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Long-term monitoring of carbon and oxygen isotope ratios of stratospheric CO_2 over Japan

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Abstract. We have been measuring stable isotopic ratios of carbon ($\delta^{13}C$) and oxygen ($\delta^{18}O$) of carbon dioxide in the stratosphere (18-35 km altitudes) over Japan since 1985, presenting here the first temporal $\delta^{13}C$ and $\delta^{18}O$ records between 1985 and 1991. The stratospheric $\delta^{13}C$ is gradually decreasing due to anthropogenic effects with a rate of approximately -0.03‰ y^{-1}, which is similar to the tropospheric value. The previously found ^{18}O enrichment in stratospheric CO_2 has been maintained almost steadily during the 6 years, with a monotonous $\delta^{18}O$ increase with increasing altitude up to 35 km over Japan.

Introduction

Stratospheric CO_2 is well characterized by its $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios. As for carbon isotopes, the annual increase of stratospheric CO_2 concentration due to anthropogenic effects (Bischof *et al.*, 1985) is expected to be accompanied by the decrease of the $^{13}C/^{12}C$ ratio, because the anthropogenic CO_2 from fossil fuels and deforestation has lower $^{13}C/^{12}C$ values ($\delta^{13}C_{PDB}$: ~-25‰) than that of the stratospheric CO_2 ($\delta^{13}C$: -7 to -8‰). It is well known that the increase of CO_2 in the troposphere has been accompanied by the decrease of $\delta^{13}C$ with a $\Delta\delta^{13}C/\Delta CO_2$ ratio of ~-0.02 ‰ ppmv^{-1} (Keeling *et al.*, 1979; Nakazawa *et al.*, 1993). As for oxygen isotopes, recent works have revealed that the stratospheric CO_2 is enriched in ^{18}O, possibly due to photochemically induced oxygen isotope exchange between CO_2 and O_3 in the stratosphere (Gamo *et al.*, 1989; Yung *et al.*, 1991; Thiemens *et al.*, 1991).

Monitoring the behavior of carbon dioxide including its isotopes in the stratosphere is essential for the assessment of CO_2 exchange between the troposphere and the stratosphere, data on stratospheric CO_2 has been few so far. Nakazawa *et al.* (1994) have been taking stratospheric air samples between 13 and 35 km altitudes over Japan nearly once a year since 1985. As a part of this project, we have been measuring stable isotopes of carbon and oxygen ($^{13}C/^{12}C$ and $^{18}O/^{16}O$) for the stratospheric CO_2. This paper will present the first long-term $\delta^{13}C$ and $\delta^{18}O$ records of stratospheric CO_2, compare them with the tropospheric data, and discuss stratospheric $\delta^{13}C$ and $\delta^{18}O$ characteristics in detail.

Experimental

Stratospheric air samples have been taken by using a balloon-borne cryogenic multi-sampling system of the Institute of Space and Astronautical Science (ISAS) (Itoh *et al.*, 1989; Honda, 1990), which is flown at the ISAS Sanriku Balloon Center (39°N, 142°E). During the descent of the balloon after reaching the highest altitude (~35 km), the balloon stopped at 7-12 assigned altitudes to collect stratospheric whole air samples of (1-3) × 10^4 cm^3 STP in 760 cm^3 stainless steel tubes using liquid helium as a refrigerant.

The CO_2 mixing ratio of the collected air samples has been measured using the NDIR (Non-dispersive infrared) method (Tanaka *et al.*, 1983; 1987; Nakazawa *et al.*, 1993; 1994). Analytical method for $^{13}C/^{12}C$ and $^{18}O/^{16}O$ measurements was the same as described in the previous paper (Gamo *et al.*, 1989). In brief, CO_2 gases were cryogenically extracted from the air samples at Tohoku University, being sent to the Ocean Research Institute, where carbon and oxygen isotopic ratios were measured with a triple collector mass spectrometer (Finnigan MAT 250).

