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Carbon and oxygen isotopic ratios of carbon dioxide of a stratospheric profile over Japan

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ABSTRACT

Four stratospheric air samples from 19 to 25 km altitudes over Japan were collected by using a balloon-borne cryogenic sampling system to measure the vertical profiles of carbon and oxygen stable isotopic ratios of the lower stratospheric CO_2.

The $\delta^{13}C$ value of the stratospheric CO_2 increased with increasing altitude, while the CO_2 mixing ratios decreased, in accordance with anthropogenic input of the isotopically light, fuel CO_2 into the atmosphere. However, the relationship between $\delta^{13}C$ and CO_2 mixing ratio ($-0.07‰$ ppmv^{-1}) was somehow similar to that for the seasonal variation in the troposphere rather than that for the secular variation so far observed in the troposphere ($-0.02 \sim -0.03‰$ ppmv^{-1}).

The $\delta^{18}O$ of the stratospheric CO_2 was found to be about 2‰ greater than that of the tropospheric CO_2 at an altitude of 19 km and to increase further with increasing altitude. Two possibilities for explaining this phenomenon are presented and discussed. One possibility is that the tropical CO_2 with high $\delta^{18}O$ might upwell and advect horizontally to the mid-latitudinal stratosphere, although the $\delta^{18}O$ enhancement by this process is insufficient to raise the $\delta^{18}O$ value up to the observed level. The other is that the ^{18}O might be enriched by an in-situ oxygen isotope exchange between CO_2 and O_2, which is possibly accelerated through photochemical dissociations of O_2 and CO_2. A relationship between $\delta^{18}O$ of CO_2 and ^{18}O enrichment of ozone in the stratosphere is also suggested.

1. Introduction

It has been well documented that the addition of anthropogenic carbon dioxide to the atmosphere has not only increased the mixing ratio but also decreased the $\delta^{13}C$ of CO_2 in the troposphere (Keeling et al., 1979; Mook et al., 1983; Keeling et al., 1984; Friedli et al., 1987). Bischof et al. (1985) also reported a temporal CO_2 increase in the stratosphere up to 35 km altitude. It is expected that the $\delta^{13}C$ of the stratospheric CO_2 concomitantly decreases.

In order to confirm this, we collected stratospheric air samples and measured the CO_2 mixing ratio and its $\delta^{13}C$. The $\delta^{18}O$ of stratospheric CO_2 was simultaneously measured. Although the $\delta^{18}O$ of stratospheric CO_2 had previously been measured by Hagemann et al. (1965), the reliability of the data was questioned by Craig and Begemann (1970) because of the imperfection of the sampling and storing methods. The present study paid much attention to the evacuation of sampling tubes and checked the storage effect of the sampling tubes as described below.

2. Experimental

A balloon-borne cryogenic sampling system of the Institute of Space and Astronautical Science (ISAS) was employed for collecting stratospheric

air samples. A detailed description of the system will be published elsewhere by Itoh et al. Briefly, the system used liquid helium as a refrigerant to condense air samples of 3-8 l STP in 6 stainless steel (270–280 cm^3) tubes (nos. 1, 2, 3, 4, 5 and 7). The tubes were all evacuated for more than 24 h at a temperature of 250°C under vacuum of 10^{-7} torr by using a turbo molecular pump, and subsequently evacuated for about 1 week at room temperature under vacuum of less than 10^{-8} torr just before their use.

The sampling system was flown and recovered at ISAS Sanriku Balloon Center (39°N, 142°E), on 3 September 1985. Although 2 samples (nos. 1 and 2) were lost after the recovery due to the destruction of rupture disks, 4 samples were successfully obtained at the altitudes of 25, 23, 21 and 19 km (sampler nos. 3, 4, 5, and 7, respectively). The tropopause was 15.5 km altitude on the sampling day.

Upon recovery, a few percent of each sample was aliquoted for the analysis of freons, methane etc. by H. Makide and K. Tominaga of the Department of Chemistry, University of Tokyo (the results are not reported here). Then, the remaining samples were sent to the Upper Atmosphere and Space Research Laboratory of Tohoku University, and CO_2 mixing ratios were measured with a non-dispersive infrared gas analyzer: NDIR (Tanaka et al., 1983a, b). The NDIR was calibrated by using the air-based CO_2 standard gases; the overall precision of CO_2 analyses was within ± 0.1 ppmv (Tanaka et al., 1987a, c).

