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Age and gravitational separation of the stratospheric air over Indonesia

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Abstract. Stratospheric air samples were collected over Biak, Indonesia in February 2015 using four large plastic balloons, each loaded with two compact cryogenic samplers. With a vertical resolution of better than 2 km, air samples from seven different altitudes were analyzed for CO_2 and SF_6 mole fractions, $\delta^{15}N$ of N_2, $\delta^{18}O$ of O_2, and $\delta(Ar/N_2)$, to examine vertically dependent age and gravitational separation of air in the Tropical Tropopause Layer (TTL) and the equatorial stratosphere. By comparing their measured mole fractions with aircraft observation in the upper tropical troposphere, we have found that CO_2 and SF_6 age increases gradually with increasing altitude from the TTL to 22 km, and then rapidly from there up to 25 km. The CO_2 and SF_6 age agrees well with each other in the TTL and in the lower stratosphere, but shows a significant difference above 24 km. The average values of $\delta^{15}N$ of N_2, $\delta^{18}O$ of O_2, and $\delta(Ar/N_2)$ all show small but distinct upward decrease due to the gravitational separation effect. Simulations with a two-dimensional atmospheric transport model indicate that the gravitational separation effect decreases as tropical upwelling is enhanced. From the model calculations with enhanced eddy mixing, it is also found that the upward increase in air age is magnified by horizontal mixing. These model simulations also show that the gravitational separation effect remains relatively constant in the lower stratosphere. The results of this study strongly suggest that the gravitational separation, combined with the age of air, can be used to diagnose air transport processes in the stratosphere.

1 Introduction

The age of air in the stratosphere provides important information about various stratospheric transport processes. It is expected that possible long-term changes in the Brewer–Dobson (BD) circulation are detectable from changes in the mean age of air evaluated from measurements of the stratospheric CO_2 and SF_6 mole fractions. Balloon and satellite observations

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(Engel et al., 2009; Stiller et al., 2012) found that the age of air derived from CO_2 and SF_6 in the stratosphere over the northern mid-latitudes did not show any significant trend over the last 30 years, although satellite observations have indicated that the SF_6 age might have increased for the period 2002–2010. More recently, Haenel et al. (2015) reported a negative trend in the age of air in the lowermost tropical stratosphere, by revising the MIPAS/SF_6 age data. To further add fire to the debate, results obtained from balloon and satellite observations do not agree with the recent model predictions that the BD circulation is accelerated due to an enhancement of mass flux from the tropical troposphere into the stratosphere (Austin and Li, 2006; Li et al., 2008).

A clock tracer, such as CO_2 or SF_6, is lifted up from the tropical upper troposphere into the stratosphere and is transported to mid-latitudes; part of this then returns to the lower latitudes via mixing process in the stratosphere, which results in increasing the clock tracer age in the lower latitudes. Therefore, to discuss a change in the mean age estimated using the clock tracer, it is important to separately evaluate the respective effects of mean circulation and mixing processes on the air age. Recently, it was shown by high-precision measurements of the isotopic ratios of N_2, O_2, and Ar and the Ar/N_2 ratio that the gravitational separation of the air is clearly observable in the northern mid-latitude stratosphere (Ishidoya et al., 2006, 2008a, 2008b, 2013). Ishidoya et al. (2013) also reported that the gravitational separation could be used as a new indicator to detect long-term behavior of the BD circulation.

Most stratospheric air originates in the Tropical Tropopause Layer (TTL) and is then slowly lifted up from lower to upper levels. Therefore, observations of stratospheric air compositions, from which the age and gravitational separation of air are deduced, are necessary in the equatorial region to understand the various transport processes in the stratosphere. Collecting whole air with balloon-borne samplers is the most reliable method so far to precisely observe the mole fractions of atmospheric compositions from the tropopause to about 35 km. Unfortunately, due to the limited availability of balloon launching facilities, only a few air sampling programs have been carried out in the low latitude stratosphere (Patra et al., 1997; Andrews et al., 2001), and no air sampling has been conducted in the equatorial mid-stratosphere.

To measure the CO_2 and SF_6 mole fractions in the equatorial stratosphere, we conducted whole air sampling with balloon-borne cryogenic samplers over Biak, Indonesia in February 2015 as part of an observation campaign called "Synthesis of Dynamics and Chemistry for the Understanding of Atmospheric Processes in the Tropical Tropopause Layer over Indonesia" (Hasebe et al., submitted to BAMS), in cooperation with the National Institute of Aeronautics and Space of the Republic of Indonesia (LAPAN). In this paper, we present measured vertical profiles of the CO_2 and SF_6 mole fractions, and discuss some of the implications of these measurements on the age and gravitational separation of stratospheric air. We also simulated the age and gravitational separation of air using a two-dimensional model (SOCRATES) (Huang et al., 1998; Park et al., 1999; Khosravi et al., 2002). Based on the simulation results, we discuss the effects of tropical upwelling and horizontal mixing on the age and gravitational separation of air.

2 Experimental Procedures

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The collection of stratospheric air over Indonesia was performed using a balloon-borne cryogenic sampler. A map of the balloon launch site is shown in Figure 1. The cryogenic air sampler is equipped with a cooling device called "Joule–Thomson (J–T) mini cooler" in which neon is liquefied to be used as a refrigerant for collecting stratospheric air cryogenically (Morimoto et al., 2009). Eight sets of cryogenic air samplers and four large plastic balloons were prepared for the present observation. Each balloon was loaded with two air samplers to collect stratospheric air at two different altitudes. The balloons were launched from the LAPAN observatory at Biak (001° 10'32" S 136° 06'02" E) on February 22, 24, 26, and 28, 2015; the samplers were successfully recovered from a coastal area of Biak on the same day of each launch. Thus, we successfully collected stratospheric air samples at 8 altitudes from 17.2 to 28.7 km, with one at 17.2 and another at 18.5 km inside the Tropical Tropopause Layer (TTL). One sampler assigned to 21 km leaked after landing due to a trouble in electric circuit. Overall, the amount of air collected ranged from 2.0 to 9.3 L at standard temperature (0°C) and pressure (1013.25 hPa), depending on the sampling altitude, enough to measure the mole fractions and isotopic ratios of various gases. The collected air samples were sent to Japan, and then analyzed for $\delta^{15}N$ of N_2, $\delta^{18}O$ of O_2, and $\delta(Ar/N_2)$ using a mass spectrometer and for CO_2 and SF_6 mole fractions using a non-dispersive infrared gas analyzer (NDIR) and a gas chromatograph (GC) equipped with an electron capture detector, respectively.

In this study, $\delta^{15}N$, $\delta^{18}O$, and $\delta(Ar/N_2)$ are defined as:

$$\delta^{15}\mathrm{N} = \left(\frac{\left[n\left({}^{15}\mathrm{N}{}^{14}\mathrm{N}\right) / n\left({}^{14}\mathrm{N}{}^{14}\mathrm{N}\right) \right]_{\mathrm{sample}}}{\left[n\left({}^{15}\mathrm{N}{}^{14}\mathrm{N}\right) / n\left({}^{14}\mathrm{N}{}^{14}\mathrm{N}\right) \right]_{\mathrm{standard}}} - 1 \right) \times 10^6 \quad (per\ meg), \tag{1a}$$

$$\delta^{18}\mathrm{O} = \left(\frac{\left[n\left({}^{18}\mathrm{O}{}^{16}\mathrm{O}\right) / n\left({}^{16}\mathrm{O}{}^{16}\mathrm{O}\right) \right]_{\mathrm{sample}}}{\left[n\left({}^{18}\mathrm{O}{}^{16}\mathrm{O}\right) / n\left({}^{16}\mathrm{O}{}^{16}\mathrm{O}\right) \right]_{\mathrm{standard}}} - 1 \right) \times 10^6 \quad (per\ meg), \tag{1b}$$

and

$$\delta(\mathrm{Ar}/\mathrm{N}_2) = \left(\frac{\left[n\left({}^{40}\mathrm{Ar}\right) / n\left({}^{14}\mathrm{N}{}^{14}\mathrm{N}\right) \right]_{\mathrm{sample}}}{\left[n\left({}^{40}\mathrm{Ar}\right) / n\left({}^{14}\mathrm{N}{}^{14}\mathrm{N}\right) \right]_{\mathrm{standard}}} - 1 \right) \times 10^6 \quad (per\ meg), \tag{1c}$$

where n means the amount of each substance, and "sample" and "standard" denote the sample and standard gases, respectively. Technical details of our mass spectrometry analyses have been described in Ishidoya and Murayama (2014). In this study, we were able to determine $\delta^{15}N$, $\delta^{18}O$, and $\delta(Ar/N_2)$ more precisely than Ishidoya et al. (2013), with the respective reproducibility of about ±2, ±5, and ±7 per meg (±1σ), precise enough to detect small variations of interest in the stratosphere over the equatorial region. A detailed technical aspect of our CO_2 analysis has been given in Nakazawa et al. (1995) and Aoki et al. (2003). The CO_2 mole fraction was measured using an NDIR with analytical precision of better than 0.02 μmol mol^{-1}, employing our new CO_2 standard gases prepared in 2010 by a one-step dilution gravimetric method with an estimated uncertainty of 0.1 μmol mol^{-1}.

