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Ion microprobe analysis of graphite from ca. 3.8 Ga metasediments, Isua supracrustal belt, West Greenland: Relationship between metamorphism and carbon isotopic composition

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Abstract—In-situ ion microprobe measurements of carbon isotopic compositions of graphite were made in seven metasediments and two carbonate rocks from the ca. 3.8 Ga Isua supracrustal belt, West Greenland. The $\delta^{13}C$ values of micron-scale graphite globules in the metasediments and the carbonate rocks vary from –18 to +2‰ and from –7 to –3‰, respectively. The maximum $\delta^{13}C$ value of graphite globules in the metasediment rises from –14 to –5‰, as the metamorphic grade increases from epidote-amphibolite to upper amphibolite facies. In a single hand specimen, the $\delta^{13}C$ values of graphite inclusions in garnet are ~7‰ lower on average than those outside garnet. Similarly, graphite armored by quartz apparently shows a few permil lower $\delta^{13}C$ values than those on grain boundaries between noncarbonate minerals. The fact that early crystallized minerals include relatively ^{13}C-depleted graphite indicates that the regional metamorphism increased the $\delta^{13}C$ values of the Isua graphite. This is consistent with the regional trend of ^{13}C-enrichment accompanied by the increase of metamorphic grade. The minimum fractionation between graphite and carbonate is consistent with the equilibrium fractionation at about 400 to 550 °C. These observations indicate that isotopic exchange with isotopically heavy carbonate caused ^{13}C-enrichment of Isua graphite. The $\delta^{13}C$ values of graphite reported here ($\delta^{13}C > -18$‰) were produced either as a metamorphic modification of organic carbon with initially much lower $\delta^{13}C$ values, or as an abiological reaction such as decomposition of carbonate. If the isotopic exchange between carbonate and graphite during regional metamorphism controlled the ^{13}C-enrichment of Isua graphite, previously reported large ^{13}C-depletion of graphite, especially armored by apatite (Mojzsis et al., 1996) was probably premetamorphic in origin. This supports the existence of life at Isua time (ca. 3.8 Ga). *Copyright © 2002 Elsevier Science Ltd*

1. INTRODUCTION

The timing of emergence of life on Earth is still debated, though carbon isotope analyses of sedimentary organic matter have revealed that autotrophic organisms, which preferentially fix isotopically light carbon, had already existed at least by 3.5 Ga (Schidlowski, 2001). The oldest (ca. 3.8 Ga) sedimentary rocks on Earth occur in the Isua supracrustal belt, southern West Greenland. These rocks are substantially metamorphosed up to amphibolite facies (Hayashi et al., 2000; Nutman, 1986). The graphitization by the intense thermal metamorphism would have eliminated the records of morphologically preserved microfossils and biologically produced specific organic compounds. However, the carbon isotopic signature of graphite has a better chance to survive. Previous isotope analyses of reduced carbon in the Isua metasediments yielded a range of $\delta^{13}C$ values from –6 to –28‰ by the conventional bulk technique (Hayes et al., 1983; Naraoka et al., 1996; Oehler and Smith, 1977; Perry and Ahmad, 1977; Rosing, 1999; Schidlowski et al., 1979; Shimoyama and Matsubaya, 1992). Some have relatively ^{13}C-depleted isotopic compositions, comparable to those of biologically fixed carbon. In addition, a recent ion microprobe study recorded a large ^{13}C-depletion (below –30‰) of graphite inclusions in apatite grains both from the Isua supracrustal belt and from the >3.85 Ga granulite-facies metamorphic rocks on Akilia island (Mojzsis et al., 1996). This strongly suggests the existence of life at >3.85 Ga.

Despite the presence of highly ^{13}C-depleted graphite, most Isua graphite are more enriched in ^{13}C (typically –10 to –15‰). Such ^{13}C-enriched graphite could have been produced by inorganic processes such as siderite decomposition at ~400 to 500 °C (Perry and Ahmad, 1977) and deposition from CO_2- and CH_4-bearing fluids at 400 to 700 °C during regional metamorphism (Naraoka et al., 1996). Moreover, Oehler and Smith (1977) and Naraoka et al. (1996) suspected highly ^{13}C-depleted reduced carbon to be postdepositional in origin, because of its very low reduced carbon concentration (below 0.01 wt.%).

One of the most fundamental and unsolved questions is whether the carbon isotopic composition of the Isua graphite is primary or not. Indeed some $\delta^{13}C$ values of the Isua graphite are comparable to those of biogenic reduced carbon (Rosing, 1999), but it is likely that the intense regional metamorphism may have modified their carbon isotopic compositions. Eiler et al. (1997) pointed out the possibility that the Rayleigh distillation process during metamorphism could have produced highly ^{13}C-depleted graphite without biologic fractionation. On the other hand, earlier workers (Hayes et al., 1983; Schidlowski et al., 1979) suggested that the Isua graphite may have been enriched in ^{13}C by isotopic exchange with carbonate during the metamorphism. The latter hypothesis supports a biologic origin for the Isua graphite, but has not yet been verified (Naraoka et al., 1996). The magnitude and trend of the metamorphic effect on isotopic compositions of the Isua graphite are still unknown.

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Therefore, calculation of the metamorphic effect is particularly important for deducing primary carbon isotopic compositions.

To evaluate the metamorphic effect on carbon isotopic compositions, in-situ analyses by ion microprobe were performed in this study. The history of isotopic modification during the metamorphism was potentially traced in micron-scale graphite crystals included in silicate minerals grown under different pressure and temperature conditions. In-situ analysis by the ion microprobe can differentiate the isotopic variability of graphite at a scale of ~5 μm with <3‰ precision (House et al., 2000; Ueno et al., 2001). The isotopic distribution of Isua graphite has the potential to identify the primary carbon isotopic signature preserved in early formed minerals, as well as to indicate the trend of isotopic modification during metamorphism.

Recently, Hayashi et al. (2000) identified the progressive metamorphism in the Isua supracrustal belt. The isotopic compositions of graphite from three different metamorphic zones were compared to evaluate the relationship between the isotopic composition of graphite and their degree of metamorphism.

In this paper, we report the results of in-situ carbon isotope analyses of the micron-scale graphite in nine rock samples from three different metamorphic zones. We suggest that the isotopic exchange between carbonate carbon and graphite controlled the ^{13}C-enrichment of the Isua graphite.

2. GEOLOGICAL OUTLINE AND METAMORPHIC ZONATION

The Isua supracrustal belt lies approximately 150 km northeast of Nuuk, Greenland. It forms a 35-km-long arcuate tract and is the largest fragment of early Archean supracrustal rocks in the Akulleq terrane (Fig. 1). Despite later discoveries of older geological terrains such as the Acasta gneiss (Bowring et al., 1989), the Isua supracrustal belt is the oldest greenstone belt, containing the oldest (≥3810 Ma) supracrustal rocks on the Earth (Nutman et al., 1996; Nutman et al., 1997). Well-preserved primary structures, such as pillows in lava (Komiya et al., 1999) and graded bedding in sedimentary rocks (Nutman et al., 1984) in the least metamorphosed zone enable us to understand their precursor material (Komiya et al., 1999). The Isua supracrustal belt comprises the following four major lithologic units: (1) mafic-felsic turbidites, including interlayered minor conglomerate; (2) chert and banded iron-formation (BIF); (3) basaltic volcanics including pillow lava, pillow breccia, and related intrusive rocks; and (4) ultramafic rocks. These rocks were intruded by mid-Archean Ameralik dykes, and NS-trending high-Mg andesite dykes (2215 Ma; Nutman et al., 1995).

