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Carbon dioxide variations in the stratosphere over Japan, Scandinavia and Antarctica

By S. AOKI[1]*, T. NAKAZAWA[1], T. MACHIDA[2], S. SUGAWARA[3], S. MORIMOTO[4], G. HASHIDA[4], T. YAMANOUCHI[4], K. KAWAMURA[1] and H. HONDA[5], [1]*Center for Atmospheric and Oceanic Studies, Tohoku University, Sendai 980-8578, Japan;* [2]*National Institute for Environmental Studies, Tsukuba 305-8506, Japan;* [3]*Faculty of Education, Miyagi University of Education, Sendai 980-0845, Japan;* [4]*National Institute of Polar Research, Tokyo 173-8515, Japan;* [5]*The Institute of Space and Astronautical Science, Sagamihara 229-8510, Japan*

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ABSTRACT

Systematic collections of stratospheric air samples have been conducted over Japan since 1985 using a balloon-borne cryogenic sampler. The collection of stratospheric air samples was also carried out twice over Scandinavia and once over Antarctica. Vertical profiles of CO_2 concentration thus obtained over these locations were quite similar to each other; CO_2 concentration decreased with increasing altitude in the lower stratosphere and reached an almost constant value in the mid-stratosphere. $\delta^{13}C$ of stratospheric CO_2 observed over these locations enriched with increasing altitude. A negative correlation between $\delta^{13}C$ and CO_2 concentration with $\Delta\delta^{13}C/\Delta CO_2$ of $-0.02‰$ ppmv^{-1} was found in the lower stratosphere. Although CO_2 concentration was almost constant in the mid-stratosphere, the $\delta^{13}C$ enrichment was observed in succession. $\delta^{18}O$ of stratospheric CO_2 also enriched with increasing altitude. The enrichment was significant; $\delta^{18}O$ was almost $0‰$ at the tropopause and reached a maximum value of about $11‰$ at a layer with N_2O concentration of about 10 ppbv. A compact relation between $\delta^{18}O$ and N_2O concentration was consistently observed for these locations. Stratosperic CO_2 over Japan showed a secular increase with an average rate of 1.4 ppmv yr^{-1} for the period 1985–2000. The secular increase was not constant with time, and temporal stagnation of the CO_2 increase was observed in 1997.

1. Introduction

In order to enhance our understanding of the global carbon cycle, a large number of CO_2 data have been collected in the troposphere by using ground-based stations, ships and aircraft (e.g. Keeling et al., 1995; Conway et al., 1994; Nakazawa et al., 1991a, b; Morimoto et al., 2000). On the other hand, a limited number of CO_2 data have been collected in the stratosphere by using balloons and aircraft (Bischof et al., 1985; Schmidt and Khedim, 1991; Nakazawa et al., 1995; Boering et al., 1996; Harnish et al., 1998; Ray et al., 1999; Strunk et al., 2000; Andrews et al., 2001a). Data obtained from aircraft indicated that a small but detectable seasonal CO_2 cycle was observable in the lowest stratosphere (Nakazawa et al., 1991b; Boering et al., 1996; Andrews et al., 1999). A secular increase of CO_2 concentration was also seen in the stratosphere (Bischof et al., 1985; Schmidt and Khedim, 1991; Nakazawa et al., 1995; Andrews et al., 2001a).

To understand the stratospheric CO_2 variations, knowledge of CO_2 sources and sinks in the upper atmosphere is required. There are two CO_2 sources in the stratosphere; one is carbon monoxide (CO) and the other is methane (CH_4). CO is rapidly oxidized to CO_2 in the lower stratosphere. Since the abundance is very small relative to CO_2, the source would

*Corresponding author.
e-mail: aoki@mail.cc.tohoku.ac.jp

contribute 0.1 ppmv at most. Oxidation of CH_4 is a larger CO_2 source and its strength increases with increasing height. However, the contribution adds positive offset of less than 1 ppmv to the CO_2 distribution even in the upper stratosphere (Hall and Prather, 1993). On the other hand there is no CO_2 sink in the stratosphere. In the upper mesosphere, above 80 km, CO_2 is photodissociated into CO and O. However, this process is not an irreversible sink for CO_2 because CO is chemically recycled back to CO_2 before the air returns to the stratosphere (Allen et al., 1981). Consequently, these sources and sinks of CO_2 in the upper atmosphere hardly affect stratospheric CO_2 variations.

Therefore, much of the stratospheric CO_2 variations are attributed to inflow of tropospheric air masses into the stratosphere. This feature implies that CO_2 is a very good tracer and it has been used to deduce stratospheric transport mechanisms (Hall and Prather, 1993; Bacmeister et al., 1998; Hall et al., 1999; Fleming et al., 1999; Andrews et al., 1999; 2001b; Jones et al., 2001).

