



Stratospheric ozone isotope fractionations derived from collected samples

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Received 31 July 2006; revised 31 October 2006; accepted 21 November 2006; published 17 April 2007.

[1] Oxygen isotope ratios in ozone show an unusual enrichment when compared with expected values. New results are reported that have been determined from samples collected in the stratosphere on board balloons. Flights were conducted from three locations, near the equator, at middle latitudes, and in the polar region. To about 27 km the temperature of the atmosphere determines the isotope enrichment of the two heavy isotopes ⁴⁹O₃ and ⁵⁰O₃; above that altitude the enrichments increase more strongly. Highest values measured near the equator are 13% in ⁵⁰O₃ and 10% in ⁴⁹O₃ around 32 km, implying an additional photolysis-induced isotope effect which accounts for 1/4 of the total enrichments measured. Results above Kiruna, Sweden, show a marked increase in heavy ozone from early winter to early summer in agreement with laboratory studies which established the significance of the gas temperature during ozone production. The new data quantitatively establish an additional enrichment in heavy ozone for the upper stratosphere. It is more pronounced near the equator than at middle latitudes and was not detectable in the polar region.

Citation: Krankowsky, D., P. Lämmerzahl, K. Mauersberger, C. Janssen, B. Tuzson, and T. Röckmann (2007), Stratospheric ozone isotope fractionations derived from collected samples, *J. Geophys. Res.*, 112, D08301, doi:10.1029/2006JD007855.

1. Introduction

[2] Almost 25 years ago an unusual isotope effect in stratospheric ozone was discovered and confirmed in many balloon-borne and ground-based experiments [Mauersberger *et al.*, 2005]. The two heavy isotopomers with mass 49 (a combination of ¹⁶O¹⁶O¹⁷O and ¹⁶O¹⁷O¹⁶O) and 50 (¹⁶O¹⁶O¹⁸O and ¹⁶O¹⁸O¹⁶O) showed unexpectedly large enrichments over the theoretically predicted isotope ratios [Kaye and Strobel, 1983]. Different experimental techniques, however, resulted initially in a large scatter in the ozone isotope data. Instruments and analysis processes have been refined over the last decade and the magnitude of the enrichments in ⁴⁹O₃ and ⁵⁰O₃ between 20 and 30 km are now much better known and usually range approximately between 6% and 12%. The isotope effect gained additional interest in atmospheric research when a transfer of the ozone isotope signature to stratospheric CO₂ was discovered [Thiemens *et al.*, 1991; Lämmerzahl *et al.*, 2002].

[3] Ozone isotope enrichments (or depletions) are defined by the expression

$$\delta(^M\text{O}_3) = \frac{([\text{M}\text{O}_3]/[^{48}\text{O}_3])_{\text{sample}}}{([\text{M}\text{O}_3]/[^{48}\text{O}_3])_{\text{reference}}} - 1 \quad (1)$$

with mass M = 49 or 50, respectively. The reference isotope ratios in ozone are calculated from the oxygen isotope distribution in air, which is well known, assuming a statistical distribution of the oxygen atoms within ozone.

[4] Parallel to atmospheric investigations extensive laboratory research has provided detailed descriptions of the temperature and pressure dependence of the ozone isotope effect. Morton *et al.* [1990] found that the isotope enrichments are produced during the ozone gas phase formation process, and their magnitude decreases as the temperature of the gas in which ozone is produced decreases while a decrease of gas pressure leads to higher enrichments. It is interesting to note that at temperatures somewhat below 200 K the enrichments in the two heavy isotopes are about equal [Heidenreich and Thiemens, 1983; Morton *et al.*, 1990] while at 300 K the enrichment in ⁵⁰O₃ is higher than that of ⁴⁹O₃. Laboratory results permit predictions for the stratosphere, and indeed good agreement with measured ratios was found, considering stratospheric low pressures and temperatures [Krankowsky *et al.*, 2000]. Most of the enrichments, however, were measured below 30 km. Mauersberger *et al.* [2001] critically analyzed all data obtained in the stratosphere and proposed that early measurements particularly those obtained with mass spectrometers flown on balloon gondolas [Mauersberger, 1987] were often too high and unreliable and should be disregarded.