According to Komiya et al. (1999), the northeastern part of the Isua supracrustal belt is divided into three units bounded by low-angle thrusts. The southern unit is subdivided into 14 thrust-bound subunits (horses), which share a similar lithostratigraphy. Duplex structures are widespread, and vary from a few meters to kilometers in size. The reconstructed lithostratigraphy of each horse reveals a simple pattern, which consists of greenstone with a low-K tholeiitic composition with or without pillow lava, chert/BIF, and turbidite in ascending stratigraphic order. The cherts and underlying low-K tholeiites do not contain continent- or arc-derived material. The lithostratigraphy is similar to typical Phanerozoic "oceanic plate stratigraphy," except for the abundance of mafic material in the turbidites. The evidence of duplex structures and "oceanic plate stratigraphy" indicates that the Isua supracrustal belt was an accretionary complex in the Early Archean (Komiya et al., 1999). The dominantly mafic turbidite composition suggests that the accretionary complex was formed in an intraoceanic environment comparable to the present-day western Pacific Ocean. The depositional environment is estimated to range from basaltic volcanism at a mid-oceanic ridge, through deposition of pelagic sediments (chert) in an open sea, to terrigenous sediments (turbidite) at a subduction zone (Komiya et al., 1999).

In their study of metamorphism in the Isua supracrustal belt, Hayashi et al. (2000) reported a systematic change of mineral parageneses in metabasites and metapelites, and a corresponding progressive change of composition of major metamorphic minerals, including plagioclase, amphibole, chlorite, epidote, and garnet. Their petrochemical and geothermobarometric study of more than 1500 rock samples defined a progressive metamorphic zonation from greenschist (Zone A) through epidote-amphibolite (Zone B) to amphibolite facies (Zones C and D) in the northeast of the Isua belt. Metamorphic pressures and temperatures were estimated to be 5 to 7 kbar from garnet-hornblende-plagioclase-quartz geobarometry and 380 to 550 °C from garnet-biotite geothermometry in Zones B and D. These P-T estimates indicate an intermediate P/T ratio metamorphic facies series (Hayashi et al., 2000; Komiya et al., 1999).

3. SAMPLES

To find graphite, 337 rock specimens including BIF (n = 69), metachert (n = 214), muddy metachert (n = 13), psammitic schist (n = 19), metaconglomerate (n = 7), and carbonate rock (n = 15) were scanned by optical microscopy under transmitted and reflected light and by scanning electron microscopy (JEOL JSM5310) with an X-ray analysis system (OxFord Link ISIS). All samples were collected during our field mapping in 1990 and 1993. Among the 337 specimens, 18 specimens contain graphite, which include metachert (n = 6), muddy metachert (n = 3), psammitic schist (n = 2), and carbonate rock (n = 7). These 18 graphite-bearing samples are from metamorphic Zones B, C, and D, but unfortunately not from Zone A, which has the lowest metamorphic grade.

We selected nine graphite-bearing rock samples for ion microprobe analysis; metachert (n = 2), muddy metachert (n = 3), psammitic schist (n = 2), and carbonate rock (n = 2). The metachert, psammitic schist, and carbonate rock are all from Zone B, and the three muddy metachert samples K463, K612, and K244 are from Zones B, C, and D, respectively. Their mineralogy is listed in Table 1. The mode of occurrence of the graphite in the four lithologies is as follows.

3.1. Metachert

Metachert is mainly composed of quartz (>70%) with small amounts of amphibole (grunerite/cummingtonite) and chlorite. In K424, graphite is disseminated as 2- to 5-μm globular grains and often occurs in thin magnetite-rich layers (Fig. 2A). They occasionally form aggregates up to 50 μm diameter. Most are on grain boundaries of quartz, and others are enclosed within quartz. However, graphite in K426 is the largest (10 to 30 μm)

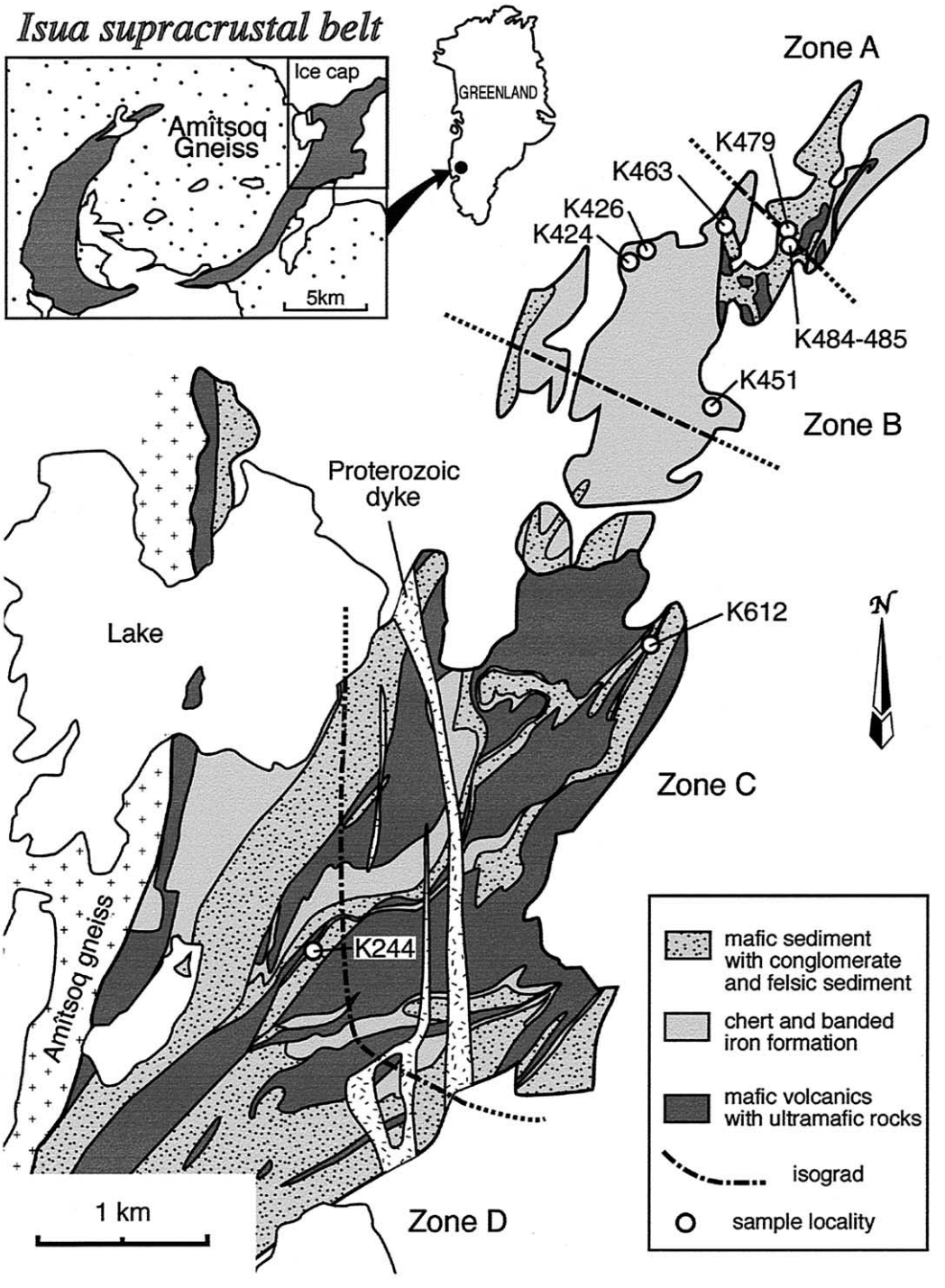

Fig. 1. Simplified geologic map of the eastern Isua supracrustal belt showing locations of metasediment samples, compiled from maps by Nutman (1986) and Komiya et al. (1999). Metamorphic zonation after Hayashi et al. (2000).

of all graphites in the nine samples (Fig. 2B), most occurrence as inclusions in quartz and rarely enclosed within garnet (almandine) porphyroblasts of ~2 mm diameter.

