

## Multi-oxygen isotope analysis of ground based ozone: implications to tropospheric chemistry

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**Multi-isotope analysis of tropospheric O<sub>3</sub> in an urban area shows that the range of seasonal variations in δ<sup>18</sup>O and δ<sup>17</sup>O is in good agreement with that predicted based on pressure dependency of O<sub>3</sub> isotope enrichment. However, the mean values are depleted by about 10–15‰ relative to that derived from pressure dependency and also from the data reported by previous workers. The observed depletion indicates a sink of O<sub>3</sub>, presumably from surface destruction that possesses non-mass dependent isotopic fractionation.**

ISOTOPIC analysis of atmospheric trace gases has proved to be useful in identifying their sources and sinks<sup>1–6</sup>. Multi-isotope analysis of some of these gases, such as CO<sup>7,8</sup>, N<sub>2</sub>O<sup>9</sup> also provides additional information on their transport and transformation, which are difficult to obtain by single isotope or concentration measurement<sup>10</sup>. Three isotope (<sup>16</sup>O, <sup>17</sup>O, <sup>18</sup>O) analysis of synthetic O<sub>3</sub> was first carried out by Thieme and Heidenreich<sup>11</sup> who discovered a new type of chemical fractionation in a terrestrial sample in which oxygen isotopes were anomalously enriched and followed a non-statistical distribution<sup>11</sup>. The large isotopic enrichment in ozone observed in the laboratory was considered to be a powerful tool in investigating some of the atmospheric processes. However, isotopic analysis of tropospheric O<sub>3</sub> was not possible until mid 1990s due to technical problems arising from its extremely low concentration and fragile behaviour. Krankowsky *et al.*<sup>12</sup> first successfully analysed tropospheric O<sub>3</sub> isotopes and demonstrated that they were indeed anomalously enriched similar to that observed in the laboratory. Subsequently, Stehr *et al.*<sup>13</sup> and Johnston and Thieme<sup>14</sup> reported the techniques and analysis of tropospheric O<sub>3</sub> in different environments.

In these initial attempts the analytical precision was not adequate enough to distinguish sources and sinks of O<sub>3</sub>. The O<sub>3</sub> isotopes showed significant spatial variability<sup>14</sup>, which remained unexplained. Krankowsky *et al.*<sup>12</sup> observed large annual variations of 27 and 46‰ in δ<sup>18</sup>O and δ<sup>17</sup>O respectively. Though O<sub>3</sub> isotope enrichment depends on temperature and pressure<sup>15,16</sup> such large change could not be explained by seasonal change in temperature and pressure. The stable isotope distribution in trace atmospheric species is largely controlled by the isotopic composition

of precursor molecules<sup>17</sup>. However, such kind of causative relationship was not found in case of O<sub>3</sub> (ref. 18).

The tropospheric O<sub>3</sub> isotope composition is known to be controlled by *in situ* photochemical production, O<sub>3</sub> decomposition and vertical and horizontal transport. Unlike several other atmospheric trace species, the isotopic composition of O<sub>3</sub> during its formation is believed to be independent of its precursor molecules (NO and NO<sub>2</sub>). This is due to the fact that O(<sup>3</sup>P), a photolysis product of NO<sub>2</sub>, rapidly exchanges its isotopes with O<sub>2</sub> and hence loses its isotopic integrity<sup>19</sup>. However, the extent of fractionation associated with O<sub>3</sub> decomposition processes shows considerable variation and needs to be quantified in order to precisely determine the tropospheric O<sub>3</sub> isotope ratio.

There are various pathways of O<sub>3</sub> decomposition in atmosphere, such as (i) photolysis, (ii) thermal dissociation, (iii) deposition on earth surface and (iv) chemical reaction with trace gases. O<sub>3</sub> photolysis<sup>20</sup> and wall effect are believed to be mass dependent, while thermal decomposition undergoing homogeneous reaction at elevated temperature (>90°C) is known to be mass independent<sup>21</sup>. Not much experimental evidence exists regarding the nature and degree of fractionation during O<sub>3</sub> decomposition by various chemical reactions. One such reaction:



is responsible for considerable amount of O<sub>3</sub> loss, particularly in the stratosphere<sup>22</sup>. In our earlier paper<sup>23</sup> we have reported the extent of fractionation that ozone isotopes suffer while reacting with NO. In this communication I make an attempt to understand the behaviour of ozone isotopes with its precursors, viz. NO and NO<sub>2</sub>.