Many people have believed that CO_2 gave no information about the stratospheric chemistry because it was a nonreactive gas in the stratosphere. In 1989, however, Gamo et al. (1989) found oxygen isotopic enrichment of stratospheric CO_2. To address those observations, Yung et al. (1991) constructed a kinetic model. They proposed that isotope exchange reaction involving $O(^1D)$ produced from O_3 photolysis could provide a mechanism for transfer of the stratospheric ^{18}O enrichment in ozone to CO_2. Thiemens et al. (1991) measured both ^{17}O and ^{18}O of stratospheric CO_2 and showed that the enrichment was mass-independent. Afterwards, stratospheric chemistry that relates oxygen isotopes in O_3–$O(^1D)$–CO_2 cycling has been investigated (Wen and Thiemens, 1993; Thiemens et al., 1995a, b; Yung et al., 1997; Barth and Zahn, 1997; Thiemens, 1999). It is known that the mass-independent enrichment in the stratospheric CO_2 occurs when CO_2 quenches $O(^1D)$ atoms formed by the photolysis of O_3, but the details of this process remain uncertain (Johnston et al., 2000).

For a better understanding of the concentration variations of stratospheric CO_2 and its isotopic compositions ($\delta^{13}C$ and $\delta^{18}O$), we have collected stratospheric air samples since 1985 using a cryogenic air sampler. In this paper, temporal and spatial variations of the CO_2 concentration, $\delta^{13}C$ and $\delta^{18}O$ in the stratosphere, obtained from our measurements, are presented and discussed.

2. Experimental procedures

We initiated the collection of stratospheric air samples in 1985 over Japan using a balloon-borne cryogenic sampler (Nakazawa et al., 1995) and the program has continued up to the present. The sampler was launched once a year from the Sanriku Balloon Center (39°10′N, 141°50′E) of the Institute of Space and Astronautical Science for the last 16 yr. In addition, stratospheric air samples were also collected over the Scandinavian Peninsula on 22 February and 18 March 1997 and over Antarctica on 3 January 1998 by launching the same sampler at the respective locations of ESRANGE, Kiruna (67°53′N, 21°06′E) and the Japanese Antarctic Station, Syowa (69°00′S, 39°35′E), to examine the behavior of stratospheric CO_2 in the polar regions. The locations of Sanriku, Kiruna and Syowa are shown in Fig. 1.

Since technical details of the air sampler used in this study have already been given elsewhere (Honda et al., 1996), only a brief description will be presented here. The sampler consisted mainly of 12 stainless-steel sample containers, a liquid helium dewar, motor-driven valves, a control unit and batteries. All these components were housed in an airtight aluminium chamber. The volume of each sample container was 760 mL. The sampler was equipped with external shock absorbers made of aluminium honeycomb to protect it from the shock at landing on the ground or the ice shelf when it was used for the collection of air samples at Kiruna and Syowa. On the other hand we did not use the shock absorbers for the sampler launched at Sanriku, because the sampler was recovered from the Pacific Ocean or the Japan Sea. The

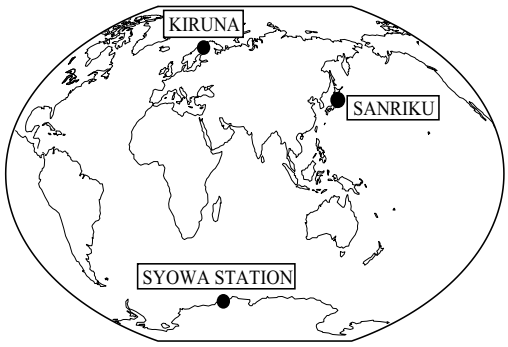

Fig. 1. Map showing the locations of Kiruna, Sanriku and Syowa Station, where the cryogenic sampler was launched to collect stratospheric air samples.

total weight of the sampler with and without the shock absorbers was 330 and 250 kg, respectively.

After recovery of the sampler, air samples were analyzed for concentrations and isotopic ratios of many constituents such as CO_2, CH_4, N_2O, H_2, SF_6 and halocarbons. The CO_2 concentration was measured by using a non-dispersive infrared (NDIR) analyzer with a precision of ± 0.01 ppmv. Standard gases used for the measurements were prepared by the gravimetric method. Uncertainties of the standard gases were almost ± 0.13 ppmv (Tanaka et al., 1983; Tanaka et al., 1987). Air samples were injected into the analyzer after removing water vapor with a water trap cooled at $-78\,^{\circ}$C. Each air sample was analyzed three times for its concentration, and the resulting values were averaged to attain high-quality measurements.

To measure δ^{13}C and δ^{18}O of CO_2, pure CO_2 was first extracted cryogenically from each air sample of 550 mL_{STP}. Its extraction procedures were the same as those described previously by Nakazawa et al. (1997a). The mass spectrometer used in this study was a Finnigan MAT-δS. The values of δ^{13}C and δ^{18}O are defined as relative isotope abundance ratios of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ with respect to those of the international standard, Vienna Peedee Belemnite (VPDB) (Allison et al., 1995). The external reproducibilities were estimated to be 0.02‰ and 0.05‰ (one standard deviation) for δ^{13}C and δ^{18}O, respectively (Nakazawa et al., 1993; 1997b).

We employed the mass-independent enrichment for ^{17}O and ^{18}O, which was found by Thiemens et al. (1991) in the stratosphere over the U.S.A., for calculating δ^{13}C and δ^{18}O from the measured mass ratios of 45/44 and 46/44, as described in Gamo et al. (1995). Correction factors of δ^{13}C and δ^{18}O for the presence of N_2O were determined experimentally, after Friedli and Siegenthaler (1988).

