

## ***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.***

**Anonymous Referee #2**

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### General comments

Sofen et al presents a novel approach to constrain preindustrial oxidant concentrations based on the triple oxygen isotopic composition of sulfate preserved in ice cores. The question to which extent the “oxidizing capacity” of the atmosphere has changed since preindustrial times is relevant within the scope of ACP and their findings should be published. The idea of constraining preindustrial oxidant concentrations based on the triple oxygen isotopic composition of sulfate is excellent, however, the necessity to derive more than one parameter from a single measurement makes the system very sensitive to assumptions such as cloud water pH and model input parameters.

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The Autor’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 parameters such as NO<sub>x</sub> and VOC emissions and stratosphere-troposphere exchange of O<sub>3</sub> (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 Hemispheres 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. NO<sub>x</sub> 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.

### Specific comments

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

Page 3, paragraph 1

The author’s do not specify why the reconstruction of O<sub>3</sub> measurements from the

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nineteenth century should be doubted, neither is this point elaborated in the discussion or conclusions.

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? 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?

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

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