

Review of egusphere-2025-5800: “Gas loss and isotopic fractionation induced by pumping during ice core gas extractions”

The $\delta\text{O}_2/\text{N}_2$ ratio in bubbles trapped in ice provides a useful tool for dating and reconstructing past atmospheric pO_2 . However, O_2 is susceptible to various gas loss effects from the initial bubble formation to gas extraction for measurements. This study by Li et al. aims to quantify gas loss fractionation associated with the necessary pumping out of ambient air during the gas extraction process. Using a horizontal core from an ice stream in coastal East Antarctica, they perform systematic pumping experiments relative to control samples to investigate the effects of pumping-induced fractionation on measured $\delta\text{O}_2/\text{N}_2$, $\delta\text{Ar}/\text{N}_2$ and $\delta^{18}\text{O}-\text{O}_2$. By using a horizontal ice core, the authors assume/argue that the ice can be considered homogenous over that depth layer and thus any differences between replicates are attributed to pumping-induced fractionation. They find that while there is no clear relationship between pumping time and gas loss fractionation, turbo pumping induces more variance in $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ than rotary pumping. They then try to quantify this effect and apply it to existing data.

While the motivation for the study is clearly demonstrated, I have concerns about the choice of samples/core used for these experiments and as such, the conclusions drawn. As it stands, I am not convinced that the core sections represent a homogenous (apparent trend in initial samples), or unaltered (low total air content and positive $\delta\text{O}_2/\text{N}_2$) ice core. The authors should address these concerns, outlined in detail below, before the manuscript can be considered for publication. Some specific comments and technical corrections are then given.

General comments

1. My initial concern relates to the validity of the core used for this analysis. The low total air content (TAC) of these samples (0.06 scc/g) suggests bubble formation occurred at a high-altitude site, on the order of 6000 m elevation (e.g., Martinerie et al., 1992). An alternative explanation could be that the low TAC is melt-induced, which may also explain the positive $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ measurements - not typical for traditional ice cores – given that O_2 and Ar are more soluble than N_2 (e.g., Hu et al., 2022). Did the authors consider that these samples may have experienced some melting? If melting has influenced these samples, they do not necessarily provide an acceptable analogue for typical ice cores unaffected by melt. Overall, the choice of these samples for the experiments described in this manuscript seem unsuitable for the scope of this study.
2. Secondly, the experiments rely on the assumption that the core is homogenous. However, there is notable internal variability between the different "initial samples" (e.g., $\delta\text{O}_2/\text{N}_2$ ranges from 9 ‰ to 28.09 ‰) making it difficult to assess the effect of pumping time. When looking at the initial samples included in Table S1, it looks like there is a trend in the data that may be inherent

to the core – assuming that the subsamples are in order from NJ-1 to NJ-4. Can the authors confirm whether they account for this trend before assessing the slope of the pumping experiment data. It is important to first demonstrate that the samples are identical, which I am not convinced of as it stands. In addition, the authors do not acknowledge other processes which could modify gases in ice samples that have presumably been exposed to UV for an extended period of time (e.g., photochemical reactions). For example, $\delta^{15}\text{N}$ values are particularly low (initial sample average of 0.015 ‰), and sometimes negative, suggesting that additional processes beyond simple firnification may have modified the signal.

3. The purpose and application of gas loss corrections in Section 3.3 would benefit from further clarification. Specifically, it is not clear whether Eq. 4 and Eq. 5 are intended to correct for pumping-induced fractionation. If so, it is not immediately apparent that the correction using Eq. 5 achieves this goal, nor how the experimental results have informed this correction. As discussed by Oyabu et al. (2021), differences in replicate samples prepared using the same extraction method may instead be showing fractionation processes inherent to the ice itself, such as heterogeneity in bubble close-off fractionation, differential post-coring gas loss, or fractionation associated with bubble-clathrate transition.

Alternatively, if these corrections are intended to correct for combined gas loss processes more broadly, the authors may want to consider whether this is within the scope of the manuscript, which is specifically investigating pumping-induced fractionation. It is worth noting that Eq. 4 correcting $\delta^{18}\text{O}-\text{O}_2$ for gas loss using $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ has previously been demonstrated and applied to correct for gas loss effects in fractured ice (e.g., Severinghaus et al., 2009). The authors are encouraged to clearly distinguish the novelty of their work relative to existing approaches, so that the importance and relevance of any new correction is well understood by the reader.

4. Given the previous points, it is difficult to accept the conclusions drawn regarding pumping-induced gas loss as they do not appear to be adequately supported by the data. For example, one would expect $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$ values to become more depleted with gas loss. However, as stated by the authors in Line 185-186, the pair difference plots in Figure 4 suggest that the values are equally likely to be depleted or enriched relative to the initial samples with pumping time. The effects of pumping on fractured ice is an interesting avenue, but I am not convinced that the chosen samples are suitable to address this.

Specific Comments

Lines 83-85: The authors could include the melt-refreeze technique which is also widely used (e.g., Petrenko et al., 2006; Klüssendorf et al., 2026).

Lines 106-112: As mentioned in the general comments, the manuscript would benefit from a more thorough site description. Specifically, providing information about the ice stream source region and the climate conditions at the core site.

Figure 2: This is a useful figure (as is Figure 1) and clearly shows the core site and subsampling method. It would be helpful to also show where exactly the horizontal core was extracted from, if possible. Was it along the wall of the ice stream or are those holes in Figure 2C the boreholes? If the latter, gases trapped in the outer ice closest to the wall may have experienced more alteration than the gases trapped in inner ice.