3. Results and discussion

Air sampling over Japan has been tried once a year since 1985, and we have succeeded in collecting air samples 11 times so far. Because of failure in launching or recovery of the sampler, we could not collect air samples in 1987, 1992 and 1993. In addition, we rejected CO_2 data obtained in 1996 and 1999 because of contamination due to instrumental troubles of the sampler. The air sampling was conducted only in late spring and early autumn when weak easterly winds prevailed in the stratosphere over Japan. This wind condition is necessary for ship recovery of the sampler near the coast of the northern part of the main island of Japan, because westerly winds usually prevail throughout the year in the troposphere over Japan.

Figure 2 shows vertical profiles of CO_2 concentration in the stratosphere over Japan. As seen in this figure, the CO_2 concentration in the stratosphere has been

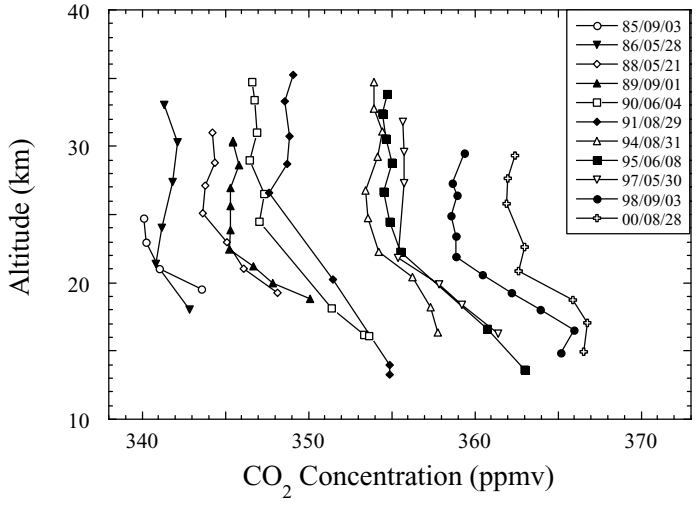

Fig. 2. Vertical profiles of CO_2 concentration in the stratosphere over Japan during the period 1985–2000.

increasing year by year. The cause is intrusion of tropospheric air into the stratosphere, because there is no stratospheric CO_2 source that can induce such a secular CO_2 increase. A major process of the CO_2 transport into the stratosphere is upwelling of tropospheric air by cumulus convection in the tropical region. Air enters the stratosphere, rises to higher altitudes, and then moves polewards at middle and high latitudes, eventually returning to the troposphere (Holton et al., 1995). Therefore, tropospheric CO_2 increase propagates into the stratosphere.

Another distinctive feature of the profiles is that the CO_2 concentration was high in the lowest part of the stratosphere and decreased rapidly with increasing altitude until the value became almost constant at heights above 20–25 km. The difference in CO_2 concentration between the middle and the lower stratosphere was 7–8 ppmv at most. The standard deviations of CO_2 concentration over 20–25 km for the respective profiles were 0.2–0.5 ppmv. The characteristic profile implies that the meridional exchange of air is most rapid near the tropopause and that it decreases with increasing altitude. The fact that almost constant values of CO_2 concentration appeared at heights over 20–25 km is caused by a large-scale slow airmass mixing due to the Brewer–Dobson circulation. Consequently, the CO_2 profiles observed over Japan are formed basically by the height-dependent poleward transport of tropospheric air intruded into the stratosphere in the tropical region.

A similar CO_2 profile was obtained by Bischof et al. (1985) in the stratosphere over France using a balloon-borne cryogenic air sampler; the CO_2 concentration decreased by about 7 ppmv from the tropopause to the layer above 20–22 km, where CO_2 was almost constant. Schmidt and Khedim (1991) and Harnish et al. (1998) also obtained CO_2 profiles over France, Sweden and India. Their profiles over France and India were quite similar to ours obtained over Japan. However, their profiles over Sweden were somewhat different; a larger variability was observed even in the mid-stratosphere.

Boering et al. (1994) showed the compact correlations between mixing ratios for stratospheric CO_2 and N_2O at heights below 21 km. In order to identify whether our data also indicate a similar correlation or not, CO_2 concentrations obtained over Japan were plotted in Fig. 3 as a function of N_2O concentration. Because N_2O concentrations have been measured since 1991, only six profiles were available. As seen in Fig. 3, CO_2 correlated positively with N_2O in the lower stratosphere, where N_2O was higher than 150 ppbv. The correlation curves between CO_2 and N_2O were not linear but rather quadratic. These features are quite similar to those obtained by Boering et al. (1996). We also collected air samples from higher altitudes. In the mid-stratosphere, where N_2O was lower than 150 ppbv, the positive correlation was hardly observable and the CO_2 concentration was almost constant for the respective profiles.

