B-1.10   Study on Exchange of CO_2 between Atmosphere, Hydrosphere and Biosphere Using Isotope Analysis (Final Report)

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Abstract

Variation of carbon isotope ratio of carbon dioxide is considered to be one of key information to study a carbon cycle on the earth. In this study, measurements of carbon and oxygen isotope ratios of carbon dioxide in oceanic atmosphere were tried. Oceanic air samples were collected over the Pacific ocean by using two cargo ships which ply periodically between Japan and Australia, and between Japan and Canada respectively. By this sampling, the air samples from wide latitudinal range and at various seasons could be obtained. The methods for isotope ratios measurements were studied and the precision under 0.07 permil was obtained for carbon isotope ratio measurement finally, in addition to the correction factor (about 0.2 permil) by the interference of nitrous oxide. This methods were applied to the some samples, and carbon isotope ratio was found to decrease with increase of its concentration. As for oxygen isotope ratio, the variation pattern was different from that of carbon dioxide, suggesting that both isotope ratios had potentials to trace their behavior.

Key Words: Carbon dioxide, Isotope ratios, Ocean, Soil , latitudinal distribution

1. Introduction

Carbon dioxide moves during atmosphere, ocean and biosphere, through various processes.   The global increase of carbon dioxide concentration in the atmosphere corresponds to the increase of production of carbon dioxide by human activities, however, the increase rate of carbon dioxide concentration is influenced by the exchange amount of carbon in the atmosphere with that in both biosphere and ocean. In this study, we try to clarify the movement of carbon dioxide during such carbon pools, by using carbon and oxygen isotope ratio measurements.

Carbon isotope ratio of fossil fuel is usually around -25 permil (-27 to -30 for petroleum, -23 to -26 for coal). This value is lighter than the ratio of atmospheric carbon dioxide (i.e., -9 permil).   Therefore, accumulation of carbon dioxide which is produced by fossil fuel combustion makes the carbon isotope ratio in the atmosphere lighter than before.
Biological activities also put lighter carbon dioxide to the atmosphere and at the same time they fix lighter carbon (-25 permil for C4 plant) from the atmosphere by photosynthesis. These processes will change carbon isotope ratio by -0.04 permil per 1 ppm.   On the other hand, when ocean absorbed carbon dioxide, its fractionation effect is so small that the change of isotope ratio with change of the concentration is not observed.   Such differences in isotope ratio changes during processes allow us to trace the movement of carbon dioxide by using carbon isotope ratio measurements.

Oxygen isotope ratio of carbon dioxide can also be a tracer of carbon dioxide. Since oxygen in the atmosphere has lighter oxygen isotope ratio, carbon dioxide produced by combustion will have lighter oxygen isotope ratio than that which is produced by biological processes such as respiration and degradation. When carbon dioxide is processed through plant, oxygen in the carbon dioxide can be exchanged with oxygen in water in plant. Since oxygen isotope ratio of water depends on the origin of water, the isotope ratio varies with region. Thus, these two isotope ratios are considered to be good tracers for studying behavior of carbon dioxide in the atmosphere.

2. Research objective

We tried to study the following two themes
(1) to clarify the movement of carbon dioxide by using isotope ratio measurements of carbon dioxide in the oceanic atmosphere.
(2) measurement of carbon isotope ratio in the soil air to know the seasonal variation of biological activity which produce carbon dioxide from the soil .

Especially in theme (1), we decided to use two cargo ships which ply in the Pacific ocean to collect air samples for long times and over wide latitudinal range.

3. Method
3.1 Air sampling over the Pacific

Air sampling bottle is made of stainless steel and has 3.3 liters volume. Sampling air was pressurized to 3 kgw/cm^2 in the bottle after removing moisture by -60 degree C trap. This sampling equipment was installed in Hakubamaru (Nippn Yusen) which plies between Japan and Australia (Fig.1). Air was sampled periodically from Australia to Japan and 21 air samples were obtained in one cruse. In the case Skaugran (Jahre Wallen Management AS) which ply between Canada and Japan (Fig.1), about 14 air samples were collected manually in one cruse. Such samplings were performed about 10 times a year. These samplings covered the position from 20 degree south to 55 degree north.