After the CO_2 measurements, CO_2 gases were extracted cryogenically from the remaining samples (about 2 l STP) and sent to the Ocean Research Institute, University of Tokyo, for the stable isotope analyses. The $\delta^{13}C$ (relative to PDB) and $\delta^{18}O$ (relative to SMOW) were measured with a triple collector mass spectrometer (Finnigan MAT 250). For the calculation of $\delta^{18}O$, we employed the fractionation factor between CO_2 and water at 25°C of 1.04115 (O'Neil et al., 1975; Brenninkmeijer et al., 1983). For both δ values, replicate analyses of the same sample showed a reproducibility of less than 0.02‰; the overall precision is estimated to be 0.1‰.

Tropospheric air samples over Japan in August and September, 1985, were also analyzed for comparisons. They were taken aboard domestic jetplanes, with no contamination due to engine exhaust (Tanaka et al., 1983a, b). The analytical methods were the same as those for the stratospheric samples.

In order to remove the N_2O effect on $\delta^{13}C$ and $\delta^{18}O$ data (Craig and Keeling, 1963), N_2O content in the CO_2 samples was measured by gas chromatography (Gamo and Horibe,1985) and the $\delta^{13}C$ and $\delta^{18}O$ values were empirically corrected according to Sakai et al. (1982). The corrections for the tropospheric samples are $+0.25$‰ and $+0.36$‰ for $\delta^{13}C$ and $\delta^{18}O$, respectively. These values are almost the same as $+0.23$‰ and $+0.33$‰ reported by Mook and Van der Hoek (1983) and Mook and Jongsma (1987). The correction for the stratospheric data depended on each sampling altitude because the N_2O content decreases with altitude in the stratosphere.

3. Results and discussion

3.1. Storage effects of the sampling tubes

As pointed out by Craig and Begemann (1970), there is a fear that remaining water or other contaminants in air samplers gives incorrect isotope data, because isotope fractionation of CO_2 could occur during the sample storage. We checked the storage effect of our sampling tubes as follows. Immediately after the analyses of the stratospheric samples, the sampling tubes (nos. 3, 4, 5 and 7) were evacuated in the same way as before, and then charged at a pressure of about 17 kg cm^{-2} with the air-based standard CO_2 gas (for which the CO_2 mixing ratio, $\delta^{13}C$ and $\delta^{18}O$ were known, see Table 1). The storage pressures of the stratospheric samples were 11–27 kg cm^{-2}. The tubes were allowed to stand for 50 days (the stratospheric samples were also stored for 50 days before analyses) and the CO_2 gases were analyzed in the same way as for the samples.

Table 1 shows values of CO_2, $\delta^{13}C$ and $\delta^{18}O$ measured after the storage period. It was confirmed that the CO_2 mixing ratio and $\delta^{13}C$ values remain constant during the storage, within ± 0.1 ppm and ± 0.03‰, respectively. On the other hand, the $\delta^{18}O$ value increased by 0.8‰, probably due to the oxygen isotope exchange between CO_2 and the water vapor in the tubes.

Table 1. *Results of air storing test (50 days) for the stainless steel tubes used for stratospheric air samplings*

Sample tube no.	CO_2 (ppm)	$\delta^{13}C$ (‰)	$\delta^{18}O$ (‰)
3	337.22	−30.10	11.10
4	336.94	−30.14	10.89
5	337.17	−30.14	10.82
7	336.95	−30.14	10.86
(average value:	337.07	−30.13	10.92)

The stored air is dried (dew point: −73°C), air-based CO_2 standard gas, whose initial CO_2, $\delta^{13}C$, and $\delta^{18}O$ values are 337.06 ppm, −30.11‰, and 10.10‰, respectively.

