P-09

Poster Session Day 1

What's missing in current theory about O-MIF transfer in atmospheric reactive nitrogen: insight from atmospheric $\Delta^{17}O(NO_2)$ observations and modeling

Zhuang Jiang[1], Zhongyi Zhang[1], Lei Geng[1]

[1] School of Earth and Space Sciences, University of Science and Technology of China, Hefei, Anhui, China
*Presenting Author Email: pb1300@ustc.edu.cn

The oxygen mass-independent fractionation signal (O-MIF) offers a powerful tool to study the oxidation mechanism of atmospheric nitrate or probe the oxidation capacity of paleo atmosphere. These relevant studies heavily rely on the theoretical framework proposed by Michalski et al. (2003), which was based on the assumption of photochemical steady-state of NO_2 and unidirectional transfer of $\Delta^{17}O$ during NO_2 oxidation. Over twenty years, only a few modeling or observational studies have tried to verify this theory through atmospheric $\Delta^{17}O(NO_3^-)$ observations. Recent advance in atmospheric NO_2 sampling and $\Delta^{17}O$ analysis technics allow a more precise validation of the Michalski's theory. In this study, we report the high resolution (2h) atmospheric $\Delta^{17}O(NO_2)$ observations in Hefei City of China and results from a zero-dimensional, oxygen isotope tagging, gas phase kinetic model. We found that $\Delta^{17}O(NO_2)$ displays a clear diurnal cycle of being higher in daytime than nighttime, and the extremely high $\Delta^{17}O(NO_2)$ (>37‰) peaking in noon can be hardly explained with Michalski's theory. By adjusting the model mechanism, we show that the model-observational contradictory can be reconciled via 1) enhance the gas phase nitrate photolysis rate constant (i.e., particulate nitrate photolysis) and 2) assuming NO_2 photolysis would induce extra O-MIF fractionation. Our results highlight the importance of many other factors controls $\Delta^{17}O(NO_2)$ not considered by the Michalski's theory: the fresh emission, the isotope exchange reactions and the unknown chemical processes and the associated isotopic effect. Interestingly, from the sensitivity test results of the isotope kinetic model, we also found the modeled $\Delta^{17}O(O_3)$ value is impacted by the prescribed $J(NO_2)$ and NO_2 concentration, which may partly explain the deviation of observed tropospheric $\Delta^{17}O(O_3)$ from the theoretical expectation based on laboratory measured relationships between $\Delta^{17}O(O_3)$ and temperature/pressure.