

High Precision Measurements of the Atmospheric O₂/N₂ Ratio on a Mass Spectrometer

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(Manuscript received 16 January 2002, in revised form 28 October 2002)

Abstract

Employing a mass spectrometry method, a high precision measurement system was developed for analysis of the atmospheric O₂/N₂ ratio. Sample air and reference air were introduced into the mass spectrometer through thermally-insulated thin fused silica capillaries from an inlet system. Interference by CO generated in the ion source of the mass spectrometer from CO₂ in the sample air, and the O₂/N₂ ratio biased due to pressure imbalance between the sample air and the reference air during their introduction into the mass spectrometer were experimentally corrected. Deterioration of sampled air during storage in flasks, as well as air sampling procedures, was also examined. The precision of our measurement system was estimated to be 5.4 per meg for the O₂/N₂ ratio, which corresponds to 1.1 ppmv of the atmospheric O₂ concentration. Our standard air with 6 different O₂/N₂ ratios were prepared by drying the atmosphere and then stored in 47 L high-pressure cylinders; their O₂/N₂ ratios were confirmed to be stable within 20.0 per meg over the last 2 years. This system has been used for actual measurements of the atmospheric O₂/N₂ ratio since May 1999. Preliminary results of the measurements made in the suburbs of Sendai, Japan showed clear evidence for the seasonal cycle and the secular trend of the atmospheric O₂/N₂ ratio, which are opposite in phase with those of the CO₂ concentration.

1. Introduction

On Earth, there are three major carbon reservoirs of the atmosphere, the ocean and the terrestrial biosphere. For understanding global climate change due to human activities, it is very important to estimate the partitioning of anthropogenic CO₂ into these three reservoirs. Recently, simultaneous measurements of the atmospheric CO₂ and O₂ concentrations have attracted considerable attention in this regard (Keeling and Shertz 1992; Bender et al. 1994, 1996; Battle et al. 1996, 2000; Keeling et al. 1996, 1998a, b; Langenfelds et al. 1999a, b;

Manning et al. 1999; Tohjima 2000). The atmospheric O₂ and CO₂ concentrations are expected to change inversely with each other at some specific rate, by producing and oxidizing biospheric organic matter, as well as by burning fossil fuel (Keeling 1988; Severinghaus 1995; Lueker et al. 2001). On the other hand, the atmospheric O₂ concentration is not affected by oceanic CO₂ uptake. By using these different behaviors of atmospheric O₂ and CO₂, it is possible to separate the terrestrial biospheric and oceanic sinks of CO₂. However, to obtain meaningful information about the global carbon budget, it is necessary to measure the atmospheric O₂ concentration with a precision of about 1 ppmv (Keeling et al. 1993). To attain such high precision, substantial efforts have been devoted to establishing its measurement technique. Keeling (1988) succeeded for the first time in developing a measurement system with a precision of 1.3 ppmv by employing an

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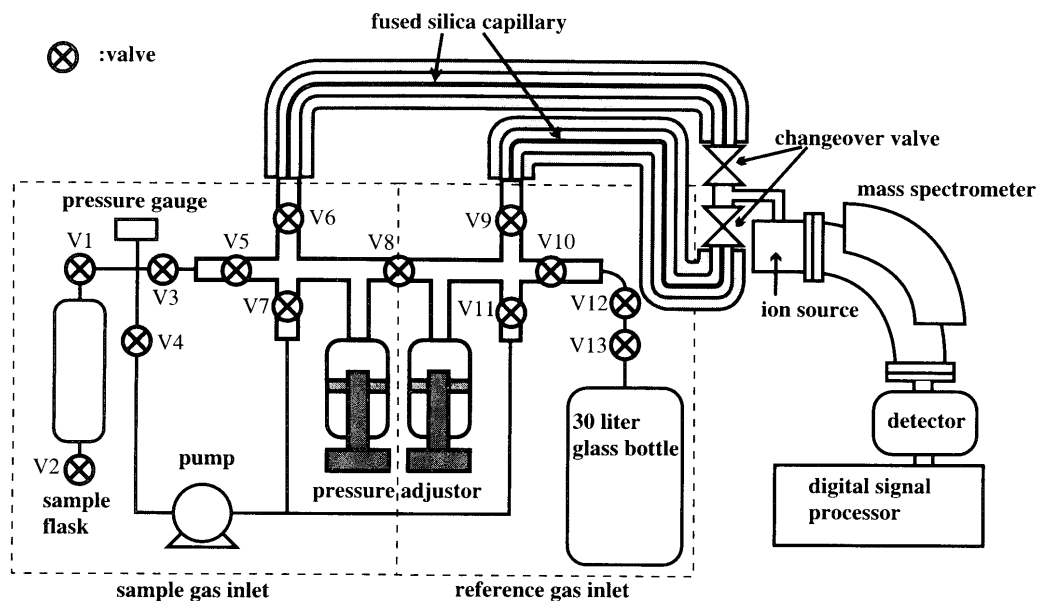


Fig. 1. Schematic diagram of the measurement system for atmospheric $\delta(O_2/N_2)$.

interferometric method. Since then, Bender et al. (1994b), Manning et al. (1999) and Tohjima (2000) made it possible to measure the atmospheric O_2/N_2 ratio with similar precision, using a mass spectrometer, a paramagnetic oxygen analyzer and a gas chromatograph, respectively. We have also developed a high precision measurement technique based on the mass spectrometry method and examined it from many facets.

This paper primarily focuses on a detailed description of the O_2 measurement technique, but preliminary results of the actual atmospheric observation in the suburbs of Sendai, Japan since May 1999 are also briefly presented.

2. Method

2.1 Measurement system and procedures

Our newly developed measurement system is schematically illustrated in Fig. 1. In order to avoid a dilution effect caused by changes in the total number of molecules in the atmosphere, changes in the atmospheric O_2 concentration are conveniently expressed in terms of changes in the ratio of O_2 relative to N_2 which can be assumed to be constant, instead of those in the O_2 mole fraction (Keeling et al. 1998a). Values are usually reported in per meg units

$$\delta(O_2/N_2) = \left(\frac{(O_2/N_2)_{\text{sample}}}{(O_2/N_2)_{\text{standard}}} - 1 \right) \times 10^6 \text{ (per meg)}, \quad (1)$$

where the subscripts 'sample' and 'standard' indicate the O_2/N_2 ratios of the sample air and the standard air, respectively. A value of 4.8 per meg of $\delta(O_2/N_2)$ corresponds to 1.0 ppmv of the O_2 concentration in the atmosphere. For measuring $\delta(O_2/N_2)$ of the sample air, we employed a mass spectrometer, Finnigan MAT-252, in which corrector cups were adjusted to measure the ion beam currents for masses 32 ($^{16}O^{16}O$) and 29 ($^{15}N^{14}N$). The reason why we did not use masses 28 ($^{14}N^{14}N$) and 32 ($^{16}O^{16}O$) is that the spread of both ion beams is so wide that our mass spectrometer cannot measure their currents simultaneously. An inlet system used for introducing the sample air and the reference air into the mass spectrometer was made of Pyrex glass, and Viton O-rings were employed for all stopvalves. The tubing of the inlet system was designed symmetrically, so that selective O_2 adsorption on and desorption from its insides, as well as different O_2 fractionations possibly occurring by passing through different length tubes, were equalized for both the sample air and the reference air.