The carbon and oxygen isotopic ratios are expressed as $\delta^{13}C$ and $\delta^{18}O$ in the traditional way: $\delta=(R_x/R_{STD}-1)\times1{,}000$ (‰), where R_x and R_{STD} are $^{13}C/^{12}C$ (or $^{18}O/^{16}O$) ratio of an unknown sample and that of the PDB (or SMOW) standard, respectively. It should be noted that, in calculating $\delta^{13}C$ from the measured mass ratios of 45/44 and 46/44, we slightly modified the usual calculation procedure (Craig, 1957) which is based on the mass-dependent isotope fractionation between ^{17}O and ^{18}O ($\delta^{18}O = 2\cdot\delta^{17}O$). This modification is due to the recent discovery of mass independent enrichment in both ^{17}O and ^{18}O for stratospheric CO_2 over U.S.A. (Thiemens *et al.*, 1991): $\Delta\delta^{18}O \cong \Delta\delta^{17}O$, where $\Delta\delta$ = δ (stratosphere) - δ (troposphere). Assuming that this mass-independent effect is also applicable for the stratospheric CO_2 over Japan, we corrected the usually calculated $\delta^{13}C$ values. The method of the correction will be

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published elsewhere in detail. The maximum $\delta^{13}C$ correction added to the usual values was -0.24‰ in case of $\Delta\delta^{18}O$= 6.8‰ (the maximum $\Delta\delta^{18}O$ value observed in this study). The $\delta^{13}C$ and $\delta^{18}O$ values were also corrected for the presence of N_2O using the usual procedure (Friedri and Siegenthaler, 1988). The estimated precision is ±0.1‰ for both δ values.

Results and discussion

$\delta^{13}C$ data

Figure 1 summarizes the stratospheric CO_2 mixing ratio (Nakazawa *et al.*, 1994) and its $\delta^{13}C$ data from 1985 to 1991. The profiles of CO_2 mixing ratio (Fig.1a) are characterized by steep decrease with increasing altitude above the lowest part of the stratosphere (~15 km altitude) to reach nearly constant CO_2 values at heights above 20-25 km. It is apparent that the averaged CO_2 mixing ratio in the stratosphere above 25 km altitude has increased with a rate of ~1.4 ppmv y^{-1} since 1985, possibly due to the anthropogenic effects (Nakazawa *et al.*, 1994). The $\delta^{13}C$ and CO_2 data are almost mirror images of each other; the $\delta^{13}C$ values increase steeply between ~15 km and ~25 km altitudes and then become nearly constant. The yearly averaged $\delta^{13}C$ values above 25 km altitude show gradual decrease with year. The $\delta^{13}C$ decrease coupled with the increase of CO_2 mixing ratio strongly supports that the stratospheric CO_2 increase is caused by the anthropogenic CO_2 emission in the troposphere.

It should be noted, however, that the yearly $\delta^{13}C$ decreasing pattern is not so regular as the increasing pattern of the CO_2 mixing ratio. Keeling *et al.* (1989) and Nakazawa *et al.* (1993) showed that the yearly $\delta^{13}C$ decrease of tropospheric CO_2 between 1977 and 1990 is characterized by temporal variations, suggesting substantial release of biospheric CO_2 with lower $\delta^{13}C$ values in 1980, 1983, and 1987-88, which may be associated with the ENSO events. Such temporal variations in the troposphere are likely to be transferred to the stratosphere with a time lag of a couple of years. The relatively low $\delta^{13}C$ values observed in 1986 (Fig.1b) may reflect the 1983 ENSO event.

Figure 2 shows that the annually averaged $\delta^{13}C$ values (altitude ≥ 25 km) decreased from -7.35‰ (1985) to -7.54‰ (1991) with the rate of about -0.03‰ yr^{-1}, and that the changing ratio of $\Delta\delta^{13}C/\Delta CO_2$ is -0.017±0.006 ‰ $ppmv^{-1}$ between 1985 and 1991. These rate and ratio are in good agreement with the tropospheric values of -0.03 to -0.04 ‰ yr^{-1} and -0.02 to -0.03 ‰ $ppmv^{-1}$, respectively (Keeling *et al.*, 1979; Nakazawa *et al.*, 1993). This consistency suggests that the variations of CO_2 and $\delta^{13}C$ occur almost only in the troposphere, and that the secular CO_2 - $\delta^{13}C$ variations in the troposphere are conservatively transferred to the stratosphere.

