Atmos. Chem. Phys. Discuss., 13, 4839–4861, 2013
www.atmos-chem-phys-discuss.net/13/4839/2013/
doi:10.5194/acpd-13-4839-2013

Atmospheric Chemistry and Physics
Open Access
Discussions

Gravitational separation in the stratosphere – a new indicator of atmospheric circulation

S. Ishidoya[1], S. Sugawara[2], S. Morimoto[3], S. Aoki[4], T. Nakazawa[4], H. Honda[5], and S. Murayama[1]

[1]National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba 305–8569, Japan
[2]Miyagi University of Education, Sendai 980–0845, Japan
[3]National Institute of Polar Research, Tokyo 190-8518, Japan
[4]Center for Atmospheric and Oceanic Studies, Tohoku University, Sendai 980–8578, Japan
[5]Institute of Space and Astronautical Science (ISAS), Japan Aerospace Exploration Agency (JAXA), Sagamihara 252-5210, Japan

Received: 30 December 2012 – Accepted: 12 February 2013 – Published: 20 February 2013

Correspondence to: S. Ishidoya (s-ishidoya@aist.go.jp)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

As a basic understanding of the dynamics of the atmospheric circulation, it has been believed that the gravitational separation of atmospheric components is observable only in the atmosphere above the turbopause. However, we found, from our high-precision measurements of not only the isotopic ratios of N_2, O_2 and Ar but also the concentration of Ar, that the gravitational separation occurs even in the stratosphere below the turbopause; their observed vertical profiles are in good agreement with those expected theoretically from molecular mass differences. The O_2/N_2 ratio observed in the middle stratosphere, corrected for the gravitational separation, showed the same mean air age as estimated from the CO_2 concentration. Simulations with a 2-dimensional model of the middle atmosphere indicated that a relationship between the gravitational separation and the air age in the stratosphere would be significantly affected if the Brewer-Dobson circulation is enhanced due to global warming. Therefore, the gravitational separation is usable as a new indicator of changes in the atmospheric circulation in the stratosphere.

1 Introduction

The gravity of the earth prevents the atmosphere from dissipating into space. It is also known that the gravity causes atmospheric molecules to separate depending on their molar masses, which is called "gravitational separation". It is widely recognized that the gravitational separation of atmospheric components occurs in the atmosphere above the turbopause (Lewis and Prinn, 1984; Jacobs, 1999). On the other hand, we have suggested from our measurements of the stable isotopic ratios of major atmospheric components ($\delta(^{15}N)$ of N_2 and $\delta(^{18}O)$ of O_2) (Ishidoya et al., 2006; Ishidoya et al., 2008a, b) that the gravitational separation exists even in the stratosphere. However, in our earlier studies, we were not able to exclude the possibility that some other factors affect our measurement results.

In this paper, we present a new concrete evidence for the existence of the gravitational separation in the stratosphere. We also show a significant effect of the gravitational separation on the O_2 concentration ($\delta(O_2/N_2)$) value measured in the stratosphere. Furthermore, we propose to use the gravitational separation as a new indicator to detect a change in the Brewer-Dobson Circulation (BDC) (Brewer, 1949) in the stratosphere. Atmospheric general circulation models have shown that the mean age of stratospheric air decreases as the BDC is enhanced under global warming (Austin and Li, 2006; Li et al., 2008), but a significant change of the air age has not been observed so far (Engel et al., 2009). Since the gravitational separation occurs physically due to gravity, its effect is expected to become more pronounced as the stratospheric air is slowly transported poleward after its intrusion from the troposphere in the tropics. Therefore, in this conceptual framework, by measuring the gravitational separation, it would be possible to obtain information about changes in the stratospheric circulation. To confirm this supposition, we simulate the stratospheric gravitational separation using a 2-dimensional model of the middle atmosphere (SOCRATES) (Huang et al., 1998), and then examine the relationship between the gravitational separation and the stratospheric circulation.

2 Stratospheric air collection and sample analyses

The collection of stratospheric air has been carried out using a balloon-borne cryogenic air sampler over Sanriku (39° N, 142° E) and Taiki (43° N, 143° E), Japan since 1985 (e.g. Nakazawa et al., 1995; Aoki et al., 2003). Our air sampler consists mainly of 12 stainless-steel sample containers, a liquid helium dewar, a receiver, a transmitter, a control unit and batteries; all these components are housed in a water- and pressure-proof aluminum chamber (Honda, 1990; Honda et al., 1996). The volume of each sample container is about 760 mL, and its inner wall is electrically polished. A motor-driven metal-to-metal seal valve is attached to each sample container. The other end of the motor-driven valve is connected to a sample intake, located 3.5 m below the bottom of

ACPD
13, 4839–4861, 2013

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |
Title Page
Abstract Introduction
Conclusions References
Tables Figures
◀ ▶
Back Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

the aluminum chamber, through a manifold and a stainless-steel bellows tube with an inner diameter of 15 mm reinforced with mesh. Before sampling, all the sample containers were evacuated with heating and then cooled by filling the dewar with liquid He. Then, the cryogenic air sampler was connected to a large balloon, launched from the balloon center at Sanriku or Taiki early in the morning and recovered from the Pacific Ocean around noon. Air samples were collected in the containers at assigned altitudes by opening and closing the motor-driven valves using a telecommand system. The flow rates of sample air at the respective altitudes were 50–100 $\mathrm{L\,min^{-1}}$ at ambient pressures, and typical amounts of air samples collected were about 25 L at standard temperature (0 °C) and pressure (1013.25 hPa).