3.2. CO_2 and $\delta^{13}C$ results

Fig. 1 shows the results for the 4 stratospheric samples together with the tropospheric data. The CO_2 mixing ratio in the stratosphere steeply decreased with increasing altitude from 19 to 21 km, and became almost constant at altitudes of 23 and 25 km, averaging 340.1 ± 0.1 ppmv. These features are similar to those observed in the stratosphere over mid-latitudinal Europe between 1979 and 1984 by Bischof et al. (1985). However, if their stratospheric CO_2 mixing ratios averaged above 22 km altitude are corrected for the NDIR carrier gas effect of +4 ppmv (Bischof et al., 1985), a value of 337 ppmv is obtained as the extrapolated CO_2 mixing ratio in 1985. This value is 3 ppmv smaller than our result in 1985. At the present stage, we suspect that this discrepancy is attributable to problems of measurement. Detailed discussion on this subject will be given in a subsequent paper.

Below the tropopause, the CO_2 mixing ratio decreased toward the surface. This is a trend specific to the summer season, because the photosynthetic uptake of CO_2 by the biosphere reaches its maximum state in August to cause the CO_2 mixing ratio on the surface to be the lowest during the year.

The annual mean of the CO_2 mixing ratio in the troposphere over Japan in 1985 was 345 ppmv (Tanaka et al., 1987b), as shown by the dotted line in Fig. 1. Since the rate of CO_2 increase over a recent decade is about 1.3 ppmv $year^{-1}$, the stratospheric air at 23–25 km altitude (CO_2: 340.1 ppmv) has an apparently 4-year older age than that of the tropospheric air. This time lag is in reasonable agreement with the

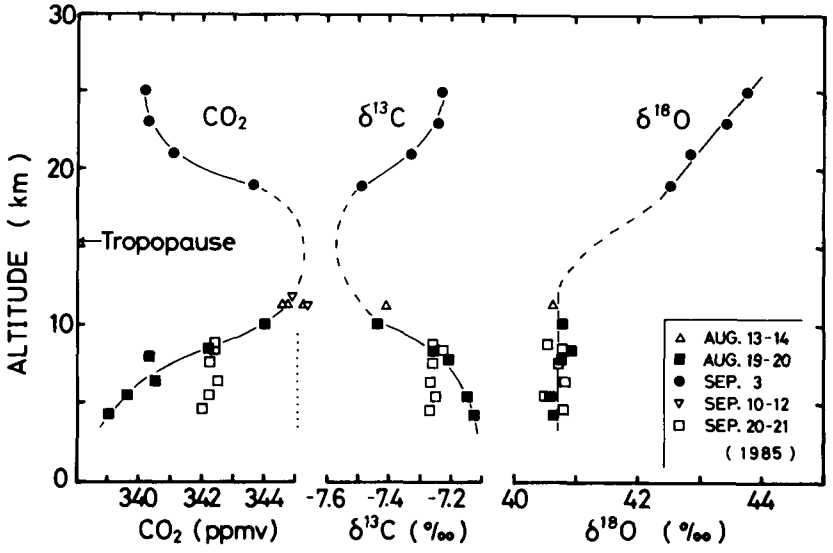

Fig. 1. Vertical profiles of the CO_2 mixing ratio, $\delta^{13}C$, and $\delta^{18}O$ of the CO_2 at heights up to 25 km over Japan in August to September, 1985. Solid circles are the data of stratospheric air samples collected by the balloon-borne cryogenic sampler. Triangles and squares represent samples collected by airplanes on the dates indicated in the insert. The dotted line stands for the annual mean CO_2 mixing ratio in the troposphere in 1985 (Tanaka et al., 1987b). The stratospheric $\delta^{18}O$ has not been corrected for the storage effect mentioned in Section 3.

value of 5.2 ± 0.8 years obtained by Bischof et al. (1985) over mid-latitudinal Europe. The origin of the stratospheric CO_2 will be discussed later by using CO_2–$\delta^{13}C$ relationship and $\delta^{18}O$ data.

