



Stratospheric $\delta^{13}\text{CO}_2$ observed over Japan and its governing processes and potential as an air age tracer

Satoshi Sugawara¹, Shinji Morimoto², Shigeyuki Ishidoya³, Taku Umezawa^{4,2},

5 Shuji Aoki², Takakiyo Nakazawa², Sakae Toyoda⁵, Kentaro Ishijima⁶,

Daisuke Goto⁷, and Hideyuki Honda²

¹Miyagi University of Education, Sendai 980-0845, Japan

²Center for Atmospheric and Oceanic Studies, Tohoku University, Sendai 980-8578, Japan

10 ³National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8569, Japan

⁴National Institute for Environmental Studies, Tsukuba 305-8506, Japan

⁵Institute of Science Tokyo, Yokohama 226-8503, Japan

⁶Meteorological Research Institute, Japan Meteorological Agency, Tsukuba 305-0052, Japan

⁷National Institute of Polar Research, Tachikawa 190-8518, Japan

15 *Correspondence to:* Satoshi Sugawara (sugawara@staff.miyakyo-u.ac.jp)

Abstract. Due to very few reports of $\delta^{13}\text{CO}_2$ (the stable carbon isotopic ratio of CO_2) observations in the stratosphere, its variations are not well understood. In order to elucidate stratospheric $\delta^{13}\text{CO}_2$ variations and their governing mechanisms, and to investigate usefulness of $\delta^{13}\text{CO}_2$ as an air age tracer, we have collected stratospheric air samples using balloon-borne cryogenic samplers over Japan since 1985 and analyzed them for $\delta^{13}\text{CO}_2$. To obtain precise $\delta^{13}\text{CO}_2$ values, we incorporated the mass-independent fractionation of ^{17}O and ^{18}O in the $\delta^{13}\text{CO}_2$ calculation. $\delta^{13}\text{CO}_2$ has decreased through time in the mid-stratosphere with an average rate of change of $-0.026 \pm 0.001 \text{ ‰ yr}^{-1}$ for the period 1985–2020, consistent with that in the troposphere. However, mid-stratospheric $\delta^{13}\text{CO}_2$ values did not show a time delay compared to the tropical tropospheric values. This could be explained by the production of CO_2 by CH_4 oxidation and the gravitational separation of $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$. To confirm this hypothesis, we used a two-dimensional model to simulate the stratospheric $\delta^{13}\text{CO}_2$ values while accounting for these processes. The results indicate that these two effects strongly impact the vertical distribution of $\delta^{13}\text{CO}_2$. We newly defined ‘stratospheric potential $\delta^{13}\text{C}$ ’ ($\delta^{13}\text{C}_\text{p}$) as a quasi-conservative parameter incorporating the kinetic isotope effect of CH_4 oxidation and gravitational separation, and we used it to estimate the mean age of stratospheric air. Despite large uncertainties, the mean age derived from $\delta^{13}\text{C}_\text{p}$ was consistent with that derived from the CO_2 mole fraction, suggesting its usefulness for further investigation of stratospheric transport processes.

1 Introduction

The isotopic ratio of carbon in CO_2 (here, we use ‘ $\delta^{13}\text{CO}_2$ ’ to distinguish it from that in CH_4 , ‘ $\delta^{13}\text{CH}_4$ ’) is thought to provide information on the carbon cycle, and observations have been carried out mainly using ground stations, ships, and aircraft in the troposphere (e.g. Keeling et al., 1995; Francey et al., 1995; Nakazawa et al., 1993; Morimoto et al., 2000).



35 However, there have been very few reports of $\delta^{13}\text{CO}_2$ observations in the mid-stratosphere, mainly because of the
difficulty in collecting air samples at such altitudes; the only available reports are balloon observations over Japan and
Scandinavia (Gamo et al., 1995; Aoki et al., 2003). It is well known that tropospheric $\delta^{13}\text{CO}_2$ values have decreased with
time due to anthropogenic emissions with low $\delta^{13}\text{CO}_2$ values resulting from fossil fuel consumption. Gamo et al. (1995)
have reported that $\delta^{13}\text{CO}_2$ values observed in the mid-stratosphere were higher than those in the troposphere over the
40 same period and that the average stratospheric $\delta^{13}\text{CO}_2$ value during 1986–1992 was about -7.5‰ and decreasing with
time. Aoki et al. (2003) have reported that the mid-stratosphere (25–32 km altitude) $\delta^{13}\text{CO}_2$ value over Japan in 1997 was
approximately -7.7‰ ; this value is consistent with the expected value extrapolated from the results of Gamo et al. (1995),
suggesting that their estimated secular decreasing trend is plausible.

Anomalous ^{18}O enrichment in stratospheric CO_2 was first reported in balloon observations (Gamo et al., 1989),
45 which spurred extended studies of the mass-independent isotopic effect (MIE) on the triple oxygen isotope system (e.g.
Thiemens, 1999; Kawagucci et al., 2008). These MIE studies have clarified that the relationship between ^{17}O and ^{18}O
enrichment in stratospheric CO_2 is quite different from that in the troposphere. This fact is very important for stratospheric
 $\delta^{13}\text{CO}_2$ measurements because mass spectrometry measures the ratios $^{45}\text{CO}_2/^{44}\text{CO}_2$ and $^{46}\text{CO}_2/^{44}\text{CO}_2$, and an assumed
relationship between ^{17}O and ^{18}O enrichment is needed to calculate $\delta^{13}\text{CO}_2$. The influence of the MIE on oxygen in
50 stratospheric $\delta^{13}\text{CO}_2$ has not been taken into account in previous studies. Although Aoki et al. (2003) have found that
 $\delta^{13}\text{CO}_2$ values increase with increasing altitude in the stratosphere over Japan and have suggested that the MIE on ^{17}O
and ^{18}O should be considered when interpreting such a vertical distribution, no quantitative investigation of these factors
has been conducted.

Stratospheric methane (CH_4) is destroyed by reactions with hydroxyl (OH), excited singlet oxygen ($\text{O}(^1\text{D})$),
55 and chlorine (Cl) radicals, and thus plays an important role in stratospheric chemistry. However, the quantitative
contributions of these chemical processes to CH_4 loss and their temporal variations remain poorly understood. It is thought
that $\delta^{13}\text{CH}_4$ provides useful information about CH_4 destruction in the stratosphere because characteristic isotopic
fractionations occur in each reaction (e.g. Saueressig et al., 1995; Sugawara et al., 1997; Rice et al., 2003; Röckmann et
al., 2011). However, only a few measurements have been made so far in the mid-stratosphere, mainly due to the difficulty
60 of collecting air samples at such altitudes. Oxidation of CH_4 produces CO , which is eventually oxidized to CO_2 . In general,
the isotopic fractionations in the above reactions cause the faster destruction of $^{12}\text{CH}_4$ relative to $^{13}\text{CH}_4$, making the
chemical products depleted in ^{13}C (decreased $\delta^{13}\text{C}$) while the remaining CH_4 becomes enriched in ^{13}C (increased $\delta^{13}\text{CH}_4$).
Indeed, Brenninkmeijer et al. (1996) have found that CO in the lower Antarctic stratosphere is extremely depleted in ^{13}C
(decreased $\delta^{13}\text{CO}$) mainly because of the local production of CO via the reaction of CH_4 with Cl . Recently, Gromov et al.
65 (2018) and Röckmann et al. (2024) have discussed $\delta^{13}\text{CO}$ variations associated with the $\text{CH}_4 + \text{Cl}$ reaction. From these
studies, it is expected that the $\text{CH}_4\text{--CO--CO}_2$ chain reaction could be an airborne source of CO_2 with extremely low $\delta^{13}\text{C}$
values, depressing stratospheric $\delta^{13}\text{CO}_2$ values. However, no study has yet quantitatively assessed this effect.

The age of stratospheric air is the transit time of air from around the tropical tropopause to a certain location
in the stratosphere, which is a powerful tool for diagnosing stratospheric transport (see Garny et al., 2024 for a review of
70 the latest developments in air age studies). It is expected that possible changes to the Brewer–Dobson circulation induced



by climate change are detectable as long-term changes in the mean age of air. For this purpose, age tracers, such as mole fractions of CO₂ and SF₆, have been measured in air samples collected by scientific balloons and satellites (e.g. Engel et al., 2009, 2017; Stiller et al., 2012). CO₂ mole fractions observed in the mid-stratosphere over Japan have been combined with SF₆ data to provide the longest record of the mean age of air, as reported by Engel et al. (2009, 2017) and Ray et al. (2014). Engel et al. (2017) has reported that the mean age of air in the mid-stratosphere does not indicate a significant trend over the period 1975–2016, with only a slightly positive increase of $+0.15 \pm 0.18$ years decade⁻¹. However, recent models predict accelerating circulation throughout the stratosphere (e.g. Butchart, 2014), which will decrease the mean age of air. Such a decreasing trend is consistent with observational results in the lower stratosphere (Ray et al., 2014). Despite many efforts to elucidate the trend of age of air, a discrepancy remains between mid-stratosphere age trends in models and observations. One reason for this discrepancy is the large uncertainties on the observational trends. To resolve this problem, it is necessary to increase the frequency of high-altitude balloon observations and observe additional age tracers beyond CO₂ and SF₆. Perfluorocarbons and hydrofluorocarbons with extremely long lifetimes could be alternative age tracers (Leedham Elvidge et al., 2018; Laube et al., 2025; Umezawa et al., 2024), and observations of such multiple age tracers should reduce the uncertainties on mean age of air estimates.

The gravitational separation (hereafter, ‘GS’) of major atmospheric constituents in the stratosphere was first reported from balloon observations (Ishidoya et al., 2006, 2008a, 2008b, 2013). They showed that vertical gradients of the isotopic and elemental ratios of major atmospheric components (N₂, O₂, and Ar) in the stratosphere are caused by molecular diffusion and depend on molecular mass. Stratospheric GS has now been observed in polar and equatorial regions (Ishidoya et al., 2018; Sugawara et al., 2018) and reproduced in numerical models (Belikov et al., 2019; Birner et al., 2020). Alongside age of air, stratospheric GS can be used to diagnose stratospheric transport processes (Ishidoya et al., 2013; Sugawara et al., 2018; Birner et al., 2020). These findings also suggest that GS could affect the mole fractions and isotopic ratios of all stratospheric constituents, although no studies have addressed the impact of GS on stratospheric $\delta^{13}\text{CO}_2$ values.

The main objective of this study is to clarify the mechanisms governing $\delta^{13}\text{CO}_2$ variations in the stratosphere and understand the long-term variations. A comprehensive understanding of the variations of stratospheric $\delta^{13}\text{CO}_2$ requires that the MIE on oxygen, CH₄ oxidation and associated isotopic fractionation, mean age of air, and GS be considered. Balloon observations provide a unique opportunity to evaluate these effects by studying a variety of atmospheric constituents using high-precision measurements. In this study, we constructed a new $\delta^{13}\text{CO}_2$ record for the stratosphere over Japan spanning the 35 years from 1985 to 2020, primarily by newly analyzing archived CO₂ samples and in part by including previously published data (Gamo et al., 1995; Aoki et al. 2003). We then examined vertical and temporal variations in the record. Furthermore, we investigated in detail the various mechanisms affecting the vertical distribution of stratospheric $\delta^{13}\text{CO}_2$ and propose herein a new concept called ‘stratospheric potential $\delta^{13}\text{C}$ ’. We also investigated the possibility of estimating the age of stratospheric air from the $\delta^{13}\text{CO}_2$ record.

2 Experimental Procedures

2.1 Air sample collection



We have continuously collected stratospheric air samples over Japan since 1985 using balloon-borne cryogenic samplers (e.g. Nakazawa et al., 1995). A large scientific balloon equipped with a sampler was launched nearly once a year during 1985–2002 from the Sanriku Balloon Center (SBC; 39° 10' N, 141° 50' E). The frequency of observations has decreased since 2004, with the longest interval between observations being 5 years. During this period, the balloon launch site was relocated from SBC to the Taiki Aerospace Research Field in Hokkaido (TARF; 42° 30' N 143° 26' E) in 2008. Balloon observations conducted so far over Japan are summarized in Table S1 of the Supplement. The cryogenic air sampler consists mainly of a liquid helium dewar, stainless steel bottles, motor-driven valves, and a control unit (Honda et al., 1996). Liquid helium was used as a refrigerant for collecting stratospheric air cryogenically under low atmospheric pressures, and 20–30 L STP of stratospheric air was collected in each bottle, depending on the altitude and valve operation. Air sampling was performed typically at 11 different altitudes, spaced about 2 km apart, between 14 and 35 km altitude. Occasionally, anomalously low CO₂ mole fractions were observed, probably due to sample deterioration in the bottle. In such cases, both CO₂ mole fraction and $\delta^{13}\text{CO}_2$ data were excluded from the data record. In 2020, the CO₂ mole fraction and $\delta^{13}\text{CO}_2$ value at 28.8 and 30.9 km altitude were not available due to water contamination of the air samples.

2.2 Analytical methods of mole fractions and isotopic ratios

Collected air samples were distributed to several institutes in Japan for analysis of the mole fractions and isotopic compositions of various gases. The CO₂ mole fraction was measured using a nondispersive infrared gas analyzer at Tohoku University (TU) with an analytical precision of $<0.02 \mu\text{mol mol}^{-1}$; the CO₂ measurement protocol has been described in detail in previous studies (Nakazawa et al., 1995; Aoki et al., 2003; Sugawara et al., 2018). N₂O and CH₄ mole fractions were measured using gas chromatographs equipped with an electron capture detector and flame ionization detector, respectively, at TU. The N₂O mole fraction was used both for mass spectrometry analyses to determine $\delta^{13}\text{CO}_2$ and to investigate the MIE between ^{17}O and ^{18}O in CO₂, as described below. The analytical precisions for the N₂O and CH₄ mole fractions were $0.3 \text{ nmol mol}^{-1}$ and 3 nmol mol^{-1} , respectively (Nakazawa et al., 2002; Aoki et al., 2003; Ishijima et al., 2007).

