



## Assessing the anthropogenic influence on atmospheric oxidants using the oxygen isotopic composition of sulfate and nitrate from the WAIS-Divide ice core

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The degree of non-mass dependent fractionation in the oxygen isotopic composition of sulfate and nitrate, described by  $\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$ , reflects the relative contributions of different oxidation pathways to the formation of sulfate and nitrate in the atmosphere. The  $\Delta^{17}\text{O}$  of nitrate and sulfate extracted from ice cores can provide insight into past variations in atmospheric sulfur and nitrogen chemistry and oxidative conditions. We present a model-based interpretation of measurements of oxygen isotopes of nitrate and sulfate from the West Antarctic Ice Sheet Divide (WAIS-Divide) ice core spanning the past 2400 years. Features of the measurements include stable values for the first 2200 years of the record, indicating no significant change in atmospheric oxidation chemistry from 428 BCE to 1800 CE, followed by opposite trends in the  $\Delta^{17}\text{O}$  of nitrate and sulfate in the past two centuries. We observe a large (1.2 ‰), sudden increase in the  $\Delta^{17}\text{O}$  of sulfate around 1800 CE and a later, less abrupt, downward trend (5 ‰/century) in the nitrate  $\Delta^{17}\text{O}$ . Using box models of atmospheric sulfate and nitrate chemistry, we conduct Monte Carlo simulations to determine the atmospheric chemistry conditions that explain the observed changes in the  $\Delta^{17}\text{O}$  of sulfate and nitrate. Sulfate simulations alone suggest a large (10 nmol mol<sup>-1</sup>) increase in tropospheric ozone in the high-latitude Southern Hemisphere across the stepwise increase in  $\Delta^{17}\text{O}$ , which is consistent with the magnitude, but not the timing, of the change in observed surface ozone concentrations based on late-1800s and modern measurements of tropospheric ozone. Combined modeling of both sulfate and nitrate indicates that a single set of oxidant conditions cannot explain the isotopic composition changes observed in both species, consistent with our expectation that nitrate and sulfate form in different regions of the troposphere (continental vs. oceanic). We will present results of Monte Carlo simulations investigating oxidant changes in the respective source regions for nitrate and sulfate constrained by ice core observations.