Carbon and oxygen isotope studies of graphite bearing carbonates in the Kasuga area, Gifu Prefecture, central Japan

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Abstract— $^{13}\text{C}/^{12}\text{C}$ and $^{18}\text{O}/^{16}\text{O}$ ratios were determined for carbonate minerals and graphites in marbles from the contact metamorphic aureole in the Kasuga area, Gifu Prefecture, central Japan. $^{13}\text{C}/^{12}\text{C}$ ratios were determined also for carbonaceous materials in pelitic rocks.

$^{13}\text{C}/^{12}\text{C}$ ratios of graphites in marbles approach the carbon isotopic range of coexisting carbonates, although they are considered according to their occurrence to be of biogenic origin. In a typical traverse of the carbonate aureole, carbon isotopic fractionation between calcite and coexisting graphite becomes regularly smaller toward the igneous contact. This strongly suggests that calcite and coexisting graphite approached isotopic equilibrium during contact metamorphism.

When we assume an isotopic equilibrium between calcite and graphite, we can estimate carbon isotopic temperatures, which reasonably agree with temperatures estimated from the solubility of magnesium in calcite coexisting with dolomite and from a heat flow model.

Carbon isotopic temperatures for the maximum contact temperature are estimated to be from 600 to 650°C. The thermal gradient estimated from carbon isotopic ratios is gentle and agrees with that estimated from a heat flow model. Carbon isotopic temperature is considered to represent a temperature, which is closest to the maximum temperature during metamorphism.

Dolomite and coexisting calcite are considered to be in disequilibrium as to oxygen isotopes, although equilibrium between calcite and graphite is attained. This is probably due to the difference in resistivity between calcite and dolomite to oxygen isotopic exchange with hydrothermal water.

INTRODUCTION

Dispersed carbonaceous materials occur in sedimentary rocks and pelitic metamorphic rocks. Carbonaceous materials in highly metamorphosed rocks are changed to graphite forming scaly or fine-grained crystals. Progressive graphitization has been discussed in connection with the grade of metamorphism (QUINN and GLASS, 1958; FRENCH, 1964; KATO and NAKAI, 1966; GRIFFIN, 1967; IZAWA, 1968; LANDIS, 1971). LANDIS (1971) studied especially the relationship between the structure of carbonaceous materials and metamorphic facies.

DEGENS (1969) summarized carbon isotopic studies from biogeochemical point of view. RANKAMA (1948a, b, 1954) and WICKMAN and UBISCH (1951) suggested that graphites in Precambrian gneiss are classified by the carbon isotopic composition into two types, of organic and inorganic origins. CRAIG (1953, 1954), however, emphasized that it is impossible to identify the origin of a carbonaceous material by only its carbon isotopic ratios, because the isotopic composition may have shifted according to chemical and isotopic reactions.

HAHN-WEINHEIMER (1960, 1966) investigated carbon isotopic compositions of carbonate and graphite coexisting in metamorphic and igneous rocks, and showed that

graphites could be classified in two groups, one is of organic origin and the other of inorganic. HAHN-WEINHEIMER *et al.* (1969) further showed a possibility that the heavy graphite from Kropfmühl in Bavaria, Germany was derived from ^{13}C -rich carbonate by the Boudouard reaction ($2\text{CO} = \text{CO}_2 + \text{C}$).

BOTTINGA (1969) calculated fractionation factors for carbon isotopic exchange equilibria between carbonaceous materials (C, CO, CO_2 , CH_4 , CaCO_3) over a wide temperature range from 0 to 700°C . He estimated carbon isotopic temperatures for graphite-calcite pairs from Kropfmühl mentioned above, applying his fractionation factors between calcite and graphite. Many of these temperatures, however, are too high or too low as compared with inferred metamorphic temperatures (BOTTINGA, 1969). SHABO and MAMCHUR (1973) observed that the concentration of the light carbon in graphite samples increased with increasing distance from limestone to gneiss. They also estimated equilibrium temperatures in the system of calcite and graphite. Some isotopic temperatures, however, are inconsistent with geological evidence. Carbonate-graphite pairs in these cases are considered not to have attained isotopic equilibrium.

