Stable isotopic evidence for migration of metamorphic fluids along grain boundaries of marbles

YOKO ARITA* and HIDEKI WADA**

Institute of Geosciences Shizuoka Univ. Ohya 836, Shizuoka 422, Japan

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In order to elucidate carbon and oxygen isotopic systematic in metamorphosed limestone and isotopic behavior during metamorphism, microscale carbon and oxygen isotopic compositions of graphite and calcite in crystalline limestone were determined for the contact metamorphic aureole of the polymetamorphosed Hida metamorphic belt, central Japan. In this area granulite facies metamorphic rocks were overprinted by contact metamorphism related to a granitic intrusion.

Carbon isotopic fractionation between individual crystalline graphites and the cores of coexisting calcite grains gives a constant value independent of the sampling localities. Graphites armored by silicates have the same $\delta^{13}C$ as other graphites in calcite. These indicate that carbon isotopic equilibrium between graphite and calcite was completely attained during granulite facies metamorphism.

Values of $\delta^{18}O$ in the cores of individual calcite grains vary over about 2% near the granite contact, and the range of variation tends to become smaller with increasing distances from the contact. In calcite grains near the granite contact, $\delta^{18}O$ values sharply decrease by up to 7% within 200–300 $\mu$m wide zones toward grain boundaries, whereas $\delta^{13}C$ remain almost constant. This $\delta^{18}O$ trough at the grain boundaries is less pronounced with increasing distance from the granite contact and is almost no longer seen at distance about 1.3 km.

Oxygen isotopic zonation of calcite at grain boundaries strongly suggests partial isotopic exchange with water-rich metamorphic fluids that migrated along grain boundaries. This fluid-rock interaction occurred preferentially in the grain boundaries with very limited scale at distances up to 1.3 km from the granite contact, although the contact aureole defined by the mineralogical paragenesis is limited to within several tens of meters of the contact.

Skeletal graphites growing over the substrata of large hexagonal graphite grains have lower $\delta^{13}C$ values than those of the host graphite. It is considered that the fine-grained graphite crystals were formed in isotopic equilibrium with low $\delta^{13}C$ carbon in the metamorphic fluids.

INTRODUCTION

Stable isotopic studies of metamorphic rocks are the powerful tools for determining the scale of fluid migration and water-rock interaction. Many recent studies involving stable isotopic and petrologic investigations have revealed the presence of steep gradients in metamorphic fluid composition with regards to the mole fraction of $CO_2$ and carbon and oxygen isotopes (see summary by Valley, 1986). The dimensions of oxygen isotopic exchange reactions have been examined at scales from centimeter to meter for marbles and calc-silicate rocks of regional metamorphic terranes (Rye et al., 1976; Rumble et al., 1982; Valley and O’Neil, 1984; Bebout and Carlson, 1986; Baker et al., 1989) and of contact metamorphic aureoles (Shieh and Taylor, 1969; Taylor and O’Neil, 1977). The results of these studies showed that the nature of metamor-
phic fluid migration is highly variable and may depend on many factors including the development of fracture systems, and the permeability of rocks. Marbles are often believed to have been relatively impermeable during metamorphism (Sheppard and Schwarcz, 1970; Schwarcz et al., 1970; Rye et al., 1976; Nebelek et al., 1984; Baker et al., 1989).

Examination of isotopic zonings of metamorphic minerals would provide an important clue to elucidate isotopic environment of mineralization and/or metamorphic fluid migration. Recently, Wada (1988) reported the first study of micro-scale isotopic zoning within individual calcite and graphite crystals from the Hida metamorphic belt, central Japan. The cause of the isotopic zonation is best explained by exchange with metamorphic fluids infiltrated during the last stage of polymetamorphism. Such microscale determinations of the isotopic composition of calcite and graphite in individual crystals are fundamental for understanding metamorphic fluid migration during metamorphism.

Marbles exposed in the central part of the Hida metamorphic belt (Fig. 1) provide an excellent opportunity for microscale investigations of carbon and oxygen isotopes in calcite and graphite during regional granulite-facies metamorphism and subsequent contact metamorphism related to granitic intrusion. The Hida metamorphic rocks were partially transformed from regionally metamorphosed mineral assemblages to contact mineral assemblages by the granitic intrusion (Inazuki, 1982; Okui, 1985). Coarse-grained calcite and graphite crystals, formed during the granulite facies metamorphism, were micro-sampled by the technique developed by Wada (1988).