3.2. Muddy Metachert

Muddy metachert is now banded schist composed of quartz and amphibole (grunerite/cummingtonite) (Figs. 2C, D, and E). The highly metamorphosed samples (i.e., K612 and K244) show more conspicuous banding than the least metamorphosed sample (K463). The grain size of amphibole porphyroblasts in K612 and K244 is large (up to 500 μm long) relative to those in K463 (~50 μm). Regardless of their metamorphic grade, disseminated graphite globules occur both within quartz and amphibole and on their grain boundaries. The grain size of

Table 1. Mineralogy of graphite-bearing rocks.

Sample no.	Zone	Mineralogy		
		major	minor	trace
Metachert				
K424	B	Qtz	Mag, Gr, Cum	Chl, Ank
K426	B	Qtz	Gru, Chl, Alm	Ilm, Gr
Muddy metachert				
K463	B	Qtz	Cal, Cum, Ath	Po, Gr
K612	C	Gru, Qtz	Alm	Gr, Po, Ilm
K244	D	Gru, Qtz	Cal, Gr	
Psammitic schist				
K484	B	Qtz	Act, Cal (vein)	Gr
K485	B	Qtz	Act, Ath, Cal	Po, Ccp, Gr, Mag
Carbonate rock				
K479	B	Cal, Qtz	Cum, Ath, Bt	Po, Gr
K451	B	Ank	Qtz, Cum, Py	Chl, Po, Gr

Minerals: Act = actinolite; Alm = almandine; Ath = anthophyllite; Ank = ankerite; Bt = biotite; Cal = calcite; Ccp = chalcopyrite; Chl = chlorite; Cum = cummingtonite; Gr = graphite; Gru = grunerite; Ilm = ilmenite; Mag = magnetite; Py = pyrite; Po = pyrrhotite; Qtz = quartz.

graphite globules in K463 is 1 to 5 μm, whereas those in K612 and K244 are slightly larger (2 to 10 μm) and often aggregated up to 50 μm (Fig. 2E). In K612, graphite globules also enclosed within garnet (almandine) porphyroblasts along with pyrrhotite (Fig. 3).

3.3. Psammitic Schist

Psammitic schist is mainly composed of quartz and a small amount of amphibole (mainly actinolite) and calcite. Disseminated graphite globules are small ($<$1 to 2 μm) relative to those in other lithologies (Fig. 2H). Most are concentrated at the grain boundaries of quartz, and others occur as inclusions in quartz. A secondary carbonate vein cuts the K484; such veins do not contain graphite (Fig. 2H).

3.4. Carbonate Rock

Carbonate rock is mainly composed of carbonate (calcite or ankerite) and small amounts of quartz and amphibole (mainly cummingtonite). K479 shows banding formed by the alternation of carbonate/quartz and amphibole/biotite layers, whereas K451 has a saccharoidal texture without obvious foliation (Fig. 2G). Graphite globules (1 to 5 μm) are concentrated on grain boundaries of calcite (Fig. 2G); they rarely occur as inclusions in quartz and carbonate (Fig. 2F).

4. ANALYSES

4.1. Carbon Isotope Analysis of Carbonate

Concentrations and $\delta^{13}C$ values of carbonate were determined by conventional methods. Carbonate powders were reacted in anhydrous phosphoric acid ($\rho \geqq 1.89$ g/mL) at 50°C for 48 h to produce CO_2. Isotopic compositions of CO_2 were determined with a Finnigan MAT δ-S mass spectrometer at Tokyo Metropolitan University. All carbon isotope data are reported against Pee Dee belemnite (PDB) standard ($^{12}C/^{13}C$ = 88.99; Craig, 1957). Analytical reproducibility of $\delta^{13}C$ values, based on replica of NBS19 standards, is better than $\pm$0.1‰.

4.2. In-situ Carbon Isotope Analysis of Graphite

Carbon isotopic measurements of graphite were performed by secondary ion mass spectrometry (SIMS) using a CAMECA ims1270 at the Tokyo Institute of Technology. Gold-coated graphite in thin section was sputtered by a focused 20-keV Cs^+ primary beam. Measurements of $^{12}C^-$ and $^{13}C^-$ secondary ions were made under a high mass resolution mode ($m/\Delta m$ = $\sim$4500) to separate the $^{12}CH^-$ interference at mass 13. A normal incident electron flood gun was used to compensate electrostatic charging of the analysis area by the Cs^+ sputtering. The primary beam was focused into a small spot ($<$10 μm), and a field aperture (20 μm $\times$ 20 μm image field of sample surface) was inserted into the secondary ion optics. A 150 μm field setting for the transfer optics was used. Secondary ions were collected through an energy window of $\pm$75 eV. Constant count rates of 4×10^5 cps and 3 to 4×10^5 cps of $^{12}C^-$ were maintained to eliminate uncertainties in dead-time correction of the electron multiplier pulse counting system for standard and unknown, respectively. Dead-time of the counting system is 21.2 $\pm$ 0.8 ns. These count rates were achieved with a primary beam current of $\sim$10 pA. Signals of $^{12}C^-$ and $^{13}C^-$ were accumulated for 2 and 5 s during each cycle, respectively. Carbon isotopic composition was usually determined by averaging the ratios of $^{13}C^-/^{12}C^-$ from 100 data cycles.

The $^{13}C^-/^{12}C^-$ ratios, after the correction of dead-time and of instrumental mass fractionation, are reported as a $\delta^{13}C$ value relative to the $^{13}C/^{12}C$ ratio of the Chicago PDB standard ($^{12}C/^{13}C$ = 88.99; Craig, 1957). Instrumental mass fractionation was corrected using the USGS24 graphite standard ($\delta^{13}C_{PDB}$ = –15.90 $\pm$ 0.25‰) mounted on a separate glass plate. The standard and unknown samples were set in the same sample holder. Measurements of this standard were performed several times at the beginning, during, and at the end of each analytical session. The procedure of mass fractionation correction assumes that the degree of bias for the lighter isotope inherent in the sputtering process is the same for the sample as for the graphite standard. In most analyses, the focussed beam overlapped graphite and the surrounding silica or silicate. How-

