

Carbon and oxygen isotope analyses of Chinese carbonate reference samples

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Introduction

Stable isotopes are becoming a very useful tool for studying origin of rocks and ore deposits, their formation temperatures, origin of thermal fluids and water-rock interaction in hydrothermal systems. Stable isotope compositions are normally reported relative to a standard sample. In order to discuss isotopic data on world-wide scale, we need intercalibration of reference samples between laboratories to verify the scale on a common standard. Intensive efforts in intercalibration of stable isotope analyses have been made by IAEA (GONFIANTINI, 1984) and some other groups (e.g. BLATTNER and HULSTON, 1978). The intercalibration work is particularly desired between the Chinese and Japanese laboratories because the direct comparison of data between the two areas is becoming essential for understanding the geology of East Asia. In the present study we analyzed four Chinese carbonate reference samples together with the laboratory reference sample of the Geological Survey of Japan, and compared

with the results reported by Chinese laboratories.

Carbonates are one of the most important minerals which occur commonly in hydrothermal systems and gangue minerals of ore deposits. Carbonates are also the mineral being most commonly analyzed for stable isotopes among Chinese laboratories. Among the four samples analyzed in the present study, TTB-1 and TTB-2 calcite are the nation-wide reference samples of China, for which more than ten laboratories have reported carbon and oxygen isotope data. The other two, CaCO₃-7901 and S2S-1 calcite, are the laboratory reference samples of the Nanjing Institute of Geology and Mineral Resources, for which quite few reliable isotopic data are available.

Experimental

Isotopic analyses were done on carbon dioxide which was obtained by reaction of the calcite samples with 100 percent phosphoric acid at 25°C (McCREA, 1950). The sample size of calcite is about 20 mg which yields 0.2 mmole carbon dioxide. Since the reaction rate of natural carbonates is quite variable, the overnight reaction was performed. After the reaction was over, carbon dioxide was purified through a two-step trap system with liquid nitrogen/dry ice cooling agent. For fur-

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ther details of the experimental procedures, see the reference paper by MORISHITA and MATSUHISA (1984).

The isotopic ratios were measured using a MAT-250 triplecollector mass-spectrometer. The measured results were corrected for background, tailing, cross-talk in change-over valves and systematic shift on SLAP/SMOW scale (GONFIANTINI, 1984), then calculated to $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios according to CRAIG (1957). The ratios are reported in the δ -notation in per mil relative to PDB. Oxygen isotope ratios are reported relative to SMOW as well.

$$\delta = \frac{R_x - R_{st}}{R_{st}} \times 1,000 \quad (\text{per mil}),$$

where R is $^{13}\text{C}/^{12}\text{C}$ or $^{18}\text{O}/^{16}\text{O}$ ratio, and x and st refer to unknown sample and standard sample, respectively.

Results

The results of isotopic analyses are given in Table 1. Analyses were duplicated for CaCO_3 -1 (GSJ laboratory reference sample), TTB-1 and TTB-2. Reproducibility in both carbon and oxygen isotope determinations is better than ± 0.05 per mil. The PDB scales were determined by assuming $\delta^{13}\text{C} = -1.06$ and $\delta^{18}\text{O} = -4.14$ per mil for NBS-20 relative to PDB (CRAIG, 1957). The SMOW scale for

Table 1 Carbon and oxygen isotope data of the Chinese carbonate reference samples analyzed in the Geological Survey of Japan.

Sample	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)	$\delta^{18}\text{O}_{\text{PDB}}$ (‰)	$\delta^{18}\text{O}_{\text{SMOW}}$ (‰)
TTB-1	+ 0.58	- 8.48	+21.75
	+ 0.58	- 8.50	+21.73
	Av. + 0.58	Av. - 8.49	Av. +21.74
TTB-2	-10.82	-12.41	+17.70
	-10.83	-12.39	+17.72
	Av. -10.83	Av. -12.40	Av. +17.71
CaCO_3 -7901	-25.12	-11.07	+19.08
S2S-1	+ 0.82	- 8.12	+22.12
TTB-1/TTB-2	11.53	3.96	

oxygen isotopes was determined using the V-SMOW water reference sample. The fractionation factors of $\alpha\text{CO}_2/\text{H}_2\text{O}$ at 25°C and $\alpha\text{CO}_2/\text{CaCO}_3$ at 25°C were taken as 1.0407 and 1.01025, respectively. The laboratory reference sample of GSJ, CaCO_3 -1, has $\delta^{13}\text{C}_{\text{PDB}} = +2.59$, $\delta^{18}\text{O}_{\text{PDB}} = -15.00$ and $\delta^{18}\text{O}_{\text{SMOW}} = +15.03$ per mil (MORISHITA and MATSUHISA, 1984) and all the data of other samples were normalized to these values.

Discussion

TTB-1 and TTB-2

The δ -values of TTB-1 and TTB-2 obtained in the Nanjing Institute of Geology and Mineral Resources (NIGMR) are shown in Table 2. The agreement of these values with the present results is excellent. So far as being normalized to TTB-1 and TTB-2, the data obtained in the two laboratories will be compared directly. This is very promising for the future studies of geologic samples.

All the data for TTB-1 and TTB-2 obtained in Chinese laboratories are taken from ZHANG *et al.* (1985), and compared with the present results in Figs. 1 and 2 for carbon and oxygen isotopes, respectively.

The $\delta^{13}\text{C}$ values for both samples seem to show normal distributions with total variation ranges of 0.4 per mil for TTB-1 and 0.25 per mil for TTB-2. The majority of the laboratories is confined within 0.15 per mil range for both samples, and its magnitude of variation would be acceptable as experimental error in interlaboratory calibration. Fortunately, the present results and the NIGMR results

Table 2 Carbon and oxygen isotope data of the Chinese carbonate reference samples obtained in the Nanjing Institute of Geology and Mineral Resources.