To detect the gravitational separation in the stratosphere, we measured $\delta(^{15}N)$ of N_2, $\delta(^{18}O)$ of O_2 and $\delta(O_2/N_2)$ of the air samples collected over Sanriku on 31 May 1999, 28 August 2000, 30 May 2001, 4 September 2002, 6 September 2004, 3 June 2006 and 4 June 2007, as well as of those over Taiki on 22 August 2010, using a mass spectrometer (Finnigan MAT-252) (Ishidoya et al., 2003). $\delta(^{15}N)$ of N_2 and $\delta(^{18}O)$ of O_2 were also measured for the samples collected over Sanriku on 8 June 1995. Furthermore, the air samples over Sanriku on 4 June 2007 were analyzed for $\delta(^{15}N)$ of N_2, $\delta(^{18}O)$ of O_2, $\delta(O_2/N_2)$, $\delta(Ar/N_2)$ and $\delta(^{40}Ar)$ using a new mass spectrometer (Thermo Scientific DELTA-V). In this study, $\delta(^{15}N)$ of N_2, $\delta(^{18}O)$ of O_2, $\delta(O_2/N_2)$, $\delta(Ar/N_2)$ and $\delta(^{40}Ar)$ are reported in per meg (one per meg is equal to 1×10^{-6}),

$$\delta(^{15}\mathrm{N}) = \frac{\left[n(^{15}\mathrm{N}^{14}\mathrm{N})/n(^{14}\mathrm{N}^{14}\mathrm{N})\right]_{\mathrm{sample}}}{\left[n(^{15}\mathrm{N}^{14}\mathrm{N})/n(^{14}\mathrm{N}^{14}\mathrm{N})\right]_{\mathrm{reference}}} - 1, \tag{1a}$$

$$\delta(^{18}\mathrm{O}) = \frac{\left[n(^{18}\mathrm{O}^{16}\mathrm{O})/n(^{16}\mathrm{O}^{16}\mathrm{O})\right]_{\mathrm{sample}}}{\left[n(^{18}\mathrm{O}^{16}\mathrm{O})/n(^{16}\mathrm{O}^{16}\mathrm{O})\right]_{\mathrm{reference}}} - 1, \tag{1b}$$

ACPD
13, 4839–4861, 2013

$$\delta(O_2/N_2) = \frac{\left[n(^{16}O^{16}O)/n(^{15}N^{14}N)\right]_{\text{sample}}}{\left[n(^{16}O^{16}O)/n(^{15}N^{14}N)\right]_{\text{reference}}} - 1, \tag{1c}$$

$$\delta(Ar/N_2) = \frac{\left[n(^{40}Ar)/n(^{14}N^{14}N)\right]_{\text{sample}}}{\left[n(^{40}Ar)/n(^{14}N^{14}N)\right]_{\text{reference}}} - 1, \tag{1d}$$

and

$$\delta(^{40}Ar) = \frac{\left[n(^{40}Ar)/n(^{36}Ar)\right]_{\text{sample}}}{\left[n(^{40}Ar)/n(^{36}Ar)\right]_{\text{reference}}} - 1. \tag{1e}$$

Here, n means the amount of each substance. The measurement precision of Finnigan MAT-252 for $\delta(O_2N_2)$, $\delta(^{15}N)$ and $\delta(^{18}O)$ of the stratospheric air samples were estimated to be ±30–40, ±12 and ±26 per meg, respectively, by repeating the analysis of the same air sample (Ishidoya et al., 2006). On the other hand, Thermo Scientific DELTA-V showed the respective precision of ±5, ±7, ±35 and ±22 per meg for $\delta(^{15}N)$ of N_2, $\delta(^{18}O)$ of O_2, $\delta(Ar/N_2)$ and $\delta(^{40}Ar)$.

3 Results and discussion

3.1 Vertical profiles of the isotopic ratios of N_2, O_2 and Ar, and the Ar/N_2 ratio

Figure 1 shows the vertical profiles of the isotopic ratios of N_2, O_2, and Ar, and the Ar/N_2 ratio over Sanriku on 4 July 2007. Since the differences in mass number (Δm) for $\delta(^{18}O)$, $\delta(Ar/N_2)$ and $\delta(^{40}Ar)$ are 2, 12 and 4, respectively, the measured values of each variable plotted in this figure are normalized to the values corresponding to

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

ACPD
13, 4839–4861, 2013

Gravitational separation in the stratosphere

S. Ishidoya et al.

$\Delta m = 1$, i.e. $\delta(^{18}O)/2$, $\delta(Ar/N_2)/12$ and $\delta(^{40}Ar)/4$. As seen in Fig. 1, all the vertical profiles show a gradual decrease with height, their average difference between the lowermost part of the stratosphere and 32 km being about 45 per meg, and the fluctuations of their profiles are correlated well with each other. A vertical profile calculated using a 1-dimensional steady state eddy-diffusion/molecular-diffusion model for $\Delta m = 1$ is also shown in Fig. 1. The model is based on Eq. (33) in Lettau (1951). The vertical eddy-diffusion and molecular-diffusion coefficients for the model were taken from Massie and Hunten (1981) and Lettau (1951), respectively. Atmospheric temperatures and pressures of the model were given by the meteorological data obtained from rawinsonde observations. The calculated vertical profile is highly consistent with the observational results, suggesting that the gravitational separation due to molecular diffusion can occur even in the stratosphere. However, as pointed out in our previous studies (Ishidoya et al., 2006; Ishidoya et al., 2008a), the air intake of our cryogenic air sampler is gradually heated by the solar radiation during ascent, possibly causing lighter molecules to enter the sample air preferentially at high altitudes by a process called thermal diffusion (Blaine et al., 2006). If this is the case, such an effect would yield a vertical profile similar to that expected from the gravitational separation. Therefore, for providing a definitive evidence of the existence of the gravitational separation in the stratosphere, it is indispensable to quantitatively evaluate the magnitude of the thermal diffusion effect.