The photochemical oxidation of methane to CO_2 in the stratosphere could have had some effects on the temporal decrease of $\delta^{13}C$ of the stratospheric CO_2, because the atmospheric CH_4 has a significantly low $\delta^{13}C$ value of ~-50‰ (e.g. Stevens and Engelkemeir, 1988). The present CH_4 mixing ratio in the troposphere (~1.8 ppmv) is increasing with the rate of ~0.02 ppmv y^{-1} (Blake and Rowland, 1988). If we assume as an extreme case that the CH_4 oxidation in the stratosphere is increasing by 0.02 ppmv per year, the decrease of $\delta^{13}C$ of stratospheric CO_2 due to the CH_4 oxidation is calculated to be -0.003‰ y^{-1}. This is an order of magnitude smaller than the $\delta^{13}C$ decreasing rate due to the anthropogenic CO_2 emission in the troposphere.

$\delta^{18}O$ data

In contrast to the case of $^{13}C/^{12}C$ ratio mentioned above, the variation of $^{18}O/^{16}O$ ratio is much more significant in the stratosphere than in the troposphere. Gamo *et al.* (1989)

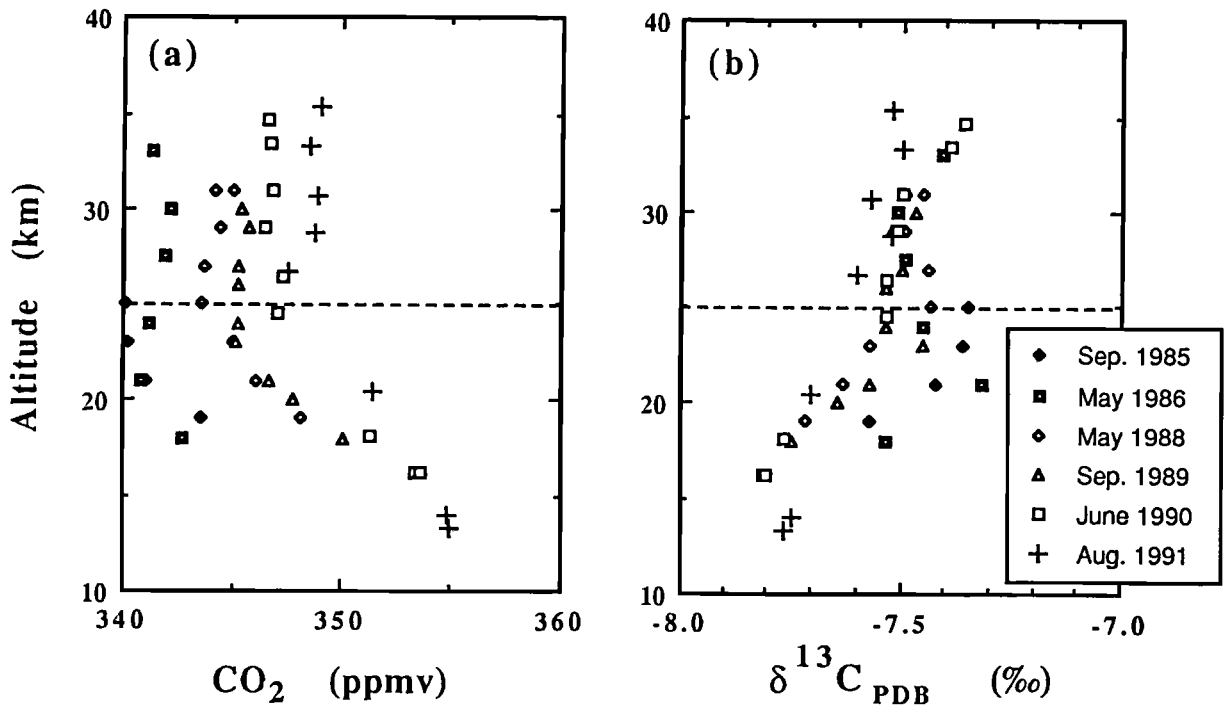

Figure 1. Vertical profiles of stratospheric CO_2 (a) (Nakazawa *et al.*, 1994) and of $\delta^{13}C$ (b) measured during 1985 and 1991 over Japan. The altitude of tropopause was estimated to be at approximately 15.0, 11.0, 12.0, 15.0, 13.5, and 16.5 km for 1985, 1986, 1988, 1989, 1990, and 1991, respectively (Nakazawa *et al.*, 1994).