Each side of the inlet system was equipped with a pressure adjustor of which the volume varies between 19 and 27 ml, to equalize the pressures of the sample air and the reference air before introducing them into the mass spectrometer. A Pyrex glass container, with a volume of 30 L, was filled with the reference air that was prepared by drying natural air using the same procedure as our standard air to be described later. The inlet system and a change-over valve of the mass spectrometer were connected with each other using 1.35 m-length fused silica capillaries with an inner diameter of 25 μm . These capillaries were chosen so that not only the ion beam currents for N_2 and O_2 were suitably measurable when the sample air and the reference air were introduced into the mass spectrometer at near atmospheric pressures, but also so that air flow passing through them was kept viscous.

Our analytical procedures of sample air are as follows. Prior to sample analysis, the fused silica capillaries and an ion source of the mass spectrometer were conditioned by flowing dry natural air for at least 48 hours, to reduce the remarkable drift of the measured $\delta(\text{O}_2/\text{N}_2)$ value which occurs after evacuating them over a long time. After this process, the reference air was introduced through one side of the inlet from the glass container until the detector output for the ion beam of N_2 (29) indicated approximately 3.0 V, corresponding to a pressure of about 0.8×10^5 Pa in the reference reservoir, while the sample air was introduced from the other side. The operation of the respective valves related to this air introduction was made every 30 seconds, to ensure air transfer to the mass spectrometer without fractionation, a discussion of which will be given in section 2.2. The volume of each pressure adjustor was then varied so that detector outputs for the sample air and the reference air agreed with each other to within ± 0.005 V, and the mass spectrometry measurement of $\delta(\text{O}_2/\text{N}_2)$ was then started. Each measurement consisted of 10 alternate analyses for the sample air and the reference air. We usually introduced the sample air into the inlet system twice and a series of 10 analyses was repeated twice for each sample, which took about 60 minutes. Four values, thus measured, were simply averaged to express the $\delta(\text{O}_2/\text{N}_2)$ value of the sam-

ple air as a deviation from the reference air. The required final value of $\delta(\text{O}_2/\text{N}_2)$ for the sample air was determined against the working standard air, by measuring it by the same procedure as above. The measurement of the working standard was done before and after each-day sample analyses, to correct for a gradual temporal drift of the detector output of the mass spectrometer, as well as for zero enrichment to be discussed later. The standard air system will be described below.

Our analytical procedures of the sample air are somewhat different from those in Bender et al. (1994b). By employing the above-mentioned procedures, analytical time of each sample was greatly reduced, compared with that of Bender et al. (1994b), while maintaining analytical precision level similar to theirs.

2.2 Changes in O_2/N_2 during air transfer to the mass spectrometer

There are several possibilities of changing the O_2/N_2 ratio during the introduction of air into the mass spectrometer, such as selective O_2 or N_2 adsorption onto and desorption from solid surface, diffusive fractionations of O_2 and N_2 induced by temperature, pressure and water vapor gradients, and fractionations of O_2 and N_2 during air flow, for example, due to Knudsen diffusion (Keeling et al. 1998a). As mentioned above, the effect of the selective adsorption and desorption of O_2 or N_2 was minimized in our measurement system. In addition, it is thought that there are no pressure or water vapor gradients in the inlet system. Therefore, we inspected two fractionation effects which are related to the operation of the valves and the temperature of the tubing of the inlet system. To examine the former effect, we tried to introduce air into the inlet system in three different ways: (a) leaving the central stopvalve (V8 in Fig. 1) open, the air was introduced into the sample and reference sides of the inlet from the sample side, and then the central stopvalve was immediately closed, (b) same as in case (a), but the air introduction was made from the reference side, and (c) leaving the central stopvalve closed, the air was introduced into the reference side, and then the central stopvalve was opened and closed. In cases (a) and (b), $\delta(\text{O}_2/\text{N}_2)$ of the air in the sample side showed the respective values of

45.5 and -83.9 per meg relative to the air in the reference side, the difference between both results being as much as about 130.0 per meg. The cause may be due to the fact that the molecular velocities of N_2 and O_2 are different when the air expands in an evacuated tube. In such a circumstance, N_2 diffuses faster than O_2 , because the mean velocity of a molecule is inversely proportional to the square root of its mass (Dushman 1949). On the other hand, it was found in case (c) that $\delta(O_2/N_2)$ of the air in the sample side was independent of the time interval between the opening and the closing of the central stopvalve, if we took as much as 30 seconds for that operation.

To examine the temperature effect on O_2/N_2 , we compared the measured values of $\delta(O_2/N_2)$ for the sample air introduced into the mass spectrometer at room temperatures with those obtained by cooling the glass trap, inserted temporarily between stopvalves V3 and V5 (see Fig. 1), at -78.0°C . From this comparison, the latter values were found to be lower by about 100.0 per meg than the former. A similar phenomenon was reported previously by Bender et al. (1994b). Keeling et al. (1998a) also mentioned in their paper that O_2 molecules concentrated on places with lower temperatures. The potential degree of diffusive fractionation of O_2 and N_2 by temperature gradients is approximated by $\delta = -\alpha\Delta T/T$, if molecular diffusion is the only gas transport mechanism. By assigning $\alpha = 0.018$ for the thermal diffusion coefficient for O_2 and N_2 (Grew and Ibbs 1952) and 22.0°C (295 K) for the room temperature, the potential O_2 enrichment relative to N_2 in the glass trap was calculated to be 6102.0 per meg. Since the volume of the glass trap accounted for about 27% of the tubing partitioned by the stopvalves V3, V6, V7 and V8, we can expect that the O_2/N_2 ratio of air in the tubing except the glass trap is lower by about 2260.0 per meg $((6102.0 \times 0.27)/(1 - 0.27))$ than that obtained at room temperatures. Considering these results, we decided to introduce the sample air into the mass spectrometer with no use of a cold trap, to avoid the preferential accumulation of O_2 in a cold trap. The discrepancy between the measured and calculated decreases of the O_2/N_2 ratio could be attributable to thermally disequilibrium between the sample air and the wall of the glass trap. In the

context of the above experimental examination, the sample air was therefore introduced into the mass spectrometer by operating the relevant stopvalves in order with a time interval of 30 seconds, as was done in actual sample analysis.

To reduce the temperature effect on the O_2/N_2 ratio as much as possible, we installed our measurement system in an air-conditioned room of around 22.0°C . The room temperature fluctuation was kept at $\pm 0.5^\circ\text{C}$, at least over a whole day. In addition, the fused silica capillaries connecting the inlet system to the changeover valve were thermally insulated using two kinds of Teflon tubes with different diameters. By making these devices, the standard error of each measurement for the sample air was considerably decreased from 9.0–30.0 per meg to below 6.0 per meg. We also tried to insulate other parts of the inlet system, but no further improvement was obtained.

During the above examination of case (c), it was found that the measured value of $\delta(O_2/N_2)$ was never equal to zero, showing typical values of about -30.0 per meg, even though sufficiently long time was taken to close the central stopvalve after its opening. This phenomenon is known as zero enrichment effect (Bender et al. 1994b), which is seen, to a greater or lesser extent, in mass spectrometers used in isotope analyses. In this regard, by measuring the air introduced from the sample side of the inlet system, we confirmed that its $\delta(O_2/N_2)$ had the same magnitude as that of case (c). We also found that the degree of zero enrichment varied quite slowly with time. Taking this into account, we corrected the $\delta(O_2/N_2)$ value of the sample air for the zero enrichment effect, by interpolating those of the working standard air obtained before and after each-day sample analyses.