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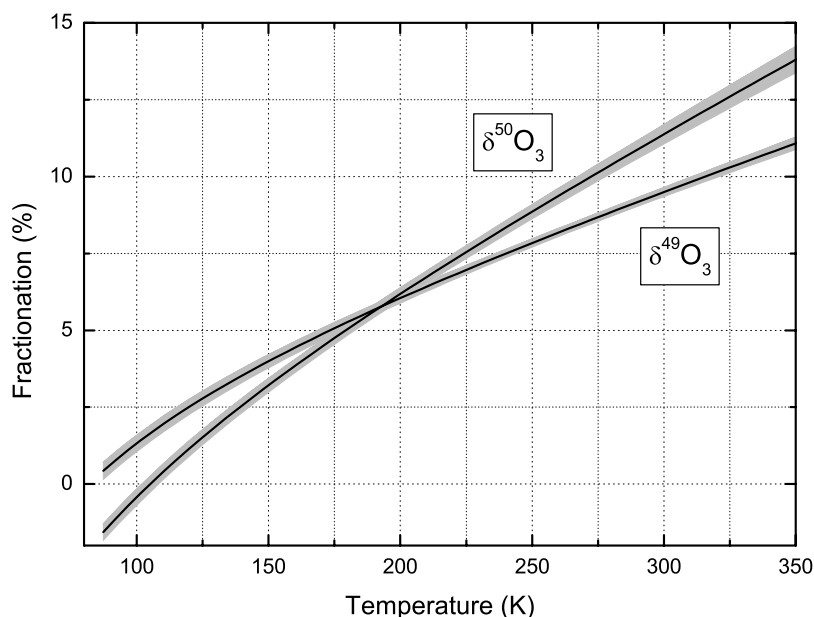


Figure 1. Temperature dependence of isotope fractionations derived from laboratory data. The fits to the data take into account measured rate coefficients, their temperature dependence, and recent precise and accurate measurements of enrichments. The shaded areas correspond to the 95% confidence limits.

[5] Still missing from stratospheric ozone isotope data are cryosample measurements at high altitudes and at equatorial latitudes. Recent balloon flights have closed this gap, and results from Teresina, Brazil (5.1°S, 42.9°W) are presented in this paper together with a summary of all measurements obtained in ozone collector flights since 1998. Included are also new data from Kiruna, Sweden (67.9°N, 21.1°E) and high-altitude measurements from Aire-sur-l'Adour, France (43.7°N, 0.3°W). Thus isotope data are now available for the entire Northern Hemisphere. The role of temperature in ozone isotope formation will be of particular interest in our discussion as we try to quantify an additional isotope effect in the stratosphere which has been proposed by a number of researchers including *Chakraborty and Bhattacharya* [2003], *Haverd et al.* [2005], *Miller et al.* [2005], *Liang et al.* [2006], and others. They based their analysis on laboratory UV absorption studies and on atmospheric isotope measurements concluding that enrichments rise faster in the stratosphere than derived from temperatures alone. The data from *Krankowsky et al.* [2000] and *Mauersberger et al.* [2001] do not permit to quantitatively identify the existence of an additional isotope effect, although *Krankowsky et al.* [2003] and *Mauersberger et al.* [2005] have not ruled out additional fractionation above about 32 km. *Brenninkmeijer et al.* [2003], analyzing the same data, concluded that 1 to 2% of the heavy ozone enrichment may be attributed to ozone photodissociation. With new precise and accurate relations between temperature and enrichments (see Figure 1), a detailed analysis of stratospheric temperature data during past balloon flights, and new high-altitude isotope data available, we can now identify and quantify such an effect.

