B-7.6 Japan-Australia cooperative study on observation of atmospheric CO_2 in Asia-Pacific region

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Abstract Although high precision was required for the measurement of carbon isotope ratio of CO_2 in the atmosphere, data provided by various labs was known to have systematic gaps with each other. To assimilate these data we have to study the cause of the gaps and develop methods for removing these gaps. In this study, one reference material for atmospheric CO_2 isotope analysis was prepared to be distributed to the researchers in the world. The reference CO_2 (NACIS) had isotope values similar to those of atmospheric CO_2. In terms of homogeneity, NACIS could be a good reference to compare isotopic scale in each laboratory. Several cooperative analyses showed a good agreement in C isotope ratio with a range of 0.1 per mil. Systematic shift of the scale was considered to be related to cross contamination effects in Mass spectrometer. The cross contamination effect for the mass spectrometer in NIES was about 0.3% for C isotope analysis and 1.1% for O analysis, which gave a considerable shift on our scale compared to CSIRO in Australia. In November, a workshop was held to discuss such technical problem on isotope analysis and newly proposed inter-comparison plan for GHGs (GLOBALHUBS). The researchers from 8 countries gave their presentations for 2 days.

Key words Carbon dioxide, Carbon isotope analysis, Oxygen isotope analysis, Cross contamination, ^{17}O correction.

1. Introduction

Isotope ratio of CO_2 in the atmosphere was important tracer to study its behavior in nature. But the shifts are usually very small (e.g. 1 per mil). Primary standard of carbon isotope ratio was a Belemnite (PDB) in Peedee formation in South Carolina[1]. Usually C and O isotope ratio was expressed by the deviation from PDB in per mil. PDB calcite is carbonate, people have to produce CO_2 from the carbonate by phosphoric acid. Therefore,

some contamination could be introduced at that chemical treatment. The variation of primary standard and stability of working standards were often problem in precious analysis.

Concerning Mass spectrometer, there were several problems. One is about ^{17}O correction[2]. Mass spectrometer usually observes 45/44 and 46/44 ratio, instead of 13/12 and 18/16.

$$R45 = R13+2 \times R17 \quad \text{---------- (1)}$$

$$R46 = 2xR18 + 2x(R13)(R17) +(R17)^2 \quad \text{---------- (2)}$$

Craig[1] estimated, as (R17)sample/(R17)reference = ((R18)sample/(R18)reference)$^{0.5}$

In general,

$$R17 = K \times (R18)^a \quad \text{---------- (3)}$$

δ notation was introduced in the equation.

$$\delta 45= (R45sample - R45reference)/R45reference \quad \text{--------(4)}$$

Craig presented the 17O correction equation as follows.

$$\delta^{13}C = 1.0676 \times \delta 45 - 0.0338 \times \delta^{18}O \quad \text{----------(5)}$$

However, as PDB was exhausted and NBS19 was used as a new standard with a new scale as Vienna-PDB scale. VPDB had a different ratio from original PDB in R17 and R18 in relation to the definition of NBS19 value. Therefore, if we solve equation (1), (2) and (3) numerically[2] for VPDB with proper values for K and a, the result is different from equation (5).

Another problem is cross contamination[3] in an ion chamber in mass spectrometer. The ratio of contamination between reference gas and sample gas was expressed by η. The deviation of the value from correct value is proportional to η value.

$$(\delta meas - \delta corr) = (-2\eta - \eta\delta meas)\, \delta corr = (-2 - \delta meas)\, \eta\delta corr \sim -2\eta\delta corr \quad \text{-----} \quad (6)$$

(because $\delta meas < 0.03$)

To minimize the cross contamination effect, we have to use a reference, which has isotopic values similar to the atmospheric CO_2. However, good reference CO_2 gas does not exist. In this study, we tried to prepare a reference CO_2 gas to be analyzed by various laboratories in the world. Such a kind of reference material must be useful to compare the scales used in each lab. By using several reference gases, inter-comparison was carried out with Commonwealth Scientific and Industrial Research

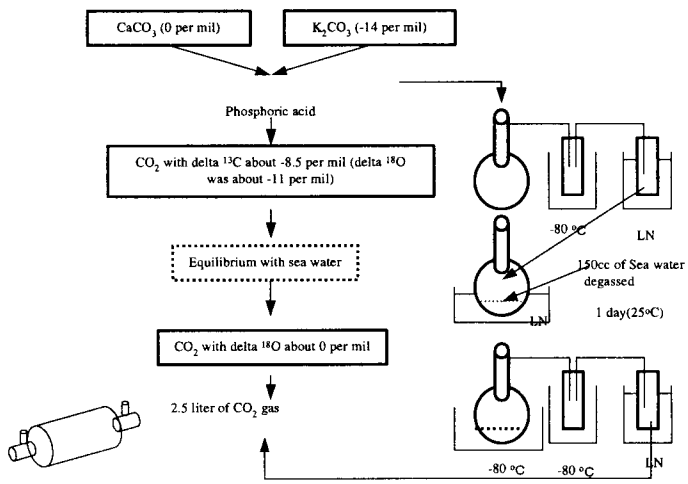

Fig.1 Procedure of making NACIS

Organization (CSIRO) in Australia and Tohoku University.

2. Method

2.1 Preparation of reference gas

Two kinds of regent carbonates with 0 per mil and −14 per mil for isotope ratio respectively were used to adjust C isotope ratio to −8.5 per mil. After CO_2 was prepared from the mixture of the regents, CO_2 was equilibrated with seawater to adjust O isotope ratio to around zero. After removing water, about 2.5 liter of CO_2 was obtained in a glass bottle, as shown in Fig.1. The CO_2 was sealed in 1300 glass tubes carefully. This reference gas was named as NIES Atmospheric CO_2 Isotope ratio Standard (NACIS).

