Review of Li et al.: Gas loss and isotopic fractionation induced by pumping during ice core gas extractions

This paper investigates the effects of gas-loss fractionation during vacuum pumping on δ18O, O2/N2, and Ar/N2 in air bubbles trapped in ice cores. The authors use a horizontal core drilled from a coastal ice stream in East Antarctica and assume that the composition is completely uniform. Then they vary the type of pump and the evacuation time. Although the authors find no clear dependence of gas loss on evacuation time, they identify a relationship based on pair differences of O2/N2, Ar/ N2 and d18O and attempt to apply a correction to the data.

Gas fractionation induced by vacuum pumping has been discussed for some time, and I agree that it is important, particularly for samples such as firn-ice transition layers, where many bubbles are close to close-off, and ice with abundant cracks. The research question is clearly defined. However, the ice samples used in this study are not suitable for the intended discussion, and the arguments and conclusions drawn from the data are not convincing. I do not agree with their claim that the relationship between O2/N2 and Ar/N2 in the pair differences of this study reflects gas loss during vacuum pumping. The observed variability more likely reflects differences in composition between samples. Given these concerns, I do not see a clear path for revision and therefore cannot recommend this manuscript for publication. Some comments that overlap with those of Reviewer 1 are not repeated here.

Major comments:

1. Sample homogeneity

To assess the effects of vacuum pumping, the ice samples used for comparison must have a uniform composition. For this purpose, “ideal” ice formed by continuous layer accumulation and normal bubble close-off, such as vertical cores from dome sites, would generally be more appropriate. At glacier ablation zones, the composition of trapped gases can be altered by contamination with modern air, surface melting, or in situ production within the ice sheet (e.g., Baggenstos et al., 2017, https://doi.org/10.5194/cp-13-943-2017; Lee et al., 2025, https://doi.org/10.5194/tc-19-3295-2025). The reported data show substantial variability even between samples only a few centimeters apart. For example, O2/N2 differs by more than 10 ‰ over distances of ~2 cm. Such large differences are unlikely to be caused solely by vacuum-induced gas loss and instead indicate that the original composition is heterogeneous. Also, the values themselves are unusual and may indicate post modification of the trapped air. In addition to the lower TAC values as already noted by Reviewer 1, both O2/N2 and Ar/N2 are consistently positive. Under normal close-off conditions, O2 and Ar are preferentially lost relative to N2 from closing or closed pores into open pores, resulting in negative O2/N2 and Ar/N2 values relative to the modern atmosphere. The reason for the positive values observed here is unclear, but such features are often reported in the upper sections of blue ice cores from ablation areas (e.g., Lee et al., 2025). The d15N values are also unusual, including negative values and inconsistent values between adjacent samples.

For these reasons, I do not agree with the assumption that the ice samples used in this study have a uniform composition and are suitable for the intended discussion. Consequently, the subsequent discussion of gas loss appears to reflect differences in composition between samples rather than effects of the vacuum pumping procedure itself.

2. Data interpretation

Gas loss during vacuum pumping should cause depletion of O_2/N_2 and Ar/N_2 and enrichment in $\delta^{18}O$ relative to the original composition. As the authors concluded, their ice core data do not show a clear dependence of gas loss on evacuation time. This also suggests that the data do not support further discussion of the effects of vacuum pumping. It is therefore unclear why the authors proceed with further interpretation along these lines. The slope observed between $\Delta\delta O_2/N_2$ and $\Delta\delta Ar/N_2$ in this study likely reflects fractionation of O_2 and Ar that occurred at some stage within the ice, rather than the effect under vacuum pumping. I also note that the slope in BCGL is not necessarily close to 0.5, as shown in Table C2 in Oyabu et al. (2021). Therefore, slopes greater than 0.5 in bubbly ice cannot be taken as clear evidence of gas loss effects.

3. Applying the correction to the Dome Fuji data

The authors of Oyabu et al. (2021) explicitly concluded that these data were not affected by vacuum pumping based on their experiments (they reported no clear dependence of depletion in O_2/N_2 and Ar/N_2, nor enrichment in $\delta^{18}O$ on evacuation time, Fig. B2). Based on this result, the large variability observed in the BCTZ of the Dome Fuji core has been interpreted as reflecting strong fractionation between bubbles and clathrate hydrates. Given this, it is unclear why applying the proposed correction to BCTZ data would provide a meaningful assessment of gas loss effects. In addition, the filtered curve obtained through this correction does not appear to reproduce the insolation signal better than the original data, which does not support the authors' conclusions. The authors need to clarify the discussion in Section 3.3.

More specific comments:

Line 70 and Fig. 1: Where does the value of 0.54 comes from?

Section 2.1 and Fig. 2:

More information on the core drilling and the samples would be helpful. Was the core drilled horizontally from an exposed ice face? At what depth below the surface were the samples taken? For panel (b), where and how was the photograph taken? In panel (c), which feature is the borehole? For panel (d), does the left-to-right direction from NJ-1 to NJ-4 represent a direction perpendicular to the ice flow?

Section 2.2

More detailed information on the analytical methods would be helpful. For example, clarification on the materials used for the sample containers and tubing, the procedure for releasing the gases from the silica gel trap and introducing them into the mass spectrometer, the reproducibility of the ice core measurements, and the sampling and analytical procedures for atmospheric air measurements would improve the clarity of the manuscript.

Lines 136 – 139:

As noted, the TAC values reported here are relatively low, and most of the O_2/N_2, Ar/N_2, and $\delta^{15}N$ values fall outside the range typically observed in deep ice cores. Therefore, the physical properties of these samples cannot be assumed to be comparable to those of deep ice cores.

Table 2
I would suggest including δ15N values in this table.

Lines 164 – 166: As described above, I do not find this statement convincing.

Line 203 – 205: The logic is unclear. What is the point of comparing the difference between the maximum and minimum values?

Lines 205 – 207: Also, it is unclear what the authors mean here.

Lines 222 – 224: Unclear. Please provide a more detailed explanation of this point.

Line 226: This relationship appears to arise from natural fractionation processes within the ice.

Section 3.3
I do not understand the basis for the equations and corrections presented in this section. The authors should carefully reconsider the entire discussion in this section.

In addition to the points already raised in the major comments, I am not convinced by the interpretation of the Dome Fuji vacuum pumping experiments. The authors analyze the results of vacuum pumping experiments on the Dome Fuji core reported by Oyabu et al. (2021), identify a relationship between ΔδO2/N2 and ΔδAr/N2, and attempt to use this relationship to correct the data. However, this relationship cannot necessarily be attributed to the effects of vacuum pumping. A relationship is observed in the bubbly ice (446.4 m), however, this may reflect fractionation that occurred during and after bubble formation. In addition, the relatively larger slope of 0.72 may be due to the limited dataset. It is derived from five subsamples taken from a quarter core section spanning ~10 cm in depth, and these are represented as a single point in Fig. 10f of Oyabu et al. (2021). Therefore, the observed slope of 0.72 may arise by chance. Oyabu et al. also report bubbly ice data with slopes close to 1 in other cores (Table C2), suggesting that this relationship is not unique to vacuum pumping. For the clathrate hydrate ice at 2001.1 m, the slope appears to be strongly influenced by a single outlier and its significance is therfore questionable.