

MEASUREMENT OF ^{14}C CONCENTRATIONS OF STRATOSPHERIC CO_2 BY ACCELERATOR MASS SPECTROMETRY

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ABSTRACT. In order to measure the concentrations of anthropogenically influenced gases in the stratosphere, we have collected air samples from the lower stratosphere since 1985, by a balloon-borne cryogenic sampling method, developed at the Institute of Space and Astronautical Science (ISAS). Air samples of ~16 liters at STP were collected in the stratosphere at altitudes from 18.6 to 30.4 km, over the northeastern part of Japan (39.5°N, 139-142°E), on 1 September 1989. We conducted ^{14}C analyses to study the vertical and horizontal air-mass movement in the stratosphere, and to investigate the air transport mechanism between troposphere and stratosphere. Carbon dioxide (containing a few mg carbon) was separated cryogenically from the air samples, and the ^{14}C concentration of the CO_2 was measured by a Tandetron accelerator mass spectrometer, using Fe-graphite targets prepared by reducing CO_2 on Fe-powder with hydrogen in a Vycor tube at 650°C. The ^{14}C concentrations, expressed as $\Delta^{14}\text{C}$, of CO_2 were 267-309‰ at altitudes of 21-30 km, and 134‰ at 19-20 km. The $\Delta^{14}\text{C}$ values at 21-30 km were higher than those of the current tropospheric CO_2 , of around 80-200‰. The observed ^{14}C concentrations, higher in the stratosphere than the troposphere, seem to be explained by large bomb-produced ^{14}C inventories and/or high ^{14}C production by cosmic rays, as well as weak vertical mixing of air masses in the stratosphere.

INTRODUCTION

Since the 1950s, environmental radiocarbon (^{14}C) has been investigated by many researchers, who have measured ^{14}C concentrations of tropospheric CO_2 by collecting CO_2 with sodium hydroxide solutions from open air at ground level (Rafter & Fergusson 1957; Nydal & Løvseth 1983), and by using biological samples, which have photosynthetically incorporated atmospheric CO_2 (Cain & Suess 1976). However, the traditional methods, based on radioactivity measurements, could be used only for samples containing a few grams of carbon. It has required very laborious efforts to analyze air at high altitudes, where aircraft could not reach and where large-volume air sampling was rather difficult (Hagemann *et al.* 1959). Accelerator mass spectrometry (AMS) has overcome this difficulty. The amount of carbon required for AMS is 100 μg to a few milligrams (Vogel, Nelson & Southon 1987), almost three orders of magnitude less than that of traditional radiocarbon measurements.

We have developed a balloon-borne cryogenic sampling system at the Institute of Space and Astronautical Science (ISAS) to collect lower stratospheric air samples, and to measure the content of anthropogenically influenced gases such as CO_2 , CH_4 and halocarbons (Honda, Minagawa & Itoh 1987; Gamo *et al.* 1989; Honda 1990). We used a Tandetron accelerator mass spectrometer to measure the ^{14}C concentration of lower stratospheric air samples collected in 1989 with the ISAS sampling system, and for comparison, of tropospheric air samples collected in 1989 and 1990.

EXPERIMENTAL

Sample Collection and Preparation

Lower stratospheric air samples were collected at nine altitudes from 18.6 to 30.4 km on 1 September 1989, over Iwate and Akita Prefectures, northeast Japan (39.5°N, 139-142°E), as shown

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in Figure 1. A cryogenic air-sampling system with 12 stainless steel sampling tubes, each of 760 cm³ volume/capacity, with a liquid helium refrigerant, sampling manifold, monitoring circuit and valve-controlling unit, was launched from the Sanriku Balloon Center (SBC) on the Pacific coast (39.16°N, 141.83°E). Itoh *et al.* (1989) and Honda (1990) have described the apparatus in detail.

