Isotopic fractionation of the O₃-nitric oxide reaction

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Atmospheric ozone is known to possess mass-independent isotopic enrichment in both ³¹⁸O and ³¹⁷O (relative to ambient oxygen) and at the ground level it exhibits high regional variability, which is reflected through the different slope values in the three-isotope plot and is believed to be controlled by transport and chemical transformation processes. The fractionation factors associated with these processes are essential to model the observed distribution of isotopic composition. We show here that one of the important in situ ozone destruction processes, i.e. reaction with nitric oxide (NO), proceeds in a mass-dependent way with an instantaneous fractionation factor of 30.5‰.

The isotopic composition of atmospheric ozone is found to be isotopically anomalous; it is enriched in both ³¹⁸O and ³¹⁷O (with respect to atmospheric oxygen) and their relative enrichment does not obey the conventional mass-dependent fractionation relationship (\(\delta^18O = 0.52 \delta^{17}O\)). The enrichments in stratospheric ozone are very high\(^1\)–\(^3\) and it increases with increase in altitude following a slope value of 0.62 in a three-isotope plot (\(\Delta^18O \text{ vs } \Delta^17O\)) (ref. 4). Unlike stratosphere, tropospheric ozone is not well constrained. The tropospheric ozone measurements were reported by Krankowsky et al.\(^5\) and Johnston and Thiemens\(^6\), which show that the tropospheric ozone possesses relatively lower enrichments compared to that of stratosphere. Interestingly, measurement of Johnston and Thiemens\(^6\) reflects the regional variation of isotopic composition. They sampled ozone from three different environments (two urban and one remote locations) and found that the enrichment in ³¹⁸O for the three environments are comparable (La Jolla: 82.3 ± 6.7; Pasadena: 86.1 ± 5.6; White Sand Missile Range (WSMR): 89.7 ± 4.3) but having large variations in ³¹⁷O enrichment within rural and urban environments (La Jolla: 69.1 ± 6.5; Pasadena: 66.0 ± 3.3; WSMR: 78.0 ± 5.4), which is reflected in the slope values in a three-isotope plot (La Jolla: 0.72; Pasadena: 0.54; WSMR: 1.1) for the three regions (see figure 5 of ref. 6). In addition to the observed regional variation, large range of values for \(\delta^{18}O\) (27‰) and \(\delta^{17}O\) (46‰) were also observed for a particular location due to seasonal variation\(^5\). Though some of the differences in isotopic signatures of stratospheric and troposphere ozone can be explained in terms of temperature and pressure dependence of the \(O + O_3\) recombination reaction\(^7\)–\(^8\), many features still remain unaccounted for.

The tropospheric ozone has two major sources: (1) transport from stratosphere, and (2) in situ photochemical production. These two are balanced by two major decomposition pathways, (1) decomposition on the Earth’s surface and (2) chemical destruction. Operation of these processes in differential temporal and spatial scales makes the tropospheric ozone budget complex. Each of the sources and sink processes have the potential to control the enrichment value of a region, nevertheless, all these processes may not have the potential to vary the slope values to any large extent. Among the two source processes, the transported component would only reflect the stratospheric composition and the in situ production would reflect nearly a slope of unity\(^8\), therefore, the observed variation in the slope values (sometimes close to the mass dependent slope of 0.52) might only be explained through the sink processes. Among the two sink processes; destruction at the Earth surface is very difficult to estimate. There is only one recent study, which shows dissociation of ozone on a glass or a quartz surface proceeds in a mass-independent way\(^9\). The other sink processes, i.e. in-situ chemical destruction may be of interest in this respect. The chemical chain reactions, which comes under this group can be represented simplistically by the pair of reactions

\[
\begin{align*}
X + O_3 & \rightarrow XO + O_2 \\
XO + O & \rightarrow X + O_2 \\
O + O_3 & \rightarrow O_2 + O_2. 
\end{align*}
\]

Several species have been suggested for the catalytic ‘X’ in the atmosphere. The most important of these are X = NO, Cl, Br, and possibly iodine. Moreover, among this group, NO is one of the major species contributing significantly particularly in the stratosphere\(^10\) and in polluted urban areas\(^11\) through the reaction,

\[
O_3 + NO \rightarrow NO_2 + O_2. \tag{R2}
\]

The ambient NO\(_x\) mixing ratio varies significantly in the above three-mentioned sample locations. The NO\(_x\) concentrations in WSMR is quite low about < 1 ppbv and at La Jolla the concentration is highly variable with a mean value of 11 ± 15 ppbv. At Pasadena, the NO\(_x\) concentration is consistently high with an average of 55 ± 12 ppbv (ref. 6). Unfortunately, there is no direct correlation observed between the ozone and NO\(_x\) concentration\(^6\). At the same time it is evident from the data that with the increasing NO\(_x\) concentration, the slope value decreases.