Since our SF_6 analysis procedure has not been published yet, a brief description is given here. The SF_6 mole fraction of each

sample was determined twice at Tohoku University (TU) and twice at the Miyagi University of Education (MUE) against our SF_6 standard gas scale using their respective GCs. The analytical procedures at TU and MUE were basically the same, with a mixture of Ar (95%) and CH_4 (5%) used as a carrier gas for both GCs, but while TU employed Agilent 6890 with a packed column, MUE used 7890N with a capillary column. The volume of a sample loop was 10 mL for the TU's GC and 1 mL for the MUE's GC. Our SF_6 working standard gases used for the sample analysis were calibrated against our primary standard gases that were produced by the seven-step dilution gravimetric method. We prepared the primary standard gases twice in 2001 (2001 scale) and 2002 (2002 scale), and found that the 2001 scale provides higher values by 0.10-0.15 pmol mol^{-1} than the 2002 scale in a range of observed atmospheric SF_6 mole fractions. The 2001 scale was compared with those of other institutes in the 5th and 6th WMO/IAEA Round Robin Comparison Experiment programs (https://www.esrl.noaa.gov/gmd/ccgg/wmorr/), and the results showed that the 2001 scale is higher by 0.15 pmol mol^{-1}, on average, than the WMO X2006 scale. We also made an intercomparison of the SF_6 standard gas among TU, MUE, and the National Institute of Environmental Studies (NIES), Japan in August 2016. The results indicated that the 2001 scale is higher by 0.10-0.15 pmol mol^{-1} than the NIES gravimetric scale, implying a good agreement between the 2002 scale and the NIES scale. Therefore, we decided to employ the 2002 scale for our measurements of the SF_6 mole fraction. The reproducibility of our SF_6 analysis was estimated to be better than 0.09 pmol mol^{-1}, based on one standard deviation (1σ) obtained from three replicate analyses of one air sample. The CH_4 mole fraction of the air sample was also determined against our gravimetrically prepared CH_4 standard gas system using the GC with a flame ionization detector (Sugawara et al., 1997), since the measured value is necessary for the estimation of CO_2 age, as described below.

Possible deterioration of an air sample during storage should be closely examined and taken into account to accurately estimate the age of air from the measured mole fraction. From our experience of collecting air samples using the cryogenic sampler in Antarctica and Eastern Equatorial Pacific, we have found that the CO_2 mole fraction of air collected in stainless-steel bottle changes during sample storage, presumably due to CO_2 absorption on inner wall of the bottle. Although all the stainless-steel bottles used in this study were repeatedly evacuated prior to use, the CO_2 mole fraction still showed a slight decrease. Therefore, we carried out a sample storage test for each bottle to correct for the deterioration effect. The amounts of the correction ranged from 0.0 μmol mol^{-1} to 0.7 μmol mol^{-1}, depending on the bottle.

3 Results and Discussion

3.1 Vertical profiles

Vertical profiles of the CO_2 and SF_6 mole fractions, $\delta^{15}N$ of N_2, $\delta^{18}O$ of O_2, and $\delta(Ar/N_2)$ in the TTL and stratosphere over Biak are shown in Figure 2. The exact values are given in Table 1 and 2. As shown in Figure 2, the CO_2 and SF_6 mole fractions are high in the TTL and decrease with increasing altitude. Considering that there are no sources and sinks of CO_2 and SF_6 in the stratosphere, except for a small amount of CO_2 production by CH_4 oxidation, the observed vertical profiles of

the two variables are mainly formed by atmospheric transport processes. In particular, tropical upwelling in the atmosphere plays an important role in the mole fraction decrease with altitude, i.e., temporal variations of the mole fraction in the upper tropical troposphere are recorded as a vertical distribution due to the upward air transport from the TTL to the stratosphere. It is also seen from Figure 2 that the mole fractions do not change monotonically with altitude but decrease gradually from the TTL to 24 km and then rapidly to near constant values above 25 km. Such complicated vertical CO_2 and SF_6 profiles can be produced by height-dependent upwelling and/or vertical and horizontal mixing. Similar CO_2 and SF_6 profiles have been reported by previous studies primarily in the northern mid-latitudes (Bischof et al., 1985; Schmidt and Khedim, 1991; Nakazawa et al., 1995, 2002; Aoki et al., 2003; Engel et al., 2009). However, the vertical gradient of the stratospheric CO_2 profile is much smaller in the tropics than in the mid-latitudes (e.g., Nakazawa et al., 1995; Aoki et al., 2003); a typical difference of the CO_2 mole fraction between the lowermost and middle stratosphere (~30 km) over Japan is about 8 μmol mol^{-1}, whereas in the tropical stratosphere the difference is almost half of that observed in the mid-latitudes. We also measured vertical distributions of CO_2 and SF_6 from 15 to 35 km (unpublished data) over Hokkaido, Japan (42° 30' N 143° 26' E) in August 2015, using our traditional cryogenic sampler with liquid He (Nakazawa et al., 1995; Aoki et al., 2003). By comparing the mole fractions of mid-stratospheric CO_2 and SF_6 in the tropics (Biak) with those observed in the northern mid-latitudes (Hokkaido), the latitudinal differences in the CO_2 and SF_6 mole fractions were found to be 5.7 ± 0.8 μmol mol^{-1} and 0.8 ± 0.2 pmol mol^{-1}, respectively. Considering that the air sampling over Hokkaido was carried out 6 months after Biak, these differences were obtained after taking into account the effects of the CO_2 and SF_6 increase and CO_2 production by CH_4 oxidation using the recent tropospheric increase rates of CO_2, SF_6 and CH_4. If the transit time of an atmospheric tracer from the tropics to mid-latitudes can be simply obtained by dividing the latitudinal difference of the mole fraction between the two regions by its recent tropospheric increase rate, then the above observed differences would yield 2.4 ± 0.4 yrs for CO_2 and 2.5 ± 0.8 yrs for SF_6. These transit times correspond to aging of the air during the poleward transport from the equatorial region to mid-latitudes through the middle stratosphere. If we compare the average mole fraction values of these two gases at higher altitudes (30–35 km) in mid-latitudes with those above 25 km over Biak, the latitudinal difference is 5.5 μmol mol^{-1} for CO_2 and 1.1 pmol mol^{-1} for SF_6, corresponding to the respective transit times of 2.4 and 3.6 yrs. These results indicate that the difference between the transit times of CO_2 and SF_6 becomes larger at these higher altitudes. Since the estimation of the age of stratospheric air is seriously affected by the transit time, the different transit times derived from CO_2 and SF_6 will be discussed later.

As shown in Figure 2, $\delta^{15}N$ of N_2, $\delta^{18}O$ of O_2, and $\delta(Ar/N_2)$ decrease gradually with increasing altitude. Differences between the values at the lowermost and uppermost height levels (hereafter written as Δδ) are 11.2, 18.4, and 153.3 per meg for $\delta^{15}N$, $\delta^{18}O$, and $\delta(Ar/N_2)$, respectively. Considering that the mass number differences of the related molecules are 1, 2, and 12 for $\delta^{15}N$, $\delta^{18}O$, and $\delta(Ar/N_2)$, respectively, Δδ seems to increase with increasing mass number difference. Vertical distributions of the stable isotopic ratios of the major atmospheric components in the stratosphere were first reported by Ishidoya et al. (2006, 2008a, 2008b). They concluded that the overall vertical structures of the isotopic ratios are basically caused by

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gravitational separation (Ishidoya et al., 2013), based on mass-dependent relationships between the related molecules. In this study, we also found, by examining Δδ in terms of the mass number differences of related molecules, that the relationship can be approximated by a linear function, as shown in Figure 3. This suggests that the upward decreases of $\delta^{15}N$, $\delta^{18}O$, and $\delta(Ar/N_2)$ are mass dependent and that gravitational separation is observable in the stratosphere, not only in the mid-latitudes but also in the tropics. After arranging all the observed $\delta^{15}N$, $\delta^{18}O$, and $\delta(Ar/N_2)$ measurements so that the values of the respective variables measured in the lowermost level become zero, we define an average value of $\delta^{15}N$, $\delta^{18}O$, and $\delta(Ar/N_2)$ as,

$$\langle\delta\rangle = \frac{1}{3}\left[\delta^{15}N + \delta^{18}O/2 + \delta\left(Ar/N_2\right)/12\right], \quad (2)$$

which is normalized for the mass number differences. Ishidoya et al. (2013) reported that the <δ> difference between the tropopause and 32 km was approximately 45 per meg in the mid-latitude stratosphere. On the other hand, our result shows that the <δ> difference between the lowermost and uppermost levels is only 11 per meg in the tropical stratosphere. This implies that the gravitational separation in the stratosphere is much weaker in the tropics than in the mid-latitudes.

3.2 Age of air

To estimate the age of stratospheric air using a clock tracer such as CO_2 or SF_6, a long-term record of its mole fraction observed in the upper troposphere is necessary as a reference. Since the tropospheric reference record is critical for calculating the stratospheric air age from the clock tracer data, it needs to be standardized. However, different data records have been used as a reference in different studies. For example, the data obtained at ground-based monitoring sites in tropical or subtropical regions were widely used for the tropospheric record after correcting for the mole fraction differences between the surface and the upper troposphere. Therefore, the estimated air ages have been plagued with large uncertainties due not only to the selection of the monitoring site, but also to the correction for the mole fraction difference between the site and the tropical upper troposphere. Uncertainties in the transport time from the boundary layer to the tropopause in the tropics have also been pointed out by Stiller et al. (2012). However recently, 10 or more-year mole fraction records of upper tropospheric CO_2 and SF_6 have become available from the Automatic Air Sampling Equipment (ASE) employed in the Comprehensive Observation Network for TRace gases by AIrLiner (CONTRAIL) program (Machida et al., 2008, Matsueda et al., 2015). In this study, we have exploited the opportunity and constructed a set of tropical upper tropospheric CO_2 and SF_6 records from the CONTRAIL data obtained between 5° S and 5° N, between 142° E and 150° E and between 10 and 13 km over Southeast Asia. The selected CO_2 and SF_6 data are shown in Figures 4 and 5, respectively, together with their best-fit curves obtained by using the Nakazawa et al. (1997) algorithm. Although we do not have sufficient knowledge about the temporal variations of their mole fractions near the top of the TTL to obtain a definitive age of the stratospheric air (Waugh and Hall, 2002), we decided to use the upper tropospheric CONTRAIL data records as a reference. Therefore, the age of air estimated in this study could be slightly overestimated.

