Isotopic studies of marbles in the Sanbagawa metamorphic terrain, central Shikoku, Japan

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Carbon, oxygen and strontium isotopic studies were carried out on marbles occurring in crystalline schists and epidote amphibolites of the Sanbagawa metamorphic terrain, central Shikoku, Japan, in order to estimate metamorphic temperatures and to elucidate their origin. Carbon isotopic fractionation between calcite and graphite shows the metamorphic temperature of 460°C at the transitional part between the garnet and albite-biotite zones.

Marbles are isotopically classified into two groups. (1) some marbles in epidote amphibolite masses show characteristically negative $\delta^{13}\text{C}$ values and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. These marbles are interpreted as have been derived from magmatic or deep-seated carbonates. (2) marbles collected from the crystalline schists and from the marginal part of epidote amphibolite masses, have high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{13}\text{C}$ values similar to those of typical sedimentary carbonates. They were probably derived from sedimentary carbonates and/or carbonates re-equilibrated with metamorphic fluid segregated from crystalline schists during the Sanbagawa metamorphism.

INTRODUCTION

Graphite-bearing marbles occur commonly in many regional and contact metamorphic terrains in the world. Carbon isotopic fractionation between calcite and graphite has been reported from several localities of various grades of metamorphism (WADA and OANA, 1975; PINEAU et al., 1976; HOEFS and FREY, 1976; WADA, 1977; VALLEY and O'NEIL, 1981; WADA and SUZUKI, 1983). The temperature dependence of carbon isotopic fractionation between calcite and graphite was estimated by BOTTINGA (1969) on the basis of theoretical calculations for a temperature range from 0 to 700°C. VALLEY and O'NEIL (1981) and WADA and SUZUKI (1983) showed that the carbon isotopic geothermometer, using calcite-graphite pairs, is useful for the determination of metamorphic temperature in medium- to high-grade zones.

DEINES and GOLD (1973) suggested that magmatic or deep-seated carbonates have $\delta^{13}\text{C}$

values distinctly lower than those of marine carbonates. HOEFS (1980) reviewed stable isotopic studies of carbonates from various geological settings and concluded that carbon isotopic composition is useful to reveal the origin of carbonates.

Strontium isotopic studies as well as carbon and oxygen isotopic studies would provide powerful constraints on any viable theories of petrogenesis of marbles.

Twenty-two marbles were collected from crystalline schists and epidote amphibolites of the Sanbagawa metamorphic terrain, central Shikoku, Japan. Petrogenesis of the epidote amphibolite masses of this area has been discussed by many authors. These masses were once considered to represent massive and coarse-grained parts of metavolcanic sequence (basic schists) (e.g., HIDE, 1961; BANNO, 1964). One of the main bases of their arguments is that some marbles are intercalated concordantly within the epidote amphibolite masses. They

considered that marbles in the epidote amphibolite masses are sedimentary in origin. These masses, however, are now believed to have been emplaced as solid bodies in the Sanbagawa terrain from the lower crust or the upper mantle and subjected to the Sanbagawa metamorphism later (e.g., BANNO *et al.*, 1976; YOKOYAMA, 1980). If so, as pointed out by BANNO *et al.* (1976), the origin of the marble remains unsolved.

The present study is intended to estimate metamorphic temperatures of some graphite bearing marbles in the Sanbagawa metamorphic terrain, central Shikoku, Japan, applying the carbon isotopic geothermometer, and to elucidate the origin of marbles, especially of those in epidote amphibolites by means of carbon, oxygen and strontium isotopic compositions.

OUTLINE OF GEOLOGY AND PETROGRAPHY

The Sanbagawa metamorphic terrain of central Shikoku is a part of the typical intermediate high-pressure metamorphic belt in Japan (MIYASHIRO, 1961). On the basis of mineral parageneses in pelitic schists, BANNO *et al.*, (1978) and ENAMI (1982, 1983) have divided the metamorphic terrain into four mineral zones; chlorite, garnet, albite-biotite and oligoclase-biotite zones, with increasing metamorphic grade. Figure 1 shows the metamorphic zonation with sampling localities. In the Sanbagawa terrain, marbles occur as thin layers or in lenticular form (less than 1m in width) in epidote amphibolites and crystalline schists. Marbles examined in this study were collected from such layers or beds. Samples are from the following four rock types; pelitic schist, epidote amphibolite, basic schist and quartz schist.