Metamorphosed areas are formed under physico-chemical conditions, which are ruled by factors usually different in time and space. This may result in isotopic disequilibrium.

MIYAMURA (1967) and SUZUKI (1975) studied geologically the contact metamorphic aureole in Kasuga, Gifu Pref., central Japan and made clear that it was formed by a single metamorphism. The mineral and thermal zoning is simple and clear. Here we intend to demonstrate the feasibility of carbon isotopic temperature determinations in connection with geologic field evidence.

SAMPLING AND GEOLOGICAL SETTING

The Kasuga area, Gifu Pref. is composed of limestone, dolomite, chert and green rocks of the Permian (Fig. 1) (MIYAMURA, 1967; SUZUKI, 1975). Carbonate rocks form lenticular beds concordant with other formations. These sedimentary rocks were subjected to a contact metamorphism by a granite body in the north of this district. An absolute age determination with the K-Ar method (73 m.y) (KONO and UEDA, 1966) showed that the granite was intruded in the upper Cretaceous. The metamorphic aureole extends about 2 km outward perpendicular to the granite contact, and limestone and dolomite change to marble and other rocks to hornfels and/or crystalline schist.

High amphibolite facies near the granite contact changes to green-schist facies about 1 to 1.5 km outward from the contact (SUZUKI, 1975).

The strike of the contact surface seems to be nearly parallel to that of sedimentary rocks. The isograds of this area, therefore, are parallel to the strike of the formations (SUZUKI, 1975).

Fig. 1. Index map of the Kasuga area, Gifu Pref., showing the distribution of a granite intrusive, marble and sample locality. Legend; 1: granite intrusive rocks. 2: limestone and dolomite. 3: green rocks, chert, shale, slate and sandstone. 4: fault. 5: sampling points of limestone and dolomite. 6: sampling points of pelitic rocks. (geology after SUZUKI, 1975)

Considerable amounts of wollastonite are formed near the contact between limestone marble and granite. Skarn minerals such as diopside, forsterite and garnet are found near the contact between dolomite marble and granite. Many quartz veins stretch out from the granite body, filling fissures in sedimentary rocks. Zones of chemical reactions between quartz and minerals in sedimentary rocks are several centimeters wide.

In order to investigate the relationship between the contact metamorphic grade and the carbon isotopic composition, we collected samples successively along lines perpendicular to the contact.

A valley in the west of Nakayama runs perpendicular to the contact and cuts six limestone beds. Successive outcrops are located along Kasu river in the north of Komikami. Some faults, however, are found along the river, making it difficult to estimate exactly the distance from the contact to each outcrop.

Samples nearest the granite contact were collected in a tunnel of the Shirako dolomite mine. Pure calcite marble consists of rather large grains of a few millimeters and is black or dark gray in color. Dolomite marble consists of small grains, contains at least 10% of calcite, and is light gray or gray in color, containing carbonaceous material less than does pure calcite. These evidences contradict the inhibiting effect of organic substances on the crystallization of limestone (ROBINSON, 1971), but do not conflict with the fact that dolomite is more resistant to alteration than is calcite (EPSTEIN *et al.*, 1964).

EXPERIMENTAL

Carbon isotopic ratios in carbonate samples were determined for CO₂ liberated from them with 100% H₃PO₄ at 25°C in vacuum (MC CREA, 1950). For the separate collection of CO₂ from calcite and dolomite a chemical technique developed by EPSTEIN *et al.* (1964) was slightly modified (SUWA *et al.*, 1969) and used.

Carbonate-free material is collected as follows: About 100g of a powdered sample is treated with hydrochloric acid (1 : 1) on a water bath, then treated with a mixture of concentrated hydrofluoric and hydrochloric acids on a water bath to decompose silicate minerals. The residual matter is composed almost of carbonate-free carbonaceous matter. Several milligrams of carbonaceous matter is put into a quartz vessel, and is burnt to CO₂ in pure oxygen at 900°C. When the sample contains some amounts of sulfide minerals, evolved SO₂ is removed from CO₂ at the melting point of *n*-pentane (MIZUTANI and OANA, 1973). Carbon dioxide thus purified is used for mass spectrometric determinations.