3.2 CO$_2$ extraction from samples

Glass line was made to purify carbon dioxide (Fig.2). Three hundreds milliliters of sampled air were transferred to the stainless cylinder from the sampling bottle. Sample air was passed through water trap cooled by hexan-liquid nitrogen and then carbon dioxide was trapped in U tube cooled by liquid nitrogen. This trapping was operated under the condition of sample pressure of 1 torr. Trapped CO$_2$ in U tube was transferred to glass tube and CO$_2$ was enclosed in the glass tube.

3.3 Isotope ratio measurement

For making working standards of carbon and oxygen isotope ratios, vacuum line which has three Baratoron pressure gauges and a reduction furnace was made (Fig.3). To investigate the effect of N$_2$O to measured values of CO$_2$, CO$_2$/N$_2$O mixed gas samples were prepared using this line.

PRISM isotope mass spectrometer (VG) which had 10 ports auto manifold and triple trap (Fig.4), was used to determine the isotope ratios. In order to study the way of sample introduction to the mass spectrometer, several methods were tried and checked.

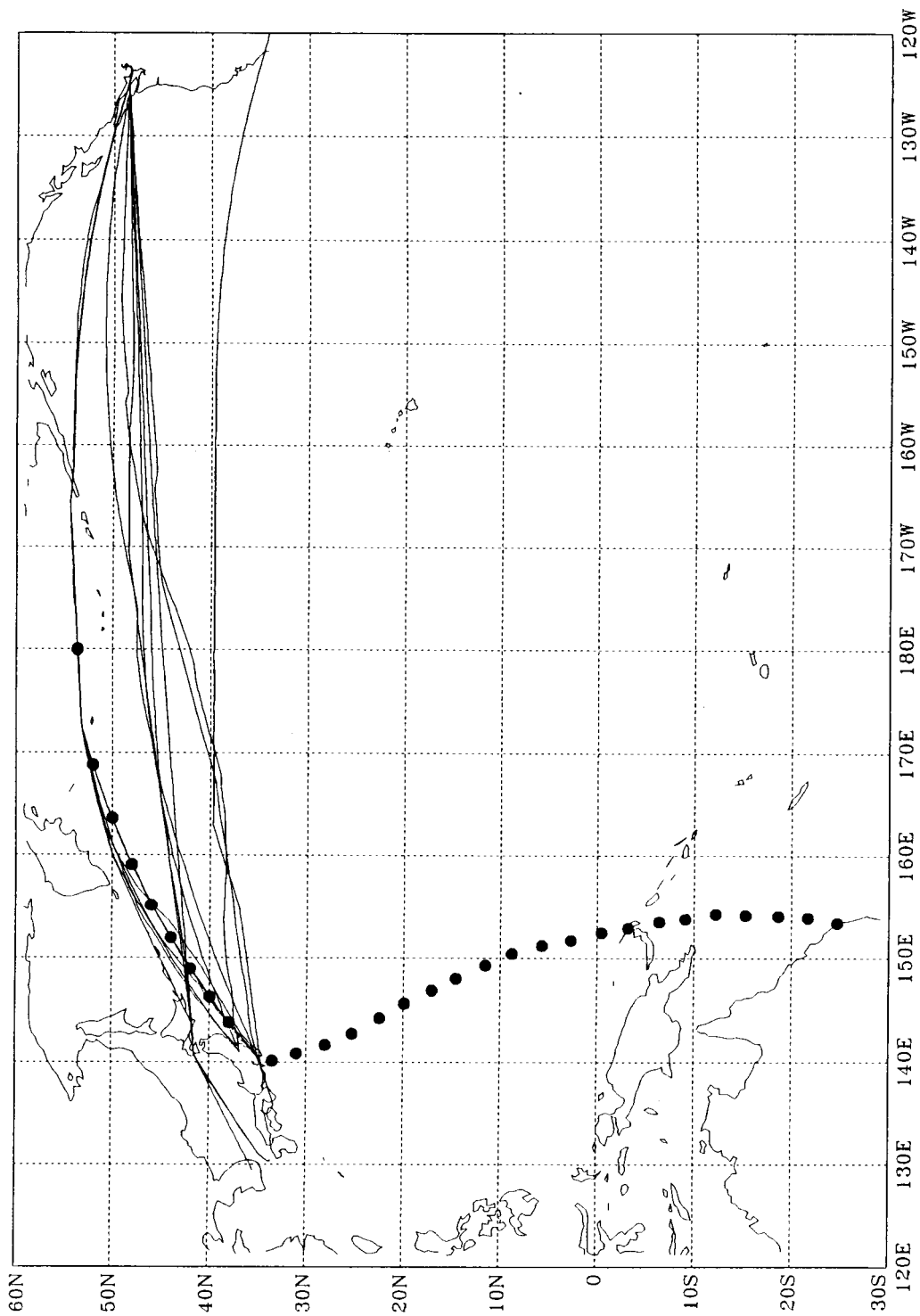### 3.4 Measurement of isotope ratio in soil air