The $\delta^{13}C$ profile correlates inversely with that of CO_2 both in the troposphere and stratosphere as shown in Fig. 1. At first, we discuss the tropospheric result. It is known that the $\delta^{13}C$ of tropospheric CO_2 changes seasonally due to photosynthesis in spring and summer and biomass decay in fall and winter (e.g., Mook et al., 1983); the $\delta^{13}C$ of the tropospheric CO_2 reaches a maximum in summer because $^{12}CO_2$ is preferentially removed from the atmosphere into vegetation by photosynthesis.

The tropospheric $\delta^{13}C$ profile seems to exhibit the seasonal variation as well as that of the CO_2 mixing ratio. In order to confirm this, the relationship between $\delta^{13}C$ (‰) and the CO_2 mixing ratio (μ in ppmv) was examined, as shown in Fig. 1. If the tropospheric CO_2 variation is only due to biospheric uptake and release of CO_2, a linear mixing relationship is expected between the CO_2 mixing ratio and its $\delta^{13}C$ (Keeling, 1958). The least squares fit for the tropospheric $\delta^{13}C$ and the reciprocal of μ (a broken line in Fig. 2) gave us the following equation:

$$\delta^{13}C = -(24.6 \pm 2.3) + (5924 \pm 773)/\mu, \quad r = 0.92, \tag{1}$$

where r is a correlation coefficient.

The first term of eq. (1), which stands for the $\delta^{13}C$ of CO_2 added (or subtracted) to (or from) the atmosphere, is in good agreement with previous results (Levin, 1987; Friedli et al., 1987; Heimann et al. quoted in Friedli et al., 1987). The slope of eq. (1), $d\delta^{13}C/d\mu$, was calculated to be $-(0.050 \pm 0.006)$‰ ppmv^{-1} for $\mu = 345$ ppmv. This slope is also in good agreement with the previous results of the seasonal variation of $-0.05 \sim -0.06$‰ ppmv^{-1} in the northern hemisphere (Keeling et al., 1979; Friedli et al., 1987). The reasonable parameter values together with the good correlation between CO_2 and $\delta^{13}C$ strongly supports that the tropospheric CO_2 variation in Fig. 1 was a seasonal variation caused by the mixing of biospheric CO_2 ($\delta^{13}C = \sim -25$‰) with the atmospheric CO_2.

On the other hand, the stratospheric $\delta^{13}C$ of CO_2 was thought to reflect rather the secular variation due to the burning of fossil fuel than the seasonal variation, because the CO_2 mixing ratio in the stratosphere suggests a time lag of 4 years as mentioned above. The general air circulation theory (Kida, 1983) also estimated the age of the mid-latitudinal stratospheric air to be about 2 years or more. Although fossil fuel carbon has a $\delta^{13}C$ value of -27‰ (Tans, 1981) close to that of biospheric CO_2, the secular CO_2–$\delta^{13}C$ slope is not similar to that of the seasonal variation but significantly suppressed to be $-0.02 \sim -0.03$‰ ppmv^{-1} (Keeling et al., 1979; Mook et al., 1983; Francey, 1985), due to the interaction between the atmosphere and the ocean (Keeling et al., 1979, 1980).

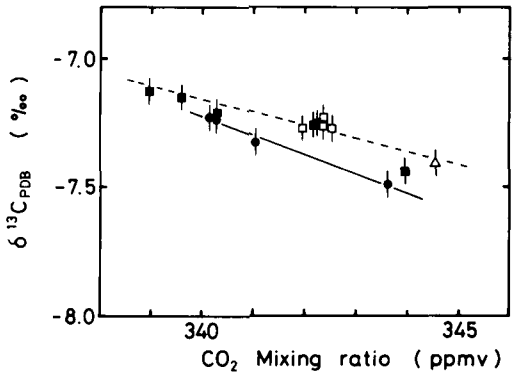

Fig. 2. A relationship between CO_2 and its $\delta^{13}C$ from the data shown in Fig. 1. The symbols are the same as in Fig. 1. The solid and broken lines were obtained by applying the least squares fit to the stratospheric and tropospheric data, respectively.

