Geophysical Research Abstracts
Vol. 13, EGU2011-1385, 2011
EGU General Assembly 2011

Measurement of the oxygen isotopic anomaly of tropospheric ozone using a nitrite-coated filter

William Vicars, Sourendra Bhattacharya, Joseph Erbland, and Joël Savarino
Université Joseph Fourier, Laboratoire de Glaciologie et Géophysique de l'Environnement, Grenoble, France
(williamcvicars@gmail.com)

The oxygen isotope anomaly (Δ^{17}O) of ozone (O_3) serves as a useful marker in studies of atmospheric oxidation pathways and provides researchers with a means of elucidating the atmospheric cycles of many key oxygen-bearing compounds. While there have been numerous studies which report Δ^{17}O values for various species carrying the anomalous O_3 isotopic signature, there are presently very few published observations of Δ^{17}O for tropospheric O_3 itself. This remains a major barrier to the robust interpretation of Δ^{17}O measurements for other atmospheric species. Because O_3 is the predominant source of the oxygen isotope anomaly in the troposphere, it is critical to know the starting isotopic composition of O_3 in order to extract quantitative information regarding oxidation pathways from isotopic measurements.

In this study, we present a new method for the collection and subsequent isotopic characterization of tropospheric O_3 using a simple, active air sampler with a nitrite-coated filter sampling substrate. This method is inexpensive and easy to implement in nearly any sampling environment; furthermore, it does not involve the complex and specialized sampling technology utilized in prior isotopic studies of tropospheric O_3 and also precludes many of the measurement errors and uncertainties that are associated with these initial investigations. The coated filter method employs the aqueous phase ozone/nitrite oxidation reaction ($NO_2^- + O_3$ — $NO_3^- + O_2$) to obtain quantitative information on O_3 via the oxygen atom transfer to nitrate (NO_3^-). $\Delta^{17}O(O_3)$ is then determined through the triple-oxygen isotope analysis of the resulting NO_3^- product via the bacterial denitrifier method. Preliminary studies of reaction efficiency indicate that the coated filter sampler collects ambient O_3 (at a flow rate of 2.9 L min^{-1}) with a reaction efficiency of 65-70 %, a significant improvement over prior studies. Isotope transfer experiments were conducted by exposing nitrite-coated filters to anomalous O_3 produced via electrical discharge. Linear regression analysis reveals a strong correlation ($r^2 = 0.98$) between the Δ^{17}O of the bulk O_3 produced in the experiment and that of the resulting NO_3^-, with a slope of 0.49, as is expected in a terminal atom transfer. This result indicates that the Δ^{17}O of O_3 is quantitatively transferred to the filter and suggests that the method is sufficiently robust and reliable to be applied to the routine analysis of stable isotope ratios of tropospheric O_3. Preliminary data for the first field measurements made using this method reveal tropospheric $\Delta^{17}O(O_3)$ values in Grenoble air ranging from 22 to 32 per mil, with a mean value of 27 per mil. Diurnal variations in $\Delta^{17}O(O_3)$ seem to be anti-correlated with O_3 mixing ratio, with the highest values being observed in the morning and late-afternoon (low O_3) and the lowest in the mid-afternoon (high O_3). This finding is consistent with our understanding of the fractionation associated with O_3 formation and destruction. Observations such as these are critical to developing a quantitative view of natural Δ^{17}O variation and its transfer in the troposphere.