In the present paper, we clarified the characteristics of carbon and oxygen isotopes resulting from polymetamorphism and tried to distinguish the individual metamorphic processes based on the isotopic records. Special attention was paid to isotopic heterogeneities in grain boundaries of calcite and graphite. The relationship between the distance from the granitic contact and the microscale isotopic zonation was interpreted in terms of migration of metamorphic fluids.

**GEOLOGY AND SAMPLES**

The Hida metamorphic belt located along the Japan Sea side of Central to Southwest Japan is the oldest regional metamorphic belt in Japan. The Hida metamorphic rocks were subjected to metamorphism at least three times; granulite facies metamorphism occurred more than 500 Ma, amphibolite facies about 300 Ma and greenschist facies about 180 Ma (Suzuki, 1977). The last metamorphism is believed to have been accompanied by intrusion of the Funatsu granitic rocks.

In the central part of the Hida metamorphic belt, the Utsubo granite, which is one of the Funatsu granitic rocks, intruded the gneiss and crystalline limestone as a body of about 4 km wide and 12 km long in a ENE-WSW direction with a distinct contact boundary (Fig. 1). These gneissose rocks are mainly composed of clinopyroxene-gneiss with minor amounts of hornblende-biotite gneiss and biotite-gneiss. Although the crystalline limestone is expected to have developed a contact metamorphic aureole due to the emplacement of the Utsubo granite, there is little sign of contact metamorphism except for a narrow zone at the granite contact. The ages of the Utsubo granite have been determined to be 200 Ma by the Rb-Sr method as a mineral age and 175 Ma by the K–Ar method for biotite (Nozawa, 1975).

Samples were collected from the crystalline limestone along a traverse with increasing distances from the granite contact (Fig. 1). They are UTS-1 through UTS-9, for which a brief description is given in Table 1. The distance from the Utsubo granite was measured in a direction perpendicular to the contact. Some skarn minerals such as wollastonite and diopside are observed in the narrow contact zone (several meters wide) around the Utsubo granite (e.g. UTS-1). The present samples (mono mineralic marbles) consist of mainly calcite with only a small amount of silicate minerals and graphite.
flakes. An exception UTS-1 contains abundant skarn minerals as shown in Fig. 2. Calcite grains of all samples are roughly equigranular and graphites are flake crystals (Table 1).

The cores and rims of the calcite crystals were sampled from thin sections of seven limestones (UTS-1, UTS-2, UTS-3, UTS-4, UTS-6, UTS-8 and UTS-9), and isotopically analyzed. Isotopic compositions were determined for narrow zanes of calcite-calcite grain boundaries in four crystalline limestone samples (UTS-2, UTS-4, UTS-8 and UTS-9) and for individual graphite crystals from five crystalline limestones (UTS-3, UTS-4, UTS-6, UTS-8 and UTS-9). Microscale isotopic determinations of graphite crystals were achieved for three samples (UTS-3, UTS-4 and UTS-9) using the exfoliation technique developed by Wada (1988).

**ANALYTICAL TECHNIQUES**

**Graphite**

Graphitic crystalline limestone was dissolved in 6N hydrochloric acid solution. An individual flake of a graphite crystal was picked from the acid insoluble residue for isotopic analysis. In order to determine the isotopic heterogeneity of the flaky graphite especially along its c-axis, the graphite crystal was cut into a small piece with a cross-section of about 1 mm² and exfoliated repeatedly perpendicular to its c-axis using an adhesive tape.

Graphite flakes of appropriate thickness were separated from the tape and washed with toluene. The graphite flakes were then scooped up by molybdenum mesh. The average thickness of a graphite flake was calculated from the volume of CO₂ evolved and the area of the...
Fig. 2. A sketch of thin section of UTS-1 with isotopic results. The blank areas with grain boundaries indicate calcite. The dotted areas C and B represent loci of crystal cores and boundaries analyzed, respectively. Figures without and within parentheses indicate δ¹³C and δ¹⁸O values, respectively. Calcite is surrounded by skarn minerals such as diopside (Di) or wollastonite (Wo). Only seven loci (five cores and two boundaries) are shown in this sketch.