2.3 Relationship between measured value of $\delta(O_2/N_2)$ and O_2/N_2 ratio

To measure the atmospheric O_2/N_2 ratio using our measurement system, it is important to examine the relationship between the measured value of $\delta(O_2/N_2)$ and the actual O_2/N_2 ratio. For this purpose, five O_2 - N_2 mixtures were prepared by employing a volumetric method with a precise pressure gauge, and then analyzed them. The mixing ratios of O_2 to

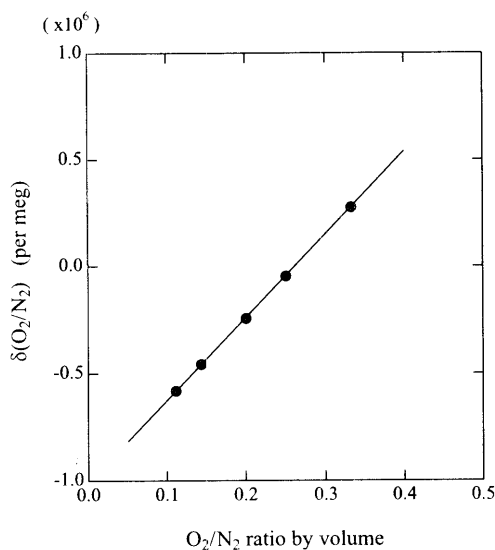


Fig. 2. Relationship between the measured value of $\delta(O_2/N_2)$ and the O_2/N_2 ratio for air sample. Closed circles represent experimental values, and solid line is a regression line obtained by applying a least-squares fit to the data.

N_2 were 0.33, 0.25, 0.2, 0.14 and 0.11, and their accuracy uncertainties were estimated to be less than 0.2%. The results are shown in Fig. 2. It was found that the relationship between the O_2/N_2 ratio and the $\delta(O_2/N_2)$ value can be approximated well with a linear equation, with a correlation coefficient of 0.99999. For further confirmation of the linear relationship, we calculated the change rates of $\delta(O_2/N_2)$ relative to the O_2/N_2 ratio from two successive data, and found no appreciable trend of the change rate against the O_2/N_2 ratio. In addition, given that the atmospheric O_2/N_2 ratios are around 0.26, we also examined the change rate of $\delta(O_2/N_2)$ relative to the O_2/N_2 ratio using the $\delta(O_2/N_2)$ data for the O_2/N_2 ratios of 0.33 and 0.25. From these two data, the change of $\delta(O_2/N_2)$ per unit O_2/N_2 ratio was found to be 3887768.4 per meg. On the other hand, by assuming that $\delta(O_2/N_2)$ of pure N_2 is -1.0×10^6 per meg, the change of $\delta(O_2/N_2)$ per unit O_2/N_2 ratio was calculated to be 3879123.9 and 3824520.8 per meg from the respective values of $\delta(O_2/N_2)$ for the O_2/N_2 ratios of 0.33 and 0.25. The discrepancies between the change rates of $\delta(O_2/N_2)$ relative to the O_2/N_2 ratio obtained by the former and lat-

ter methods were within 2%. This implies that uncertainties of $\delta(O_2/N_2)$ for samples with different values by 100.0 per meg are less than 2.0 per meg. From this experimental fact, we decided not to apply any correction regarding the non-linear effect of the detector response of the mass spectrometer to our measured values of $\delta(O_2/N_2)$.

2.4 Interference by CO with molecular mass of 29

When the sample air is introduced into the ion source of the mass spectrometer, CO_2 molecules involved are partly decomposed to generate CO. As mentioned above, we measure the molecular mass ratio of 32 ($^{16}O_2$) to 29 ($^{14}N^{15}N$) to obtain $\delta(O_2/N_2)$. Therefore, resultant ^{13}CO molecules with mass of 29 interfere with $^{14}N^{15}N$. If the CO_2 concentrations of the sample air and the reference air are different, the interference is given by the following equation under the assumption that the sensitivities of the mass spectrometer for CO and N_2 are assumed to be the same (Bender et al. 1994b):

$$I_{13CO}/I_{14N15N} = (\Delta CO_2/N_2) \times (^{13}C/^{12}C)/(^{14}N^{15}N/^{14}N_2) \times f, \quad (2)$$

where I_{13CO} and I_{14N15N} are the ion beam currents of ^{13}CO and $^{14}N^{15}N$, respectively, ΔCO_2 is the difference of the CO_2 concentration in ppmv between the sample air and the reference air, N_2 is the atmospheric N_2 concentration in ppmv (typically 780,840 ppmv), and the atmospheric $^{13}C/^{12}C$ and $^{14}N^{15}N/^{14}N_2$ are 0.0112 and 0.0074, respectively. The factor f denotes the ratio of the ion beam current of CO^+ to that of CO_2^+ when pure CO_2 is introduced into the mass spectrometer, which is slightly dependent on the ion source condition. In our case, $f = 0.095$. To confirm whether equation (2) is applicable to our mass spectrometer, we mixed two gases of pure CO_2 with $\delta^{13}C$ of -10.92 and -25.0% with purified and dried air in glass flasks, and then analyzed their CO_2 concentrations and the $\delta(O_2/N_2)$ values by using a gas chromatograph and the mass spectrometer, respectively. $\delta(O_2/N_2)$ and CO_2 concentration values obtained using CO_2 with $\delta^{13}C$ of -10.92% are plotted in Fig. 3. The results obtained for CO_2 with $\delta^{13}C$ of -25.0% are in agreement with those in Fig. 3. It is obvious that both factors are linearly related with each

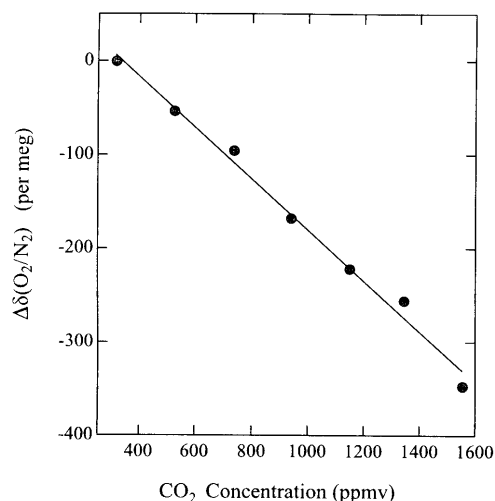


Fig. 3. Relationship between the CO₂ concentration of air sample and the decrease of its δ(O₂/N₂).

other. The best-fitted line to the data yielded a gradient of -0.3 per meg/ppmv, with a correlation coefficient of -0.9955 . As was expected, the sample air with higher CO₂ concentrations show lower values of δ(O₂/N₂) due to the apparent increase of ¹⁴N¹⁵N by ¹³CO. Therefore, the measured values of δ(O₂/N₂) were corrected for the interference of CO from CO₂ using this experimentally-determined relationship and the measured CO₂ concentration values.

As mentioned above, the experimental results showed that the relationship between δ(O₂/N₂) and the CO₂ concentration was independent of δ¹³C of CO₂, although some dependence can be expected from equation (2). The cause is attributable to its extremely small effect on δ(O₂/N₂); the difference between the respective values of I_{13CO}/I_{14N15N} calculated for δ¹³C of -25.0 and -10.92% is only 0.003×10^{-6} , so that a change in δ(O₂/N₂) for ΔCO₂ of 1000 ppmv is only 3.0 per meg. One could also consider correction for the interference of ¹⁴N¹⁸O with ¹⁶O₂. However, this effect is negligible, because N₂O concentrations of the sample background air and the reference air are almost identical with each other.