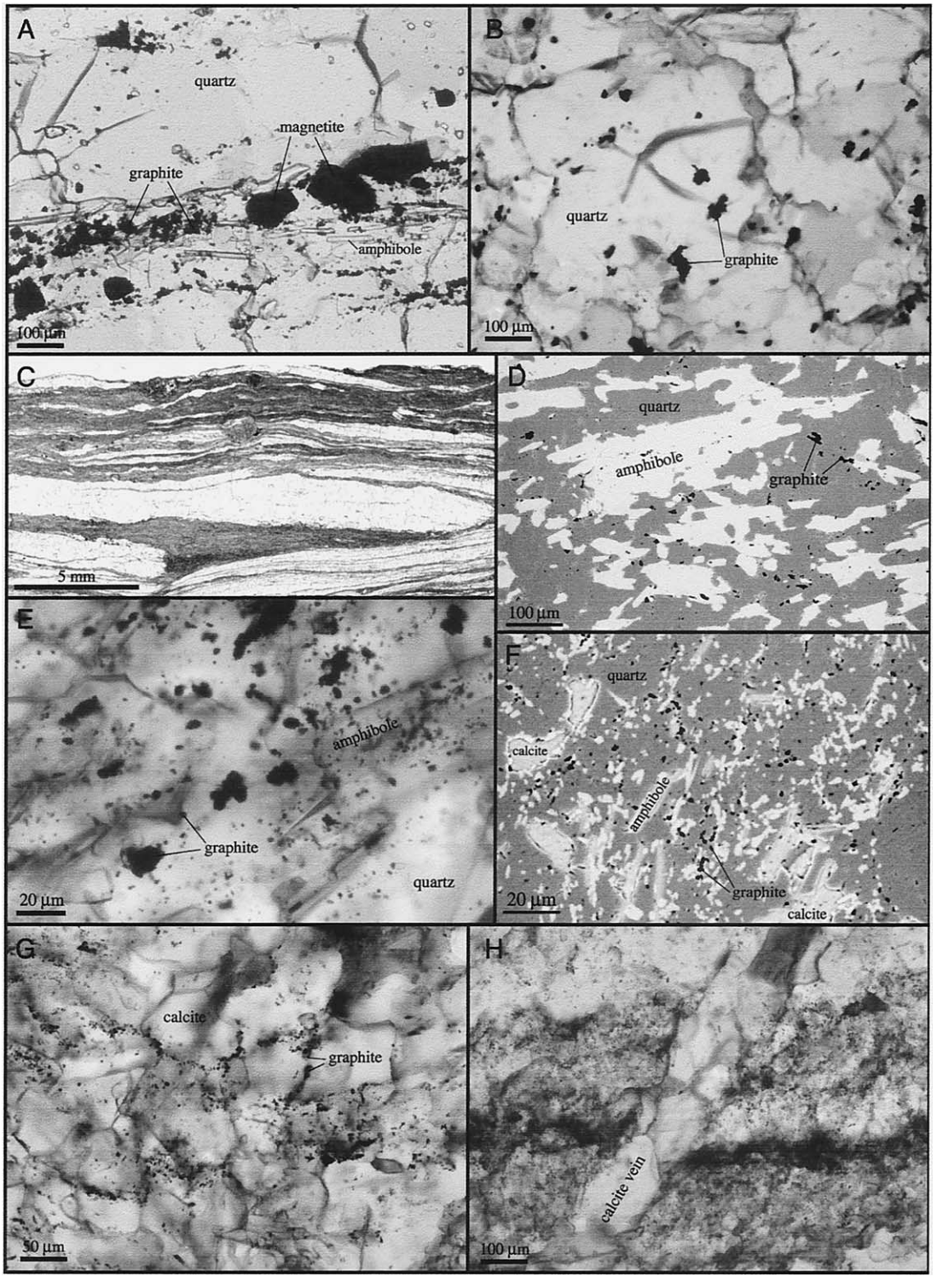

Fig. 2. Photomicrographs (A–C, E, G, and H) and backscattered electron images (D and F) showing the distribution of graphite in metasediments and carbonate rocks. (A) Metachert sample K424 showing the occurrence of graphite concentrated on a magnetite-rich layer. (B) Metachert sample K426 showing relatively coarse-grained (up to 30 μm) globular graphite mostly enclosed within quartz. (C) Muddy metachert sample K612 from Zone C showing conspicuous banding composed of quartz (white) and grunerite (gray) along with a garnet porphyroblast (upper middle). (D and E) Muddy metachert sample K244 from Zone D showing relatively coarse-grained graphite disseminated uniformly. (F) Carbonate rock sample K479 showing very fine-grained ($\sim$1 μm) graphite surrounded by quartz (black dots). (G) Carbonate rock sample K451 showing the distribution of graphite mostly on grain boundaries of calcite and quartz. (H) Psammitic schist sample K484 showing the distribution of graphite (black). Note that the graphite occurs mostly along the grain boundaries of quartz but not in a secondary calcite vein.

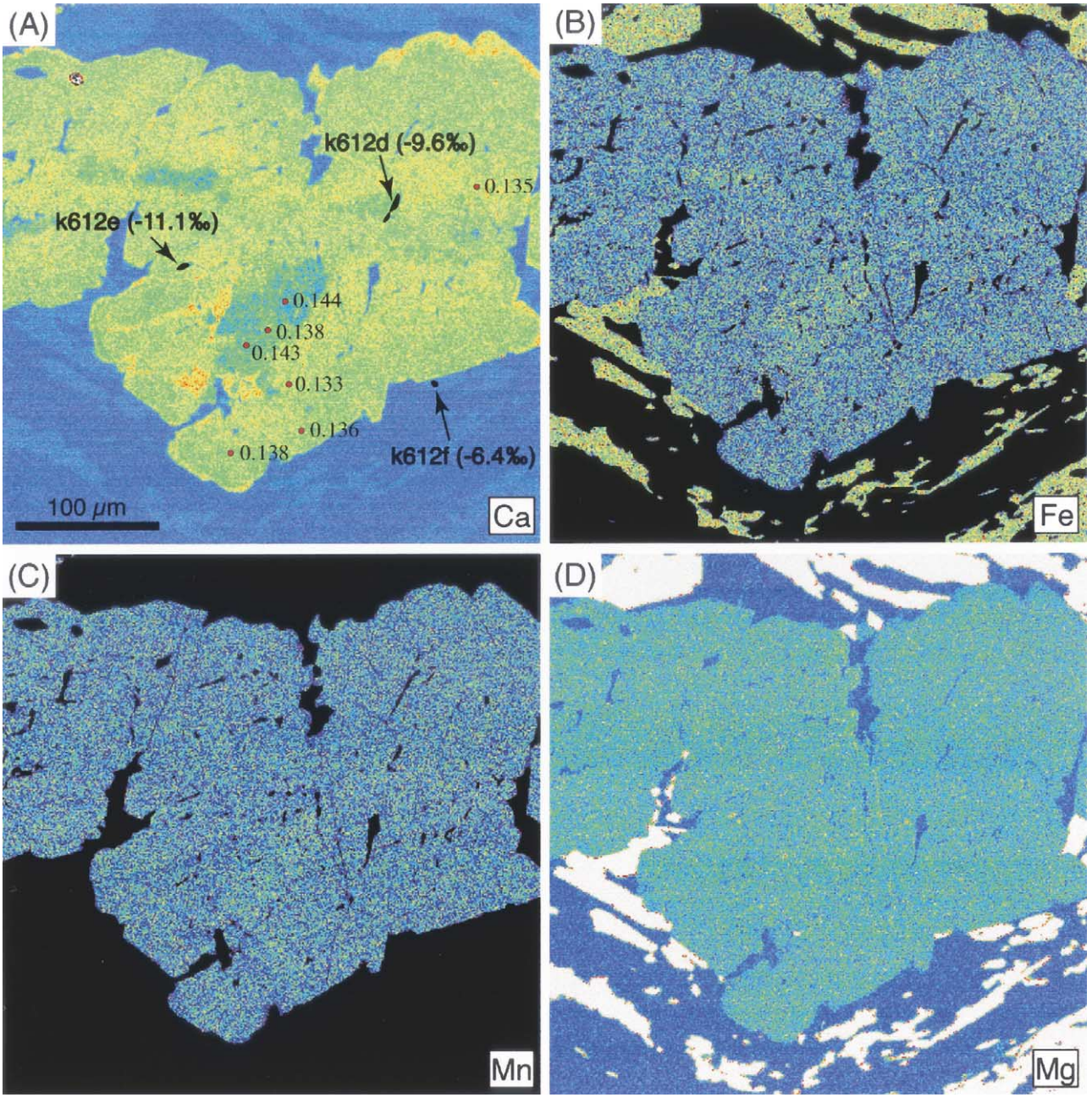

Fig. 3. Compositional variation in Ca, Fe, Mn, and Mg within a garnet porphyroblast in K612. The brighter part is more enriched in respective elements. Arrows in (A) indicate graphite globules exposed on the surface of the thin section. Values in parentheses indicate their $\delta^{13}C$ values (see Table 2). Red dots and values on their right-hand side indicate the ratios of spessartine component of garnet. Scale bar in (A) shows 100 μm for all figures.

ever, secondary C^- ions are only emitted from the graphite because the surrounding silica and silicate were C-free. Where the targets were smaller than the primary beam size, the emitted secondary carbon ion intensities often changed during the analysis. This is because the irradiated target area changes by sputtering. The variations of the $^{12}C^-$ intensities for the standard and unknown samples were less than 25% of the average intensity.