3.2 Laboratory experiments on the thermal diffusion effect

To examine the thermal diffusion effect at the air intake, laboratory experiments were carried out. Dry natural air was first filled into two 2700 mL Pyrex glass flasks connected in series at an over-pressure of 0.07 MPa, and then one was gradually cooled to −57 °C, while the other was kept at room temperature (25 °C). During this period, the air in the flask with room temperature was introduced into an inlet system of the mass spectrometer (Thermo Scientific DELTA-V). The air introduced was exhausted from the

ACPD
13, 4839–4861, 2013

inlet system with a flow rate of 4 mL min^{-1} and only a smidgen of air was transferred to an ion source of the mass spectrometer through a thermally-insulated fused silica capillary, to continuously measure $\delta(^{15}N)$, $\delta(^{18}O)$, $\delta(O_2/N_2)$, $\delta(Ar/N_2)$ and $\delta(^{40}Ar)$. The reproducibility of our laboratory experiments were estimated to be ±8, ±20, ±5, ±10 and ±70 per meg for $\delta(^{15}N)$, $\delta(^{18}O)$, $\delta(O_2/N_2)$, $\delta(Ar/N_2)$ and $\delta(^{40}Ar)$, respectively. Details of our measurements of these variables will be described somewhere (Ishidoya and Murayama, 2013, manuscript in preparation).

In general, the gravitational separation is completely mass-dependent (proportional to the difference between the mass numbers of related molecules), while the fractionation of molecules due to thermal diffusion is slightly mass independent (Severinghaus et al., 2001). The relationships of $\delta(^{18}O)/2$, $\delta(Ar/N_2)/12$ and $\delta(^{40}Ar)/4$ with $\delta(^{15}N)$ of N_2, obtained from our laboratory experiments, are shown in Fig. 2, together with those observed in the stratosphere. The experimentally determined ratios of $\delta(^{18}O)/\delta(^{15}N)$, $\delta(Ar/N_2)/\delta(^{15}N)$ and $\delta(^{40}Ar)/\delta(^{15}N)$ are (1.55±0.02), (16.2±0.1) and (2.75±0.05) per meg per meg^{-1}, respectively. These ratios are clearly different from the corresponding values of (2.1 ± 0.2), (11.9 ± 1.4) and (4.2 ± 0.6) per meg per meg^{-1} derived from the observational results shown in Fig. 2, as well as of 2, 12 and 4 expected from the gravitational separation. These statistically significant differences clearly show that the effect of thermal diffusion on our observation data is negligibly small. Previous studies have reported the respective thermal diffusion factors' ratios of approximately 1.6 (Grew and Ibbs, 1952; Severinghaus et al., 2001) and 2.6 (Severinghaus et al., 2001) for $\delta(^{18}O)/\delta(^{15}N)$ and $\delta(^{40}Ar)/\delta(^{15}N)$, which are consistent with our experimental results. Therefore, we conclude that the gravitational separation of the major atmospheric components is clearly observable, not only above the turbopause but also in the stratosphere.

ACPD
13, 4839–4861, 2013

3.3 Effect of the gravitational separation on the $\delta(O_2/N_2)$ and CO_2 concentration in the stratosphere

In order to determine the magnitude of the gravitational separation in the stratosphere, we define a parameter "δ" as an average value of $\delta(^{15}N)$ of N_2, $\delta(^{18}O)/2$ of O_2, $\delta(Ar/N_2)/12$ and $\delta(^{40}Ar)/4$ for each collected air sample. From its vertical profile, we are able to evaluate the effects of the gravitational separation on the concentration (ΔC_{grav}) and the isotopic ratio (ΔR_{grav}) of a specified atmospheric component at a certain altitude using the respective equations,

$$\Delta C_{grav} = [X] \times (m - m_{air}) \times \Delta\delta \text{ (ppm)}, \quad (2)$$

and

$$\Delta R_{grav} = \Delta m \times \Delta\delta \text{ (per meg)}. \quad (3)$$

Here, $[X]$ is the mole fraction of the specified component, m and m_{air} denote the relative molecular masses of the specified component and air, respectively, and $\Delta\delta$ is the difference in the measured δ value from its tropospheric value.

The data of $\delta(O_2/N_2)$ and CO_2 concentration taken at altitudes above 18–25 km since 1999 were corrected for the gravitational separation using the above-mentioned equations, and their averages for each year are shown in Fig. 3. As seen in the figure, the corrected values of $\delta(O_2/N_2)$ are significantly higher than the observed values. In addition, variability in the $\delta(O_2/N_2)$ value, represented by the error bars in Fig. 3, is much reduced by applying the gravitational separation correction. On the other hand, the difference between the CO_2 concentrations with and without the correction is quite small. These results imply that the gravitational separation correction is necessary when extremely small variations of abundant atmospheric component are discussed.

It is also obvious in Fig. 3 that the stratospheric $\delta(O_2/N_2)$ value, corrected for the gravitational separation, decreases secularly following a similar temporal change in the

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

ACPD

13, 4839–4861, 2013

Gravitational separation in the stratosphere

S. Ishidoya et al.

troposphere (Ishidoya et al., 2012). The mean age of the stratospheric air has usually been calculated from the stratospheric CO_2 and SF_6 concentrations by comparing them with their concentration histories in the equatorial troposphere (Waugh and Hall, 2002). To validate our gravitational separation correction, we estimated the mean age of the stratospheric air independently using the corrected middle stratospheric and upper tropospheric $\delta(O_2/N_2)$ values shown in Fig. 3. The average "$\delta(O_2/N_2)$ age" obtained is (3.9 ± 0.9) yr, which is consistent with the "CO_2 age" of (4.0 ± 0.4) yr calculated by the same procedure.