Marbles in pelitic schists were collected from the Hadeba (samples PS01~PS05), Fujiwara (sample PS06) and Matsuno (samples PS07~PS08) areas. Mg-Fe partition coefficient between garnet and chlorite ($K_{\text{Mg-Fe}}^{\text{Ga-Chl}}$) is 0.070 in

the pelitic schists from the Hadeba area and 0.072 in the rocks from the Fujiwara area (ENAMI, 1980). These values correspond to the higher grade part of the garnet zone or the transitional part between the garnet and albite-biotite zones (see HIGASHINO, 1975). Taking into account the $K_{\text{Mg-Fe}}^{\text{Ga-Chl}}$ values and local occurrences of biotite flakes in host pelitic schists of the marbles (BANNO, 1964; HIGASHINO *et al.*, 1977; ENAMI, 1980), we deduce that the Hadeba and Fujiwara areas belong to the higher-grade part of the garnet zone or the transitional part between the garnet and albite-biotite zones. In both areas, marbles occur in lenticular form (3–40cm in width, Fig. 2 a) and show a banded structure with the alternation of graphite-rich and -poor layers (Fig. 2b).

The Matsuno marble occurs as a block (about 1m across) on a river bed of the River Dozan. Although the Matsuno area lies in the transitional part between garnet and albite-biotite zones, the marble block itself might probably have been derived from the albite-biotite or oligoclase-biotite zone, since siliceous part of the block contains biotite as a major constituent mineral.

Except the Fujiwara sample (PS06), the marbles are composed mainly of calcite, graphite, diopside, tremolite and zoisite with subordinate amounts of chlorite, muscovite, albite, quartz and sphene. The sample PS06 has a mineral assemblage of calcite+graphite+paragonite+muscovite+zoisite+albite+quartz+sphene.

Marbles in epidote amphibolites (samples EA01~EA08) were collected from the Iratsu and Tonaru masses. These masses are metamorphosed layered gabbro complexes, which were subjected to the Sanbagawa metamorphism of the epidote amphibolite facies (BANNO *et al.*, 1976; TAKASU and MAKINO, 1980; YOKOYAMA, 1980). Samples EA01~EA04 and EA05~EA08 belong to the oligoclase-biotite and albite-biotite zones, respectively. These marbles occur in lenticular form (about 1m maximum in width) intercalated concordantly or subconcordantly in the host epidote amphibolite (Fig.

Fig. 1 Metamorphic zonation maps with sample localities. For the locality of sample QS01, see the text.

(a) Central Shikoku (after BANNO et al., 1978). The mark "b" denotes the area where biotite-bearing pelitic schists occur, see the text. TO: Tonaru mass, HA: Higashi-Akaishi mass, IR: Iratsu mass. Sample localities of the Bessi area are shown in an enlarged map of Fig. 1(b).

(b) Bessi area (after ENAMI, 1982). Broken line shows the lithologic boundary between dunite-epidote amphibolite complex and the surrounding crystalline schists.

Fig. 2 Mode of occurrence of some selected marbles.

- (a) A lenticular marble in the pelitic schist of the Fujiwara area.
- (b) Polished surface of a marble in the pelitic schist of the Matsuno area.
- (c) A marble layer in the Tonaru epidote amphibolite mass. Arrows indicate the boundary between the marble and the epidote amphibolite.
- (d) Close up view of the lower left part in (c). Small chips of epidote amphibolite are observed in the marble layer.

M: marble, EA: epidote amphibolite, PS: pelitic schist, GR: graphite-rich layer, GP: graphite-poor layer.

2 c), and usually contain small chips (about 10cm maximum across) of epidote amphibolite (Fig. 2 d). These marbles are composed mainly of calcite, diopside, hornblende and epidote with subordinate amounts of chlorite, muscovite, albite, quartz and sphene. Sample EA08 contains grossular in addition to these minerals.

Marbles in basic schists were taken from the Shirataki (samples BS03~BS05) and Otoji (samples BS01~BS02) areas. The Shirataki marble occurs in the Shirataki Dai-ichi amphibolite of HIDE (1954) in irregular or lenticular form (about 1m maximum in width) subparallel to the schistosity (HIDE, pers. com., 1980). The Shirataki amphibolite is a massive and coarse-

grained basic schist. It is apparently similar to the metamorphosed layered gabbros of the Iratsu and Tonaru masses, but is considered to be metamorphosed basaltic tuff or hyaloclastite (KAWACHI *et al.*, 1973, 1982; WATANABE and KAWACHI, 1975). Typical mineral assemblage of the Shirataki amphibolite is hornblende + epidote + chlorite + muscovite + albite + quartz (HIDE, 1954), suggesting the metamorphic grade of the albite-biotite zone. Except the sample BS05, the Shirataki marbles have a mineral assemblage of calcite + epidote + chlorite + muscovite + albite + quartz + sphene. The sample BS05 contains diopside and hornblende in addition to the above assemblage.