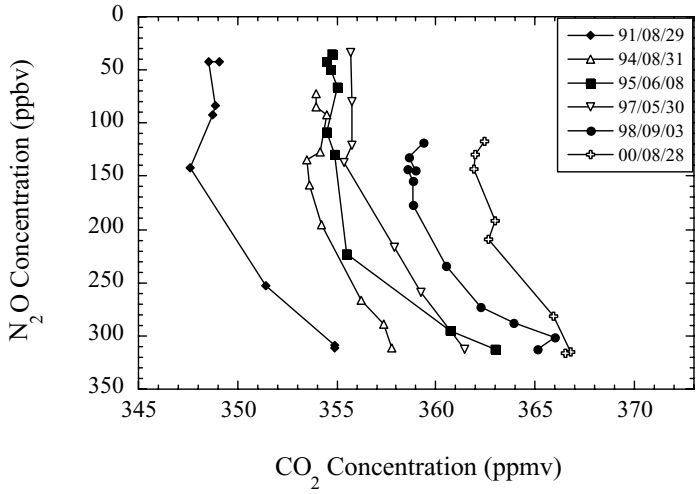

Fig. 3. Profiles of CO_2 concentration observed in the stratosphere over Japan plotted against N_2O concentration.

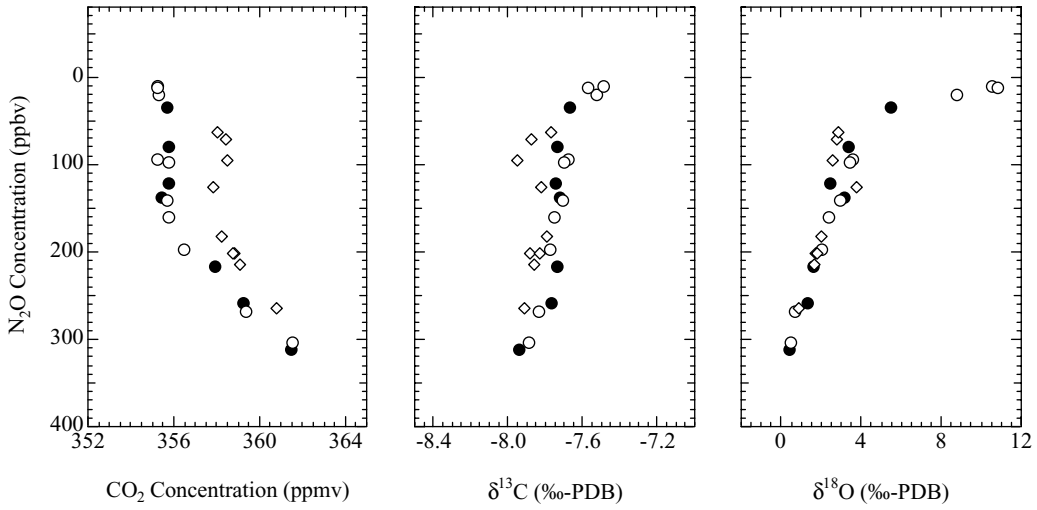

Fig. 4. Vertical profiles of CO_2 concentration, $\delta^{13}C$ and $\delta^{18}O$ observed in the stratosphere over Japan on 30 May 1997 (solid circles), Scandinavia on 18 March 1997 (open circles) and Antarctica on 3 January 1998 (open squares).

The shape of the correlation curves obtained over Japan resembled each other. However, the shape was not necessarily identical because a larger variability can be found in the lower stratosphere. The cause was probably spatial variations of tropospheric CO_2 in the northern and southern hemispheres and complex mixing of lower stratospheric air originating from the tropical and mid-latitudinal troposphere. In addition, the seasonal CO_2 cycle also propagated from the troposphere. Boering et al. (1996) found that the propagation of the seasonal CO_2 cycle made a maximum CO_2 peak in the stratosphere at a layer where the N_2O concentration was almost 300 ppbv in October and November. This CO_2 maximum was seen in our profile obtained on 3 September 1998 at a height where the N_2O concentration was 301 ppbv. A portion of such a CO_2 peak was also seen in profiles obtained on 31 August 1994 and 28 August 2000.

Figure 4 shows the CO_2 concentration and $\delta^{13}C$ and $\delta^{18}O$ plotted against the N_2O concentration observed over Japan on 30 May 1997, over Scandinavia on 18 March 1997 and over Antarctica on 3 January 1998. It should be noted that these data were obtained in different latitudes and seasons. Air samples over Scandinavia were collected in the polar vortex. Air samples over Antarctica were collected after breakdown of the polar vortex, since the last sudden warming of the season occurred at the beginning of November 1997. In order to compare stratospheric CO_2 data obtained in the different situations directly, the N_2O concentration was used as a pseudo-vertical coordinate (see Boering et al. 1996). It is clearly seen in this figure that the observed vertical profiles of stratospheric CO_2 concentration were quite similar to each other, although air samples were collected at distant locations under quite different meteorological conditions. The CO_2 concentration decreased rapidly with increasing altitude where the N_2O concentration was higher than 150 ppbv and became almost constant at altitudes above the layer. Mean CO_2 values at the constant-concentration layer over Scandinavia, Japan and Antarctica were 355.6 ± 0.4, 356.0 ± 0.5 and 358.3 ± 0.4 ppmv, respectively. The difference in the respective mean values would be mainly attributable to the secular increase, as well as to the spatial variability the CO_2 concentration in the stratosphere.