3.4 Numerical simulation of the gravitational separation

Existence of the gravitational separation in the stratosphere was also confirmed theoretically by numerical model simulations. As a first attempt, a 2-dimensional model of the middle atmosphere (SOCRATES) developed by NCAR was used to evaluate the basic structure of the gravitational separation in the stratosphere. In this model, mass transport processes caused by molecular diffusion were originally taken into account only above the mesosphere, since the molecular diffusion effect was thought to be negligibly small in the stratosphere, compared with the eddy diffusion effect. In this study, we simply lowered its vertical domain to the tropopause for the calculation of molecular diffusion. Molecular diffusion theory included in SOCRATES is based on Banks and Kockarts (1973),

$$f_i = -K_i \left[\frac{\partial n_i}{\partial z} + \frac{n_i}{H_i} + (1 + \alpha_{Ti}) \frac{n_i}{T} \frac{\partial T}{\partial z} \right], \tag{4}$$

where f_i, K_i, n_i, H_i, α_{Ti} are the vertical flux by molecular diffusion, the molecular diffusion coefficient, the number density, the scale height and the thermal diffusion factor for species i, respectively. We assumed α_{Ti} to be zero, since the thermal diffusion effect would be of no importance in the stratosphere. The molecular diffusion coefficient is given by,

$$K_i = 1.52 \times 10^{18} \left(\frac{1}{m_{\text{air}}} + \frac{1}{m_i} \right)^{1/2} \frac{\sqrt{T}}{N} \ (\text{cm}^2\,\text{s}^{-1}), \tag{5}$$

where m_{air} has the same meaning as above, m_i and N are the mean relative molecular mass of species i and the number density of air, respectively. The coefficient of 1.52×10^{18} has the dimension of "$\text{cm}^{-1}\,\text{s}^{-1}\,\text{kg}^{-1/2}\,\text{K}^{-1/2}$". Based on this model set-up, we calculated height-latitude distributions of $^{44}CO_2$ and $^{45}CO_2$ concentrations, and then derived the isotopic ratio (per meg),

$$\delta\left(^{45}\text{CO}_2\right) = \frac{\left[n\left(^{45}\text{CO}_2\right)/n\left(^{44}\text{CO}_2\right)\right]_{\text{strat}}}{\left[n\left(^{45}\text{CO}_2\right)/n\left(^{44}\text{CO}_2\right)\right]_{\text{trop}}} - 1. \tag{6}$$

Here, subscripts "trop" and "strat" denote the tropospheric and stratospheric values, respectively. In the actual atmosphere, the $^{45}CO_2/^{44}CO_2$ ratio has been decreasing secularly due to the emissions of isotopically light CO_2 by human activities. However, in this study, we assumed the $^{45}CO_2/^{44}CO_2$ ratio to be constant in the lowermost layer of the model, since our aim is to simulate the gravitational separation on $^{44}CO_2$ and $^{45}CO_2$ molecules. The boundary conditions and other input data for the present simulations were the same as SOCRATES baseline-atmosphere run. At first, a 20-yr spin-up calculation was carried out with no CO_2 increase in the troposphere, and then a 30-yr simulation was performed with monotonically increasing CO_2 at the model surface, to evaluate both the CO_2 age and the gravitational separation on $^{44}CO_2$ and $^{45}CO_2$. The CO_2 age was simply defined as a time difference between the appearance of the same CO_2 concentration in the stratosphere and the troposphere. Since the CO_2 age obtained from the model simulation was obviously underestimated compared with the observational result, probably due to atmospheric circulation moving too fast, the meridional mass transport was arbitrarily suppressed by changing the meridional mass stream function in this study so that the model-calculated CO_2 ages at northern mid-latitudes were close to the results observed over Japan. The results obtained under this condition are referred to as "Control Run". The annual mean distributions of the δ value and the CO_2 age calculated using SOCRATES are shown in Fig. 4a, b, respectively. The height-latitude distribution of the CO_2 age is close to those summarized by Waugh and Hall (2002) on the basis of the observations and model simulations. Simulated vertical distributions of the δ value and the CO_2 age at northern mid-latitudes are almost consistent with the observational results. The model result predicts that the vertical gradient of the δ value increases with increasing height especially at mid- and high latitudes and that the differences between low and high latitudes will be also observable. The basic structure of the vertical-meridional distribution of the δ value reproduced by model calculations can be interpreted as a result of a balance between the mass-dependent molecular diffusions and the mass-independent transport processes in the stratosphere.

3.5 Gravitational separation as a new indicator of atmospheric circulation

Mean vertical δ profiles always show a negative gradient due to the gravitational separation effect, but its magnitude depends on the observation. To examine the temporal variations of the vertical gradient, we calculated an average vertical profile of δ using all the data obtained in this study and then obtained deviations of the respective δ values from the average profile. The average of the deviation values of δ above 18–25 km for each observation is shown in Fig. 5 as δ anomaly, together with the CO_2 age calculated from our stratospheric and equatorial tropospheric concentration data (Nakazawa et al., 1997). The results indicate that the δ anomaly is negatively correlated with the CO_2 age, which means that the gravitational separation becomes stronger when the relevant stratospheric air becomes older.

As described in the previous section, the magnitude of the gravitational separation at a certain altitude in the stratosphere is basically determined by the molecular diffusion

ACPD
13, 4839–4861, 2013

and the mass-independent atmospheric transport. Therefore, the CO_2 age and the δ value would be affected to some extent by changes in the stratospheric circulation, such as an enhanced BDC due to global warming. To examine how the CO_2 age and the δ value are influenced by changes in the stratospheric circulation, model simulations were further made by arbitrarily changing the meridional mass stream function so that the CO_2 age decreased to about 80 % at 30 km over northern mid-latitudes, in accordance with the prediction made by a past study (Austin and Li, 2006) for potential global warming effect over the period 1960–2100, in which the BDC is accelerated due to global warming. The results obtained under this condition are referred to as "Enhanced BDC". The annual mean distributions of the δ value and the CO_2 age calculated using SOCRATES for Enhanced BDC are shown in Fig. 4c, d, respectively. The annual mean relationships between the CO_2 age and the δ value obtained from the Control Run and Enhanced BDC simulations for northern mid-latitudes are also shown in Fig. 6, together with the observational results over Japan.

