

We would like to thank the referee for the time taken and the thoughtful suggestions on our manuscript. They have been an asset to the study and have led to an improved manuscript.

#### Reviewer comment 2

This manuscript outlines the development of the age scale and associated chemistry records for the ISOL-ICE project. The manuscript looks at standard kinds of atmospheric and index correlation to understand the climatology driving the site specific characteristics. The manuscript is clear and readable, and well referenced. I have a few concerns (outlined below) which will likely require a bit of extra analysis, however I recommend the manuscript for publication once these are addressed. I have selected major revisions, but it is somewhere between minor and major revisions as what I suggest to do is not too onerous and I doubt will change the conclusions hugely, but will make the methods more defensible and easier to interpret.

#### Major comments:

I think the abstract needs a final sentence or two explaining where this work fits toward the eventual quantification of natural variability in ozone. At the moment the opening of the abstract doesn't follow to the results and conclusions section of the abstract very well.

*Text added in L32-33 "...and thereby leaving the UV imprint in the  $\delta^{15}\text{N}(\text{NO}_3^-)$  ice core record to quantify natural ozone variability."*

What proportion of years in the accumulation record are less than 6 cm (the minimum to preserve the nitrate seasonal cycle cited at line 50)? What effect will low accumulation years have on the ability to interpret the nitrate record for ozone variability? Also, it might be good to explain a bit more the need for at least 6 cm per annum to preserve the nitrate seasonal cycle, and that Akers et al., 2022 cite 4-20 cm. Finally, its not clear to me how a sampling resolution of 0.3 to 0.5 years provides a robust seasonal cycle – that is only 2-3 samples per year. How will this affect how you interpret the nitrate record? Also I suggest you change sentence at line 50 to 'higher rates' or similar rather than 'increases'. Reading further – perhaps I have misunderstood the sampling resolution for different analytes, so maybe this could be clarified with a table (see comment below).

The proportion of years in the accumulation record  $<6 \text{ cm a}^{-1}$  is 46 %. When annual accumulation decreases below  $6 \text{ cm a}^{-1}$  the seasonal  $\text{NO}_3^-$  signal is not preserved, reducing noise in  $\text{NO}_3^-$  and  $\delta^{15}\text{N}(\text{NO}_3^-)$  from the impact of accumulation on nitrate photolysis and concurrent isotope fractionation and therefore rather improves detection of multi-year trends in TCO, but at the expense of temporal resolution.

The  $4\text{-}20 \text{ cm a}^{-1}$  accumulation rate range refers to the accumulation rate of ice core sites that are suitable for reconstructing surface mass balance from  $\delta^{15}\text{N}(\text{NO}_3^-)$  due to the strong inverse relationship of  $\delta^{15}\text{N}(\text{NO}_3^-)$  and accumulation across the continent as proposed by Akers et al. (2022). This is different to the  $6 \text{ cm a}^{-1}$  average accumulation rate at the ISOL-ICE core site which is high enough to preserve a seasonal cycle of  $\text{NO}_3^-$  and  $\delta^{15}\text{N}(\text{NO}_3^-)$  ( $6 \text{ cm a}^{-1}$  water equivalent is around 30 cm of snow, largely enough to correctly sample annual layers near the surface). It was the large volume snow pit samples in Winton et al. (2020) that allowed us to seasonally resolve the nitrate isotope record. While we produced the highest possible resolution nitrate isotope record from the ISOL-ICE core (not published), the

resolution is annual rather than seasonal due to the lower sample volume. This is still significantly higher resolution than what could be produced from Dome C, and sufficient to achieve the goal of investigating the nitrate isotope variability over the last millennium. Therefore, the large proportion of years  $<6 \text{ cm a}^{-1}$  is irrelevant in the case of the ISOL-ICE core.

However, the proportion of years in the accumulation record  $<4 \text{ cm a}^{-1}$  is 12 %. At these low accumulation rates, signal preservation (drift, wind erosion, accumulation patch, seasonal bias) at the seasonal resolution can be compromised. Therefore, an accumulation rate reconstruction based on the Akers et al. (2022) rate transfer function, should remove these very low accumulation years or if statistically not frequent smooth them by averaging longer time scale.

Apologies for the confusion over the sample resolution. We have edited the text with the average number of data points per year at the top and bottom of the core. Due to the high sample resolution of the chemical markers used for annual layer counting (e.g., sodium and magnesium), we can confidently interpret the record on a sub-annual resolution. The lower sample resolution of 0.3-0.5 years refers to the soluble ion data which was not used to date the core.