The analyses were performed in six independent analytical sessions (see Table 2). The degree of variation in instrumental mass fractionation was within ±3‰ among independent analytical sessions. The variation was ±1 to ±3‰ in each analytical session (Table 2). The variation among independent analytical sessions may be due to small conditional changes in the instrumental setting. Therefore, for precise analysis, the instrumental mass fractionation was corrected using the fractionation factor determined in each session. The results of the in-situ graphite analyses are listed in Table 2.

Table 2. Summary of carbon isotopic compositions of Isua graphite.

Standard	$F^{13}C$[a] (‰)	Graphite	$\delta^{13}C_{PDB}$[b] $\pm$ σ_m (‰)	Occurrence[c]	Host rock
8/27/98 session					
		k612a	−14.3 ± 3.0	Qtz-Amp grain boundary	K612
USGS24	−23.7 ± 2.9	k612b	−10.5 ± 3.0	in Qtz	K612
		k612c	−9.5 ± 3.0	Amp-Amp grain boundary	K612
		k612d	−9.6 ± 3.0	in Grt	K612
		k612e	−11.1 ± 3.0	in Grt	K612
		k612f	−6.4 ± 3.0	in Amp	K612
		k612h	−1.9 ± 3.0	Qtz-Qtz grain boundary	K612
		k612i	−9.6 ± 3.0	Amp-Qtz grain boundary	K612
8/28/98 session					
		k451a	−2.7 ± 2.1	Qtz-Amp grain boundary	K451
USGS24	−24.3 ± 2.0	k451i	−3.1 ± 2.1	Qtz-Qtz grain boundary	K451
		k612j	−1.7 ± 2.2	Qtz-Amp grain boundary	K612
9/10/98 session					
		k244a	−5.2 ± 1.4	in Amp	K244
USGS24	−22.3 ± 1.3	k244b	−7.0 ± 1.4	in Qtz	K244
		k244c	−6.6 ± 1.5	in Qtz	K244
		k244d	−4.5 ± 1.4	in Amp	K244
		k485a	−17.5 ± 1.4	Qtz-Qtz grain boundary	K485
		k485b	−14.6 ± 1.4	Qtz-Qtz grain boundary	K485
		k485c	−14.0 ± 1.4	Qtz-Amp grain boundary	K485
		k485d	−16.5 ± 1.4	Qtz-Amp grain boundary	K485
9/11/98 session					
		k479a	−6.9 ± 1.5	Qtz-Amp grain boundary	K479
USGS24	−25.3 ± 1.4	k479b	−4.2 ± 1.7	in Qtz	K479
		k479c	−6.9 ± 1.6	Qtz-Amp grain boundary	K479
		k479d	−7.4 ± 1.5	in Qtz	K479
10/13/98 session					
		612a	1.8 ± 2.5	in Qtz	K612
USGS24	−27.0 ± 2.4	612b	−15.3 ± 2.5	in Grt with Po	K612
		612c	−17.3 ± 2.5	in Grt with Po	K612
		612d	−11.5 ± 2.4	in Grt	K612
		612e	−12.9 ± 2.5	in Grt with Po	K612
		612f	−0.5 ± 2.5	in Qtz	K612
		612g	−8.3 ± 2.5	Qtz-Amp grain boundary	K612
		426a	−14.5 ± 2.5	in Qtz	K426
		426b	−15.5 ± 2.5	Qtz-Qtz grain boundary	K426
11/12/98 session					
		424a	−12.5 ± 2.2	Qtz-Qtz grain boundary	K424
USGS24	−21.6 ± 2.1	424b	−7.6 ± 2.2	Qtz-Amp grain boundary	K424
		424c	−10.2 ± 2.2	in Mag	K424
		424d	−12.0 ± 2.4	Qtz-Qtz grain boundary	K424
		424e	−15.1 ± 2.2	in Qtz	K424
		426c	−14.4 ± 2.2	in Qtz	K426
		426e	−9.1 ± 2.3	Qtz-Qtz grain boundary	K426
		484a	−13.4 ± 2.2	in Qtz	K484
		484b	−16.1 ± 2.3	in Qtz	K484
		484c	−10.5 ± 2.9	Amp-Amp grain boundary	K484
		463A	−9.6 ± 2.3	Qtz-Amp grain boundary	K463
		463B	−12.6 ± 2.2	in Qtz	K463
		463C	−9.2 ± 2.2	Qtz-Amp grain boundary	K463

[a] Instrumental mass fractionation factors relative to $^{13}C/^{12}C$ isotope ratio of PDB ($^{12}C/^{13}C$ = 88.99; Craig, 1957). Errors denote standard deviation of reproducibility among several independent analyses during the day.

[b] Corrected $\delta^{13}C$ values relative to PDB. Errors, σ_m, are calculated from error propagation of the estimated standard deviations of the mean for sample and standard deviation of reproducibility for standard of the day. The standard deviations of the mean for sample is estimated by statistical fluctuation of secondary ions.

[c] Minerals: Qtz = quartz; Amp = amphibole; Grt = garnet; Po = pyrrhotite; Mag = magnetite.

5. RESULTS

$\delta^{13}C$ values of carbonate ($\delta^{13}C_{carb}$) in seven hand-specimens range from −4 to +2‰ (Table 3). The $\delta^{13}C_{carb}$ values fall within the range of previously reported carbonate carbon from the Isua supracrustal belt (−8 to +5‰, average −2‰; Naraoka et al., 1996; Oehler and Smith, 1977; Perry and Ahmad, 1977; Schidlowski et al., 1979; Schidlowski et al., 1983; Shimoyama and Matsubaya, 1992).

Table 3. Concentrations and the $\delta^{13}C$ values of carbonate in graphite-bearing rocks.

Sample no.	Zone	CO_2 content (wt%)	$\delta^{13}C_{carb}$ (‰)
Metachert			
K424	B	0.18	−4.09
K426	B	—[a]	—
Muddy metachert			
K463	B	0.24	−2.37
K612	C	—[a]	—
K244	D	0.66	+1.69
Psammitic schist			
K484	B	4.40	−4.12
K485	B	0.60	−4.02
Carbonate rock			
K479	B	2.96	−3.17
K451	B	5.46	−1.25

[a] Below the detection limit (≈0.04 wt.%: CO_2 content).

The $\delta^{13}C$ values of graphite ($\delta^{13}C_{graph}$) in this study are –18 to +2‰ (Table 2). The $\delta^{13}C_{graph}$ values of all but three of these 45 graphite globules fall within the range reported for whole-rock reduced carbon from the Isua belt (–28 to −6‰, average –15‰; Hayes et al., 1983; Naraoka et al., 1996; Oehler and Smith, 1977; Perry and Ahmad, 1977; Rosing, 1999; Schidlowski et al., 1979; Shimoyama and Matsubaya, 1992). However, large ^{13}C-depletion below –20‰ was not observed for the graphite in this study (Fig. 4). It is unknown what makes the discrepancy of the isotopic variations between minute graphite globules (–18 to +2‰; this study) and the whole-rock reduced carbon (–28 to −6‰; Fig. 4). The whole-rock reduced carbon was possibly derived both from graphite and from other reduced carbon components besides graphite (Oehler and Smith, 1977; Rosing, 1999). Thus, the presence of ^{13}C-depleted non-graphitic reduced carbon can not be ruled out.

Variation of $\delta^{13}C_{graph}$ values of graphite globules among a single hand specimen is 20‰ for K612 and falls within 8‰ for others. Such variations exist within a small (6 mm × 6 mm) area in thin sections. Thus, the Isua graphite in some metasediments is isotopically heterogeneous at a scale of a millimeter.