The regression analysis was also applied to the stratospheric CO_2–$\delta^{13}C$ data (a solid line in Fig. 2) to yield the following equation,

$$\delta^{13}C = -(32.6 \pm 2.4) + (8638 \pm 808)/\mu, \quad r = 0.99. \tag{2}$$

The parameters obtained are statistically different from those in the eq. (1), which supports the stratospheric CO_2 variation in Fig. 1 being different from the seasonal process observed in the troposphere. However, it should be noted that $d\delta^{13}C/d\mu$ of eq. (2) is $-(0.072 \pm 0.007)$‰ ppmv^{-1} for $\mu = 345$ ppmv, which is 2–3 times greater in its absolute value than the value of -0.02 to -0.03‰ ppmv^{-1} expected above as a value for the secular variation. At the present

stage, we have no conclusive idea to explain this discrepancy, because of the lack of latitudinal stratospheric data. Horizontal air transportation above the tropopause with a different CO_2–$\delta^{13}C$ characteristic may play an important role. More global and temporal CO_2–$\delta^{13}C$ data in the stratosphere should be acquired for further discussion.

3.3. $\delta^{18}O$ results

The tropospheric $\delta^{18}O$ data in Fig. 1 show no significant seasonal variation in contrast with the $\delta^{13}C$ data. It has been believed that the dominant process determining the $\delta^{18}O$ of tropospheric CO_2 is an oxygen isotope exchange with ocean water (Bottinga and Craig, 1969). The average value of 40.7 ± 0.1‰ (shown by a solid straight line in Fig. 1) corresponds to the equilibrium temperature of 22–24°C (Bottinga, 1968; O'Neil and Adami, 1969). On the other hand, the $\delta^{18}O$ of the stratospheric CO_2 was found to be surprisingly higher than that in the troposphere, increasing steadily with altitude as shown in Fig. 1.

As already mentioned in Subsection 3.1, the oxygen isotope exchange with the remaining water vapor in the sampling tube during storage might have slightly changed the $\delta^{18}O$ value of the CO_2. However, the steady increase in $\delta^{18}O$ with altitude cannot be explained by the storage effect, because the storage period is almost the same for all stratospheric samples. If water vapor had been condensed in the sampling tube to cause an isotope exchange between CO_2 and H_2O, the CO_2 would have had smaller $\delta^{18}O$ values than that in the troposphere (Craig and Begemann, 1970). Therefore, the $\delta^{18}O$ increase cannot be artificial.

Fossil fuel combustion would produce CO_2 with $\delta^{18}O$ of +23‰ or lower, because atmospheric oxygen has a uniform $\delta^{18}O$ value of +23‰ (Dole et al., 1954). It was actually observed that the CO_2 in the urban atmosphere in Tokyo has an approximately 1.5‰ lower $\delta^{18}O$ value than the background (uncontaminated) tropospheric value (Gamo and Horibe, 1985). Thus, the addition of fossil fuel CO_2 would never raise the $\delta^{18}O$ of stratospheric CO_2.

It is known that the $\delta^{18}O$ of tropospheric CO_2 increases as we go south in the northern hemisphere (Mook et al., 1983; Keeling et al., 1984). Recently, Francey and Trans (1987) measured the detailed meridional $\delta^{18}O$ distribution of tropospheric CO_2 on land stations from 71°N to 90°S, showing that the $\delta^{18}O$ is smallest at 71°N, increases steeply by 1–1.5‰ as we go south from 71°N to the tropical region (20°N and 14°S), and remaining relatively constant in the southern hemisphere. They attributed this pattern to the enzyme-catalyzed oxygen isotope exchange between CO_2 and leaf (and possibly soil) water, rather than that between CO_2 and ocean water.

The global air circulation theory (Kida, 1983) predicts that the air in the mid-latitudinal stratosphere is supplied mainly through the tropical tropopause. Therefore, it is likely that the low-latitudinal CO_2 with relatively high $\delta^{18}O$ would upwell and diverse horizontally toward the stratosphere over Japan to result in the higher $\delta^{18}O$ values than those in the troposphere. The CO_2 and $\delta^{13}C$ profiles in the stratosphere (Fig. 1) are consistent with this idea, because the low-latitudinal CO_2 and $\delta^{13}C$ values are lower (by about 1.5 ppmv) and higher (by about 0.15‰), respectively, than those in the mid-latitudes (Mook et al., 1983; Keeling et al., 1984). However, this process cannot completely explain the stratospheric $\delta^{18}O$ enrichment of about 3‰, because the $\delta^{18}O$ difference between the tropical and mid-latitudinal troposphere of the northern hemisphere is not more than 1‰ (Keeling et al., 1984; Francey and Tans, 1987).