The Otoji samples belong to a higher-grade part of the chlorite zone. They occur as veins (about 0.5–2cm in width) cutting the schistosity of the host basic schists, and contains calcite, epidote, chlorite, stilpnomelane, albite and quartz.

Marble in quartz schist (sample QS01) was collected in the Bessi mine about 1,500m below the sea level (point 15SL) (HIDE, pers. com. 1980). The host rock consists mainly of subcalcic hornblende, garnet, epidote, chlorite, muscovite, albite and quartz. Its metamorphic grade is of the garnet zone. The marble contains calcite, diopside, tremolite, epidote and subordinate amounts of muscovite, albite, quartz and sphene.

SAMPLES AND EXPERIMENTS

Carbonaceous matter is observed in all marbles occurring in pelitic schists. When marble has some obscure beddings or strips, graphite is concentrated mostly in the darker part. In order to know the isotopic variation in a sample, isotopic analyses were carried out on two or three splits of a fist-size marble. Isotopic compositions of calcite and graphite are averages for such splits with a size of 3cm × 5cm × 1~2cm.

The carbon and oxygen isotopic compositions are reported in the δ -notation relative to PDB (CRAIG, 1957) and SMOW (CRAIG, 1961), respectively.

$$\delta (\text{‰}) = (R(\text{sample})/R(\text{standard}) - 1) \times 1,000$$

where R is $^{13}\text{C}/^{12}\text{C}$ or $^{18}\text{O}/^{16}\text{O}$ in a sample and the standard. The working standard was calibrated with respect to NBS-20 (CRAIG, 1957). The relationship between PDB and SMOW standard on the $\delta^{18}\text{O}$ value of calcite was adopted from FRIEDMAN and O'NEIL (1977).

The carbon isotopic fractionation factor α between calcite and graphite is defined as follows;

$$\alpha_{\text{Cc-Gr}} = (^{13}\text{C}/^{12}\text{C})_{\text{Cc}} / (^{13}\text{C}/^{12}\text{C})_{\text{Gr}}$$

where subscripts Cc and Gr stand for calcite and graphite, respectively. Since α is very close to unity,

$$1,000 \ln \alpha_{\text{Cc-Gr}} = \Delta^{13}\text{C}_{\text{Cc-Gr}} \\ \doteq \delta^{13}\text{C}_{\text{Cc}} - \delta^{13}\text{C}_{\text{Gr}}$$

Calcite was reacted with 100% phosphoric acid at 25°C (MCCREA, 1950).

Graphite was separated from carbonate with hydrochloric acid. An aliquot of several milligrams of carbon was burnt to CO_2 in oxygen atmosphere at 950°C. The carbon dioxide was purified and then analyzed with a Nier-McKinney type dual collector mass-spectrometer, Varian Mat CH-7, at Department of Earth Sciences, Nagoya University.

Replicate analyses were made on many samples, and errors quoted in Tables 1 and 2 indicate the average deviation from the mean. However, no estimate for error was given when only single analysis was made.

Strontium isotopic measurements were made with a 30cm, 90 degrees solid source mass-spectrometer JEL-05RB at Department of Geology, Kyushu University. Rb and Sr concentrations were determined by isotopic dilution method using strontium-84 and rubidium-87 spikes and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was determined separately on unspiked samples. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the E and A SrCO_3 standard was measured to be 0.7080. The uncertainty in Tables 1, 2 and 5 are at 2 sigma level.

Degree of graphitization was confirmed of four samples with a X-ray powder diffractometer of Rigaku Denki Co., Ltd. at Department of Earth Sciences, Nagoya University under the following conditions; Cu-K α , 35 kv, 15 mA, Ni filter, slit 1-0.15-1 degree and scanning rate 1/8 deg./min. Silicon was used as the internal standard. The results were shown in Table 3. The spacing d (002) and the crystallite thickness Lc (002) are 3.35-3.36 Å, and 622-714 Å, respectively, showing that the carbonaceous matter belongs to fully ordered graphite of

Table 1. Isotopic compositions of graphite and calcite in marbles collected from pelitic schists of the Sanbagawa metamorphic terrain, central Shikoku.