An ozone collection system was made consisting of four cold traps (77 K to trap moisture, CO<sub>2</sub> and other condensable). Atmospheric air was passed through these traps and made to enter a stainless steel chamber known as 'O<sub>3</sub> trap' maintained at 5.75 torr (7.65 mbar) and 55 ± 0.2 K by means of liquid helium. At this thermodynamic condition, O<sub>3</sub> and Xe were distilled off from all other gases and got condensed. Other gases, such as O<sub>2</sub>, N<sub>2</sub> were pumped out. After about 5–8 h of collection O<sub>3</sub> and Xe were released into the vapour phase and then collected onto the molecular sieve kept at 77 K. The initial experimental design has been described in Johnston and Thieme<sup>14</sup>. However Johnston and Thieme<sup>14</sup> made no attempt to separate Xe from O<sub>3</sub>. It was shown that if O<sub>3</sub> is analysed for its isotopic composition contaminated with Xe, significant enrichment (both δ<sup>18</sup>O and δ<sup>17</sup>O) takes place due to isobaric interference<sup>24</sup>. Hence in the present case, an off-line separation column was made to separate O<sub>2</sub> (derived from O<sub>3</sub>) nearly completely free from Xe. The oxygen, carrying the signature of O<sub>3</sub> was then measured in a MAT251 triple collector mass spectrometer. The precision of the overall analytical procedure was ± 3‰ for both δ<sup>18</sup>O and δ<sup>17</sup>O, where the δ's represent deviation from the atmospheric oxygen isotope ratios in per mill.

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Tropospheric ozone samples were collected in La Jolla, San Diego, California and also from White Mountain, Central California. Figure 1 shows the three-isotope diagram of La Jolla O<sub>3</sub> collected during the period of December '97 to October '98. The range of  $\delta^{18}\text{O}$  is 20‰ (63 to 83‰) and  $\delta^{17}\text{O}$  is 14‰ (47 to 61‰). The best-fit line through these points is represented by:

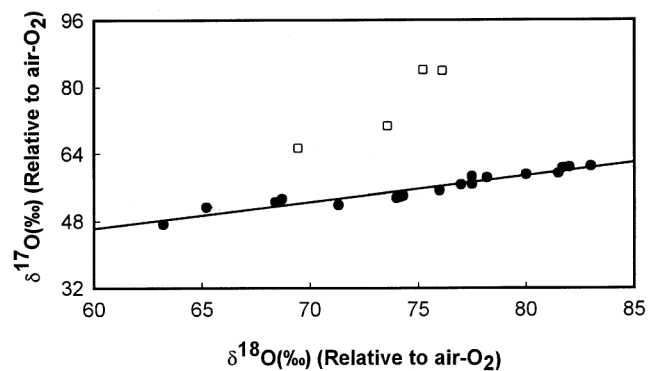
$$\delta^{17}\text{O} = (0.64 \pm 0.046) \delta^{18}\text{O} + (7.5 \pm 3.5),$$

$$(R^2 = 0.92, n = 18). \quad (1)$$

In a 3-isotope diagram if the isotopic composition of air-O<sub>2</sub> (O<sub>3</sub> precursor) is considered as origin, the O<sub>3</sub> formation line is represented by  $\delta^{17}\text{O} = \delta^{18}\text{O}$  (ref. 16), a pure mass independent process. On the other hand, the O<sub>3</sub> decomposition, which is believed until recently to be mainly a mass dependent process, would have a form  $\delta^{17}\text{O} \approx 0.5 \delta^{18}\text{O}$  (ref. 20). However, it is reported very recently that O<sub>3</sub> destruction on a surface is associated with a mass independent process<sup>25</sup>. The extent of fractionation due to decomposition will depend on the proportion of ozone being decomposed by different means. So a steady state balance of O<sub>3</sub> formation and decomposition would produce an 'O<sub>3</sub>-line' of slope between 1 and 0.5 passing through the origin.