Table 1. Sample description and mineralogy of the metamorphosed limestone from the Hida metamorphic belt, Japan

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Distance from the granite (m)</th>
<th>Grain size (mm)</th>
<th>Mineralogy</th>
</tr>
</thead>
<tbody>
<tr>
<td>UTS-1</td>
<td>1</td>
<td>2.2</td>
<td>Cc-Wo-Di-Ap-Sph-Tr</td>
</tr>
<tr>
<td>UTS-2</td>
<td>10</td>
<td>4.8</td>
<td>Cc-Qz-Chl-Gr-Ap-Sph</td>
</tr>
<tr>
<td>UTS-3</td>
<td>15</td>
<td>2.0</td>
<td>Cc-Gr-Qz-Di-Sph-Chl-Se-Tour-Kfs</td>
</tr>
<tr>
<td>UTS-4</td>
<td>25</td>
<td>3.5</td>
<td>Cc-Gr-Qz-Kfs</td>
</tr>
<tr>
<td>UTS-5</td>
<td>200</td>
<td>3.4</td>
<td>Cc-Gr-Qz-Chl-Se</td>
</tr>
<tr>
<td>UTS-6</td>
<td>220</td>
<td>3.4</td>
<td>Cc-Gr-Qz-Chl-Mus</td>
</tr>
<tr>
<td>UTS-7</td>
<td>240</td>
<td>3.5</td>
<td>Cc-Gr-Qz</td>
</tr>
<tr>
<td>UTS-8</td>
<td>500</td>
<td>3.6</td>
<td>Cc-Gr-Kfs-Mus</td>
</tr>
<tr>
<td>UTS-9</td>
<td>1250</td>
<td>3.2</td>
<td>Cc-Gr-Qz-Chl-Mus</td>
</tr>
</tbody>
</table>

Abbreviation: Ap=apatite, Cc=calcite, Chl=chlorite, Di=diopside, Gr=graphite, Kfs=K-feldspar, Mus=muscovite, Qz=quartz, Se=sericite, Sph=sphane, Tour=tourmaline, Tr=tremolite, Wo=wollastonite.
Stable isotopes along grain boundaries of marbles

Graphite samples were sealed in Vycor glass tubes which had been pre-heated at 1100°C for 10 hours to remove any contamination (Wada et al., 1984) and oxidized to CO₂ by reaction with vanadium pentoxide at 1100°C for 2 hours. The blank CO₂ derived from Vycor glass tube was less than 0.1 μl in this experimental procedure. The evolved CO₂ was completely recovered for isotopic analysis.

**Calcite**

To examine the carbon and oxygen isotope compositions of the core and rim of an individual calcite grain, about 1 mm² area of the mineral grain was scraped from a thin section using an edge of a knife. Carbon and oxygen isotope compositions in narrow zones (~700 μm) of calcite-calcite grain boundaries were determined precisely by the step by step splitting technique using a freezing-microtome (Wada, 1988). The calcite crystals were sliced together with an ice block at intervals of 20–50 μm. Pulverised calcite sample was placed in a small stainless steel cup. The cup was dropped into a reaction vessel containing concentrated phosphoric acid at 60°C in vacuo to liberate CO₂ (Wada et al., 1982; Wada et al., 1984).

Isotopic analyses were carried out on a Finnigan MAT 250 mass spectrometer at Shizuoka University. The isotopic composition is reported in the conventional δ notation relative to the Chicago Pee Dee Belemnite (PDB) described by Craig (1957) for carbon and Standard Mean Ocean Water (SMOW) for oxygen by Craig (1961). The working standard was calibrated with respect to the NBS-20 calcite standard. The reproducibility of δ¹³C measurements of graphite is 0.05‰ and those of δ¹³C and δ¹⁸O measurements of calcite are 0.03‰ and 0.05‰, respectively.

The fractionation between calcite(Cc) and graphite (Gr) (Δ¹³Cₐ₁₃Cₐ-Gr) is defined as follows in this paper;

$$\Delta^{13}C_{Cc-Gr} = 1000 \ln \alpha_{Cc-Gr} = \delta^{13}C_{Cc} - \delta^{13}C_{Gr}$$

where $\alpha$ is $(^{13}C/^{12}C)_{Cc}/(^{13}C/^{12}C)_{Gr}$.