Sample No.	Locality	Calcite		Graphite	$\Delta^{13}\text{C}$	Metamorphic temperature	Acid insoluble residue	Graphite content	$^{87}\text{Sr}/^{86}\text{Sr}$ ratio
		$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$\delta^{13}\text{C}$	Cc-Gr				
		SMOW, ‰	PDB, ‰	PDB, ‰	‰	°C	%	%	
PS01	Hadeba	+14.5±0.4	+0.4±0.1	-7.9±0.1	+8.3	450	2.1	0.06	0.70705±0.00016
PS02a	Hadeba	+15.7±0.1	+1.9±0.0	-6.5	+8.4	450	1.1	0.14	
PS02b	Hadeba	+15.6	+2.0	-6.3±0.1	+8.3	450	1.6	0.07	
PS03a	Hadeba	+15.2	+1.3	-8.1	+9.4	420	0.4	0.01	
PS03b	Hadeba	+15.1	+1.4	-7.9* ¹	+9.3	430	0.9	0.03	
PS04a	Hadeba	+15.3	+1.9	-7.4* ²	+9.3	430	1.5	0.03	0.70804±0.00024
PS04b	Hadeba	+15.3	+1.8	-7.5* ³	+9.3	430	0.6	0.03	
PS05	Hadeba	+15.2	+2.1	-7.0±0.3	+9.1	430	2.5	0.07	
PS06a	Fujiwara	+15.4±0.1	-1.0±0.2	-9.2±0.0	+8.2	460	0.6	0.01	
PS06b	Fujiwara	+15.5	-1.6	-9.9±0.1	+8.3	450	0.5	0.01	
PS07a	Matsuno	+14.7±0.0	+2.0±0.1	-5.8±0.1	+7.8	470	1.3	0.08	0.70804±0.00024
PS07b	Matsuno	+14.6	+0.7	-6.7±0.0	+7.4	480	3.5	0.13	
PS07c	Matsuno	+14.5	+0.8	-6.8±0.2	+7.6	480	1.2	0.01	
PS08a	Matsuno	+14.7±0.0	+0.1±0.1	-7.6	+7.7	470	0.7	0.01	
PS08b	Matsuno	+14.8	+0.5	-6.6±0.1	+7.1	500	0.5	0.02	

*¹(-7.2, -7.6, -8.0, -8.8), *²(-6.1, -7.5, -8.6), *³(-5.8, -7.7, -8.2, -8.2), the $\delta^{13}\text{C}$ value in this Table shows the average value.

Table 2. Whole-rock isotopic compositions of marbles collected from the Sanbagawa metamorphic terrain, central Shikoku.

Sample No.	Locality	Host rock type	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$^{87}\text{Sr}/^{86}\text{Sr}$ ratio
			SMOW, ‰	PDB, ‰	
EA01	Tonaru mass	Epidote amphibolite	+13.0	+2.8	0.70697±0.00018
EA02	Tonaru mass	Epidote amphibolite	+12.9	+2.8	
EA03	Tonaru mass	Epidote amphibolite	+12.1	+1.6	
EA04	Iratsu mass	Epidote amphibolite	+12.9	-4.3	0.70522±0.00018
EA05	Iratsu mass	Epidote amphibolite	+ 8.6	-8.9	
EA06	Iratsu mass	Epidote amphibolite	+17.1	+2.6	
EA07	Iratsu mass	Epidote amphibolite	+10.8	-5.1	0.70664±0.00010
EA08	Iratsu mass	Epidote amphibolite	+11.7	+2.7	
BS01	Otoji	Basic schist	+15.5	+1.9	0.70731±0.00016
BS02	Otoji	Basic schist	+10.3	-0.2	
BS03	Shirataki mine	Basic schist	+13.6	+2.0	
BS04	Shirataki mine	Basic schist	+14.0	+1.9	0.70731±0.00016
BS05	Shirataki mine	Basic schist	+14.4	+1.3	
QS01	Bessi mine	Quartz schist	+22.1	+1.6	

Table 3. The degree of graphitization of some selected carbonaceous matter in marbles of the Sanbagawa metamorphic terrain, central Shikoku.

Sample No.	Locality	d(002) Å	Lc(002) Å	D.G.*	
				(1)	(2)
PS04	Hadeba	3.35	635	FO	FG
PS05	Hadeba	3.35	714	FO	FG
PS06a	Fujiwara	3.35	687	FO	FG
PS06b	Fujiwara	3.35	622	FO	FG
PS07a	Matsuno	3.35	654	FO	FG
PS07b	Matsuno	3.36	653	FO	FG

*Degree of graphitization. (1): LANDIS (1971), (2): TAGIRI and TSUBOI (1979).