2. Experiment

[6] Mass spectrometry of collected ozone samples has produced the most precise results in total enrichment data of

both $^{49}\text{O}_3$ and $^{50}\text{O}_3$, while remote sensing instruments operated from the ground or from space, or as part of balloon payloads have provided information on symmetric ($^{16}\text{O}^{18}\text{O}^{16}\text{O}$) and asymmetric ($^{16}\text{O}^{16}\text{O}^{18}\text{O}$) molecules although sometimes with considerably lower accuracy [*Irion et al.*, 1996; *Meier and Notholt*, 1996; *Johnson et al.*, 2000; *Haverd et al.*, 2005]. The technique of collecting ozone samples has been described previously, for example, in some detail by *Stehr et al.* [1996]. Over the years the atmospheric research group at the Max-Planck-Institut for Nuclear Physics at Heidelberg, Germany has developed a new generation of collectors, trapping carbon dioxide and ozone samples in separate low temperature traps at 80 K and 63 K, respectively. Four sets of dual traps are part of a balloon payload. Stratospheric air is forced through the first trap in which CO_2 will condense, and will continue through a second trap where ozone is collected without condensing any of the major atmospheric gases. After sufficient amount of ozone is collected during float or during a slow descent the inlet is closed and the traps are briefly connected to a small pump to remove residual air before another pair of traps is switched to the inlet. Of the four samples obtained during a flight, two are usually collected during float and the other two during the descent. Either atmospheric temperature sensors were part of the payload or Vaisala ozone sondes were launched during or immediately before or after a balloon flight to provide temperature, total pressure, and ozone partial pressures.

[7] Below is a brief discussion about the advantages and limitations of such a system. The altitude range is defined by the partial pressure of the gases to be collected and by other gases in air such as O_2 . Saturated vapor pressures of ozone [*Hanson and Mauersberger*, 1986] are such that below about 20 km O_2 collection may interfere and thus a sample of O_3 would be diluted, while above 35 km the ozone pressure is starting to be too low for an almost

complete trapping at 63 K, the triple point of liquid nitrogen. Such limitations do not exist for CO₂, however. Within the altitude region from about 20 km to above 30 km almost pure ozone samples are usually obtained in the collector cells.

[8] Collection efficiency, flow rates and the presence of impurities can be simulated in the laboratory before a flight and again evaluated thereafter. The entire system will also be treated in the laboratory with ozone to establish inert surfaces, and it will be kept evacuated until float is reached thus minimizing ozone losses during the flight. Collected CO₂ will be used for both to determine isotope ratios and to estimate the amount of air transported through the system. Together with the measurements of an external ozone monitor, collection efficiencies can be obtained; a typical value is above 70%. The laboratory analysis is performed after ozone has decomposed into O₂, a process in which the isotope signature is preserved [Heidenreich and Thiemens, 1983]. Impurities of air can be determined through the amount of N₂ present in a sample. From this the O₂ contamination is derived and applied to correct the ozone isotope results. It should be noted that together with ozone atmospheric xenon is found in the second trap. Xenon is removed before the mass spectrometer analysis of O₃ now present as O₂ is started.

[9] The technique of sample collection and laboratory analysis has the advantage that the mass spectrometer can be calibrated with standard atmospheric O₂ gas which in turn may be referenced to the international oxygen standard of SMOW (Vienna Standard Mean Ocean Water). The enrichments for ⁴⁹O₃ and ⁵⁰O₃ are therefore reported with respect to atmospheric O₂, as has been done in the past. Zero enrichment would mean that ozone has the isotope ratios which are calculated from the isotope distribution of oxygen in air. Collection at high stratospheric altitudes must be controlled to insure that sufficient ozone is present in the atmosphere, allowing for a high collection efficiency such that fractionation due to isotope-dependent condensation and collection becomes negligible. Atmospheric ozone densities were monitored and the data presented in this paper have been carefully checked, that mass discrimination as a result of insufficient collection, the most significant source for systematic errors, can be excluded. Because of the preparations made before and the tests performed after each flight, we believe systematic errors will be less than 0.5% absolute, which is about less than or equal to the 2 σ statistical error resulting in a total uncertainty of less than $\pm 1\%$ absolute.