**RESULTS AND DISCUSSION**

**Isotope compositions of graphite**

Graphite crystals separated from five crystalline limestones (UTS-3, UTS-4, UTS-6, UTS-8 and UTS-9) were examined for their surface microstructure. All graphite crystals were flake graphite about 0.5–1.0 mm in diameter. Scanning electron microscope images indicate that there are two types of surface structure of graphite crystals with "rough" and "smooth" surfaces. The rough surfaces which consist of fine-grained graphite crystals of a few μm in diameter were observed to have rough surfaces. In UTS-6 and UTS-8, some rough graphite crystals were also found, but their relative abundance was small. However, for graphites from UTS-9, located about 1.3 km from the granite, all graphite crystals have smooth surfaces.

Figure 3 shows the carbon isotopic results of three graphite crystals. Two graphite crystals (UTS-3 and UTS-4) with rough surfaces gave the lowering of δ¹³C up to 1% at the rim. The graphite in UTS-9 with the smooth surface gave a nearly constant δ¹³C value along its c-axis with a slight decrease at the margin. Because such depletion in ¹³C of the two crystals with rough surface was observed only in the rim of the crystal, it is considered that tiny graphite crystals newly formed on the surface of host hexagonal graphite flake during retrograde metamorphism were depleted in ¹³C. Weis (1980) also reported the results similar to ours; skeleton graphite formed on hexagonal graphite in later stage and gave a δ¹³C value 2.3‰ lower than those of the hexagonal flake graphite. He pointed out that there is small-scale disequilibrium despite the high metamorphic grade of the host rock. The isotopic pattern observed in UTS-9 (Fig. 3) is considered to be representative, and a similar
Fig. 3. Carbon isotopic zoning in graphite crystals in the direction of c-axis. The surface of the graphite crystals from UTS-3 and UTS-4 was rough, while that of the graphite crystal from UTS-9 was smooth (see text).

Table 2. Carbon and oxygen isotopic ratios of calcite and graphite from the Hida metamorphic belt, Japan

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>CALCITE</th>
<th>GRAPHITE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta^{13}C$ (%PDB)</td>
<td>$\delta^{18}O$ (%SMOW)</td>
</tr>
<tr>
<td></td>
<td>Core</td>
<td>Boundary</td>
</tr>
<tr>
<td>UTS-1</td>
<td>$-2.31 \pm 0.35(7)$</td>
<td>$-2.09 \pm 0.29(3)$</td>
</tr>
<tr>
<td>UTS-2</td>
<td>$2.20 \pm 0.03(7)$</td>
<td>$2.21 \pm 0.02(3)$</td>
</tr>
<tr>
<td>UTS-3</td>
<td>$0.23 \pm 0.12(7)$</td>
<td>$0.37 \pm 0.12(3)$</td>
</tr>
<tr>
<td>UTS-4</td>
<td>$2.27 \pm 0.12(6)$</td>
<td>$2.28 \pm 0.05(4)$</td>
</tr>
<tr>
<td>UTS-6</td>
<td>$2.75 \pm 0.10(7)$</td>
<td>$2.72 \pm 0.16(4)$</td>
</tr>
<tr>
<td>UTS-8</td>
<td>$2.11 \pm 0.14(7)$</td>
<td>$2.13 \pm 0.04(3)$</td>
</tr>
<tr>
<td>UTS-9</td>
<td>$1.60 \pm 0.07(7)$</td>
<td>$1.45 \pm 0.13(3)$</td>
</tr>
</tbody>
</table>

* graphite coexisting with silicate minerals
** graphite armored by calcite

Figures in parentheses indicate the number of independent analyses.
Error is 1σ value.
isotopic pattern was reported in other localities of the Hida metamorphic belt (Wada, 1988).

As reported by Wada and Suzuki (1983), carbon isotopic compositions of some graphite crystals armored by silicate minerals are significantly deviated from those expected from equilibration with the host calcite even in the temperature range higher than 600°C during contact metamorphism. We examined the isotopic ratios of two types of graphites from the UTS-3 marble; one is graphite armored by calcite and the other is graphite coexisting with silicate minerals in the marble (Table 2). The $\delta^{13}C$ values for both types of graphite agreed well, indicating that carbon isotopic homogenization was completely attained at least within a specimen size (a few cm across) during high grade metamorphism.

