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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Carbonyl sulfide in air extracted from a South Pole ice core: a 2000 year record" *by* M. Aydin et al.

Anonymous Referee #2

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I have been looking forward to reading this paper since 2002 when Aydin et al. published their first manuscript for atmospheric COS concentrations from an Antarctic ice core in the time period from the mid 1600's. It showed a minimum at the beginning of the industrial revolution about 1800 and then a strange peak even earlier at the end of the 1600's where the conventional anthropogenic paradigm would have had it remaining flat. These earlier results were interesting to scientists who were accustomed to making measurements of the modern atmosphere. Since the 1970s the mixing ratios have always been about the same – about 500 ppt with some scatter – and people assumed that it was more or less invariant, perhaps with a seasonal cycle. However, these earlier measurements highlighted the impact of the anthropogenic industrialization in increasing COS mixing ratios, and they hinted that atmospheric COS may somehow respond to long-term climate change because the COS at the end of the 1600's occurred at about the time of the period of colder temperatures during the Little Ice Age. There was great scope for future work and analysis of longer ice cores extending back further in time, and these have been addresses in the present manuscript under review.

The current manuscript shows how atmospheric COS has varied over the past 2000 years in the period before intense industrialization after AD 1800. There has been an increasing trend in COS across the entire period, but most of the increase was concentrated in the interval between AD 500–1100, which is strange because this was a period associated with collapse of organized human societies in Europe and western Asia when there less likelihood of human impact of climate. Because time series encompasses the pre-industrial period, the observed variations are most likely due to natural phenomenon and section 4 discusses the results in light of the current understanding of the atmospheric COS budget. For sources, the potential role of the oceanic source is not ruled out. The role of a volcanic source is intriguing, but the discussion is somewhat weak because the record of volcanic eruptions only goes back to AD 1000 and thus does not encompass the period when most of the COS increase was observed between AD 500–1100. Is it true that there is no other proxy for volcanic eruptions before this time? Other potential sources are mentioned, but little is known about their impacts.

Long-term variations in the sinks of COS can also give rise to the observed trends in atmospheric mixing ratios. Because the photosynthetic sink of COS and CO2 are thought be linked, then long term variations in photosynthesis should have an impact on the atmospheric concentrations of both chemical species. However, this is shown not to be the case. This is significant for present investigations because much of the current drive for monitoring sites and aircraft campaigns to measure COS is aimed ultimately toward obtaining a better understanding of the CO2 photosynthetic sink. The limitations of using COS to understand CO2 are highlighted by the authors in the very

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last sentence of their paper.

The measurements of COS in the ice core were carefully performed. The authors describe the procedure that they use to assess possible contamination with modern air. Nevertheless, they identify outliers that could not be eliminated with this procedure. They hypothesize that it could be due to the in situ production of COS within the ice matrix because a real short term atmospheric anomaly would have diffused away in the processed of being trapped in the ice matrix. Were all the measurements somehow affected by this process to a greater or lesser degree? What makes some ice layers susceptible to this type of production and not other ice layers. The authors mention that future measurements with different cores are likely to address these issues.

There is one aspect of this manuscript that I found disturbing. The problem is illustrated in Fig. 3 of the manuscript, and it concerns the different time scales of all the data sets being compared. Different temperature proxy records are difficult to compare at longer time scales and show a wide variability in the palaeotemperature reconstructions. Some scientific workers feel that that proxy records support the existence of a Medieval climate warm period and a Little Ice Age, but others do not feel the same way. Certainly, it is difficult to compare the temperature proxy records in Fig. 3. They are presented after being smoothed with an (arbitrary?) 40 year filter. Why not an 80 or 160 year filter?

At the other extreme is the volcanic eruption data. Volcanic eruptions last a few days, but the authors present this information after being passed through a 5-year filter. How do they decide on the bandwidth of this filter? Is it based on the residence time of sulfate in the stratosphere or the lifetime of atmospheric COS? The radiative forcing is presented without the application of a filter but it still looks smooth. Is this correct? How should the reader two time series filtered with a 5 year band-width filter compared with one filtered with a 40 year band-width filter?

The issue is most serious for the COS in the ice core. Each measurement is associated

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with large band of age uncertainty due to the vertical diffusion of air in the firn before it is locked in ice. In the caption to Fig. 2, the authors refer to age uncertainty associated with counting ice bands and to age smearing due to vertical diffusion (Schwander et al., 1988). It would be very helpful to have an estimate of the approximate width of the age uncertainty kernel due to vertical diffusion plotted as a horizontal bar in Fig. 2, rather than just the average age as it currently presented. 106 data points are presented in Fig. 1, but because of the overlap in the age distribution for each point, there is somewhat less than 106 degrees of freedom, and the ability of the ice core to record short, transient fluctuations in atmospheric COS is limited. The reader would have a very different interpretation of Fig. 2 if they knew that each point had been passed through a 200–500 year bandwidth filter, for example. If the authors were to filter their COS point data according to the age kernels for each measurement, then it may be possible to generate a smooth COS trace that is more directly comparable with the other data sets that have been plotted in Fig. 3. As it is, it is difficult to compare the COS and volcanic eruption spikes.

Otherwise, I thought that the manuscript was an interesting and valuable contribution to the field and that it fits into the scope of ACP. The data is novel, the interpretation is thought-provoking, and substantial conclusions are reached. Except for the concerns in the last two paragraphs I thought that the scientific methods and assumptions were valid and clearly outlined, and the results sufficient to support interpretations and conclusions. There is enough information to replicate the results on a different ice core. The manuscript is properly referenced, and title and abstract reflect the contents of the manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 16763, 2008.