3. Results and Discussion

[10] Summarized and discussed below are all ozone isotope enrichment data which have been obtained over a ten year period with our cryogenic-collector payload on board a balloon gondola. Because of the substantial improvements made over an earlier collector system [Schueler *et al.*, 1990], only the Heidelberg data are presented. Table 1 is a summary of 11 balloon flights from Kiruna, Sweden (4 flights), Aire-sur-l'Adour, France (5 flights) and Teresina, Brazil (2 flights). No systematic coverage over seasons was attempted or possible but it is important to note that 2 flights from Kiruna were made by

the end of November and early December while two others were flown in May. Those four flights will be discussed beside the Teresina results from Brazil and the high-altitude data from Aire-sur-l'Adour in greater detail. It is a demonstration of the quality of the data when enrichments of two samples agree very well that were obtained successively at float altitudes. This is the case, besides others, for ⁴⁹O₃ and ⁵⁰O₃ on 3 May 1999 above Kiruna or on 11 October 1999 and 25 April 2002 above Aire-sur-l'Adour.

[11] Laboratory studies by Morton *et al.* [1990] revealed a pronounced dependence of the ozone isotope enrichments on temperature and pressure of the gas in which ozone is formed. In the low pressure limit below 100 mbar, the enrichments remain constant. This is the case for the stratosphere, and many laboratory studies are available to serve for comparisons [Morton *et al.*, 1990; Thiemens and Jackson, 1990]. The influence of temperature is more complex when comparisons between laboratory and stratosphere are made. The first laboratory enrichment data measured at different temperatures by Morton *et al.* [1990] showed a large scatter as the gas temperature in which ozone was formed varied, and average values were derived. Recently, precise measurements by our group in the temperature range 87 to 340 K have refined the average Morton data. Those new data agree with the average data by Morton *et al.* [1990] reasonably well (a detailed account of the new data will be given in a separate paper). In addition, a number of rate coefficients and their temperature dependence have been experimentally determined [Janssen *et al.*, 2001, 2003; Janssen, 2005]. Both sets of information, temperature dependence of total enrichments and of rate coefficients, are used to derive the functional dependence of the enrichments for ⁴⁹O₃ and ⁵⁰O₃. Figure 1 shows the result with the shaded parts representing the 95% confidence limit. For the temperature range of the stratosphere which is as low as 185 K in the winter polar atmosphere and as high as 250 K above 30 km at middle and equatorial latitudes, the temperature dependence of the ozone isotope effect is now very well defined and can be used for comparison with atmospheric measurements to find out if other processes influence the isotope ratios, processes that may not be present during laboratory experiments. The discussion below will start with results above Air-sur-l'Adour followed by a presentation of polar and equatorial data.

3.1. Middle Latitude, Aire-sur-l'Adour, France

[12] Five flights, three in October, one in May and one in April have provided a total of 19 enrichment measurements. During spring of 2002 the atmospheric ozone densities were sufficiently high to collect samples near 36 km. Shown in Figure 2 are enrichments versus altitude together with profiles that were derived from measured stratospheric temperatures during the balloon flights and from laboratory data shown in Figure 1. While to an altitude of about 27 km measured and according to atmospheric temperatures predicted enrichments agree well, above that, measured values rise faster and are clearly higher.

[13] There are 8 pairs of measurements between 31 and 34 km from four flights (Table 1), two were conducted in spring and two in fall. Averaging those high-altitude ozone isotope data results in enrichments of $9.3 \pm 0.4\%$ for ⁴⁹O₃ and $10.8 \pm 0.4\%$ for ⁵⁰O₃, respectively. They would

Table 1. Measured δ -Values of Oxygen in Stratospheric O₃ at High, Middle, and Tropical Latitudes^a