**Isotope compositions of calcite**

The $\delta^{13}C$ and $\delta^{18}O$ values of calcite grains in a thin section of the UTS-4 limestone are shown in Fig. 4. Figure 4 indicates the isotopic values and positions where six core (C) and four boundary (B) samples were taken from the calcite grains. The average $\delta^{13}C$ values of cores ($2.27 \pm 0.12\%$) and boundaries ($2.28 \pm 0.05\%$) are almost identical. The $\delta^{18}O$ values of the cores and boundaries, however, are significantly variable and different depending on the positions and grains. The average values are $19.70 \pm 0.90\%$ for the cores and $17.97 \pm 0.22\%$ for the boundaries. As listed in Table 2, such isotopic variability between the cores and boundaries are ubiquitously observed in the whole area studied.

Figure 5 indicates the relationship between the $\delta^{18}O$ value of calcite and the distance of the
Fig. S. Relationship between the δ¹⁸O values of calcite grains and the distance from the granite contact. Bars indicate the range of δ¹⁸O values.

Sample from the granite contact. The range of δ¹⁸O values for cores in samples UTS-2, UTS-4 and UTS-6 (near the contact) is relatively large and that of the samples far from the contact (UTS-8 and UTS-9) is relatively small. Calcite in sample UTS-1, collected at only 1 meter away from the granite contact, shows a very narrow range of variation. In contrast to the other samples, there is no difference in δ¹⁸O between core and boundary, and the δ¹⁸O values are considerably low (12.23±0.26‰). The δ¹³C values of UTS-1, however, are rather variable (−2.31±0.35‰). Skarn minerals such as diopside and wollastonite are formed in UTS-1 (Fig. 2). As discussed in many studies (Shieh and Taylor, 1969; Taylor and O’Neil, 1977; Wada, 1978; Taylor and Bucher-Nurminen, 1986), carbon and oxygen isotopic values of calcite are lowered during decarbonation accompanied with silica metasomatism. Thus, our results shown in Fig. 5 indicate that oxygen isotopic homogenization was accompanied by the decarbonation at least within the scale of mm to cm.

Calcite-graphite thermometry

Figure 6 shows the variation in the δ¹³C values of calcite cores and graphite crystals separated from the same limestone specimen as a function of the distance from the granite contact. The mean carbon isotopic fractionation between calcite and graphite is also shown for five samples (UTS-3, UTS-4, UTS-6, UTS-8 and UTS-9). The carbon isotopic fractionation between calcite and graphite is almost constant at +3.48±0.12‰ irrespective of the distance from the contact. It is, therefore, suggested that carbon isotopic equilibrium was attained at each locality and that the isotopic temperature was constant throughout this area. Using the carbon isotopic geothermometry by Wada and Suzuki (1983), which is in agreement with Valley and O’Neil (1981) above 600°C, the calculated carbon isotopic temperatures range from 690 to 710°C. These metamorphic temperatures ap-
Stable isotopes along grain boundaries of marbles

Fig. 6. Variation in the $\delta^{13}C$ values of calcite cores and graphite crystals as a function of the distance from the granite contact. Bars indicate the ranges of $\delta^{13}C$ values (see Table 2).

Isotopic zonation

In order to clarify isotopic zonation in the calcite grain boundary, microscale sampling for isotopic analyses was made at intervals of 20–50 $\mu$m and to a distance of about 700 $\mu$m across the grain boundary. Four calcite-calcite grain boundaries were examined and the results are shown in Figs. 7 and 8. In Fig. 7, the results of UTS-2 and UTS-4 are shown. Although a slight decrease in the $\delta^{13}C$ up to 0.2‰ within 100 $\mu$m of the grain boundary can be observed in UTS-4, most part of the core shows almost constant $\delta^{13}C$ values (about 2‰ PDB). In contrast, the $\delta^{18}O$ values are highly variable. The $\delta^{18}O$ value just at the boundary of the calcite grains in UTS-4 is about 7‰ lower than that of the core. The $\delta^{18}O$ value increases with increasing distance from the grain boundary and becomes constant at 200–300 $\mu$m inside the grain. Figure 8 shows the results for UTS-8 and UTS-9. The $\delta^{18}O$ value of the calcite grain boundary of UTS-8 is about 2‰ lower than that of the core. UTS-9 shows a relatively flat distribution with small lowering of $\delta^{18}O$ about 1‰ in the left hand side of the calcite grain in Fig. 8.