Table 4. *Magnesite and siderite components in calcite of marbles from the Sanbagawa metamorphic terrain, central Shikoku.*

Locality	Sample No.	Host rock type	Magnesite (mol. %)	Siderite (mol. %)
Tonaru	EA01	Epidote amphibolite	1.7±0.9	0.6±0.2
	EA03	Epidote amphibolite	0.4±0.1	0.2±0.1
Iratsu	EA06	Epidote amphibolite	1.9±0.6	0.3±0.1
	EA08	Epidote amphibolite	<0.1	<0.1
Hadeba	PS02	Pelitic schist	0.9±0.3	<0.1
	PS05	Pelitic schist	0.8±0.4	<0.1
Fujiwara	PS06	Pelitic schist	0.3±0.1	0.3±0.2
Matsuno	PS07	Pelitic schist	0.4±0.2	<0.1
Shirataki	BS04	Basic schist	1.8±0.2	0.7±0.1
	BS05	Basic schist	0.3±0.3	0.2±0.2
Bessi	QS01	Quartz schist	0.3±0.1	0.3±0.1

LANDIS (1971)'s classification or FG type of TAGIRI and TSUBOI (1979).

Chemical analyses of calcite were carried out on eleven samples by the method described by YUSA (1976) using JXA-5A electron microprobe analyzer of JEOL at Department of Earth Sciences, Nagoya University. The accelerating voltage, specimen current and beam diameter were kept at 15kv, 0.01 μ A and 20 μ m, respectively. As shown in Table 4, calcite has little magnesite and siderite components. For other marbles, X-ray diffraction analyses show that calcite is the only carbonate present.

a subsample (PS07a) is +2.0‰ that is larger than the others (PS07b and c) by more than 1‰, but $\Delta^{13}\text{C}_{\text{Cc-Gr}}$ values of these three are the same within analytical error. These results show that calcite and graphite in the Matsuno and Fujiwara samples, are in the carbon isotopic equilibrium, although isotopic heterogeneity seems to exist within a short distance (a few cm).

As shown in Table 1, the Hadeba marble (PS01~05) has $\Delta^{13}\text{C}_{\text{Cc-Gr}}$ values from +8.3 to +9.4‰. Calcites in subsamples of the Hadeba marbles have the same $\delta^{13}\text{C}$ values, showing

RESULTS AND DISCUSSION

Carbon isotopic temperature Carbon isotopic compositions of calcite and graphite in marbles collected from pelitic schists are given in Table 1 with the carbon isotopic fractionation between them. The relationship between $\delta^{13}\text{C}_{\text{Cc}}$ and $\delta^{13}\text{C}_{\text{Gr}}$ values is illustrated in Fig. 3. The $\delta^{13}\text{C}$ values of calcite range from -1.6 to +2.1‰ and those of graphites from -9.9 to -5.8‰.

$\delta^{13}\text{C}$ values of two subsamples of the Fujiwara marble are slightly scattered (-1.0 and -1.6‰ for calcite and -9.2 and -9.9‰ for graphite), but their $\Delta^{13}\text{C}_{\text{Cc-Gr}}$ values are identical (+8.2 and +8.3‰) within analytical error. Two samples (PS07 and PS08) from the Matsuno area show $\Delta^{13}\text{C}_{\text{Cc-Gr}}$ values from +7.1 to +7.8‰ (Table 1). $\delta^{13}\text{C}$ value of calcite of

Fig. 3 Relationship between $\delta^{13}\text{C}_{\text{Cc}}$ and $\delta^{13}\text{C}_{\text{Gr}}$ values of the marble collected from pelitic schists in the Sanbagawa metamorphic terrain, central Shikoku. For the error bar of the Hadeba samples, see the text. Dashed lines indicate the carbon isotopic fractionations at 450, 460 and 480°C, respectively given by WADA and SUZUKI (1983).