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The CONTRAIL CO_2 and SF_6 mole fractions are determined against the NIES scales, while the stratospheric data obtained in this study are expressed in the TU scales. However, as pointed out above, the differences in the SF_6 mole fraction scales between NIES and TU/MUE were found to be negligibly small. Therefore, our SF_6 data can be directly compared with the CONTRAIL SF_6 data. On the other hand, since we found that the TU CO_2 mole fraction scale gives slightly higher values than the NIES scale, the TU CO_2 data were shifted down by 0.20 μmol mol^{-1}, based on the results of the 5th and 6th Round Robin inter-comparison programs (https://www.esrl.noaa.gov/gmd/ccgg/wmorr/wmorr_results.php?rr=rr6&param=co2).

The age of stratospheric air at each altitude was estimated by comparing the corresponding CO_2 or SF_6 mole fraction with the related reference curve obtained from the CONTRAIL data. In the case of a linear time variation of the clock-tracer mole fraction, the mean age of air is determined by the difference in time between the observed mole fraction of a tracer in the stratosphere and the same value observed in the upper troposphere reference record. This is called the lag time (Waugh and Hall, 2002). As seen in Figure 5, the SF_6 mole fraction shows no clear seasonal cycle in the tropical upper troposphere and its secular increase for the last 10 years can be approximated by a linear function. Therefore it is possible that the SF_6 age can be approximated by the lag time. On the other hand, the tropospheric CO_2 mole fraction shows large seasonal cycle, as seen in Figure 4. Such a seasonal cycle propagates into the TTL and the lower stratosphere, and then gradually diminishes with increasing altitude, due to air transport processes. Therefore, we cannot determine the CO_2 age from the lag time. The damping and phase delay of the seasonal CO_2 cycle in the stratosphere should be calculated theoretically using age spectra (Waugh and Hall, 2002). However, actual age spectra are usually unknown. Therefore, we used hypothetical age spectra to calculate the age of air. A simple formulation of the age spectrum was originally introduced by Hall and Plumb (1994) as a theoretical expression for a 1D atmosphere. Their proposed function is mathematically equivalent to the inverse-Gaussian distribution (Waugh and Hall, 2002). We assumed that the width of the age spectrum (d) is parameterized using the mean age (Γ), i.e., $d^2 = 0.7\Gamma$ (Waugh and Hall, 2002; Engel et al., 2008). In this study, the mole fraction of CO_2 or SF_6 in the stratosphere, $x(\Gamma, t)$, was calculated as a convolution of the tropospheric reference curve, $x_0(t)$, and the age spectrum, $G(\Gamma, t)$;

$$x(\Gamma,t) = \int_{t-\Delta t}^{t} x_0(t')\, G(\Gamma, t-t')\, dt', \quad (3)$$

where Δt is the integration time interval. Then, the CO_2 or SF_6 age was determined by comparing the observed mole fraction with x(Γ, t). As mentioned before, a small amount of CO_2 is produced by the chemical destruction of CH_4 in the stratosphere. To correct for this effect, each observed CO_2 mole fraction was adjusted using the CH_4 mole fraction measured from the same air sample prior to the age calculation. The corrections were less than 0.1 and 0.36 μmol mol^{-1} for the lowermost and uppermost altitudes, respectively.

Ishidoya et al. (2013) pointed out that the mole fractions and isotopic ratios of all atmospheric constituents are influenced by gravitational separation and that its effect on a specified constituent can be evaluated from the <δ> value and the mass number difference between the constituent and the air. Since the molecular mass numbers of CO_2 and SF_6 are larger than the mean molecular mass of air, it is expected that their mole fractions are slightly separated gravitationally in the stratosphere, resulting in lower mole fractions compared to those in the absence of gravitational separation. In this study, we calculated

the gravitational separation effect on the CO_2 and SF_6 mole fractions observed in the tropical stratosphere, and found that the respective effects are utmost −0.07 μmol mol^{-1} and −0.01 pmol mol^{-1}, respectively. Therefore, the correction for gravitational separation is not necessary, at least up to ~30 km.

The CO_2 and SF_6 ages estimated in this study are shown in Figure 6, together with the <δ> values. These data are also tabulated in Table 1 and 2. The CO_2 and SF_6 ages gradually increase with increasing altitude from the TTL to 22 km and then rapidly up to 25 km. The CO_2 and SF_6 ages show a good agreement with each other from the TTL to approximately 24 km, but they are significantly different above approximately 25 km. The average values of the CO_2 and SF_6 ages above 25 km were 2.4 ± 0.1 and 3.4 ± 0.2 yrs, respectively.

Our results show that the CO_2 and SF_6 ages were 0.5 - 0.6 yrs at the altitude of 18.5 km (~70 hPa), which roughly corresponds to the thermal tropical tropopause around the top of the TTL. In addition to this, the CO_2 and SF_6 ages increased slightly with increasing altitude inside the upper layer of the TTL. These results suggest that the CO_2 and SF_6 ages increased by 0.5 – 0.6 yrs from the secondary tropical tropopause (approximately 11 ~ 13 km) to the thermal tropical tropopause. This indicates that a strict specification of the tropospheric reference record around the TTL is essential for the comparison between different observations. In this connection, it should be noted that our age estimates could be positively biased to some extent, since we used the CONTRAIL data as the tropospheric reference record.

Andrews et al. (2001) estimated the tropical lower stratospheric air age at 20 ± 0.5 km to be approximately 1.0 yrs, using the ER-2 aircraft. Note that their ages were estimated relative to the tropical tropopause. Even though it is not clear how different our age estimates are from the values estimated relative to the tropical tropopause, depending on the different tropospheric reference records, our CO_2 and SF_6 ages at 22 km are nearly consistent with their results. The ages of air observed in the 25-30 km by balloon experiments were tabulated by Waugh and Hall (2002). Andrews et al. (2001) and Ray et al. (1999) estimated the CO_2 and SF_6 ages in the tropical mid-stratosphere (25–30 km) to be 3.5 and 4.0 yrs, respectively, from their balloon observations conducted at Juazeiro do Norte, Brazil (7° S) in 1997. Our results show that the CO_2 and SF_6 ages were 2.4 and 3.4 yrs on average at the altitudes of 25 - 29 km. If we compare our age data directly with those observed over Brazil, the CO_2 and SF_6 ages in this study are smaller by approximately 1.1 and 0.6 yrs, respectively. This would be partly due to the different observation location.

The SF_6 age obtained in this study can be compared with the result obtained from the MIPAS satellite observations (Haenel et al., 2015). Haenel et al. (2015) estimated zonal mean SF_6 ages for each season by using the SF_6 mole fraction data from MIPAS for the period 2002-2012. They showed that the SF_6 age over the equatorial region in the northern winter season was approximately 1.0 yrs at 17 km and 5.0 yrs at 30 km, with the age increasing almost linearly with increasing altitude. Since the tropospheric reference record used for the MIPAS SF_6 age is ground-based global mean surface data, their age estimates are systematically larger than our estimates over the entire altitude range of the TTL to 30 km. By comparing our and the MIPAS SF_6 ages at 17 km, the difference in the two ages is found to be approximately 0.8 yrs. Taking this difference into account, the middle stratospheric SF_6 age obtained in this study is nearly consistent with the MIPAS SF_6 age.

In general, the age values obtained in this study are smaller than those reported previously for the mid-latitude middle

stratosphere (Engel et al., 2008; Ray et al., 2010; Ishidoya et al., 2013). Ishidoya et al. (2013) reported that the average value of CO_2 age at heights above 20 – 28 km over Japan was 5.2 ± 0.4 yrs for the period 1995-2010. However, their CO_2 age was estimated using ground-based data as the tropospheric reference record. Therefore, we re-evaluated their CO_2 age using the CONTRAIL data and found it to be 4.6 ± 0.4 yrs. Our latest observation over Japan in August 2015 showed the average middle stratospheric CO_2 age to be 4.9 ± 0.3 yrs (our unpublished data). The two values are also close to the CO_2 ages reported by Engel et al. (2008). From these results, we conclude that the middle stratospheric CO_2 age difference between the tropics and the mid-latitudes is approximately 2.2–2.5 yrs, which is consistent with the transit time estimated from the CO_2 mole fraction in section 3.1. In summary, the CO_2 age increases vertically by approximately 3.0 yrs from the TTL to the middle stratosphere in the tropics and also horizontally in the middle stratosphere by approximately 2.0 yrs from the tropics to the mid-latitudes.

3.3 Difference in the CO_2 and SF_6 ages

The SF_6 age is obviously larger than the CO_2 age in the middle stratosphere, whether in the tropics or mid-latitudes. As mentioned before, this study shows that the average CO_2 and SF_6 ages above 25 km over Biak are 2.4 ± 0.1 and 3.4 ± 0.2 yrs, respectively. On the other hand, our balloon observation over Japan in 2015 indicated the average SF_6 age of 6.8 ± 0.8 yrs for the middle stratosphere (25-35km), which is 1.9 ± 0.9 yrs larger than the CO_2 age of 4.9 ± 0.3 yrs (our unpublished data). This result suggests that the difference in the middle stratospheric CO_2 and SF_6 ages increases with latitude from the tropics (1.0 yrs) to the mid-latitudes (1.9 yrs).

The difference in the CO_2 and SF_6 ages has also been discussed in previous studies (Harnisch et al., 1998; Strunk et al., 2000, Andrews et al., 2001). Harnisch et al. (1998) reported that the CO_2 age is smaller by up to 3 yrs than the SF_6 age in the middle stratosphere, and then discussed the origin of excess CO_2. On the other hand, Strunk et al. (2000) showed from their balloon observation in 1997 that the CO_2 and SF_6 ages agree well with each other, and concluded that the discrepancy between the CO_2 and SF_6 ages reported by Harnisch et al. (1998) was caused by air sample degradation, such as CO_2 production during its storage in flasks. In this study, the sample degradation in the cryogenic sampler, as well as the mole fraction scales of CO_2 and SF_6 for stratospheric and tropospheric data, was carefully checked, as described in section 2. Therefore, we were forced to find other causes for the difference between the CO_2 and SF_6 ages.