2.5 Pressure imbalance between sample air and reference air

The ion beam current of the mass spectrometer depends on the kind and pressure of gas to

be introduced, as well as on the ion source condition. Actually, we measured the ion beam current ratios of ¹⁶O₂/¹⁴N¹⁵N and ¹⁴N¹⁵N/¹⁴N₂ by changing the pressure of air introduced into the mass spectrometer. From this measurement, we found that the ratio of ¹⁴N¹⁵N/¹⁴N₂ was almost unchanged, while that of ¹⁶O₂/¹⁴N¹⁵N showed strong and non-linear dependence on the pressure. Therefore, for a precise determination of δ(O₂/N₂), it is necessary to equalize the pressure of the sample with that of the reference. In this regard, the detector output of ¹⁴N¹⁵N can be used as a good indicator of the pressure of air introduced into the mass spectrometer.

We also found experimentally that the measured value of δ(O₂/N₂) changed in proportional to the pressure difference between the sample and the reference, at least in a range of the detector output of ± 300 mV for ¹⁴N¹⁵N. Before obtaining this result, we made various tests to find the ion source condition suitable for measurements of δ(O₂/N₂). Consequently, we selected a condition for which the sensitivity of the ion beam current of ¹⁴N₂ was high, because the dependence of δ(O₂/N₂) on pressure difference was minimized and sufficient ion beam current was obtained for both N₂ and O₂. One example of the obtained relationships between the measured δ(O₂/N₂) value and the pressure imbalance is represented in Fig. 4. Both factors are clearly correlated linearly with each other. The change rate of δ(O₂/N₂) relative to the detector output was also observed to vary very slowly with time in a range of 0.5–2.5 per meg/mV. Even if we tried to equalize the pressures on both sides of the inlet system as strict as possible, the limitation was ± 5 mV in the detector output. Therefore, prior to each-day sample analyses, we measured δ(O₂/N₂) two or three times, varying the pressure difference between the sample and the reference, and corrected the measured δ(O₂/N₂) value of the sample air for the pressure difference using the obtained relationship. A typical correction was ± 3.0 per meg, hardly exceeding ± 8.0 per meg.

2.6 Deterioration of air sample during storage in flask and air sampling procedures

For precise determination of the atmospheric O₂/N₂ ratio, it is necessary to minimize the deterioration risk of the sampled air during their

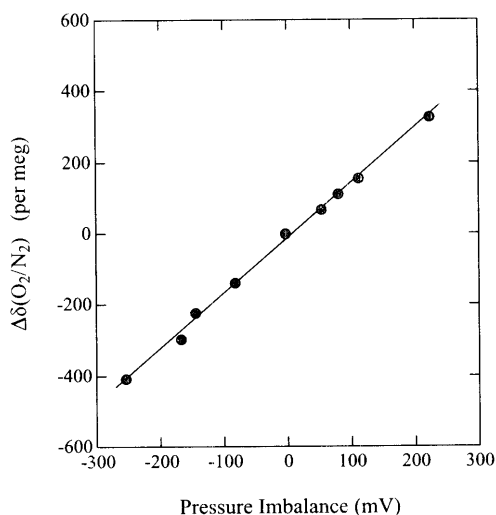


Fig. 4. Dependence of $\delta(\text{O}_2/\text{N}_2)$ on the pressure difference between the sample air and the reference air at their introduction into the mass spectrometer. The pressure difference is expressed as a detector output for $^{14}\text{N}^{15}\text{N}$.

storage in flasks. We examined this effect by filling our Pyrex glass flasks with stopvalves at both ends with purified natural air from a high pressure cylinder, and then analyzing for their $\delta(\text{O}_2/\text{N}_2)$ after storing for assigned time. The volume of each flask was 550 ml, and O-rings greased very thinly with Apiezon N were used for sealing the stopvalves. The results obtained using Viton and Nitrile as O-ring materials are shown in Fig. 5. The Viton O-ring flasks filled with air at atmospheric pressures showed that the $\delta(\text{O}_2/\text{N}_2)$ values were stable for at least over 185 days within our analytical precision. However, the pressurized flasks indicated gradual decrease of $\delta(\text{O}_2/\text{N}_2)$ with time until the value reached about -100.0 per meg after 220 days. On the other hand, the $\delta(\text{O}_2/\text{N}_2)$ values for the Nitrile O-ring flasks were less stable. In particular, the pressurized flasks showed remarkable steep decline of $\delta(\text{O}_2/\text{N}_2)$ with time, with a rate of -3.9 per meg/day.

The observed long-term decrease of $\delta(\text{O}_2/\text{N}_2)$ may be caused by selective absorption of O_2 on the inner walls of the flasks and O-rings, and/or differential escape of O_2 and N_2 through the O-rings. With regard to the last cause, we repeated the storage test, using Pyrex glass

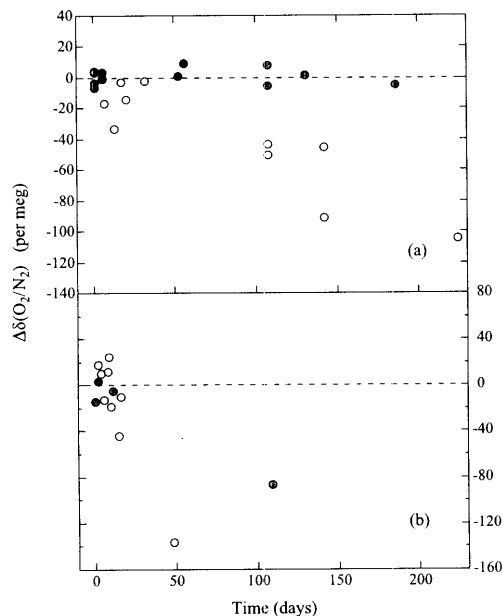


Fig. 5. Deterioration of sample air stored in Pyrex glass flasks with (a) Viton O-rings and (b) Nitrile O-rings. Closed and open circles represent the results for the flasks filled with air at atmospheric pressures and an over-pressure of 1.5×10^5 Pa, respectively.

flasks with double stopvalves with Viton O-rings at both ends in which air was filled to an over-pressure of 1.5×10^5 Pa. The results showed no appreciable decrease of $\delta(\text{O}_2/\text{N}_2)$ over 400 days. This suggests that O_2 escapes faster than N_2 in our flasks with a single stopvalve on each end.

We also examined the deterioration risk of sample air stored in all stainless-steel flasks. The volume of the flask was 1 L, and its inside was electrically polished and then washed by steam. These flasks were filled with air from a high pressure cylinder at various pressures, from atmospheric to a pressure of 2.5×10^6 Pa, and then analyzed their $\delta(\text{O}_2/\text{N}_2)$ values using the same procedure as above. In contrast to Pyrex glass flasks, stainless-steel flasks with air at atmospheric pressures showed that the $\delta(\text{O}_2/\text{N}_2)$ value decreased almost linearly with time, until the value reached about -300.0 per meg after 450 days. The pressurized flasks also showed an obvious decreasing trend of $\delta(\text{O}_2/\text{N}_2)$, but the decrease after 450 days was about

120.0 per meg, which is less than half that of flasks filled with air at atmospheric pressures. These decreasing trends are probably due to O₂ consumption by oxidation of residual organic material, oxidation of the inner wall of the flasks, and selective O₂ adsorption on the inside surface of the flasks. In this examination, we found that one of the stainless-steel flasks showed an appreciable increase of $\delta(\text{O}_2/\text{N}_2)$ and $\delta^{15}\text{N}$ with time, if the air was pressurized. A similar phenomenon was also found by Langenfelds et al. (1999a) for archive air at Cape Grim, Australia. The cause may be attributable to selective escape of N₂ from the pressurized flask due to leakage of the stopvalve. In this regard, it is known that molecular diffusion through very narrow space occurs in inverse proportion to the square root of the mass (Moore 1962). The $\delta(\text{O}_2/\text{N}_2)$ values corrected by applying this theoretical basis to the measured values indicated almost the same temporal decreasing trend as other flasks did, except for the data with remarkable upward shifts of $\delta(\text{O}_2/\text{N}_2)$ and $\delta^{15}\text{N}$.

