

We want to thank Reviewer #1 for their thoughtful and helpful comments, which have improved the manuscript. We greatly appreciate your input. Our response is below.

**The total air content of the SPC14 ice core is displayed here at very high resolution over the last 54,000 years. It shows orbital (albeit on a short period) and variability and variability at millennial scale on some periods. By comparing this TAC record to records of other proxies and integrated insolation curves, the authors elaborate on the mechanisms which can explain the observed variations. Accumulation rate seems to be an important control on the variations but it also seems that the mechanism at play is not the same as in Greenland.**

**In general, the manuscript is well-written and well-illustrated. I recommend its publication after the following comments are taken into account.**

**105 : Replace « = » by « is »**

Line 105, was replaced as recommended.

**153 : Can you explain how you estimate accurately the line temperature for the portion outside of the GC oven ?**

Replaced [line 153] with: *“This relied on an accurate estimation of the line temperature for the portion outside of the GC oven.”* With *“The line temperature for the portion outside the GC oven was estimated by averaging the measured temperature at multiple points adjacent to the line. The variation in temperature of the line was less than 0.1°C.”*

**154 : remove « is »**

Removed, as recommended

**165 : the use of V1 and V2 are confusing since V1 was used and defined before (eq. 1, l. 105) and I am not sure that it refers to the same volume. Or is it the same volume ? Please clarify.**

Thanks for pointing out this potential confusion. To avoid this, we removed subscripts on equation 1, (line 105). Also changed the paragraph that begins on [line 110] to: *“The effective temperature of the line can change from day to day due to differences in air temperature, ethanol bath temperature, chiller efficiency, and flask headspace variation due to sample size. Because of the daily variation, it is problematic to use a weighted average calculation of  $T_{eff}$  in our calculation of TAC, as this would require a daily estimate of  $T_{eff}$  or an assumption that it is constant. To avoid this issue, we take advantage of the methods for methane measurement. During the methane measurement, we expand the air released from the melted ice four times, with each subsequent expansion releasing lower pressures from the flask headspace. The ratio between the subsequent expansion pressures allows us to calibrate the TAC measurement, as follows.”*

**Similarly, I am not sure that you refer to the same P1 and P2 than before (in equation 3, P1 and P2 were the pressures of first and second expansion).**

See the explanation, addressing Line 165, above.

**175 – can you explain clearly what is the ratio of pressures ? Which pressures ?**

This refers to the ratio of the pressure for the second expansion relative to the first, the third to the second and the fourth to the third. Changed the last paragraph of section 2.1 (beginning line 176) to read *“Finally, multiple expansions of air from the front array to the GC volume consistently give a ratio of pressures (between the four subsequent expansions for one measurement) of 0.56. When this ratio is combined with equation (5), yields a final  $\frac{T_{gc}}{V_{gc}}$  of 12.79 (K/cc).” This change, combined with the change on [line 110], outlined above, give a clearer explanation of what is meant by ‘the ratio of pressures’.*

**The confusions between notations noted above make it very difficult to properly understand the description of the analytical device and the way TAC is calculated. This part should be thoroughly rewritten.**

See changes detailed above.

**195 and after – not enough information is given on the cut-bubble correction for this study. Can you explain in more details how the correction has been derived and how the micro-CT measurements have been used? Is it possible to show the correction for the top 200 m since it appears that this correction is variable from sample to sample ?**

The micro-CT measurements were done by Fegyveresei et al (2018) whose methods are not yet published. The micro-CT measurements were done in conjunction with traditional bubble size and count methods, and only serve to validate the traditional methods. We propose the following edits to lines 195 and after, and the inclusion of the below figure, which outline the cut bubble correction applied.

*“This cut-bubble correction is based on a statistical relationship between the total number and average size of bubbles in a given sample, and the amount of exposed surface area that is cut during sample preparation (Saltykov, 1976). Bubble numbers and average sizes were determined during number-density, physical property measurements, and micro-CT measurements as described in Fegyveresi et al. (2011), Fitzpatrick et al., (2014), and Fegyveresi et al. (2018). Following the methods in Martinerie et al., (1990) and Fegyveresi (2015), we interpolated the bubble size and density data to the depth of each TAC sample, and applied the correction based on the bubble size distribution for each sample across the dataset. 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 trimming on the edges of samples, but the variation is small.” We calculated a cut-bubble correction that gives a maximum of 8% loss in the first 200 m of ice, decreasing to 1.9% TAC loss at the base of the bubbly ice at ~1200m at the onset of the clathrate-ice transition, as shown in figure 2. We applied no correction below the base of the bubbly ice.”*