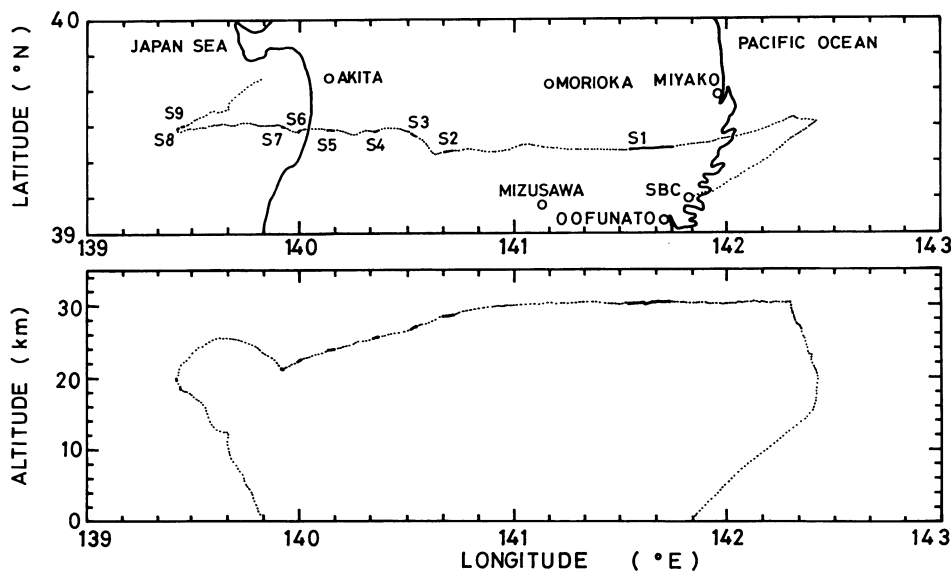


Fig. 1. Trajectory of the cryogenic air sampler. S1 to S9 are collection sites of stratospheric air samples

Before being installed in the sampling system, the sample tubes and manifold were pretreated as follows: they were evacuated for 4 days at room temperature, then for 24 h at 110°C under a vacuum of 10^{-7} Torr, and finally, for 7 days at room temperature, using a turbo-molecular pump. Figure 1 shows the flight trajectory of the balloon and the air-sampling points. We calculated the altitude of the sampler from the distance from the ground station to the sampler, and the elevation angle of the sampler. The accuracy of altitude determination is generally about ± 200 m. After launch, the balloon reached its highest altitude, 31.1 km, in 2 h, and the sampling system was reeled down to 100 m below the flight-control gondola, to avoid any possible contamination from the balloon or the launch and recovery systems. While the system was descending after release of helium gas from the balloon, we collected air samples of *ca.* 16 liters at STP of 9-altitude intervals of 30.4–30.2, 28.7–28.5, 27.1–26.8, 25.7–25.5, 24.0–23.8, 22.6–22.3, 21.3–21.1, 20.1–19.8, 19.0–18.6 km, by condensing air inside the sampling tubes with liquid helium. We actuated the valve sequence of the sampling tubes with microwave signals from the ground station, in a programmed way controlled by a microcomputer. After collection of stratospheric air, the sampling system was cut off from the balloon, landed in the Sea of Japan (Fig. 1) and was recovered.

We removed the sample tubes from the sampling system, transported them to the ISAS, and stored them horizontally for about two weeks to reduce any sample fractionation that may have been introduced during the cryogenic sampling. Gamo *et al.* (1989) and Tanaka *et al.* (1987) studied the effects of storing the sampling tubes on the isotopic fractionation of CO₂ and CO₂ concentrations, and found them to be negligible. We analyzed the air samples for ¹⁴C, and also made routine measurements of halocarbons, CH₄ and CO₂ concentrations (Makide *et al.* 1987; Nakazawa *et al.* 1991), and the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of their CO₂ (Gamo *et al.* 1989), which will be reported elsewhere.

The ^{14}C samples were transported to the Upper Atmosphere and Space Research Laboratory, Tohoku University, where CO_2 concentrations were measured with a non-dispersive infrared gas analyzer (NDIR) to a precision of ± 0.1 ppmv (Tanaka, Nakazawa & Aoki 1987). After this analysis, the CO_2 gas was extracted from the air samples using a cryogenic method. Two U-shaped gas traps of 20 mm diameter and 50 cm effective length, with several small glass tubes to increase the gas-trapping surface, were installed in a vacuum line. The first was cooled to -100°C with an ethanol and liquid N_2 mixture to trap H_2O , and the second to -196°C with liquid N_2 to trap CO_2 . The air samples were passed through the two traps at a reduced pressure of about 1 Torr with a flow rate of about $40\text{ cm}^3\text{ min}^{-1}$. When all the air had passed through the line, H_2O was separated from CO_2 by changing the coolant from -197°C to -100°C in the second trap. We condensed the purified CO_2 samples from the nine altitudes into five samples by averaging them with samples from the adjacent two altitudes (Table 1). These five CO_2 samples, each containing 2.5–3.9 mg carbon, were sealed in pyrex tubes of 6 mm diameters and sent to Nagoya University for carbon isotopic analysis. Gamo *et al.* (1989) tested the effects of pretreatment of the sampling tubes and the CO_2 extraction method on the carbon-isotopic fractionation, and found them to be negligible.

