Hydrothermal syntheses of graphite from bituminous coal at 0.5-5 kbar water vapor pressure and 300-600°C

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Hydrothermal experiments were carried out to synthesize graphite from bituminous coal at water vapor pressure of 0.5-5 kbar using 1% Li_2CO_3 or 2% Ni metal as a catalyst. Oxygen fugacities were controlled by hematite+magnetite (HM), nickel+nickel oxide (NNO) or quartz+fayalite+magnetite (QFM) buffers during six runs at 1 kbar. Graphite crystallized from bituminous coal at about 375°C, 0.5 kbar; 405°C, 1 kbar; 390°C, 2 kbar and 320°C, 5 kbar under uncontrolled f_{O_2} conditions. The transition boundary from bituminous coal to graphite has a positive inclination below 1 kbar and a negative inclination over 1 kbar under uncontrolled f_{O_2} conditions. The negative inclination of the transition boundary was probably due to the experiments that the oxygen fugacity was incompletely buffered by the escape of hydrogen gas from the system through the Ag-Pd capsule-wall. Under the f_{O_2} controlled conditions by NNO buffers, graphite crystallized between 400°C and 420°C at 1 kbar. When f_{O_2} were controlled by NNO or QFM, the crystallinity of graphite increased abruptly to reach a fully-ordered state at 420°C.

The experimental results were compared with graphitization of carbonaceous material in black schists from some metamorphic districts, and also with oxygen isotope geothermometry. In natural systems, graphitization depends on metamorphic temperature and oxygen fugacity, but not on metamorphic pressure to a great extent.

Introduction

Carbonaceous materials in sedimentary and meta-sedimentary rocks are mainly composed of carbon, oxygen and hydrogen. They change to graphite through a process creating an intermediate coaly product during progressive diagenesis and metamorphism. This successive phenomenon has been called coalification in part and graphitization in other part (e.g. French, 1964; Griffin, 1967; Izawa, 1968; Landis, 1971; Grew, 1974; Diessel *et al.*, 1978). Graphitization depends on temperature, because the crystallinity of carbonaceous material gradually changes with increasing temperature (Itaya, 1981; Tagiri, 1981). Buseck and

Bo-Jun (1985) reported the graphite-crystallizing mechanism in metamorphic rocks by means of the high resolution electron microscopy.

The synthesis of graphite has been ordinarily done at very high temperatures above 1300°C for industrial uses. On the other hand, only one study of French and Rosenberg (1965) has made from the viewpoint of geological significances. However, the experiments by French and Rosenberg (1965) were to determine the stability field of siderite in CO_2 atmosphere at 350-500°C, and not to examine graphitization. They made a disordered graphite at about 450°C, 1 kbar through the breakdown reaction of siderite. It is necessary for an advanced study of graphitization to

examine the transformation of coal to graphite.

The degrees of coalification and graphitization has been believed to be strongly influenced by duration of heating (e.g. Hood *et al.*, 1975). We intended to show how the duration of heating influences the degree of graphitization. Our experimental results clearly indicate, however, that the degree of graphitization must be controlled strongly by temperature and f_{O_2} conditions.

Reaction relation in the graphitization

Crystallization of graphite probably takes place through at least three distinct types of reactions:

M represents a metal.

Reaction (1) proceeds easily at temperatures above 1300°C. Industrial carbon black is made from carbonaceous material at those high temperatures. No one has synthesized graphite through this reaction at much lower temperatures, such as several hundred degree C. Direct crystallization of graphite from amorphous carbon requires an activation energy of about 60–100 kcal/mol (Tensner and Rafal'kes, 1952; Murphy *et al.*, 1985; Hirt and Palmer, 1963; Hirai and Yajima, 1967), which corresponds to the activation energy of hydrocarbon dehydrogenation. Extrapolating the formation rate constant (Tensner and Rafal'kes, 1952) from 800° to 450°C provides a value of $10E-30$ g/cm²/min, an extremely small rate of production of graphite during metamorphism within the earth crust.

Reaction (2) has been investigated by many authors (e.g. Osetzky, 1974; Baird, 1977). The activation energy of reaction (2) is

relatively low, e.g. 16 kcal/mol at 500°C in the presence of Ni₃C (Baird, 1977). Baird (1977) produced turbostratic graphite ($d_{002}=3.36$) on Ni foils by pyrolysis of propylene at 380°C and a pressure of 50 mmHg. This order of temperatures is possible in natural graphitization. However, metal carbides do not appear to be abundant in natural rocks. Reaction (2) may not represent the dominant process of graphitization in nature.