6. DISCUSSION

The variation of $\delta^{13}C$ values of the Isua graphite (–28 to −6‰) has been interpreted as a result of metamorphic modification, which enriched the graphite in ^{13}C (Hayes et al., 1983; Schidlowski et al., 1979). On the other hand, Rayleigh-type degassing of CO_2 during metamorphism could have depleted the graphite in ^{13}C (Eiler et al., 1997).

To evaluate the direction and magnitude of the metamorphic effect on the carbon isotopic composition of the Isua graphite, we will discuss (1) the recrystallization process of graphite-bearing minerals in three different metamorphic zones (i.e., Zones B, C, and D), and (2) the isotopic distribution of graphite globules in the three zones. Based on these evaluations, we will finally discuss the origin of the Isua graphite.

In the following section, we concentrate our discussion on the carbon isotopic composition of graphite and carbonate in metasediments except for carbonate rocks, because the carbonate rocks are largely of secondary metasomatic origin (Rose et al., 1996; Rosing et al., 1996).

6.1. Isotopic Variation of Graphite Globules and Their Mode of Occurrence

6.1.1. Zone B (epidote-amphibolite facies)

$\delta^{13}C_{graph}$ values of graphite globules in Zone B vary from –18 to −8‰ (Fig. 5). Isotopic fractionation between carbonate and graphite ($\Delta_{carb\text{-}graph} = \delta^{13}C_{carb} - \delta^{13}C_{graph}$) varies from 4 to 13‰ (Fig. 6). The results clearly show that graphite globules

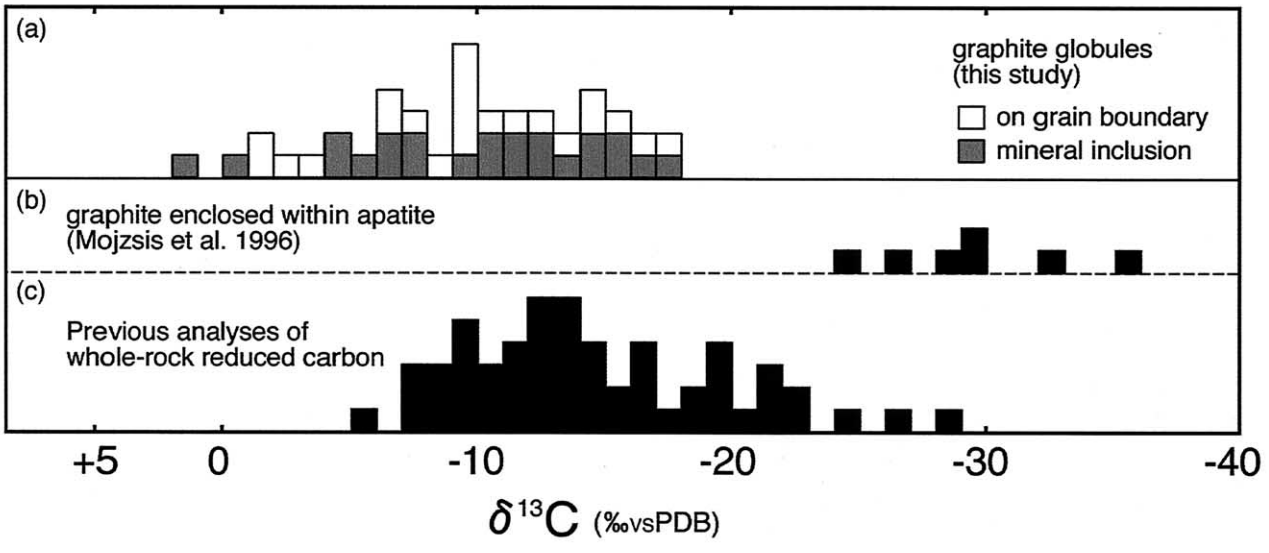

Fig. 4. Distributions of $\delta^{13}C$ values of graphite globules (a; this study), apatite-hosted graphite (b; Mojzsis et al., 1996), and whole-rock reduced carbon (c; Hayes et al., 1983; Naraoka et al., 1996; Oehler and Smith, 1977; Perry and Ahmad, 1977; Rosing, 1999; Schidlowski et al., 1979; Shimoyama and Matsubaya, 1992) from the Isua supracrustal belt.

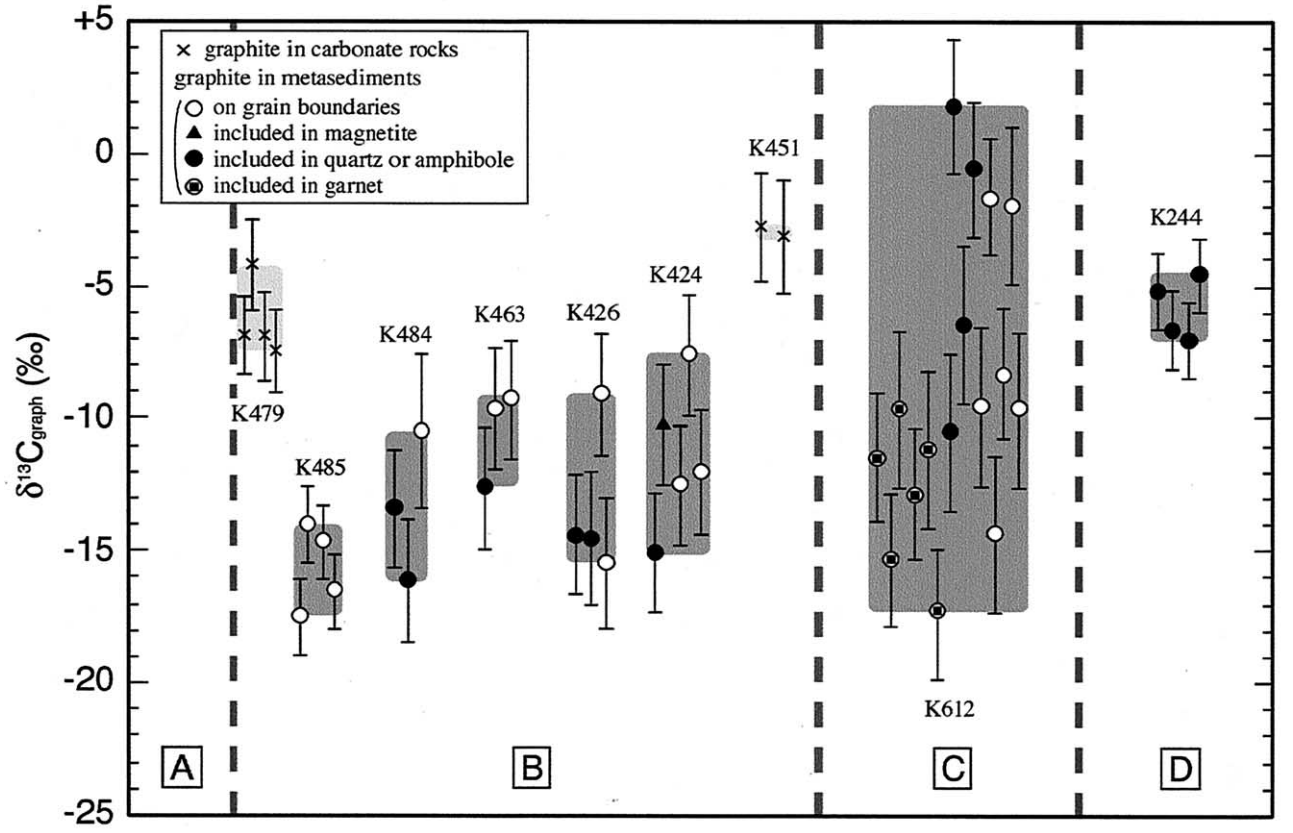

Fig. 5. Carbon isotopic compositions of minute graphite globules. "A" to "D" show the metamorphic grade, based on mineral parageneses and compositions of metabasites and metapelites (Hayashi et al., 2000).

in Zone B are not in isotopic equilibrium with each other, and suggest that the isotopic distribution was not reset completely by the metamorphism.