$\delta^{13}C$ of stratospheric CO_2 observed over Scandinavia, Japan and Antarctica increased with increasing altitude, showing small irregular variations. A negative correlation between CO_2 concentration and $\delta^{13}C$ was found in the lower stratosphere, where the N_2O concentration was higher than 150 ppbv. A mean value of $\Delta\delta^{13}C/\Delta CO_2$ calculated from these two variables obtained in the lower stratosphere was $-0.02‰\,\mathrm{ppmv}^{-1}$. In the troposphere, the CO_2 concentration and $\delta^{13}C$ have been increasing and decreasing, respectively, due to fossil-fuel combustion and deforestation (Keeling et al., 1995; Francy et al., 1995; Morimoto et al., 2000). From our aircraft measurements over Japan and shipboard measurements in the western Pacific region

(Nakazawa et al., 1993; 1997a), the changing rate of $\delta^{13}C$ relative to the CO_2 concentration with respect to their secular components was found to be $-0.02‰$ ppmv^{-1}. This quantitative agreement of $\Delta\delta^{13}C/\Delta CO_2$ indicates that the vertical profiles of CO_2 concentration and $\delta^{13}C$ observed in the lower stratosphere over Japan, Scandinavia and Antarctica were thought to be formed by the height-dependent poleward transport of tropospheric air intruded into the stratosphere in the tropical region.

As mentioned above, the CO_2 concentration was almost constant at the mid-stratosphere, where the N_2O concentration was lower than 150 ppbv, while $\delta^{13}C$ enriched with increasing altitude, especially over Scandinavia and Japan. In the stratosphere, CO_2 is produced by oxidation of CH_4, by which its concentration decreased rapidly with height, but the $\delta^{13}C$ values of CO_2 thus produced are expected to be much lower than those of atmospheric CO_2 (Sugawara et al., 1997). Therefore, this process would not be effective for explaining the observed profiles of $\delta^{13}C$ of CO_2. Another possible cause may be related to the isotopic enrichments of $\delta^{17}O$ and $\delta^{18}O$ in the stratosphere. Thiemens et al. (1991) discovered mass-independent enrichment in both ^{17}O and ^{18}O for stratospheric CO_2 over the U.S.A.: $\Delta\delta^{18}O \times \Delta\delta^{17}O$, where $\Delta\delta = \delta$(stratosphere) $-$ δ(troposphere). To obtain $\delta^{13}C$, we applied this mass-independent effect of $\Delta\delta^{18}O = \Delta\delta^{17}O$. Assuming that the enrichment of ^{17}O is larger than that of ^{18}O in the mid-stratosphere, the $\delta^{13}C$ increase with height could be reduced or cancelled. To interpret the observed $\delta^{13}C$ profiles, further studies are required.

$\delta^{18}O$ of stratospheric CO_2 observed over Japan, Scandinavia and Antarctica became enriched significantly with increasing altitude. Such a large enrichment of $\delta^{18}O$ was first pointed out by Gamo et al. (1989) from their measurements in the stratosphere over Japan and then confirmed by Thiemens et al. (1991) over the U.S.A. From our measurements, it is obvious that a similar phenomenon also occurred in the stratosphere in northern and southern high latitudes. The rapid increase of $\delta^{18}O$ with height is thought to be due to exchange of isotopically heavy oxygen between CO_2 and O_3 through O_3–$O(^1D)$–CO_2 cycling (Yung et al., 1991, Wen and Thiemens, 1993; Thiemens et al., 1995a, b; Yung et al., 1997; Barth and Zahn, 1997; Thiemens, 1999). $\delta^{18}O$ was almost $0‰$ at the tropopause and increased slowly with increasing altitude up to a layer where N_2O concentration was about 50 ppbv. Above the layer, $\delta^{18}O$ increased rapidly to the maximum value of about $11‰$ with a N_2O concentration of about 10 ppbv. From this figure, the compact correlation is also clearly seen between $\delta^{18}O$ and N_2O concentration.

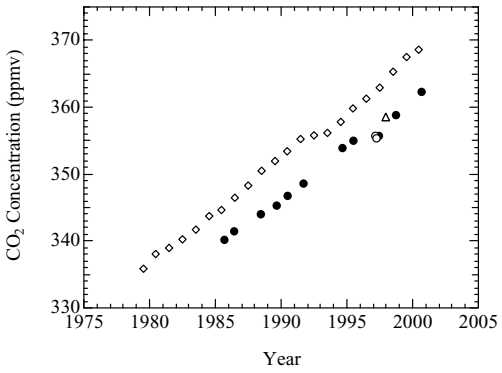

Fig. 5. Average values of stratospheric CO_2 concentration at heights above 15–25 km over Japan (solid circles), Scandinavia (open circles) and Antarctica (open triangle). Yearly mean concentrations of upper tropospheric CO_2 over Japan are also shown by open diamonds.