As seen in Fig. 6, the relationships between the CO_2 age and the δ value for Control Run at northern mid-latitudes are fairly close to the observational results over Japan, which implies that both the CO_2 age and the δ value can be almost reproduced by SOCRATES. However, the relationships for Enhanced BDC are clearly different from those of Control Run, indicating that the CO_2 age and the δ value respond differently to changes in the stratospheric transport, i.e. the gravitational separation for the air molecules with the same age is enhanced when the BDC is accelerated. For example, the δ value of about −50 per meg and the CO_2 age of about 5.0 yr are found at 30 km over the northern mid-latitudes for Control Run, while Enhanced BDC shows −100 per meg for the δ value and 5.0 yr for the CO_2 age at 40 km over the same latitude region. This phenomenon is caused by a strong height dependency of the gravitational separation due to the fact that the molecular diffusion coefficient increases with increasing height.

It is difficult to detect a long-term change in the BDC only from the CO_2 and SF_6 ages because of their variability (Engel et al., 2009). But by using the definite relationship

ACPD
13, 4839–4861, 2013

Gravitational separation in the stratosphere

S. Ishidoya et al.

between the δ value and the air age found in this study, such a long-term change would be detectable. However, it is interesting to note that the observational results shown in Fig. 6 indicate the gravitational separation for the air with the same age slightly weakening with time for the period 1995–2010. This tendency is just the opposite of that expected from the Enhanced BDC simulation. Balloon and satellite observations (Engel et al., 2009; Stiller et al., 2012) reported that the CO_2 and SF_6 ages in the stratosphere over northern mid-latitudes showed no significant trend over the last 30 yr, while the satellite measurements indicate that the SF_6 age might have increased for the period 2002–2010. Our long-term record of the middle stratospheric CO_2 concentration over Japan for the period 1985–2010 also shows a slight secular increase in the CO_2 age (our unpublished data, but the CO_2 age values for a limited time period of 1986–2001 are available from Engel et al. (2009)). These observational results on the gravitational separation and the air age could imply that the BDC has not changed significantly or weakened slightly over the past 10–30 yr, in conflict with the model prediction of an enhancement of the BDC due to global warming (Austin and Li, 2006; Li et al., 2008).

With respect to this interpretation, it may be worthwhile to describe the results of simulations made by Ray et al. (2010) using a tropical leaky pipe (TLP) model. Ray et al. (2010) reported that a weakening of the mean circulation in the middle and upper stratosphere is of importance for obtaining an agreement with the observed mean age over the past 3 decades. Their finding would strongly support the above-mentioned observational results. However, they also pointed out that the mean age trend is sensitive to the horizontal mixing into the tropics. Therefore, it is further necessary to examine how the horizontal mixing affects not only on the mean age but also on the gravitational separation using stratospheric transport models.

4 Conclusions

To detect the gravitational separation in the stratosphere, the stratospheric air samples collected over Japan were analyzed for $\delta(^{15}N)$ of N_2, $\delta(^{18}O)$ of O_2, $\delta(O_2/N_2)$, $\delta(Ar/N_2)$

ACPD
13, 4839–4861, 2013

Gravitational separation in the stratosphere

S. Ishidoya et al.

and $\delta(^{40}Ar)$. The vertical profiles of $\delta(^{18}O)/2$, $\delta(Ar/N_2)/12$, $\delta(^{40}Ar)/4$ and $\delta(^{15}N)$ of N_2 showed a gradual decrease with height, their average difference between the lowermost part of the stratosphere and 32 km being about 45 per meg. The relationships of $\delta(^{18}O)$, $\delta(Ar/N_2)$ and $\delta(^{40}Ar)$ with $\delta(^{15}N)$ of N_2 were (2.1 ± 0.2), (11.9 ± 1.4) and (4.2 ± 0.6) per meg per meg^{-1}, respectively. These ratios are consistent with the corresponding values of 2, 12 and 4 per meg per meg^{-1} expected from the gravitational separation, but are clearly different from (1.55 ± 0.02), (16.2 ± 0.1) and (2.75 ± 0.05) per meg per meg^{-1} determined experimentally for a possible thermal diffusion effect at the air intake of the cryogenic air sampler. This fact indicates that the gravitational separation of the major atmospheric components is clearly observable even in the stratosphere.

By using a parameter "δ" defined as an average of $\delta(^{15}N)$ of N_2, $\delta(^{18}O)/2$ of O_2, $\delta(Ar/N_2)/12$ and $\delta(^{40}Ar)/4$ for each collected air sample, we corrected the values of $\delta(O_2/N_2)$ observed in the middle stratosphere for the gravitational separation. The $\delta(O_2/N_2)$ values, thus corrected, were found to be significantly higher than the observed values. This implies that the gravitational separation correction is necessary when extremely small variations of abundant atmospheric component are discussed. It was also found that the corrected values of $\delta(O_2/N_2)$ show a secular decrease similar to temporal change in the troposphere, and that the mean age of the middle stratospheric air calculated from $\delta(O_2/N_2)$ is consistent with the CO_2 age.

To examine how the CO_2 age and the δ value are influenced by changes in the stratospheric circulation, we made numerical simulations using the SOCRATES model. It was found from the simulations that the CO_2 age and the δ value respond differently to changes in the stratospheric transport. The simulation results also indicate that the gravitational separation for the air with the same age is strengthened if the BDC is enhanced due to global warming, which is just the opposite of our observational result for the period 1995–2010.

The δ value is a new, unique and excellent indicator to represent how much the gravitational separation occurs in the stratosphere. Therefore, analyses of the δ value,

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

ACPD

13, 4839–4861, 2013

Gravitational separation in the stratosphere

S. Ishidoya et al.

in addition to the CO_2 and SF_6 ages, would provide us with useful information about the stratospheric circulation. However, observations of the gravitational separation are still sparse. By taking longer records of the δ value we can detect a change in the BDC due to global warming, a feat that has not been achieved so far. Knowledge obtained from observations of the gravitational separation also contributes to further progression of atmospheric science, especially for the middle atmosphere.

