VERTICAL PROFILES OF THE O2/N2 RATIO IN THE STRATOSPHERE
OVER JAPAN AND ANTARCTICA

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ABSTRACT
To examine vertical distributions of the O2/N2 ratio in the stratosphere, air samples were collected using a cryogenic
sampler over Sanriku, Japan and Syowa, Antarctica. It was clearly seen that δ(O2/N2), as well as simultaneously
measured δ15N of N2 and δ18O of O2, decreased gradually with increasing height in the stratosphere. The observed
profiles of stratospheric δ15N and δ18O were in agreement with those calculated using a steady state 1-dimensional
eddy-diffusion/molecular-diffusion model suggesting that the upward decrease of stratospheric δ(O2/N2) is caused
by O2 and N2 molecules fractionated differently by gravity. The stratospheric δ(O2/N2) 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 δ(O2/N2) value over Japan at the corresponding time, and that it has decreased secularly, as was
found in the troposphere.

INTRODUCTION
The atmospheric O2/N2 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 O2/N2 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 O2/N2 ratio calculated for the stratosphere using a 1-dimensional
diffusion model, that the measured O2/N2 ratios at 15-22 km would constrain net O2 sink over the past 5 years
and that those at 30-40 km, where the tropospheric O2 loss has little influence, would be useful for validating models of
eddy mixing. Therefore, it is worthwhile to measure the stratospheric O2/N2 ratio. In this paper, we present the O2/N2
ratio observed in the stratosphere over Japan and Antarctica, together with simultaneously measured δ15N of N2 and
δ18O of O2.

EXPERIMENTAL PROCEDURES
We analyzed the δ(O2/N2) ratio, δ15N of N2 and δ18O of O2 of the stratospheric air samples collected over Sanriku,
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 δ(O2/N2), δ15N and δ18O, respectively. The present precision of δ(O2/N2) 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 δ(O2/N2), δ15N and δ18O. Although the values of δ(O2/N2), δ15N and
δ18O are highly variable with respect to height, it is clearly seen that they all decrease gradually with increasing
height. The decreases of δ(O2/N2), δ15N and δ18O between the middle and lowermost parts of the stratosphere
amount to about 250, 100, and 180 per meg, respectively. Considering that δ15N and δ18O 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 δ15N and δ18O 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 δ(O2/N2) was caused by the separation of O2 and N2 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 CO2 distribution in the mesosphere, although its
heights are higher than those of our study. Using the measured values of stratospheric δ15N and δ18O, 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.

REFERENCES


