VERTICAL PROFILES OF THE O_2/N_2 RATIO IN THE STRATOSPHERE OVER JAPAN AND ANTARCTICA

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ABSTRACT

To examine vertical distributions of the O_2/N_2 ratio in the stratosphere, air samples were collected using a cryogenic sampler over Sanriku, Japan and Syowa, Antarctica. It was clearly seen that $\delta(O_2/N_2)$, as well as simultaneously measured $\delta^{15}N$ of N_2 and $\delta^{18}O$ of O_2, decreased gradually with increasing height in the stratosphere. The observed profiles of stratospheric $\delta^{15}N$ and $\delta^{18}O$ were in agreement with those calculated using a steady state 1-dimensional eddy-diffusion/molecular-diffusion model suggesting that the upward decrease of stratospheric $\delta(O_2/N_2)$ is caused by O_2 and N_2 molecules fractionated differently by gravity. The stratospheric $\delta(O_2/N_2)$ corrected for the gravitational separation indicated that the average value at heights above 20-25 km over Sanriku was always higher than the upper tropospheric $\delta(O_2/N_2)$ value over Japan at the corresponding time, and that it has decreased secularly, as was found in the troposphere.

INTRODUCTION

The atmospheric O_2/N_2 ratio have been observed precisely at the ground surface to constrain the global carbon budget (IPCC, 2001). However, there are only a few observations for the O_2/N_2 ratio in the free troposphere [e.g. *Langenfelds et al.,* 1999; *Ishidoya*, 2003], and no measurement has been made so far in the stratosphere. *Keeling* [1988] suggested, from the vertical profiles of the O_2/N_2 ratio calculated for the stratosphere using a 1-dimensional diffusion model, that the measured O_2/N_2 ratios at 15-22 km would constrain net O_2 sink over the past 5 years and that those at 30-40 km, where the tropospheric O_2 loss has little influence, would be useful for validating models of eddy mixing. Therefore, it is worthwhile to measure the stratospheric O_2/N_2 ratio. In this paper, we present the O_2/N_2 ratio observed in the stratosphere over Japan and Antarctica, together with simultaneously measured $\delta^{15}N$ of N_2 and $\delta^{18}O$ of O_2.

EXPERIMENTAL PROCEDURES

We analyzed the $\delta(O_2/N_2)$ ratio, $\delta^{15}N$ of N_2 and $\delta^{18}O$ of O_2 of the stratospheric air samples collected over Sanriku, Japan (39°N, 142°E) on May 31, 1999, August 28, 2000, May 30, 2001, September 4, 2002 and September 6, 2004 and Syowa, Antarctica (69°S, 40°E) on January 5, 2004 [*Aoki et al.,* 2003; *Nakazawa et al*. 1995], using a mass spectrometer (Finnigan MAT-252). Our overall analytical precision were estimated to be ±34, ±12 and ±26 per meg for $\delta(O_2/N_2)$, $\delta^{15}N$ and $\delta^{18}O$, respectively. The present precision of $\delta(O_2/N_2)$ is worse than ±5.4 per meg of our ordinary flask sample analyses [*Ishidoya et al*., 2003], probably due to deterioration of air samples stored in the cryogenic sampler.

RESULTS AND DISCUSSION

Figure 1 shows measured vertical profiles of $\delta(O_2/N_2)$, $\delta^{15}N$ and $\delta^{18}O$. Although the values of $\delta(O_2/N_2)$,$\delta^{15}N$ and $\delta^{18}O$ are highly variable with respect to height, it is clearly seen that they all decrease gradually with increasing height. The decreases of $\delta(O_2/N_2)$, $\delta^{15}N$ and $\delta^{18}O$ between the middle and lowermost parts of the stratosphere amount to about 250, 100, and 180 per meg, respectively. Considering that $\delta^{15}N$ and $\delta^{18}O$ are expected to uniformly distribute in the troposphere at least over a timescale of a few or several 100 years, such vertical differences are attributable to the gravitational fractionation effect occurred in the stratosphere. In fact, the observed vertical profiles of stratospheric $\delta^{15}N$ and $\delta^{18}O$ are in agreement with those calculated using a steady state 1-dimensional eddy-diffusion/molecular-diffusion model, as used in *Keeling* [1988]. Taking this into account, it is thought that the observed upward decrease of the stratospheric $\delta(O_2/N_2)$ was caused by the separation of O_2 and N_2 by molecular diffusion depending on their molecular masses (gravitational separation). *Chabrillat et al* [2002] also reported that molecular diffusion has a non-negligible impact on the vertical CO_2 distribution in the mesosphere, although its heights are higher than those of our study. Using the measured values of stratospheric $\delta^{15}N$ and $\delta^{18}O$, we corrected the stratospheric $\delta(O_2/N_2)$ values for the effects of gravitational separation and other possible fractionation processes. The averages of the corrected $\delta(O_2/N_2)$ data, at heights above 18-25 km, for the respective years are shown in Fig. 2. The $\delta(O_2/N_2)$ value over Sanriku is always higher than the upper tropospheric value over Japan [*Ishidoya*, 2003] at the corresponding time, and age differences of air between the middle stratosphere and the upper troposphere over Japan, estimated from the measured values of $\delta(O_2/N_2)$ and CO_2 concentration, are almost consistent with each other. It is also seen from Fig.2 that stratospheric $\delta(O_2/N_2)$ decreased secularly. By calculating the age of stratospheric air from its CO_2 concentration and a history of the tropospheric CO_2 concentration, the rate in secular decrease of $\delta(O_2/N_2)$ for the period 1993-2003 was estimated to be about –16 per meg/yr. This estimate indicates that O_2 consumption by fossil fuel combustion can be detectable not only in the troposphere but also in the stratosphere.

