficult exercise to make, because the input time series of temperature and accumulation are not well known themselves, but the lack of consistency between GISP2 and NGRIP is a red flag for me, especially because they are consistent in terms of $d_{15}N$ and $d_{40}Ar$. I would suggest that you would instead use the known and measured dAr/N_2 (or dO_2/N_2) from shallow ice cores all over Greenland and Antarctica, where we have a good constraint on present day temperature and accumulation. This would allow you to explore a larger parameter space in terms of T and acc , and perhaps find a stronger relationship between climate

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and gas loss (dAr/N₂ grav corr).

2. Uncertainties in the permeation model

In Section 5, the authors use the permeation model of Ikeda-Fukasawa et al. (2005) to estimate gas loss. There are a number of unknown parameters in equation (3). The authors make an honest attempt at finding reasonable values for them, but do not give uncertainty estimates in the parameters. A propagation of uncertainty would be necessary for us to understand what conclusions can be drawn from this model.

- You do not comment on what you use for Δl , the thickness of the ice layer, which is an essential parameter.

- You use constant values for D and X , but it is very likely that they strongly depend on temperature, otherwise we would not witness that there is less gas loss at -50°C than at -10°C . You may not know what it should be (I don't know either), but it would be useful to include a range of possible permeabilities that would fit the data. The conclusion of Section 5 is that the model doesn't match the data, but perhaps, you could instead use the data to constrain the permeability used in the model, and see if you can learn something. (Here again, I would use data for many core sites, to have better constraints)

- You use for your S/V the geometric shape of the core, rather than the distance from one bubble to the next. This is very surprising. What's the reason for this? I would have imagined that what matters for gas loss is how much the bubbles near the edges of the core can lose their gas, not have a model where all the air is in the middle, and has to go through solid ice of 9.8cm diameter.

- In the end, I suspect that the uncertainty in the amount of post-coring fractionation (section 5) completely erases the possibility to detect any sign of microbubble fractionation, which has a much smaller amplitude, but it would be nice if you could quantify that.

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3. Microbubble concentration

You make an interesting point about microbubble concentration. As I understand, although the volume of gas is very small, the fractionation is so intense that they matter. This argument depends strongly on the microbubble concentration in a sample, but you make no attempt at quantifying it from observations. Only you quote a concentration of 0.3% from Vostok, which is a very different site from GISP2 and NGRIP, and I doubt that the bubble shapes are the same at a cold low accumulation like Vostok and at warmer Greenland sites. In addition, you use in your model a concentration of 1 to 3%, which is one order of magnitude higher than the 0.3% documented at Vostok without justification.

Since your argument depends very strongly on the presence of microbubbles, I think that a documentation/quantification of their presence is needed. You can do this by imaging a few thin sections from the core at these sites, or look at tomography data from Greenland firn cores. I'm sure that such data exists already, and including them would considerably strengthen your argument.

4. Link between the two process studies

Your dominant mechanism for linking dAr/N_2 gravcor and (T, accum) is through bubble pressure, affecting permeation through the ice. I could imagine that for cores with different bubble pressure (perhaps because of different depths), the post-coring fractionation would be more or less important.

- This study is complicated if we look at different depths because of clathrate formation, but you could look for a trend in the first 500m where there are few clathrates. Perhaps you could take a look at what we expect bubble pressure to be with depth, and run your gas loss model for an expected range of bubble pressures to see if we could see any change that would match your data

- In your time series, you are looking at the fractionation of micro-bubbles due to differ-

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ent bubble pressure for different (T , accum), but what about the fact that if the bubble pressure is higher, you will also have more post-coring fractionation? Perhaps you could make a plot of bubble pressure in the x axis, and expected dAr/N_2 from post-coring fractionation after 15 years, with the parameters used in Section 5, to estimate whether this could have a significant impact on the correlation of dAr/N_2 with temperature or accumulation. You could also use this graph to add the expected fractionation of dAr/N_2 from the presence of microbubbles, since bubble pressure depends on firm thickness. This would be a way to put both studies together in a comparable framework, and estimate what can be said. If your model runs have error bars, even better.

5. link between model and data

The link between the observed time series and the model could be made more clear. For instance, you could have run the model for the input temperature and accumulation time series shown in Fig 3, and do a model/data comparison. If you follow my advice #1 to show multiple sites, you could instead make a 2D plot of temperature, accumulation and dAr/N_2 , on which to compare data and model.

6. Conclusions

You emphasize in the abstract and conclusion the importance of process #2 (microbubbles), but you find that process #1 is responsible for -2.7 to -6.6 per mil of dAr/N_2 , whereas process #2 accounts for $0.38\% \cdot ^\circ C$ (and Holocene changes are on the order of $1^\circ C$), or $-0.11\% \cdot (cm/yr)$, with Holocene changes on the order of 2-5cm/yr. It's hard for me to believe that, in the presence of noisy data, and with a moderately well known amount of post-coring gas loss (process #1), you could identify the contribution of microbubbles (process #2). It does not make the modeling study any less valuable, but I believe that with such data, and uncertainty in the model, you can not conclude that you have observed it, or that this process is significant.

As it stands, the conclusions of the paper are not sufficiently strong, and the articulation between the observation and models not clear, but there is potential for making this a

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much stronger paper, or at least, clearly state the limits of current knowledge and offer suggestions for better observations. I hope that you will take this into account in rewriting the paper.

Specific comments :

Page 15717 | 6-7 : It's confusing to use dAr/N_2 , and it would be ore clear to keep the $dAr/N_2_{gravcor}$ (or dAr/N_2_{gc} if you want to be more compact), during the remainder of the manuscript, like you did for equation (2).