One possible cause is the propagation of the seasonal cycle of tropospheric CO_2 into the stratosphere. The propagation effect of periodic tracer variations into the stratosphere was also discussed in Andrews et al. (2001) and Waugh and Hall (2002). Since the seasonal cycle of the CO_2 mole fraction is significantly large in the tropical upper troposphere, its signal propagates into the TTL and then into the lower stratosphere via slow tropical upwelling. At the same time, the atmospheric mixing process broadens the width of the age spectra, resulting in damped seasonal amplitude with increasing altitude. If the CO_2 seasonal cycle is still significantly large at the observation altitude, it is difficult to estimate the CO_2 age precisely from the mole fraction at that altitude, because it is not necessarily guaranteed that $x(\Gamma, t)$ is a single-valued function of time. However, if the upward propagation of the CO_2 seasonal cycle is responsible for the difference between the CO_2 and SF_6

ages, the age difference should be larger in the lower stratosphere than in the middle stratosphere, which is opposite to our observational results. Therefore, it is likely that the propagation of the CO_2 seasonal cycle would be a minor contributor to the difference in the middle stratospheric CO_2 and SF_6 ages.

We also examined the influence of mesospheric air, because SF_6 is decomposed by UV absorption and electron reactions in the mesosphere (e.g., Reddmann et al., 2001). Andrews et al. (2001) reported that the CO_2 and SF_6 ages observed by ER-2 are in agreement with each other for ages less than 3.0 yrs, while the SF_6 age is 10–20% larger than the CO_2 age if older. They also suggested that the loss of mesospheric SF_6 would lead to an excess in age at higher altitudes. The age-dependent difference between the CO_2 and SF_6 ages obtained by Andrews et al. (2001) is nearly consistent with that observed in this study. However, it is not yet clear how much the mesospheric SF_6 loss affects the SF_6 age observed in the tropical middle stratosphere.

The contribution of the mesospheric air subsidence to the stratospheric SF_6 age was also discussed by Stiller et al. (2012). They proposed that the "over-aging" of SF_6 in the mid- and high-latitude stratosphere could be due to the mixing of air with less SF_6 inside the polar vortex with the mid-latitude air, and estimated a rate of change in the northern hemispheric air age caused by the mixing to be 0.04 yrs per year of age. They also suggested that this effect is halved (0.02 yrs per year of age) if the mixing of the polar vortex air occurs throughout the stratosphere. Therefore, if the SF_6 age is estimated to be 5.0 yrs for a certain altitude in the northern hemisphere, the "true" SF_6 age should be 4.8 yrs or 4.9 yrs. However, the difference between the CO_2 and SF_6 ages obtained in this study is so large that the "polar vortex mixing" effect is not a major factor.

The vertical distribution of gravitational separation, shown by $<\delta>$ in Figure 6, could also point to another possible process that produces the observed difference in the CO_2 and SF_6 ages in the middle stratosphere. As seen in Figure 6, the degree of disagreement between the CO_2 and SF_6 ages correlates well with the gravitational separation enhancement. The SF_6 age, for example, increases with altitude above 25 km, showing a good correlation with the decrease in $<\delta>$. Gravitational separation is completely independent of any chemical processes in the atmosphere, and therefore it could be an indicator of atmospheric transport processes (Ishidoya et al., 2013). Since gravitational separation is especially sensitive to vertical air transport, the correlation between the SF_6 age and gravitational separation suggests that the SF_6 age observed in the middle stratosphere is influenced by horizontal and vertical mixing with upper atmosphere air impacted with greater SF_6 losses.

3.4 Numerical simulations of gravitational separation

The gravitational separation effect of atmospheric constituents is mainly governed by two factors: (1) mass-independent transport and (2) mass-dependent molecular diffusion; the former reduces the effect and the latter enhances it. In general, since the mass-dependent molecular diffusion flux of a specific constituent, i, (hereafter written as F_{mi}) is much smaller than the mass-independent flux, F_{mi} is usually neglected except for the mass transport above the mesosphere. A theoretical expression for the vertical component of the molecular diffusion flux ($F_{mi,z}$) is given by:

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$$F_{mi,z} = -D_{mi}\left\{\frac{\partial n_i}{\partial z} + \frac{m_i g}{RT} n_i + \left(1+\alpha_{Ti}\right)\frac{\partial\left(\ln T\right)}{\partial z} n_i\right\}, \quad (4)$$

where n_i, D_{mi}, m_i, and α_{Ti} are the number density, the molecular diffusion coefficient, the molecular mass, and the thermal diffusion factor of a specific constituent, i, respectively, and g, R, and T denote the gravitational acceleration, the gas constant and temperature, respectively (Banks and Kockarts, 1973). The relative difference in the number density (n) ratio of constituent i and j between the stratosphere and the troposphere, $\delta_{i,j}$, is defined as:

$$\delta_{i,j} = \left(\left[\frac{n_j}{n_i}\right]_{str} \Big/ \left[\frac{n_j}{n_i}\right]_{trp} - 1\right), \quad (5)$$

where subscripts *str* and *trp* denote the stratosphere and the troposphere, respectively. In the theoretical expression given by equation (4), the mass dependency arises from m_i, D_{mi}, and α_{Ti}. As described in section 3.1, $\Delta\delta$ is nearly proportional to the mass number differences of the related molecules (see Figure 3), suggesting that the molecular mass difference is a main cause of molecular separation and α_{Ti} does not play an important role. If m_j is larger than m_i, the number density ratio, n_j/n_i, decreases with increasing altitude due to the mass-dependent flux, resulting in the upward decrease in the δ value (see Figure 6). In our observations of the major atmospheric constituents, i and j correspond to ^{14}N and ^{15}N, ^{16}O and ^{18}O, or N_2 and Ar, for which $m_i < m_j$. Therefore, gravitational separation of two related molecules is enhanced as the δ value is lowered. In addition, the separation effect by molecular diffusion is enhanced with increasing altitude due to the strong height dependency of the molecular diffusion coefficient, D_{mi}. Ishidoya et al. (2013) made a similar comment related to their results observed in the northern mid-latitude stratosphere. The most striking result obtained in this study is that the magnitude of gravitational separation is significantly different between the mid-latitude and the equatorial regions. The TTL and the stratosphere over the tropics are characterized by a slow upward motion of air. We suggest that this tropical upwelling has a relatively large contribution to the mass-independent flux and significantly weakens the gravitational separation effect.

To examine the relative contributions of the tropical upwelling to the gravitational separation effect, 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). Since details of our model calculation have already been described in Ishidoya et al. (2013), a brief description is given here. In the present simulations, we neglected the thermal diffusion flux by setting α_{Ti}, which appears in equation (4), to zero. Even by doing this, the term involving the temperature gradient still remains in equation (4). This term does not represent the thermal diffusion flux, but is theoretically arisen from the flux components caused by concentration and pressure gradients (Banks and Kockarts, 1973). Then we calculated the $^{44}CO_2$ and $^{45}CO_2$ mole fractions to derive the <δ> value. Note that the mass number difference between $^{44}CO_2$ and $^{45}CO_2$ molecules is 1. Therefore the model-calculated <δ> value can be directly compared with the observed <δ> value. Because our purpose is to simulate the gravitational separation in $^{44}CO_2$ and $^{45}CO_2$ molecules, it is not necessary to reproduce $\delta(^{45}CO_2)$ variations in the actual atmosphere. Taking this into account, their mole fractions in the

lowermost layer of the model were fixed at known values, assuming their mole fraction ratio, $n(^{45}CO_2)/n(^{44}CO_2)$, to be constant. Before simulating the gravitational separation, we performed preliminary calculations to evaluate the time constant that characterizes how long it takes to attain a steady state. In the preliminary calculation, the initial <δ> value was set to zero in the entire atmosphere (i.e., molecules are not gravitationally separated), and then a 50-year calculation was performed for $^{44}CO_2$ and $^{45}CO_2$ mole fractions. From this calculation, the time constant of the gravitational separation was estimated to be about 5 to 8 years at altitudes of 20–30 km. Considering this result, a 20-year spin-up calculation was carried out with no $^{44}CO_2$ and $^{45}CO_2$ increases in the lowermost layer, and then a 30-year simulation was performed in which $^{44}CO_2$ and $^{45}CO_2$ were monotonically increased at the model surface, keeping their mole fraction ratio constant. The age of air was also calculated from the model-simulated CO_2 mole fraction. The age of air was determined as the difference between the time when the same CO_2 mole fraction value was found in the tropical upper troposphere and at a certain altitude in the stratosphere. Systematic difference between the calculated and observed ages was adjusted so that the age calculated for the TTL agrees with the observed value.

In our model simulations, we first calculated the <δ> value and the age of air under the SOCRATES baseline-atmospheric condition (Huang et al., 1998). However, the air age and <δ> calculated from this standard run were found to be significantly lower and higher, respectively, compared to the observed values. Previous studies also pointed out that the air age calculated by the SOCRATES standard run is underestimated, probably due to a faster residual mean circulation (Park et al., 1999; Ishidoya et al., 2013). By examining the SOCRATES baseline condition, we found that the mean ascending rate at levels 18 to 24 km over the equator to be approximately 0.5 mm s^{-1} (~16 km yr^{-1}). This value was obviously larger than the typical values of 0.2–0.3 mm s^{-1} (6–10 km yr^{-1}) reported by previous studies (Mote et al., 1996; Randel et al., 2001). Therefore, we calculated the <δ> value and the age of air again by arbitrarily suppressing the residual mean meridional circulation to 60% of the standard run (hereafter written as the "control run"), corresponding to a mean ascending rate of 0.3 mm s^{-1} (~10 km yr^{-1}) over the equator. The average meridional distributions of the <δ> value calculated by the control run for DJF are shown in Figure 7, together with the results for the age of air. As shown in Figure 7, the calculated vertical distributions of the <δ> value and the age of air at northern mid-latitudes are nearly consistent with the results observed over Japan (Ishidoya et al., 2013). The model result also shows that the vertical <δ> gradient is very small over the equator, rapidly increasing toward the pole. The vertical gradient of the age of air shows a similar variation (Figure 7 (b)). However, the latitudinal difference in the vertical age gradient is smaller than that of the <δ> value. This phenomenon is caused by a strong dependence of the gravitational separation on the vertical air transport. In general, the gravitational separation is enhanced with increasing altitude due to the height dependency of the molecular diffusion coefficient. However, the upward mean flow from the lower part, where air compositions are not gravitationally separated, significantly weakens the molecular separation effect at a certain altitude in the stratosphere.