Fig 1. Typical sampling points and some cruise tracks.

Sampling probes were installed in forest soil in Tsukuba up to 170cm depth.   Soil air was sampled through these sampling probes and kept in vacuums vials.   Carbon isotope ratio was measured by GC-on line combustion-mass spectrometry[1-2)].

4. Results and discussion

4.1 Precision of measurements

Carbon and oxygen measurements were tried by several sample introduction methods using manifold and trap.   Finally we obtained optimum condition of the measurement.   Data for standard sample was shown in Table 1.

Correction factors for N_2O interference were also obtained as following equations.

$$\Delta \text{ C (permil)} = -192 \times (N_2O/CO_2)$$
$$\Delta \text{ O (permil)} = -295 \times (N_2O/CO_2)$$

Table1.Precision of measurements of standard sample

sample No.	delta C 1 3 (permil)
1	− 2 6 . 3 6
2	− 2 6 . 4 6
3	− 2 6 . 2 7
4	− 2 6 . 2 3
5	− 2 6 . 3 6
6	− 2 6 . 3 2
7	− 2 6 . 3 2
Average	− 2 6 . 3 3
C V	0 . 0 6 8

4.2 Carbon and oxygen isotope ratio in carbon dioxide in the oceanic atmosphere

In Fig 5 and 6,   an example of latitudinal distribution of carbon and oxygen isotope ratios in October in 1994.   Carbon isotope ratio showed clear anti-correlation to its concentration.   When carbon isotope ratio and a reciprocal of its concentration were plotted (Fig.7), we obtained the intercept as the isotope ratio of end member which is added to the atmosphere.   Since this intercept was around -25 permil, its value was similar to the values of fossil fuel and biological activities.   If there is addition from ocean source around equator, we have to observe the concentration increase without change of isotope ratio.   However, this time we did not observed such behavior in the graph.

As for oxygen isotope ratio, it was found that the relation between the value and its concentration was very different from that of carbon.   Decrease of oxygen isotope ratio and increase of its concentration were observed near Japan, which meant that carbon dioxide from combustion source was added to the atmosphere.   Although oxygen isotope ratio decreased at the higher latitude than 20 degree north,   the concentration decreased in this case. Therefore, the other explanation should be considered the variation of oxygen isotope ratio beside addition of combustion source carbon dioxide.

These kinds of observation will be continued to clarify the carbon cycle through the atmosphere.

4.3 Carbon isotope ratio in soil air

The carbon isotope ratio in the soil air deeper than 1m was within the range from -24 to -22 permil.   In summer time,   this value was observed until surface soil, suggesting active production of carbon dioxide occurred in all depth.