Pqge 15718 | 19 : it's unclear now that dAr/N_2 has been corrected for gravitation. If it has not, this is a trivial result, but I assume it is, and it would reduce confusion if you keep a clearer notation.

P 15719 | | 7 : colder temperature induce more fractionation. This is opposite the conventional wisdom that colder ice has less gas loss. Can you comment on it? It would be good to add the plots of the stated correlations (scatter plots) in the online supplement.

P 15721 |17-19 : "not in the shallower part", does it mean that it is better than "weakly correlated", or not correlated at all? You commented on the fact that the accum rate is smaller at NGRIP, but you don't comment on the lack of correlation with temperature. Could you say something?

Figure 5 : put the data points in (+), so that we can see the original scatter in the data
page 15724, line 23 : " using these values ", add a table with the values used for D, X, and KX.

page 15724: impact on the uncertainty of the values for k, and X?

- why use S/V ice core rather than S/V bubbles?
- S/V bubbles changes with depth due to compression, does it affect your results?

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P 15725, l 2 : " several orders of magnitude larger " : what impact on results?

l 16: close-off with dash, not one word (valid for the whole document)

p 15726, l5 : vostok vs gisp2 ? is vostok data relevant for a very different firm?

p 15727 : above the depth -> that depth

fig 7 : would be a more efficient use of space in a table

p 15728 : equation 7 is wrong for 2 reasons :

- it's not homogeneous : P is unitless, V is a volume (m³) or maybe unitless like C(l)? (unclear), rho is a density (kg/m³), you probably want to divide the right hand side by rho_ice.

- you are neglecting the change in total porosity by multiplying by (rho_ice - rho(l)), and an equivalent term of (rho_ice - rho(l+1)) should appear, probably in the form of : [p_open(l)*(rho_ice - rho(l))-p_open(l+1)*(rho_ice - rho(l+1))]

Actually, many equations loosely described in line 8-13 should be written explicitly, with a clear definition of variables to be understandable. I don't understand how you relate C(l) with v0(l)

Page 15729, section 6.3, figure 11a

Can you explain why the dAr/N2 in normal bubbles decreases and increases again before stabilising ? What are the competing effects ?

You mention competing effects between micro and normal bubbles, but not in the normal bubbles themselves.

page 15730 : You conclude that the micro-bubble effect is one order of magnitude too small, and you have likely overestimated the micro-bubble fraction by an order of magnitude (see my earlier comment). The reader can naturally conclude that micro-bubbles are not a dominant contributor to the fractionation. I believe that there is a lot

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of value in quantifying the micro-bubble contribution, as you did, but I would not reach the conclusion that " they dominate the total $\delta\text{Ar}/\text{N}_2$ changes in spite of their smaller volumes. " as you state in the abstract on line 18-19. Instead, perhaps you could hint at other processes, or highlight the limits of your model, due to unconstrained parameters that we could perhaps quantify experimentally, by doing an uncertainty estimation including a range of possible values for the permeation coefficients, the geometry of the bubbles, etc.

Page 15730, lines 25-30. As you know, gases take some time to diffuse through the firn, and take about 10 years to reach the lock-in depth. You use a densification model (Goujon et al 2003) to infer $d\text{Ar}/\text{N}_2$, but neglect gas diffusion. The time-lags you find are 81 and 21 years for bubble pressure changes, which are the parameter you are most interested about, and these timelags are in the same ballpark as the timelag due to gas diffusion. Therefore, I wonder how including gas diffusion would change your time-lag estimates. In particular, gas diffusion does not affect bubble pressure, but it affects gravitational fractionation, and thus what time lag we include in the gas-age ice-age difference used for the chronology.

page 15730 : " Apparently, the surface temperature anomaly takes longer time to reach the maximum increase in the overloading pressure than that of the accumulation rate anomaly, which is consistent with the observation (68 and 38 years, respectively). " Perhaps you could add that when you have an accumulation increase, you increase the downward advection in the firn, so the propagation of the anomaly is quicker. (At least, that's how I interpret this difference)

Pages 15731-33 : the discussion is great, and very thorough

Page 15734 (conclusion) line 20: " Therefore, the observed negative correlation of $\delta\text{Ar}/\text{N}_2$ and accumulation rate can be explained by the processes on the micro-bubbles through the changes in the overloading pressure. " I disagree. You are overstating your conclusions. You find that micro-bubbles have the right sign, but produce a much

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smaller (10x) fractionation than observed. This could be due to poor knowledge of the diffusivity/sorptivity, or to the fact that post-coring permeation is dominant, or to unknown additional processes. Also, you don't talk about post-coring fractionation, which you calculated to be highly significant. Why ?

Figure 2 (and also in the text). Did you plot dAr/N_2 or $dAr/N_2\text{gravcor}$? Of course, we expect dAr/N_2 to be subject to gravitational fractionation, which depends on T and accumulation. This is not new at all to find a correlation between gravitational fractionation and T or acc. I suspect that you meant to plot $dAr/N_2\text{gravcor}$, and you should make it clear throughout the manuscript.

Figure 3 : Can you be sure that the correlation you find between dAr/N_2 and T or accumulation is not due to a remnant of gravitational fractionation that was not corrected well by $d^{15}N$? Is there a way that you can test that ?

Figure 5 : Perhaps you could add to Fig 5 the comparison of $d^{15}N$ for both cores, which shows good agreement.

Figure 9 : I don't understand what all the colored lines show. What is your point in this figure ?

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