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Isotopic anomaly transfer during the $NO_2 + O_3 \longrightarrow NO_3 + O_2$ reaction

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Oxygen isotopes in most natural compounds form a linear array in a three-isotope plot ($\delta^{17}O$ versus $\delta^{18}O$) having slope 0.52. Any deviation from this correlation is termed isotopic anomaly and is expressed as: $\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O$. Ozone is a key oxidizing molecule in the atmosphere and has a large isotopic anomaly which can be transferred to other atmospheric compounds. It is confirmed that atmospheric nitrate anomaly (ranging from 20 to 40 ‰) is inherited from ozone but experimental quantification has been lacking.

We have addressed this issue by studying $NO_2 + O_3$ reaction, a key reaction in the formation of nitrate from nitrogen oxide precursors in atmosphere, followed by isotopic analysis of the initial ozone and the oxygen produced. Ozone with $\Delta^{17}O$ values of 5 to 40 ‰ was made by electrical discharge of oxygen and used to react with NO_2 in gas phase. The isotopic data were analyzed under three assumptions: i) the anomaly in O_3 is due to terminal atoms, ii) the reaction of O_3 with NO_2 occurs only with the terminal atoms, and iii) the reaction produces only mass dependent fractionation if any. Isotope mass balance then imposes: $3 \times \Delta^{17}O(NO_3) = 3 \times \Delta^{17}O(O_3) - 2 \times \Delta^{17}O(O_2)$. The reproducibility of calculated $\Delta^{17}O(NO_3)$ for the same $\Delta^{17}O(O_3)$ is within about ± 2 ‰.

In addition, we also obtain the internal composition of O_3 from two relations involving δ–values of bulk O_3 and resulting O_2. Under the assumptions listed above one would expect: $\Delta^{17}O(\text{terminal } O_3) = 1.5 \times \Delta^{17}O(\text{bulk } O_3)$ and $\Delta^{17}O(NO_3) = 1/3\times \Delta^{17}O(\text{terminal } O_3) = 0.5 \times \Delta^{17}O(\text{bulk } O_3)$. The $\Delta^{17}O(NO_3)$ values calculated from experimental data using the mass balance equation obey this rule reasonably well (within 0.5 ‰) for $\Delta^{17}O(\text{bulk } O_3)$ values above 20 ‰ and a best fit line through the data points yields: $\Delta^{17}O(NO_3) = 0.48 (\pm 0.12) \times \Delta^{17}O(\text{bulk } O_3) + 0.62 (\pm 0.72)$ ‰.

However, it was observed that there is a small deviation from linearity between $\Delta^{17}O(\text{terminal } O_3)$ versus $\Delta^{17}O(\text{bulk } O_3)$ if one considers the whole range of values from 5 to 40 ‰. In particular, for values below 20 ‰, the $\Delta^{17}O(\text{terminal } O_3)$ values are much higher (~ 6.7‰) than predicted by the 1.5 rule. This implies that $\Delta^{17}O(\text{central } O_3)$ values are correspondingly negative. This is a surprising result since the present models can only predict a positive $\Delta^{17}O$ value for the terminal position of ozone molecule and zero $\Delta^{17}O$ value for the central position.