For comparison, we analyzed 11 tropospheric air samples, collected over Japan in 1989 and 1990, and at Syowa Station (60.0°S , 39.6°E) in Antarctica in 1990 (Table 1), using an evacuated stainless-steel flask of 6-liter capacity (*ca.* 1 mg C). We collected some samples aboard aircraft at altitudes of 1400 and 8845 m, with no contamination from engine exhaust (Tanaka, Nakazawa & Aoki 1983), and others at ground level. Pretreatment was similar to that for stratospheric air samples.

Carbon Isotope-Ratio Measurement

For CO_2 gas extracted from air samples, the carbon stable-isotope ratio was measured with a triple collector mass spectrometer (Finnigan MAT 251) at the Water Research Institute, Nagoya University. The results were normalized to the PDB-Chicago standard, and given as $\delta^{13}\text{C}_{\text{PDB}}$

$$\delta^{13}\text{C}_{\text{PDB}} = \left(\left(\frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}} \right)_{\text{sample}} / \left(\frac{^{13}\text{C}/^{12}\text{C}}{^{13}\text{C}/^{12}\text{C}} \right)_{\text{PDB}} - 1 \right) \times 1000 \text{ (‰)}. \quad (1)$$

The error for $\delta^{13}\text{C}_{\text{PDB}}$ is $< \pm 0.1\%$. No correction was made for the effect on $\delta^{13}\text{C}$ values of residual N_2O in sample CO_2 gas, which was investigated by Gamo and Horibe (1985) in detail. According to them, N_2O in CO_2 samples reduces $\delta^{13}\text{C}$ by 0.25‰, that is negligible for correcting carbon isotopic fractionation to evaluate ^{14}C concentrations ($\Delta^{14}\text{C}$ defined by Eq. (3)).

We then prepared an Fe-graphite target by reducing CO_2 on Fe-powder with hydrogen in a sealed Vycor tube at 650°C for 4–6 h (Kitagawa *et al.* 1991), modifying the method of Vogel, Nelson and Southon (1987). We measured the $^{14}\text{C}/^{13}\text{C}$ ratio, $\delta^{14}\text{C}(13)$, in the Tandetron spectrometer at the Dating and Materials Research Center, Nagoya University (Nakai *et al.* 1984; Nakamura, Nakai & Ohishi 1987)

$$\delta^{14}\text{C}(13) = \left(\left(\frac{^{14}\text{C}/^{13}\text{C}}{^{14}\text{C}/^{13}\text{C}} \right)_{\text{sample}} / \left(\frac{^{14}\text{C}/^{13}\text{C}}{^{14}\text{C}/^{13}\text{C}} \right)_{\text{standard}} - 1 \right) \times 1000 \text{ (‰)}. \quad (2)$$

As a radiocarbon standard, we used charcoal prepared from the 1840–1860 annual rings of a Japanese cypress tree, with their $^{14}\text{C}/^{12}\text{C}$ ratio calibrated to NBS oxalic acid (SRM-4990) (Nakamura *et al.* 1985). The sample $\Delta^{14}\text{C}$ value, corrected for carbon isotopic fractionation, was calculated as

$$\Delta^{14}\text{C} = \delta^{14}\text{C}(13) - (25 + \delta^{13}\text{C}_{\text{PDB}}) \times \left(1 + \delta^{14}\text{C}(13)/1000 \right) \text{ (‰)}. \quad (3)$$

We can routinely measure ^{14}C concentrations to a precision of $\pm 1\%$ for modern samples of more

TABLE 1. $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ values of CO_2 , and CO_2 mixing ratios for air samples at different locations and altitudes