5. Conclusion

In this study,   platforms and system for sampling oceanic air were established.   The methods for extraction of carbon dioxide and measurement of its isotope ratio were investigated in detail.   Latitudinal distribution of carbon and oxygen isotope ratios will be continuously monitored by using this method which was established here, and by this monitoring , carbon cycle through the atmosphere will be better understood in the future.

6. Reference

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2)   Y.Sano, M. Masuda, N. Takahata, H. Wakita, Y. Zeng, Y. Nojiri, H. Mukai, H. Bandow (1992) Carbon isotope measurement of natural and anthropogenic methane, Chikyukagaku 26, 105-114.
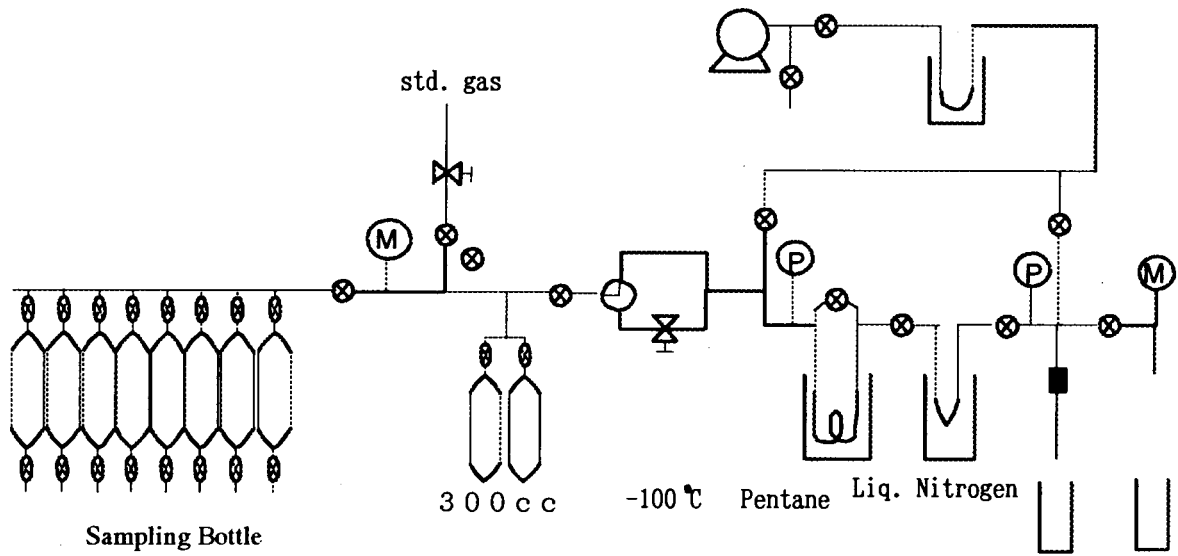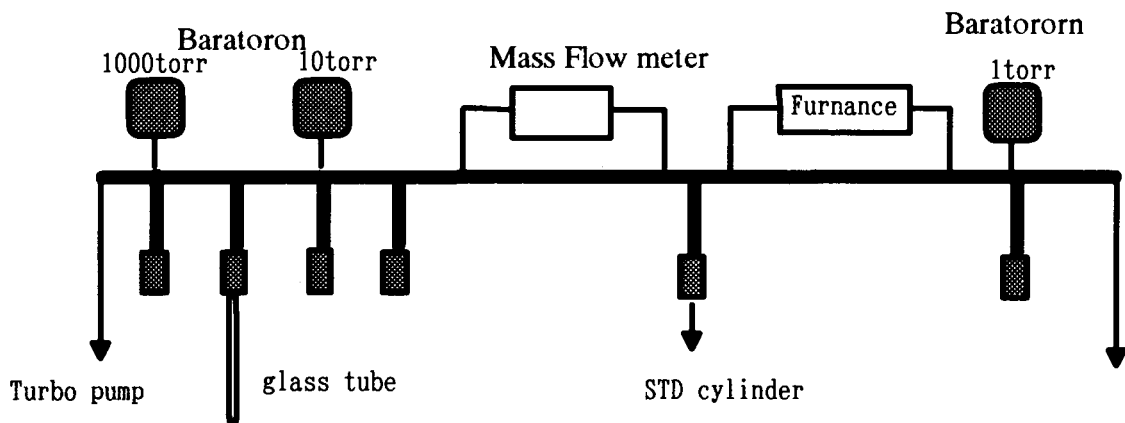
Fig.2 Glass line for sample extraction