Date	Sampling Period, UT (hhmm)	Height Range, km	⁴⁹ O ₃ % Versus O ₂	⁵⁰ O ₃ % Versus O ₂	Source of O ₃ Data ^b
<i>Kiruna, Sweden, 67.9°N, 21.1°E</i>					
10 May 1998	0537–1330	22.09 ± 0.53	8.48 ± 0.74	8.73 ± 0.46	1
10 May 1998	0537–1330	22.01 ± 0.52	7.51 ± 0.53	9.11 ± 0.33	1
10 May 1998	0537–1330	22.40 ± 0.23	8.05 ± 0.53	9.21 ± 0.35	1
10 May 1998	0537–1330	22.05 ± 0.61	8.00 ± 0.49	8.39 ± 0.30	1
3 May 1999	0739–1341	30.76 ± 0.06	8.35 ± 0.48	9.25 ± 0.31	1
3 May 1999	0739–1341	30.64 ± 0.03	8.17 ± 0.48	9.29 ± 0.30	1
3 May 1999	0739–1341	28.96 ± 1.65	7.91 ± 0.62	9.03 ± 0.39	1
3 May 1999	0739–1341	25.53 ± 1.69	7.77 ± 0.48	7.86 ± 0.30	1
3 Dec 2001	1059–1243	28.60 ± 0.18	6.54 ± 0.54	6.1 ± 0.34	2
3 Dec 2001	1059–1243	27.37 ± 1.39	6.07 ± 0.55	5.35 ± 0.34	2
3 Dec 2001	1059–1243	24.47 ± 1.09	5.39 ± 0.55	5.11 ± 0.34	2
3 Dec 2001	1059–1243	23.17 ± 0.16	5.19 ± 0.52	5.11 ± 0.34	2
28 Nov 2002	1733–1847	26.56 ± 0.91	5.82 ± 0.54	6.03 ± 0.30	2
28 Nov 2002	1733–1847	24.05 ± 1.05	5.88 ± 0.46	6.26 ± 0.29	2
28 Nov 2002	1733–1847	21.47 ± 0.82	6.14 ± 0.47	6.18 ± 0.30	2
28 Nov 2002	1733–1847	19.84 ± 0.32	5.67 ± 0.45	6.01 ± 0.31	2
<i>Aire-sur-l'Adour, France, 43.7°N, 0.3°W</i>					
3 Oct 1998	1639–2009	28.74 ± 0.38	7.65 ± 0.48	8.46 ± 0.30	1
3 Oct 1998	1639–2009	25.30 ± 2.90	6.97 ± 0.46	7.45 ± 0.28	1
3 Oct 1998	1639–2009	21.09 ± 1.45	6.91 ± 0.51	7.08 ± 0.33	1
11 Oct 1999	1055–1444	31.71 ± 0.15	8.71 ± 0.57	10.50 ± 0.36	1
11 Oct 1999	1055–1444	31.64 ± 0.20	9.24 ± 0.57	10.78 ± 0.35	1
11 Oct 1999	1055–1444	28.50 ± 2.71	8.12 ± 0.54	9.14 ± 0.35	1
11 Oct 1999	1055–1444	23.35 ± 2.20	6.84 ± 0.53	8.09 ± 0.34	1
4 Oct 2000	1326–1833	33.35 ± 0.63	9.55 ± 0.56	10.86 ± 0.34	3
4 Oct 2000	1326–1833	33.15 ± 0.60	8.95 ± 0.56	10.34 ± 0.34	3
4 Oct 2000	1326–1833	30.07 ± 2.41	7.82 ± 0.62	8.01 ± 0.40	3
4 Oct 2000	1326–1833	25.86 ± 1.48	6.69 ± 0.35	6.59 ± 0.56	3
11 May 2001	1429–1839	32.81 ± 0.12	9.70 ± 0.75	10.76 ± 0.51	4
11 May 2001	1429–1839	32.53 ± 0.40	9.60 ± 0.56	10.98 ± 0.35	4
11 May 2001	1429–1839	30.82 ± 1.05	8.71 ± 0.53	9.55 ± 0.34	4
11 May 2001	1429–1839	25.47 ± 0.86	7.32 ± 0.55	7.02 ± 0.34	4
25 Apr 2002	0949–1358	35.75 ± 0.11	10.14 ± 0.81	11.81 ± 0.51	2
25 Apr 2002	0949–1358	35.53 ± 0.41	10.08 ± 0.55	11.83 ± 0.35	2
25 Apr 2002	0949–1358	33.39 ± 1.53	9.62 ± 0.53	11.64 ± 0.33	2
25 Apr 2002	0949–1358	31.37 ± 0.35	9.35 ± 0.54	10.81 ± 0.34	2
<i>Teresina, Brazil, 5.1°S, 42.9°W</i>					
29/30 Nov 2004	2353–0139	29.38 ± 0.27	8.67 ± 0.54	10.33 ± 0.34	2
29/30 Nov 2004	2353–0139	25.83 ± 3.03	8.35 ± 0.50	9.39 ± 0.31	2
29/30 Nov 2004	2353–0139	20.88 ± 1.13	6.26 ± 0.57	6.84 ± 0.34	2
4 Jun 2005	1036–1443	32.92 ± 0.08	9.67 ± 0.64	12.06 ± 0.40	2
4 Jun 2005	1036–1443	32.83 ± 0.15	9.98 ± 0.64	12.99 ± 0.39	2
4 Jun 2005	1036–1443	31.85 ± 0.83	10.39 ± 0.63	12.76 ± 0.40	2
4 Jun 2005	1036–1443	30.14 ± 0.76	9.60 ± 0.62	12.34 ± 0.40	2