The analytical procedures for $\delta^{13}\text{CO}_2$ in air samples collected after 1988 have already been described in previous studies (Nakazawa et al., 1993, 1997a; Morimoto et al., 2000, 2006), and is briefly summarized here. An aliquot of each air sample (about 550 mL STP) was introduced into a CO₂ extraction system, and the pure extracted CO₂ was divided and sealed in small glass tubes; some tubes were archived for future study. The carbon and oxygen isotopic ratios ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) of the sample CO₂ were measured using a mass spectrometer (Finnigan MAT-8S) installed at TU against an in-house reference CO₂ calibrated to Vienna Pee Dee Belemnite (VPDB). The analytical precision of $\delta^{13}\text{CO}_2$ was $\pm 0.02 \text{ ‰}$ (Morimoto et al., 2000). Air samples collected in 1985, 1986, 1988, and 1989 were analyzed for $\delta^{13}\text{CO}_2$ using a mass spectrometer (Finnigan MAT250) with a reproducibility of less than $\pm 0.02 \text{ ‰}$ at the University of Tokyo (Gamo et al., 1989, 1995).

In this study, we modified the calculation of isotopic ratios to take into account the stratospheric MIE and GS. Hereafter, the isotopic ratios of ^{13}C to ^{12}C , ^{17}O and ^{18}O to ^{16}O , and $^{45}\text{CO}_2$ and $^{46}\text{CO}_2$ to $^{44}\text{CO}_2$ are expressed as $^{13}R = n(^{13}\text{C})/n(^{12}\text{C})$, $^{17}R = n(^{17}\text{O})/n(^{16}\text{O})$, $^{18}R = n(^{18}\text{O})/n(^{16}\text{O})$, $^{45}R = n(^{45}\text{CO}_2)/n(^{44}\text{CO}_2)$, and $^{46}R = n(^{46}\text{CO}_2)/n(^{44}\text{CO}_2)$, respectively,



where n is the amount of each isotopologue. $\delta^{13}\text{CO}_2$ is defined as:

$$\delta^{13}\text{CO}_2 = \left(\frac{^{13}R}{^{13}R_{\text{VPDB}}} - 1 \right) \times 10^3 \text{ (‰)}, \quad (1)$$

145 where $^{13}R_{\text{VPDB}}$ is the known ^{13}R value of VPDB (Cowple and Shrestha, 2016). The isotopic ratios ^{45}R and ^{46}R are expressed as (Santrock et al., 1985):

$$^{45}R = ^{13}R + 2 \cdot ^{17}R, \quad (2a)$$

$$^{46}R = 2 \cdot ^{18}R + 2 \cdot ^{13}R \cdot ^{17}R + (^{17}R)^2. \quad (2b)$$

To calculate $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values from ^{45}R and ^{46}R , the relationship between ^{17}O and ^{18}O should be known, because $^{45}\text{CO}_2$ contains $^{12}\text{C}^{17}\text{O}^{16}\text{O}$, whereas $^{46}\text{CO}_2$ contains both $^{13}\text{C}^{17}\text{O}^{16}\text{O}$ and $^{12}\text{C}^{17}\text{O}_2$. The relationship between ^{17}R and ^{18}R can be expressed as (e.g. Meijer and Li, 1998) :

$$\frac{^{17}R}{^{17}R_{\text{VSMOW}}} = \left(\frac{^{18}R}{^{18}R_{\text{VSMOW}}} \right)^{\beta}, \quad (2c)$$

155 where $^{17}R_{\text{VSMOW}}$ and $^{18}R_{\text{VSMOW}}$ are the known ratios of VSMOW (Coplen and Shrestha, 2016). In measurements of tropospheric $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, the mass-dependent relationship between ^{17}O and ^{18}O can be assumed, i.e. $\beta = 0.528$ (Meijer and Li, 1998; Assonov and Brenninkmeijer, 2003). However, the MIE between ^{17}O and ^{18}O is non-negligible in the stratosphere (Gamo et al., 1995; Thieme et al., 1999). Therefore, the $\delta^{17}\text{O}$ value is essential for accurately determining the $\delta^{13}\text{C}$ value in the stratosphere. Our air samples were also measured for triple oxygen isotopes, as reported by Kawagucci et al. (2008). However, $\delta^{17}\text{O}$ measurements were not performed for all of our stratospheric samples. In such cases, the following method was applied to obtain $\delta^{17}\text{O}$ values. The values of ^{17}R and ^{18}R calculated from $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ observed by Kawagucci et al. (2008) were fitted to Eq. (2c), and the average value of β was calculated to be 1.7 ± 0.2 using the least squares method. For samples for which $\delta^{17}\text{O}$ was not analyzed, we used Eq. (2c) with this β value to calculate $\delta^{13}\text{C}$. By substituting Eqs. (2a) and (2c) into (2b), we obtained the following equation:

$$3(^{17}R)^2 - 2 \cdot ^{45}R \cdot ^{17}R - 2\gamma(^{17}R)^{\frac{1}{\beta}} + ^{46}R = 0, \quad (3a)$$

where, γ is defined as,

$$165 \quad \gamma = ^{18}R_{\text{VSMOW}}(^{17}R_{\text{VSMOW}})^{-\frac{1}{\beta}}. \quad (3b)$$

Eq. (3a) was solved for ^{17}R numerically using the bisection method and the measured ^{45}R and ^{46}R values, and then ^{13}R and $\delta^{13}\text{C}$ were calculated by Eqs. (2a) and (1), respectively. We note that GS occurs in CO_2 molecules with different mass numbers (44, 45, 46). Therefore, it is not accurate to correct $\delta^{13}\text{C}$ by assuming a mass number difference of uniquely $\Delta m = 1$. To obtain the correct $\delta^{13}\text{C}$ of stratospheric CO_2 , it is necessary to first apply the GS correction to the measured values of ^{45}R and ^{46}R , and then to calculate $\delta^{13}\text{C}$ using the method described above. The method used to correct ^{45}R and ^{46}R for GS will be discussed in Sect. 3.3.

The MIE calculation described above was not considered in Gamo et al. (1995) and Aoki et al. (2003), and it is therefore likely that their $\delta^{13}\text{C}$ values are not correct, especially at higher altitudes. $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in CO_2 increase rapidly with increasing altitude in the stratosphere (Gamo et al., 1995; Kawagucci et al., 2008), and the deviations from mass-dependent values also increase with altitude, meaning that the overestimation of $\delta^{13}\text{C}$ also increases with altitude. The influence of the oxygen MIE on $\delta^{13}\text{C}$ is almost zero near the tropopause, but at an altitude of about 35 km over Japan,



it is approximately 0.6 ‰. Therefore, this effect significantly impacts the vertical distributions of $\delta^{13}\text{C}$. We reanalyzed some of the CO_2 samples used by Gamo et al. (1995) and Aoki et al. (2003) to determine the differences between their results (not accounting for the oxygen MIE) and ours to allow us to correct their data and add them to our long-term record. The MIE on $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ occurs through photochemical reactions in O_2 , O_3 , and CO_2 (e.g. Thiemens et al., 1999), which are relatively tightly correlated with the mole fraction of N_2O , which is also destroyed through photochemical processes. Figure 1 shows the relationships between the N_2O mole fraction and $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in CO_2 in the stratosphere over Japan. These results show that $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values calculated using $\beta = 1.7$ are consistent with the values observed by Kawagucci et al. (2008).

While cryogenically extracting CO_2 from the air sample, N_2O was simultaneously trapped with the CO_2 . Because N_2O and CO_2 have the same mass number, we must correct for N_2O to obtain the true $\delta^{13}\text{C}$ value. The correction method was described in detail by Nakazawa et al. (1993), and we summarize it here. The ionization efficiency of N_2O was measured in advance, and the measured $\delta^{13}\text{C}$ value was corrected using the $\text{N}_2\text{O}/\text{CO}_2$ mole fraction ratio of the air sample. In the troposphere, the $\text{N}_2\text{O}/\text{CO}_2$ mole fraction ratio does not change significantly, and the N_2O correction is almost constant (approximately +0.2 ‰) (Nakazawa et al., 1997a). However, because the N_2O mole fraction decreases rapidly with increasing altitude in the stratosphere (e.g. Toyoda et al., 2001), the $\text{N}_2\text{O}/\text{CO}_2$ mole fraction ratio decreases with altitude, and the magnitude of the N_2O correction also varies vertically. Therefore, the N_2O correction also strongly influences the observed vertical distribution of $\delta^{13}\text{C}$ in the stratosphere.

Stratospheric air samples were also measured for $\delta^{13}\text{CH}_4$ using a gas chromatograph-combustion-isotope ratio spectrometer developed at the National Institute of Polar Research (NIPR), Japan. The method has been described in detail by Morimoto et al. (2006) and is briefly summarized here. Each air sample was flushed by pure helium, and the contained CH_4 was trapped in a HayeSep D trap at -120°C . Then, the CH_4 was released and transferred into a PoraBOND Q cryofocusing trap at -197°C . The CH_4 released from the trap when brought to room temperature was separated from the residual components using a PoraPLOT Q capillary column and combusted into CO_2 in a furnace with a Pt-Ni-Cu catalyst at 940°C . The converted CO_2 was analyzed using a continuous-flow mass spectrometer (Finnigan MAT252). The precision was reported to be 0.06 ‰ (Morimoto et al., 2006). Before 1996, $\delta^{13}\text{CH}_4$ measurements were performed using off-line oxidation equipment (Sugawara et al., 1997), in which CH_4 in the sample was converted to CO_2 using a catalyst (0.5% Pt supported on alumina pellets) at 750°C , and the pure CO_2 sample thusly prepared was analyzed using the mass spectrometer installed at TU in the same way as for $\delta^{13}\text{CO}_2$, except using a micro-volume inlet system. The overall analytical precision was 0.07 ‰ (Sugawara et al., 1997). To produce a high-quality data record, we needed to verify that these two methods produced the same results. Therefore, several sets of stratospheric air samples were analyzed using both methods, and the $\delta^{13}\text{CH}_4$ results differed by about 0.85 ‰. To correct for this difference, the off-line measurement results were adjusted to match the on-line measurements. In this study, $\delta^{13}\text{CH}_4$ value is reported relative to VPDB. The international comparison of $\delta^{13}\text{CH}_4$ measurements described in detail by Umezawa et al. (2018) revealed a difference of 0.2 ‰ between NIPR and the Institute of Arctic and Alpine Research (INSTAAR) results. Therefore, all $\delta^{13}\text{CH}_4$ values observed by National Oceanic and Atmospheric Administration Earth System Research Laboratories (NOAA/ESRL) and INSTAAR were shifted to match the NIPR scale.



The method used to analyze GS is described in Appendix A.

215 **3 Results and Discussion**

3.1 Vertical profiles of CO₂ mole fraction and $\delta^{13}\text{CO}_2$

Figure 2 shows vertical profiles of the CO₂ mole fraction and $\delta^{13}\text{CO}_2$ over Japan throughout the study period. CO₂ mole fractions and $\delta^{13}\text{CO}_2$ values have increased and decreased, respectively, from 1985 to 2020. Vertical $\delta^{13}\text{CO}_2$ profiles observed by Gamo et al. (1995) in 1985 and 1986 are included in this figure after MIE correction. Previous studies reported that the CO₂ mole fraction decreases with increasing altitude from the tropopause to around 20–25 km, and then it becomes almost constant at higher altitudes (Nakazawa et al., 1995, 2002). Our CO₂ mole fraction data show a similar vertical distribution during the observation period. Because our $\delta^{13}\text{CO}_2$ data are more scattered with respect to altitude than the CO₂ mole fraction, we calculated detrended vertical $\delta^{13}\text{CO}_2$ profiles as follows. First, the long-term trend of the tropospheric $\delta^{13}\text{CO}_2$ at Mauna Loa, Hawaii (hereafter, MLO) (White et al., 2024) was calculated as a representative tropospheric trend, and all our stratospheric $\delta^{13}\text{CO}_2$ observation data were shifted up or down based on that trend to produce values corresponding to August 2016 for comparison with the model results described below. Then, the $\delta^{13}\text{CO}_2$ values thusly obtained for the entire study period were grouped into eleven 2-km vertical bins, and the average value for each bin was calculated (Fig. 2c). The results showed that $\delta^{13}\text{CO}_2$ values increased with increasing altitude from near the tropopause to around 25 km and then decreased slightly above that altitude. Gamo et al. (1989) originally reported that $\delta^{13}\text{CO}_2$ values increased by approximately 0.4 ‰ from the tropopause to 25 km altitude in September 1985, whereas our recalculated results showed an increase of about 0.2 ‰ (Fig. 2b). The average increase shown in Fig. 2c was even smaller, only about 0.1 ‰. This difference between the vertical profiles originally reported by Gamo et al. (1989) and our present results is due to our incorporation of the MIE on ¹⁷O and ¹⁸O (Sect. 2.2).

Below an altitude of ~17 km, $\delta^{13}\text{CO}_2$ values are quite variable, often being irregularly high or low depending on the observation year, which is exhibited by the large error bars in Figure 2c. Based on detailed aircraft observations of $\delta^{13}\text{CO}_2$ variations in the troposphere over Japan, Nakazawa et al. (1993) have reported that the seasonal cycle of $\delta^{13}\text{CO}_2$ between 8 km altitude and the tropopause show a minimum around May and a maximum around September, with a peak-to-peak amplitude of 0.36 ‰. Indeed, our balloon observations were conducted in either spring (late May to early June) or summer (late July to early September), and the observed $\delta^{13}\text{CO}_2$ values at lower altitudes tended to be lower in spring and higher in summer. Accordingly, we attribute the large $\delta^{13}\text{CO}_2$ variations below an altitude of 17 km to the upper tropospheric air itself, or air directly influenced by it.

