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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The sensitivity of the oxygen isotopes of ice core sulfate to changing oxidant concentrations since the preindustrial" *by* E. D. Sofen et al.

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Thanks to the reviewer for taking the time to read our paper and provide comments on it. Your suggestions have been valuable for improving the clarity of the paper, especially the description of how the uncertainty due to pH is handled. Responses to the specific critiques are below.

Author's assume a cloud water pH of 4.5 for the Northern and 5 for the southern Hemisphere, because these assumptions lead to the best match between modeled DELTA17O and measurements from multiple measurement stations and different seasons. This method of assuming a cloud water pH requires that other critical input pa-

rameters such as NOx and VOC emissions and stratosphere-troposphere exchange of O3 (which would also directly impact DELTA17O) are correct by definition, rather than a major source of inter-model variability. Cragin et al., 1987 reconstructed a pH of 5.4 for the precipitation in the southern Hemi- spheres over the past 2000 years. This value is higher than the one used by Sofen et al. for the southern Hemispheres and the pH of the PI northern Hemisphere. The acidity of precipitation in the Northern Hemisphere is routinely monitored in measurement networks such as EMEP and additional datasets for cloud, fog and rainwater pH are available from many measurement campaigns. I think that the conclusions would become more certain, if cloud water pH was constraint by measurements and the match between modeled and measured DELTA17O in the PD scenario was used to study the sensitivity to other critical input parameters which are far more difficult to constrain by measurements and major sources of inter- model variability e.g. NOx and VOC emissions. I do not think that the system is sufficiently constraint as long as pH is treated as a parameter that can be assumed, and the other parameters which are the source of the variability recorded in the literature are assumed to be accurate in the current study.

In Section 4 on sensitivity studies, we have now elaborated on how the uncertainty associated with cloud water pH is handled. As the reviewer points out, there is some observational evidence with which to constrain cloud water pH. Unfortunately, precipitation pH is not identical to that of cloud water, making the EMEP and ice core acidity measurements of limited value for our work. Most cloud water pH measurements have been made in the polluted Northern Hemisphere mid-latitudes. Precipitation drops represent the largest droplets in a cloud, and therefore are likely to have a more neutral pH than the average cloud water, as the large precipitation are more dilute solutions. This is born out by measurements of the pH of both cloud water and precipitation during the same event (Aleksic et al., 2009) that show on average a 0.3 higher pH in precipitation than cloud water (e.g. factor of 2 lower [H+]). Thus, we expect the cloud pH in the Antarctic to be lower than 5.4, perhaps 5.1, which is close to our best-fit case (pH = 5.0) for WAIS-Divide. In the Discussion section, we have included more on the pH=5.5

simulation, as the change in $\Delta^{17}O_{SO_4}$ at pH=5.5 is also consistent with that observed at WAIS-D. We show that no matter what we assume for pH (4.5, 5.0, 5.5), the calculated change in $\Delta^{17}O_{SO_4}$ is within the uncertainty of the measured change. It is the absolute magnitude of the $\Delta^{17}O_{SO_4}$ that differs with pH. Thus, by focusing on the change in the $\Delta^{17}O_{SO_4}$, our conclusions are less sensitive to the pH assumption, particularly in the Southern Hemisphere where pH does not change.

Specific comments caption: "preindustrial" is an adjective not a noun it would be better to add time or period

I assume this comment refers to the title? Added “era” to the title.

Page 3, paragraph 1 The author's do not specify why the reconstruction of O_3 measurements from the nineteenth century should be doubted, neither is this point elaborated in the discussion or conclusions.

Additional information has been added to section 5 about potential sources of error in the late-1800s O_3 reconstructions, including interference from other oxidizing or reducing gases, humidity, and the influence of local sources. Furthermore, the statements in the discussion and conclusion have been revised to reflect that either the model or measurements may be responsible for the mismatch.

Page 6, sensitivity studies and page 7 results and discussion The Author's use pH 5.0 instead of 5.5, which is much closer to the measured 5.4 for the southern Hemisphere, because “Simulations at pH=5.5 yield unrealistically high DELTA17O values”. What are these values?

At a pH of 5.5, the model overestimates $\Delta^{17}O_{SO_4}$ by >2.5 per mil. This has been added to the 3rd paragraph of Section 5.

Since lowering the lightening and soil NOx and doubling the VOC emissions decreases the DELTA17O values for the PI scenario compared to the baseline PI scenario, could similar changes in the PD scenario lead to better agreement between measured and

modeled DELTA17O while maintaining the pH at the measured 5.4?

A low-NOx/high-VOC (low-O3) simulation was not run at pH=5.5. However, as described above, the PD-PI $\Delta^{17}O_{SO_4}$ difference is consistent across pH assumptions in our base simulation.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 20607, 2010.