The mass spectrometer used is a double collector Nier-McKinney type instrument, Varian Mat CH7.

The isotopic composition of a sample is reported in δ -notation,

$$\delta (\text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1,000$$

where R is ¹³C/¹²C or ¹⁸O/¹⁶O ratio in sample or standard. The standards are PDB (CRAIG, 1957) for carbon and SMOW (CRAIG, 1961) for oxygen. A working standard is used in practice. Its isotopic ratios are determined with respect to the NBS-Solenhofen standard (CRAIG, 1957).

The fractionation factor, α_{A-B} , between two substances A and B is defined as

$$\alpha_{A-B} = \frac{R_A}{R_B}$$

where R is ¹³C/¹²C or ¹⁸O/¹⁶O in A and B.

When α is very close to unity, $1,000 \ln \alpha_{A-B} = \delta_A - \delta_B$. $1,000 \ln \alpha_{A-B}$ is denoted

by Δ_{A-B} in this paper.

Carbonate minerals, graphite and other carbonaceous materials are identified by the X-ray powder method.

DISCUSSION

Carbon and oxygen isotopic compositions of carbonates Carbonate samples are composed of dolomite and calcite except for 73080406A,B and 73080407, which are nearest the granite contact, and Ka-02, which is farthest from the contact.

The dolomite component is more abundant in almost all samples than the calcite component.

The isotopic ratios of calcite and dolomite from the Kasuga area are listed in Table 1.

Table 1. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of carbonates and coexisting graphites.

Sample No.	Distance from the contact (m)	Calcite dolomite ratio	$\delta^{13}\text{C}$ (‰) Calcite part	$\delta^{18}\text{O}$ (‰) Calcite part	$\delta^{13}\text{C}$ (‰) Dolomite part	$\delta^{18}\text{O}$ (‰) Dolomite part	$\delta^{13}\text{C}$ (‰) Graphite or carbonaceous material
<i>Nakayama traverse</i>							
1. 73080408	1,680	20 : 100	+3.9	+25.2	+5.0	+28.4	-5.6
2. 73050503	1,150	8 : 100	+3.5	+24.0	+4.0	+28.1	-5.4
3. 73050504	1,060	100 : 30	+4.1	+26.4	+4.7	+28.5	-4.4
4. 73050505	960	50 : 50	+4.3	+24.6	+5.2	+27.3	-4.4
5. 73080401	610	100 : <5	+3.5	+26.0	+4.2	+27.4	-4.6
6. 73080405A	410	12 : 100	+0.5	+21.9	+1.3	+25.3	-5.9
73080405B	410	17 : 100	+2.2	+23.1	+3.9	+25.8	-3.6
7. 73080406A	190	100 : 0	+3.8	+26.9			-2.1
73080406B	190	100 : 0	+4.2	+29.0			-1.6
73080407	190	100 : 0	+3.3	+26.6			-2.9
<i>Others</i>							
8. 72082301B	100	14 : 100	+3.0	+23.0	+2.9	+25.0	-3.4
9. 72082305A	<50	11 : 100	+4.2	+24.2	+4.8	+27.4	-1.8
10. 72082305C	<50	10 : 100	+2.5	+17.6	+4.8	+30.4	-4.7
11. 72082309	600	11 : 100	+0.8	+22.0	+2.0	+25.1	-8.6
12. 72082311B	700	9 : 100	+2.1	+17.0	+4.1	+26.5	-4.9
13. Ka-02	>2,000	100 : 0	+4.1	+26.8			-25.0

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the dolomite component are distributed from +1.3 to +5.2‰ with respect to PDB, and from +25.1 to +30.4‰ with respect to SMOW, respectively. The extent of these variations is usual in marble (SHIEH and TAYLOR, 1970).

OSAKI (1973) reported carbon and oxygen isotopic compositions of dolomite from Miyama, Gifu Pref., where Permian dolostone and limestone are distributed. These Permian formations have not been subjected to any thermal metamorphism, and are correlated with the marble in the Kasuga area. Carbon and oxygen isotopic ratios for the dolomite component is similar for Kasuga and Miyama samples. Therefore, the isotopic composition of dolomite in the Kasuga area is considered not to have changed since dolomite was formed, though it was subjected to a thermal metamorphism.