Our data clearly reveal a secular decrease in mid-stratospheric $\delta^{13}\text{CO}_2$ values. To compare the temporal variations of $\delta^{13}\text{CO}_2$ in the mid-stratosphere with those in the troposphere, the $\delta^{13}\text{CO}_2$ values obtained by averaging mid-stratospheric data above 24 km altitude (≤ 30 hPa) from each year and the continuous MLO data are shown in Figure 3. When comparing our data with the NOAA/ESRL and INSTAAR data at MLO (White et al., 2024), any possible offset of $\delta^{13}\text{CO}_2$ measurements should be taken into account. The inter-comparison results of the WMO/IAEA Round Robin Comparison Experiment (<https://gml.noaa.gov/ccgg/wmorr/>; accessed 20 February 2025) show that our values are approximately 0.07 ‰ lower than INSTAAR values. In this study, we directly compared $\delta^{13}\text{CO}_2$ data at Ny-Ålesund,



Svalbard observed by Goto et al. (2017) with the INSTAAR data at the Zeppelin Observatory (ZEP) in Ny-Ålesund (White et al., 2024) because we used the same $\delta^{13}\text{CO}_2$ measurement system and standard scale as Goto et al. (2017). Monthly average $\delta^{13}\text{CO}_2$ values at Ny-Ålesund from both studies were calculated by applying a curve-fitting procedure (Nakazawa et al., 1997b) over the years 1996–2014 compared. As a result, we estimated the difference between this study and INSTAAR data to be insignificant ($-0.005 \pm 0.067 \text{ ‰}$) and did not apply any further correction to our $\delta^{13}\text{CO}_2$ data. Annual average $\delta^{13}\text{CO}_2$ values at MLO were calculated by applying the same curve-fitting procedure as described above. The average rate of change of $\delta^{13}\text{CO}_2$ in the mid-stratosphere was calculated to be $-0.026 \pm 0.001 \text{ ‰ yr}^{-1}$ for the period 1985–2020, consistent with the average rate of change at MLO from 1990 to 2022 ($-0.027 \pm 0.000 \text{ ‰ yr}^{-1}$) despite the slightly different time periods. Tropospheric $\delta^{13}\text{CO}_2$ values are known to decrease over time due to the emission of CO_2 with low $\delta^{13}\text{CO}_2$ by anthropogenic fossil fuel consumption, and our results show that a similar decreasing trend is observable in the stratosphere. It is also well known that mid-stratospheric air over the mid-latitudes is ‘aged’, mainly because of the slow transport of air from the tropical tropopause to the mid-latitude mid-stratosphere. Indeed, the age of mid-stratospheric air estimated from CO_2 mole fractions was approximately 4.4 years older on average than that of tropical tropospheric air (see Sect. 3.5). Nevertheless, the $\delta^{13}\text{CO}_2$ values observed in the mid-stratosphere over Japan did not seem to show any significant time delay compared with the observed values in the tropical troposphere. Although systematic observations of $\delta^{13}\text{CO}_2$ have not yet been performed in the tropical upper troposphere where stratospheric air originates, Assonov et al. (2010) have found from CARIBIC aircraft observations that $\delta^{13}\text{CO}_2$ variations in the tropical upper troposphere are close to those at MLO. Therefore, if we assume no difference between the $\delta^{13}\text{CO}_2$ values at MLO and those in the tropical upper troposphere, the lack of a delay between the values in the mid-stratosphere over Japan and those at MLO clearly contradicts the concept of the age of air. Simply following the logic of the age of air, we would expect the decrease of stratospheric $\delta^{13}\text{CO}_2$ to lag behind the tropospheric trend, such that the $\delta^{13}\text{CO}_2$ value at any given time should be higher in the mid-stratosphere than in the troposphere. This discrepancy suggests that $\delta^{13}\text{CO}_2$ is not a conserved quantity in the stratosphere and is instead modified not only by air transport but also by other mechanisms. In the following sections, we discuss possible mechanisms in detail.

3.2 Airborne CO_2 source from CH_4 oxidation

In the stratosphere, CH_4 is destroyed by reactions with OH, $\text{O}(^1\text{D})$, and Cl, which produce intermediate products such as CH_3O_2 and CH_2O . These products are immediately converted to CO because of their short lifetimes. However, CO is also destroyed by reaction with OH. Therefore, the chemical budget of CO in the stratosphere is expressed as (Minschwaner et al., 2010):

$$\frac{d[\text{CO}]}{dt} = [\text{CH}_4](k_{\text{CH}_4+\text{OH}}[\text{OH}] + k_{\text{CH}_4+\text{Cl}}[\text{Cl}] + k_{\text{CH}_4+\text{O}}[\text{O}(^1\text{D})]) + J_{\text{CO}_2}[\text{CO}_2] - k_{\text{CO}+\text{OH}}[\text{CO}][\text{OH}], \quad (4)$$

where $k_{\text{CH}_4+\text{OH}}$, $k_{\text{CH}_4+\text{Cl}}$, $k_{\text{CH}_4+\text{O}}$, and $k_{\text{CO}+\text{OH}}$ are the reaction rates for the respective chemical reactions, and J_{CO_2} is the rate of photodissociation of CO_2 . The last term on the right-hand side of this equation represents the oxidation of CO to CO_2 . Although the amount of CO_2 produced this way is small compared to the stratospheric abundance, it cannot be ignored as an airborne source, especially in terms of isotopic signatures. The timescales for the photochemical loss and production of CO in the mid-latitude mid-stratosphere ($\sim 35 \text{ km}$ altitude) are about 30 days (Minschwaner et al., 2010),



quite short compared to the timescale of the stratospheric mean meridional circulation (more than several years). If we assume that the chemical budget of CO is in a steady state and that CO₂ photodissociation is negligibly small below the mid-stratosphere, the rate of CH₄ loss should equal the rate of CO₂ production. Indeed, to estimate the age of stratospheric air from the CO₂ mole fraction, a small amount of CO₂ produced by the chemical destruction of CH₄ was taken into account (e.g., Engel et al., 2002; Sugawara et al., 2018). To correct for this effect, each observed CO₂ mole fraction was adjusted using the CH₄ mole fraction measured from the corresponding air sample prior to age calculation (see Appendix C). The adjustment increases with increasing altitude and becomes larger than 1 μmol mol⁻¹ at the highest altitudes. As with the CO₂ mole fraction, ¹³C can be corrected by assuming a steady state ¹³CO budget in which ¹³C is added to ¹³CO₂ from ¹³CH₄ through a series of oxidation reactions from CH₄ to CO₂. Indeed, it is well known that isotopic fractionation occurs during CH₄ oxidation (Saueressig et al., 1995; Sugawara et al., 1997; Rice et al., 2003; Röckmann et al., 2011).

Figures 4a, b shows the vertical CH₄ mole fraction and δ¹³CH₄ profiles observed over Japan, respectively. A common feature of both profiles is their rapid change with altitude, although δ¹³CH₄ values increase, whereas the mole fractions decrease with increasing altitude. Such vertical distributions have been attributed to large kinetic isotopic effects (KIEs) associated with the chemical destruction of CH₄ in the stratosphere (Sugawara et al., 1997; Rice et al., 2003; Röckmann et al., 2011). KIEs on CH₄ have also been studied using numerical models (Saueressig et al., 2001; Wang et al., 2002; McCarthy et al., 2003). In previous studies, the apparent fractionation factor was derived from the Rayleigh distillation model by assuming that the chemical destruction of CH₄ occurs in a closed system (Sugawara et al., 1997; Rice et al., 2003). In general, the Rayleigh distillation model for the CH₄ mole fraction and δ¹³CH₄ is expressed as:

$$\delta^{13}\text{CH}_4 = (\delta^{13}\text{CH}_{4,0} + 1)\mu^{\alpha-1} - 1, \quad (5)$$

where δ¹³CH_{4,0}, μ, and α are the isotopic ratio before CH₄ is destroyed, the ratio of mole fractions (μ = [CH₄]/[CH₄]₀), and the apparent fractionation factor, respectively. The apparent fractionation factor can be estimated by applying Eq. (5) to observed data. We note that [CH₄]₀ and δ¹³CH_{4,0} change with time and should be taken here as the values in the tropical upper troposphere at the time when air entered into the stratosphere through the tropical tropopause layer (TTL). Therefore, the tropical upper tropospheric records of CH₄ and δ¹³CH₄ were used to give [CH₄]₀ and δ¹³CH_{4,0} values going back in time based on the mean age estimated from CO₂ mole fractions (see Appendix C). Details of the tropical upper tropospheric records of CH₄ and δ¹³CH₄ are described in Sect. 3.5. Figure 4c shows that the relationship between ln{(δ¹³CH₄ + 1)/(δ¹³CH_{4,0} + 1)} and ln([CH₄]/[CH₄]₀) can be approximated by linear functions if we divided the data between the lower (<24 km) and mid-stratosphere (>24 km), with the upper layer showing larger isotopic fractionation effects. The apparent fractionation factors calculated using the least-squares method were 0.9889 ± 0.0003 and 0.9866 ± 0.0007 for the lower and mid-stratosphere, respectively. We attributed these differences in apparent fractionation factors to differences in the relative contributions of the CH₄ reactions with OH, O(¹D), or Cl over the air transport pathway, and/or the effect of air mixing (Röckmann et al., 2011).

Eq. (5) expresses the relationship between the mole fraction and isotopic ratio of the remaining CH₄. Similarly, focusing on the CH₄ lost via the CH₄–CO–CO₂ chain reaction, the relationship between the CH₄ mole fraction and isotopic ratio of lost CH₄ (hereafter, δ¹³CH_{4,L} is derived from Eq. (5) as:

$$\delta^{13}\text{CH}_{4,L} = (\delta^{13}\text{CH}_{4,0} + 1)^{\frac{1-\mu}{1-\mu^{\alpha}}} - 1. \quad (6)$$



Here, the removed CH_4 includes the total amount of CH_4 loss integrated over the air transport pathway. Based on this equation, we calculated $\delta^{13}\text{CH}_4_{\text{L}}$ for each year's data from the observed CH_4 mole fractions and apparent fractionation factors by grouping them into altitudes below and above 24 km. Typical $\delta^{13}\text{CH}_4_{\text{L}}$ values were about -57 , -56 , and -55 ‰ around altitudes of 20, 30, and 35 km, respectively. The stratospheric $\delta^{13}\text{CO}_2$ values were corrected for airborne sources simply by assuming that carbon with the isotopic ratio of $\delta^{13}\text{CH}_4_{\text{L}}$ was added to ambient CO_2 . We note that the amount of CO_2 added by CH_4 oxidation was estimated from the difference between the CH_4 mole fraction observed in the mid-latitude stratosphere and that estimated at the tropical upper troposphere; this does not represent chemical production at the observed location, but apparent production, because CH_4 oxidation occurs along the transport pathway of the air mass and is accompanied by air mixing. Consequently, the depression of CH_4 integrated over the air transport pathway is observed at a certain location in the stratosphere. Because we assumed simple Rayleigh distillation model, the $\delta^{13}\text{CH}_4_{\text{L}}$ estimated here is also apparent value in a similar sense as described above. Accordingly, our assumption described above was a first-order approximation to correct $\delta^{13}\text{CO}_2$ for airborne CO_2 sources.

As an example, we corrected the vertical distributions of the CO_2 mole fraction and $\delta^{13}\text{CO}_2$ (Fig. 5a) and compared with the CH_4 mole fraction and $\delta^{13}\text{CH}_4$ (Fig. 5b) observed on 22 August 2010. The results indicated that the $\delta^{13}\text{CO}_2$ value decreased by 0.14 ‰ and the CO_2 mole fraction increased by approximately $1.1 \mu\text{mol mol}^{-1}$ at the highest altitude (~ 34 km) when corrected for airborne CO_2 sources. Therefore, such a correction for the airborne CO_2 source with low $\delta^{13}\text{CO}_2$ values produced by CH_4 oxidation is essential for understanding CO_2 mole fraction and $\delta^{13}\text{CO}_2$ variations in the mid-stratosphere. This effect is particularly strong on $\delta^{13}\text{CO}_2$ and significantly impacted the shape of the vertical distribution.

We note that the transport of CO from the troposphere into the stratosphere and its oxidation in the lower stratosphere are not considered in the above discussion. Because the photochemical timescales of CO are longer in the lower stratosphere than in the mid-stratosphere, tropospheric CO could be a stratospheric CO_2 source associated with troposphere–stratosphere exchange and may be important in the lower stratospheric CO budget. Observational results on the stable carbon isotopic ratio of CO, $\delta^{13}\text{CO}$, have been reported not only for the troposphere (Brenninkmeijer, 1993; Röckmann and Brenninkmeijer, 1997; Röckmann et al., 1999, 2002; Kato et al., 2000) but also for the lower stratosphere (Brenninkmeijer et al., 1996; Röckmann et al., 2024). In particular, Brenninkmeijer et al. (1996) have found that extremely low $\delta^{13}\text{CO}$ values in the southern high-latitude lower stratosphere are accompanied by increasing $\delta^{13}\text{CH}_4$ values and have suggested that the large KIE of CH_4 destruction by Cl plays an important role. The local production of CO by CH_4 destruction depleted ^{13}C in stratospheric CO is consistent with the above discussion if CO is rapidly oxidized to CO_2 depleted in ^{13}C . However, tropospheric CO could be an additional airborne CO_2 source if it is transported into the lower stratosphere and oxidized to CO_2 . Previous studies have reported that $\delta^{13}\text{CO}$ values in the free troposphere are around -30 ‰ to -25 ‰ (Brenninkmeijer, 1993; Röckmann and Brenninkmeijer, 1997; Röckmann et al., 1999, 2002; Kato et al., 2000), and the KIE on carbon in the reaction $\text{CO} + \text{OH}$ depends on atmospheric pressure (Stevens and Wagner, 1989; Bergamaschi et al., 2000). Its fractionation factor is 0.994 (expressed as the ratio of rate constants, $^{13}k/^{12}k$) at 1013 hPa, but increases to about 1.000 at 400 hPa and further to 1.003–1.005 above the tropopause. Therefore, CO_2 produced from the reaction $\text{CO} + \text{OH}$ should be slightly enriched in ^{13}C in the stratosphere, contrary to CO_2 produced in the lower



troposphere. Accordingly, tropospheric CO could be an airborne CO₂ source with $\delta^{13}\text{C}$ values lower than around -25‰ to -20‰ in the lower stratosphere. Assuming that tropospheric air containing 250 nmol mol^{-1} CO with $\delta^{13}\text{CO} = -30\text{‰}$ is transported to the stratosphere where 200 nmol mol^{-1} CO is lost by reaction with OH, $\delta^{13}\text{CO}_2$ values should decrease by only about 0.01‰ when $0.2\text{ }\mu\text{mol mol}^{-1}$ CO₂ with $\delta^{13}\text{CO}_2 = -28\text{‰}$ is added to $390\text{ }\mu\text{mol mol}^{-1}$ CO₂ with $\delta^{13}\text{CO}_2 = -8.5\text{‰}$. Therefore, this effect would be negligibly small compared with the influence of CH₄ oxidation. Unfortunately, we could not further evaluate the effect of tropospheric CO from our observations, and further study including measurements of $\delta^{13}\text{CO}$ is needed.