In the light of these results, we decided to usually collect air samples in the 550 ml Pyrex glass flasks with Viton O-rings at atmospheric pressures. Our flasks are smaller than 5, 2 and 1 L glass flasks employed by Keeling (1998a), Bender et al. (1996) and Tohjima (2000), respectively but comparable to the 0.5 L glass flasks used by Langenfeld et al. (1996). Keeling (1998a), Bender et al. (1996) and Langenfeld et al. (1996) also collected air samples in the flasks at atmospheric pressures, but Tohjima (2000) pressurized samples to 2.5×10^5 Pa.

In addition to the deterioration of air samples during their storage in the flasks, we also examined air sampling procedures. To collect air samples in two different glass flasks for measurements of $\delta(\text{O}_2/\text{N}_2)$ and CO₂ concentration, we arranged a sample intake, a diaphragm pump with a flow rate controller and a water vapor trap cooled to -78.0°C in that order, and then separated the sample line into two, each connected to a flask. The air samples were collected by closing the inlet of the flask first, and then the outlet, for the $\delta(\text{O}_2/\text{N}_2)$ analysis, and subsequently by closing the stopvalves of the other flask in reverse order to pressurize the air for the CO₂ concentration analysis. We also made another sampling ap-

paratus, in which the two flasks were arranged in series, the flask for CO₂ first and then that for $\delta(\text{O}_2/\text{N}_2)$. In this arrangement, the air samples were pressurized into the former flask and collected in the latter at atmospheric pressures, by closing the stopvalve between the two flasks. By operating these two sampling apparatuses simultaneously, the air samples were collected from the same place, and their $\delta(\text{O}_2/\text{N}_2)$ values were compared to each other. We repeated this test 23 times, and found that the former sampling apparatus yielded values lower by 24.0 per meg, on average, than the latter apparatus. Considering this experimental result, we decided to arrange two flasks in series to collect air samples for $\delta(\text{O}_2/\text{N}_2)$ and CO₂ concentration analyses.

We also examined the influence of water vapor contained in sample air on $\delta(\text{O}_2/\text{N}_2)$, by comparing the results obtained from air samples with and without drying. As a result, it was found that the $\delta(\text{O}_2/\text{N}_2)$ values of wet samples were lower than those of dry samples, while simultaneously analyzed $\delta^{15}\text{N}$ showed an opposite trend. This phenomenon is attributable to the process that water vapor included in the air sample is decomposed into H⁺ and OH⁻ in the ion source of the mass spectrometer, and the bonding of resultant H⁺ with ¹⁴N¹⁴N (28) produces ¹⁴N¹⁴NH⁺ (29). By this process, the ion beam current of mass 28 decreases and that of mass 29 increases, which leads to higher values of $\delta^{15}\text{N}$ and lower values of $\delta(\text{O}_2/\text{N}_2)$. In the light of these results, our air samples were usually dried. However, in cases in which the air sample could not be dried, we corrected their measured values of $\delta(\text{O}_2/\text{N}_2)$ using the relationship between $\delta(\text{O}_2/\text{N}_2)$ and $\delta^{15}\text{N}$ determined experimentally from wet samples, which shows a change of 0.38 per meg in $\delta(\text{O}_2/\text{N}_2)$ against that of 1.0 per meg in $\delta^{15}\text{N}$. For example, the maximum corrections amounted to 360 and 30 per meg for the air samples collected at the ground surface in Sendai, Japan in summer and winter, respectively. However, no correction was needed for the air samples collected at heights higher than 2 km in winter and 8 km throughout the year.

2.7 Standard air

Since the mass spectrometer analysis is a relative measurement method, stable standard

Table 1. Standard air used for measurements of atmospheric $\delta(O_2/N_2)$.

Cylinder No.	Filling	$\delta(O_2/N_2)$ (per meg)	CO ₂ (ppmv)
PLM37172	98. 11. 16	0.0	355.01
PLM37171	99. 02. 05	348.0	545.39
CQB08442	98. 10. 24	679.4	300.90
CQB06531	98. 09. 12	-107.4	335.23
CQB08443	00. 04. 13	412.4	326.16
CQB09379	00. 05. 01	120.0	360.36

air with known $\delta(O_2/N_2)$ values are required to determine the $\delta(O_2/N_2)$ values of sample air. We can easily obtain a large amount of purified air from gas companies. However, we found that such industrially prepared air are not suitable for standard air of atmospheric $\delta(O_2/N_2)$ measurements, because their $\delta(O_2/N_2)$ values are significantly lower by 2500–4500 per meg than the atmospheric values. Therefore, we took natural air from the roof of our laboratory building and filled 47 L high pressure cylinders at about 1.0×10^7 Pa after drying by using Molecular Sieve 4A. As shown in Table 1, 6 standard air with dew points of -63°C to -77°C have been prepared so far. PLM37172 and PLM37171 are manganese steel cylinders and others are aluminum cylinders. Their CO₂ concentrations were somewhat different; 5 standards showed concentration values from 300.9 to 360.4 ppmv mainly due to different CO₂ absorption by Molecular Sieve, while a very high concentration value of 545.4 ppmv was found for PLM37171 probably due to CO₂ desorption from Molecular Sieve. We arbitrarily selected PLM37172 as our primary standard, and all the $\delta(O_2/N_2)$ values of the sample air are expressed as deviation from this standard. Other standard air was used as working standards. It is crucial for long-term measurements of $\delta(O_2/N_2)$ to maintain self-consistency in the data. Therefore, we have repeatedly compared PLM37172 with the remaining 5 standards to confirm the stability of their $\delta(O_2/N_2)$ values. As seen from Fig. 6, almost all cylinders showed that their $\delta(O_2/N_2)$ values were stable to within 20.0 per meg over the last 2 years, but the values of PLM37171 somewhat exceeded that range. We also found from this comparison that the $\delta(O_2/N_2)$ values depend slightly on whether the cylinder is laying down or standing up on the floor, the differences being about 20.0–30.0 per meg. Keel-

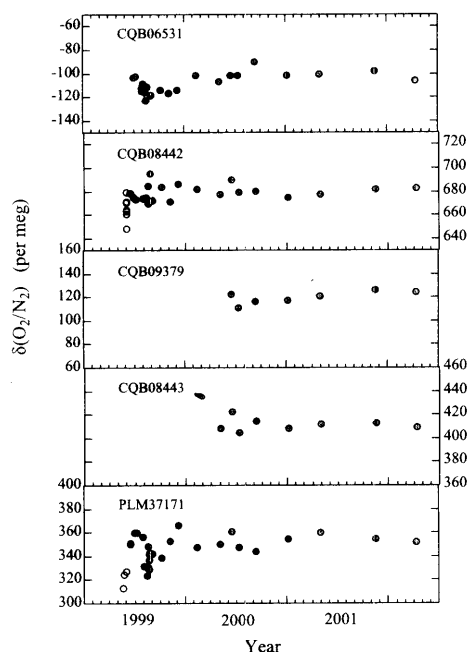


Fig. 6. $\delta(O_2/N_2)$ of 5 standard air determined against the primary standard air. Open and closed circles represent the results obtained when the cylinders are standing up and laying down on the floor, respectively.

ing et al. (1998a) also found an upward shift of 5.0–10.0 per meg in O_2/N_2 by relocating their standard cylinders from a vertical to a horizontal position. They ascribed its plausible cause to thermal diffusion in the cylinders, rather than to gravimetric fractionation, because a time on the order of 1 year is required to achieve a barometrically equilibrium gradient of the O_2/N_2 ratio between the top and the bottom of a high pressure cylinder. If we assume the temperature difference of 0.5°C between the top and the bottom of our standing-up cylinders, it can be expected from the above-mentioned equation (section 2.2) that

the gradient of 30.0 per meg is produced by the thermal diffusion effect.

