

We want to thank Reviewer # 3 for their thoughtful and helpful comments, which have improved the manuscript. We greatly appreciate your input. Our response is below.

The manuscript contributes to deeper understanding of the complicated nature of the variability of the total air content of polar ice by providing and interpreting the high-resolution air content record from the South Pole ice core covering the last 54 ka. The local insolation effect on TAC is confirmed for the site without a diurnal cycle in solar insolation and with an accumulation rate that is 3 times higher than at the Antarctic sites where this effect was first discovered (Dome C and Vostok), thus further promoting TAC as a useful tool for orbital dating of the ice cores. The high resolution of the obtained record made it possible to study millennial-scale variations in TAC and to relate them to changes in the snow accumulation rate. This relationship appears to be different from that earlier observed in and explained for the NGRIP ice core, even though the amplitude of the millennial variations of TAC is similar in both cores. The authors propose a rather plausible mechanism by which pore volume at the close-off can be affected by changes in accumulation through accompanying changes in grain size in the near-surface snow. I would only suggest that the authors develop the description of this mechanism a little in order to make it clearer and more consistent with what has already been published on this topic. They also attempt to explain the difference in mechanisms linking TAC to accumulation at the cold and relatively dry sites in Antarctica and at the warmer sites with higher accumulation in Greenland, and this explanation also sounds quite plausible.

In general it is a good paper, but it needs a number of minor improvements and corrections (see my comments below).

-L39-40. 'For temperature, Martiniere et al. (1992) demonstrated a spatial correlation between site temperature and pore volume at close-off, using data from late Holocene ice core samples'.

Since this spatial correlation is mentioned for the first time in the manuscript, it is more correct here to refer to the 1979 paper by Reynaud and Lebel in which it was initially presented.

Changed lines 39-40 to include the Reynaud and Lebel reference. Changed to: "For temperature, Raynaud and Lebel (1979), first introduced a spatial correlation between site temperature and pore volume at close-off. This was later refined by Martiniere et al. (1992) using data from late Holocene ice core samples."

- L45-48 'The proposed mechanism for this relationship requires that higher local summer insolation increases the size of snow grains in the first few meters of firn, which then decreases the pore volume in these same layers as they reach bubble close-off (Raynaud et al., 1997, Arnaud, 2000).' Replace Raynaud et al., 1997 with Raynaud et al., 2007.

Replaced, as suggested.

2.1 Total air content measurements.

-The description of the measuring technique, though it is detailed in many technical aspects, lacks important information about absolute accuracy of the TAC measurements and their reproducibility. The latter is important for evaluating the contribution of experimental uncertainties to the total variance of the experimental TAC record.

We suggest adding the following text at the bottom of paragraph 1 of section 3.1:

“Samples measured in duplicate at OSU have a pooled standard deviation of 0.0006 cm³/g and samples measured at PSU (130 -1150 m) have a pooled standard deviation of 0.002 cm³/g. Differences in methods between the OSU and PSU labs created a mean offset of 0.0072 cm³/g. To correct for this offset, PSU values were increased to be comparable to OSU values. The pooled standard deviation of measurements for the combined dataset (130 – 1150 m) is 0.002 cm³/g, data from 1151 -1751 m OSU only have a pooled standard deviation of 0.0006 cm³/g. Data are available at the USAP data repository including details in standard deviation and sample resolution of datasets (Epifanio, et al., 2022).”

-Caption for Fig 1: ‘Measurements are averaged duplicate measurements’. Does it mean that for each depth two parallel samples were measured and the average value is shown in the figure? If so, please provide the discrepancy between the individual measurements. If not, please explain what you meant to say.

See revised caption, below and new figure 1, in response to reviewer 3’s earlier comments about differences between OSU and PSU data.