3.3 Gravitational separation of $\delta^{13}\text{CO}_2$

The standardized GS is defined as $\langle\delta_G\rangle$, which is normalized by the mass number differences of corresponding molecules (see Appendix A). With respect to $\delta^{13}\text{CO}_2$, the upward decrease due to GS is equal to $\langle\delta_G\rangle$ for $^{13}\text{C}^{16}\text{O}_2$ and $^{12}\text{C}^{17}\text{O}^{16}\text{O}$ ($\Delta m = 1$), and is 2 times larger for $^{12}\text{C}^{18}\text{O}^{16}\text{O}$, $^{13}\text{C}^{17}\text{O}^{16}\text{O}$, and $^{12}\text{C}^{17}\text{O}_2$ ($\Delta m = 2$). Therefore, GS equal to and twice the magnitude of $\langle\delta_G\rangle$ can be considered to act on $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$, respectively:

$$\Delta_G(\delta^{45}\text{CO}_2) = \langle\delta_G\rangle - \langle\delta_G\rangle_0, \quad (7a)$$

$$\Delta_G(\delta^{46}\text{CO}_2) = 2(\langle\delta_G\rangle - \langle\delta_G\rangle_0). \quad (7b)$$

Here, $\Delta_G(x)$ represents the change in isotopic value x due to GS. Because $\langle\delta_G\rangle - \langle\delta_G\rangle_0$ is negative in the stratosphere (see Appendix A), $\Delta_G(\delta^{45}\text{CO}_2)$ and $\Delta_G(\delta^{46}\text{CO}_2)$ are also negative. When $\delta^{13}\text{CO}_2$ was corrected for GS, Eqs. (7a) and (7b) were first applied to $\delta^{45}\text{CO}_2$ and $\delta^{46}\text{CO}_2$, respectively, and then $\delta^{13}\text{CO}_2$ was determined using the MIE algorithm described in Sect. 2.2. As shown in Figure 5c, $|\Delta_G(\delta^{13}\text{CO}_2)|$ was slightly smaller than (about 82% of) $|\Delta_G(\delta^{45}\text{CO}_2)|$ in the mid-stratosphere, mainly because of $^{12}\text{C}^{17}\text{O}^{16}\text{O}$ enrichment due to the MIE in the stratosphere.

The same method can be applied to the mole fraction of a specific molecule as (Ishidoya et al., 2006):

$$\Delta_G(C) = C_0 \times (m - m_{\text{air}}) \times (\langle\delta_G\rangle - \langle\delta_G\rangle_0). \quad (8)$$

Here, C_0 and C denote the mole fractions of the molecule before and after GS, respectively, and m and m_{air} are the respective mass numbers of the molecule and air. The maximum depression of the CO₂ mole fraction amounts to about $0.6\text{ }\mu\text{mol mol}^{-1}$ at the highest altitude, assuming $C_0 = 400\text{ }\mu\text{mol mol}^{-1}$ and $\langle\delta_G\rangle - \langle\delta_G\rangle_0 = -100$ per meg. As an example, the vertical profile of the CO₂ mole fraction obtained by correcting the 22 August 2010 observations for GS is shown in Figure 5a. Compared to the profiles corrected for airborne CO₂ sources, GS correction increases the CO₂ mole fraction by $0.4\text{ }\mu\text{mol mol}^{-1}$ and the $\delta^{13}\text{CO}_2$ by approximately 0.06‰ at 34 km altitude. Although the effect of GS on the CO₂ mole fraction is small, that on $\delta^{13}\text{CO}_2$ is non-negligible, significantly influencing the vertical profile along with CH₄ oxidation.

Correcting for both CH₄ oxidation and GS, $\delta^{13}\text{CO}_2$ values increase with altitude and become nearly constant above $\sim 25\text{ km}$; they are clearly anticorrelated with the CO₂ mole fraction. Assuming a linear relationship between the CO₂ mole fraction and $\delta^{13}\text{CO}_2$ (Fig. 5d), the slope calculated by least-squares is $-0.005 \pm 0.003\text{‰} (\mu\text{mol mol}^{-1})^{-1}$ for the raw observational data and $-0.023 \pm 0.002\text{‰} (\mu\text{mol mol}^{-1})^{-1}$ for the corrected data. This rate of change for the corrected data is less negative than approximately $-0.05\text{‰} (\mu\text{mol mol}^{-1})^{-1}$ for the seasonal cycles in the troposphere (Nakazawa et al., 1993) and is near the rate of change for their secular trends (Morimoto et al., 2000; Goto et al., 2017). Generally, because of the Brewer–Dobson circulation, air at higher altitudes is older. Therefore, we consider that this rate of change



for the corrected data basically reflects different ages of air.

395 **3.4 Two-dimensional model of stratospheric $\delta^{13}\text{CO}_2$**

The mechanisms governing the vertical $\delta^{13}\text{CO}_2$ profile in the stratosphere are schematically shown in Figure 6, including the influence of the age of air as well as the effects of CH_4 oxidation and GS discussed in Sects. 3.2 and 3.3. Tropospheric $\delta^{13}\text{CO}_2$ values have been decreasing through time due to the combustion of fossil fuels. If it is assumed that $\delta^{13}\text{CO}_2$ has no sink or source in the stratosphere, the air that intrudes from the tropical upper troposphere is slowly transported to the mid-latitude stratosphere by the Brewer–Dobson circulation. Therefore, based on the concept of age of air, it is expected that $\delta^{13}\text{CO}_2$ values should also decrease with time in the stratosphere after a certain lag time. Accordingly, $\delta^{13}\text{CO}_2$ values should be higher in the mid-stratosphere than in the troposphere (dotted line in Fig. 6). In contrast, GS decreases $\delta^{13}\text{CO}_2$ values at higher altitudes because $^{13}\text{C}^{16}\text{O}_2$ is heavier than $^{12}\text{C}^{16}\text{O}_2$ (dashed line in Fig. 6). In addition, ^{13}C -depleted CO_2 produced by CH_4 oxidation further decreases $\delta^{13}\text{CO}_2$ values at high altitudes (solid line in Fig. 6). The observed stratospheric vertical $\delta^{13}\text{CO}_2$ profile should therefore be formed by a combination of these effects.

To verify this hypothesis, we performed numerical simulations using a two-dimensional model of the middle atmosphere (SOCRATES) developed by the National Center for Atmospheric Research (NCAR; Huang et al., 1998; Park et al., 1999; Khosravi et al., 2002). Details of the model calculations are described in Appendix B. The monthly average meridional $\delta^{13}\text{CO}_2$ distribution calculated by SOCRATES for August 2016 is shown in Figure 7, which includes the effects of CH_4 oxidation and GS. The effect of the CO_2 production associated with the KIE on CH_4 destruction is included in a simplified manner (see Appendix B). The $\delta^{13}\text{CO}_2$ values decrease with increasing altitude up to about 14 km and then increase up to about 20 km in the mid-latitudes of the northern hemisphere during summer. The distribution of $\delta^{13}\text{CO}_2$ from the troposphere to the lower stratosphere should therefore be closely related to the propagation of its seasonal cycle in the troposphere. $\delta^{13}\text{CO}_2$ values reach a maximum at around 20 km and then gradually decrease. At high latitudes in the southern (winter) hemisphere, the vertical decrease of $\delta^{13}\text{CO}_2$ is significant, suggesting that the effects of CH_4 oxidation and GS are enhanced by the descending upper atmosphere.

To investigate the vertical $\delta^{13}\text{CO}_2$ profile in detail, we compared this model with our observations in Figure 2c. The modeled $\delta^{13}\text{CO}_2$ profile calculated without accounting for CH_4 oxidation and GS increased with increasing altitude, and it was 0.14 ‰ higher at altitudes around 35 km than near the tropopause. Because the average rate of change of the long-term $\delta^{13}\text{CO}_2$ record at MLO is -0.027 ‰ yr^{-1} for the period 1990–2022, the lag time at 35 km (0.14 ‰ divided by 0.027 ‰ yr^{-1}) should be approximately 5.2 years, nearly consistent with the calculated mean age of air (see Appendix C). If the effect of GS is further taken into account, the $\delta^{13}\text{CO}_2$ decreased by approximately 0.07 ‰ at 35 km. The most significant impact on the modeled vertical profile was the effect of CH_4 oxidation, which imparted a decrease of 0.26 ‰ at around 35 km. The vertical profile calculated including all effects exhibited a maximum at an altitude of about 20 km and then decreased monotonically at greater altitudes, mainly because of the effect of CH_4 oxidation. However, the observed $\delta^{13}\text{CO}_2$ profile increased to about 25 km altitude, indicating that the model results clearly overestimated the ^{13}C depletion at higher altitudes. We note, though, that this model calculation included the seasonal cycle of tropospheric $\delta^{13}\text{CO}_2$ and nearly reproduced the vertical distribution observed at 14–20 km altitude, which is mainly due to the upward



propagation of the seasonal cycle from the upper troposphere to the lower stratosphere. Therefore, the difference between
430 the observed and modeled results above 20 km was likely due mainly to an overestimation of the effect of CH₄ oxidation.

One possible reason for this difference was an overestimation of CH₄ loss at high altitudes. The observed CH₄
mole fraction at ~35 km altitude ranged between about 500 and 900 nmol mol⁻¹ (Fig. 4), but the model results indicated
a monthly average of about 600 nmol mol⁻¹ for August, which was lower than the observed average value (see Fig. B1c
in Appendix B). This discrepancy may be related to the fact that we weakened the mass stream function to reproduce a
435 realistic age of air (see Appendix B). Another reason may be that the model simulation set the KIE on CH₄ destruction in
a simplified manner, with the apparent fractionation factors set uniformly at 0.9889 and 0.9866 for the lower and mid-
stratosphere, respectively. In reality, the apparent fractionation factor for CH₄ oxidation varies with altitude and latitude,
and it is determined not only by a complex process that depends on the paths of air masses, but also by the chemical
reactions that occur along the pathway (e.g. Röckmann et al., 2011). In this study, the KIEs on the CH₄–CO–CO₂ reaction
440 processes were not calculated explicitly, but rather in a simplified manner, which may have resulted in an overestimation
of the effect on δ¹³CO₂. However, the present model simulation was able to prove our hypothesis that three factors – CH₄
oxidation, GS, and air age – are essential to determining vertical δ¹³CO₂ profiles.

3.5 Stratospheric potential δ¹³C

445 From the above discussion, we considered that the total amount of ¹³C in both CO₂ and CH₄, δ¹³C_T, was conserved. We
defined δ¹³C_T as:

$$\delta^{13}\text{C}_T = \frac{n(\text{CO}_2) \times \delta^{13}\text{CO}_2 + n(\text{CH}_4) \times \delta^{13}\text{CH}_4}{n(\text{CO}_2) + n(\text{CH}_4)}, \quad (9)$$

which is quasi-conservative with respect to the KIEs associated with CH₄ oxidation and consequent CO₂ production in
the stratosphere. Furthermore, as mentioned above, the effect of GS cannot be ignored in the stratosphere. Taking this
450 into account, we defined the stratospheric potential δ¹³C, δ¹³C_P, by correcting δ¹³C_T for GS as:

$$\delta^{13}\text{C}_P = \delta^{13}\text{C}_T - \Delta_G(\delta^{13}\text{CO}_2), \quad (10)$$

where Δ_G(δ¹³CO₂) denotes the GS correction for δ¹³CO₂. Normally, Δ_G(δ¹³CO₂) gives a negative value, which means that
it has a positive effect on δ¹³C_P. This equation does not include the effect of GS on δ¹³CH₄, but that contribution to δ¹³C_P
is negligibly small (about 10⁻⁴ ‰). Eqs. (9) and (10) were applied to the observed results to calculate stratospheric δ¹³C_T
455 and δ¹³C_P profiles. For some air samples without δ¹³CH₄ measurements, values were estimated from the CH₄ mole fraction
using a linear function fitted to the log-log plot of the observed data shown in Figure 4. The <δ_G> values were also
partially complemented by applying the average vertical profile. The average vertical profile of δ¹³C_P thus calculated is
shown in Figure 8, alongside the CO₂ mole fraction. The data plotted in this figure were detrended and normalized to
August 2016. The CO₂ mole fractions were also corrected for CH₄ oxidation and GS, although the magnitude of these
460 corrections was relatively small. δ¹³C_P increased with increasing altitude from the tropopause to about 25 km, then was
almost constant with increasing altitude. Unlike δ¹³CO₂ (Fig. 2c), δ¹³C_P was inversely correlated with the CO₂ mole
fraction. Figure 9 shows the temporal variations of the averaged δ¹³CO₂, δ¹³C_T, and δ¹³C_P values above 24 km altitude.
δ¹³C_T and δ¹³C_P changed almost in parallel with δ¹³CO₂, showing a similar decreasing trend through time. The average
difference from δ¹³CO₂ was -0.079 ± 0.025 ‰ for δ¹³C_T and -0.034 ± 0.027 ‰ for δ¹³C_P.



465 To estimate the age of stratospheric air based on $\delta^{13}\text{C}_\text{P}$ observations in the stratosphere, $\delta^{13}\text{C}_\text{P}$ at the tropical upper troposphere was required. However, there are no long-term data records of $\delta^{13}\text{C}$ values in CO_2 and CH_4 in the tropical upper troposphere. Therefore, we hypothetically synthesized a $\delta^{13}\text{C}_\text{P}$ record in the tropical upper troposphere based on surface data observed at MLO and in the equatorial Pacific region by INSTAAR (White et al., 2024; Michel et al., 2023). In our previous study, we employed CO_2 mole fraction data obtained in the tropical upper troposphere using
470 the Automatic Air Sampling Equipment in the Comprehensive Observation Network for TRace gases by AirLiner (CONTRAIL) program (Machida et al., 2008; Sawa et al., 2008; Matsueda et al., 2015) to estimate the mean age of stratospheric air (Sugawara et al., 2018). A similar method was used in this study. We first estimated the average seasonal cycle of $\delta^{13}\text{CO}_2$ in the tropical upper troposphere from the observed seasonal cycle of CO_2 mole fraction, assuming that the correlation between the seasonal cycles of CO_2 mole fraction and $\delta^{13}\text{CO}_2$ in the upper troposphere was approximately
475 $-0.05 \text{ ‰} (\mu\text{mol mol}^{-1})^{-1}$ (Nakazawa et al., 1993). The long-term $\delta^{13}\text{CO}_2$ trend was calculated from the observation data at MLO and then adjusted to match the observations in the equatorial Pacific region. The average seasonal cycles were then added to the long-term $\delta^{13}\text{CO}_2$ trend estimated in the equatorial Pacific region. The difference between $\delta^{13}\text{CO}_2$ values at the surface and those in the upper troposphere in the equatorial region is currently unknown. However, Sugawara et al. (2018) have reported that the CO_2 and SF_6 ages in the TTL are 0.5–0.6 years, consistent with the SF_6 age of 0–1.5 years
480 in the TTL based on Michelson Interferometer for Passive Atmospheric Sounding (Stiller et al., 2008). Taking this into account, we assumed the difference between surface and upper troposphere $\delta^{13}\text{CO}_2$ values in the equatorial region to be equivalent to 0.5 years. Because systematic measurements of CH_4 mole fraction and $\delta^{13}\text{CH}_4$ in the upper troposphere were performed in the CONTRAIL program (Umezawa et al., 2012), the MLO data obtained by INSTAAR were adjusted to fit the CONTRAIL data in the equatorial upper troposphere to produce long-term records of CH_4 mole fraction and
485 $\delta^{13}\text{CH}_4$ in the equatorial upper troposphere. Because the seasonal cycle of $\delta^{13}\text{CH}_4$ in the equatorial upper troposphere is not clear (Umezawa et al., 2012), the seasonal cycle was ignored in the calculation of the upper tropospheric $\delta^{13}\text{C}_\text{P}$. Since GS, i.e. $\langle \delta_\text{G} \rangle - \langle \delta_\text{G} \rangle_0$, should be zero in the equatorial upper troposphere, tropospheric $\delta^{13}\text{C}_\text{P} = \delta^{13}\text{C}_\text{T}$.