The line in Figure 1 shows a slope of 0.64, which is closer to mass dependent fractionation line (i.e., slope = 0.5). This possibly implies that tropospheric O<sub>3</sub> isotopes at this location are dominated by O<sub>3</sub> destruction rather than formation. The 1 $\sigma$  error on the intercept is  $\pm 3.5\%$ , so a positive intercept of 7.5‰ probably indicates the presence of an external O<sub>3</sub> enriched in <sup>17</sup>O relative to the local air mass. Since this line is a best fit line of samples collected over a period of ~1 year, this intercept possibly indicates a background component of stratospheric O<sub>3</sub>, enriched in <sup>17</sup>O.

The pressure and temperature dependency of isotope enrichment in O<sub>3</sub> have been determined in the laboratory<sup>15,26</sup>.



**Figure 1.** The three isotope diagram of La Jolla ozone (filled circles). The line represents a least square fit. The open squares represent the isotopic values of ozone collected at the White Mountain Research Station, where the  $\delta^{17}\text{O}$ s are significantly higher than the La Jolla values.

At normal atmospheric pressure  $\delta^{18}\text{O}$  should be about  $90 \pm 10\%$ <sup>15</sup>. However, the mean La Jolla O<sub>3</sub>  $\delta^{18}\text{O}$  ( $75 \pm 5.8\%$ ) shows a depletion of about 15%. The values are also depleted relative to that of tropospheric O<sub>3</sub> analysed by Johnston and Thiemens<sup>14</sup> (mean  $82.2 \pm 6.7\%$ ), and Krankowsky *et al.*<sup>12</sup> (mean  $90.5 \pm 6.2\%$ ). This discrepancy is an important aspect of our observation and possible causes and their implications are discussed below.

Laboratory investigations<sup>15,26</sup> of O<sub>3</sub> formation show a value of  $\delta^{18}\text{O} \sim 90\%$  and  $\delta^{17}\text{O} \sim 80\%$  relative to starting O<sub>2</sub> composition at normal atmospheric pressure and temperature condition. Assuming these as the starting isotope values, the final O<sub>3</sub> isotope ratios at a given location will be determined by O<sub>3</sub> transformation and transport. O<sub>3</sub> decomposition undergoing a mass-dependent process like photolysis would produce heavier O<sub>3</sub> relative to its starting composition<sup>20</sup>. O<sub>3</sub> destruction through chemical pathways is also a mass-dependent process; an example is reaction R1, which destroys considerable amount of O<sub>3</sub>, particularly in the stratosphere.

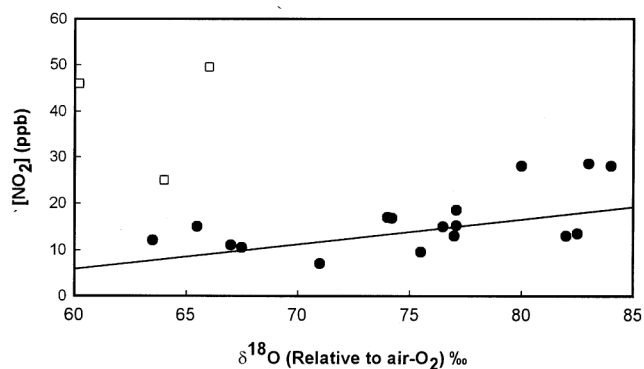
There is one pathway of O<sub>3</sub> destruction, which produces lighter O<sub>3</sub>. Wen and Thiemens<sup>21</sup> demonstrated that thermal decomposition of ozone following reaction:



results in leftover O<sub>3</sub> lighter than the initial O<sub>3</sub>. However, this process is extremely slow and only a small fraction of O<sub>3</sub> is decomposed thermally. The net effect of O<sub>3</sub> decomposition would be a balance between ozone destruction by different means.

The tropospheric O<sub>3</sub> analysed by Johnston and Thiemens<sup>14</sup> had a mean value of  $82.2 \pm 6.7\%$ , slightly higher than our mean  $75 \pm 5.8\%$ . This discrepancy could be explained in terms of 'Xe effect'. As mentioned earlier the samples analysed by Johnston and Thiemens<sup>14</sup> contained significant amount of Xe. We have shown that the presence of Xe during mass spectrometric measurement of O<sub>2</sub> could enrich the O<sub>2</sub> isotopes by more than 10%<sup>24</sup>. In the present case Xe was separated from O<sub>2</sub> (derived from O<sub>3</sub>) and hence its effects were completely eliminated.