Section 2.2: It would be useful to include more information in the methods section, specifically regarding the extraction process. For example, how long were the sample transfer and subsequent de-trapping from the silica gel? What was the method of releasing samples from the silica gel? The authors reference Emerson et al. (1995) describing an extraction method for water samples from the ocean, which presumably differs from the method for ice core samples. Some clarity on the method modifications would be helpful. It would also be nice to see the modern air measurements in a figure.

Lines 165-166: “*the original gas ratios and isotopic compositions were considered identical.*” As mentioned before, the data does not seem to support this (e.g., Table 2).

Section 2.3: The pumping experiments in Oybau et al. (2021) mentioned later in this study show small trends in the data even after 5 hours of pumping on the samples. The maximum pumping duration in this study was 90 minutes which seems relatively short. Did the authors consider pumping for several hours?

Lines 205-207: It is not clear what the authors mean by the suggestion of “*stronger disturbance to trapped gases caused by turbo pumping*”. Is the suggestion that turbo pumping fractionates gases in the bubbles/ice lattice in addition to gases trapped in the fractures, which both pumping techniques are thought to disturb?

Lines 218-219: While the $\Delta\delta\text{Ar}/\text{N}_2 - \Delta\delta\text{O}_2/\text{N}_2$ slopes indicate close to pure size-dependent fractionation, the slope of $\delta\text{Ar}/\text{N}_2$ and $\delta\text{O}_2/\text{N}_2$ from the initial samples alone is 0.73 which ought to be considered before interpreting any pumping effects.

Lines 239-240: “*Our results demonstrate that pump-induced gas loss exhibits a size-dependent fractionation signature for O₂ and Ar and causes greater oxygen isotopic fractionation than BCGL and PCGL.*” Maybe the authors could provide some more explanation on what is thought to be driving isotopic fractionation of $\delta^{18}\text{O}-\text{O}_2$. Is this thought to be a separate process to the near-pure size-dependent fractionation of $\delta\text{O}_2/\text{N}_2$ and $\delta\text{Ar}/\text{N}_2$?

Table 3: It is useful to have this comparison to existing studies. Just a note that the slopes presented for pumping gas loss in Dome Fuji samples appear to be those for the actual values instead of the pair difference values. The authors may want to check this. Similarly, it seems that some of the slopes for other cores are also different to those presented in Table C2 from Oyabu et al. (2021).

Line 276: The $\Delta\delta\text{Ar}/\text{N}_2$ - $\Delta\delta\text{O}_2/\text{N}_2$ pair difference slopes defined here are different from those presented in Oyabu et al. (2021). For example, the authors give a slope of 0.6066 for the upper BCTZ (450-800 m) compared to 0.92 in Oyabu et al. Figure 10f. Is there a reason for this?

Lines 280-281: This sentence implies that orbital-scale signals were not recoverable in the BCTZ of the Dome Fuji core without the application of Eq. 5, which is misleading as Oyabu et al. (2021) demonstrated that orbital signals could still be recovered, even in the scattered data. The authors may want to reconsider this.

Technical corrections:

Lines 93-94: “, *has been shown...*” should be “, *have been shown...*”

Line 101: I think this should either be “*we applied $\delta\text{Ar}/\text{N}_2$ -based gas loss corrections...*” or “*we applied a $\delta\text{Ar}/\text{N}_2$ -based gas loss correction...*”.

Line 236: “*from the surface*” instead of “*from surface*”.

References

Hu, H., Li, Q., Zhang, W., Wu, S.-y., Song, J., Liu, K., et al. (2022). $\delta^{18}\text{O}$ of O_2 in a Tibetan ice core constrains its chronology to the Holocene. *Geophysical Research Letters*, 49, e2022GL098368.

Klüssendorf, A., Harris Stuart, R., Brückner, L., Prié, F., Brugère, E., Orsi, A., Jacob, R., Stüki, C-M., Morici, L.C., Fourné, E., Salaün, S. & Landais, A. (2026). Extraction of air from ice core samples using trapping and detrapping on silica gel. *International Journal of Mass Spectrometry*, 117606.

Martinierie, P., Raynaud, D., Etheridge, D. M., Barnola, J.-M. and D. Mazaudier. (1992). Physical and climatic parameters which influence the air content in polar ice. *Earth and Planetary Science Letters*, 112(1-4):1–13, [https://doi.org/10.1016/0012-821X\(92\)90002-D](https://doi.org/10.1016/0012-821X(92)90002-D).

Oyabu, I., Kawamura, K., Uchida, T., Fujita, S., Kitamura, K., Hirabayashi, M., Aoki, S., Morimoto, S., Nakazawa, T., Severinghaus, J. P., and Morgan, J. D. (2021). 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, *Cryosphere*, 15, 5529-5555, <https://doi.org/10.5194/tc-15-5529-2021>.

Petrenko, V. V., Severinghaus, J. P., Brook, E. J., Reeh, N., & Schaefer, H. (2006). Gas records from the West Greenland ice margin covering the Last Glacial Termination: a horizontal ice core. *Quaternary Science Reviews*, 25(9-10), 865-875.

Severinghaus, J. P., Beaudette, R., Headly, M. A., Taylor, K., and Brook, E. J. (2009). Oxygen-18 of O_2 Records the Impact of Abrupt Climate Change on the Terrestrial Biosphere, *Science*, 324, 1431-1434, <https://doi.org/10.1126/science.1169473>.