2.2 Measurement of cross contamination effect

To assess cross contamination effect, several reference materials provided by NIST [4] were measured under two kinds of conditions of mass spectrometer (MAT252, ThermoQuest). (i.e. VISC close and open). Other condition was the same as usual one (delay time: 60 sec).

2.3 Inter-comparison of reference materials

Two working standards (MWSTD −8.3, MWSTD −8.8) and NACIS were used for inter-comparison analysis between CSIRO and NIES. NACIS was distributed to several laboratories including Tohoku University to compare their basic scales.

3.Results

3.1 Homogeneity of NACIS

As shown Fig.2, NACIS showed good homogeneity. Standard deviation of 24 samples was 0.0033 per mil in delta 13C and 0.0085 in delta 18O. Therefore, this gas could be used for the inter-comparison, because that the target precision was 0.001 per mil in delta 13C.

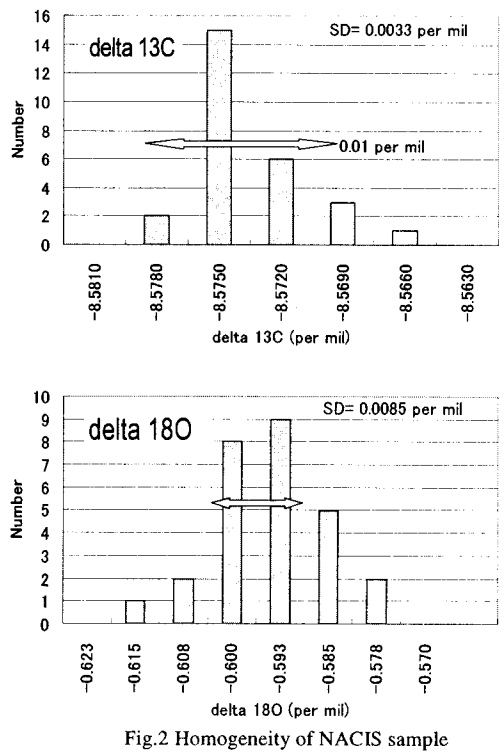

Fig.2 Homogeneity of NACIS sample

3.2 Cooperative analysis

Several labs provided the value of NACIS. These values are summarized in Fig.3. The range of reported values for delta 13C was about 0.1 per mil. This range was considerably small, compared to previous results of inter-comparison. If we use this kind of common reference gas, it may be possible to adjust the scale for each other. As for NIES 98 scale, it showed relatively large shift in delta 13C from other data (but not delta 18O), suggesting that the calibration for working standards was biased by some reason.

The results of inter-comparison between CSIRO and NIES were shown in Table 1. NIES 98 scale showed 0.08 per mil higher delta 13C value than that in CSIRO, suggesting

that the values between working standards themselves were consistent with each other. This shows that NIES data can adjusted to CSIRO by adding systematic bias.

Table 1, Difference of isotopic data between NIES and CSIRO

	MWST-8.8			NACIS			MWSTD-8.3		
	NIES (98)	CSIRO (CG99)	difference	NIES (98)	CSIRO (CG99)	difference	NIES (98)	CSIRO (CG99)	difference
δ13C	-8.729	-8.814	0.085	-8.504	-8.586	0.082	-8.235	-8.319	0.084
SD		0.017		0.003	0.004			0.006	
δ18O	-3.620	-3.611	-0.009	-0.731	-0.734	0.003	-11.301	-11.282	-0.019
SD		0.019		0.009	0.020			0.047	

3.3 Cross contamination effect

By using RM8562, 8563, and 8564, η was measured to be 0.3 % and 1.1 % in the case of VISC close. It was concluded that we should use reference CO_2, which has the difference in delta within 2 per mil against sample to minimize deviation due to the cross contamination effect. Close values to data previously reported by Tohoku University were obtained when the measurements were done under the condition of VISC open.

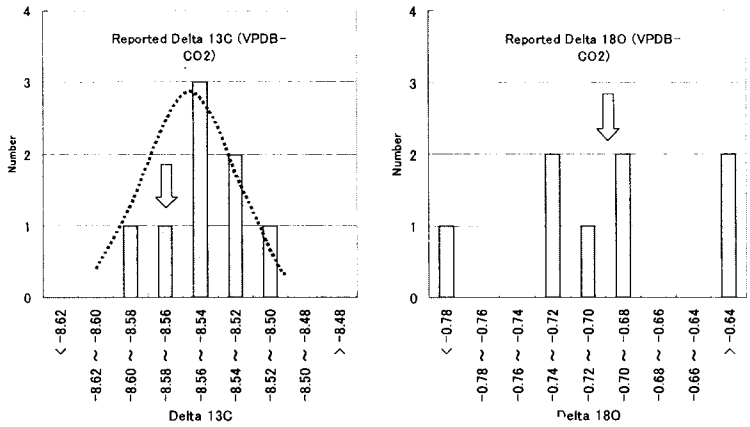

Fig. 3 Reported value for NACIS

4. Discussion

In the workshop, related discussion to above results was done by several researchers. As for the GLOBALHUBS, Dr. Roger Francey introduced basic idea of it and several questions related to present inter-comparison activities were also discussed.

Newly prepared reference material (NACIS) was considered to be very handy to use it, because it was separated by sealed glass tubes. More data on NACIS by various labs in the world is expected in the near future.

5. References

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