Evaluating the sensitivity of nitrate and sulfate $\Delta^{17}O$ to changes in atmospheric oxidant concentrations on the preindustrial-industrial timescale

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Atmospheric oxidants are the primary sink for reduced trace gases such as methane. Knowledge of past oxidant abundances is critical for closing paleoatmospheric reduced trace gas budgets. Ice core measurements of $\Delta^{17}O$ of nitrate and sulfate ($\Delta^{17}O = \delta^{17}O - 0.52\times (\delta^{18}O)$) provide a tracer of paleoatmospheric changes in the oxidation chemistry of nitrate and sulfate production that may be quantitatively interpreted using atmospheric photochemical modeling. We use an atmospheric global chemical transport model of $\Delta^{17}O$ of nitrate and sulfate (GEOS-Chem, www-as.harvard.edu/chemistry/ trop/geos/) with both preindustrial and industrial simulations to investigate the sensitivity of sulfate and nitrate $\Delta^{17}O$ to oxidant concentration changes on this timescale. Model results are compared with existing ice core records from Site A, Greenland, as well as a new record from the West Antarctic Ice Sheet (WAIS Divide).

Our global model results show a 40-50% preindustrial-industrial increase in global mean ozone concentrations in the troposphere, while preindustrial-industrial changes in global mean OH concentrations are much smaller (decrease of <10%). Despite significant preindustrial-industrial differences in atmospheric ozone abundance in the global model, modeled preindustrial-industrial changes in $\Delta^{17}O$ of sulfate over Site A and WAIS Divide are insignificant (-0.1 and 0 per mil), in agreement with available ice core records (0.1±0.5 per mil and 0.2±0.3 per mil, respectively (±1σ error)). This reflects the relatively minor contribution of ozone to sulfate formation in both time periods in the remote southern hemisphere, and the rise in importance of metal-catalyzed SO_2 oxidation by O_2 during northern hemisphere industrialization. In contrast to sulfate, global model results for $\Delta^{17}O$ of nitrate show significant preindustrial-industrial changes for Site A (2.6 per mil) and WAIS Divide (1.1 per mil), reflecting the greater model sensitivity of $\Delta^{17}O$ of nitrate to changes in ozone abundance. This change is not mirrored in ice core records of preindustrial-industrial changes in $\Delta^{17}O$ of nitrate at Site A (0.7±0.6 per mil (±1σ error)). Because the global model also underpredicts $\Delta^{17}O$ of nitrate at Site A for both simulations (by 4.6 and 2.7 per mil in preindustrial and industrial, respectively), we suggest that the influence of halogen chemistry (i.e., BrO), not yet included in the global model, may play an important role in nitrate formation in polar regions, reducing the sensitivity of $\Delta^{17}O$ of nitrate to ozone abundance changes.