The oxygen isotopic depletion at the grain boundary tends to become smaller with increasing distance from the granite contact. Consequently UTS-9 collected about 1.3 km away from the contact showed minimum $\delta^{18}O$ depletion. As shown in Fig. 4, the maximum isotopic variation of cores is 2.4‰ ($\delta^{18}O_{\text{max}}=21.32‰$ and $\delta^{18}O_{\text{min}}=18.91‰$) among the UTS-4 calcite grains which are partly contiguous to each other. The variation of the core $\delta^{18}O$ in individual calcite grains of UTS-8 and UTS-9 is apparently small (about 1‰) as shown in Fig. 5 and Table 2. In this context, it may be interpreted that the ox-
Fig. 7. Microscale isotopic results across calcite-calcite grain boundaries for samples UTS-2 (solid bars) and UTS-4 (open bars). Vertical dashed line represents the grain boundary.

Fig. 8. Microscale isotopic results across calcite-calcite grain boundaries for samples UTS-8 (solid bars) and UTS-9 (open bars). Vertical dashed line represents the grain boundary.
Stable isotopes along grain boundaries of marbles

Yogen isotopic composition of the limestone which was less affected by the contact metamorphism was homogenized within 1% during the regional metamorphism, probably at temperature of 700±10°C as estimated from calcite-graphite thermometry. The large variations of δ¹⁸O values of cores came from closer localities to the granite contact as observed in UTS-2, UTS-4 and UTS-6 (Fig. 5). UTS-3 seems to have a relatively small range of the δ¹⁸O values of cores. Because our thin section samples are 2-dimensional analyses, the plane of the section may not strictly pass through the center of each grain sampled. Furthermore the maximum depth and width of the oxygen isotopic trough observed in UTS-4 which is relatively close to the granite contact is about 7% and about 600 μm across the grain boundary. Therefore, much of the apparent variation of core δ¹⁸O values could simply be due to the effect of marginal zone. Symmetrical oxygen isotopic troughs at the boundary were observed for UTS-8 and UTS-9 (Fig. 8). The δ¹⁸O distribution across the boundaries of UTS-2 and of UTS-4, however, is asymmetrical (Fig. 7). The oxygen isotopic differences between both sides of cores in UTS-2 and UTS-4 are about 1 and 3%, respectively. Wada (1988) also reported a distinct asymmetrical oxygen isotopic pattern in the rims of calcite grains sandwiching a graphite crystal in marble from the Wada-gawa area of the Hida metamorphic belt. The irregularity of oxygen isotopic variation from rim to core was explained by the irregular surface of the boundary and subsequent differences in fluid permeability of calcite-graphite contact. Otherwise, the core δ¹⁸O values could simply be due to that the apparent “core” of the grain was actually marginal zone cut by the plane of the section.

If such an isotopic trough was formed by self-diffusion of oxygen in calcite during metamorphism, the diffusion coefficient is expected to depend on the direction of crystal axis or crystal face of calcite. Although no data are available for calcite, it is known that diffusion of oxygen in quartz parallel to c-axis is about 2 orders of magnitude faster than that normal to the c-axis at 700°C (Giletti and Yund, 1984). Therefore, it is plausible that the penetrating depth to which the isotopic exchange may affect is dependent on the crystal orientation. Heterogeneity in the permeability of individual crystals may also be responsible for the isotopic trough. This may be the cause of the difference of the isotopic exchange depth in different crystals. According to Anderson (1969), oxygen self-diffusion coefficients in calcite experimentally determined by isotopic exchange with CO₂ were higher than the corresponding carbon values by up to a factor of 4 in the interested temperature range. This implies that oxygen atoms are transported into calcite by not only CO₂ migration but also migration of other species such as water molecule. As shown in Figs. 2 and 4 of Wada (1988), the penetrating depths of oxygen isotopic troughs were two to three times larger than that of carbon. This is consistent with the Anderson’s experiments. In the present study, there is a case where only the oxygen isotopic trough was observed (Fig. 7), implying that the metamorphic fluid was dominantly water (i.e., carbon-poor).

Isotopic zoning shown in this study is considered to have resulted from isotopic exchange between calcite and metamorphic fluids during the intrusion of the Utsubo granite. In the studied area, skarn minerals such as wollastonite and/or diopside are locally observed within only a few meters away from the granite contact. A small amount of diopside crystals is only found under the microscope at the grain boundaries of calcite in UTS-3. There is no mineralogical evidence that metamorphic fluids infiltrated into the limestone in the localities far from the granite contact. The effect of contact metamorphism accompanying with decarbonation and metasomatic reactions due to the Funatsu granitic intrusion is considered to have affected only the narrow areas around the granite.