As seen in Figure 9, $\delta^{13}\text{CO}_2$ values did not differ significantly between the troposphere and the mid-stratosphere. However, the $\delta^{13}\text{C}_\text{P}$ values calculated from observed values in the mid-stratosphere were, on average, about
490 $0.14 \pm 0.03 \text{ ‰}$ higher than those calculated for the tropical troposphere. This means that $\delta^{13}\text{C}_\text{P}$ is conservative in the stratosphere and that the decreasing tropospheric $\delta^{13}\text{C}_\text{P}$ trend through time propagates into the stratosphere with a time delay. Roughly calculated, this lag time is about 5 years, consistent with the age of air estimated from CO_2 mole fractions (Appendix C) and the model calculation. If the mid-stratospheric $\delta^{13}\text{C}_\text{P}$ values were shifted by -5 years, they were in good agreement with the tropospheric $\delta^{13}\text{C}_\text{P}$ trend (Fig. 9).

495 It is thus possible to estimate the mean age of air using $\delta^{13}\text{C}_\text{P}$, which can serve as an additional air age tracer. Therefore, we estimated the mean age of air not only from the CO_2 mole fraction but also from $\delta^{13}\text{C}_\text{P}$ using a convolution method (Ray et al., 2017; Sugawara et al., 2018) (described in Appendix C). It was necessary to consider that both the uncertainties on individual mole fraction or isotopic ratio measurements and those on the tropospheric reference record propagated to the uncertainties on individual age estimates (e.g. Leedham Elvidge et al., 2018). Regarding our CO_2 ages,
500 Umezawa et al. (2024) have estimated a total uncertainty of 0.72 years, and we estimated the uncertainties on $\delta^{13}\text{C}_\text{P}$ ages



in a similar manner: by adding normal pseudo-random numbers to all measured values and calculating $\delta^{13}\text{C}_\text{P}$ values using Eqs. (9) and (10). The uncertainty on individual $\delta^{13}\text{C}_\text{P}$ values was almost the same as that on $\delta^{13}\text{C}$, ± 0.02 ‰. In contrast, the uncertainty on the tropospheric reference record for $\delta^{13}\text{C}_\text{P}$ was calculated to be ± 0.03 ‰, which was the standard deviation when the curve fitting was applied to the MLO $\delta^{13}\text{C}$ data used as the tropospheric reference record. Taking into account all these uncertainties and the tropospheric trend of -0.027 ‰ yr^{-1} , the total uncertainty on individual $\delta^{13}\text{C}_\text{P}$ ages was estimated to be ± 1.9 years. This rather large uncertainty means that $\delta^{13}\text{C}_\text{P}$, with its smaller tropospheric secular change compared to other age tracers, was somewhat disadvantageous for age estimations. Because the seasonal cycle of $\delta^{13}\text{C}_\text{P}$ is significantly large in the troposphere, its signal propagates into the TTL and then into the stratosphere via the slow air transport. Simultaneously, atmospheric mixing broadens the width of the age spectrum, attenuating seasonal amplitudes with increasing altitude. Because some of the $\delta^{13}\text{C}_\text{P}$ values in the lower stratosphere showed high variability, with values lower than the tropospheric reference record, the convolution method could not provide reasonable age estimations for those data. We attributed these irregularities and low values to the large seasonal variations in the upper troposphere and the stratosphere–troposphere air exchange in the lower stratosphere. Therefore, only mid-stratospheric (>24 km altitude) data were taken into account for age estimations, and the average values of the mean age were calculated.

The results are shown in Figure 10, along with the mean age calculated from the CO_2 mole fraction using the same method (see Appendix C). The average $\delta^{13}\text{C}_\text{P}$ and CO_2 ages were 5.5 ± 1.6 and 4.4 ± 0.6 years, respectively. Because the uncertainty of the $\delta^{13}\text{C}_\text{P}$ age was large, no significant difference was apparent between the two values. The ratio of moments and its influence on age estimates have been examined in previous studies (e.g. Hauck et al., 2019; Nguyen et al., 2021). Here, as a sensitivity test, the mean age calculation was repeated for different ratios of moments ranging from 0.05 to 2.00 years. As a result, the mean ages derived from $\delta^{13}\text{C}_\text{P}$ were found to be within the observational uncertainties on the $\delta^{13}\text{C}_\text{P}$ age. To examine the long-term trend of mean age, a linear function was fitted to both the CO_2 and $\delta^{13}\text{C}_\text{P}$ age data using the least squares method. A slightly positive trend (0.04 ± 0.01 years yr^{-1}) was observed for the CO_2 age, but no specific trend was observed for the $\delta^{13}\text{C}_\text{P}$ age. It is important to note that our data were unevenly distributed over time, with sparse observations in recent years and more frequent observations before 2007. This made it difficult to clarify the exact 35-year trend from our data alone. However, the result that $\delta^{13}\text{C}_\text{P}$ age and CO_2 age are roughly consistent implies that $\delta^{13}\text{C}_\text{P}$ age could be used in addition to SF_6 , halocarbons, etc., for better multi-component age estimations (Umezawa et al., 2024).

4 Conclusions

Previous studies on $\delta^{13}\text{CO}_2$ have mainly focused on observations in the troposphere and on elucidating the global CO_2 budget based on monitoring programs. However, little research has been performed on $\delta^{13}\text{CO}_2$ in the stratosphere, and the mechanisms of its distribution and variations are not fully understood. This study presented a comprehensive analysis of stratospheric $\delta^{13}\text{CO}_2$ obtained from balloon observations over Japan during the period 1985–2020. The following four factors were found to be important for understanding the variations of $\delta^{13}\text{CO}_2$ in the stratosphere. (1) Appropriate corrections for the MIE on ^{17}O and ^{18}O in isotopic analyses are essential. However, even after applying this correction, we found that the average values of $\delta^{13}\text{CO}_2$ in the northern mid-latitude mid-stratosphere and the tropical troposphere



were almost identical, despite the secular decreasing $\delta^{13}\text{CO}_2$ trend and the expected time lag (age of air). We attributed this strange agreement to the other three factors: (2) airborne production of ^{13}C -depleted CO_2 by the oxidation of CH_4 in the stratosphere, (3) GS of $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ in the stratosphere, and (4) propagation of the decreasing tropospheric $\delta^{13}\text{CO}_2$ trend into the stratosphere. Based on these considerations, we introduced 'stratospheric potential $\delta^{13}\text{C}$ ' ($\delta^{13}\text{C}_\text{P}$) as a new concept and inspected $\delta^{13}\text{C}_\text{P}$ in terms of the age of air in detail. Mean age of air was estimated by using $\delta^{13}\text{C}_\text{P}$ value with the convolution method. The average $\delta^{13}\text{C}_\text{P}$ age was calculated to be 5.5 ± 1.6 years for the period of 1985–2020. Although the $\delta^{13}\text{C}_\text{P}$ age has larger uncertainties than the CO_2 age at present, our results showed that stratospheric $\delta^{13}\text{C}_\text{P}$ can serve as an additional age tracer alongside CO_2 and SF_6 mole fractions, and it should prove a useful tool for investigating stratospheric transport processes.

$\delta^{13}\text{C}_\text{P}$ age is slightly larger than CO_2 age (4.4 ± 0.6 years) by about 1.1 years on average. In this regard, Engel et al. (2009) reported that CO_2 age and SF_6 age observed in the mid-stratosphere at mid-latitudes during the period 1975–2005 ranged from 4.7 to 5.3 years. Compared to their reported ages, our $\delta^{13}\text{C}_\text{P}$ age and CO_2 age tend to be slightly larger and smaller, respectively. It is likely that $\delta^{13}\text{C}_\text{P}$ age is overestimated because the effect of methane oxidation was underestimated in the calculation of $\delta^{13}\text{C}_\text{T}$. The discrepancy between the two CO_2 ages would be due to differences in the age estimation methods, the tropospheric reference records, and the ratios of moments used in the two studies. Our GS correction for the CO_2 mole fraction also has the effect of lowering CO_2 age. Therefore, it is necessary to perform age estimations by analyzing all observational data using the same method in future study. It is also needed to reduce uncertainty in age estimation by performing multi-component age estimations using additional age tracers, such as halocarbons and $\delta^{13}\text{C}_\text{P}$.

The observation of numerous stratospheric air constituents, as in this study, requires the collection of a large amount of stratospheric air with a high-quality method and multi-component gas analyses of each air sample. GS of atmospheric constituents in the stratosphere was first revealed by our previous balloon observations, and this knowledge is indispensable for a better understanding of the variations of stratospheric $\delta^{13}\text{CO}_2$. The quality of air sampling is particularly important for observing GS in the mid-stratosphere, because even slight separations due to molecular diffusion during air sampling could prevent GS observations. At present, the only method capable of such sampling is our cryogenic air sampler.

The 2-D model reproduced the basic structure of stratospheric $\delta^{13}\text{CO}_2$ and elucidated the mechanisms governing $\delta^{13}\text{CO}_2$ behavior. However, our numerical model simulations remained insufficient because the mean age of stratospheric air could not be reproduced adequately without arbitrarily tuning the model. Accordingly, our model overestimated the effect of airborne CO_2 production via CH_4 oxidation because the reaction process was treated in a very coarse manner. To improve upon this model, it will be necessary to incorporate KIEs into all reactions related to stratospheric carbon. Although a two-dimensional model was used in this proof-of-concept study, a three-dimensional model is desirable for more realistic simulations in the future.

Appendix A: Gravitational separation of major atmospheric components



The gravitational separation (GS) of atmospheric components in the stratosphere was first reported from our balloon observations in Japan (Ishidoya et al., 2006, 2008a, 2013), in which the isotopic and elemental ratios of major atmospheric compositions, such as $\delta^{15}\text{N}$ in N_2 , $\delta^{18}\text{O}$ in O_2 , and $\delta(\text{Ar}/\text{N}_2)$, were measured by mass spectrometry at the National Institute of Advanced Industrial Science and Technology (AIST) (e.g. Ishidoya et al., 2006, 2008a; Sugawara et al., 2018). Technical aspects of our mass spectrometry analyses are described in detail in Ishidoya and Murayama (2014). In this study, we used $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\delta(\text{Ar}/\text{N}_2)$ to evaluate GS, which are defined as:

$$\delta^{15}\text{N} = \frac{[n(^{15}\text{N}^{14}\text{N})/n(^{14}\text{N}^{14}\text{N})]_{\text{sp}}}{[n(^{15}\text{N}^{14}\text{N})/n(^{14}\text{N}^{14}\text{N})]_{\text{st}}} - 1, \quad (\text{A1a})$$

$$\delta^{18}\text{O} = \frac{[n(^{18}\text{O}^{16}\text{O})/n(^{16}\text{O}^{16}\text{O})]_{\text{sp}}}{[n(^{18}\text{O}^{16}\text{O})/n(^{16}\text{O}^{16}\text{O})]_{\text{st}}} - 1, \quad (\text{A1b})$$

and

$$\delta(\text{Ar}/\text{N}_2) = \frac{[n(^{40}\text{Ar})/n(^{14}\text{N}^{14}\text{N})]_{\text{sp}}}{[n(^{40}\text{Ar})/n(^{14}\text{N}^{14}\text{N})]_{\text{st}}} - 1, \quad (\text{A1c})$$

where ‘sp’ and ‘st’ denote the sample and standard gases, respectively. The 1σ reproducibilities of our $\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\delta(\text{Ar}/\text{N}_2)$ measurements were ± 2 , ± 5 , and ± 7 per meg, respectively, which was sufficient to detect GS in the stratosphere. Ishidoya et al. (2013) have concluded that vertical variations of the isotopic ratios of major atmospheric components are dominated by differences in molecular mass, based on mass-dependent relationships among related molecules such as $\delta^{15}\text{N}$ in N_2 , $\delta^{18}\text{O}$ in O_2 , and the Ar/N_2 ratio. Such GS in the stratosphere is known to be proportional to the mass difference, as would be expected for pure molecular diffusion, even though eddy diffusion obviously far exceeds molecular diffusion in the stratosphere. Therefore, GS can be expressed as follows:

$$\delta - \delta_0 = \Delta m \times (\langle \delta_G \rangle - \langle \delta_G \rangle_0), \quad (\text{A2})$$

where Δm is the mass number difference, the suffix “0” refers to the value before GS occurs (i.e. corresponding to the relevant value in the upper troposphere), and $\langle \delta_G \rangle$ is the average of δ values normalized to $\Delta m = 1$ as reported by Ishidoya et al. (2013) and Sugawara et al. (2018). $\langle \delta_G \rangle$ is defined by:

$$\langle \delta_G \rangle = \frac{1}{3} \left[\delta^{15}\text{N} + \delta^{18}\text{O}/2 + \delta(\text{Ar}/\text{N}_2)/12 \right]. \quad (\text{A3})$$

Figure A1 shows vertical profiles of $\langle \delta_G \rangle$ obtained from balloon observations over Japan (Ishidoya et al., 2013). The value of $\langle \delta_G \rangle$ decreases gradually with increasing altitude. By fitting a linear function to the vertical profiles, the average difference of $\langle \delta_G \rangle$ between the lowermost and uppermost altitudes was found to be -66 ± 17 per meg. Here, it is important to mention the relationship between the GS of $\delta^{18}\text{O}$ and photochemical processes. As mentioned in Sect. 2.2., in the stratosphere, O_3 and CO_2 are significantly enriched in ^{17}O and ^{18}O by MIEs associated with photochemical reaction processes. Because stratospheric O_2 molecules are the source of the ^{17}O and ^{18}O enrichment, $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ values of O_2 are thought to be lower in the stratosphere than in the troposphere due to photochemical processes. This assumption is crucial not only for the Dole–Morita effect, but also for the ^{17}O budget of tropospheric O_2 (Bender et al., 1994; Luz et al., 1999; Luz and Barkan, 2011; Ishidoya et al., 2025). However, $\delta^{18}\text{O}$ values of stratospheric O_2 measured in our balloon observations show a very large decrease, i.e. by approximately -130 per meg, at around 35 km that is almost entirely dominated by GS. This decrease is probably also due in part to photochemical effects, but their contribution should be



negligible, amounting to only a few per meg (Ishidoya et al., 2025).