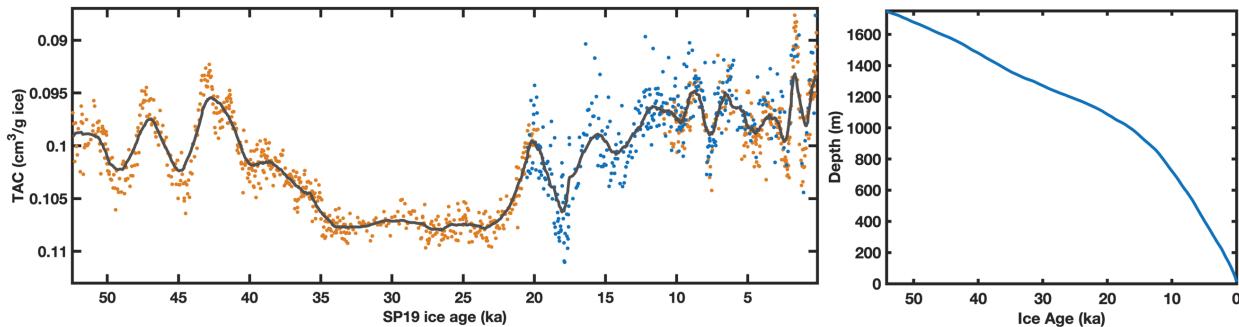


Figure 1: Total air content of the SPC14 ice core. (Left) Measurements are individually shown, plotted on the SP19 ice age scale (Winski et al., 2019). Black line is the smoothed record using a running 10-point average. TAC is expressed in units of cm³ air at standard temperature and pressure, per gram of ice. Orange markers are TAC measurements collected at OSU (depths 130 – 841m, 1150-1751 m, pooled standard deviation = 0.0006 cm³/g). Blue markers are TAC measurements collected at PSU (depths 130-1150 m, pooled standard deviation = 0.002 cm³/g). (Right) Ice age as a function of depth. Data from Winski et al., (2019).

-There is no information about the mass and shape of the ice samples used (important for estimating the cut bubble effect since this effect depends on the specific surface area of the samples).

We used a standard surface area for each sample, though we recognize we are likely missing some variation here. The variation would be small across the 2300 samples. We added the following after paragraph 3, sentence 3:

"To estimate the exposed surface area of each sample, we used a standard rectangular dimension (2.5cm x 2.5 cm x 9 cm), and a mass of 51.2 g across all samples. While there is likely some missed variation due to sample trimming, the variation is small."

L183-186. The amount of air trapped in refrozen ice (I wouldn't call it "solubility") depends, in addition to the air pressure in the flasks, on the number and size of air bubbles formed in this ice. These values can vary considerably from one experiment to another and are difficult to predict.

We recognize that some air is trapped in the melted sample which is then refrozen prior to measuring the air content. Because of this, we conducted multiple melt-refreeze experiments to determine this correction (1.3%). These were done as outlined in Mitchell et al., (2015), and give consistent results.

L193-202 Cut bubble correction.

1. One could understand from this text that cut bubble correction depends on the number and size of the bubbles. In fact (see Saltykov, 1976; Martienerie et al., 1990) this correction depends only on the size of the bubbles (or more precisely, on the bubble-size distribution) and on the specific surface area of the sample. How did you estimate the latter?

We estimated the surface of each sample by using a standard size for each sample. We recognize we are likely missing some variation here, due to trimming the edges of a cubic prism shape to fit in the sample flask. The variation would be small across the 2300 samples. We added the following after section 2.2, paragraph 3, sentence 3:

"To estimate the exposed surface area of each sample, we used standard dimensions (2.5cm x 2.5 cm x 9 cm) across all samples. There is likely some missed variation due to sample trimming, the variation is small."

2. Bubbles efficiently expand during ice storage at a relatively elevated temperature (e.g. at -20 °C), so, with other things being equal, the correction increases with the time of storage and therefore bubble measurements should be done at the same time as TAC measurements.

Because of the nature of the research being completed at multiple organizations, the TAC and bubble measurements were not done at the same time. We recognize that effect of bubble expansion occurs over time, though we do not believe this would invalidate the data set or largely change the correction. Some of our TAC measurements (26 samples) were measured in duplicate 2 years apart. These measurements have a standard deviation of 0.001 g/cm³, which is well within the precision of our measurements.

3. The correction for gas loss for bubble-free ice (i.e. ice containing only hydrates) is needed in the same way as it is needed for bubbly ice, because the ice sample loses its gas from cut hydrates as it does from the cut bubbles. In addition, if the temperature of storage was not low enough (say, above -40...-30 °C) many hydrates in ice can dissociate with formation of air cavities whose size also needs to be measured.

We have no way to quantify the gas loss due to clathrates since clathrate size and density have not been measured. However, the correction would be small, and no more than recorded at the base of the bubbly ice, since bubbles contain more air than clathrates, individually.

As per our response to reviewer 2, above, we suggest the following statement be added to the bottom of the last paragraph of 2.2:

“While clathrate ice will still have a gas-loss correction, it is likely constant and no more than 1.9%. We applied no correction after the base of the bubbly ice.”

L209-211. I understand that for each depth two samples were measured with the OSU vacuum line using the method described in section 2.1. Can you estimate the repeatability of the measurements and present it in the paper?