Krankowsky *et al.*<sup>12</sup> reported a mean  $\delta^{18}\text{O}$  value of tropospheric O<sub>3</sub> as  $90.5 \pm 6.2\%$ . The range of  $\delta^{18}\text{O}$  was 27% and that of  $\delta^{17}\text{O}$  was 46%. The large range observed in this case cannot be explained by means of temperature and pressure change. Our mean value of La Jolla O<sub>3</sub> is again depleted relative to Krankowsky *et al.*<sup>12</sup>. The ranges of delta values of our La Jolla samples agree well with those predicted from the pressure dependency of O<sub>3</sub> enrichment<sup>15,26</sup>. If reaction of O<sub>3</sub> with NO is responsible for the observed isotopic enrichment, a linear correlation between NO<sub>2</sub> concentration and O<sub>3</sub> isotope ratio is expected. For a mass-dependent process, the kinetic theory predicts that lighter O<sub>3</sub> isotopes will preferentially be removed by NO. This will result in isotopic enrichment in remaining O<sub>3</sub> co-varying with NO<sub>2</sub> concentration. A scatter plot (Figure 2) between



**Figure 2.** The relationship between  $\delta^{18}\text{O}$  of La Jolla  $\text{O}_3$  and the  $\text{NO}_2$  mixing ratio. The line is a best fit plot. The open squares represent  $\text{O}_3$  samples collected in absence of sunlight.

$[\text{NO}_2]$  and  $\delta^{18}\text{O}$  of La Jolla  $\text{O}_3$  tests this hypothesis, where  $y$ -axis represents  $\text{NO}_2$  concentration (in ppb) of an area (Kearny Mesa) near our sampling site. Most of the  $\text{O}_3$  samples were collected during 10:00 to 18:00 h and the  $y$ -axis is the mean of the hourly  $\text{NO}_2$  concentration for the same period. The plot shows a positive trend between  $\text{NO}_2$  concentration and  $\delta^{18}\text{O}$  of  $\text{O}_3$ . Similar behaviour was also observed in case of  $[\text{NO}_2]$ - $\delta^{17}\text{O}$ ; but the correlation is not strong in either case ( $R^2 = 0.37$ ). A strong  $[\text{NO}_2]$ - $\delta^{18}\text{O}$  correlation would imply faster  $\text{O}_3$  decomposition, while a weak relationship means only a fraction of  $\text{O}_3$  is getting decomposed by reacting with  $\text{NO}$ . Another evidence of this assertion is apparent from Figure 2. The open squares in this figure are samples collected in absence of sunlight (during 2100–0500). Isotopic compositions of these  $\text{O}_3$  samples are not significantly different compared to the contemporaneous day samples. This was also observed by other investigators<sup>12,14</sup>. In the absence of sunlight photolysis stops, whereby  $\text{O}_3$  source and  $\text{NO}_2$  sink are cut-off, but the  $\text{NO} + \text{O}_3$  sink remains active. This enhances the  $\text{NO}_2$  concentration, which is seen in Figure 2. Despite  $\text{NO} + \text{O}_3$  reaction,  $\text{O}_3$  isotopes were not significantly enriched. This is a strong indication that chemical mode of  $\text{O}_3$  decomposition does not significantly affect its isotopic composition in this area. Hence in order to explain the depletion in  $\text{O}_3$  isotopes there must be a missing source and/or sink which would produce isotopically lighter  $\text{O}_3$ . But since  $\text{O}_3$  formation produces isotopic enrichment there must be a decomposition process that is responsible for a light  $\text{O}_3$ . Until recently it was believed that  $\text{O}_3$  decomposition on earth surface was a mass-dependent process. However detailed investigation made by Chakraborty and Bhattacharya<sup>25</sup> revealed that surface destruction of ozone is a mass independent process. Since mass independent process produces lighter ozone, it appears that most of the ozone in this area is getting decomposed on the earth surface, thereby producing lighter ozone.