that the carbon isotopic compositions of calcite is homogeneous within a sample. Two samples PS01 and PS02 give the same $\Delta^{13}\text{C}_{\text{Cc-Gr}}$ value of +8.3‰. This seems to show that the carbon isotopic equilibrium was attained in both samples. Carbon isotopic analyses of PS03~05, however, show that there is a wide variation in $\delta^{13}\text{C}$ values of graphite even within a hand specimen. For example, the replicate measurements show that $\delta^{13}\text{C}$ values of graphite of PS3b fall in the range from -7.2 to -8.8‰, scattering well over the range of analytical uncertainty. This isotope heterogeneity of graphite may be explained as follows; graphite in marbles of the Sanbagawa metamorphic terrain occurs usually as scattered aggregates of small graphite crystals enclosed in calcite grains or clustered along the boundary between crystal grains of calcite. Such dispersed graphite in marbles are considered to be biogenic carbon $\delta^{13}\text{C}$ values of which might have been originally around -25‰ or lower (WADA and OANA, 1975). As listed in Table 1, calcite is predominant in marbles and the graphite content of marbles is mostly less than 0.1 weight percent. Therefore, it is considered that the carbon isotopic composition of graphite disproportionately become enriched in ^{13}C during the exchange reaction with calcite. In PS02, graphite occurs mostly in the boundary of calcite, but PS04 marble has some crystals of graphite characteristically adhering to silicates or quartz. WADA and SUZUKI (1983) have reported a case in which graphite adhering to or being armored by silicates or quartz is enriched in ^{12}C in comparison with graphite coexisting only with calcite. In addition, the average $\Delta^{13}\text{C}_{\text{Cc-Gr}}$ value of PS03~05 is apparently larger than that of PS01 and PS02, therefore the large $\Delta^{13}\text{C}_{\text{Cc-Gr}}$ values of three Hadeba marbles (PS03~05) could be explained in terms of the disequilibrium in the isotopic exchange reaction between calcite and graphite at the peak metamorphic temperature.

The metamorphic temperatures of these samples were estimated on the basis of the carbon isotopic geothermometer formulated by WADA and SUZUKI (1983) as follows;

$$1,000 \ln \alpha_{\text{Cc-Gr}} \\ = 5.6 \times 10^6 \times T^{-2} (\text{K}) - 2.4$$

Results are listed in Table 1. The isotopic temperatures of the Matsuno marble are from 470 to 500°C, averaging 480°C. The temperature is calculated to be 460°C for the Fujiwara marble and 450°C for Hadeba marble (for PS01 and PS02). As already described, the Hadeba and Fujiwara marbles are in the upper part of the garnet zone and/or in the transitional part between the garnet and albite-biotite zones, and the Matsuno marble is considered to have been derived from the albite-biotite zone or from the oligoclase-biotite zone. Therefore, the temperature at the boundary between the garnet zone and the albite-biotite zone is estimated to be between 450 and 480°C, or most probably 460°C as shown in Fig. 3.

TAYLOR and COLEMAN (1968) have determined the oxygen isotopic compositions of quartz and magnetite in a basic schist collected from the Shirataki mine, in central Shikoku, and reported that a compatible oxygen isotopic fractionation between quartz and magnetite is +10.7‰. This value may give a metamorphic temperature of about 500°C when the quartz-water fractionation curve of CLAYTON *et al.* (1972) is combined with magnetite-water fractionation of BERTENRATH *et al.* (1973). Since the Shirataki mine is situated on the higher metamorphic side of biotite isograd (HIGASHINO, 1975) and hence lies in the albite-biotite zone, this temperature is consistent with the temperatures estimated from the carbon isotopic fractionation.

Isotopic compositions of carbonates Carbon and oxygen isotopic compositions of 14 samples besides 8 samples mentioned in the previous section, and strontium isotopic ratios of 6 samples were determined to elucidate the origin of marbles.

1) *Carbon and oxygen isotopic compositions* Carbon and oxygen isotopic compositions are listed in Tables 1 and 2, and illustrated in Fig. 4.

Of eight marbles (15 data for subsamples) collected from the pelitic sequences, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values range from -1.6 to $+2.1\text{‰}$ and from $+14.5$ to $+15.7\text{‰}$, respectively. These $\delta^{13}\text{C}$ values are in the range of typical sedimentary carbonate values of KEITH and WEBER (1964). The $\delta^{18}\text{O}$ values, however, are limited in a narrow range and evidently lower than those of the typical sedimentary carbonates. These marbles probably exchanged oxygen isotopes with metamorphic fluid or surrounding silicates during the metamorphism, and hence their $\delta^{18}\text{O}$ values were lowered (RYE *et al.*, 1976; SHIEH and TAYLOR 1969; WADA, 1977). The Matsuno samples show a constant $\delta^{18}\text{O}$ value of $+14.6 \pm 0.1\text{‰}$, being more strongly depleted in ^{18}O than the Fujiwara and Hadeba samples ($\delta^{18}\text{O} = +15.3 \pm 0.3\text{‰}$).

Marbles intercalated in basic schists also have $\delta^{13}\text{C}$ values similar to the typical sedimentary carbonate values.