To examine the equatorial <δ> dependency on the mean meridional circulation, average vertical profiles over the equator for DJF simulated by assuming different mean ascending rates, are shown in Figure 8, together with the observational results

over Indonesia. As seen in this figure, the suppression of the mean meridional circulation improves the discrepancy between the model-calculated and observed <δ> values over the equatorial region. However, the air age calculated by the control run is still underestimated, in particular above 24 km. To reduce the air age difference between the observation and simulation, we further suppressed the mean meridional circulation to 50% of the standard run. It is obvious from Figure 8 (b) that the age difference is reduced as expected, but the calculated age is still smaller than the observed value above 22 km. On the other hand, the further suppression of the mean meridional circulation yields an anomalous overestimation of gravitational separation, implying that the vertical gradient of the <δ> value is sensitive to the ascending air motion. The overestimated effect of gravitational separation could arise from unrealistic mixing processes in the model atmosphere, such as horizontal and/or vertical eddy diffusion. To examine the contribution of horizontal mixing to the model-simulated air age and <δ> value, these two variables were re-calculated by intensifying the horizontal eddy diffusivity, K_{yy}, by a factor of 1.5. As shown in Figure 8, the result indicates that an upward increase in the air age is further enhanced due to additional aging by the horizontal mixing. However, gravitational separation does not show any appreciable change, especially in the lower stratosphere, suggesting that gravitational separation is insensitive to horizontal mixing. From these results, it is suggested that the changes in the mean meridional circulation and the horizontal eddy diffusion have different impact on the gravitational separation and the age of air.

4 Conclusions

To investigate the age and gravitational separation of air in the equatorial stratosphere, we observed CO_2 and SF_6 mole fractions, $\delta^{18}O$ of O_2, $\delta^{15}N$ of N_2, and δ (Ar/N_2) at altitudes of 17 to 29 km over Biak, Indonesia in February 2015, using a set of cryogenic samplers. The CO_2 and SF_6 ages were carefully estimated from their measured mole fractions by comparing with the CONTRAIL tropical upper tropospheric data, after applying necessary corrections to the mole fraction scales used in different laboratories. The SF_6 and CO_2 ages showed a general increase with height. The SF_6 age and its vertical gradient obtained in this study are nearly consistent with those obtained by MIPAS satellite observations. The SF_6 age is in good agreement with the CO_2 age below 24 km, but increases at heights above 25 km, probably due to an over-aging of SF_6 resulting from the influence of upper air with low SF_6 mole fractions. To better understand the difference between the SF_6 and CO_2 ages above 25 km, it is necessary to investigate the effect of mesospheric SF_6 losses on the stratospheric SF_6 age in detail. We also found a very small but significant upward decrease in <δ>. This implies that gravitational separation occurs within the entire stratosphere and its magnitude is altitude dependent. By comparing with the observational results at mid-latitudes, it was confirmed that the tropical upwelling weakens gravitational separation in the TTL and in the lower stratosphere. Simulations with the SOCRATES two-dimensional transport model revealed that gravitational separation is highly sensitive to the strength of tropical upwelling.

Uncertainties and issues raised in this study require further observations of the air compositions and model analyses for a better understanding of gravitational separation and age of air in the stratosphere. The knowledge obtained would be crucial

for investigating stratospheric air transport processes. To enhance our understanding of the dynamics and chemistry in the TTL and the equatorial stratosphere in more detail, more comprehensive studies that include water vapor "tape recorder", other atmospheric constituents and their isotopic signatures are also necessary.

Statement. The authors declare that they have no conflict of interest.

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References

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

Aoki, S., Nakazawa, T., Machida, T., Sugawara, S., Morimoto, S., Hashida, G., Yamanouchi, T., Kawamura, K., and Honda, H.: Carbon dioxide variations in the stratosphere over Japan, Scandinavia and Antarctica, *Tellus*, **55B**, 178-186, 2003.

Austin, J., and Li, F.: On the relationship between the strength of the Brewer–Dobson circulation and the age of stratospheric air. *Geophys. Res. Lett.*, **33**, L17807, doi:10.1029/2006GL026867, 2006.

Banks, P. M., and Kockarts, G.: Aeronomy, Parts A and B, Academic Press, Inc. New York, 1973.

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

Engel, A., Möbius, T., Bönisch, H., Schmidt, U., Heinz, R., Levin, I., Atlas, E., Aoki, S., Nakazawa, T., Sugawara, S., Moore, F., Hurst, D., Elkins, J., Schauffler, S., Andrews, A., and Boering, K.: Age of stratospheric air unchanged within uncertainties over the past 30 years, *Nature Geoscience*, **2**, 28–31, doi:10.1038/Ngeo388, 2009.

Haenel, F. J., Stiller, G. P., von Clarmann, T., Funke, B., Eckert, E., Glatthor, N., Grabowski, U., Kellmann, S., Kiefer, M., Linden, A., and Reddmann, T.: Reassessment of MIPAS age of air trends and variability, *Atmos. Chem. Phys.*, **15**, 13161-13176, doi:10.5194/acp-15-13161-2015, 2015.

Hall, T. M., and Plumb, R. A.: Age as a diagnostic of stratospheric transport, *J. Geophys. Res.*, **99**, 1059–1070, 1994.

Harnisch, J., Bischof, W., Borchers, R., Fabian, P., and Maiss, M.: A stratospheric excess CO_2 – due to tropical deep convection, *Geophys. Res. Lett.*, **25**, 63-66, 1998.

Huang, T. Walters, S., Brasseur, G., Hauglustaine, D., and Wu, W.: *Description of SOCRATES - A chemical dynamical radiative two-dimensional model*, *NCAR/TN-440+EDD NCAR TECHNICAL NOTE*, 1998.

Ishidoya, S., Sugawara, S., Hashida, G., Morimoto, S., Aoki, S., Nakazawa, T., and Yamanouchi, T.: Vertical profiles of the O_2/N_2 ratio in the stratosphere over Japan and Antarctica, *Geophys. Res. Lett.*, **33**, L13701, doi:10.1029/2006GL025886, 2006.

Ishidoya, S., Sugawara, S., Morimoto, S., Aoki, S., and Nakazawa, T.: Gravitational separation of major atmospheric components of nitrogen and oxygen in the stratosphere, *Geophys. Res. Lett.*, **35**, L03811, doi:10.1029/2007GL030456, 2008a.

Ishidoya, S., Morimoto, S., Sugawara, S., Watai, T., Machida, T. Aoki, S., Nakazawa, T., and Yamanouchi, T.: Gravitational separation suggested by O_2/N_2, $\delta^{15}N$ of N_2, $\delta^{18}O$ of O_2, Ar/N_2 observed in the lowermost part of the stratosphere at northern middle and high latitudes in the early spring of 2002, *Geophys. Res. Lett.*, **35**, L03812, doi:10.1029/2007GL031526, 2008b.

Ishidoya, S., Sugawara, S., Morimoto, S., Aoki, S., Nakazawa, T., Honda, H., and Murayama, S.: Gravitational separation in the stratosphere – a new indicator of atmospheric circulation, *Atmos. Chem. Phys.*, **13**, 8787-8796, doi:10.5194/acp-13-8787-2013, 2013.

Ishidoya, S., and Murayama, S.: Development of high precision continuous measuring system of the atmospheric O_2/N_2 and Ar/N_2 ratios and its application to the observation in Tsukuba, Japan, *Tellus* **66B**, 22574, http://dx.doi.org/10.3402/tellusb.v66.22574, 2014.

Khosravi, R., Brasseur, G., Smith, A., Rusch, D., Walters, S., Chabrillat, and Kockarts, G.: Response of the mesosphere to human-induced perturbations and solar variability calculated by a 2-D model, *J. Geophys. Res.,* **107** (D18), 4358, doi:10.1029/2001JD001235, 2002.

Li, F., Austin, J., and Wilson, J.: The Strength of the Brewer–Dobson Circulation in a changing climate: Coupled chemistry–climate model simulations, *J. Climate*, **21**, 40-57, doi: 10.1175/2007JCLI1663.1, 2008.

Machida, T., Matsueda, H., Sawa, Y., Nakagawa, Y., Hirotani, K., Kondo, N., Goto, K., Nakazawa, N., Ishikawa, K., and Ogawa, T.: Worldwide measurements of atmospheric CO_2 and other trace gas species using commercial airlines, *J. Atmos. Oceanic Technol.*, **25**(10), 1744-1754, doi:10.1175/2008JTECHA1082.1, 2008.

Matsueda, H., Machida, T., Sawa, Y., and Niwa, Y.: Long-term change of CO_2 latitudinal distribution in the upper troposphere, *Geophys. Res. Lett*., **42**, doi:10.1002/2014GL062768, 2015.

Morimoto, S., Yamanouchi, T., Honda, H., Iijima, I., Yoshida, T., Aoki, S., Nakazawa, T., Ishidoya S., and Sugawara, S.: A new compact cryogenic air sampler and its application in stratospheric greenhouse gas observation at Syowa station, Antarctica. *J. Atmos. Oceanic Technol.*, **26**, 2182–2191, doi: 10.1175/2009JTECHA1283.1., 2009.

Mote, P. W., Rosenlof, K. H., McIntyre, M. E., Carr, E. S., Gille, J. C., Holton, J. R., Kinnersley, J. S., Pumphrey, H. C., Russell III, J. M., and Waters, J. W.: An atmospheric tape recorder: The imprint of tropical tropopause temperatures on stratospheric water vapor, *J. Geophys. Res.*, **101**(D2), 3989–4006, doi:10.1029/95JD03422, 1996.