As seen in Fig. 2, the CO_2 concentration measured over Japan increased year by year, especially at heights above 20–25 km where the N_2O concentration was lower than 200–150 ppbv. To estimate an average rate of the secular CO_2 increase, CO_2 concentrations above 20–25 km for each year were simply averaged. The values thus obtained are plotted in Fig. 5, together with annual mean CO_2 concentrations observed by our aircraft measurements at altitudes between 8 km and the tropopause over Japan. The rate of secular increase was found to be 1.4 ppmv yr^{-1} applying a linear equation to the averaged values by using the least-squares fit technique. This rate was comparable with that of 1.5 ppmv yr^{-1} obtained by our aircraft measurements in the upper troposphere for the same period.

The mean values of CO_2 concentration in the stratosphere above 20–25 km were lower by about 4–8 ppmv than those obtained at the uppermost troposphere with an average difference of 5.9 ppmv. These concentration differences suggest that the mid-stratospheric air over Japan was older by about 3–5 yr than the upper tropospheric air, considering that the CO_2 increase in the stratosphere was induced by intrusion of tropospheric air with an annual increase of 1.5 ppmv yr^{-1}. This delay time corresponds to the average mixing time of the transport processes that mix tropospheric air into the middle stratosphere. This delay was also supported by the Pinatubo anomaly. As seen in Fig. 5,

the secular increase of tropospheric CO_2 stagnated temporarily for a few years after the eruption of Mt. Pinatubo, in the Philippines in June 1991. Such a stagnation was also seen in the stratospheric CO_2 in 1997.

Andrews et al. (2001a) observed the CO_2 mixing ratio on the 215 ppbv N_2O isopleth for 1992–1998 using the ER-2. Their data increased linearly with time and did not show such stagnation. A major difference between their and our experimental conditions was sampling altitudes. However, it is difficult to explain the cause of the discrepancy because our samples were obtained from higher altitudes.

The mean CO_2 concentrations in the mid-stratosphere over Scandinavia and Antarctica are also plotted in Fig. 5. These values agreed quite well with those expected from their contiguous data over Japan; this suggests that the spatial variability of CO_2 concentration in the mid-stratosphere was quite small for northern middle, northern high and southern high latitudes.

4. Summary

(1) Vertical profiles of CO_2 concentration in the stratosphere over Japan, Scandinavia and Antarctica were quite similar; the CO_2 concentration decreased with increasing altitude in the lower stratosphere, where the N_2O concentration was higher than 150 ppbv and reached almost constant values in the middle stratosphere, where the N_2O concentration was lower than 150 ppbv.

(2) $\delta^{13}C$ of stratospheric CO_2 observed over Japan, Scandinavia and Antarctica increased with increasing altitude. A negative correlation between CO_2 concentration and $\delta^{13}C$ with $\Delta\delta^{13}C/\Delta CO_2$ of $-0.02‰$ $ppmv^{-1}$ was found in the lower stratosphere, where the N_2O concentration was higher than 150 ppbv. On the other hand, $\delta^{13}C$ enriched with increasing altitude even at mid-stratosphere, where the N_2O concentration was lower than 150 ppbv, while the CO_2 concentration was almost constant.

(3) $\delta^{18}O$ of stratospheric CO_2 observed over Japan, Scandinavia and Antarctica increased significantly with increasing altitude. A compact relation between $\delta^{18}O$ and N_2O concentration was consistently observed for all locations.

(4) Stratosperic CO_2 over Japan showed a secular increase, with an average rate of 1.4 ppmv yr^{-1} for the period 1985–2000. The CO_2 concentration in the mid-stratosphere was lower by about 4–8 ppmv than that of the upper troposphere, with an average of 5.9 ppmv. These concentration differences suggest that the mid-stratospheric air over Japan is "older" by about 3–5 yr than the upper tropospheric air.

5. Acknowledgments

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REFERENCES

Allen, M., Yung, Y. L. and Waters, J. W. 1981. Vertical transport and photochemistry in the terrestrial mesosphere and lower thermosphere (50–120 km). *J. Geophys. Res.* **86**, 3617–3627.

Allison, C. E., Francy, R. J. and Meijer, H. A. J. 1995. Recommendations for the reporting of stable isotope measurements of carbon and oxygen in CO_2 gas. In: *References and intercomparison materials for stable isotopes of light elements*, Int. Atomic Energy Agency, Vienna. 155–162

Andrews, A. E., Boering, K. A., Daube, B. C., Wofsy, S. C., Hintsa, E. J., Weinstock, E. M. and Bui, T. P. 1999. Empirical age spectra for the lower tropical stratosphere from in situ observations of CO_2: Imprications for stratospheric transport. *J. Geophys. Res.* **104**, 26 581–26 595.

Andrews, A. E., Boering, K. A., Daube, B. C., Wofsy, S. C., Loewenstein, M., Jost, H., Podorske, J. R., Webster, C. R., Herman, R. L., Scott, D. C., Flesch, G. J., Moyer, E. J., Elkins, J. W., Dutton, G. S., Hurst, D. F., Moore, F. L., Ray, E. A., Romashkin, P. A. and Strahan, S. E., 2001a. Mean age of stratospheric air derived from in situ observations of CO_2, CH_4, and N_2O. *J. Geophys. Res.* **106**, 32 295–32 314.