^a2 σ random errors for ozone fractionation are quoted. Systematic errors are about 0.5% absolute for both isotopes. δ -values for O₃ are with respect to atmospheric O₂: $\delta^{17}\text{O} = 1.22\%$ and $\delta^{18}\text{O} = 2.35\%$ referenced to V-SMOW.

^bReferences: 1, *Krankowsky et al.* [2000]; 2, this work; 3, *Mauersberger et al.* [2001]; 4, *Lämmerzahl et al.* [2002] (some sampling heights have been revised slightly because of improved trajectory information).

correspond (for an average altitude of 32.5 km) to an atmospheric temperature of about 290 K, too high compared with measured temperatures of about 230 to 240 K for which enrichments of 7.4% and 8.1% (Figure 1) would be expected if only the ozone formation process would determine the isotope fractionation. Therefore in approximately 32 km the additional isotope effect at middle latitudes is 1.9% and 2.7%, respectively or 20% and 25% of the total measured enrichments.

3.2. Equatorial Latitude, Teresina, Brazil

[14] Two flights, one in June and the other in November resulted in 4 high-altitude data only and provided three enrichments on descent during the second flight. They are shown together with Kiruna data (to be discussed shortly) in

Figure 3. During both flights the tropopause was near 18 km. At 21 km the temperature was only 210 K and the lowest enrichments measured were almost equal and just above 6% as predicted from Figure 1. Near 26 km values are considerably higher (8.4 and 9.4%, respectively) while the temperature has increased to 220 K. Using the same procedure as before, an additional isotope effect of approximately 1.5 and 2% can be estimated. Very pronounced is the increase when considering the high-altitude data of the second flight: Again around 32.5 km the three averaged enrichments show 10.0 and 12.6%, respectively for the two isotopes. Atmospheric temperatures were between 240 to 250 K which would correspond to enrichments of 7.6% for ⁴⁹O₃ and 8.7% for ⁵⁰O₃. Now the additional contributions are 2.4% and 3.9%, respectively, and they make 25 and 30%