Appendix B: Two-dimensional model

We used a two-dimensional model of the middle atmosphere (SOCRATES) developed by the National Center for Atmospheric Research (NCAR) (Huang et al., 1998; Park et al., 1999; Khosravi et al., 2002). The advantage of using this model is that we have already calculated $^{13}\text{C}^{16}\text{O}_2$ and $^{12}\text{C}^{16}\text{O}_2$ and examined stratospheric GS in our previous studies (Ishidoya et al., 2013; Sugawara et al., 2018). Therefore, we give only a brief description of the model calculation here. To reproduce GS, the molecular diffusion flux must be calculated. The vertical component of the molecular diffusion flux ($F_{m_i,z}$) is given by:

$$F_{m_i,z} = -D_{m_i} \left\{ \frac{\partial n_i}{\partial z} + \frac{m_i g}{RT} n_i + (1 + \alpha_{T_i}) \frac{\partial(\ln T)}{\partial z} n_i \right\}, \quad (\text{B1})$$

where n_i , D_{m_i} , m_i , and α_{T_i} are the number density, molecular diffusion coefficient, molecular mass, and thermal diffusion factor of atmospheric constituent i , respectively, and g , R , and T are the gravitational acceleration, gas constant and temperature, respectively (Banks and Kockarts, 1973). However, because the thermal diffusion flux is not important in this case, we ignored it in the model calculations. Because it is cumbersome to include all CO_2 isotopologues in the model calculations, only $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$ were calculated independently in the model, and $\delta^{13}\text{CO}_2$ was approximated using the respective mole fractions of $n(^{13}\text{C}^{16}\text{O}_2)$ and $n(^{12}\text{C}^{16}\text{O}_2)$ as:

$$\delta^{13}\text{CO}_2 = \left(\frac{1}{^{13}\text{R}_{\text{VPDB}}} \frac{n(^{13}\text{C}^{16}\text{O}_2)}{n(^{12}\text{C}^{16}\text{O}_2)} - 1 \right). \quad (\text{B2})$$

Because $\delta^{13}\text{CO}_2$ has a large seasonal cycle in the troposphere, we used NOAA/ESRL data to give latitude-dependent seasonal cycles as boundary conditions at the model surface. In addition, a secular decrease of $\delta^{13}\text{CO}_2$ in the troposphere was given by the MLO data (White et al., 2024). SOCRATES originally included a series of carbon reactions starting with CH_4 oxidation. Model calculations were repeated with and without GS, the secular trend and seasonal cycle of tropospheric $\delta^{13}\text{CO}_2$, and airborne CO_2 production, and comparisons were made between them (Fig. 2c). The chemical budget of CO_2 in SOCRATES is calculated as:

$$\frac{d[\text{CO}_2]}{dt} = k_{\text{CO}+\text{OH}}[\text{CO}][\text{OH}] + k_{\text{CO}+\text{O}(^3\text{P})}[M][\text{CO}][\text{O}(^3\text{P})] - J_{\text{CO}_2}[\text{CO}_2], \quad (\text{B3})$$

where $k_{\text{CO}+\text{OH}}$ and $k_{\text{CO}+\text{O}(^3\text{P})}$ are the reaction rates of their respective chemical reactions, and M is the third body which carries off excess energy in a termolecular reaction. Because CO_2 photodissociation is important only above the mesosphere (e.g. Garcia et al., 2014), it was ignored in this study. KIEs in the CH_4 – CO – CO_2 chain reaction were not included explicitly in these simulations but were rather treated in a coarse manner as follows. Simulations were performed with and without the chemical production of CO_2 . Taking the CO_2 mole fractions simulated with (‘wP’) and without chemical production (‘nP’) to be $n(\text{CO}_2)_{\text{wP}}$ and $n(\text{CO}_2)_{\text{nP}}$, respectively, the CO_2 mole fraction difference between the two simulations, $n(\text{CO}_2)_{\text{wP}} - n(\text{CO}_2)_{\text{nP}}$, was calculated as the apparent CO_2 production in the stratosphere. The apparent CO_2 production is distinct from the local production calculated in Eq. (B3) because it is an apparent value influenced by the accumulated chemical processes along the pathway of the air mass, including transport and mixing. A typical value of the apparent CO_2 production was simulated to be about $1.5 \mu\text{mol mol}^{-1}$ at 35 km altitude in the mid-latitudes. Similarly, the $\delta^{13}\text{CO}_2$ value simulated excluding chemical CO_2 production was expressed by $\delta^{13}\text{CO}_{2,\text{nP}}$. After both these simulations, the



$\delta^{13}\text{CO}_2$ value including airborne CO_2 sources from the CH_4 destruction, $\delta^{13}\text{CO}_{2,\text{WP}}$, was calculated as:

$$\delta^{13}\text{CO}_{2,\text{WP}} = \frac{\delta^{13}\text{CO}_{2,\text{NP}} \times n(\text{CO}_2)_{\text{NP}} + \delta^{13}\text{CH}_4 \times [n(\text{CO}_2)_{\text{WP}} - n(\text{CO}_2)_{\text{NP}}]}{n(\text{CO}_2)_{\text{WP}}} \quad (\text{B4})$$

In this equation, $\delta^{13}\text{CH}_4$ was calculated using Eq. (6) assuming apparent fractionation factors of 0.9889 and 0.9866 at lower (<24 km) and upper (>24 km) altitudes, respectively (see Sect. 3.2). Note that $\delta^{13}\text{CH}_4$ values were estimated from the apparent fractionation factors by assuming Rayleigh distillation relationships between vertical profiles of CH_4 mole fraction and $\delta^{13}\text{CH}_4$. Therefore, these apparent fractionation factors differed from fractionation factors *sensu stricto* and were influenced by the accumulated KIEs along the pathway of the air mass, as with the apparent CO_2 production described above. Eq. (B4) means that $\delta^{13}\text{CO}_2$ was simulated by combining the apparent fractionation factors estimated from observations with the apparent CO_2 production simulated by the model.

A virtual clock tracer was used to calculate the mean age of air. However, previous research has shown that the speed of the Brewer–Dobson circulation in SOCRATES is fast, leading to an underestimation of age of air. Therefore, similar to Sugawara et al. (2018), we reduced the mass stream function to approximate a realistic mean age, which also improved the reproduction of GS. The model results of GS reproduced well the almost linear decrease with increasing altitude above the tropopause in the observational results (Fig. A1). The model calculations were carried out over the 25 years from 1995 to 2020. The monthly average meridional distribution of the mean air age, GS, and CH_4 mole fraction calculated by SOCRATES for August 2016 is shown in Figure B1.

Appendix C: CO_2 mole fraction and age calculations

Corresponding to the secular decrease of $\delta^{13}\text{CO}_2$, an increase in CO_2 mole fraction was also clearly observed in the mid-stratosphere. To compare the temporal variations of the CO_2 mole fraction in the mid-stratosphere with those in the troposphere, the average values above 24 km altitude were calculated for each year, shown in Figure C1 alongside the monthly average data obtained by NOAA/ESRL at MLO. The results of the WMO/IAEA Round Robin Comparison Experiment showed that our CO_2 mole fraction values were approximately $0.2 \mu\text{mol mol}^{-1}$ higher than the NOAA/ESRL values; accordingly, our CO_2 mole fraction values are plotted in Figure C1 only after subtracting $0.2 \mu\text{mol mol}^{-1}$. The CO_2 mole fraction in the mid-stratosphere over Japan increased monotonously and reached about $400 \mu\text{mol mol}^{-1}$ in 2020, lagging behind that at MLO by about 5 years. The average rate of change of the CO_2 mole fraction in the mid-stratosphere was calculated to be $1.68 \pm 0.04 \mu\text{mol mol}^{-1} \text{ yr}^{-1}$ by applying the least-squares method to the observed values. However, this increasing trend was not linear, gradually steepening over the last 40 years. Therefore, a quadratic function of the form $n(\text{CO}_2) = K_0 + (K_1 \times t) + (K_2 \times t^2)$ would better represent the observed variations. Here, t (years) is the elapsed time since 1980. The coefficients of CO_2 mole fraction in the mid-stratosphere K_0 , K_1 , and K_2 were calculated to be 333.7, 1.0448, and 0.014755, respectively. The standard deviation of residuals was $0.8 \mu\text{mol mol}^{-1}$. The same procedure was applied to the annual mean CO_2 mole fractions at MLO for the period 1980–2015, considering a time lag of 5 years between the mid-stratosphere and the troposphere. The coefficients K_0 , K_1 , and K_2 for the MLO data were calculated to be 338.85, 1.2307, and 0.014577, respectively. As seen in Figure C1, the two quadratic functions thusly obtained agreed well to within $\pm 0.7 \mu\text{mol mol}^{-1}$. This result suggested that even temporal changes in the rate of increase in the troposphere



propagate to the mid-stratosphere with a certain time delay.

The CO₂ age based on our balloon observations has been partly reported in previous studies (Engel et al., 2002; Ishidoya et al., 2013; Umezawa et al., 2024). CO₂ ages estimated using air samples collected from 1995 to 2010 have been published as supplementary data in Ishidoya et al. (2013). However, the method of age estimation was subsequently updated in Sugawara et al. (2018). In this study, we further improved the estimation method by correcting the CO₂ mole fraction data for GS and created a new 35-year CO₂ age record. We estimated the mean age of air from the CO₂ mole fraction using the convolution method (Ray et al., 2017; Leedham Elvidge et al., 2018; Sugawara et al., 2018); this method has been described in detail by Sugawara et al. (2018), so only a brief explanation is given here. Hypothetical age spectra were used in the convolution method to estimate the mean age (Waugh and Hall, 2002). Expected temporal variations in the CO₂ mole fraction in the stratosphere, $x(I, t)$, were calculated by convolution of the tropospheric reference curve, $x_0(t)$, and the age spectrum, $G(I, t)$:

$$x(I, t) = \int_{t-T_B}^t x_0(t') G(I, t - t') dt', \quad (C1)$$

where T_B is the integration time interval. T_B should theoretically be ∞ , but we truncated it to 20 years for the calculations.

Actual age spectra, $G(I, t)$ are usually unknown. Therefore, we used the inverse Gaussian distribution (Waugh and Hall, 2002) as:

$$G(I, t) = \left(\frac{I^3}{4\pi\Delta^2 t^3} \right)^{1/2} \exp \left[-\frac{I(t-I)^2}{4\Delta^2 t} \right], \quad (C2)$$

where Δ denotes the width of the age spectrum, which was parameterized using the mean age (I), i.e. the ratio of moments, Δ^2/I . This value has usually been assumed to be 0.7 years, as suggested by Hall and Plumb (1994) based on results from a General Circulation Model calculation, and was used to estimate SF₆- and CO₂-derived mean ages in the northern mid- and high-latitude stratosphere (Engel et al., 2002). Recently, however, Fritsch et al. (2020) have reported that a value of 1.25 years is better for estimating ages from the SF₆ mole fraction. Therefore, we used 1.25 years for the ratio of moments in this study. After calculating the convolutions, the CO₂ age was determined by substituting the observed CO₂ mole fractions, x_{obs} , into the inverse function, $I(x, t)$.

As described in the main text, the influences of CO₂ production by CH₄ oxidation and GS should be considered to precisely estimate the CO₂ age. Therefore, the CO₂ mole fraction was corrected as follows. At first, the tropical upper tropospheric CH₄ data, $x_{\text{CH}_4, \text{tp}}(t)$, were created by adjusting the annual mean data at MLO to fit the CONTRAIL data in the tropical upper troposphere (Umezawa et al., 2012). Then, we corrected x_{obs} as:

$$x_{\text{cor}}(t) = x_{\text{obs}}(t) - [x_{\text{CH}_4, \text{tp}}(t - I) - x_{\text{CH}_4, \text{obs}}(t)] - \Delta_G(x_{\text{obs}}(t)), \quad (C3)$$

where x_{cor} and $x_{\text{CH}_4, \text{obs}}$ denote the corrected CO₂ mole fraction and observed CH₄ mole fraction, respectively. Δ_G is the correction for GS (see Sect. 3.3.). The CO₂ mole fractions corrected for CH₄ oxidation and GS are shown with the convolutions in Figure C2. Finally, the CO₂ age was determined as $I_{\text{CO}_2} = I(x_{\text{cor}}, t)$. We note that Eq. (C3) contains the mean age of air, I , because the CH₄ mole fraction in the troposphere has increased with time and CH₄ is destroyed over the air transport pathway from the tropical upper troposphere to the observation altitude in the stratosphere. Therefore, I_{CO_2} was solved iteratively by starting from $I_{\text{CO}_2} = 0$. This iteration converged sufficiently after the second time of I_{CO_2} calculation. The vertical profiles of I_{CO_2} , corresponding to CO₂ age, are shown in Figure C3. The $\delta^{13}\text{C}_\text{p}$ age was also



calculated using the same method, except that the corrections for CH₄ oxidation and GS were already included when calculating $\delta^{13}\text{C}_\text{P}$. The convolutions are shown with the calculated $\delta^{13}\text{C}_\text{P}$ values in Figure C4.

715 **Data availability.** The observational data obtained by our balloon measurements are included as an electronic supplement to the manuscript.

Author contributions. SS designed the study, conducted the measurements of mole fractions of greenhouse gases, and drafted the manuscript. SM, TN, SA, and SS conducted the measurements of carbon isotopic ratios of CO₂. SM, SS, and
720 TU conducted the measurements of carbon isotopic ratios of CH₄. SI conducted the measurements of isotopic and elemental ratios of atmospheric major compositions. KI conducted the measurements of N₂O mole fraction. HH, TN, SA, SM, and SS conducted the balloon experiments. SI, ST, and DG participated in balloon experiments. All authors approved the final manuscript.