Acknowledgements. We deeply thank the balloon engineering group of the Institute of Space and Astronautical Science, JAXA for their cooperation in our stratospheric air sampling. This work is partly supported by the Grants-in-Aid for Creative Scientific Research (2005/17GS0203), the Grants-in-Aid for Scientific Research (2006/18710004) and the subsidized project "Formation of a virtual laboratory for diagnosing the earth's climate system" of the Ministry of Education, Science, Sports and Culture, Japan.

References

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 B, 55, 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.

Blaine, T. W., Keeling, R. F., and Paplawsky, W. J.: An improved inlet for precisely measuring the atmospheric Ar/N_2 ratio, Atmos. Chem. Phys., 6, 1181–1184, doi:10.5194/acp-6-1181-2006, 2006.

Brewer, A.: Evidence for a world circulation provided by the measurement of helium and water vapor in the stratosphere, Q. J. Roy. Meteor. Soc., 75, 351–363, 1949.

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

ACPD

13, 4839–4861, 2013

Gravitational separation in the stratosphere

S. Ishidoya et al.

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion

Boering, K.: Age of stratospheric air unchanged within uncertainties over the past 30 years, Nat. Geosci., 2, 28–31, doi:10.1038/Ngeo388, 2009.
Grew, K. E. and Ibbs, L. T.: Thermal Diffusion in Gases, Cambridge Univ. Press., New York, 1952.
Honda, H.: Balloon-borne cryogenic whole air sampling system, The Institute of Space and Astronautical Science, Sagamihara, Japan, 1990.
Honda, H., Aoki, S., Nakazawa, T., Morimoto, S., and Yajima, N.: Cryogenic air sampling system for measurements of the concentrations of stratospheric trace gases and their isotopic ratios over Antarctica, J. Geomagn. Geoelectr., 48, 1145–1155, 1996.
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, http://nldr.library.ucar.edu/repository/collections/TECH-NOTE-000-000-000-383, 1998.
Ishidoya, S., Aoki, S., and Nakazawa, T.: High precision measurements of the atmospheric O_2/N_2 ratio on a mass spectrometer, J. Meteorol. Soc. Jpn., 81, 127–140, 2003.
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, δ^{15}N of N_2, δ^{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., Aoki, S. Goto, D., Nakazawa, T., Taguchi, S., and Patra, P. K.: Time and space variations of the O_2/N_2 ratio in the troposphere over Japan and estimation of global CO_2 budget, Tellus B, 64, 18964, doi:10.3402/tellusb.v64i0.18964, 2012.
Jacob, D. J.: Introduction to Atmospheric Chemistry, Princeton University Press, 1999.
Lettau, H.: Diffusion in the upper atmosphere, Compendium of Meteorology American Meteorological Society, Boston, 1951.

ACPD
13, 4839–4861, 2013

Lewis, J. S. and Prinn R. G.: Planets and Their Atmosphere: origin and evolution, International Geophysics Series, 33, Academic Press Inc., 1984.
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.
Massie, S. T. and Hunten, D. M.: Stratospheric eddy diffusion coefficients from tracer data, J. Geophys. Res., 86, 9859–9868, 1981.
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, 1229, doi:10.1029/95GL01188, 1995.
Nakazawa, T., Morimoto, S., Aoki, S., and Tanaka, M.: Temporal and spatial variations of the carbon isotopic ratio of atmospheric carbon dioxide in the western Pacific region, J. Geophys. Res., 102, 1271–1285, 1997.
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.
Severinghaus, J. P., Grachev, A., and Battle, M.: Thermal fractionation of air in polar firn by seasonal temperature gradients, Geochem. Geophy. Geosy., 2, 1048, doi:10.1029/2000GC000146, 2001.
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.
Waugh, D. W. and Hall, T. M.: Age of stratospheric air: theory, observations, and models, Rev. Geophys., 40, 1010, doi:10.1029/2000RG000101, 2002.

ACPD
13, 4839–4861, 2013

Gravitational separation in the stratosphere

S. Ishidoya et al.

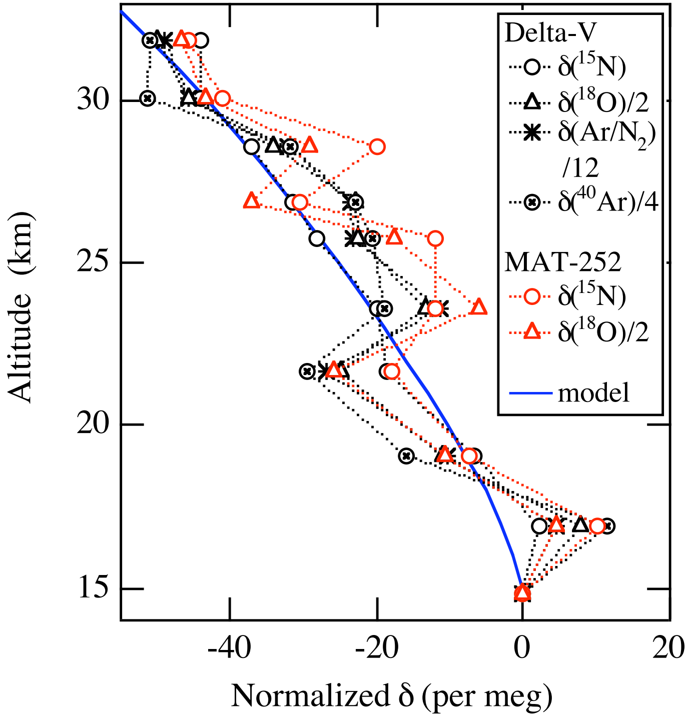

Fig. 1. $\delta(^{15}N)$ of N_2, $\delta(^{18}O)/2$ of O_2, $\delta(Ar/N_2)/12$ and $\delta(^{40}Ar)/4$ observed over Sanriku, Japan on 4 July 2007. Also shown is the vertical profile of δ value calculated using a 1-dimensional steady state eddy-diffusion/molecular-diffusion model for the mass number difference of 1. The tropopause height on 4 July 2007 was estimated to be about 12 km.