I have also collected a few samples from a high altitude area, viz. White Mountain, Central California ( $37^\circ 30'\text{N}$ ,

$118^\circ 2'\text{W}$ , 3800 m). The samples were collected during March 1997; the typical time when  $\text{O}_3$  shows spring maxima. These samples show significantly high enrichment in  $\delta^{17}\text{O}$  compared to La Jolla samples (open squares in Figure 1). Though these samples were not purified from  $\text{Xe}$ , the  $\delta^{17}\text{O}/\delta^{18}\text{O}$  ratio is little affected, which is also significantly enriched. The possible reason of this enrichment is, presence of a different air-mass, such as stratospheric intrusion and/or local *in-situ*  $\text{O}_3$  production that dominates over the decomposition. In order to decouple these two possibilities, multi-tracer approach using  $^{35}\text{S}$  and  $^7\text{Be}$  (refs 27, 28 respectively) may be helpful.

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## Continuous observations of surface air concentration of carbon dioxide and methane at Maitri, Antarctica

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**A 23-month record of continuous hourly averaged carbon dioxide observations over the February 2002–January 2004 period and 16-month record of methane over the February 2003–June 2004 period for the Indian Research**

**Station, Maitri (Antarctica) have been examined to reveal baseline values in the atmosphere. During the observational period, CO<sub>2</sub> surface air concentration showed mean yearly value of 368.43 ppm in the year 2002 and 369.72 ppm in the year 2003, indicating an increase by 1.3 ppm. This corresponds to a growth rate of 0.35% per year. Mean CH<sub>4</sub> concentration for a 16-month period has been observed to be 1.699 ppm, with standard error of ± 0.0025. Unlike CO<sub>2</sub>, CH<sub>4</sub> does not show any evidence for an increase during the observation period. In the present communication, the experimental set-up and results obtained are discussed.**

THE current important issues in atmospheric sciences which affect life on the earth are global greenhouse warming, global increase in carbon dioxide, regional increase in tropospheric ozone, urban and regional atmospheric pollution and decrease in stratospheric ozone and ozone hole over Antarctica<sup>1,2</sup>. The distribution of greenhouse gases (GHGs) in the atmosphere, particularly those due to human and biosphere activities, is quite heterogeneous<sup>3</sup>. Increase in the atmospheric concentration of GHGs such as carbon dioxide, methane, nitrous oxide, halocarbons and tropospheric ozone since the industrial period (1750) has been identified as one of the major causes of the warming of the earth's surface<sup>4–6</sup>. CO<sub>2</sub> has the largest radiative effect. Now it has been recognized that the global warming due to infrared active gases like O<sub>3</sub>, CFCs, CH<sub>4</sub>, N<sub>2</sub>O, etc. is collectively as much as that due to CO<sub>2</sub> alone<sup>7</sup>, while it was only due to CO<sub>2</sub> during the pre-industrial era to 1950s. Recent studies have demonstrated that during 1999–2000, CO<sub>2</sub> alone had been responsible for about 60% of the increase in radiative forcing due to emissions from all GHGs<sup>8</sup>. Keeling and Whorf<sup>9</sup> analysed that the average rate of increase in CO<sub>2</sub> since 1980 is 0.4% per year. Direct measurements of CO<sub>2</sub> concentrations made over 40 years show that year-to-year fluctuations in the rate of increase of atmospheric CO<sub>2</sub> are large<sup>9</sup>. In the 1990s, the annual rates of CO<sub>2</sub> increase in the atmosphere<sup>8</sup> had fluctuated from 0.9 to 2.8 ppm/yr. Next to carbon dioxide, methane is the most abundant and important organic trace gas in the atmosphere. It absorbs infrared radiation<sup>10</sup> and is also involved in tropospheric and stratospheric photochemical reactions<sup>11</sup>. A downward trend was observed in the surface concentrations of methane in the northern and southern hemispheres between 1987 and 1992 and even larger downward trends were observed<sup>12</sup> for the period 1992–93. These trends have again reversed to the previous upward trend, almost 1% for methane. Dlugokencky *et al.*<sup>12</sup> reported that the global methane increase averaged 3.9 ppb per year during the three-year period 1995–97, but it was 12.7 ppb in 1998. In 1999 the increase was 2.6 ppb, suggesting that the large increase in 1998 was temporary<sup>12</sup>. The large increase in global methane abundance during 1998 corresponds to an increase in methane emissions of about 5% of the total emissions. Dlugokencky *et al.*<sup>13</sup> noted that the globally-averaged atmospheric methane abundance was constant at ~1751 ppb from 1999 through 2002, which suggests that

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