We suggest adding the following text at the bottom of paragraph 1 of section 3.1:

“Samples measured at OSU have a pooled standard deviation of 0.0006 cm³/g and samples measured at PSU (130 -1150 m) have a pooled standard deviation of 0.002 cm³/g. Differences in methods between the OSU and PSU labs created a mean offset of 0.0072 cm³/g. To correct for this offset, PSU values were increased to be comparable to OSU values. The pooled standard deviation of measurements for the combined dataset (130 – 841 m) is 0.002 cm³/g, data from 1151 -1751 m have a pooled standard deviation of 0.001 cm³/g. Data are available at the USAP data repository including details in standard deviation and sample resolution of datasets (Epifanio, et al., 2022). To our knowledge, this is the first ice core TAC record with this resolution and length, allowing in-depth comparison with other climate proxies at a site that is not likely to have experienced significant elevation change over the last 54 ka (Fudge et al., 2020, Lilien et al., 2018).”

L214-217 It is not clear from the text how the data from OSU and PSU were combined (and averaged?). Were the PSU measurements made at the same depths with the same resolution as in the OSU? Might it be useful to show the OSU and PSU data (after correction for the offset) in figure 1 with a different color? Please explain and comment.

OSU and PSU data were not made at the same depths or in the same resolution, so the samples were not averaged between labs. Instead, the datasets were combined including data from both labs at individual points. The individual lab measurements are publicly available at the USAP data repository and listed in the references.

We suggest including the following figure and revised caption which uses different colors to show the two lab measurements after combining the datasets, and includes an age/depth scale as suggested by reviewer 2:

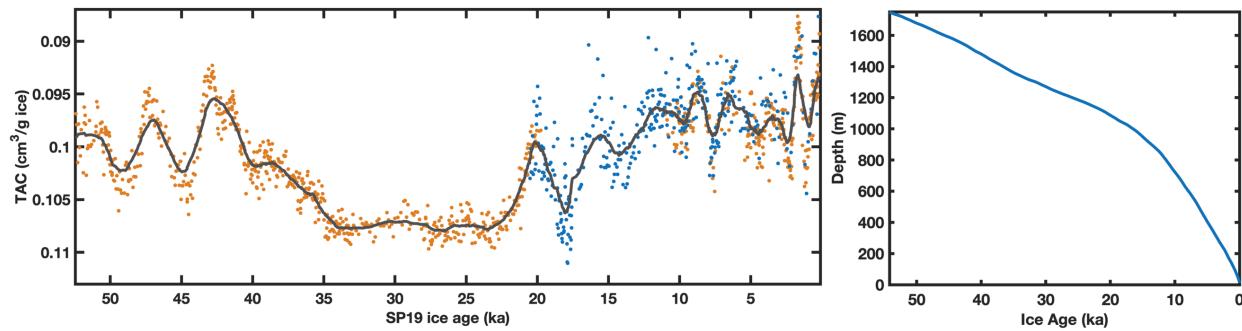


Figure 1: Total air content of the SPC14 ice core. (Left) Measurements are individually shown, plotted on the SP19 ice age scale (Winski et al., 2019). Black line is the smoothed record using a running 10-point average. TAC is expressed in units of cm^3 air at standard temperature and pressure, per gram of ice. Orange markers are TAC measurements collected at OSU (depths 130 – 841m, 1150-1751 m, pooled standard deviation = $0.0006 \text{ cm}^3/\text{g}$). Blue markers are TAC measurements collected at PSU (depths 130-1150 m, pooled standard deviation = $0.002 \text{ cm}^3/\text{g}$). (Right) Ice age as a function of depth. Data from Winski et al., (2019).

L245-248. About the Vcr.

1. The temperature used in eq. 12 (T_s) and the one in the ‘gas law’(T_c in eq. 11) are different temperatures. The first one refers to the time when snow was deposited at the ice sheet surface (corresponds to the age of the ice), the second one – to the time of pore closure (~gas age). Did you distinguish these temperatures when calculating V_{cr} using temperature reconstruction from Kahle et al (2021)? And if so, please explain how you did this, especially for the transient climatic conditions.

We use the same temperature for both the surface and the close-off depth. In reality, the latter is a little bit higher due to geothermal heat, but the difference is negligible for the current application.

We add this explanation directly after equation 13: “*We use the same temperature for the surface (T_s) and the close-off depth (T_c). While the temperature at pore close-off (T_c) is a bit warmer than T_s due to geothermal heating, the difference is small when the firn column is in*

equilibrium.”