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of calcite from calcite marble (deficient in dolomite component) fall in the relatively narrow ranges from +3.3 to +4.2‰, and from +26.6 to +29.0‰, respectively, which are similar to the ranges of δ values for dolomites. This suggests that the calcite marble did not appreciably change carbon and oxygen isotopic compositions since it was formed.

The isotopic ratios of calcite coexisting with dolomite, however, are from +0.5 to

+4.3‰ for carbon and from +17.0 to +26.0‰ for oxygen. They are distributed in wide ranges compared with δ values of coexisting dolomite.

Carbon and oxygen isotopic compositions of dolomite are heavier than those of coexisting calcite, when both minerals are in isotopic equilibrium (SCHWARCZ, 1966). SHEPPARD and SCHWARCZ (1970) showed that $\Delta^{13}\text{C}_{\text{Do-Cc}}$ and $\Delta^{18}\text{O}_{\text{Do-Cc}}$ for contact metamorphosed coexisting dolomite and calcite fall on a regression curve.

$\Delta^{13}\text{C}_{\text{Do-Cc}}$ and $\Delta^{18}\text{O}_{\text{Do-Cc}}$ values for Kasuga samples are plotted in Fig. 2. They do not fall on the regression curve by SHEPPARD and SCHWARCZ (1970) and seem to form a different regression curve.

According to these facts and oxygen fractionation factor between dolomite and calcite (EPSTEIN *et al.*, 1964; SCHWARCZ, 1966; O'NEIL and EPSTEIN, 1966; SHEPPARD and SCHWARCZ, 1970), dolomite and coexisting calcite in the Kasuga area are not considered to be in isotopic equilibrium (Fig. 3).

Fig. 2. $\Delta^{13}\text{C}_{\text{dolomite-calcite}}$ v. $\Delta^{18}\text{O}_{\text{dolomite-calcite}}$ for dolomite-calcite pairs from the Kasuga area. Diagonal dashed line is derived from regional metamorphic marble (SHEPPARD and SCHWARCZ, 1970)

Fig. 3. Relationship between $\Delta^{18}\text{O}_{\text{dolomite-calcite}}$ and carbon isotopic temperature. Dashed and dotted lines are oxygen isotopic fractionation curves obtained by O'NEIL and EPSTEIN (1966) and NORTHROP and CLAYTON (1966), respectively. (right)

When these carbonate rocks were metamorphosed, only oxygen in calcite might have exchanged with connate water or meteoric water, because calcite is less resistible in isotopic exchange than dolomite (EPSTEIN *et al.*, 1964).

Carbon isotopic ratios of carbonaceous materials in marble and pelitic rocks Carbon isotopic ratios of dispersed carbonaceous materials in marble and pelitic rocks are listed in Tables 1 and 2, respectively.

Dispersed carbonaceous materials in marbles from the Kasuga area were confirmed by the X-ray diffraction method to be finely crystalline graphites. None of scaly graphite, such as Kropfmühl graphite (HAHN-WEINHEIMER, 1966) and Kamioka graphite (NOZAWA, 1952), are found in the Kasuga area. Thus these graphites from the Kasuga area are considered according to their occurrence to be of biogenic origin.

Carbonaceous material in the non-metamorphosed limestone, Ka-02 has a low $\delta^{13}\text{C}$ value, suggesting its biogenic origin. $\delta^{13}\text{C}$ values of graphites in marbles, -8.6 to -1.6‰ are considerably heavier than those of typical biogenic carbon. Nevertheless these graphites are considered to be of biogenic origin as mentioned above.