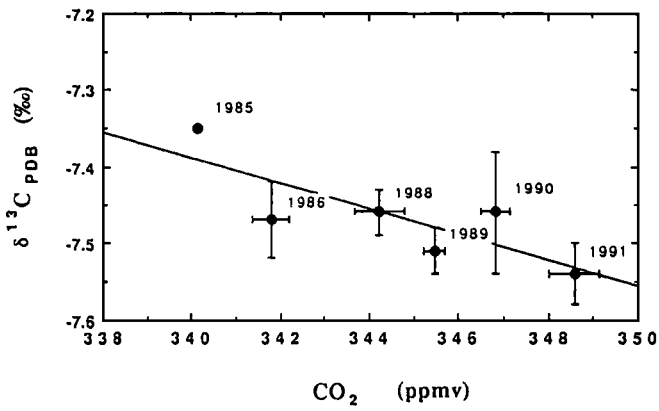

Figure 2. Relationship between annually averaged CO_2 mixing ratio and its $\delta^{13}C$ in the stratosphere over Japan (altitude ≥25km) from 1985 to 1991. The straight line was drawn by the least-squares method.

discovered ^{18}O enrichment for the stratospheric CO_2, suggesting a possibility that *in situ* photochemically induced oxygen isotope exchange might occur between CO_2 and ^{18}O-enriched ozone. The ^{18}O enrichment in O_3 had been observed by Mauersberger (1981; 1987). Yung *et al.* (1991) gave a theoretical support to Gamo *et al.* (1989) by considering an isotopic exchange mechanism between CO_2 and O_3 via $O(^1D)$ to transfer the O_3 isotope enrichment to CO_2 in the stratosphere. Furthermore, Thiemens *et al.* (1991) analyzed stratospheric CO_2 samples over U.S.A. to confirm the higher $\delta^{18}O$ values.

The $\delta^{18}O$ data obtained from 1985 to 1991 over Japan are plotted in Fig.3. These data apparently show that a trend of monotonous $\delta^{18}O$ increase with increasing altitudes in the stratosphere has been almost steadily maintained since 1985,