ACPD
13, 4839–4861, 2013

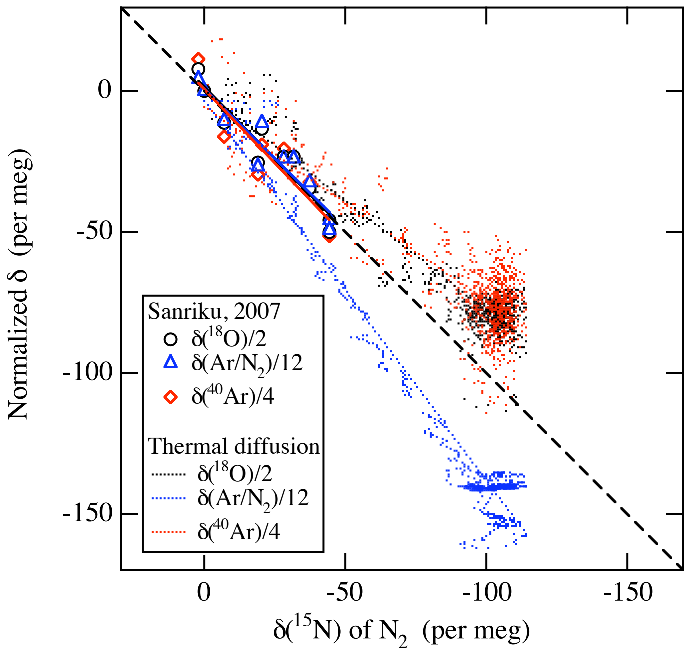

Fig. 2. Plots of $\delta(^{18}O)/2$, $\delta(Ar/N_2)/12$ and $\delta(^{40}Ar)/4$ against $\delta(^{15}N)$ for stratospheric air samples collected over Sanriku, Japan on 4 July 2007, and those for laboratory experiments to examine a possible effect of thermal diffusion at the air intake of the sampler on the collected air samples (see text). Black dashed line represents the relationship expected from the gravitational separation.

ACPD
13, 4839–4861, 2013

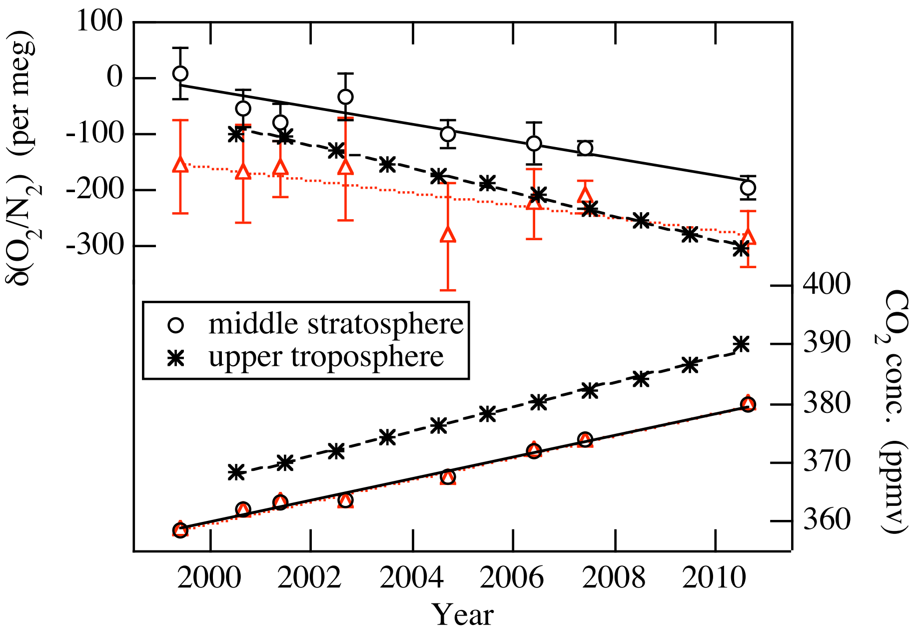

Fig. 3. Average values of $\delta(O_2/N_2)$ and the CO_2 concentration observed above 18–25 km over Sanriku and Taiki, Japan for the period 1999–2010, after (black open circles) and before (red triangles) correcting for the gravitational separation effect. Asterisks denote the annual mean values of $\delta(O_2/N_2)$ and the CO_2 concentration observed in the upper troposphere over Japan for the period 2000–2010.