2.8 Measurement precision

To estimate our measurement precision, we repeatedly filled flasks with air from a high pressure cylinder and then determined their $\delta(O_2/N_2)$ values. The total number of flask samples amounted to 278. As mentioned above, we usually introduced the sample air into the inlet system twice and a series of 10 analyses was repeated twice for each sample, and then the respective results were simply averaged to obtain its $\delta(O_2/N_2)$ value. From these flask sample analyses, it was found that the internal precision of our mass spectrometer, defined by standard error of each measurement with 10 alternate analyses, ranged between 2.0 and 6.0 per meg. The reproducibility of duplicate determinations of $\delta(O_2/N_2)$ with our mass spectrometer was also estimated on the basis of the difference between the first and the second determinations for each flask sample. From the analytical results of 278 samples, we derived 5.3 per meg for one standard deviation of their differences. With respect to the external precision of our mass spectrometer (reproducibility of $\delta(O_2/N_2)$ determined by repeatedly introducing the same air sample into the mass spectrometer), we calculated an average of the $\delta(O_2/N_2)$ values of several flasks filled at a time with air from a cylinder and then derived the differences of the respective values from it. The differences thus obtained for all flask samples of 278 are shown in Fig. 7. Our external precision, defined by one standard deviation of the respective differences, was estimated to be 5.4 per meg, which is equivalent to 1.1 ppmv of the atmospheric O_2 concentration. This precision corresponds to approximately 1/3 the currently observed decreasing rate of $\delta(O_2/N_2)$ in the atmosphere (e.g. Keeling and Shertz 1992; Bender et al. 1996; Battle et al. 2000), and it is somewhat worse than 1.0–4.0 per meg of Bender et al. (1996), Keeling et al. (1998a) and Manning et al. (1999), but better than 7.0–10.0 per meg of Langenfelds et al. (1999a) and Tohjima (2000).

3. Preliminary observational results of the atmospheric O_2/N_2 ratio

Using our newly developed system, we started systematic measurements of the tropo-

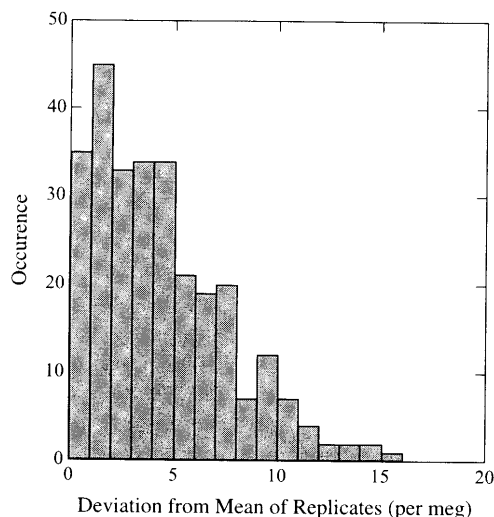


Fig. 7. Distribution of $\delta(O_2/N_2)$ obtained by repeating the analysis of the same air. The values are expressed as deviation from their mean, and a total number of data is 278.

spheric and stratospheric O_2/N_2 ratios at various places in May 1999. As an example of the measurement results, $\delta(O_2/N_2)$ values observed on the roof of our 40 m high laboratory building are shown in Fig. 8, together with the CO_2 concentrations. The building is located on the top of a hill (150 m above sea level) in the suburbs of Sendai, Japan (38°N, 140°E), and its surrounding area is covered mainly by deciduous shrubs. Since the urban area of Sendai is located to the east of the sampling site, the collection of air samples was made only during the condition of westerly winds. Each air sample was taken from an air intake situated on the west side of the building by using a diaphragm pump. Each glass flask was filled at atmospheric pressures after removing water vapor by a cold trap at $-78.0^\circ C$. After sampling, the flasks were placed in our laboratory room, and then analyzed for the CO_2 concentration and $\delta(O_2/N_2)$ within a few days. The CO_2 concentration was determined against our air-based CO_2 standard gas system using a non-dispersive infrared analyzer, with a precision of better than ± 0.05 ppmv (Tanaka et al. 1983).

As seen from Fig. 8, both the CO_2 concentration and $\delta(O_2/N_2)$ data show clear evidence of a seasonal cycle and a secular trend. To separate

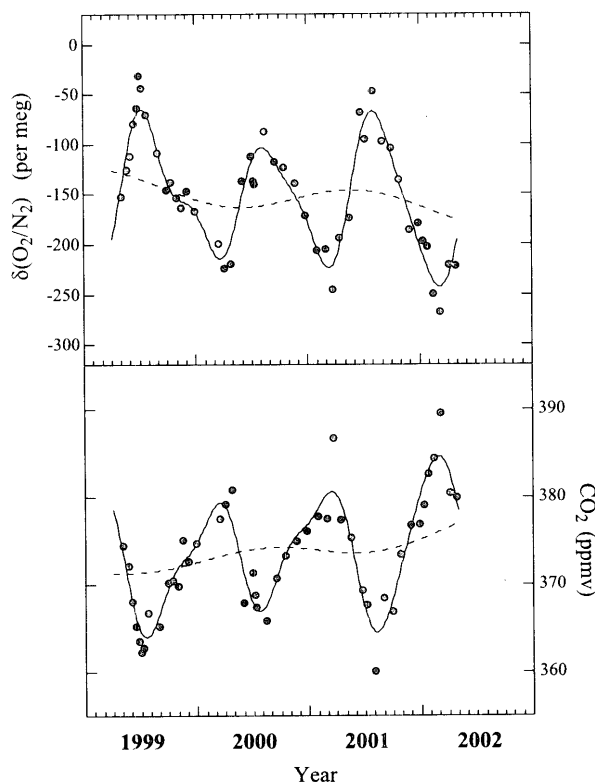


Fig. 8. Observational results of $\delta(O_2/N_2)$ and CO_2 concentration in the suburbs of Sendai, Japan.

these two factors, we applied our digital filtering technique to the data (Nakazawa et al. 1997a). In this technique, we approximated the seasonal cycle by two harmonics with 12 and 6 months cycles, and regarded the signal with period of over 21 months as secular trend. Average seasonal cycle of $\delta(O_2/N_2)$ reached a minimum in late March or early April, and a maximum in late July or early August, while the CO_2 concentration varied seasonally in opposite phase with $\delta(O_2/N_2)$. A similar seasonal cycle was also observed by other measurements in the northern hemisphere (Keeling and Shertz 1992; Keeling et al. 1996; Battle et al. 2000; Tohjima 2000). Peak-to-peak amplitude was about 150.0 per meg for $\delta(O_2/N_2)$ and about 15.0 ppmv for the CO_2 concentration. In the northern hemisphere, the seasonal CO_2 cycle is produced mainly by the CO_2 exchange between the atmosphere and the terrestrial biosphere through photosynthesis and respiration (Nakazawa et al. 1993, 1997b). However, the rela-

tionship between $\delta(O_2/N_2)$ and the CO_2 concentration was found to be approximated by a linear line with a change rate of -8.3 per meg/ppmv, showing the correlation coefficient of -0.95 . This change rate is larger than -5.3 per meg/ppmv expected from the terrestrial biospheric activities (Severinghaus 1995). The cause of the discrepancy could be ascribed to the different roles of the ocean in the O_2 and CO_2 cycles (Keeling and Shertz 1992). The exchange of CO_2 between the atmosphere and the ocean is highly suppressed due to the carbonate dissociation effect in the ocean, and a few years or so is required to equilibrate both carbon reservoirs with respect to CO_2 . On the other hand, the imbalance of O_2 partial pressure between the atmosphere and the ocean is dissolved in a few weeks, due to its rapid exchange according to Henry's law. Therefore, the observed seasonal cycle of $\delta(O_2/N_2)$ is thought to be affected by the O_2 exchange between the atmosphere and the ocean, in addition to the effect of the terrestrial biospheric O_2 flux.