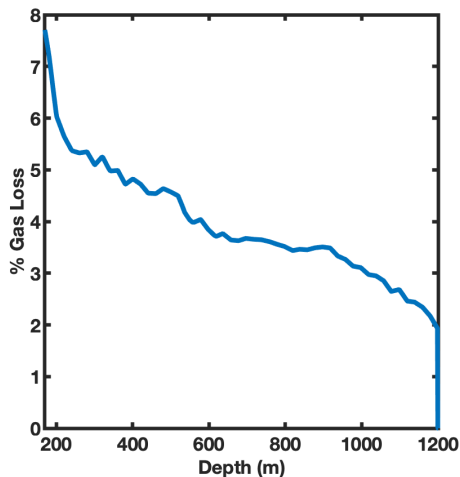


Figure 1: Cut-bubble correction for the SPC14 ice core

**206 : Did you try to have the TAC also on a gas age?**

Yes, we also explored plotting the TAC on the gas-age scale. Ice-age was chosen due to the proposed mechanism (both on orbital and millennial time scales) acting at the surface of the firn, which would be closer to the ice-age than the gas-age.

**Also, as you compare it later with the d15N of N2s, I imagine that d15N of N2 is on gas age and TAC on ice scale – what is the mechanistic link between the two if they are not on the same age scale?**

We compare TAC on the ice age scale with d15N-N2 on the gas age scale. The mechanistic link between TAC and d15N-N2 is through accumulation (an ice-age process). d15N-N2 is being trapped at bubble close-off, making the parameter a gas-age scale process. Our hypothesis is that d15N-N2 is reflecting the effect of firn thickness (a surface change) at the bubble close-off. Because of this delayed effect in 15N reflecting the firn thickness, we feel confident in our choice to compare d15N on the gas age scale with TAC on the ice age scale.

We suggest adding the following revision to the third paragraph of 3.4.1 after sentence 4 to incorporate this explanation:

*“...At this site, greater accumulation rates cause a thicker firn column and a subsequently higher  $\delta^{15}N-N_2$ . Because  $\delta^{15}N-N_2$  is not set until pore close-off, toward the base of the firn, comparison of the effect in  $\delta^{15}N-N_2$  with accumulation rate is done using the gas age scale for  $\delta^{15}N-N_2$  and ice age scale for TAC. Winski et al., (2019) also notes the close resemblance of  $\delta^{15}N-N_2$  and the Holocene accumulation rate reconstruction, which is further evidence to support the use of  $\delta^{15}N-N_2$  as an indicator of accumulation rate changes in SPC14.”*

**241 : change the « x » symbol**

Changed to '\*' to be consistent with the rest of the paper.

**251 : explain what are standardized versions of « TAC" and « Vcr\* »**

Added to the sentence after line 252.

*“The standardized data sets were created by subtracting the mean value (of TAC or Vcr, respectively) and then dividing by the respective standard deviation.”*

**290 : I know that it is explained in other places in the manuscript but it is important to document here the speed of the change. In particular, it is important to document the speed of the change because you mention that it is « abrupt ».**

Suggest changing the text on line 290 to read:

*“The approximate magnitude of the largest, abrupt, millennial-scale changes is 0.007 cm<sup>3</sup>/g in ~ 3kyr, which is similar to the abrupt millennial-scale variations observed in NGRIP, which were typically around 0.01 cm<sup>3</sup>/g in the same time frame (Eicher et al., 2016).”*

**345 : why do you mention only the resemblance between TAC and accumulation rate and between TAC and d15N of N2 ?**

- **First, you should explain on which timescale the different records are compared (the sentence « are also highly correlated with d15N-N2 at all depth » is quite confusing – indeed, if TAC and d15N-N2 are correlated on a depth timescale, then I do not understand why TAC should be on an ice scale since d15N-N2 is on a gas timescale)**

To avoid confusion about age scales, changed line 356 to *“Second, the millennial-scale changes in TAC, are also highly correlated with  $\delta^{15}N-N_2$  plotted on the SP19 gas age scale ( $r^2 = 0.51$ ,  $p < 0.001$ , Figure 5 and Table 2).”*

- **Second, why don't you also mention the resemblance between TAC and d18O of ice? I imagine that there is also a good correlation? What would be the r2 for the correlation between TAC and d18Oice**

The Pearson correlation coefficient between d18Oice and TAC is quite low (-0.13), and is listed in Table 3. We also compared the temperature reconstruction of Kahle et al (2021) and also found a low r value. These results were not discussed in the text but are available in table 3.