Nakazawa, T., Machida, T., Sugawara, S., Murayama, S., Morimoto, S., Hashida, G., Honda, H., and Itoh, T.: Measurements of the stratospheric carbon dioxide concentration over Japan using a balloon-borne cryogenic sampler, *Geophys. Res. Lett.*, **22**, No. 10, P. 1229, doi:10.1029/95GL01188, 1995.

Nakazawa, T., Ishizawa, M., Higuchi K., and Trivett, B. A. N.: Two curve fitting methods applied to CO_2 flask data, Environmetrics, 8, 197-218, 1997.

Nakazawa, T., Aoki, S., Kawamura, K., Saeki, T., Sugawara, S., Honda, H., Hashida, G., Morimoto, S., Yoshida, N., Toyoda, S., Makide, Y., and Shirai, T.: Variations of stratospheric trace gases measured using a balloon-borne cryogenic sampler, *Advances in Space Research*, **30**, 2002,1349-1357, doi:10.1016/S0273-1177(02)00551-3., 2002.

Park, J. H., Ko, M. K. W., Jackman, C. H., Plumb, R. A., Kaye, J. A., Sage, K. H.: Models and Measurements Intercomparison II, NASA/TM-1999-209554, http://www.cs.odu.edu/~mln/ltrs-pdfs/NASA-99-tm209554.pdf.

Patra, P., Lal S., Subbaraya B., Jackman C. H., and Rajaratnam P.: Observed vertical profile of sulfur hexafluoride (SF6) and its atmospheric applications, *J. Geophys. Res.*, **102**, 8855–8859, 1997.

Randel, W. J., Wu, F., Gettelman, A., Russell III, J. M., Zawodny, J. M., and Oltmans, S. J.: Seasonal variation of water vapor in the lower stratosphere observed in Halogen Occultation Experiment data, *J. Geophys. Res.*, **106**, 14,313–14,325, 2001.

Ray, E. A., Moore, F. L., Rosenlof, K. H., Davis, S. M., Boenisch, H., Morgenstern, O., Smale, D., Rozanov, E., Hegglin, M., Pitari, G., Mancini, E., Braesicke, P., Butchart, N., Hardiman, S., Li, F., Shibata, K., and Plummer, D. A.: Evidence for changes in stratospheric transport and mixing over the past three decades based on multiple data sets and tropical leaky pipe analysis, *J. Geophys. Res.,* **115**, D21304, doi:10.1029/2010JD014206, 2010.

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

Reddmann, T., Ruhnke, R., and Kouker, W.: Three-dimensional model simulations of SF_6 with mesospheric chemistry, *J. Geophys. Res.*, **106**, 14 525–14 537, 2001.

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

Stiller, G. P., Von Clarmann, T., Haenel, F., Funke, B., Glatthor, N., Grabowski, U., Kellmann, S., Kiefer, M., Linden, A., Lossow, S., and López-Puertas, M.: Observed temporal evolution of global mean age of stratospheric air for the 2002 to 2010 period, *Atmos. Chem. Phys.*, **12**, 3311–3331, doi:10.5194/acp-12-3311-2012, 2012.

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

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

Waugh, D.W., and Hall, T. M.: Age of stratospheric air: Theory, observations, and models. *Rev. Geophys.,* **40**, no. 4, 1010,

doi:10.1029/2000RG000101, 2002.

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Table 1. CO_2 and SF_6 mole fractions and ages observed over Biak, Indonesia in February 2015.

Date	Altitude (km)	CO_2 mole fractions (μmol mol^{-1})	SF_6 mole fractions (pmol mol^{-1})	CO_2-age (years)	SF_6-age (years)
Feb. 22, 2015	17.2	398.22 ±0.07	8.38 ±0.09	0.42 ±0.03	0.3 ±0.3
Feb. 24, 2015	18.5	397.88 ±0.07	8.31 ±0.09	0.53 ±0.03	0.6 ±0.3
Feb. 24, 2015	22.0	397.07 ±0.03	8.07 ±0.02	0.87 ±0.01	1.3 ±0.1
Feb. 26, 2015	23.9	395.41 ±0.33	7.92 ±0.06	1.77 ±0.14	1.8 ±0.2
Feb. 28, 2015	25.2	394.13 ±0.11	7.47 ±0.04	2.39 ±0.05	3.3 ±0.1
Feb. 26, 2015	27.4	394.10 ±0.13	7.49 ±0.07	2.45 ±0.06	3.2 ±0.2
Feb. 28, 2015	28.7	394.20 ±0.05	7.37 ±0.04	2.44 ±0.02	3.6 ±0.1

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Table 2. The values of $\delta^{15}N$ of N_2, $\delta^{18}O$ of O_2, $\delta(Ar/N_2)$, and $<\delta>$ observed over Biak, Indonesia in February 2015.

Date	Altitude (km)	$\delta^{15}N$ of N_2 (per meg)	$\delta^{18}O$ of O_2 (per meg)	$\delta(Ar/N_2)$ (per meg)	$<\delta>$ (per meg)
Feb. 22, 2015	17.2	-1.3	1.9	-109	0
Feb. 24, 2015	18.5	-1.7	-0.6	-99	-0.3 ±1.0
Feb. 24, 2015	22.0	-3.3	0.8	-109	-0.8 ±1.0
Feb. 26, 2015	23.9	-4.6	-3.6	-93	-1.6 ±2.5
Feb. 28, 2015	25.2	-5.2	-7.2	-152	-4.0 ±0.5
Feb. 26, 2015	27.4	-6.0	-12.1	-153	-5.1 ±1.7
Feb. 28, 2015	28.7	-12.6	-16.5	-262	-11.1 ±1.8

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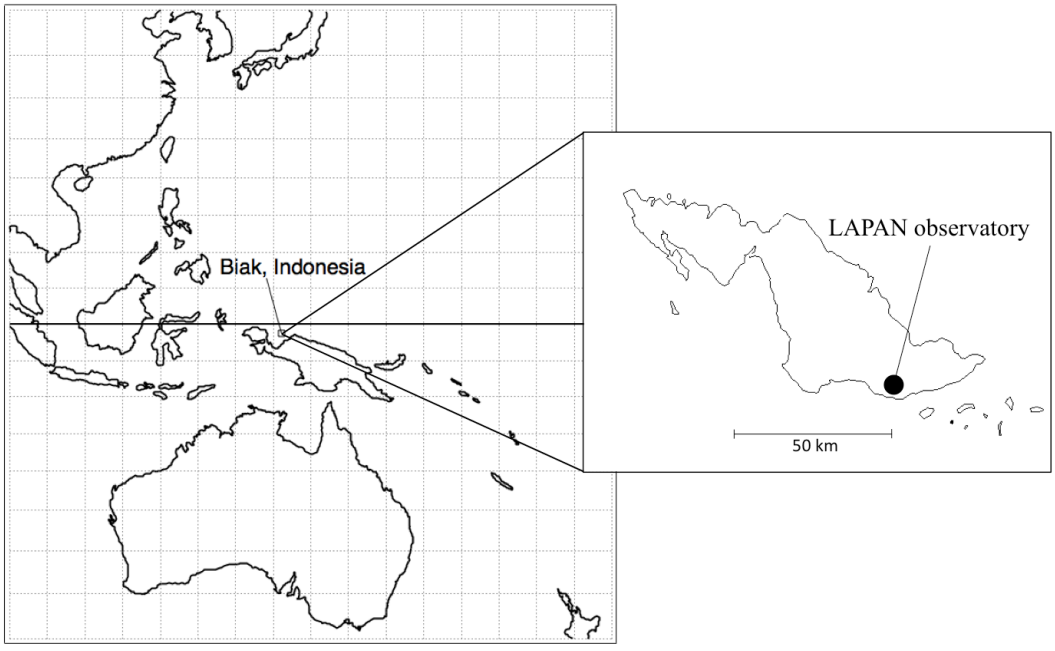

Figure 1. Map showing Biak Island, Indonesia and the LAPAN observatory on the island.

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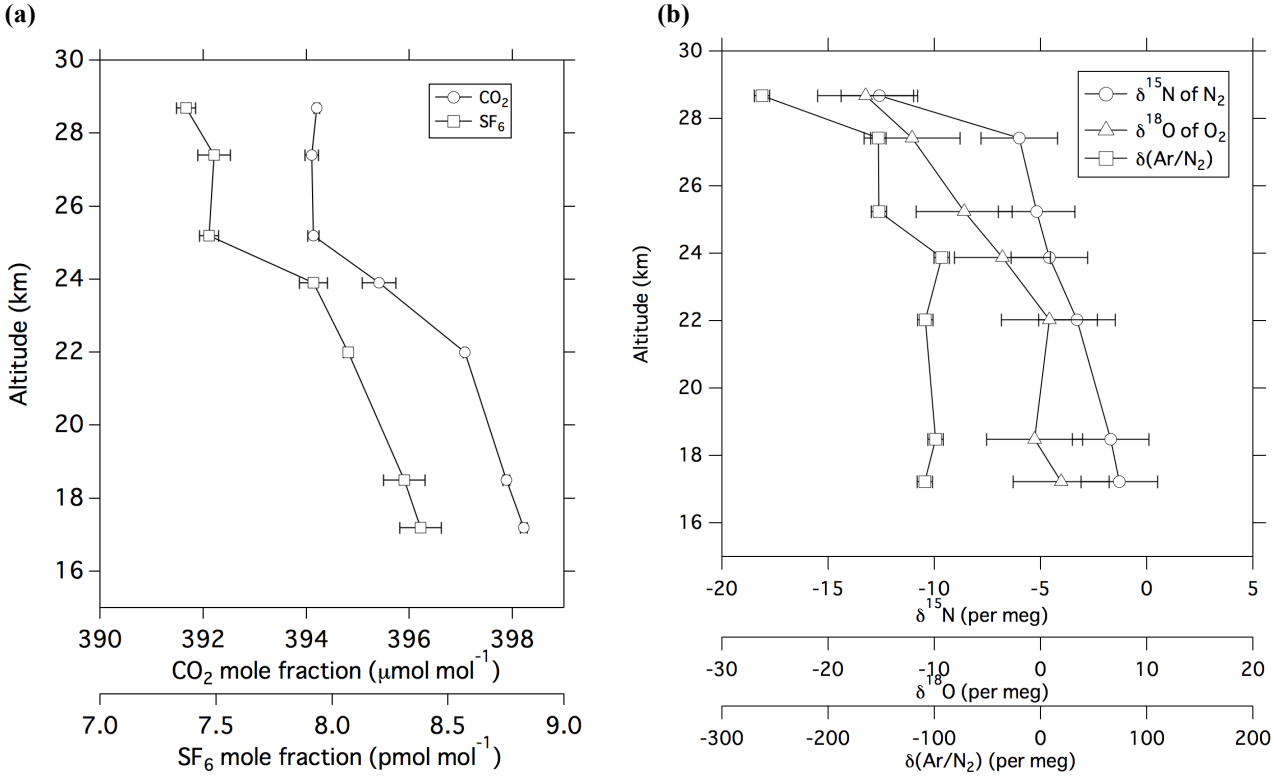