Three sources for the metamorphic water are possible: water derived from the Utsubo granite; water from dehydration reactions in the surrounding metamorphic rocks; and meteoric water. Calcite in UTS-1 has similar δ¹⁸O values in core and rim as shown in Fig. 5. The isotopic
composition of the metamorphic or metasomatic fluid which equilibrated with UTS-1 calcite at a magmatic temperature is consistent with magmatic water derived from the Utsubo granite (Wada and Iwaki, in prep.). Because the temperature gradient in metamorphic rocks around the Utsubo granitic body is not known, we can not calculate the oxygen isotopic composition of the metamorphic water except for UTS-1 in this stage. If we assume magmatic water emitted from the granite as the source of the contact metamorphic fluid, the oxygen isotopic composition of the fluid pervaded the grain boundaries of the minerals would have gradually changed during migration due to partial isotopic exchange with calcite boundaries. As shown in Fig. 5, however, δ¹⁸O values of calcite in the grain boundaries do not show a gradual change with distance from the contact. The oxygen isotopic compositions of the calcite boundaries seem to reflect those of the pre-contact metamorphic limestone because of very limited fluid amount. Since the isotopic composition of fluid of limited amount could have been modified by reaction with the host limestone, we could not specify the source of the metamorphic water.

As pointed out by many studies, infiltrations of metamorphic fluids during contact metamorphism mainly take place along the fracture or vein channelized system (Valley and O'Neil, 1984, Bebaut and Carlson, 1986, Taylor and Bucher-Nurminen, 1986). Two types of metamorphic fluid flow migration can be envisaged to explain the isotopic troughs near the contact: i) Macroscale (meter to tens meters) fracture-controlled channelized flow of metamorphic fluid; and ii) Microscale (in micrometers) grain-boundary-controlled channelized flow of metamorphic fluid. The oxygen isotopic trough in UTS-4 is larger in depth and width than that in UTS-2, although the sampling locality of UTS-2 is closer to the granite contact than that of UTS-4. The difference in the depth of the trough is simply a record of apparent differences in isotopic exchange or isotopic difference in metamorphic fluid, and that of the width of the trough might indicate the difference of diffusion coefficient of the specific surface of calcite or temperature. Otherwise the large isotopic trough in UTS-4 may be resulted from the preferentially macroscale infiltration of metamorphic fluid near the grain boundary observed at present.

Inazuki (1982) and Okui (1985) reported polymetamorphism in the Hida metamorphic rocks with special reference to the Funatsu granitic rocks. They revealed that water-rich metamorphic fluids regionally infiltrated into the metamorphic rocks coeval to the Funatsu granitic intrusion at about 180 Ma. Although our data are qualitative, fluids released from the granite might have been water-rich and very limited in amount (low fluid-to-rock ratios).

SUMMARY

(1) Small flaky graphite crystals (a few μm in diameter) growing over the surface of large, hexagonal graphite crystals near the granite contact have the δ¹³C values lower than that of the host graphites by up to 1.5‰. We believe that the new graphite crystals were formed in isotopic equilibrium with low δ¹³C carbon in the metamorphic fluid.

(2) Differences between the average δ¹³C value of the large, hexagonal graphite and the cores of calcite crystals were constant irrespective of the distance from the contact. This indicates that carbon isotopic equilibrium between graphite and calcite was completely attained during granulite facies metamorphism which preceded the contact metamorphism.

(3) The δ¹⁸O values of cores of individual calcite grains vary more than 2‰ in the granite contact zone and the range of variation tend to become smaller with distance from the contact.

(4) The calcite grains near the granite contact show isotopic zonation with δ¹⁸O decreasing up to 7‰ toward the grain boundary, thus making δ¹⁸O troughs across the boundary (within 400 ~ 600 μm across). The δ¹⁸O troughs become less conspicuous with increasing distance and almost disappear at about 1.3 km from the granite contact. There is no difference in δ¹³C between the core and rim of calcite grains.
(5) Oxygen isotopic zonation of calcite near the grain boundaries suggests that isotopic exchange between calcite and water-rich metamorphic fluid took place along the grain boundaries during contact metamorphism. The amount of fluid reacted with calcite during the contact metamorphism was very limited.

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