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The global distribution of the oxygen isotopic composition in nitrate and sulfate

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The oxygen isotopic composition of nitrate and sulfate reflect the oxidation processes that produce these species in the atmosphere. Both nitrate and sulfate contain a mass-independent fractionation (MIF) signal, quantified as Δ^{17}O where $\Delta^{17}\mathrm{O} \approx \delta^{17}\mathrm{O} - 0.52*\delta^{18}\mathrm{O} \neq 0$ per mil. The relatively large, positive Δ^{17}O signal in atmospheric nitrate originates primarily from the interaction of precursor nitrogen oxides (NOx) and ozone (O_3), since tropospheric O_3 typically has a Δ^{17}O of 35 per mil. A positive Δ^{17}O arises in sulfate produced from aqueous phase oxidation of SO_2 by hydrogen peroxide (H_2O_2) and O_3. Other oxidants in the atmosphere that influence the production of nitrate and sulfate tend to lower the resulting MIF signal because the Δ^{17}O of oxidants such as OH, HO_2 and RO_2 is near 0 per mil. Δ^{17}O of nitrate and sulfate preserved in aerosol, rain, snow and ice cores is thus a robust indicator of the importance of O_3 oxidation in the atmosphere.

A 3-dimensional global chemical transport model (GEOS-Chem) is used to quantify the impact of the different production pathways on the global distributions of Δ^{17}O in nitrate and sulfate. The modeled Δ^{17}O of surface nitrate varies globally from $\sim$10 to 34 per mil, while that of sulfate is 0 to 7 per mil. The Δ^{17}O of nitrate is dependent upon the degree to which NO_2 is produced from NO+O_3 versus other oxidants, as well as the oxidation processes that produce HNO_3 from NO_2. The Δ^{17}O of nitrate varies significantly seasonally, with the highest values occurring in the winter hemisphere extratropics, when the hydrogen abstraction pathway dominates nitrate formation. The lowest Δ^{17}O values occur year-round in the tropics, where relatively high concentrations of OH, HO_2 and RO_2 contribute to the lower values. Overall the model compares well with available observations of $\Delta^{17}O$ of nitrate in precipitation and aerosols, although observations are particularly limited in the tropics at this time. The $\Delta^{17}O$ of sulfate is dependent on the oxidation pathway of SO_2, with O_3 oxidation providing the largest values. The $\Delta^{17}O$ of sulfate exhibits a large degree of spatial and temporal variability, with highest values over the Southern Ocean due to pH dependent oxidation in sea-salt aerosols, and the lowest values in the tropics where gas-phase OH oxidation dominates. Wintertime sulfate $\Delta^{17}O$ values tend to be larger than in summer due to the decreased importance of gas-phase OH oxidation in winter. The largest discrepancies between model calculations and observations are in the high northern latitudes during winter, where there is evidence of a non-photochemical SO_2 oxidation pathway. Comparison with available observations allows for evaluation of current understanding of chemical reactions in the atmosphere, as well as the possibility for interpretation of past changes in atmospheric chemistry and its connection with changes in the climate based on ice core measurements.