It seems something is missing in the sentence ‘For the temperature at bubble close-off (Ts), a temperature reconstruction from Kahle et al (2021)’. Also, please replace Ts with Tc in this sentence.

We suggest changing the sentence to read:

“For the temperature at bubble close-off (Tc), we used the temperature reconstruction from Kahle et al (2021)”.

2. Eq. 12 shows the present-day (late Holocene) spatial relationship between pore volume at close-off and mean annual surface temperature. It is very unlikely that this relationship was the same in the past, especially during periods with different from today’s insolation. So strictly speaking one cannot use eq. 12 to calculate Vcr.

L253-256. ‘...Vcr is a quantity that essentially describes TAC in the absence of temperature effects...’

Even if we assume that eq. 12 is valid for the past, the Vcr calculated from eq. 13 will contain a significant summer-temperature signal, because the impact of changing insolation on the Vc is transmitted through corresponding changes in summer temperature and temperature gradients that affect the snow metamorphism near the ice-sheet surface (Raynaud et al., 2007; Lipenkov et al., 2011).

We are assuming the spatial relationship between pore volume and temperature remains the same. To our knowledge, the spatial relationship between pore volume and temperature has not been significantly updated. Additionally, the high r^2 value between TAC and Vcr indicate that the summer temperature signal that affects firn metamorphism at the ice sheet surface is small.

Suggest changing line 253-256 to read *“Vcr* is a quantity that describes TAC if temperature did not affect pore volume at close-off, Vcr* is a useful quantity to understand the magnitude of the direct effects of temperature.”*

L260-261. Correct references here: Raynaud et al., 2007; Lipenkov et al., 2011; Eicher et al., 2016.

Corrected references.

L317-319: I cannot understand this sentence.

Changed to read *“Accumulation rates during the glacial period were just 3 cm/yr (water equivalent), which would mean the maximum amount of elevation gain due to accumulation alone would be only about 80 meters, without considering the effects of ice layer thinning.”*

L336-337. Please provide a reference for this hypothesis or justify it.

After review, we suggest revising the last paragraph of section 3.4 to read as below. This removes the hypothesis of firn stretching affecting TAC, as this hypothesis is not supported by observation.

“Other hypotheses for changing TAC include layering due to melt, and dust affecting grain metamorphism. Layering due to melt or other effects influences the trapping of air in ice, shaping TAC. However, due to the lack of melt layers at this location, this possibility is beyond the scope of this study to investigate. Dust has also been documented to influence grain metamorphism in the firn. Due to its interior location, the ice at South Pole experiences very small amounts of dust flux. We observe no correlation between dust deposition and TAC.”

The need for Figure 6 doesn't seem obvious for me, but if you decide to keep it in the paper, it should come before Figure 5 .

Agree with removing figure 6, and references to it.

L367-369: ‘The size of the firn grains at the surface seems to predict at which density bubble close-off occurs, with larger grained firn closing off at a higher density (Gregory et al., 2014)’. In fairness, it should be noted that the mechanism by which the porosity of firn at close-off is linked to the snow grain size at the surface was first proposed by L. Arnaud (1997). Later on his model was used to qualitatively describe a possible mechanism by which summer temperature and surface temperature gradients controlled by local insolation can influence pore volume at close-off, assuming a homogenous firn column and neglecting the sealing effect on the total amount of air trapped in ice (Raynaud et al., 2007; Lipenkov et al., 2011).

Added reference to Arnaud, 1997. At this point in the manuscript, we do not feel that the summer insolation mechanism is relevant, as we are trying to express a different mechanism (accumulation instead of insolation) for grain size affecting TAC.

-L373-374: ‘Low accumulation rates create more homogeneous, spherically shaped grains which force more air to escape the ice core, leading to lower TAC’. Please provide a reference for this statement or justify it using your own observations.

We suggest a reference to Gregory et al., 2014 and Eicher et al, 2016. Suggested revisions are included in the paragraph for the next reviewer comment.

-L374-376: ‘We propose that a mechanism of grain size and shape affecting pore volume leads to a positive correlation between accumulation and TAC, which we observe in the SPC14 ice core’.

L460-461: ‘We propose that a common mechanism, grain size metamorphism in the top few meters of the firn, can explain both orbital and millennial-scale times scale of TAC variations in the SPC14 ice core’.

Since this proposed mechanism is considered by the authors as one of the main merits of their work (along with the obtained high-resolution TAC record), I would advise them to

pay a little more attention to its clear and consistent description, and correct alignment with what has already been published on this mechanism in connection with orbital variations in TAC. In the present manuscript, the entire description of this mechanism is confined to a single paragraph (L365-376) and seems neither clear nor complete.