Reaction (3) apparently proceeds under the conditions of low oxygen fugacity, for example $f_{O_2}=10E-25$ at 460°C, 1 kbar (French and Rosenberg, 1965). Some types of metals and carbonates added in aqueous fluid evidently catalyze this reaction even at low temperatures below 500°C (Tomita and Tamai, 1972; McKee, 1974; Macak *et al.*, 1978). In the system with 4.5% Ni metal or 1% Li₂CO₃, the activation energy decreases from 88 to 25 kcal/mol for Ni at 700–1000°C (Tomita *et al.*, 1974) and to 37 kcal/mol for Li₂CO₃ at 750–900°C (McKee and Chatterji, 1978). Reaction (3) seems to be one of the most probable processes for the formation of graphite in low-grade metamorphic and diagenetic environments, because of the widespread abundance (at trace levels) of such catalysts in pelitic strata (Krauskopf, 1967, p. 639).

It is still very difficult, however, to specify the reaction relation of graphitization in nature. As coal usually contains a great amount of hydrogen and oxygen, for example, graphite may be formed by the following reaction with the release of various kinds of gas.

This reaction is similar to reaction (1) from the viewpoint that graphite crystallizes directly from solid carbonaceous material.

Experimental methods

Externally-heated cold-seal pressure vessels were used in this study. The H_2O pressure medium was provided by an external hydraulic pumping system. The maximum fluctuation of temperature and pressure was 10°C and 50 bars in the experiments at 0.5–2 kb, and 20°C and 100 bars in the experiments at 5 kb, respectively. Ag70–Pd30 single capsules were used in the fo_2 uncontrolled experiments. In the fo_2 controlled experiments, sealed tubes of Ag and Ag75–Pd25 were used for the outer and inner capsules, respectively.

The method proposed by Tagiri (1981) was employed for the calculation of the crystallinity of carbonaceous material. The starting material was bituminous coal from the Pittsburgh Formation (Carboniferous) of Pennsylvania, U. S.A. It was ground in an agate mortar together with a catalyst as described below, and its crystallinity was checked by an X-ray powder diffractometer. The d_{002} and the

crystallite size ($L_c(002)$) of turbostratic layers of bituminous coal are $3.71 \text{ \AA}$ and $10 \text{ \AA}$, respectively. This starting material does not show any sharp diffraction peak except for very weak diffractions of kaolinite. The chemical composition of the bituminous coal material is as follows; C=80.84%, H=4.54%, O=13.55%, others=1.07% (wt% of dry basis).

We selected two kinds of catalysts (Li_2CO_3 and Ni metal) for the experiments, following Mckee (1974) and Mckee and Chatterji (1978). Starting charges contained about 1 wt% of Li_2CO_3 or about 2 wt% of Ni metal. These concentrations in the starting materials are geologically meaningful values, because Ni: C and Li: C ratio are similar to the ratio shown by an average shale (Krauskopf, 1967, P. 639), although it is not clear whether these catalysts are present as Ni metal or as Li_2CO_3 in such rocks. Charges were enclosed in small, sealed Ag–Pd capsules together with an adequate amount (about 50 wt%) of distilled water. During these single sealed-tube and fo_2 un-

Fig. 1. Crystallinity and nomenclature of carbonaceous material.

controlled experiments which are not truly buffered owing to escape of hydrogen gas from the system through Ag-Pd capsule-wall, certain low f_{O_2} were established by the presence of graphite or carbonaceous material and vapor (French and Eugster, 1965).

Carbonaceous material can be classified in terms of d_{002} and $L_c(002)$ of the crystallites (Honda *et al.*, 1968; Tagiri, 1981) (Fig. 1) as follows; *Fully-ordered graphite* has a $d_{002} = 3.35\text{--}3.36$ Å and an $L_c(002) > 500$ Å, *disordered graphite* a $d_{002} = 3.35\text{--}3.43$ Å and an $L_c(002) = 30\text{--}500$ Å, and *coaly material* a $d_{002} > 3.43$ Å and an $L_c(002) < 30$ Å. Coaly material transforms gradually into fully-ordered graphite with increasing temperature and its crystallinity changes abruptly at $d_{002} = 3.37$ Å and $L_c(002) = 100$ Å (see Figs. 5 and 6 of Tagiri, 1981). We apply the terms *graphite* to carbon of $d_{002} = 3.35\text{--}3.37$ Å and $L_c(002) > 100$ Å.