We suggest adding the following line at the end of paragraph 3, section 3.4.1 to alert the reader to the single regressions done on other climate parameters *“TAC was compared with temperature as well as d18Oice. Low r-values were recorded, and the results are listed in Table 2”*

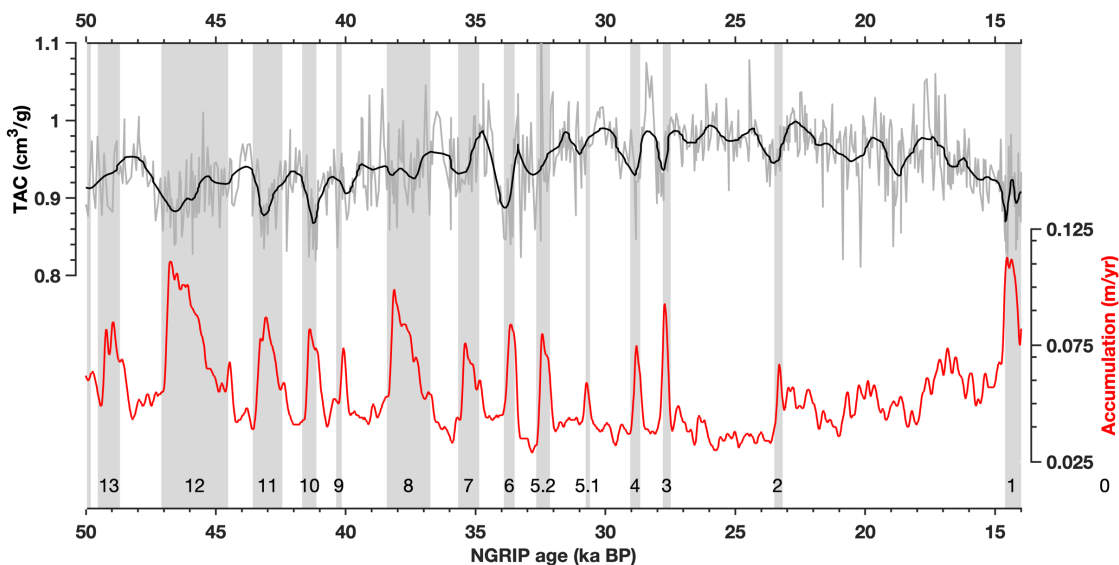
- **Any link between millennial variations of TAC and millennial variations of dust concentration? What would be the  $r^2$ ? Dust load can indeed also influence grain size and this influence has not been discussed in this manuscript. It is important to add a few sentences on this possible influence in a revised manuscript.**

The correlation between dust and TAC is very low,  $r^2 = 0.03$ . Dust levels at the South Pole are also very low, so we theorize that dust would not likely have a large impact at this site. We suggest revising the last paragraph of section 3.4 to reflect this.

*“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 dust flux. We observe no correlation between dust deposition and TAC.”*

- **It is really interesting that the TAC signal at SP can not be explained the same way as the TAC signal at NGRIP. However, it would be great to elaborate a bit more and provide one figure showing the comparison between the two records and their relationship with accumulation rate so that the reader understands clearly the different relationships between TAC and accumulation rate in the two sites.**

Eicher et al (2016) used stacked data from D-O events (defined by multiple parameters including temperature,  $d18O$ ,  $CH_4$ , and  $d15N$ ) and stacked TAC data to show a delayed change in TAC due to rapid climate changes. However, as per the reviewers request, we suggest adding the below figure and caption after figure 5 which shows the comparison of TAC and accumulation at NGRIP:



**Figure 6:** TAC and accumulation rate at North GRIP. TAC (grey, upper: Eicher et al., 2016) compared with accumulation rate (red, bottom: Kindler et al., 2014) Black line is smoothed TAC using a 10-point running average. Grey shaded areas are D-O events, numbered on the bottom for reference. Correlation coefficients are presented in Table 4.