In Zone B, graphite globules exist (1) in quartz, amphibole, and magnetite, and (2) on grain boundaries between these minerals. The graphite globules are uniformly scattered in the metasediments and are absent in crosscutting veins such as quartz and calcite (Fig. 2A, B, G, and H). This mode of occurrence indicates that some graphite was trapped by quartz, amphibole, and magnetite during the recrystallization process, and that other graphite was accumulated on their mutual grain boundaries (Fig. 2G).

According to Hayashi et al. (2000), Zone B corresponds to the epidote-amphibolite facies. Metamorphic temperature of Zone B estimated from garnet-biotite Fe-Mg exchange thermometry is ~400 to 450 °C. Equilibrium carbon isotopic fractionation between carbonate and graphite at 400 and 500 °C is 8 and 6‰, respectively (Chacko et al., 1991). Thus, about half the graphite in Zone B, which shows the smallest fractionation ($\Delta_{carb\text{-}graph}$ = 4 ~ 8‰), is apparently in equilibrium with carbonate carbon of their host rocks at epidote-amphibolite facies grade (Fig. 6).

The graphite globules with equilibrium fractionations ($\Delta_{carb\text{-}graph}$ = 4 ~ 8‰) occur only on grain boundaries (Fig. 6). Although they are not in contact with carbonate, this grain boundary graphite probably underwent fluid exchange during metamorphism. The isotopic equilibrium between the graphite and carbonate was probably achieved through a CO_2-rich metamorphic fluid.

Other graphite globules show larger fractionations ($\Delta_{carb\text{-}graph} > 9‰$), are depleted in ^{13}C, and occur not only on grain boundaries but also as inclusions in quartz crystals (Fig. 6). Within a single hand specimen, quartz-hosted graphite globules (K484, K463, and K424, Fig. 6) show a few permil larger fractionation relative to those on grain boundaries with the smallest fractionation ($\Delta_{carb\text{-}graph}$ = 4 ~ 8‰). This relationship may result from the recrystallized quartz preventing isotopic exchange between graphite inclusions and CO_2-rich fluid; this is the so-called "armoring effect" (Wada and Suzuki, 1982).

In addition, some graphite globules even on grain boundaries have a large fractionation above 9‰ (K485). Graphite in K485 shows a larger fractionation ($\Delta_{carb\text{-}graph}$ = –13 ~ –10‰; Fig. 6) than graphite in K484, which has similar mineralogy and similar grain size to K485 (Table 1). The lithological similarity between these samples suggests that the degree of the armoring effect was probably the same. However, carbonate concentration of K485 (CO_2, 0.60 wt.%; Table 3) is about one-tenth of that in K484 (CO_2, 4.40 wt.%; Table 3). This suggests that scarcity of carbonate as a carbon partner resulted in incomplete isotopic reequilibration.

Consequently, the above-mentioned carbon isotopic distributions indicate that the $\delta^{13}C_{graph}$ values in Zone B were increased toward isotopic equilibrium with carbonate, but some graphite globules were not completely reequilibrated and main-

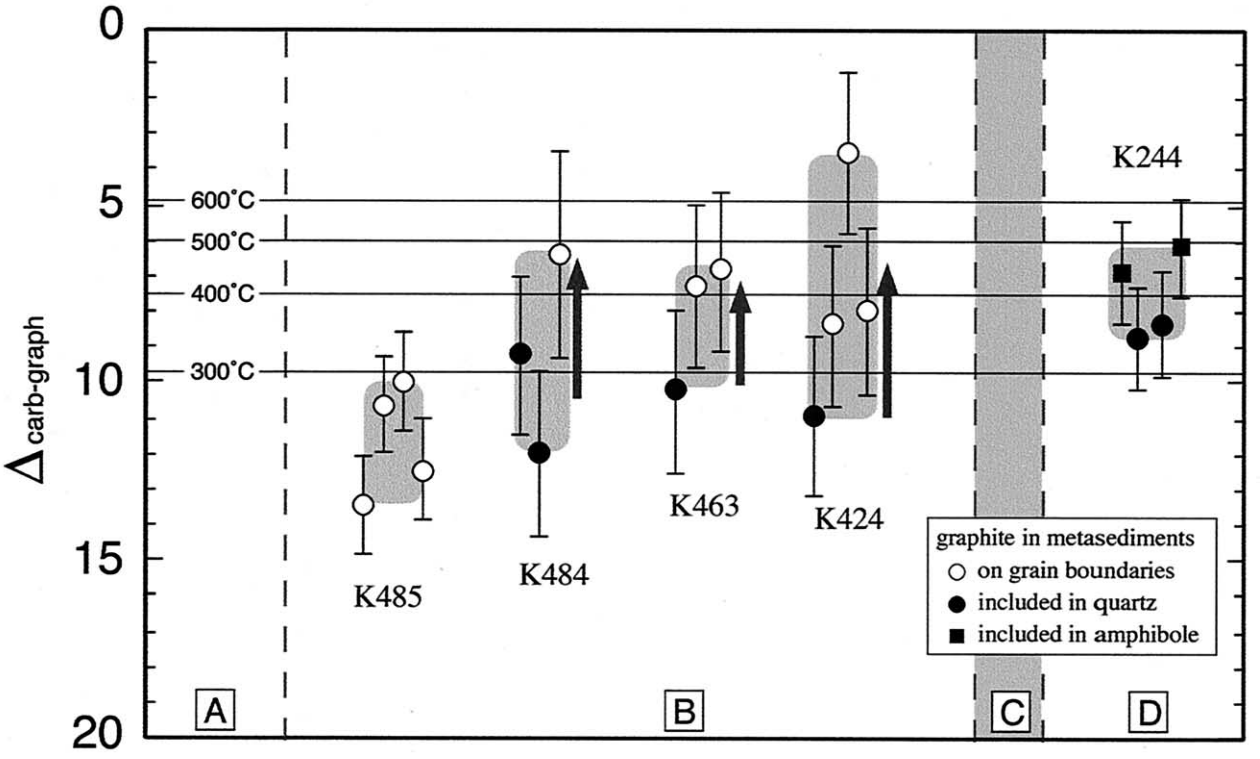

Fig. 6. Isotopic fractionations between carbonate and minute graphite globule ($\Delta_{carb\text{-}graph} = \delta^{13}C_{carb} - \delta^{13}C_{graph}$). Horizontal lines indicate the equilibrium fractionations at 300, 400, 500, and 600 °C (Chacko et al., 1991). "A" to "D" show the metamorphic grade (Hayashi et al., 2000). Arrows indicate hypothetical trend of carbon isotopic modification during prograde metamorphism.

tain earlier ^{13}C-depleted signatures before the epidote-amphibolite facies metamorphism. The escape from isotopic reequilibration was probably caused mainly by the armoring effect and additionally by lack of a carbon partner (i.e., carbonate within the host rock or fluid).

6.1.2. Zone C (lower amphibolite facies)

$\delta^{13}C_{graph}$ values of graphite globules in Zone C (K612) vary from –17 to +2‰ (Fig. 5). Isotopic fractionation between carbonate and graphite is unknown, because the sample does not contain carbonate (Tables 1 and 3). However, the isotopic heterogeneity of 19‰ within a single hand-specimen indicates that graphite globules are not in isotopic equilibrium with each other.