HAHN-WEINHEIMER (1966) and HAHN-WEINHEIMER *et al.* (1969) reported that graphites

Table 2. $\delta^{13}\text{C}$ of carbon and carbon contents of pelitic rocks

Sample No.	Rock	Distance from the contact (m)	Carbon wt. %	$\delta^{13}\text{C}$ (‰)
1. 72082304A	black schist	50	1.3	-25.2
2. 72082307	shale	500	1.3	-28.4
3. 72082307	slate	850	0.8	-22.6
4. 73050502	shale	1,200	2	-26.6

in marble could be recognized in two groups, one group was of biogenic origin and the other of non-biogenic. Non-biogenic graphite occurs in marble as scales and is enriched in ^{13}C .

$\delta^{13}\text{C}$ in slates or shales are -22.6 to -28.4‰ and fall in a relatively narrow range. The carbon isotopic ratios in Paleozoic and younger marine shales or slates have values lighter than -25‰ (CRAIG, 1953, 1954). A sample, 72082310 occurs in slate 850m from the contact and its $\delta^{13}\text{C}$ is slightly heavy. The carbon content of this sample is also slightly low compared with the other samples (see Table 2). This low carbon content may have been derived by consumption of carbonaceous material as an oxygen buffer during metamorphism. If any difference results in the $\delta^{13}\text{C}$ value, it's in the direction of making the remnant heavy.

Nakayama traverse Nakayama traverse is shown in Fig. 1 by a dashed line designated T. Several outcrops of marble are exposed along this traverse. The carbon isotopic ratios of calcites and coexisting graphites in marbles are plotted with respect to the distance from the igneous contact in Fig. 4. Figure 5 shows the relationship between $\Delta^{13}\text{C}_{\text{Cc-Gr}}$ in marbles and the distance from the contact in the same traverse. In Figs. 4 and 5 and in Table 1, we can recognize a decrease in $\Delta^{13}\text{C}_{\text{Cc-Gr}}$ toward the igneous contact. Carbon isotopic composition of calcite is almost constant regardless of the distance from the contact, whereas the carbon of graphites coexisting with carbonates becomes evidently heavier toward the igneous contact. These graphites are considered to have been derived from organic materials, $\delta^{13}\text{C}$ values of which were originally from -25 to -30‰. Organic materials in the limestone have been converted into graphite, their carbon isotopic composition becoming progressively heavier during the contact metamorphism.

Enrichment of ^{13}C in carbonaceous materials in marble may have been performed by either of the following mechanisms:

- 1) Thermal cracking of organic matter to form graphite,
- 2) Reaction with gases equilibrated with graphite, or
- 3) Isotopic exchange between calcite and graphite.

SACKET *et al.* (1966) studied thermal cracking of oil and showed that carbon isotopic fractionation between methane formed by cracking and residual organic carbon depends on the physical characters of carbon-carbon bonds in organic compounds. Numerical estimation of the carbon isotopic fractionation for the present study, however, is difficult, because original structures of organic compounds involved are unknown. This mechanism may also be considered in slate and shale. Graphites in slate or shale are not deviated in the carbon isotopic composition from organic carbon. This may suggest that they are biogenic in origin and have not changed their carbon isotopic compositions through metamorphism. This is also shown for graphites in Precambrian gneiss (ANDREAE, 1974).

Effects of the 2nd mechanism will be expected, especially when gaseous fluid from a granite body flows into sedimentary rocks and forms skarn minerals. Therefore, we assume chemical equilibrium between graphite and water, and estimate carbon isotopic fractionations between them according to BOTTINGA (1969). Dissociation pressure of calcite under 600°C is so small that we can neglect the contribution of calcite to gas components (WILLIE and TUTTLE, 1960).

FRENCH (1966) theoretically calculated mutual ratios of the amounts of carbon

dioxide and methane under various total pressures and temperatures in the stability field for graphite. The partial pressures of both gases are nearly equal at 600°C. According to BOTTINGA (1969) the fractionation factor between carbon dioxide and graphite $\Delta \text{CO}_2\text{-C}$ (graphite) is smaller than that between graphite and methane $\Delta \text{C (graphite)-CH}_4$ at temperatures lower than 280°C. At temperatures higher than 280°C, however, this relationship becomes reverse, and the $\delta^{13}\text{C}$ value of the gaseous phase should be greater than that of graphite.