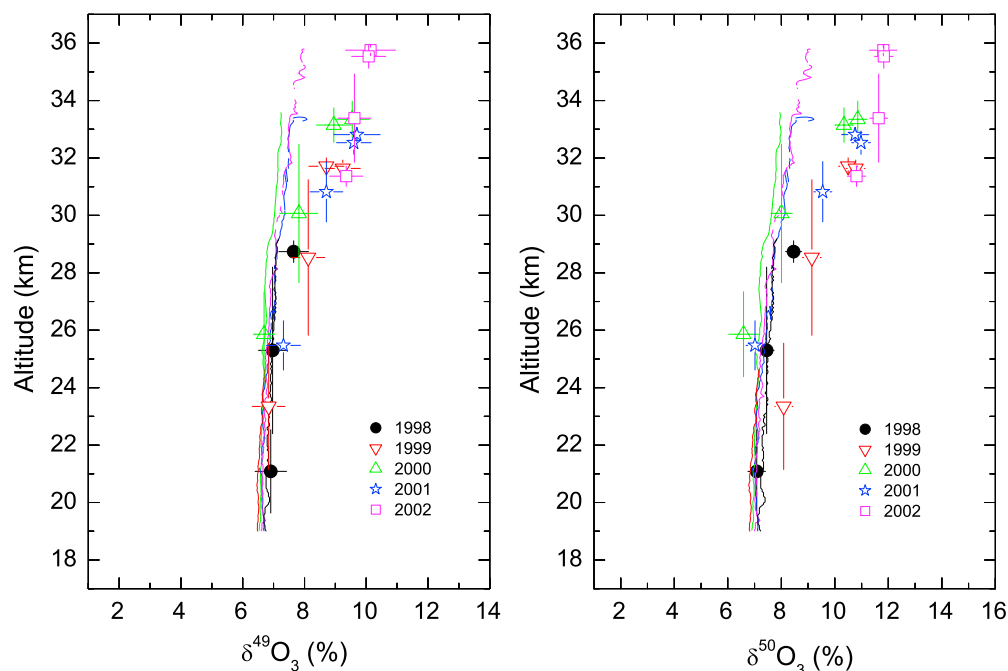


Figure 2. Altitude profiles of enrichment of (left) $^{49}\text{O}_3$ and (right) $^{50}\text{O}_3$ measured during five balloon flights at middle latitude (Aire-sur-l'Adour, France). Horizontal error bars are 2σ errors while the vertical bars indicate the height range over which ozone was collected. The lines represent the enrichment expected from measured atmospheric temperature profiles and the known temperature dependence of isotope fractionation in ozone formation (see Figure 1).

of the total values measured. There appears to be a higher contribution of this additional isotope fractionation above the equator compared to middle latitudes.

3.3. Polar Region, Kiruna, Sweden

[15] The four flights from Kiruna were flown in November/December and in May and results are also shown in Figure 3. Unfortunately in one May flight a descent system was not part of the payload and all 4 data were obtained around 22 km. For both winter flights the ozone isotope enrichments are substantially lower and almost equal, in very good agreement with prediction from the temperature dependence. Atmospheric temperatures were very low, particularly during the flight on 28 November 2002 when the payload was inside the cold polar vortex for most of the time. Considerably different is the situation in May. As expected, with higher atmospheric temperatures of about 230 to 240 K the enrichments are much higher. Averaging those values shows that atmospheric temperatures still determine the isotope ratios with no or little additional contributions.

4. Conclusions

[16] A large database of stratospheric ozone isotope data for both $^{49}\text{O}_3$ and $^{50}\text{O}_3$ is now available, covering the Northern Hemisphere. Very high enrichments, found in earlier flights, were not confirmed in the samples analyzed from the eleven balloon flights presented in this paper, consistent with the reanalysis of older data in the work by Mauerberger *et al.* [2001]. The temperature of the atmosphere determines foremost the magnitude of the enrichments in both heavy isotopomers. As the temperature in the

stratosphere increases the isotope ratios increase as well, at middle latitudes from 6.5% in 20 km to about 7.5% in 28 km for $^{49}\text{O}_3$ and from 7% to 8% for $^{50}\text{O}_3$. In the cold polar stratosphere at temperatures below 200 K both heavy isotope enrichments are lower and nearly equal around 6%. When toward summer the temperatures in the stratosphere rise enrichments increase accordingly without a sign of an additional effect even at altitudes of 30 km. Very different is the situation at middle and equatorial latitudes: The precision and accuracy of the measurements and the better known temperature dependence permit a quantification of an additional isotope effect which is more pronounced above the equator than at middle latitudes. In past publications the source of this effect has been discussed a number of times: Miller *et al.* [2005] identified the Chapman, Huggins, and Hartley band photolysis of ozone, and their calculations show that both altitude dependence as well as the magnitude of the effect agree quite well with our middle latitude data at 32 km which are 1.9% ($^{49}\text{O}_3$) and 2.7% ($^{50}\text{O}_3$). At the same altitude the calculation by Miller *et al.* [2005] results in 1.5% and 2.9%, respectively. The equatorial balloon data suggest even higher fractionations than Miller *et al.* [2005] predict. In both cases the fractionation in the heavier isotopologue is about twice that in the lighter. Liang *et al.* [2006] concluded that the ozone formation process is primarily responsible for the enrichments but that there is an additional contribution of a few percent at high stratospheric altitudes. Remote sensing results [Johnson *et al.*, 2000; Haverd *et al.*, 2005] can separate the $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ from the $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ molecules, but the absolute accuracy and precision of the data are not enough to resolve latitudinal variations. Haverd *et al.*