Another possibility is an in situ isotope exchange reaction occurring after the air mass entered the stratosphere. Bottinga and Craig (1969) suggested that the oxygen isotope exchange between CO_2 and O_2 could increase the $\delta^{18}O$ of CO_2 according to the following reaction (3).

$$C^{16}O_2 + {}^{16}O^{18}O \rightleftarrows C^{16}O^{18}O + {}^{16}O_2. \quad (3)$$

The theoretical isotope separation factor of reaction (3) was calculated to be 1.037 (at 0°C) by Urey (1947). If the $\delta^{18}O$ of stratospheric O_2 is 23‰, that of stratospheric CO_2 could be raised to as high as 60‰ relative to SMOW in an equilibrium condition at 0°C. Reaction (3) is too slow in the troposphere to be significant, but in the stratosphere, photodissociations of O_2 and CO_2 by ultraviolet light may accelerate the progress of reaction (3). At the present stage, however, there is no quantitative estimate for the extent to which

the photodissociation could contribute to accelerating the reaction (3).

Cicerone and McCrumb (1980) and Blake et al. (1984) showed that the photolysis rate of $^{18}O^{16}O$ is larger than that of $^{16}O^{16}O$ in the high stratosphere. This may relate to the high $\delta^{18}O$ value observed in this study. Recent studies on ozone have elucidated many interesting facts with regard to heavy ozone ($^{16}O_2{}^{18}O$). Thiemens and Heidenreich (1983) found by laboratory experiments a mass-independent enrichment of ^{17}O and ^{18}O in photochemically produced ozone. Mauersberger (1981, 1987) and Rinsland et al. (1985) observed the ^{18}O enrichment of stratospheric ozone. The mechanism of ozone ^{18}O enrichment has not yet been completely understood because of the disagreement between the model and observations (Kaye, 1986). It would be interesting to pursue the relationship between our $\delta^{18}O$ result and the ozone ^{18}O enrichment by measuring both parameters at the same time.

Anyway, if there occurs an in situ ^{18}O enrichment in the stratosphere, the $\delta^{18}O$ value of CO_2 would depend on the time elapsed after the air mass enters the stratosphere. This suggests that the $\delta^{18}O$ of CO_2 may be used as a useful tracer for estimating the rate of air circulation in the stratosphere.

4. Conclusions

(1) The $\delta^{13}C$ value of CO_2 in the stratosphere over Japan was observed to increase with increasing altitude from 19 to 25 km, reflecting the secular anthropogenic addition of CO_2 with a lower $\delta^{13}C$ value. There is also the possibility that a part of the $\delta^{13}C$ increase might be caused by horizontal air advection from the low-latitudinal troposphere as suggested by the $\delta^{18}O$ results. The relationship between $\delta^{13}C$ variation and the CO_2 mixing ratio (-0.07‰ ppmv^{-1}) was closer to that of the seasonal variation in the troposphere ($-0.05 \sim -0.06$‰ ppmv^{-1}) than to the secular value so far observed in the troposphere ($-0.02 \sim -0.03$‰ ppmv^{-1}). Further data acquisition is required to explain this discrepancy.

(2) It was found that the $\delta^{18}O$ of the stratospheric CO_2 at an altitude of 19 km is about 2‰ greater than that of the tropospheric CO_2 and increases further with increasing altitude. We suggested that the $\delta^{18}O$ might be enhanced by the following two processes. One is the advective inflow of low-latitudinal tropospheric air whose CO_2 has a $\delta^{18}O$ value of about 1‰ greater than that in the mid-latitudinal troposphere. The other is a photochemically accelerated oxygen isotope exchange between CO_2 and molecular oxygen in the stratosphere. The enrichment of ^{18}O of CO_2 may be related to the recent observation that the stratospheric ozone is also rich in ^{18}O.

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