Sample no.	Location* (sampling date) (yr/mo./day)	Altitude (km)	$\frac{R_{\text{sample}}}{R_{\text{AD1950}}}$	$\Delta^{14}\text{C}$ (‰)	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)	CO_2 mixing ratio (ppmv)
ST1	Sanriku (89/09/01)	30.4–30.2	1.332 ± 0.014	309 ± 14	-7.7	345.5
ST2	Sanriku (89/09/01)	28.7–28.5 27.1–26.8	1.290 ± 0.015	267 ± 15	-7.6	345.8 345.3
ST3	Sanriku (89/09/01)	25.7–25.5 24.0–23.8	1.309 ± 0.014	287 ± 14	-7.8	345.3 345.4
ST4	Sanriku (89/09/01)	22.6–22.3 21.3–21.1	1.293 ± 0.016	271 ± 16	-	345.2 346.7
ST5	Sanriku (89/09/01)	20.1–19.8 19.0–18.6	1.154 ± 0.013	134 ± 13	-8.0	347.8 350.1
TR1	Nagoya (90/07/19)	8.845	1.223 ± 0.014	203 ± 14	-8.0	
TR2	Nagoya (90/07/19)	8.845	1.212 ± 0.015	192 ± 15	-7.9	
TR3	Souma (90/07/25)	1.4	1.202 ± 0.014	182 ± 14	-8.0	
TR4	Souma (90/07/25)	1.4	1.150 ± 0.009	131 ± 9	-8.1	
TR5	Syowa Station (90/01/17)	Ground	1.099 ± 0.038	80 ± 38	-8.1	
TR6	Syowa Station (90/01/17)	Ground	1.138 ± 0.011	119 ± 11	-8.0	
TR7	Sendai (89/12/12)	Ground	1.100 ± 0.009	82 ± 9	-8.7	
TR8	Sendai (89/12/13)	Ground	1.161 ± 0.010	142 ± 10	-8.6	
TR9	Sendai (89/12/19)	Ground	1.125 ± 0.009	106 ± 9	-8.2	
TR10	Sendai (90/06/21)	Ground	1.164 ± 0.022	144 ± 22	-7.9	
TR11	Sendai (90/06/21)	Ground	1.184 ± 0.014	164 ± 14	-7.9	

*Longitude and latitude of sampling locations: Sanriku (39.2°N, 141.8°E); Sendai (38.2°N, 140.8°E); Souma (37.8°N, 140.9°E); Nagoya (35.3°N, 137.9°E); Syowa Station (69.0°S, 39.6°E)

than a few mg carbon (Nakamura *et al.* 1985). Errors usually get larger than $\pm 1\%$ for targets of less than 1 mg carbon, primarily owing to statistical counting errors.

RESULTS AND DISCUSSION

Table 1 and Figure 2 show the $^{14}\text{C}/^{13}\text{C}$, $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}_{\text{PDB}}$ values, and CO_2 concentrations (CO_2 mixing ratios) for lower-stratospheric and tropospheric air samples. The CO_2 concentration is expressed in terms of the volume mixing ratio in ppmv (10^{-6} v v^{-1}), with the error of ± 0.1 ppmv.

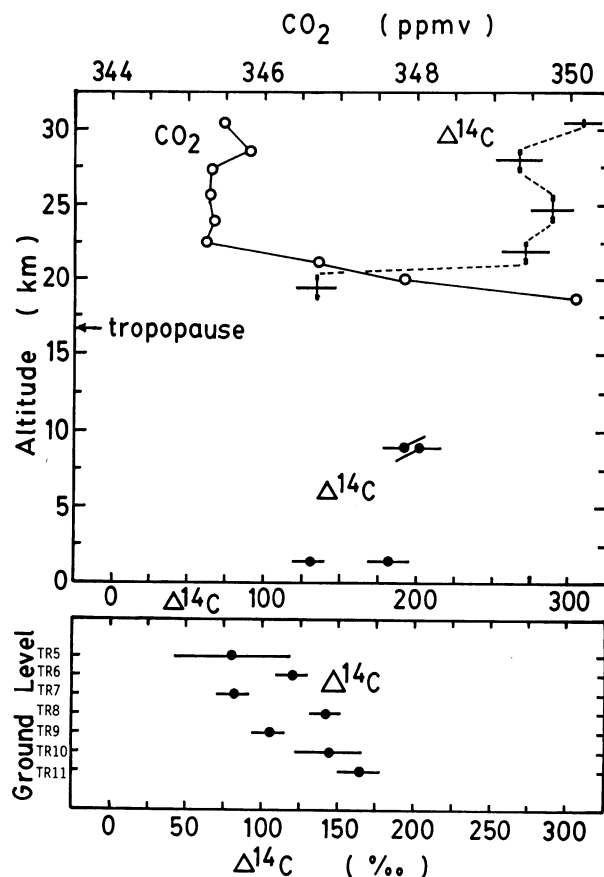


Fig. 2. $\Delta^{14}\text{C}$ values of CO_2 and the CO_2 mixing ratio vs. altitude of air samples collected in the stratosphere and troposphere