A marble from quartz schist has $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values similar to those of the typical sedimentary carbonates, and the $\delta^{18}\text{O}$ value is distinctly higher than those of the marbles from pelitic and basic schists. Since this marble occurs as a relatively large mass in the quartz schist (HIDE, pers. com. 1980), it is assumed that the rock body of the marble was too large to change its isotopic composition by the ex-

change reaction with metamorphic fluid during the metamorphism. The sample may have held the original $\delta^{18}\text{O}$ value.

All the marbles collected from crystalline schists, thus, have $\delta^{13}\text{C}$ values in the range of the typical sedimentary carbonates. As mentioned in the previous section, carbon isotopic exchange reaction between calcite and graphite is considered to have occurred in marbles of the pelitic schists. Because of the low graphite content of marbles, however, the carbon isotopic composition of calcite did not disproportionately change during the isotopic exchange reaction. These marbles seem to have originally precipitated from sea water.

Both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of eight marbles collected from the Tonaru and Iratsu epidote amphibolite masses are varied ($\delta^{13}\text{C} = -8.9$ to $+2.8\text{‰}$ and $\delta^{18}\text{O} = +8.6$ to $+17.1\text{‰}$). These samples can be classified into two groups with different ranges of $\delta^{13}\text{C}$ values. Group I which includes the samples AE04, 05 and 07, is characterized by negative $\delta^{13}\text{C}$ values (-4.3 to -8.9‰). On the other hand, group II (samples AE01, 02, 03, 06 and 08) has $\delta^{13}\text{C}$ values of $+1.6$ to $+2.8\text{‰}$, which are similar to those of marbles in crystalline schists.

2) Strontium isotopic ratios Strontium isotopic ratios are also listed in Tables 1 and 2. Rubidium content of marbles is usually negligible (HEIER and BILLINGS, 1969), and hence we regard the strontium isotopic ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) listed in these tables as the ratios when these marbles formed.

Strontium isotopic ratios of two samples collected from pelitic schists (Hadeba and Matsuno) are 0.70705 and 0.70804. A sample which came from a quartz schist has a value of 0.70731. These three isotopic values fall in the range of pre-Tertiary sea water reported by PETERMAN *et al.* (1970). This is consistent with the conclusion that the marbles in crystalline schists have precipitated from sea water. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of three marbles (samples EA01, 04 and 06) collected from the epidote amphibolite masses are 0.70697, 0.70522 and 0.70664 (Table 2). Sample EA04, which be-

Fig. 4 Relationship between carbon and oxygen isotopic compositions of marbles collected from the Sanbagawa metamorphic terrain, central Shikoku.

Table 5. *Strontium and rubidium isotopic data for epidote amphibolites and eclogites in the Iratsu mass of the Sanbagawa metamorphic terrain, central Shikoku.*

Sample No.	Rock type	Sr (ppm)	Rb (ppm)	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$
7-22-17	Epidote amphibolite	719	7.60	0.0306	0.70462±0.00006
7-23-23	Epidote amphibolite	567	9.72	0.0493	0.70520±0.00005
7-23-13	Epidote amphibolite	495	1.544	0.00902	0.70436±0.00009
7093K	Epidote amphibolite	356	4.14	0.0337	0.70462±0.00006
7055a	Epidote amphibolite	590	1.174	0.00576	0.70447±0.00012
7-23-2	Epidote amphibolite	480	—	—	0.70447±0.00006
No. 1	Zoisite rock	620	—	—	0.70433±0.00008
Gon. No. 2	Hornblende eclogite	—	26.2	—	0.70481±0.00009
Gon. No. 7	Quartz eclogite	76.6	8.00	0.302	0.70472±0.00014
Gon. Chi. No. 8	Hornblende eclogite	132.8	1.169	0.0255	0.70624±0.00009
Gon. No. 5	Quartz eclogite	74.7	12.26	0.471	0.70446±0.00005
70072102	Eclogite	201.0	9.97	0.1436	0.70400±0.00011

Unpublished data by T., YANAGI, K. YOKOYAMA and S. BANNO.

longs to the group I according to the $\delta^{13}\text{C}$ criteria, has low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio being close to the values of the amphibolites and eclogites of the Iratsu mass (Table 5). On the other hand, samples EA01 and 06 (group II) have intermediate $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between the Iratsu mass and the marbles in crystalline schists.