725 **Competing interests.** The corresponding author declares that none of the authors has any competing interests.

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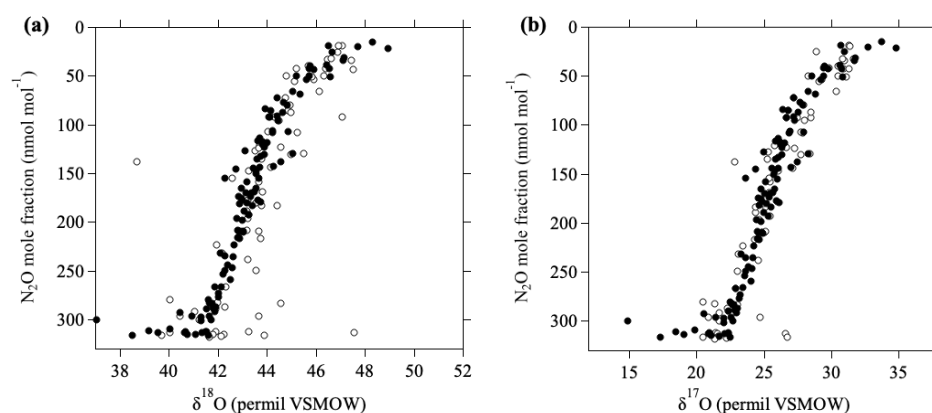
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970

Figures



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Figure 1. The relationship between the N_2O mole fraction and (a) $\delta^{18}\text{O}$ in CO_2 and (b) $\delta^{17}\text{O}$ in CO_2 . $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values measured by Kawagucci et al. (2008) are shown by open circles. $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ values calculated assuming a MIE factor of 1.7 (see text) in this study are shown by closed circles.

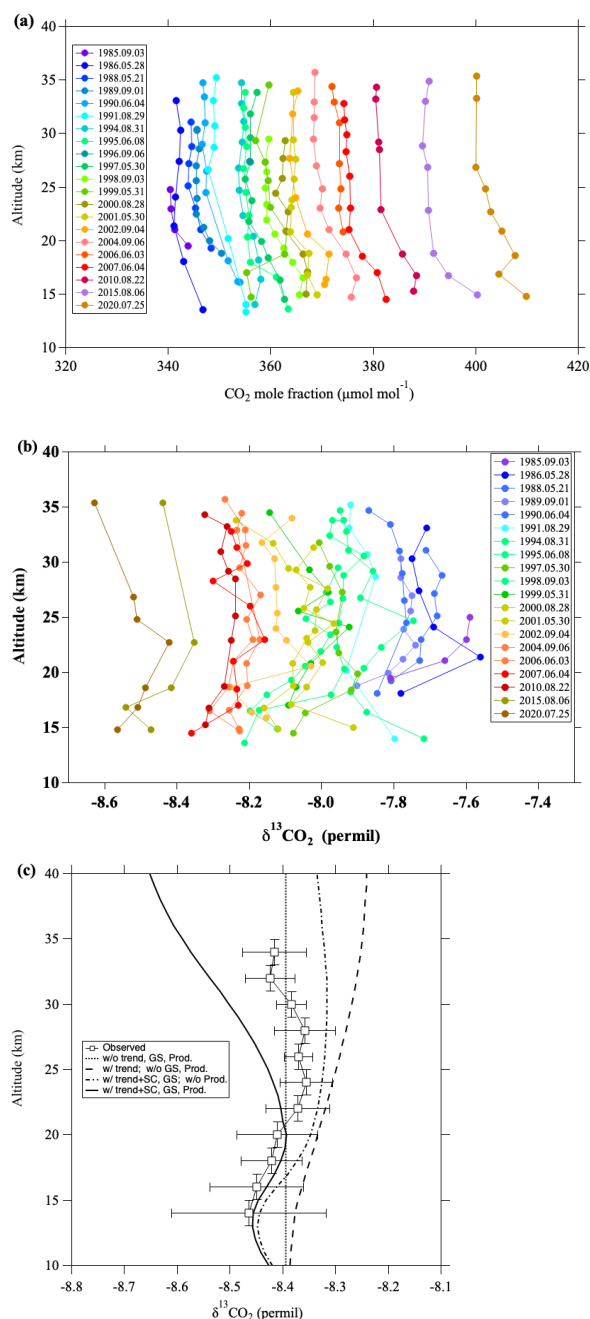
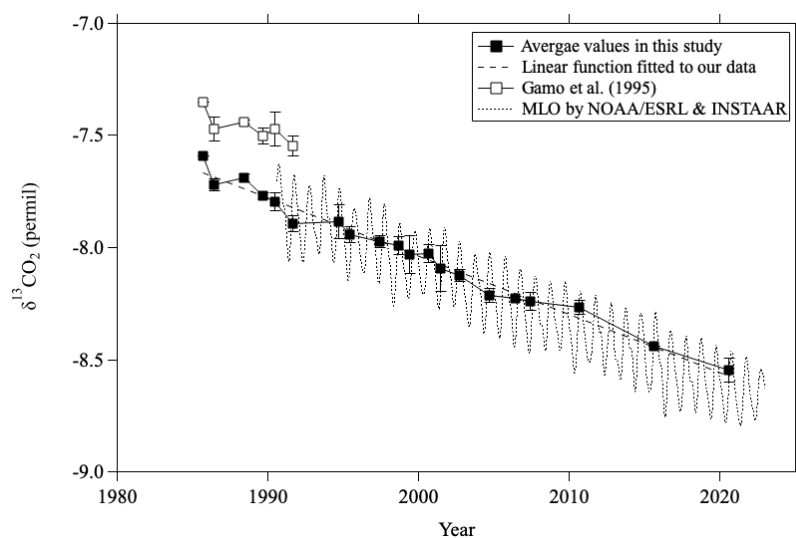


Figure 2. Vertical profiles of (a) CO₂ mole fraction and (b) δ¹³CO₂ over Japan during the period 1985–2020. (c) δ¹³CO₂ values averaged over the study period and grouped in eleven 2-km vertical bins (open squares). Curves show 2-D modeling results without the tropospheric trend, GS, or airborne sources (dotted line), including only the tropospheric trend (dashed line), including the tropospheric trend, seasonal cycle, and GS (dotted-dashed line), and including the tropospheric trend, seasonal cycle, GS, and airborne sources (solid line).



990 **Figure 3.** Average mid-stratospheric (>24 km altitude) $\delta^{13}\text{CO}_2$ values over Japan (closed squares). The linear function fitted to the average values using the least-squares method is shown by the dashed line. Values reported by Gamo et al. (1995) are shown by open squares. The best-fit curve for $\delta^{13}\text{CO}_2$ observed at Mauna Loa by NOAA/ESRL and INSTAAR is also shown by the dotted line.



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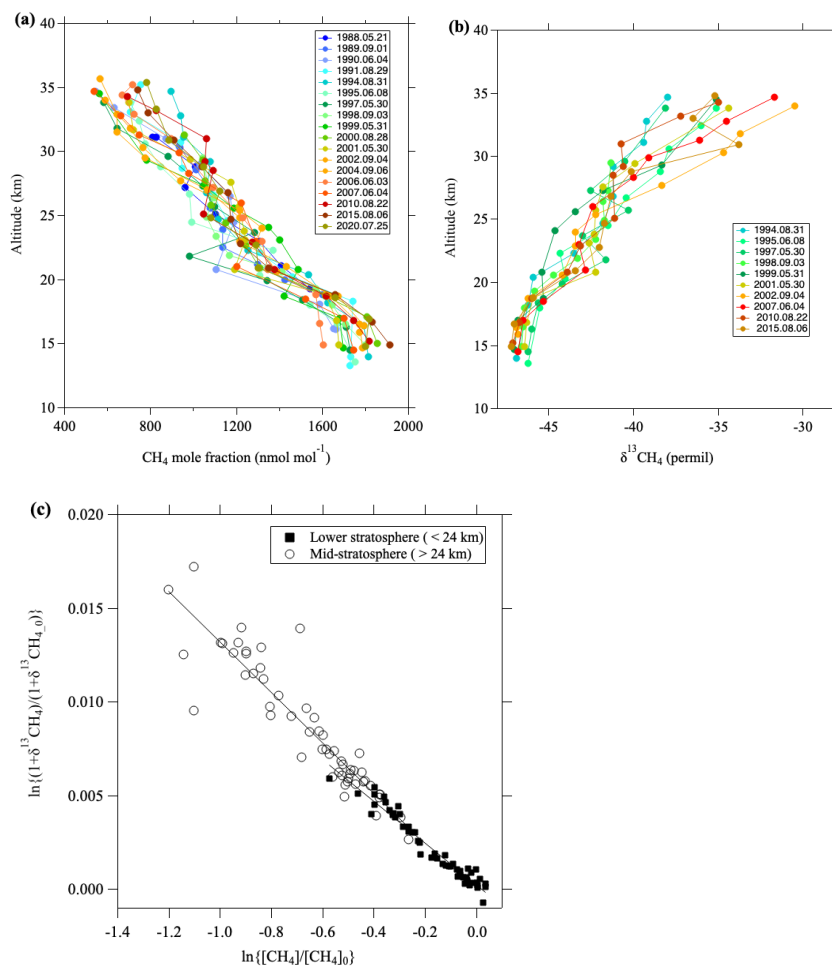


Figure 4. Vertical profiles of (a) CH₄ mole fraction and (b) δ¹³CH₄ over Japan, and (c) the relationship between $\ln\{(\delta^{13}\text{CH}_4 + 1)/(\delta^{13}\text{CH}_{4,0} + 1)\}$ and $\ln\{[\text{CH}_4]/[\text{CH}_4]_0\}$. In (c), the data are divided into the lower (<24 km, closed squares) and mid-stratosphere (>24 km, open circles), and the linear functions fitted to each dataset using the least-squares method are shown by lines.

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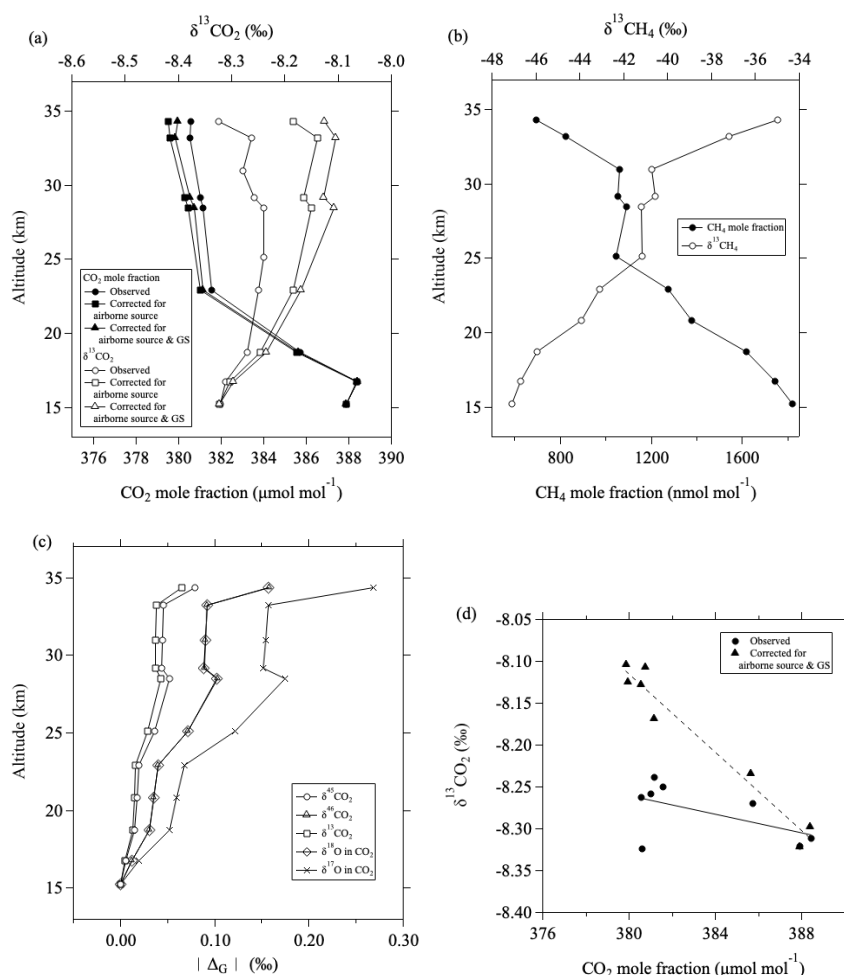
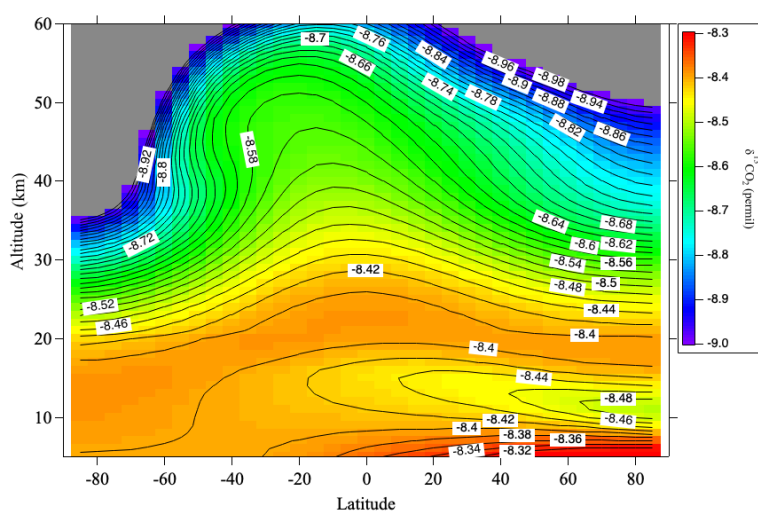


Figure 5. (a) Vertical profiles of the CO₂ mole fraction (closed circles) and $\delta^{13}\text{CO}_2$ (open circles) observed over Japan on 22 August 2010. Values corrected for airborne CO₂ sources (squares) and additionally for GS (triangles) are also shown. (b) Vertical profiles of the CH₄ mole fraction (closed circles) and $\delta^{13}\text{CH}_4$ (open circles). (c) Vertical profiles of the magnitude of GS corrections, $|\Delta_G|$, for $\delta^{45}\text{CO}_2$ (circles), $\delta^{46}\text{CO}_2$ (triangles), $\delta^{13}\text{CO}_2$ (squares), and $\delta^{18}\text{O}$ (diamonds) and $\delta^{17}\text{O}$ (crosses) in CO₂. (d) Observed $\delta^{13}\text{CO}_2$ plotted against CO₂ mole fraction (closed circles) and those corrected for airborne CO₂ sources and GS (triangles). Lines are linear functions fitted to each trend by the least-squares method.