In Zone C (K612), graphite globules exist (1) in garnet, (2) in amphibole and quartz, and (3) on grain boundaries between these minerals. Graphite-bearing garnet shows chemical zoning with decreasing Mn and Fe, and increasing Ca from core to rim (Fig. 3). Graphite exists both in core and rim. Mn-depletion in the rim of the garnet suggests that it grew during prograde metamorphism. Therefore, the garnet crystal trapped graphite at an earlier stage before amphibolite facies metamorphism. According to Hayashi et al. (2000), garnet is absent in Zone A metasediments, but becomes stable from the northeastern side of Zone B in Fe-rich pelitic rocks (e.g., K426). This is consistent with the early growth of the garnet cores. Ca-enrichment in the rim of the garnet probably resulted from the decomposition of calcite (Hayashi et al., 2000). Graphite globules in garnet core were probably isolated from released CO_2 by decomposed calcite. On the other hand, amphibole and quartz in K612 show more conspicuous banding than those in Zone B (Fig. 2C). The grain size of amphiboles is about ten times larger than those in Zone B. These textures indicate that amphibole and quartz were recrystallized at peak metamorphism in Zone C. Graphite globules were partly enclosed within amphibole and quartz during the amphibolite facies metamorphism and were partly extruded onto their grain boundaries.

$\delta^{13}C_{graph}$ values of graphite globules in quartz and amphibole and on their grain boundaries vary from –14 to +2‰. On the other hand, $\delta^{13}C_{graph}$ values of graphite globules within garnet have a narrower range of –17 to –9‰ and are more depleted in ^{13}C by 7‰ on average than those outside garnet. Similar to the discussion in Zone B, these isotopic distributions also suggest that the $\delta^{13}C_{graph}$ values of Isua graphite were increased during prograde metamorphism. It is plausible that released CO_2 from carbonate enhanced the isotopic exchange and increased the $\delta^{13}C$ graph values of some graphite outside garnet toward reequilibration, whereas the graphite within early-crystallized garnet escaped from the reequilibration and maintained an earlier ^{13}C-depleted signature before amphibolite facies metamorphism. This is consistent with the fact that the variation of $\delta^{13}C_{graph}$ values of the garnet-hosted graphite in K612 (–17 ~ –10‰) and their average (–13‰) are almost identical to those of the graphite in less metamorphosed Zone

B (–18 ~ –8‰; average –13‰). On the other hand, ^{13}C-enriched graphites ($\delta^{13}C > -10$‰) in K612 occur on grain boundaries as well as inclusions in quartz and amphibole. This characteristic isotopic distribution is dissimilar to that in Zone B. The distribution was possibly resulted from recrystallization of quartz and amphibole at peak metamophism in Zone C and entrapment of graphite in isotopic equilibrium.

6.1.3. Zone D (upper amphibolite facies)

$\delta^{13}C_{graph}$ values of graphite globules in Zone D are from –7 to –5‰ (Fig. 5). Isotopic fractionation between carbonate and graphite ($\Delta_{carb\text{-}graph}$) is from 6 to 8‰ (Fig. 6).

According to Hayashi et al. (2000), Zone D corresponds to the upper amphibolite facies. Metamorphic temperature of Zone D estimated from garnet-biotite Fe-Mg exchange thermometry is ~500 to 600 °C. Equilibrium carbon isotopic fractionation between carbonate and graphite at 500 and 600 °C is 6 and 5‰, respectively (Chacko et al., 1991). Thus, all four graphite globules in Zone D are considered to be in isotopic equilibrium with carbonate carbon of their host rock at the upper amphibolite facies metamorphism.

6.2. Isotopic Modification of Isua Graphite

On the basis of the above discussions, we conclude that regional metamorphism increased the $\delta^{13}C$ values of Isua graphite by more than 5‰. The main cause of the ^{13}C-enrichment is attributed to isotopic exchange with carbonate probably mediated by a pervasive CO_2-rich metamorphic fluid.

As the metamorphic grade increases from epidote-amphibolite facies (Zone B) to upper amphibolite facies (Zone D), the maximum $\delta^{13}C_{graph}$ values of graphite globules increase from –14 to –5‰ (Fig. 5). This trend is consistent with the inferred ^{13}C-enrichment of Isua graphite toward isotopic reequilibration. Similar increases of $\delta^{13}C$ values of sedimentary organic carbon toward isotopic reequilibrium were observed in a progressively metamorphosed section in the Swiss Alps (Hoefs and Frey, 1976), and in contact metamorphic aureoles in the Kasuga area, Japan (Wada and Suzuki, 1982), in the Tudor gabbro, Ontario, Canada (Dunn and Valley, 1992), and in the Adirondack Mountains, New York (Kitchen and Valley, 1995).

Another possibility of the cause of ^{13}C-enrichment of Isua graphite is selective loss of ^{12}C through devolatilization of graphite. This process may also have affected the isotopic composition of Isua graphite, in addition to the isotope exchange. However, the magnitude of this effect may have been negligible, because the minimum fractionation between graphite and carbonate (Fig. 6) from Zones B to D is consistent with the equilibrium fractionation at ~400 to 550 °C.

6.3. Origin of Isua Graphite

Our data support the earlier hypothesis by Schidlowski et al. (1979) and Hayes et al. (1983) that the isotopic exchange between reduced carbon and carbonate carbon during regional metamorphism caused an increase of the $\delta^{13}C$ values of Isua graphite. An important implication of this model is that the minimum $\delta^{13}C$ value (–28‰) for the previously reported whole-rock reduced carbon reflects a primary biologic signature. However, none of the graphite in this study has $\delta^{13}C$ values below –20‰ (Fig. 6). We conclude that the primary $\delta^{13}C$ values of Isua graphite were the same as or below the –18‰ of the lowest value in our study. The reduced carbon with $\delta^{13}C$ value above ~–15‰ can be produced both by a biologic carbon fixation (Preuss et al., 1989) and by an inorganic reaction such as decomposition of siderite (Perry and Ahmad, 1977). Thus, an abiological origin of most Isua graphite (>~–15‰) cannot be ruled out. If the original $\delta^{13}C$ value of all the Isua graphite was as low as ~–25‰, the isotopic modification during regional metamorphism would have been so extensive that most primary carbon isotopic signatures would have been obliterated. Unfortunately, despite thorough observation, no graphite has yet been found from the least metamorphosed area, Zone A. The graphite in our least metamorphosed specimens may preserve an earlier isotopic signature, but it is necessary to determine the isotopic composition of graphite from Zone A in a further study.

Notwithstanding, Mojzsis et al. (1996) indeed reported very low $\delta^{13}C$ values (average –30‰) of graphite armored by apatite from the Isua supracrustal belt. On the basis of the above discussion, isotopic exchange under metamorphic conditions controlled the increase of the $\delta^{13}C$ values of the Isua graphite. Thus, such a large ^{13}C-depletion of Isua graphite should be an earlier signature before epidote-amphibolite facies metamorphism and is probably close to original signature. Hence, it is plausible that at least some highly ^{13}C-depleted Isua graphite was originally produced via biologic carbon fixation. The minimum $\delta^{13}C$ value (−28‰; Hayes et al., 1983) for the reduced carbon in the rocks of the Isua belt may reflect a primary biologic signature. This supports the existence of life at Isua time (ca. 3.8 Ga).

7. CONCLUSIONS

The characteristic distributions of isotopically heterogeneous graphite globules indicate that the $\delta^{13}C$ values of Isua graphite were increased more than 5‰ by isotopic exchange with carbonate or probably a CO_2-rich fluid above 400°C. Some graphite enclosed within noncarbonate minerals escaped from isotopic reequilibration and preserve their earlier ^{13}C-depleted signature ($\delta^{13}C < \sim -15$‰) before epidote-amphibolite grade metamorphism. If the carbon isotopic exchange during metamorphism controlled the ^{13}C-enrichment of Isua graphite, the previously reported significant ^{13}C-depletion of at least some Isua graphite (up to –30‰; Mojzsis et al., 1996) should be a premetamorphic signature, which was essentially produced by biologic carbon fixation. This supports the hypothesis that life on Earth already existed at Isua time (ca. 3.8 Ga).

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