In this context, it is important to evaluate the relative role of R2 in the isotopic fractionation in ozone as well as the associated fractionation factor of this reaction to
We obtain reaction. Rewriting the Rayleigh equation in ratios of ozone and as sume a Rayleigh model of the form

\[ R = R_0 e^{(a-1) f} \]

where \( R_0 \) and \( R \) are the respective initial and final \(^{18}\)O/\(^{16}\)O ratios of ozone and \( f \) is the fraction of ozone left after the reaction. Rewriting the Rayleigh equation in \( \delta \) notation we obtain

\[ \ln(1 + 0.001*\delta) = \ln(1 + 0.001*\delta_0) + (\alpha - 1)\ln f \]  

where \( \delta_0 \) and \( \delta \) are the initial and final \( \delta \) of ozone respectively. Figure 2 shows the correlation diagram between \( \Delta \ln(1 + 0.001*\delta) \) (i.e. \( \ln(1 + 0.001*\delta) - \ln(1 + 0.001*\delta_0) \)) and \( \ln f \). The slope of this line was used to calculate the fractionation factor, and found to be \( \alpha = 1.0305 \), implying a single stage fractionation of 30.5\%.
It is known that with the decrease of NO concentration from 50 to 1 ppbv, the lifetime of ozone increases from 42 s to 30 min\(^2\). Therefore, the recycling of ozone through NO is far more efficient for Pasadena compared to WSMR. Coupling of the above fact with this experimental finding (i.e. mass-dependent fractionation with large fractionation factor) leads us to conclude that more the recycling of ozone through NO, more is the enrichment (in \(\delta^{18}O\)) and less is the slope from its expected value (from \(O + O\) recombination reaction) of unity. Hence, the slope values observed in the three environments were consistent with the NO\(_x\) concentrations of these three sampling locations. Though large enrichment variations in \(^{18}O\) were not observed consistent with their corresponding slope values, that can be interpreted as effect of other source process controlling the enrichment as described earlier. Moreover, this fractionation factor may be a useful parameter for the mathematical modelling to construct the isotopic budget of tropospheric ozone.

It was recently proposed by Bhattacharya et al.\(^{13}\) that dissociation of ozone plays a significant role over the above temperature effect\(^{14}\) in deciding the isotopic enrichment in stratospheric ozone. Moreover, the observed slope (\(\Delta^{18}O/\Delta^{16}O\)) in lower stratosphere (up to 33 km) is 0.62\(^2\) instead of what was expected from \(O + O\) recombination reaction (nearly unity). Additionally, it is also known that the observed stratospheric ozone concentration is half of that calculated from Chapman’s cycle and is attributed to the catalytic destruction cycle. Therefore, the NO\(_x\) + O\(_3\) reaction can be considered as a representative reaction for the catalytic cycles active in destroying ozone and hence, both the lowering of slope value as well as the increase in enrichment with altitude in stratospheric ozone can be accounted.

The NO\(_x\) + O\(_3\) sink reaction follows a mass-dependent path with a significantly large associated fractionation factor (\(\epsilon=1.0305, 30.5\%)\) enriching the left-over ozone. This can be used as an important parameter to model the tropospheric ozone budget. This reaction has the potential to control the relative variations of oxygen isotopic enrichments in ozone at different tropospheric environments. Additionally, this reaction can be used as a representative reaction for catalytic cycles to explain the observed slope value and the altitudinal variation of enrichment in stratospheric ozone.


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**Influence of methyl jasmonate and salicylic acid in the enhancement of capsaicin production in cell suspension cultures of Capsicum frutescens Mill**

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The cell suspension cultures of *Capsicum frutescens* were treated with two signalling compounds, salicylic acid (SA) and methyl jasmonate (MeJA), individually, and in combination. SA and MeJA were found to individually enhance capsaicin production, but when administered in combination there was no further enhancement in capsaicin production. Both the signalling compounds were also found to result in higher leaching of capsaicin into the medium. The endogenous polyamine (PA) levels were higher in the treatments with SA and lower in the treatments with MeJA. The endogenous PA levels were found to be the highest on the sixth day of culture, after which the ethylene levels were found to increase. Maximum ethylene produc-

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