Andrews, A. E., Boering, K. A., Wofsy, S. C., Daube, B. C., Jones, D. B., Alex, S., Loewenstein, M., Podorske, J. R. and Strahan, S. E. 2001b. Empirical age spectra for the midlatitude lower stratosphere from in situ observations of CO_2: Quantitative evidence for a subtropical "barrier" to horizontal transport. *J. Geophys. Res.* **106**, 10 257–10 274.

Bacmeister, J. T., Siskind, D. E. and Summers, M. E. 1998. Age of air in a zonally averaged two-dimensional model. *J. Geophys. Res.* **103**, 11 263–11 288.

Barth, V. and Zahn, A. 1997. Oxygen isotope composition of carbon dioxide in the middle atmosphere. *J. Geophys. Res*. **102**, 12 995–13 007.

Bischof, W., Borchers, R., Fabian, P. and Kruger, B. C. 1985. Increased concentration and vertical distribution of carbon dioxide in the stratosphere. *Nature* **316**, 708–710.

Boering, K. A., Daube, Jr. B. C., Wofsy, S. C., Loewenstein, M., Podolske, J. R. and Keim, E. R. 1994. Tracer-tracer relationships and lower stratospheric dynamics: CO_2 and N_2O correlations during SPADE. *Geophys. Res. Lett*. **21**, 2567–2570.

Boering, K. A., Wofsy, S. C., Daube, Jr. B. C., Schneider, H. R., Loewenstein, M., Podolske, J. R. and Conway, T. J. 1996. Stratospheric mean ages and transport rates from observations of carbon dioxide and nitrous oxide. *Science* **274**, 1340–1343.

Conway, T. J., Tans, P. P., Waterman, L. S., Thoning, K. W., Kitzis, D. R., Masarie, K. A. and Zhang, N. 1994. Evidence for interannual variability of the carbon cycle from the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory global air sampling network. *J. Geophys. Res*. **99**, 22 831–22 855.

Fleming, E. L., Jackman, C. H., Stolarski, R. S. and Considine, D. B. 1999. Simulation of stratospheric tracers using an improved empirically based two-dimensional model transport formulation. *J. Geophys. Res*. **104**, 23 911–23 934.

Francy, R. J., Tans, P. P., Allison, C. E., Enting, I. G., White, J. W. C. and Trolier, M. 1995. Changes in oceanic and terrestrial carbon uptake since 1982. *Nature* **373**, 326–330.

Friedli, H. and Siegenthaler, U. 1988. Influence of N_2O on isotope analyses in CO_2 and mass-spectrometric determination of N_2O in air samples. *Tellus* **40B**, 129–133.

Gamo, T., Tsutsumi, M., Sakai, H., Nakazawa, T., Tanaka, M., Honda, H., Kubo, H. and Itoh, T. 1989. Carbon and oxygen isotopic ratios of carbon dioxide a stratospheric profile over Japan. *Tellus* **41B**, 127–133.

Gamo, T., Tsutsumi, M., Sakai, H., Nakazawa, T., Machida, T., Honda H. and Itoh, T. 1995. Long-term monitoring of carbon and oxygen isotope ratios of stratospheric CO_2 over Japan. *Geophys. Res. Lett*. **22**, 397–400.

Hall, T M. and Prather, M. J. 1993. Simulations of the trend and annula cycle in stratospheric CO_2. *J. Geophys. Res*. **98**, 10 573–10 581.

Hall, T. M., Waugh, D. W., Boering, K. A. and Plumb, R. A. 1999. Evaluation of transport in stratospheric models. *J. Geophys. Res*. **104**, 18 815–18 839.

Harnish, J., Bishof, W., Borchers, R., Fabian, P. and Maiss, M., 1998. A stratospheric excess of CO_2 – due to tropical deep convection? *Geophys. Res. Lett*. **25**, 63–66.

Holton, J. R., Haynes, P. H., McIntyre, M. E., Douglas, A. R., Rood, R. B. and Pfister, L. 1995. Stratosphere–troposphere exchange. *Rev. Geophys*. **33**, 405–439.

Honda, H., Aoki, S., Nakazawa, T., Morimoto, S. and Yajima, N. 1996. Cryogenic air sampling system for measurements of the concentrations of stratospheric trace gases and their isotopic ratios over Antarctica. *J. Geomag. Geoelectr*. **48**, 1145–1155.

Johnston, J. C., Röckmann, T. and Brenninkmeijer, C. A. M. 2000. $CO_2 + O(^1D)$ isotopic exchange: laboratory and modeling studies. *J. Geophys. Res*. **105**, 15 213–15 229.

Jones, D. B. A., Andrews, A. E., Schneider, H. R. and McElroy, M. B. 2001. Constraints on meridional transport in the stratosphere imposed by the mean age of air in the lower stratosphere. *J. Geophys. Res*. **106**, 10 243–10 256.

Keeling, C. D., Whorf, T. P., Wahlen, M. and van der Plicht, J. 1995. Interannual extremes in the rate of rise of atmospheric carbon dioxide since 1980. *Nature* **375**, 666–670.

Morimoto, S., Nakazawa, T., Higuchi, K. and Aoki, S. 2000. Latitudinal distribution of atmospheric CO_2 sources and sinks inferred by $\delta^{13}C$ measurements from 1985 to 1991. *J. Geophys. Res*. **105**, 24 315–24 326.