Keeling et al. (1998b) defined the oceanic component of $\delta(O_2/N_2)$ by

$$\delta(O_2/N_2)_{oc} = \delta(O_2/N_2) + (1.1/0.2095)[CO_2], \quad (3)$$

where the factor of 1.1 is the O_2 - CO_2 exchange rate for terrestrial biospheric activities, the factor of 0.2095 is the atmospheric O_2 mole fraction, and $[CO_2]$ is the observed CO_2 concentration. The $\delta(O_2/N_2)_{oc}$ values, obtained by applying this equation to the detrended observational data, are shown in Fig. 9, together with their best fit curve consisting of the fundamental and its first harmonics. The peak-to-peak amplitude of $\delta(O_2/N_2)_{oc}$ was 65.0 per meg, and its maximum and minimum values appeared in July and March, respectively. The seasonal variation of $\delta(O_2/N_2)_{oc}$ is generally in phase with that of sea surface temperature in the Pacific Ocean off Sendai (IRI Climate Information System, <http://iri.columbia.edu/climate/>), but the appearance time of the maximum $\delta(O_2/N_2)_{oc}$ value preceded by about 1 month. Keeling et al. (1993) ascribed the seasonal $\delta(O_2/N_2)_{oc}$ cycle to marine biospheric activities and thermally driven air-sea gas exchanges, and they estimated the contribution of the thermal effect at $33^\circ N$ and $58^\circ N$ to be 9 per meg_{peak-to-peak}. Taking this into account, the

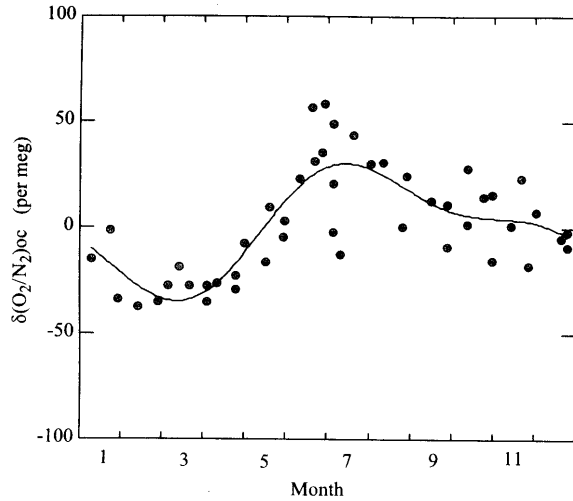


Fig. 9. Oceanic seasonal component of atmospheric $\delta(O_2/N_2)_{oc}$ in the suburbs of Sendai, Japan. Closed circles represent measured values, and solid line shows the best fit curve to the data.

seasonal $\delta(O_2/N_2)_{oc}$ cycle observed at our site could be caused mainly by marine biospheric activities which show a good correlation with variations of sea surface temperature.

It is also seen in Fig. 8 that $\delta(O_2/N_2)$ decreases secularly, in contrast to the CO_2 concentration. This suggests that a major cause of the CO_2 increase is due to fossil fuel burning and/or deforestation. An average increase rate over the period covered by this study was found to be -16.3 per meg/year for $\delta(O_2/N_2)$ and 1.9 ppmv/year for the CO_2 concentration. Assuming that the secular trends of CO_2 and $\delta(O_2/N_2)$ observed in this study are representative of their global changes, we made an estimation of the terrestrial biospheric and oceanic CO_2 fluxes from our observational data, based on an analytical method used initially by Keeling and Shertz (1992), followed by Keeling et al. (1996), Bender et al. (1994a, 1996), Battle et al. (1996, 2000) and Langenfelds et al. (1999b). The mass balances of CO_2 and O_2 in the atmosphere can be written as

$$d(CO_2)/dt = 0.471 \times (f_{fuel} + f_{cement} + f_{land} + f_{ocean}), \quad (4)$$

$$d(O_2/N_2)/dt = -4.8 \times 0.471 \times (1.43f_{fuel} + 1.1f_{land}), \quad (5)$$

where f_{fuel} , f_{cement} , f_{land} and f_{ocean} are carbon fluxes (in GtC/year) into the atmosphere due to fossil fuel combustion, cement manufacturing, the terrestrial biosphere and the ocean, respectively. The respective coefficients of 1.43, 1.1, 0.471 and 4.8 are the O_2 consumption rate by CO_2 generation for today's fossil fuel (Keeling 1988), the O_2 - CO_2 exchange rate by the terrestrial biosphere (Severinghaus 1995), the conversion factors from GtC to ppmv and from ppmv to per meg. By substituting our observational results of the $\delta(O_2/N_2)$ and CO_2 concentration trends into these equations, we found that the average net uptake of CO_2 by the terrestrial biosphere and the oceans over the period March 1999–March 2002 were 1.9 and 0.8 GtC/year, respectively. In this analysis, we assumed that f_{fuel} and f_{cement} can be given by average values over our observation period, which were derived by linearly extrapolating yearly carbon emissions from fossil fuel consumption and cement manufacture for the period 1990–1998 (Carbon Dioxide Information Analysis Center, <http://cdiac.esd.ornl.gov/>). If the statistical values for 1998 were employed for f_{fuel} and f_{cement} , we obtained 1.7 and 0.8 GtC/year for terrestrial biospheric and oceanic CO_2 uptake, respectively. On the other hand, Battle et al. (2000) found that the terrestrial biosphere and the oceans absorbed 1.4 ± 0.8 and 2.0 ± 0.6 GtC/year, respectively, on average during May 1991–May 1997. The difference between our budget estimates and those of Battle et al. (2000) is probably due to the fact that (1) the periods covered by the two measurements are different, (2) our sampling site is affected to some extent by local anthropogenic and biospheric effects and (3) our data records of $\delta(O_2/N_2)$ and CO_2 are rather short.

4. Concluding remarks

We developed a precise measurement system for the atmospheric O_2/N_2 ratio using a mass spectrometry method. The air inlet system was designed symmetrically for sample air and reference air, and each side was equipped with a pressure adjustor to equalize the pressures of the sample air and the reference air as strictly as possible. The inlet system and a changeover valve of the mass spectrometer were connected by 1.35 m long fused silica capillaries with an inner diameter of 25 μm , so that not only the

ion beam currents of molecular masses 32 (O_2) and 29 (N_2) were suitably measurable when the sample air and the reference air were introduced into the mass spectrometer at atmospheric pressures, but also air flow passing through capillaries was kept viscous. To minimize the effect of temperature fluctuation on $\delta(O_2/N_2)$, the fused silica capillaries were insulated using two kinds of Teflon tubes with different diameters, and the measurement system was set in an air-conditioned room.