We suggest the following edits to the two paragraphs beginning on L365 to better tie in the proposed mechanism to that of previous work in connection with orbital variations in TAC.

“Metamorphism of the ice in the first few meters of the firn may explain the link between accumulation rate and TAC. Lower accumulation rates allow grains to remain at or near the surface for a longer time, giving grains in the firn more time to grow while they remain at the surface (Courville et al., 2007). The size of the firn grains at the surface seems to predict the density at which bubble close-off occurs, with larger-grained firn closing off at a higher density (Arnaud, 1997; Gregory et al, 2014). Because ice density is by definition, inversely proportional to porosity, higher density bubble close-off (associated here with longer time near the surface of the ice sheet, larger grain sizes, and lower accumulation) leads to bubbles with less pore volume than firn with smaller grain sizes. Lower accumulation rates may additionally allow more time for grains to become spherically shaped before close-off, where higher accumulation rates tend to close off bubbles earlier in the densification process. Because grains tend to move toward a spherical shape with enough time, due to vapor diffusion (Eicher et al., 2016), low accumulation rates likely create more homogeneous, spherically shaped grains. These spherically shaped grains force more air to escape the ice core, leading to lower TAC. (Gregory et al., 2014) noted higher gas diffusivity at lower accumulation sites, implying that at low accumulation sites, the pores are closing off later, allowing time for more spherically shaped grains. We propose that a mechanism of grain size and shape affecting pore volume leads to a positive correlation between accumulation and TAC, which we observe in the SPC14 ice core, however the microstructure and physics behind the mechanism should be explored in future work.

In a sense, this proposed grain size mechanism is similar to the proposed mechanism for how ISI impacts TAC on an orbital timescale (Raynaud et al., 2007, Eicher et al., 2016). ISI is hypothesized to act on TAC by changing the grain size of the firn at the surface by influencing temperature gradients in the first few meters of firn. On orbital time-scales, higher ISI increases the near-surface firn metamorphism and grain size, and decreases pore volume at close off, resulting in the inverse relationship between TAC and ISI recorded in both hemispheres (Raynaud et al., 1997, Eicher et al., 2016). In our proposed mechanism for millennial-scale variations in TAC, lower accumulation increases near-surface firn metamorphism and grain size and decreases pore volume at close-off. In both scenarios (orbital- and millennial-scale changes), grain size is set in the first few meters of the firn, though by different mechanisms, and the impact is advected to the close-off depth. We propose that the relationship between grain size and accumulation rate is responsible for the large, millennial-scale changes in TAC found in the SPC14 ice core. This mechanism is complimentary to the orbital changes in TAC imposed by ISI and creates millennial-scale changes imposed on top of the orbital-scale changes.”

3.5 Multiple regression

I don't see much point in multiple regression analysis involving non-independent variables

that correlate with each other. The latter could be one of the reasons why the authors obtained such a weak contribution of the ISI to the total variance of TAC.

We suggest revising section 3.5 to include regressions only between ISI and accumulation and ISI and d15N, as discussed above, in response to reviewer 1.

Surprisingly, the authors don't even mention the so-called 'wind effect' (Martinerie et al., 1994), which could account for a significant fraction of the non-orbital variability of the air content.

Suggest adding the following line to the bottom of paragraph 2, section 3.4:

"The wind effect, as described in Martinerie et al., (1994) would require large-sustained wind changes over millennia that are not supported by modeling reconstructions (Goodwin et al., 2014)."

Technical comments

In general, the manuscript requires additional proofreading, as it still contains many minor technical errors. I will cite those which I managed to notice and remember.

L331-333 and L334-336: two identical sentences in a row.

Deleted duplicate sentences.

L348, L357, L427, L560: please check and correct the table numbers you refer to here.

Table numbers have been revised and proofread.

L371-373: the first and the second parts of the sentence seem to be poorly connected.

See edits to paragraphs starting on Line 365 (detailed above).

L420: table 2 is mentioned here for the first time, while table 3 has already been mentioned above (as table 4, I suppose).

Table numbers have been revised and proofread.

Please check units for ISI in Fig. 4. Should it be GJ/m2?

Yes. Corrected label to GJ/m2

Additional reference:

Arnaud, L., 1997. Modélisation de la Transformation de la Neige en Glace à la Surface des Calottes Polaires; étude du Transport des gaz dans ces Milieux Poreux, PhD. Université Joseph Fourier.

Added reference.