Origin of marbles in epidote amphibolite masses As discussed in the previous section, the marbles in epidote amphibolites are classified into two groups with different carbon isotopic compositions. Marbles of group I are characterized by negative $\delta^{13}\text{C}$ values and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Their carbon and oxygen isotopic compositions fall in the range of carbonates in granitic, mafic and ultramafic igneous rocks (HOEFS, 1973; FUEX and BAKER, 1973). The $\delta^{13}\text{C}$ values are also similar to those of magmatic or deep-seated carbons represented by carbonatites and carbonates associated with kimberlites (DEINES and GOLD, 1973; SUWA *et al.*, 1975). Then it follows that some magmatic or deep-seated carbon may have controlled mainly the carbon isotopic compositions of the group I marbles.

As pointed out by several authors (SHIEH and TAYLOR, 1969; TAYLOR and O'NEIL, 1977; WADA, 1978), it is expected that carbon isotopic compositions of residual calcite usually change towards negative values during decarbonation reactions. Therefore, we should evaluate a

possibility that the negative $\delta^{13}\text{C}$ values of the group I marbles have resulted from some decarbonation reactions during the Sanbagawa metamorphism. If the Sanbagawa marbles were widely affected by the decarbonation reactions, however, the negative $\delta^{13}\text{C}$ value should be observed in marbles commonly irrespective of their modes of occurrence. As the marbles having negative $\delta^{13}\text{C}$ values are found limitedly in the epidote amphibolite masses, decarbonation reactions are probably not a main mechanism to control the carbon isotopic composition of the marbles.

Furthermore, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the group I marble (EA04) fall in the range of those of the host epidote amphibolite masses, showing a marked contrast with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of marbles in the crystalline schists. This implies that the group I marbles were probably formed having an intimate genetic relation to their host epidote amphibolite masses. Taking into account the negative $\delta^{13}\text{C}$ values and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the group I marbles, we propose two possible sources of these marbles. One is that these marbles precipitated directly from a hydrothermal solution, which might be related with magmatism which formed the original layered gabbros. Another possible interpretation is that they were derived from magmatic or deep-seated carbonates segregated from the host epidote amphibolite masses during the Sanbagawa metamorphism. Although we have

little petrologic and mineralogic data to discuss which of these two is more responsible for the formation of the group I marbles, we may safely say that these marbles have isotopic characteristics similar to those of magmatic or deep-seated carbonates, and are different from sedimentary ones like those in crystalline schists.

Group II marbles from epidote amphibolite masses have isotopic compositions similar to those of the typical sedimentary carbonates. We can not consider that such high $\delta^{13}\text{C}$ values were derived from magmatic or deep-seated carbonates. It may be worthy to mention that all the marbles of the group II were collected near the boundary between the epidote amphibolites and the surrounding crystalline schists (cf. Fig. 1b). BANNO *et al.*, (1976), YOKOYAMA (1980) and ENAMI (1982) showed that the Tonaru and Iratsu epidote amphibolite masses have been subjected to the Sanbagawa progressive metamorphism with the surrounding schists. Thus, it is possible that these marbles precipitated from metamorphic fluid with high $\delta^{13}\text{C}$ which has segregated from sedimentary sequences and permeated along the lithologic boundary. Another possible explanation is that these marbles were originally co-genetic with those of the group I but their isotopic compositions changed towards higher $\delta^{13}\text{C}$ values during the Sanbagawa metamorphism.

MINAMISHIN *et al.* (1979) reported the Rb-Sr whole rock isochron of 116 ± 10 Ma with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7066 for pelitic schists in the albite-biotite zone (biotite zone of HIGASHINO, 1975) of the Asemi river area in central Shikoku (cf. Fig. 1a). They suggested that the whole rock age does not show the age of sedimentation, but may represent the final stage of dehydration reaction (the last period of the Sanbagawa progressive metamorphism). They also pointed out that the $^{87}\text{Sr}/^{86}\text{Sr}$ initial ratio may indicate the isotopic composition equilibrated with metamorphic fluid escaping from the pelitic sequences during the final stage of dehydration reactions in the Sanbagawa metamorphism. This implies that regional exchange of isotopic compositions took place

throughout crystalline schist sequences during metamorphism. Based on these strontium data, we conclude that the high $\delta^{13}\text{C}$ values of the group II marbles have resulted from re-equilibration of group I marbles with metamorphic fluid segregated from the surrounding pelitic sequences during the Sanbagawa metamorphism. This is in accord with the fact that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the group II marbles are close to the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the pelitic schists reported by MINAMISHIN *et al.* (1979). The group II marbles occur only in the marginal parts of the epidote amphibolite masses, thus the re-equilibration of isotopic composition was probably promoted by the metamorphic fluid permeating along the lithologic boundaries between the epidote amphibolites and the surrounding schists.

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