To reduce changes in the O_2/N_2 ratio occurring during the introduction of air into the mass spectrometer, stopvalves of the air inlet system were operated at least at 30-second intervals. The relationship between $\delta(O_2/N_2)$ and the O_2/N_2 ratio was experimentally confirmed to be linear, which meant that no correction was needed to apply to our measured values of $\delta(O_2/N_2)$ to express atmospheric O_2/N_2 ratios. To examine the interference by CO with molecular mass of 29 generated in the ion source from CO_2 in the sample air, we analyzed air- CO_2 mixtures with the same O_2/N_2 ratio but different CO_2 concentrations. A linear relationship between the measured value of $\delta(O_2/N_2)$ and the CO_2 concentration, thus obtained, was used to correct the measured $\delta(O_2/N_2)$ values of sample air. $\delta(O_2/N_2)$ biased due to the pressure difference between the sample air and the reference air at their introduction into the mass spectrometer was corrected by using a relationship determined experimentally prior to sample analyses, the typical correction being ± 3.0 per meg. We also found that air samples filled in Pyrex glass flasks with Viton O-rings at atmospheric pressures showed stable $\delta(O_2/N_2)$ over a long time. Our standard air was prepared by drying the atmospheric air through Molecular Sieve 4A. It was then pumped into 47 L high-pressure cylinders at 1.0×10^7 Pa. Their $\delta(O_2/N_2)$ values were confirmed to be stable by comparing with each other. The precision of our $\delta(O_2/N_2)$ measurement system was estimated to be 5.4 per meg by repeating the analysis of the same air.

Preliminary results of atmospheric $\delta(O_2/N_2)$ values measured using the newly developed system in Sendai, Japan indicated clear evidence for a seasonal cycle and a secular decrease. It is suggested that the CO_2 exchange not only between the terrestrial biosphere and

the atmosphere, but also between the ocean and the atmosphere played an important role in the observed seasonal O_2 cycle. The secular decrease in $\delta(O_2/N_2)$ was attributed mainly to the consumption of O_2 by fossil fuel burning, and by applying our observational results to global carbon and oxygen budgets, it was suggested that both the terrestrial biosphere and the oceans absorbed CO_2 from the atmosphere during the period covered by this measurement.

In order to contribute to a better understanding of the global carbon cycle, we will carry out $\delta(O_2/N_2)$ measurements over a geographically wide area for a long time, using our new system to analyze samples collected from aircraft, scientific balloons, ships and ground-based stations.

Acknowledgements

We are very grateful to Prof. Michael Bender, Princeton University for his valuable advice on our O_2 measurement system.

References

- Battle, M., M. Bender, T. Sowers, P.P. Tans, J.H. Butler, J.W. Elkins, J.T. Ellis, T. Conway, N. Zhang, P. Lang, and A.D. Clarke, 1996: Atmospheric gas concentrations over the past century measured in air from firn at the South Pole. *Nature*, **383**, 231–235.
- , M.L. Bender, P.P. Tans, J.W.C. White, J.T. Ellis, T. Conway, and R.J. Francey, 2000: Global carbon sinks and their variability inferred from atmospheric O_2 and $\delta^{13}C$. *Science*, **287**, 2467–2470.
- Bender, M.L., T. Sowers, J.M. Barnola, and J. Chappellaz, 1994a: Changes in the O_2/N_2 ratio of the atmosphere during recent decades reflected in the composition of air in the firn at Vostok Station, Antarctica. *Geophys. Res. Lett.*, **21**, 189–192.
- , P.P. Tans, J.T. Ellis, J. Orchard, and K. Habfast, 1994b: High precision isotope ratio mass spectrometry method for measuring the O_2/N_2 ratio of air. *Geochim. Cosmochim. Acta*, **58**, 4751–4758.
- , J.T. Ellis, P. Tans, R. Francey, and D.C. Lowe, 1996: Variability in the O_2/N_2 ratio of southern hemisphere air 1991–1994: Implication for the carbon cycle. *Glob. Biogeochem. Cycles*, **10**, 9–21.
- Dushuman, S., 1949: *Scientific foundations of vacuum technique*, John Wiley and Sons, Inc., New York.

- Grew, K.E. and L.T. Ibbs, 1952: *Thermal diffusion in gases*, 143 pp., Cambridge Univ. Press, New York.
- Keeling, R.F., 1988: Development of an interferometric oxygen analyzer for precise measurement of the atmospheric O₂ mole fraction, Ph.D. thesis, Harvard University, Cambridge.
- and S.R. Shertz, 1992: Seasonal and inter-annual variations in atmospheric oxygen and implications for the global carbon cycle. *Nature*, **358**, 723–727.
- , R.G. Najjar, M.L. Bender, and P.P. Tans, 1993: What atmospheric oxygen measurements can tell us about the global carbon cycle, *Global Biogeochem. Cycles*, **7**, 37–67.
- , S.C. Piper, and M. Heimann, 1996: Global and hemispheric CO₂ sinks deduced from changes in atmospheric O₂ concentration. *Nature*, **381**, 218–221.
- , A.C. Manning, E.M. McEvoy, and S.R. Shertz, 1998a: Methods for measuring changes in atmospheric O₂ concentration and their application in southern hemisphere air. *J. Geophys. Res.*, **103**, 3381–3397.
- , B.B. Stephens, R.G. Najjar, S.C. Doney, D. Archer, and M. Heimann, 1998b: Seasonal variations in the atmospheric O₂/N₂ ratio in relation to the kinetics of air-sea gas exchange. *Glob. Biogeochem. Cycles*, **12**, 141–163.
- Langenfelds, R.L., R. Francey, L.P. Steele, R.F. Keeling, M. Bender, M. Battle, and W.F. Budd, 1999a: Measurements of O₂/N₂ ratio from the Cape Grim air archive and three independent flask sampling program, *Baseline atmospheric program (Australia) 1996*, 57–70.
- , R.J. Francey, L.P. Steele, M. Battle, R.F. Keeling, and W.F. Budd, 1999b: Partitioning of the global fossil CO₂ sink using a 19-year trend in atmospheric O₂. *Geophys. Res. Lett.*, **26**, 1897–1900.
- Lueker, T.J., R.F. Keeling, and M.K. Dubey, 2001: The oxygen to carbon dioxide ratios observed in emissions from a wildfire in northern California. *Geophys. Res. Lett.*, **28**, 2413–2416.
- Manning, A.C. and R.F. Keeling, 1999: Precise atmospheric oxygen measurements with a paramagnetic oxygen analyzer. *Glob. Biogeochem. Cycles*, **13**, 1107–1115.
- Nakazawa, T., S. Morimoto, S. Aoki and M. Tanaka, 1993: Time and space variations of the carbon isotopic ratio of tropospheric carbon dioxide over Japan. *Tellus*, **45B**, 258–274.
- , M. Ishizawa, K. Higuchi, and N.B.A. Trivett, 1997a: Two curve fitting methods applied to CO₂ flask data. *Environmetrics*, **8**, 197–218.
- , S. Morimoto, S. Aoki, and M. Tanaka, 1997b: Temporal and spatial variations of the carbon isotopic ratio of atmospheric carbon dioxide in the western Pacific region. *J. Geophys. Res.*, **102**, 1271–1285.
- Severinghaus, J.P., 1995: Studies of the terrestrial O₂ and carbon cycles in sand dune gases and in Biosphere 2, Ph.D. thesis, Columbia University, New York.
- Tanaka, M., T. Nakazawa, and S. Aoki, 1983: High quality measurements of the concentration of atmospheric carbon dioxide. *J. Meteorol. Soc. Japan*, **61**, 249–256.
- Tohjima, Y., 2000: Method for measuring changes in the atmospheric O₂/N₂ ratio by a gas chromatograph equipped with a thermal conductivity detector. *J. Geophys. Res.*, **105**, 14575–14584.