L162-164 *“The sampling resolution of the ICP-MS, liquid conductivity and insoluble particle measurements was  $<1 \text{ mm}$  resulting in an average of  $190 \pm 120$  measurements per year in the top 5 m of the core and an average of  $140 \pm 60$  measurements per year in the bottom 5 m of the core.”*

L144-145 *“The sampling resolution of the FIC measurements was 5 cm at the top of the core and 4 cm at the bottom resulting in an average of  $2 \pm 1$  measurements per year.”*

L53 “increases” replaced with “higher rates.”

I'd recommend a schematic in the introduction that outlines how Winton et al. 2020 and this work sit in the larger frame of eventually being able to robustly interpret the stable isotopic composition of nitrogen in snow and ice as a TCO/ozone layer proxy. At the moment, its not totally clear from the abstract and the introduction what the prior work has done, what this manuscript does, and what the future work will be, and it would be good to have that clarified at the start of the manuscript.

Thank you for this suggestion to clearly outline the development process of the UV/TCO ice core proxy.

The first step is an air-snow transfer study where high resolution (daily and seasonal) observations of nitrate concentration and isotopes were made at the ice core site. These observations were used to quantify the effect of the accumulation rate, light attenuation and TCO on the archived snow  $\delta^{15}\text{N}(\text{NO}_3^-)$  signature using the TRANSITS model. The results, published in Winton et al. (2020), show that the accumulation rate along with e-folding depth are the dominant factors controlling the archived  $\delta^{15}\text{N}(\text{NO}_3^-)$  signature, followed by TCO and accumulation timing. The second step is the development of the age scale, accumulation rate and associated chemistry records for the ice core. These results, presented in this manuscript, provide foundational data to understand nitrate source regions and the natural variability of changes in the site specific accumulation rate. The final step is to use the ice core nitrate

concentration and accumulation rate record reported in this study, along with the measured ice core  $\delta^{15}\text{N}(\text{NO}_3^-)$ , to model the site specific surface conditions using the inverted TRANSITS model (Jiang et al., 2023). The UV (ozone) proxy is extracted from the  $\delta^{15}\text{N}(\text{NO}_3^-)$  record by constraining the accumulation rate effect on the  $\delta^{15}\text{N}(\text{NO}_3^-)$  thereby leaving the UV effect. Application of the UV (TCO) transfer function to the ice core  $\delta^{15}\text{N}(\text{NO}_3^-)$  which will be presented in a future study.

In L84-96, we believe we have now clearly incorporated these steps into the introduction as thus a schematic is not necessary.

Can you expand a bit on volcanic dates – specifically the delayed ‘arrival date’ of Huaynaputina (2 years) and Kuwae (8 years)? This seems a bit odd with an error of 3 years.

Thank you for pointing this out. We used published volcanic dates previously used to reconstruct well established age-depth models for ice cores in the DML region. We apologise for the confusion which likely arises around our explanation of the chosen dates which were taken from either the eruption date if known or ice core arrival (=deposition) dates in the literature if unknown. The deposition date in Table A2 refers to the published deposition date from ice cores in the literature rather than the ISOL-ICE deposition dates. For example, common observation of the layer attributed to Kuwae in other ice cores is around 1457-1458 (deposition date; Plummer et al. (2012); (Cole-Dai et al., 2013; Sigl et al., 2013), and the commonly accepted eruption date is 1450 (eruption date). The ISOL-ICE deposition date for Kuwae is 1453.

We have now added the deposition date for the ISOL-ICE core to the Table A2 which was accidentally omitted in the submitted version of the manuscript. We apologise for the confusion. We have edited the table caption and added text around the volcanic dates to make this clearer. Please see response to reviewer 1 concerning at dating uncertainty of 3 years.

L179-182 *“The volcanic dates were taken from either the eruption date if known or published deposition dates used to construct age-depth models for ice cores in the DML region if unknown (e.g. Cole-Dai and Mosley-Thompson, 1999; Zielinski et al., 1994; Langway et al., 1995; Traufetter et al., 2004).”*

Lines 75-77 – but how do you do this faithfully with only 2-3 measurements per year? You need some caveats here that your sample resolution limits your ability to interpret sub-annually here. Perhaps detail what sample resolution you get in the surface cores compared to at depth. Now that I have got to the results, I see at lines 218-219 I might have missed detail on what the sample resolution is for different analyses? If so, perhaps explain with a table (as I suggest above) the sample resolution for each type of analyte both at the surface and at depth so the reader can clearly see where you get seasonal / sub-annual resolution and where you don't.

