

The reviewer comments are in black font and our responses are in blue.

Reply to reviewer #2

Summary:

Aydin et al present a new 52kyr record of COS from the South Pole ice core (SPC14). The record was generated using both a dry-extraction (most of the samples) and a wet-extraction technique. An empirical solubility correction is applied to the wet-extracted samples based on comparison with dry-extraction data over the Holocene, where analytical artifacts are thought to be insignificant for the dry technique. Prior work has shown that COS appears to slowly degrade in glacial ice, with the hypothesized mechanism being hydrolysis. The authors argue that SPC14 is too cold for this process to be significant, providing an important advantage in terms of COS preservation. However, the authors find an unrealistically large amount of COS variability in the part of the record from the last glacial period. They observe a very weak but statistically significant correlation between COS and sea-salt sodium (ssNa) concentrations. The authors propose that there is a mechanism in the firn (and firn only) that somehow produces excess COS of non-atmospheric origin. On the basis of the observed correlation with ssNa, the authors develop and apply a correction for excess COS for SPC14. They also apply a version of this correction to COS data from two other ice cores: WAIS Divide and Taylor Dome. The resulting 52kyr record suggests very large changes in atmospheric COS, with 2 – 4 times greater COS in the Holocene than during the last glacial maximum (LGM). This large change is interpreted as an increase in the oceanic sources of COS during the deglaciation.

One point we would like to respond to in the summary is the passing comment about the statistics. When it comes to the validity and the accuracy of the correction, we note very high statistical significance of the relationship and its robustness across various data analysis scenarios.

Major comments:

COS is present in air in very low concentrations (ppt level), and thus is extremely challenging to measure in glacial ice. The authors are therefore to be commended on the very demanding analytical effort involved in producing this record. This is an interesting record, and I think should be published if the authors are able to address the points below, but I find this record very challenging to interpret and have some concerns and recommendations, as follows.

I am not convinced by the authors' arguments for a ssNa-based COS correction. The argument that excess COS is produced only in the firn does not make sense to me. The authors effectively propose a mechanism that "burns out" fast (so that there is nothing below the firn zone). Such a "fast burn" mechanism would be expected to be most intense near the surface, but here ventilation to atmosphere would remove any excess COS that is produced. Trapped air below the firn layer would be much more sensitive to any excess production because there is less air and because this air can't exchange with overlying air.

The manuscript includes results from a firn model that demonstrates the impacts of production in the firn. It is good to see the reviewer's expectations overlap with what we find in our modeling experiment. We do not perceive a direct challenge to the evidence presented for presence of excess COS (i.e., the disagreement between measured COS levels in different ice

cores and the same-depth correlation with impurities). We therefore assume that the reviewer's skepticism about production in the firn is due to the fact that reasons supporting a firn production mechanism were not presented in sufficient detail. We revised the manuscript to expand the arguments supporting production in the firn to emphasize the points outlined below (L632-640).

We propose a production mechanism largely confined to the firn, but strictly speaking, the production does not have to stop immediately below the close-off depth, rather any production that happens deeper in the ice sheet has little to no impact on the record. One exception to this might be the spikes that are unlikely to be atmospheric in origin as discussed in the manuscript (L667-670). We demonstrate with multiple analysis scenarios that the spikes do not impact the interpretation offered in the manuscript.

A production process confined primarily to the firn is sensible because all chemical reactions require substrates which run out over time, lowering the probability of reactions as the ice ages. Emerging laser ablation-based research shows that solid and dissolved phase ice impurities, e.g. sea salt aerosols and trace metals that can act as reaction substrates and catalysts for production of COS, can migrate to different locations in the ice via post-depositional processing (Stoll et al., The new frontier of microstructural impurity research in polar ice, *Annals of Glaciology*, 2023; this reference added to the manuscript), further lowering the probability of complex reactions deeper in the ice sheet.

As for the reaction rates, the firnification at the South Pole happens over a 1000 year time scale (2000 years during the glacial period); even at fast accumulation sites, the firn-ice transition can take hundreds of years. This is plenty of time for even slow chemical reactions to run their course and substrates to run out or get physically separated from each other.

Any production process that happens in the ice sheet has to include a firn component, with the only possible exceptions being very deep, warm and wet ice with incorporated bedrock materials. If the production continues over very long time horizons (e.g. 10,000-100,000 years) such that what is produced in the ice far exceeds what is produced in the firn, we would expect the excess gas to increase with depth (over time). There is no such evidence in our record.

The ssNa-based correction is very large (up to $\approx 70\%$ of the measured values for some samples) and results in a record that shows 2 – 4 times lower COS at LGM than at the Holocene, and the authors argue that this must be mainly source-driven. Sources are mainly linked to ocean microbiota, and I find it difficult to accept that oceanic sources could have declined this much (the surface ocean was quite productive during the LGM).