Fig.3 Vacuume line for making working standard

sample inlet

10 ports manifold

Triple trap

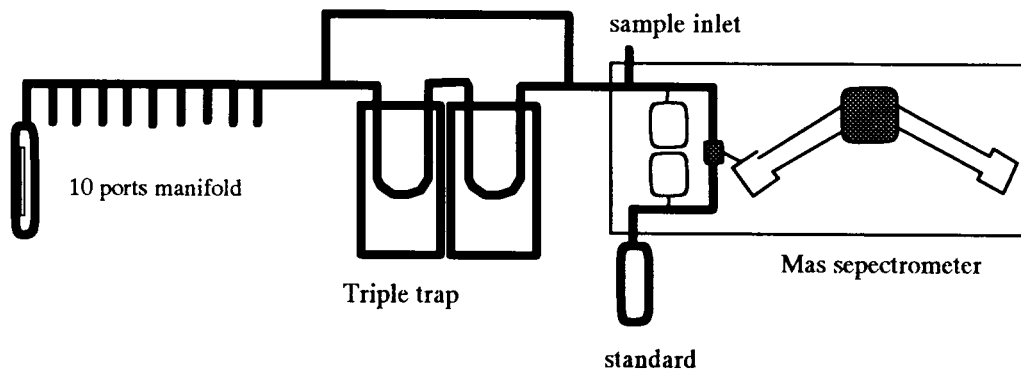standard

Mas sepectrometer

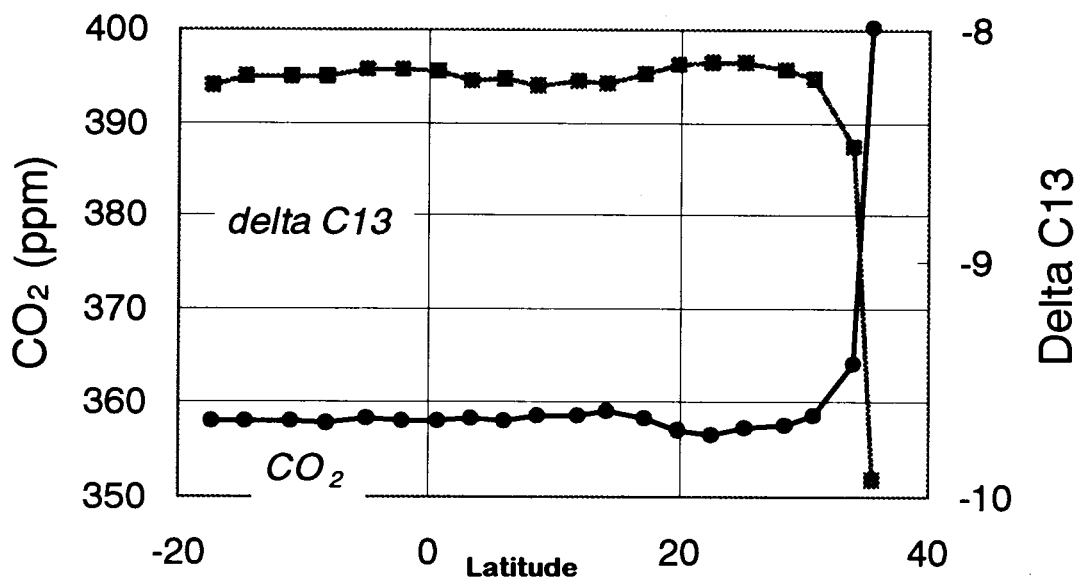Fig.4 Sample introduction system for mass spectrometer

Fig.5 Latitudinal distribution of Delta C13 in October in 1994 over the Pacific