Sample	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)	$\delta^{18}\text{O}_{\text{PDB}}$ (‰)
TTB-1	+ 0.58	- 8.49
TTB-2	-10.85	-12.49
TTB-1/TTB-2	11.56	4.05

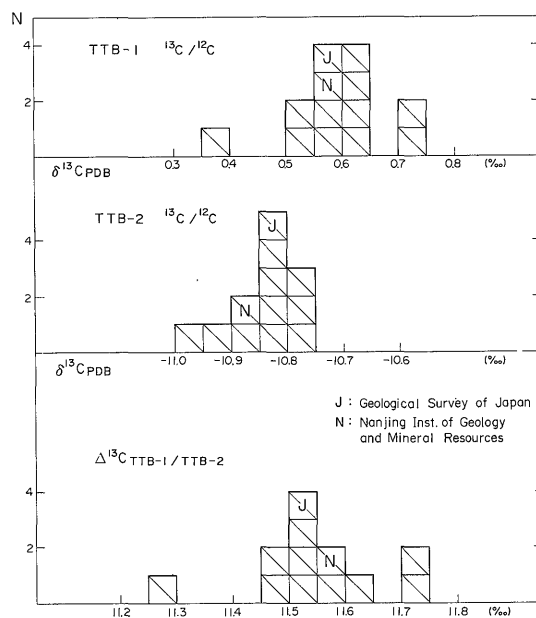


Fig. 1 Histogram of $\delta^{13}\text{C}$ values of TTB-1 and TTB-2 calcite reference samples reported by Chinese laboratories. The present results marked with J are also plotted. The $\Delta^{13}\text{C}$ stands for the relative difference in $^{13}\text{C}/^{12}\text{C}$ ratios between the two samples.

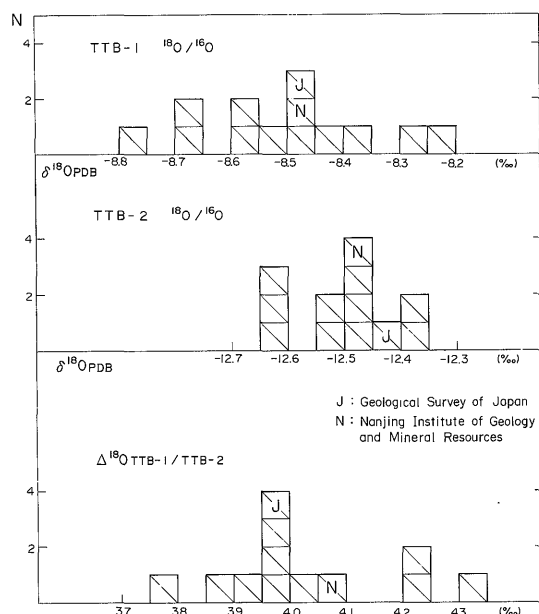


Fig. 2 Histogram of $\delta^{18}\text{O}$ values of TTB-1 and TTB-2 calcite reference samples reported by Chinese laboratories. The present results marked with J are also plotted. The $\Delta^{18}\text{O}$ stands for the relative difference in $^{18}\text{O}/^{16}\text{O}$ ratios between the two samples.

lie near the mean values in the diagrams. If determinations are done with internal consistency within a single laboratory, the relative difference in isotopic compositions between two samples should agree with that of other laboratories regardless of δ -values of individual samples. The relative difference in $^{13}\text{C}/^{12}\text{C}$ ratio of TTB-1 and TTB-2 ($\Delta^{13}\text{C}$) in Fig. 1 again shows a normal distribution with a total variation range of 0.2 per mil except for three data. The three data larger than 11.7 per mil and smaller than 11.3 per mil may be attributed to some laboratory factors other than experimental error.

The $\delta^{18}\text{O}$ values of TTB-1 have a greater variation range of 0.6 per mil, and show no distinct normal distribution (Fig. 2). Since only two third of the oxygen in carbonate is recovered as carbon dioxide, fluctuation of isotopic fractionation in the sample preparation procedures between laboratories might be much larger in oxygen isotopes than in carbon isotopes. Nevertheless, the present results and the NIGMR results for both TTB-1 and TTB-2 again lie near the mean values in the diagrams. The relative difference in $^{18}\text{O}/^{16}\text{O}$ ratio of TTB-1 and TTB-2 ($\Delta^{18}\text{O}$) shows a normal distribution for the values lower than 4.1 per mil (Fig. 2). The present result of 3.96 per mil agrees with the mean value of the normal distribution. Three laboratories give $\delta^{18}\text{O}$ values larger than 4.2 per mil, which may be due to unknown factor other than experimental error. More detailed discussion in China about experimental conditions in each laboratory would provide further understanding of these results.

CaCO_3 -7901 and S2S-1

The $\delta^{18}\text{O}_{\text{PDB}}$ value of -10.80 per mil has been obtained for CaCO_3 -7901 in NIGMR, which is about 0.3 per mil different from the present results of -11.07 per mil. This difference is larger than the experimental error and much greater if we compare with the excellent agreement in TTB-1 and TTB-2 determinations. Repeated analyses of CaCO_3 -7901

are strongly advised.

S2S-1 calcite has been proposed as a reference in NIGMR. The present results show that its δ -values of both carbon and oxygen are close to those of TTB-1. The carbon dioxide yield from this sample was about 92 percent and some gray-colored residue was observed after the reaction, suggesting an impurity of acid-insoluble minerals. It is suggested to examine the impurity before using S2S-1 as a reference.

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