In the absence of any comments on the accuracy of the correction and the related uncertainty estimates, we fail to see the merit in the comment about the magnitude of the correction.

Our argument about the change being primarily source driven is strong, which we assume is agreed by the reviewer given that they do not dispute any specific aspect. The levels of ocean productivity during the LGM is an open science question and we present a well-referenced discussion supporting our interpretation (L693-737).

The fairly good (although far from perfect) agreement among three ice cores after the ssNa correction is encouraging, but the ssNa correction may or may not be transferrable between sites.

The South Pole record is the most detailed and complete COS record and stands on its own. The other ice cores provide enough supporting information for identification and corrections of the excess COS. In fact, one of the strong piece of evidence for the presence of excess COS comes from the comparison of measurements from different sites. The measured COS levels from the different ice cores do not agree, most significantly during the deglaciation, which we can only explain by a production process linked to impurities.

Considering the above, I would recommend presenting the ssNa correction and the resulting temporal trend as speculative and one of possible scenarios (the other obvious scenario being no ssNa correction), and more clearly emphasizing how uncertain the interpretation of the measurements is, both in terms of the resulting reconstruction and implications for COS budget, which Table 1 shows to be very uncertain even today.

An interpretation of the uncorrected WAIS Divide record was published by Aydin et al. (2016), suggesting an increase in GPP might have caused the decline during mid through the late deglaciation. The uncorrected South Pole record did not agree with the WAIS Divide record during this period and indicated a different interpretation was in order. We revised the manuscript to emphasize why the previous interpretation based on the WAIS Divide ice core is not valid (in section 3.2 about comparisons with other ice core records) and further clarify why a correction for excess COS is required before any interpretation can be attempted (L430-435).

We reiterate our confidence about the completeness of our uncertainty analyses and the uncertainty estimates presented for the corrected COS record. The interpretations are limited to the likely ranges provided by the 2 sigma uncertainty estimates and do not include any over interpretations. The reviewer does not comment on any specific aspect of the interpretation for us to address.

Regarding the uncertainties in the COS budget, we offer an interpretation of the record based on the contemporary understanding of COS biogeochemistry. COS literature has been nearly unanimous for about 40 years in identifying ocean emissions as the most important natural source of COS. There is ongoing debate over how much each gas contributes but the impacts of this uncertainty on our interpretation is limited. The discussions we added based on one of reviewer #1 comments also include the possible impact on the interpretation should future research show that one or more of the ocean COS emission components (e.g. emissions from low latitudes versus emissions from high latitudes) is clearly the dominant atmospheric source. This could mean the changes in the COS record reflect more regional changes than global (L748-750).

Minor comments:

I think the manuscript could benefit from a stronger explanation for the motivation for this study, which clearly involved a great deal of effort. It seems that direct radiative forcing due to COS is negligibly small. The authors mention its link with DMS (which has a larger forcing), but

DMS appears to be a relatively smaller source of COS. COS is removed by terrestrial plant uptake – could this be a stronger motivation for the record, as a possible proxy for terrestrial biospheric productivity?

The motivation of this study is to explore what can be learned about past changes in the Earth Systems from a paleoatmospheric record of COS. The interpretation is worked out after the measurements are made and the data analyses are completed. In essence, the interpretation goes where the data takes it. Had we thought there was any possible inference to draw from this record about past GPP variability, it would have been in the manuscript.

Section 2.2:

The temperature-dependent expression for COS solubility should be given, and the actual solubility value used should be stated, and compared to the value for air. What fraction of COS is typically in the meltwater?

We deploy an empirical method in the manuscript and do not explicitly use the solubility of COS. The temperature dependent solubility equations from Sander et al. (2015) for COS and air are provided by the citation in the paper (supplemental Table 6 of Nicewonger et al., 2020). We revised the manuscript to include a more explicit citation to this previous work. The solubility correction is a factor of 1.2 on average (L149), meaning about 20% of the COS in ice core air is left in the melt water. The full distribution of corrections is shown in Fig. A3. Nicewonger et al. (2020) estimated that roughly 25% of COS would be left dissolved in the melt water. In other words, melt water is slightly undersaturated at the completion of the wet extraction. This amount varies from sample to sample (Fig. A3).

Line 149: “above” and “below” ◇ “shallower than” and “deeper than” would be less ambiguous here. “above” could mean “greater than”

Thanks, changed as suggested.

Line 215: “COS was measured over the length of the SPC14 ice core...”

Thanks, corrected.

Line 252: Do you mean “ice from the last glacial period”? All of the ice core is “glacial ice”. Please edit to clarify.

Changed to glacial period ice.

Line 254: Fig 1c does not show COS during time interval being discussed

Changed to Fig. 1b.

We thank the reviewer for their concerns and suggestions.