Products

f_{O_2} uncontrolled experiments

Typical diffraction patterns of synthesized products are shown in Fig. 2. In the experiments with the catalyst Li_2CO_3 , Li_2C_2 appears only at temperatures above 470°C . This indicates that reaction (2) proceeded above 470°C . The starting material shows a diffraction peak for Li_2CO_3 , but the peak disappears at 300°C indicating that the catalyst Li_2CO_3 changed to Li metal and CO_2 . About 80% of the charge still remains as a coaly material after the run. Graphite precipitated on the capsule walls at temperatures above 600°C . At temperatures below 500°C , graphite crystallized in the main charge.

In the experiments with Ni metal, graphite was produced only at temperatures above 500°C . The catalytic activity of Ni metal is evidently lower than that of Li_2CO_3 , because nickel metal easily combines with sulfur in coal to form nickel sulfide (Ni_3S_2) (Fig. 2). How-

Fig. 2. Selected typical X-ray diffraction patterns of carbonaceous material (Cu $K\alpha$). gr, graphite.

ever, the crystallinity of the product in the experiment with Ni is nearly the same as that catalyzed by Li_2CO_3 (see Table 1). Ni_3C sometimes crystallized only at temperatures below 500°C .

In these experiments, coaly material gradually changes to disordered graphite just as in the graphitization process of the natural system (Tagiri, 1981). We could not obtain graphite in any uncatalyzed experiment between 300° and 600°C , at 1 kbar. In all catalyzed experiments, only about 3–9 percent of the products transformed to graphite, and most of the original carbonaceous material remained as coaly material, d_{002} and $L_c(002)$ of which is about 3.45 Å and about 20 Å respectively.

Graphitization has been thought to depend greatly on the duration of heating. We checked the role of the duration of heating in the graphitization process at 1 kbar (Figs. 3

Table 1. Selected results of f_{O_2} uncontrolled experiments

P(Kbar)	T(°C)	Time(hrs)	Catalyst	d_{002} (Å)	$L_c(002)$ (Å)
0.5	410	164	Li_2CO_3	3.36	271
0.5	400	164	Li_2CO_3	3.36	224
0.5	380	164	Li_2CO_3	3.37	111
0.5	360	164	Li_2CO_3	3.45	33
0.5	340	165	Li_2CO_3	3.62	12
0.5	320	165	Li_2CO_3	3.64	13
0.5	300	165	Li_2CO_3	3.70	12
1	600	168	Ni	3.36	856
1	600	168	Li_2CO_3	3.36	763
1	500	168	Li_2CO_3	3.36	304
1	500	672	Li_2CO_3	3.36	339
1	450	168	Li_2CO_3	3.37	238
1	410	168	Li_2CO_3	3.37	111
1	410	672	Li_2CO_3	3.37	114
1	400	168	Ni	3.42	68
1	400	672	Ni	3.42	58
1	400	168	Li_2CO_3	3.43	57
1	400	672	Li_2CO_3	3.41	63
1	350	672	Ni	3.48	24
1	350	336	Li_2CO_3	3.47	27
1	350	672	Li_2CO_3	3.48	23
1	300	672	Ni	3.59	14
1	300	672	Li_2CO_3	3.60	12
2	410	165	Li_2CO_3	3.36	238
2	400	165	Li_2CO_3	3.37	111
2	380	168	Li_2CO_3	3.38	62
2	370	165	Li_2CO_3	3.45	43
2	350	165	Li_2CO_3	3.52	23
5	400	168	Li_2CO_3	3.37	292
5	350	236	Li_2CO_3	3.37	171
5	325	167	Li_2CO_3	3.38	141
5	315	175	Li_2CO_3	3.53	17
5	300	164	Li_2CO_3	3.56	14

Table 2. f_{O_2} controlled experiments at 1 kbar for a duration of 1 week

Temp(°C)	buffers	d_{002} (Å)	$L_c(002)$ (Å)
400	HM	3.51	14
400	NNO	3.47	27
400	QFM	3.35	>1000
420	HM	3.50	31
420	NNO	3.35	>1000
420	QFM	3.35	>1000

and 4). Duration of heating clearly influenced graphitization in 1 month runs below 400°C, but is not so effective at higher temperature conditions above 410°C. Based on these experiments at above 350°C, we suppose that experimental product would reach to a fixed crystallinity for four weeks.

f_{O_2} controlled experiments

Oxygen fugacities were controlled by HM, NNO or QFM buffers at 1 kbar for one week. The starting material was the same as that in

Fig. 3. Relation between d_{002} and duration of heating at 1 kbar. The solid smooth curves show the reaction rate at each temperature.