Figure 2. (a) Vertical profiles of the CO_2 and SF_6 mole fractions observed over Biak, Indonesia on February 22–28, 2015. (b) Same as panel (a) but for $\delta^{15}N$ of N_2, $\delta^{18}O$ of O_2, and $\delta(Ar/N_2)$.

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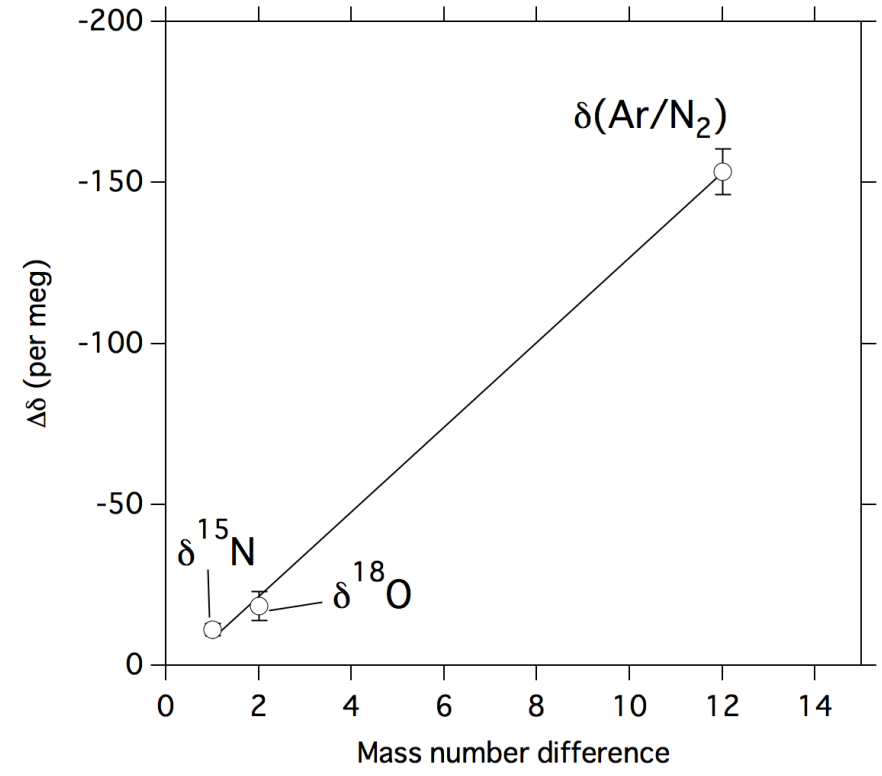

Figure 3. The relationship between the mass number difference and the Δδ value. The Δδ value denotes the difference in $\delta^{15}N$ of N_2, $\delta^{18}O$ of O_2 or $\delta(Ar/N_2)$ between 17.2 and 28.7 km. Solid line represents a linear relationship between Δδ and the mass number difference.

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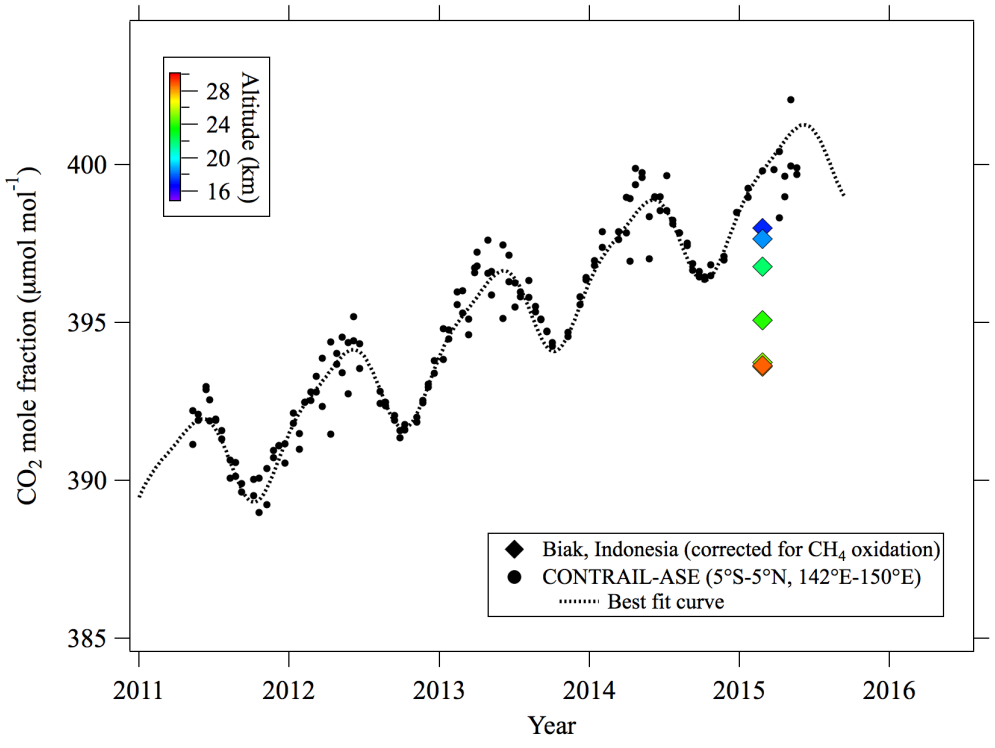

Figure 4. Stratospheric CO_2 mole fraction values observed over Biak and tropical upper tropospheric data (5° N–5° S, 142° E–150° E, 10–12.5 km) obtained by the CONTRAIL aircraft project. Also shown is the best-fit curve fitted to the CONTRAIL data.

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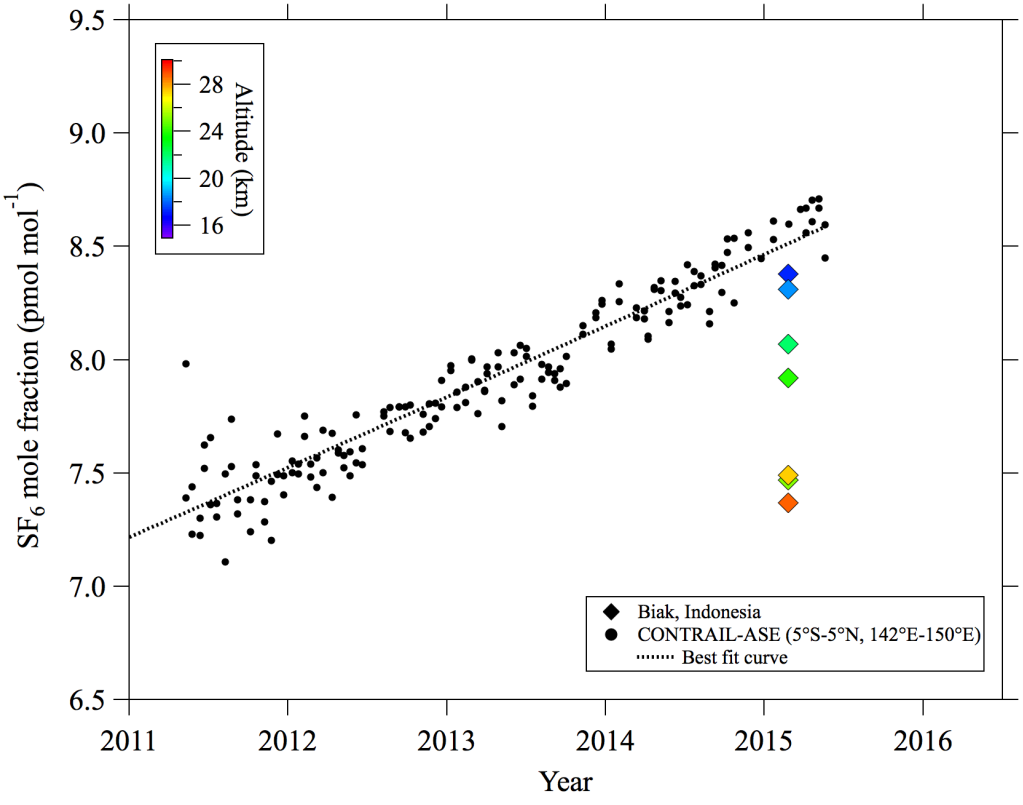

Figure 5. Same as Figure 4 but for SF_6.