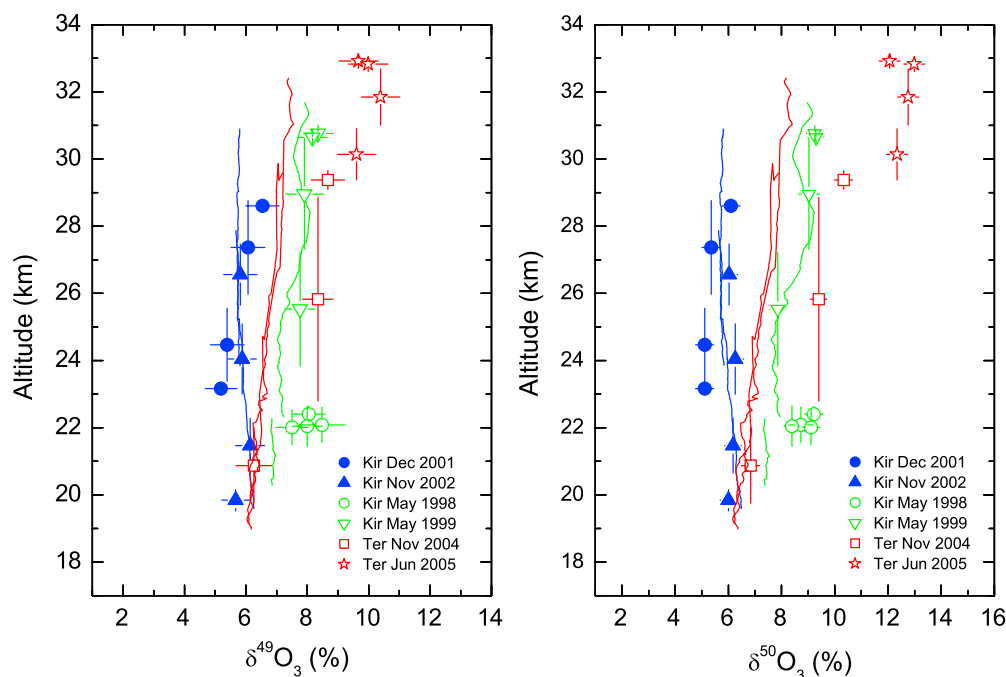


Figure 3. Altitude profiles of enrichment of (left) $^{49}\text{O}_3$ and (right) $^{50}\text{O}_3$ measured at high latitudes (Kiruna) and equatorial latitude (Teresina). Horizontal error bars are 2σ errors while the vertical bars indicate the height range over which ozone was collected. The lines represent the enrichment expected from measured atmospheric temperature profiles and the known temperature dependence of isotope fractionation in ozone formation (see Figure 1).

[2005] derive from their remote sensing data the magnitude of the additional photolytical effect on the fractionation of $^{50}\text{O}_3$ as an average over low and high latitudes and seasons. Their quoted value of 4% at 35 km is comparable to our equatorial value of 3.9% at 32.5 km.

[17] While for the lower and middle stratosphere a substantial database is available, for the upper stratosphere above 35 km precise isotope data are missing and would be very desirable. The selective cryosample technique, unfortunately, becomes marginal above that altitude as the ozone partial pressure drops too low in relation to its saturated vapor pressure at feasible collector temperatures. Similarly, limitations also exist for the remote sensing techniques when it comes to altitudes around 40 km and above. A progress in instrumental techniques for those higher altitudes would advance our knowledge of photochemical processes that control the ozone production and loss processes, would aid modeling of the ozone isotope effect, and would provide information on the transfer of the ozone isotope effect to other atmospheric constituents such as CO_2 . The isotopes of ozone remain a fascinating research object even after numerous investigations.

[18] **Acknowledgments.** The authors would like to thank support personnel from the electronic and mechanical shops as well as personnel involved in the balloon operations who made the experiments and the campaigns a success. We are particularly grateful to Reinhard Hofacker for his support during the equatorial campaigns.

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