In addition, we suggest changing the first sentence of the last paragraph of section 3.4.1 to read: “*Studies of TAC in Greenland suggest a different mechanism for similar-magnitude changes in TAC. Eicher et al. (2016) observed a complex, asynchronous relationship between rapid climate changes (D-O events) and millennial-scale TAC changes in the NGRIP ice core. Figure 6 shows the Greenland (North GRIP) TAC record compared with accumulation at the same site.*”

- **I am not sure to support the first sentence of section 3.5. Indeed, if the dependence of TAC on accumulation rate (or other influences) is not the same on different sites (+ this study does not provide a clear mechanism), we should be very cautious in using the finding on SP to better interpret « future TAC record » since the controls may be different.**

We agree that this multiple regression is not meant to be a ‘solution’ for how TAC responds to multiple parameters at all ice core sites. We suggest the following revision to the first sentence of section 3.5:

*“A multiple-regression analysis was performed to examine how climate-related variables correlate with TAC at SPC14. This analysis was performed to examine the possibility of removing non-elevation-dependent signals from the record.”*

- **The multiple regression is a bit difficult to follow. Indeed, while we can assume that ISI and accumulation rate are largely independent, there is strong links between d189ice, d15N-N2, Dage and accumulation rate so that I do not really understand why the multiple regression is not simply done on ISI and accumulation rate (or ISI and d15N-N2) ? The choice of the multiple regression on 4 parameters, 3 of them being strongly linked should be much better explained.**

The multiple regression is done on a variety of climate parameters to create a regression that fits the data best. D15N, d18Oice and Dage are all correlated through complicated climate relationships. However, their inclusion in the multiple regression serves to increase the goodness of fit of the regression model. A model that uses only accumulation and ISI (modeled parameter multiple regression) or d15N and ISI (measured parameter multiple regression) produces an adjusted R2 value of 0.51, and 0.62, respectively, which are still very strong goodness of fit values. Adding the other climate parameters only enhances the adjusted R2 value, and in the case of dDage it also helps to explain the reason behind why the predictive power of the model increases (see explanation below).

If requested, we could replace section 3.5 with:

*A multiple-regression analysis was performed to examine how climate-related variables correlate with TAC at SPC14. This analysis was performed to examine the possibility of removing non-elevation-dependent signals from the record. Because we do not expect large elevation changes at the South Pole site, SPC14 is an excellent ice core to examine this possibility. If the TAC variability in the SP14 core can be explained using measured or modeled*

climate variables, it might be possible in future projects to extract the portion of the variability due to elevation change. Here we considered two separate multiple linear regression analyses. In the first multiple regression (referred to as the 'modeled reconstruction' multiple regression), we considered ISI and accumulation rate. In the second multiple regression (referred to as the 'measured data' multiple regression), we considered ISI and  $\delta^{15}\text{N-N}_2$ . TAC data and variables considered are plotted in Figure 7.

The modeled reconstruction regression included ISI and the Kahle et al. (2021) reconstruction of accumulation rate. The modeled reconstruction multiple regression had a maximum adjusted  $r^2 = 0.51$  ( $p < 0.0001$ ), therefore the combined relationship accounts for 51% of the variation in the SPC14 TAC. The modeled reconstruction multiple regression residuals show an even distribution. The parameters are listed in Table 2 in order of how much each parameter affected the adjusted correlation coefficient.

A regression using only measured parameters incorporated  $\delta^{15}\text{N-N}_2$  instead of using the modeled accumulation rate. Results for the measured data multiple regression are listed in Table 3, again in the order of how much each variable changes the final multiple regression's adjusted correlation coefficient. We find a maximum adjusted  $r^2 = 0.62$  ( $p < 0.0001$ ). Both the modeled and measured parameter multiple regressions compare well (Figure 8).

For both the modeled and measured regression models, addition of other climate variables increased the goodness of fit. Adding temperature and  $\Delta\text{age}$  to the modeled multiple regression increased the  $r^2$  to 0.72. Adding  $\delta^{15}\text{N-N}_2$  and  $\delta^{18}\text{O}_{\text{ice}}$  to the measured parameter multiple regression increased the  $r^2$  to 0.69. While adding these parameters increased the goodness of fit of the models, suggesting that they do record phenomena important to controlling TAC, the other climate parameters are also highly correlated between themselves, which makes the interpretation of the regression parameters difficult (Gregorich et al., 2021)."

Add reference: Gregorich M, Strohmaier S, Dunkler D, Heinze G. Regression with Highly Correlated Predictors: Variable Omission Is Not the Solution. *Int J Environ Res Public Health*. 2021 Apr 17;18(8):4259. doi: 10.3390/ijerph18084259. PMID: 33920501; PMCID: PMC8073086.

• **ISI and accumulation account for 14 and 15% of the multiple regression (l. 422).**

**This is quite weak. Would these proportions be larger if the multiple regression is done only on ISI and accumulation rate?**

The proportions of how much each parameter adds to the multiple regress would increase if fewer variables were used. Using only ISI and accumulation rate to create a multiple regression, the absence of ISI would decrease the regression  $r^2$  by 0.25, and removing the accumulation term would decrease the regression  $r^2$  by 0.15.