The metamorphic temperature in the Kasuga area is supposed on mineralogical and geological evidence to have been higher than 400°C. When the gases equilibrated with graphite at this temperature were removed, the $\delta^{13}\text{C}$ value of remaining graphite could not increase to the observed values.

The 3rd mechanism seems to be natural and should be most effective, if realized. Since marble in the Kasuga area contains only small amounts of graphite, isotopic exchange between them would not significantly affect the carbon isotopic composition of marble, and should strongly control $\delta^{13}\text{C}$ of graphite (see Fig. 4). BOTTINGA (1969) calculated fractionation factors between calcite and graphite in a temperature range from 0 to 700°C. Applying these values, we can estimate carbon isotopic temperatures as shown in Table 3. Along the Nakayama traverse, the relationship between the carbon isotopic temperature and the distance of sampling sites from the contact is shown in Fig. 6. The distances from the contact are estimated on a geological map.

Table 3. Carbon isotopic temperature and magnesium solvus temperature

Sample No.	$\Delta^{13}\text{C}_{\text{Cc-Gr}}(\text{‰})$	Carbon isotopic temperature (°C)	Magnesium solvus temperature (°C)
<i>Nakayama traverse</i>			
1. 73080408	+9.5	365	<400
2. 73050503	+8.9	390	<400
3. 73050504	+8.5	430	<400
4. 73050505	+8.7	410	<400
5. 73080401	+8.1	450	—
6. 73080405A	+6.4	580	580
73080405B	+5.8	650	580
7. 73080406A	+5.9	640	—
73080406B	+5.8	650	—
73080407	+6.2	600	—
<i>Others</i>			
8. 72082301B	+6.4	580	580, 570
9. 72082305A	+6.0	630	570
10. 72082305C	+7.3	500	—
11. 72082309	+9.3	370	440
12. 72082311B	+7.0	530	510
13. Ka-02	+29.0	<0	<400

Comparison with solvus temperature GOLDSMITH *et al.* (1961) and GOLDSMITH and NEWTON (1969) studied magnesium content of magnesian calcite coexisting with dolomite and estimated solvus temperatures by magnesium content of calcite. SUZUKI (1975) analyzed magnesium in calcite coexisting with dolomite by the X-ray diffraction method and estimated solvus temperatures for some samples which were collected from the same sites as in this work. Solvus temperatures are listed in Table 3 in comparison with carbon isotopic temperatures. They agree with each other fairly well. The average isotopic temperature near the contact is about 620°C, which is consistent with the geological fact that the highest metamorphic facies near the contact is high amphibolite (SUZUKI, 1975). Figure 7 shows the relationship between the carbon isotopic temperatures and other mineralogical evidences in the Kasuga area investigated by SUZUKI (1975). On phase equi-

Fig. 4. $^{13}\text{C}/^{12}\text{C}$ ratios of calcite and coexisting graphite v. distance of sampling sites from the igneous contact along the Nakayama traverse. Numbers correspond to those in Fig. 1.

Fig. 5. $\Delta^{13}\text{C}_{\text{calcite-graphite}}$ values along the Nakayama traverse with respect to the distance from the igneous contact. Numbers correspond to those in Fig. 1.

Fig. 6. Relationship between carbon isotopic temperature and distance of sampling sites from the contact along the Nakayama traverse. The solid and dotted curves are maximum temperature curves (JEAGER, 1959). The solid curve is for the case of equal thermal properties of country rock and magma and of latent heat of 80 cal/g. The dotted curve is for the case of no latent heat and thermal properties of shale and granite porphyry. The solid curve, B.C., is oxygen isotopic temperature gradient for the Birch Creek traverse given by SHIEH and TAYLOR (1969b).

libria in metamorphosed siliceous marbles, METZ and TROMMSDORFF (1968) showed stability fields for talc and tremolite by experiment and calculation. When the total pressure is 1,000 bars, talc can be formed at temperatures between 400 and 500°C and tremolite above 500°C (SUZUKI, 1975). In Fig. 7 the distributions of tremolite and talc are consistent with carbon isotopic temperatures except for two samples, Nos. 5 and 12 (450 and 530°C, respectively).