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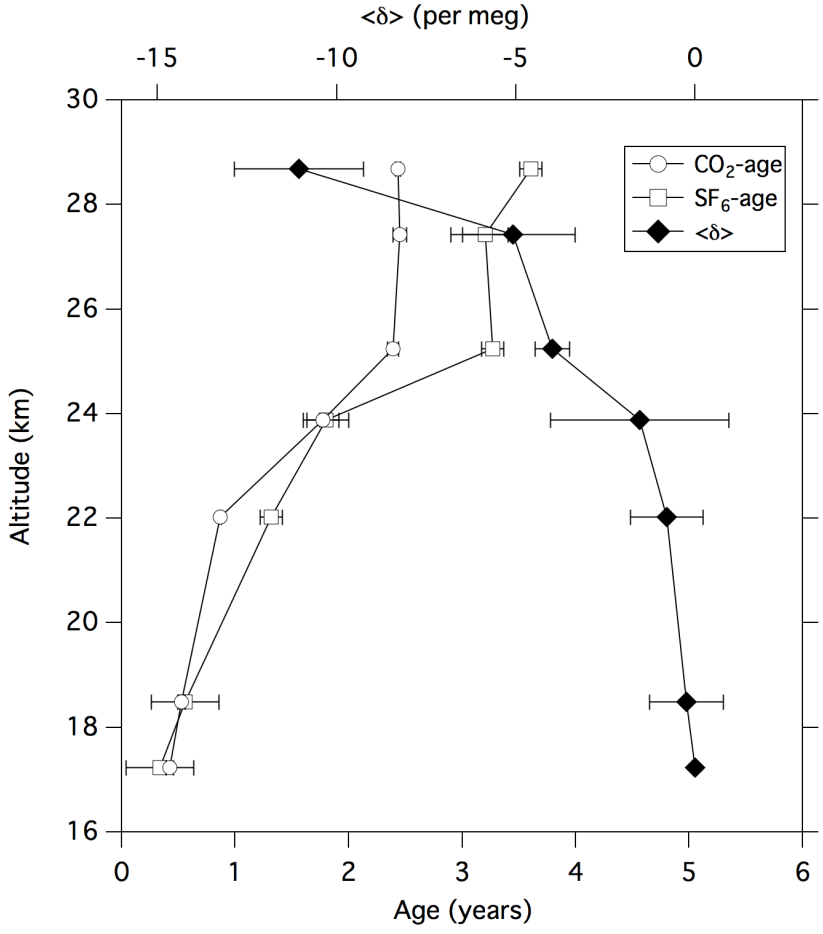

Figure 6. Vertical profiles of the CO_2 and SF_6 ages and the <δ> value over Biak, Indonesia on February 22–28, 2015. The <δ> value represents an average of $\delta^{15}N$ of N_2, ($\delta^{18}O$ of O_2)/2, and $\delta(Ar/N_2)/12$ (cf. text).

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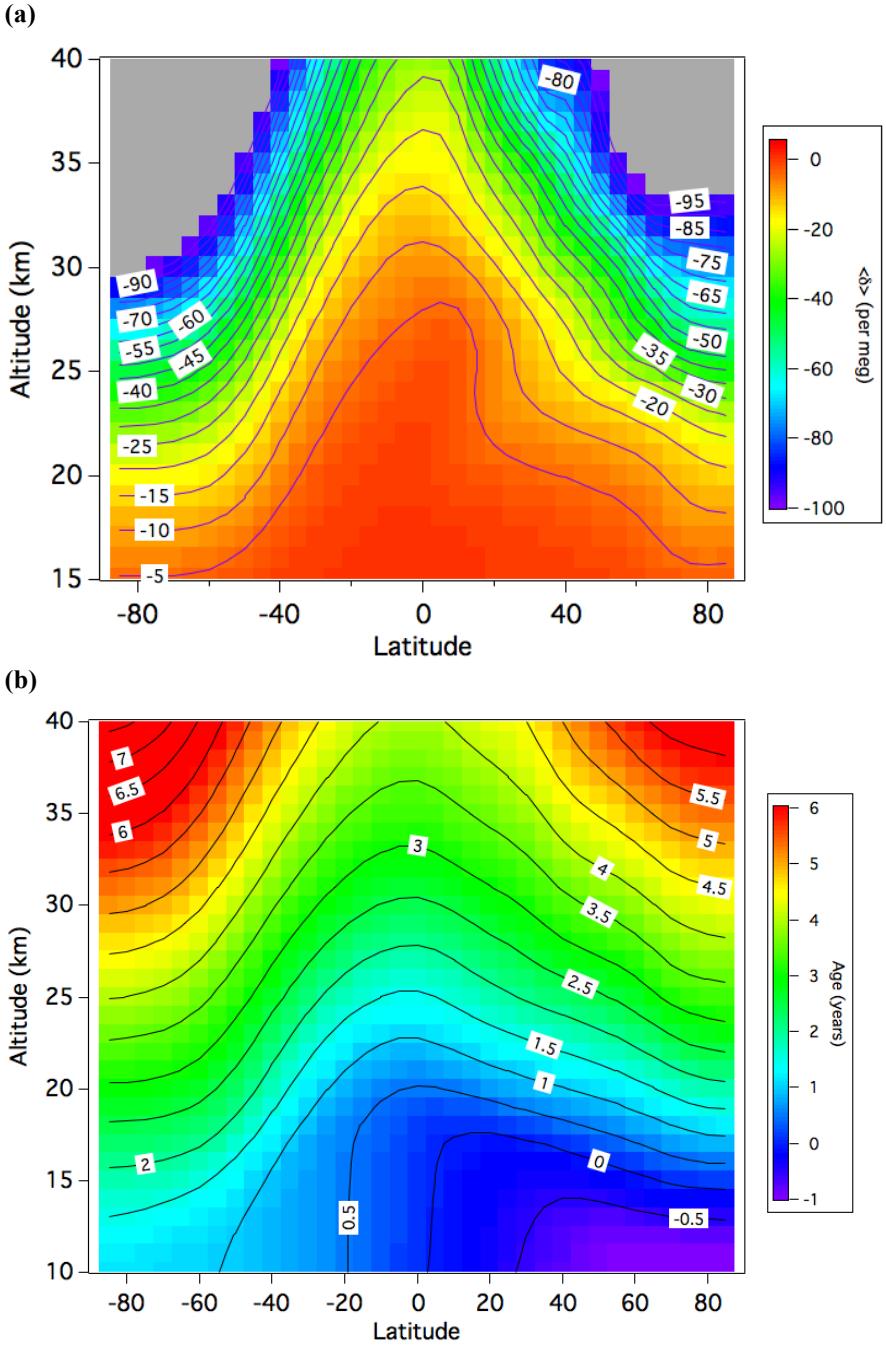

Figure 7. (a) Average meridional distributions of the <δ> value for DJF calculated using the SOCRATES model with the control run (cf. text). The <δ> values lower than −100 per meg are shown in gray.

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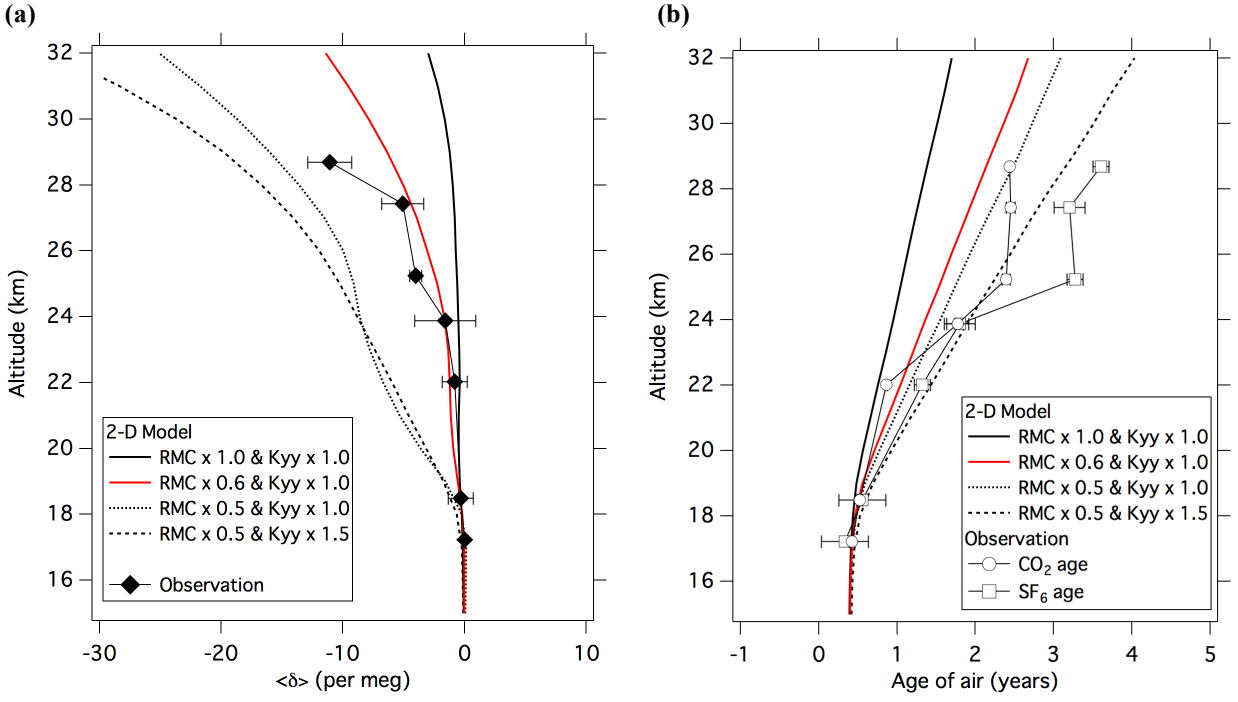

Figure 8. (a) Average vertical profiles of <δ> over the equator for DJF, calculated using the SOCRATES model as a standard run (black solid line), suppressed mean circulation runs (red and black dotted lines), and suppressed mean circulation and enhanced horizontal eddy diffusion run (black dashed line). The <δ> values observed over Biak are also plotted (closed diamonds). (b) Same as in panel (a) but for the age of air. The observed CO_2 and SF_6 ages are shown by open circles and squares, respectively.