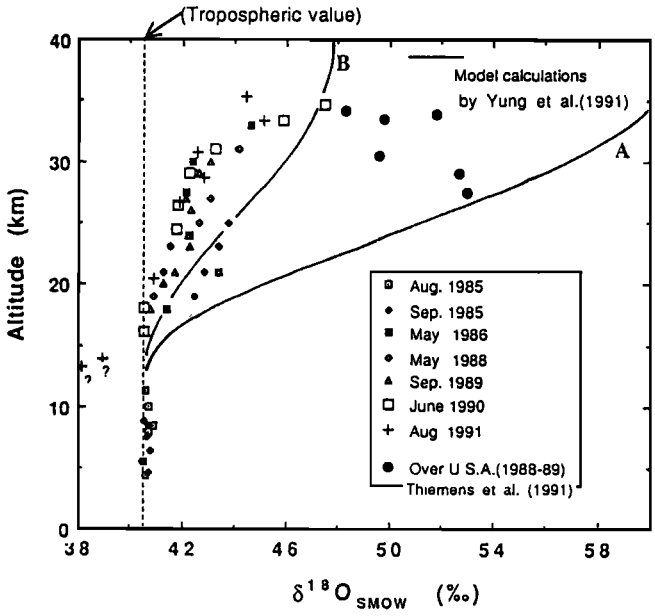

Figure 3. Vertical profiles of $\delta^{18}O$ of tropospheric (only in 1985) and stratospheric CO_2 measured during 1985 and 1991 over Japan. Two points with "?" may be erroneous data, although the cause has not been specified yet. The $\delta^{18}O$ data measured over U.S.A. (Palestine and Fort Sumner) in 1988 and 1989 (Thiemens *et al.*, 1991) are also shown. Two theoretical $\delta^{18}O$ profiles are from by Yung *et al.* (1991) (see text).

when the enrichment of ^{18}O was observed for the first time (Gamo *et al.*, 1989). The maximum $\delta^{18}O$ value reached 47.5‰ at 34.7 km altitude in June 1990. There seems to be a tendency that the slope of the $\delta^{18}O$ increase above ~30 km altitude becomes steeper than below. Such $\delta^{18}O$ profiles imply a similar increasing trend of $^{50}O_3$ with increasing altitude up to ~35 km, although no $^{50}O_3$ data is available over Japan at the present stage.

The $\delta^{18}O$ data over U.S.A. (Palestine in Texas (32°N, 96°W) and Fort Sumner in New Mexico (34°N, 104°W)) measured in 1988 and 1989 (Thiemens *et al.*, 1991) are also shown in Fig.3 for comparison. The ^{18}O enrichment of stratospheric CO_2 observed over Japan and U.S.A. suggests not only that the ^{18}O enrichment is a global scale phenomenon, but also that there may be latitudinal and/or longitudinal variations in the stratospheric $\delta^{18}O$ values. As shown in Fig.3, the $\delta^{18}O$ data over Japan (42 - 48 ‰) are significantly lower than those over U.S.A. (48 - 53 ‰) (Thiemens *et al.*, 1991), when they are compared with each other in the same altitude range of 26-35 km.

Two theoretical $\delta^{18}O$ profiles A and B in Fig.3 were referred from Yung *et al.* (1991), who regarded ^{18}O exchange between CO_2 and O_3 to be in photochemical equilibrium, with assuming a proper vertical eddy diffusivity in the stratosphere. Profiles A and B were calculated using the maximum $^{50}O_3$ enrichment at ~30 km altitude of 40% (measured value at Palestine, U.S.A., by Mauersberger (1981; 1987)) and that of 13% (laboratory results by Thiemens *et al.* (1988) and Morton *et al.* (1990)), respectively. The $\delta^{18}O$ data over U.S.A. (Thiemens et al., 1991) are in good agreement with these profiles, while our $\delta^{18}O$ values mostly deviate from the area sandwiched between the two profiles.

The areal $\delta^{18}O$ variation between Japan and U.S.A. may be explained by either of the following three possibilities: (i) the ^{18}O enrichment of O_3 might be less significant over Japan than that over U.S.A, or (ii) vertical eddy diffusivity in the stratosphere might be higher over Japan than that over U.S.A., because the increase of the diffusivity causes to lower the ^{18}O enrichment in CO_2 during ^{18}O exchange between O_3 and CO_2 (Yung *et al.*, 1991), or (iii) upward mixing of tropospheric CO_2 with less $\delta^{18}O$ values to the stratosphere might be stronger over Japan than over U.S.A.

It is of interest that Fig.3 also suggests temporal $\delta^{18}O$ variation over Japan. The $\delta^{18}O$ data in September 1985 and a part of the data in May 1986 slightly deviate from the main $\delta^{18}O$ increasing trend, which may have been caused by an episodic variation of dynamic air transport system in the stratosphere in 1985 to 1986. The $\delta^{18}O$ of stratospheric CO_2 is thought to be a useful air mass tracer. It is desirable to accumulate further temporal and spatial $\delta^{18}O$ data as well as CO_2, $\delta^{17}O$ and $^{50}O_3$ data in a global scale for more detailed discussion.

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