Comparison with a heat flow model

JEAGER (1959) calculated the temperature gradient in the vicinity of a contact between an intrusive and a country rock. We calculate a maximum temperature curve for the Nakayama traverse on a heat flow model of JEAGER. The dimension of the granite intrusion in the Kasuga area is about 5,000m in NW-SE and a little larger than 5,000m in NE-SW (SUZUKI, pers. com.). Assuming that the contact temperature is 650°C and the latent heat is 80 cal/g or zero, we get maximum temperature

Fig. 7. Carbon isotopic temperatures and mineral parageneses in the Kasuga area. Abbreviations are as follows; tr: tremolite isograd, tc: talc isograd, C.I: cordierite isograd, B.I: biotite isograd. Zone I: brown hornblende zone, Zone II: blue green hornblende zone, Zone III: actinolite zone, figures: carbon isotopic temperature. (mineral parageneses after SUZUKI, 1975).

curves in Fig. 6. We cannot estimate strictly the distance from the igneous contact, because of the irregular shape of the granite body. Therefore, the relationship between carbon isotopic temperatures and the apparent distance from the contact cannot be strictly compared with these theoretical curves. Estimated isotopic temperatures seem to decrease at places farther than 500m from the contact along a heat flow model without latent heat. We, however, do not intend to discuss the latent heat of the granite intrusive with those limited data.

SHIEH and TAYLOR (1969b) studied oxygen isotopic temperatures of contact metamorphism, and obtained an average contact temperature of 580°C from oxygen isotopic fractionations between two silicate minerals in the Birch Creek traverse. The solid line B.C. in Fig. 6 represents the oxygen isotopic temperature curve in the Birch Creek (SHIEH and TAYLOR, 1969b). Carbon isotopic temperatures farther than 500m from the contact fall on the extrapolation of the Birch Creek isotopic temperature gradient. This gentle decrease in temperature might have been realized by a large granite body as in the case of the Birch Creek traverse. High temperatures as far as 400m from the main contact might have resulted from a small intrusive, which is located 400m from the main contact on the Nakayama traverse.

Oxygen fugacity in metamorphic aureole is maintained low, as long as graphite exists (MIYASHIRO, 1964). Graphite cannot be found and oxygen fugacity should be high in marble near quartz veins, where quartz reacts with calcite and/or dolomite to form wollastonite and/or diopside and forsterite etc. Aqueous fluid containing silica is considered to have intruded into fissures of carbonate rocks in such locations, and graphite or organic carbon might have disappeared. Carbonate rocks in the Kasuga area contain only small amount of organic carbon even where they were not subjected to metamorphism. Therefore, marble with a small amount of graphite implies that it was scarcely affected by aqueous fluid during metamorphism in the Kasuga area. When isotopic equilibrium between calcite and graphite is once attained in marble, isotopic compositions of calcite and graphite are retained during the subsequent lowering of metamorphic temperature, because of the lack of aqueous fluid and the high stability of crystalline graphite. The carbon isotopic temperature is thus considered to represent the maximum temperature in the metamorphism.

CONCLUSIONS

- 1) Graphite in the Kasuga marble is finely crystalline and is considered to be of organic origin from its occurrence.
- 2) Carbon isotopic fractionation between calcite and graphite progressively decreases with increasing distance from the igneous contact along the Nakayama traverse.
- 3) When we assume carbon isotopic equilibrium between calcite and coexisting

graphite in marble, carbon isotopic temperatures reasonably agree with solvus temperatures of magnesian calcites, heat flow temperatures and mineral paragenesis.

4) Maximum contact temperature is estimated to be from 600 to 650°C, according to the carbon isotopic fractionations. Carbon isotopic maximum temperature represents the maximum metamorphic temperature.

5) ^{18}O depletion for some calcites coexisting with dolomite in the Kasuga marble results from the oxygen isotopic exchange with connate or meteoric water, since calcite constitutes small fractions of the marble and is more susceptible to isotopic exchange than dolomite.

6) Carbon in pelitic rocks of contact metamorphic aureole is of organic origin. Its isotopic composition is typically organic, and varies at most several per mils during contact metamorphism.

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