Fig. 4. Relation between L_c (002) and duration of heating at 1 kbar. Symbols are the same as Fig. 3.

the f_{O_2} uncontrolled experiments, and 1% Li_2CO_3 was included as a catalyst. The results are listed in Table 2. Disordered graphite did not appear in the experiments using HM buffers at 400°C and 420°C. Under the NNO buffer conditions, graphite crystallized at 420°C but not at 400°C. However, the crystallinity ($L_c > 1000$ Å) of the product is quite different from those ($L_c = 100$ Å) of the f_{O_2} uncontrolled experiments and of disordered graphite ($L_c = 100$ Å) in metamorphic rocks. Fully-ordered graphite appeared at 400°C in the experiment using the QFM buffers. In contrast to the f_{O_2} uncontrolled experiments, the products of these experiments did not show a gradual increase of crystallinity.

Discussions

Grew (1974) and Itaya (1981) showed that graphite ($d_{002} = 3.37$ Å, $L_c(002) = 100-200$ Å) contains minor amounts of H and O, and that graphite loses H and O with increasing metamorphic temperature. These facts indi-

cate that the change of chemical composition from coaly material to fully-ordered graphite reflects the increase of crystallinity. However, we cannot specify any phase for the coaly material during reaction (4). Accordingly, the present transition boundary from coaly material to graphite must not be univariant. The curve of Fig. 5 will be represented by a narrow transition zone.

In the f_{O_2} uncontrolled experiments, we obtained a negative P-T slope for the decomposition boundary from coaly material to graphite at the pressure field higher than 1 kbar, even though degassing-type reactions usually possess positive P-T slopes at low pressures. Some possible reasons will be considered for this phenomenon. The first is the large compressibility of gas-products. It is well known that a degassing reaction has a negative slope at high pressures because of the large compressibility of gas (e.g. the stability field of amphiboles: Hariya *et al.*, 1974). The second is the expansion of the stability range of graphite

Fig. 5. Formation curve of graphite. Italic numbers are GD values.

in the f_{O_2} versus temperature field with increasing pressure (French and Eugster, 1965). The third is the mobility of gas components, especially of H_2 gas. The formation of graphite is intensely controlled by oxygen fugacity. In sealed capsule-experiments, oxygen fugacity is buffered incompletely by gas components and carbonaceous material, because of the escape of hydrogen gas from the capsule. The permeability of hydrogen gas allows the graphite-formation boundary to make a curved line from positive to negative. The third may be most effective on the sealed capsule-experiments studied.

We could not show any gradual increase of graphite-crystallinity in the experiments externally controlled in f_{O_2} , in contrast to the experiments in which the f_{O_2} was incompletely controlled by internal buffers, carbonaceous material and water. Comparing the graphit-

ization through laboratory experiments with natural graphitization in metamorphic rocks, it appears that experimental data of uncontrolled f_{O_2} conditions are more likely applied to the graphitization in black schists than experiments under controlled f_{O_2} . The contrast between the f_{O_2} controlled and uncontrolled conditions may be noticed with the different partial pressure of hydrogen gas. That is, the f_{O_2} controlled experiments were done under higher f_{H_2} and lower f_{O_2} conditions than the f_{O_2} uncontrolled experiments. The different crystallinity between the products in the two types of experiments is probably derived from the different mechanism of graphite-crystallization. Fully-ordered graphite has a composition close to pure carbon. Reaction (3) can make pure carbon phase under very low f_{O_2} conditions because graphite precipitates from CO gas. It is possible that high f_{CO} conditions

have accelerated the formation of fully-ordered graphite in the f_{O_2} controlled experiments at low temperatures. This high f_{O_2} condition will not be realized in carbonaceous metamorphic rocks, so that the graphitization might proceed gradually with increasing temperature in the low temperature range. The studies on graphite- H_2O - CO_2 equilibrium by Yui (1968), and on the Sanbagawa metamorphism by Ernst (1972) and Itaya and Banno (1980) are consistent with this discussion.