Please see response above regarding the sample resolution.

It isn't clear to me why you used a calendar year (Jan-Dec?) mean for the ENSO indices – is that correct? If so, this would split any ENSO event in half and partition it to separate years. This doesn't make sense to me from a climatological perspective. I'd strongly suggest using a more appropriate seasonal split of either April-March or May to April (if you want to use a full 12 month mean). You could also use June to Feb. Alternatively, you could use June-

November, as the ENSO oceanic and atmospheric anomalies that are relevant to high southern latitudes commence around May / June, and intensify through to early summer, by which stage any event is well established. E.g. see Crockart et al., 2021 for an example of different seasonal splits. Lines 210-214 – this may well need a re-write once you have more appropriate seasonal boundaries for the Niño 3.4 and SOI indices. For table A3 please add in caption what monthly boundaries you end up using for calculating the indices.

Thanks for the great suggestion to examine ENSO variability based on its seasonal cycle. We have accordingly correlated the annual data with July to April (JFMA) and June to November (JJASON; Crockart et al., 2021) seasonal-mean ENSO variability noting that May is generally the transition month between ENSO cycles. We still find that annual accumulation shows no significant relationship with ENSO variability. However, we find that ENSO variability during JFMA (summer/early autumn) has moderately strong, statistically significant relationships with annual  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{MSA}^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  variability, while the correlations are much weaker and insignificant during JJASON (winter/spring). This helps shed light on the underlying seasonality of the annual correlations seen between  $\text{SO}_4^{2-}$  and ENSO shown in Table A3, in that these are likely dominated by summer ENSO variability. However, it is interesting to note that the correlations are stronger for the shorter period of 1979-2016 compared to the longer 1951-2016 period, thus may cast some uncertainty over the long-term stability of this relationship. Nevertheless, we can conclude from this analysis over the modern observation era that ENSO variability during summer does appear to be an important driver of annual chemical variability in the ice core.

We have updated Table A3 and edited the text in the methods (L231-233), results (L289-297) and discussion (L444-448) to reflect this.

Figure 4 and Discussion. A dot on each map for the ice core site would be helpful to orientate the reader. As you state, there is not a huge difference between the magnesium and sodium maps (because the records are very highly correlated, especially winter spring). Do you need to present both? At the moment its hard to interpret any differences, especially for winter spring as they may be artefacts of analysis more than anything.

Thank you for the suggestion. As there are some differences in summer, we decided to keep the text around magnesium but have moved the magnesium plots the appendix (Figure A4). We also added the location of the ISOL-ICE core to Figure 4.

Line 322 – what about orographic factors and relatively short sea salt aerosol life times of a few days? Can you prove transport across the continent, versus say short-term episodic inputs of high sea salt loads that can't be teased out in your 6 month means? I'm not suggesting you have to prove this, but I think the across continent statement is a big one and lacks evidence in this context, especially given the statement about air mass / accumulation source at lines 459-461. Would that mean that any cross-continental sea salt transport was dry deposited?

Of the two transport pathways, we agree that cross continental transport is less likely and have added text to support this.

L359-361 “...and precipitation events take four days to arrive at Kohnen Station from the Southern Atlantic Ocean consistent with the relatively short sea salt aerosol lifetime of a few days in the Southern Ocean (Landwehr et al., 2022; Reijmer et al., 2002).”

Minor comments:

In the abstract, I'd recommend separating into two sentences the sentence about the development of the age model, and then the snow accumulation and ice chemistry records and correlation. These are two separate (fairly major) steps and deserve a sentence each.

Line 27 – over the last two decades.

Done.

Line 66 – independently derived – do you mean via layer counting and volcanic horizons?

Yes. Text added L69 “...from annual layer counting and volcanic horizons...”

Line 279 – figure 4b? also, what is an ‘offshore low’ and an ‘offshore high’?

We have referred to Figure 4b. Offshore refers to the low over the ocean as opposed to over the continent.

Line 369 – sea salt

Done.

Line 390 – what do you mean by a change in the DMS oxidation pathway

Text added L426 “...change in DMS oxidation pathway from DMS to MSA and  $SO_4^{2-}$ ...”

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