• **The influence of the  $d\text{Dage}/dt$  is discussed but does not help to identify the mechanism at play (l. 439 : « the reason  $d\text{Dage}/dt$  helps explain TAC changes in the firm is not at first clear ») so why not exploring the influence of  $d\text{Accu}/dt$  or  $d(\delta^{15}\text{N-N}_2)/dt$  or ... ? The choice of the parameters used in the multiple regression line should be much more discussed.**

We recommend changing paragraph 4 of section 3.5, explaining the analysis of  $d\Delta_{age}/dt$  to read:

*“Large misfits between the multiple regression solution and measured TAC seem to occur during times when the climate is rapidly changing. An interesting feature of this analysis is that if the derivative of  $\Delta_{age}$  ( $d\Delta_{age}/dt$ ) is added to the multiple regression, it seems to explain more of the variability observed in the TAC record. A comparison between a regression that includes  $d\Delta_{age}/dt$ , and a regression that does not include  $d\Delta_{age}/dt$  is shown in Figure 8. Specifically,  $d\Delta_{age}/dt$  seems to correlate well with the magnitude of TAC change that occurs at 2,600 years as well as the large variations that occur between 45 ka and the oldest part of the record. A regression analysis that includes  $\partial\Delta_{age}/\partial x$  and the measured parameters (ISI,  $\delta^{15}N-N_2$ ,  $\delta^{18}O_{ice}$ , and  $\Delta_{age}$ ) gives an adjusted  $r^2$  of 0.77 ( $p < 0.0001$ ), meaning that  $d\Delta_{age}/dt$  and its interactions describe about 8% of the measured data multiple regression solution. Adding  $d\Delta_{age}/dt$  to the modeled reconstruction multiple regression increases the  $r^2$  adjusted by 4%.*

*A possible explanation for why  $d\Delta_{age}/dt$  explains this extra variation is that  $\Delta_{age}$  responds to changing climate conditions, and times when  $\Delta_{age}$  is changing rapidly (large  $d\Delta_{age}/dt$ ) correspond with large changes in temperature and accumulation rate. We specifically observe this at D-O 12 and 13. This agreement between large  $d\Delta_{age}/dt$  and rapid climate changes again points to a mechanism in the firn column that responds to transient accumulation changes. Following the reasoning of Eicher et al (2016), times of large changes in accumulation may not allow the firn to form spherical bubbles, creating less space, and therefore lower TAC values.”*

- **445 : The influence of ISI on TAC is not so obvious because the record is short. Is it possible that the effect of accumulation rate on TAC is inhibited because the ISI is on a minimum and thus inhibits the metamorphism mechanism leading to grain size modification?**

This is a possible explanation for the lack of variation in the TAC from ~25 to 35ka.

We suggest adding at the end of section 3.5 *“A possible explanation for the lack of variation at that time could be that the effect of accumulation rate on TAC is inhibited when ISI is at a minimum. This inhibition of accumulation effects on grain size could be due to ISI dominating the grain metamorphism mechanism during that period. However, more detailed studies including high resolution TAC through multiple orbital cycles would be needed to address this question.”*

- **The conclusion starting on l. 467 is surprising: why isn't the influence of accumulation rate on  $\Delta_{age}$  and  $d^{15}N-N_2$  not mentioned ? How much can the influence of accumulation rate on both TAC and  $d^{15}N-N_2$  ( $\Delta_{age}$ ) explain the strong link between TAC and  $d^{15}N-N_2$  ( $\Delta_{age}$ ) ? I feel that some explanations are missing here so as not to give the impression of a circular reasoning.**

Revise conclusion (2) to better explain why further high-resolution data sets of  $\Delta_{age}$  and  $d^{15}N-N_2$  are required:



*“(2) Further understanding of links between  $\delta^{15}\text{N-N}_2$ ,  $\Delta\text{age}$ , and TAC in ice cores. Accumulation rate can influence the  $\delta^{15}\text{N-N}_2$  and  $\Delta\text{age}$  depending on climate, and therefore influence the TAC differently at different sites. High-resolution sampling of  $\delta^{15}\text{N-N}_2$  in ice cores, and model-independent  $\Delta\text{age}$  determinations, could be used in future work to corroborate findings from the SPC14 ice core. Additionally, TAC sampling at locations with well-known accumulation rate histories will provide further constraints.”*