Values lower than -9.0 ‰ are colored gray.

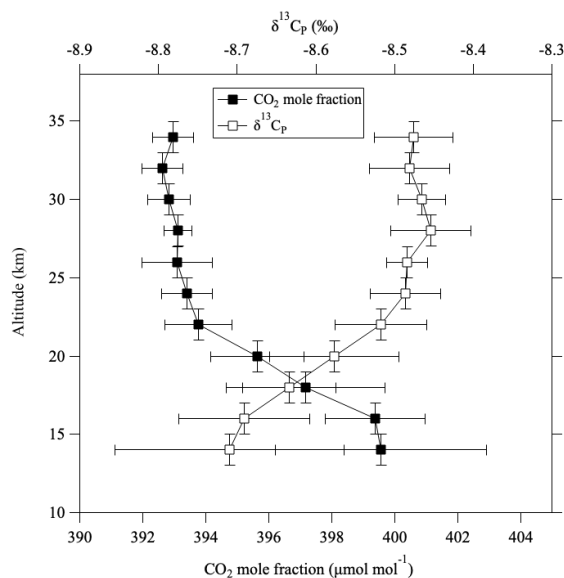


Figure 8. Vertical profiles of CO_2 mole fraction (closed squares) and stratospheric potential $\delta^{13}\text{C}$ ($\delta^{13}\text{C}_\text{P}$, open squares) based on their averages in 11 vertical bins over the period 1985–2020. All values were detrended and normalized to values in August 2016.

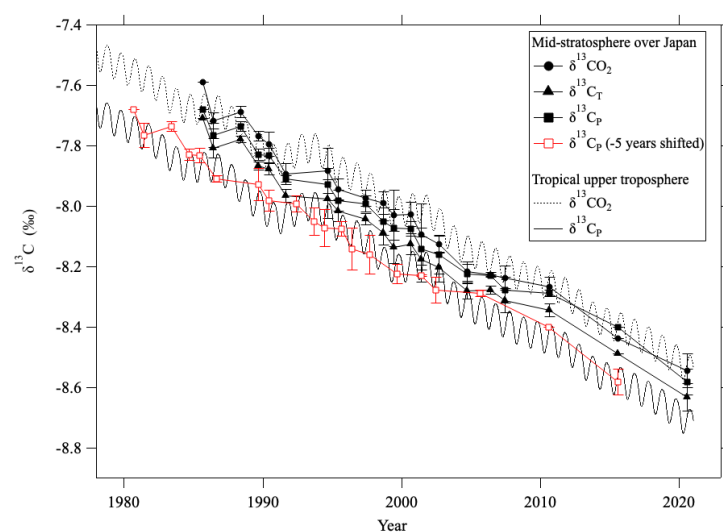
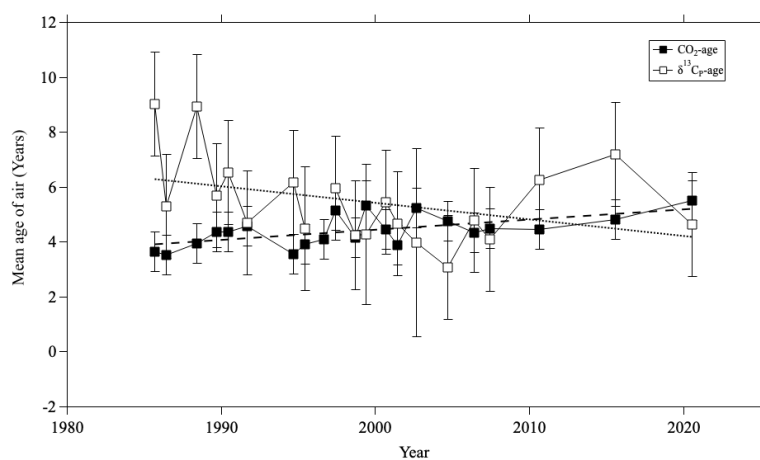


Figure 9. Average mid-stratospheric (>24 km altitude) values of $\delta^{13}\text{CO}_2$ (closed circles), $\delta^{13}\text{C}_\text{T}$ (closed triangles), and $\delta^{13}\text{C}_\text{P}$ (closed squares) over Japan. $\delta^{13}\text{CO}_2$ and $\delta^{13}\text{C}_\text{P}$ in the tropical upper troposphere are shown by dashed and solid lines, respectively. Red squares show the mid-stratospheric $\delta^{13}\text{C}_\text{P}$ shifted by -5.0 years.



1035 **Figure 10.** Temporal variations of averaged $\delta^{13}\text{C}_\text{p}$ ages (open squares) and CO_2 ages (closed squares) in the mid-
stratosphere (>24 km altitude) over Japan. Dotted and dashed lines are linear least-squares fits to the $\delta^{13}\text{C}_\text{p}$ and CO_2 ages,
1040 respectively.



Figures for appendix

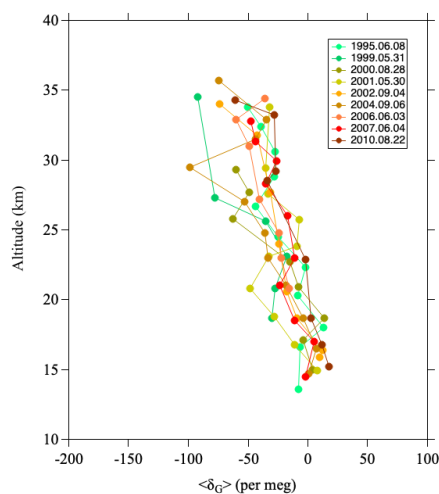


Figure A1. Vertical profiles of GS, $\langle \delta_G \rangle$, observed over Japan (Ishidoya et al., 2013).

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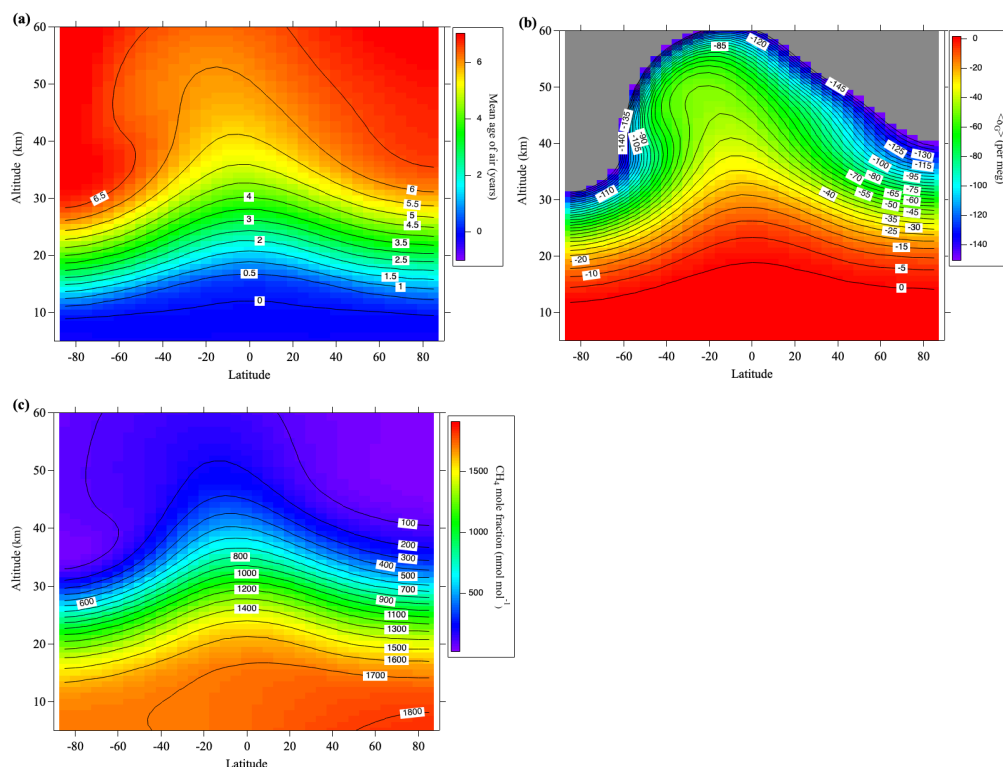


Figure B1. (a) Monthly average meridional distributions of the mean age of air for August 2016 calculated using the SOCRATES model. (b) As in (a), but for gravitational separation, $\langle \delta_G \rangle$. Values lower than -150 per meg are shown in gray. (c) As in (a), but for the CH_4 mole fraction.

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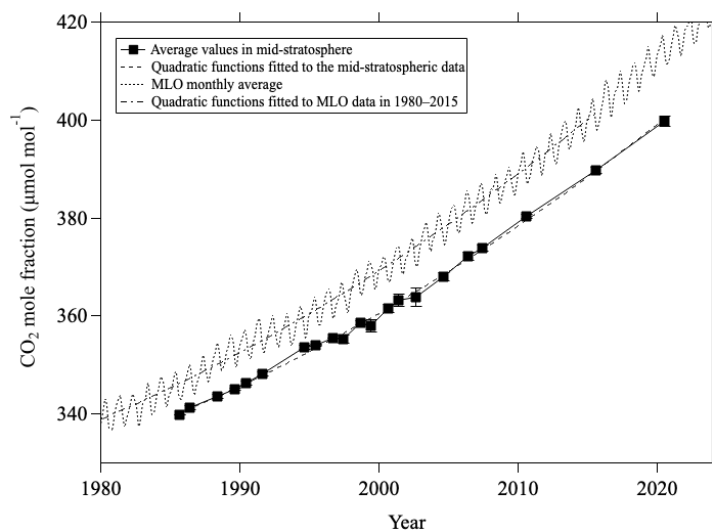


Figure C1. Average values of mid-stratospheric CO₂ mole fraction (>24 km altitude) over Japan (closed squares). Monthly average CO₂ mole fractions at Mauna Loa observed by NOAA/ESRL are shown by the dotted line. Quadratic functions fitted to the mid-stratospheric data (dashed line) and annual average MLO data from 1980 to 2015 (dashed-dotted line) are also shown.

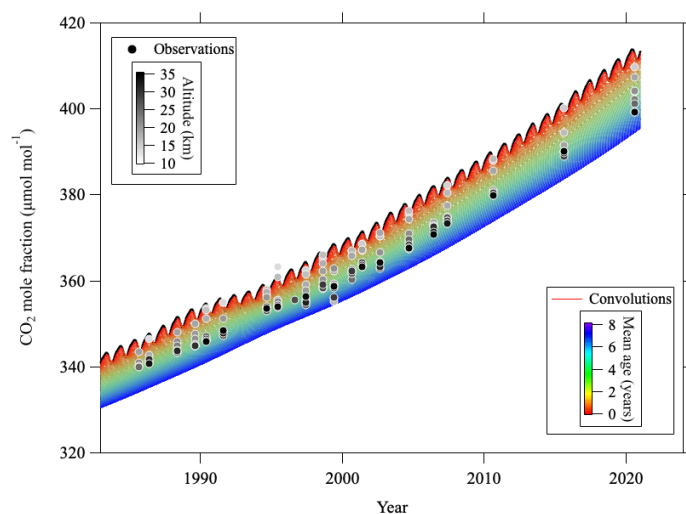


Figure C2. CO₂ mole fractions observed over Japan (circles) and convolutions (colored lines) calculated from the tropospheric reference record and age spectrum. Observation altitudes of the CO₂ mole fraction are indicated by the gray scale of the symbol colors. Note that the CO₂ mole fractions plotted have been corrected for CH₄ oxidation and GS.

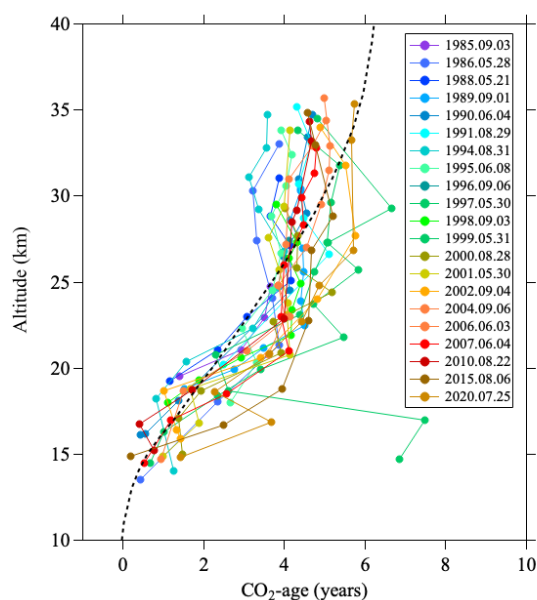


Figure C3. Vertical profiles of the CO₂ age calculated from CO₂ mole fractions from 1985 to 2020. The monthly average vertical profile of the mean age of air for August 2016 calculated using the SOCRATES model is shown by the dashed line.

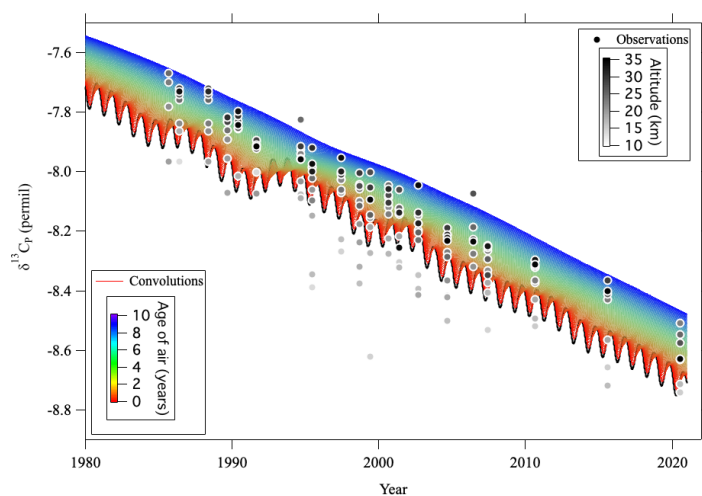


Figure C4. $\delta^{13}\text{C}_p$ observed over Japan (circles) and convolutions of $\delta^{13}\text{C}_p$ (colored lines) calculated from the tropospheric reference record and age spectrum. Observation altitudes of $\delta^{13}\text{C}_p$ are indicated by the gray scale of the symbol colors.