Our results show that the lower stratospheric CO_2 is abundant in ^{14}C , with $\Delta^{14}\text{C}$ values of 270–310‰, compared to $\Delta^{14}\text{C}$ values of 80–200‰ for tropospheric CO_2 . The $\Delta^{14}\text{C}$ value of stratospheric air also increases slightly, or is almost constant, as the altitude increases from 21.1 to 30.4 km.

It is commonly accepted that the $\Delta^{14}\text{C}$ value of tropospheric CO_2 is still affected by bomb-produced ^{14}C . The observed $\Delta^{14}\text{C}$ values are higher than the pre-bomb values. However, it is not certain whether the observed $\Delta^{14}\text{C}$ value is higher than the pre-bomb value for stratospheric CO_2 , because the exact pre-bomb value is not known. Hagemann *et al.* (1959) assumed the pre-bomb stratospheric background as 13 dpm g^{-1}C for their stratospheric excess ^{14}C estimation, but the value is not confirmed. Also, the pre-bomb value in the stratosphere may depend on the altitude. We consider two possibilities for the observed ^{14}C concentrations that are higher in the stratosphere than in the troposphere. One is stratospheric ^{14}C inventories by nuclear bomb tests. Excess ^{14}C produced by bomb tests can still be greater in the stratosphere than in the troposphere, perhaps owing to weak vertical mixing of stratospheric air. The other is higher ^{14}C production by cosmic rays and lower CO_2 content in the stratosphere than troposphere, *i.e.*, the stratospheric $\Delta^{14}\text{C}$ value can be higher than the tropospheric value in the pre-bomb steady state.

Large stratospheric ^{14}C inventories by bomb tests were noted by Hagemann *et al.* (1959). In the late 1950s, they observed ^{14}C concentrations of stratospheric CO_2 more than ten times the pre-bomb ground-level ^{14}C concentration. Much more ^{14}C must have been injected into the stratosphere during

the early 1960s than late 1950s, because larger-scale bomb tests were performed during the early 1960s at ground level. The bomb-produced ^{14}C may still exist in the stratosphere (more abundantly in the upper stratosphere) even though 30 years have passed since ground-level bomb tests ceased, if the stratosphere is not well mixed vertically. This explains qualitatively the difference in $\Delta^{14}\text{C}$ values between both spheres. It is not clear whether the weak stratospheric mixing hypothesis contradicts the CO_2 exchange time of 2.0 ± 0.5 years between lower stratosphere and troposphere, concluded by Nydal (1986).

As for the second possibility, the ratio of ^{14}C production by cosmic rays in the stratosphere to that in the troposphere is 1.6 (O'Brien 1979), and the ratio of the CO_2 content in the stratosphere to that in the troposphere is 0.24 (Junge 1963). Thus, the ratio of $^{14}\text{C}/^{12}\text{C}$ for stratospheric CO_2 to that of tropospheric CO_2 is expected to be 6.7, if each CO_2 box can be treated as a closed, internally well-mixed system. The observed $\Delta^{14}\text{C}$ values of stratospheric CO_2 are higher than those of tropospheric CO_2 , but much less than expected. This implies that the exchange of CO_2 between troposphere and stratosphere is not negligible, and also not large enough to produce the similar ^{14}C concentrations in both CO_2 boxes. This comparison between calculation and observation also supports the weak vertical mixing of stratospheric air.

At present, limited experimental data prevent us from choosing one possibility over the other for explaining the difference of the observed ^{14}C concentrations for stratospheric and tropospheric CO_2 .