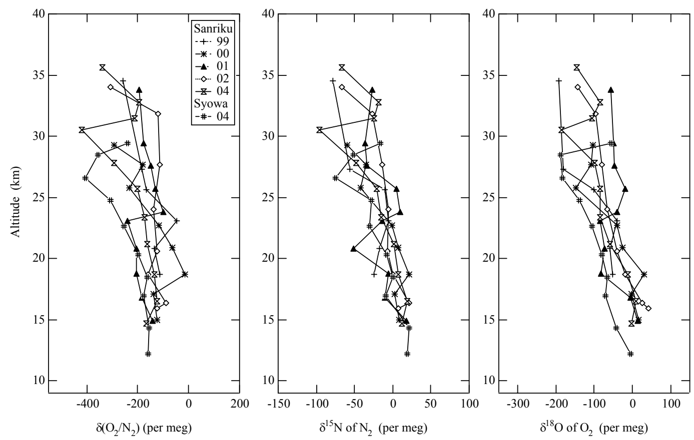

Fig. 1. Vertical profiles of $\delta(O_2/N_2)$, $\delta^{15}N$ and $\delta^{18}O$ observed over Sanriku, Japan and Syowa, Antarctica.

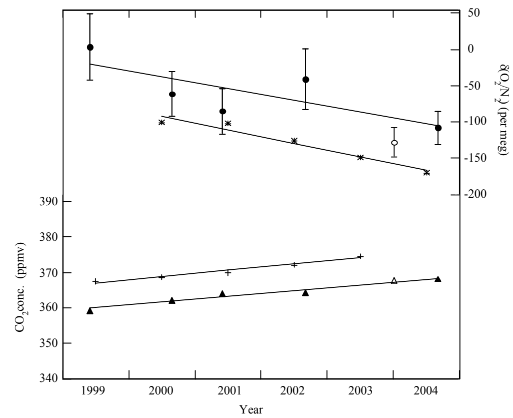

Fig. 2. Average values of $\delta(O_2/N_2)$ corrected for the gravitational separation and CO_2 concentration at heights above 18-25 km. Solid and open circles represent the results over Sanriku and Syowa, respectively. Asterisks and crosses represent annual mean values of the respective factors observed in the upper troposphere over Japan.

REFERENCES

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

Chabrillat, S., G. Kockarts, and D. Fonteyn, Impact of molecular diffusion on the CO_2 distribution and the temperature in the mesosphere, *Geophys. Res. Lett.*, *29* (15), 10.1029/2002GL015309, 2002.

IPCC, in *Climate Change 2001*, edited by J.T. Houghton, Y. Ding, D.J. Griggs, M. Noguer, P.J. Linden, X. Dai, K. Maskell, and C.A. Johnson, Cambridge University Press, Cambridge, U. K., 2001.

Ishidoya, S., S. Aoki, and T. Nakazawa, High precision measurements of the atmospheric O_2/N_2 ratio on a mass spectrometer, *J. Meteorol. Soc. Japan*, *81* (1), 127-140, 2003.

Ishidoya, S., Development of high precision measurement technique of the atmospheric O_2/N_2 ratio and its application to the global carbon cycle, Ph. D. thesis, Tohoku university, Sendai, 2003.

Keeling, R. F., Development of an interferometric oxygen analyzer for precise measurement of the atmospheric O_2 mole fraction, Ph.D. thesis, Harvard University, Cambridge, 1988.

Langenfelds, R. L., R. Francey, L. P. Steele, R. F. Keeling, M. Bender, M. Battle, and W. F. Budd, Measurements of O_2/N_2 ratio from the Cape Grim air archive and three independent flask sampling program, *Baseline atmospheric program (Australia) 1996*, 57-70, 1999.

Nakazawa, T., T. Machida, S. Sugawara, S. Murayama, S. Morimoto, G. Hashida, H. Honda, and T. Itoh, Measurements of the stratospheric carbon dioxide concentration over Japan using a balloon-borne cryogenic sampler, *Geophys. Res. Lett.*, *22* (10), 1229-1232, 1995.