ACPD
13, 4839–4861, 2013

ACPD
13, 4839–4861, 2013

Gravitational separation in the stratosphere

S. Ishidoya et al.

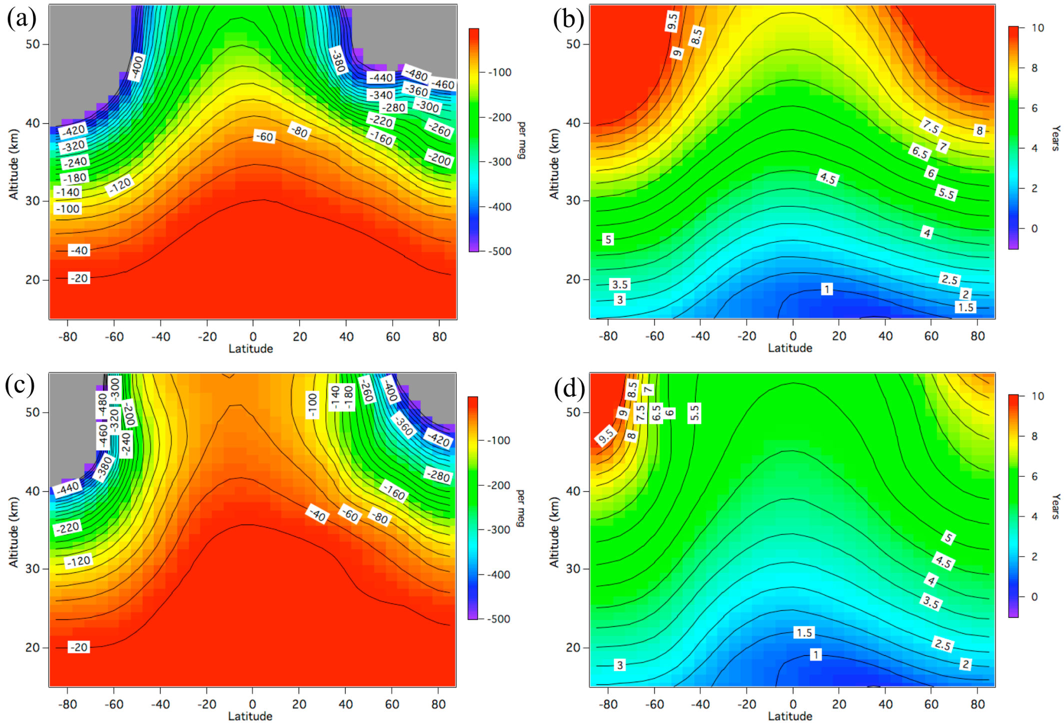

Fig. 4. Annual mean height-latitude distributions of **(a)** δ value (per meg) and **(b)** CO_2 age (years) calculated using the SOCRATES model for Control Run, and the corresponding results for Enhanced BDC (**c** and **d**). The δ values lower than −500 per meg are shown by gray shades.

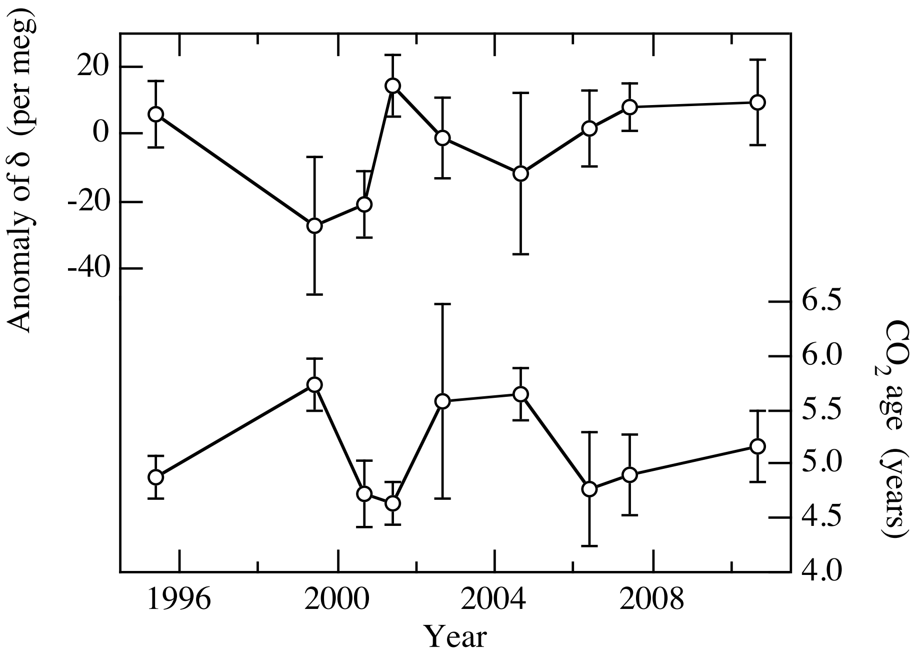

Fig. 5. Average values of the deviations of δ from its mean vertical profile over the observation period (upper) and those of the CO_2 ages (lower) at heights above 18–25 km for the respective years.

ACPD
13, 4839–4861, 2013

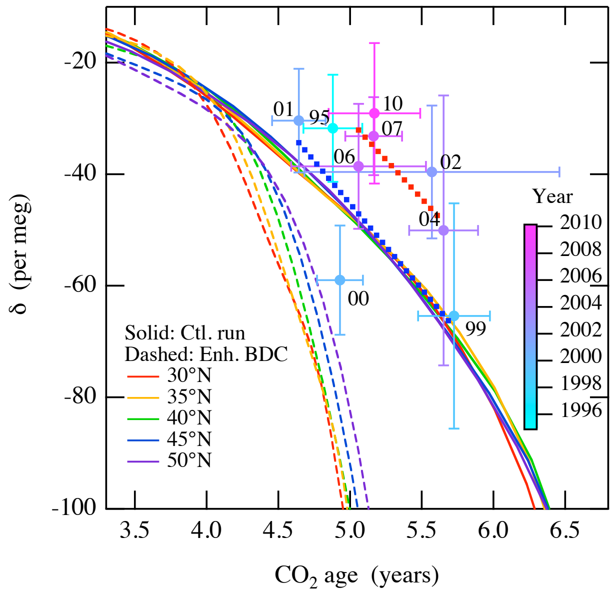

Fig. 6. Plots of the δ value at 29 km against the average values of CO_2 ages at heights above 18–25 km for the respective observations over Sanriku and Taiki, Japan (closed circles). Color bar and Arabic numerals near the symbols indicate the observation years. The results calculated using the SOCRATES model for Control Run (solid lines) and Enhanced BDC (dashed lines) are also shown. Blue and red dotted lines represent the results obtained by applying a linear regression analysis to the data for the respective periods 1995–2001 and 2004–2010. It is noted that the result for 2002 is not used in the regression analysis, since it was found to deviate significantly from those of the other years, due to large variability in the vertical CO_2 profile observed in that year. It is also noted that the observed δ values plotted are the values obtained by linearly interpolating the measured δ values of the corresponding observations for 29 km, which is approximately the highest altitude covered by all our observations.

ACPD
13, 4839–4861, 2013

Gravitational separation in the stratosphere

S. Ishidoya et al.