Concerning the exchange of CO_2 between troposphere and stratosphere, Nakazawa *et al.* (1991) clearly observed a seasonal cycle of the CO_2 mixing ratio, as well as the definite annual increase of the ratio, in lower-stratospheric air, both of which were caused most probably by air transport from the troposphere, as there are no major CO_2 sources in the stratosphere. They considered two possibilities for this transport process, *i.e.*, vertical diffusion of tropospheric air through the tropopause, and upwelling of tropospheric air through cumulus convection near the Intertropical Convergence Zone (ITCZ) and the South Pacific Convergence Zone (SPCZ). The former possibility is considered to be minor, because the CO_2 mixing ratio of lower stratospheric air varies seasonally, out of phase with that of the upper troposphere.

In the upwelling process, upper tropospheric air with low ^{14}C concentration penetrates the tropopause and mixes with lower stratospheric air in the equatorial region. The mixed air in the lower stratosphere moves through the mid-latitudes towards the North and South Poles, with velocities dependent on altitude (*i.e.*, faster at lower altitudes), and returns to the troposphere at both poles (Nakazawa *et al.* 1991).

The $\Delta^{14}\text{C}$ value for stratospheric air sample, ST5, the lowest in altitude (18.6–20.1 km), is rather low (134‰) compared to the values of the upper air samples. The tropopause was at 16.7 km altitude on 1 September 1989. We monitored the air temperature with a thermosensor mounted on the sampling apparatus. Air sample ST5 may have originated from the mixture of stratospheric air and upwelling tropospheric air, as stated above. In fact, the mixing ratio of stratospheric CO_2 showed a prominent increase as the altitude decreased from 22 to 18 km (Fig. 2). Also, the mixing ratios of halocarbons decreased only slightly from their almost constant maximum values in the troposphere, up to an altitude of a few km above the tropopause, and decreased rapidly at higher altitudes (Makide *et al.* 1987). This also suggests that air sample ST5 is closely connected with upper tropospheric air.

$\Delta^{14}\text{C}$ values of tropospheric CO_2 vary more widely than statistical uncertainties, from 80 to 200‰, with an average value of 140 ± 5 ‰. The average value coincides with the $\Delta^{14}\text{C}$ values of 134 ± 5 ‰ (in 1988) and 130 ± 4 ‰ (in 1989) for new pine needles grown in the suburbs of Nagoya City

(Nakamura, Nakai & Furukawa 1990). ^{14}C depletion relative to the average may result from local CO_2 production by the burning of fossil fuel. High ^{14}C concentrations at 8.845 km altitude may be attributed to an intrusion of stratospheric air with high $\Delta^{14}\text{C}$ value into the troposphere, through the gap near the jet stream. This effect is especially important in the upper troposphere. The jet stream is located over Japan usually from October to June, and sometimes until July, when air samples, TR1 and TR2, were collected.

CONCLUDING REMARKS

$\Delta^{14}\text{C}$ values for stratospheric air ranged from 270 to 310‰ and increased slightly or remained nearly constant as the altitude increased, and were clearly higher than those for tropospheric air. Air from the lowest stratosphere level showed a lower $\Delta^{14}\text{C}$ value compared with other stratospheric $\Delta^{14}\text{C}$ values. Perhaps this is due to the latitudinal transport of stratospheric air, produced by upwelling of upper tropospheric air with low $\Delta^{14}\text{C}$ value and mixing with lower stratospheric air in the equatorial region.

The observation of higher ^{14}C concentrations ($^{14}\text{C}/^{12}\text{C}$) for stratospheric air than for tropospheric air is rather different from the trends of halocarbons, CH_4 and CO_2 concentrations, which decrease as the altitude increases from troposphere to stratosphere (Makide *et al.* 1987). The major sources of anthropogenic gases (halocarbons, CH_4 , CO_2) are in the troposphere. On the other hand, ^{14}C is produced steadily by cosmic rays both in the stratosphere and troposphere. Also, nuclear bomb tests have produced a large amount of ^{14}C in both spheres. We cannot draw definite conclusions concerning the sources of the observed difference in ^{14}C concentrations (higher in the stratosphere than troposphere) from the present limited experimental data. We plan to continue research to obtain the annual variations of $\Delta^{14}\text{C}$ values for stratospheric CO_2 .

The production rate of ^{14}C in the air by cosmic rays depends on latitude as well as altitude, and relates to the intensity of cosmic rays incident on the atmosphere. Observations of ^{14}C concentrations for stratospheric CO_2 at higher altitudes and several different latitudes, especially high and low latitudes, are necessary, together with long-term observations, to clarify the mechanism of air-mass movement and transport of chemical substances having low concentrations in the stratosphere and troposphere.

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