Nakazawa, T., Aoki, S., Murayama, S., Fukabori, M., Yamanouchi, T., Murayama, H., Shiobara, M., Hashida, G., Kawaguchi, S. and Tanaka, M. 1991a. The concentration of atmospheric carbon dioxide at the Japanese Antarctic Station, Syowa. *Tellus* **43B**, 126–135.

Nakazawa, T., Miyashita, K., Aoki, S. and Tanaka, M. 1991b. Temporal and spatial variations of upper tropospheric and lower stratospheric carbon dioxide. *Tellus* **43B**, 106–117.

Nakazawa, T., Morimoto, S., Aoki, S. and Tanaka, M. 1993. Time and space variations of the carbon isotopic ratio of tropospheric carbon dioxide over Japan. *Tellus* **45B**, 258–274.

Nakazawa, T., Machida, T., Sugawara, S., Murayama, S., Morimoto, S., Hashida, G., Honda, H. and Itoh, T. 1995. Measurements of the stratospheric carbon dioxide concentration over Japan using a balloon-borne cryogenic sampler. *Geophys. Res. Lett*. **22**, 1229–1232.

Nakazawa, T., Morimoto, S., Aoki, S. and Tanaka, M. 1997a. Temporal and spatial variations of the carbon isotopic ratio of atmospheric carbon dioxide in the western Pacific region. *J. Geophys. Res*. **102**, 1271–1285.

Nakazawa, T., Murayama, S., Toi, M., Ishizawa, M., Otonashi, K., Aoki, S. and Yamamoto, S. 1997b. Temporal variations of the CO_2 concentration and its carbon and oxygen isotopic ratios in a temperate forest in the central part of the main island of Japan. *Tellus* **49B**, 364–381.

Ray, E. A., Moore, F. L., Elkins, J. W., Dutton, G. S., Fahey, D. W., Vömel, H., Oltmans, S. J. and Rosenlof, K. H. 1999. Transport into the northern hemisphere lowermost stratosphere revealld by in situ tracer measurements. *J. Geophys. Res*. **104**, 26 565–26 580.

Schmidt, U. and Khedim, A. 1991. In situ measurements of carbon dioxide in the winter arctic vortex and at midlatitudes: an indicator of the age of stratospheric air. *Geophys. Res. Lett*. **18**, 763–766.

Strunk, M., Engel, A., Schmidt, U., Volk, C. M. and Wetter, T. 2000. CO_2 and SF_6 as stratospheric age tracers: consistency and the effect of mesospheric SF_6-loss. *Geophys. Res. Lett*. **27**, 341–344.

Sugawara, S., Nakazawa, T., Shirakawa, Y., Kawamura, K., Aoki, S., Machida, T. and Honda, H. 1997. Vertical profile of the carbon isotopic ratio of stratospheric methane over Japan. *Geophys. Res. Lett*. **24**, 2989–2992.

Tanaka, M., Nakazawa, T. and Aoki, S. 1983. High quality measurements of the concentration of atmospheric carbon dioxide. *J. Meteorol. Soc. Jpn.* **61**, 678–685.

Tanaka, M., Nakazawa, T., Shiobara, M., Ohshima, H., Aoki, S., Kawaguchi S. and Yamanouchi, T. 1987. Variations of atmospheric carbon dioxide concentration at Syowa Station (69°00′S, 39°35′E), Antarctica. *Tellus* **39B**, 72–79.

Thiemens, M. H. 1999. Mass-independent isotope effects in planetary atmospheres and the early solar system. *Science* **283**, 341–345.

Thiemens, M. H., Jackson, T., Mauersberger, K., Schueler, B. and Morton, J. 1991. Oxygen isotope fractionation in stratospheric CO_2. *Geophys. Res. Lett*. **18**, 669–672.

Thiemens, M. H., Jackson, T. L. and Brenninkmeijer, C. A. M. 1995a. Observation of a mass independent oxygen isotopic composition in terrestrial stratospheric CO_2, the link to ozone chemistry, and the possible occurrence in the Martian atmosphere. *Geophys. Res. Lett*. **22**, 255–257.

Thiemens, M. H., Jackson, T., Zipf, E. C., Erdman, P. W. and van Egmond C. 1995b. Carbon dioxide and oxygen isotope anomalies in the mesosphere and stratosphere. *Science* **270**, 969–972.

Wen, J. and Thiemens, M. H. 1993. Multi-isotope study of the $O(^1D) + CO_2$ exchange and stratospheric consequences. *J. Geophys. Res*. **98**, 12 801–12 808.

Yung, Y. L., DeMore, W. B. and Pinto, J. P. 1991. Isotope exchange between carbon dioxide and ozone via $O(^1D)$ in the stratosphere. *Geophys. Res. Lett*. **18**, 13–16.

Yung, Y. L., Lee, A. Y. T., Irion, F. W., DeMore, W. B. and Wen, J. 1997. Carbon dioxide in the atmosphere: Isotopic exchange with ozone and its use as a tracer in the middle atmosphere. *J. Geophys. Res*. **102**, 10 857–10 866.