Comparison with natural systems

The graphite-formation boundary determined by the hydrothermal experiments is

shown in Fig. 6 together with the metamorphic facies boundaries compiled by Seki (1973) and Ernst (1976, p. 251). Here, the "graphitizing-degree (GD)" must be introduced to represent arithmetically the graphitization shown in Fig. 1. The graphitizing-degree is formulated as follows, combining d_{002} and $L_c(002)$: $GD = (d_{002} - 3.70) \times 100 / \log(L_c(002)/1000)$. Applying this formula to Fig. 1, the graphitizing-degree at the graphite-formation boundary corresponds to $GD=33$ at every P-T range. The graphitizing-degrees in some metamorphic districts are also indicated in Fig. 6. All graphitizing-degrees in Fig. 6 except for the datum from the New Caledonia metamorphic

Fig. 6. Relation among the graphite-formation curve, the metamorphic facies and the graphitizing-degree (GD). H, heulandite zone; LM, laumontite zone; WA, wairakite zone; PP, prehnite-pumpellyite meta-greywacke facies; PA, pumpellyite-actinolite facies; GS, greenschist facies; EP-AM, epidote amphibolite facies; AM, amphibolite facies; GR, granulite facies; fr, Franciscan metamorphic district; ka, Kamukotan metamorphic belt; ot, Western Otago metamorphic district; ne, New England metamorphic district; hi, Hitachi metamorphic district; ya, Yamizo district; ta, Tanzawa metamorphic district; uw, Uwajima contact metamorphic aureole; jd, jadeite; qz, quartz; ar, aragonite; cal, calcite; GD, graphitizing-degree.

Table 3. The graphitizing-degree of carbonaceous materials from some metamorphic districts

Uwajima hornfels	distances from granite contact	d_{002}	G D *
	180 m	3.35	222
	500 m	3.35	66
	1070 m	3.36	35
	1180 m	3.41	20
	1430 m	3.44	15
	1860 m	3.50	11
	2460 m	3.64	3
Yamizo sedimentary rocks			
	low grade part of greenschist facies	3.39	25
	"	3.43	16
	"	3.47	14
	lower grade than greenschist facies	3.55	8
Hitachi metamorphic rocks			
	low grade part of greenschist facies	3.43	17
New England metamorphic rocks			
	lowest grade part of sillimanite zone	3.36	765
	lowest grade part of staurolite zone	3.36	88
	lowest grade part of garnet zone	3.35	58
Sanbagawa metamorphic rocks			
	highest grade part of biotite zone	3.36	109
	lowest grade part of biotite zone	3.36	52
	highest grade part of garnet zone	3.36	48
	lowest grade part of garnet zone	3.39	29
	chlorite zone	3.42	21
	pumpellyite-actinolite zone	3.47	14
	PP-PA boundary	3.49	13
	pumpellyite-prehnite zone	3.51	10
	Chichibu belt	3.69	1
Kamuikotan metamorphic rocks			
	pumpellyite-actinolite zone	3.45	15
	Law-Pump-Chl zone	3.60	5
	"	3.63	4
	"	3.72	-1
Franciscan metamorphic rocks			
	pumpellyite-actinolite zone	3.57	7
	Law-Pump-Chl zone	3.66	2
Tanzawa metamorphic rocks			
	laumontite-mordenite zone	3.85	-8
	heulandite zone	3.88	-9

$$*G D = (d_{002} - 3.70) \times 100 / \log(Lc_{(002)} / 1000)$$

GD, graphitizing-degree; PP-PA boundary, boundary between the prehnite-pumpellyite meta-greywacke facies and the pumpellyite-actinolite facies; Law, lawsonite; Pump, pumpellyite; Chl, chlorite.

district were analyzed by the authors (Table 3 and 4). The graphitizing-degree of the New England metamorphic district were determined using the same samples as Grew's (1974). The metamorphic facies or the mineral zones of the analyzed samples are known in the literature described as follows.

The P-T conditions of the Uwajima contact metamorphic aureole were estimated from

both the mineral assemblages of pelitic hornfels (Tagiri, 1981) and the experiments uncontrolled in f_{O_2} at 1 kbar. The following studies were quoted for the estimation of the metamorphic conditions of analyzed rocks; the Tanzawa metamorphic district by Seki *et al.* (1969); the Yamizo district by Tagiri and Tsuboi (1979); the Hitachi metamorphic district by Tagiri (1973); the New England

Table 4. Comparison of the graphitizing-degree with the oxygen isotope geothermometry

	Sample	d ₀₀₂	Lc(002)	GD	T(°C)
Shuksan	216A	3.41	62	24	360
	276C	3.37	96	32	360
	297	3.41	46	22	330
	298	3.42	42	20	330
	502A	3.42	57	23	400
	502C	3.41	55	23	400
	505	3.40	57	24	400
	506C	3.42	52	22	400
	507	3.40	58	24	400
	508A	3.41	48	22	400
	710A	3.38	57	26	320-340
	710B	3.39	52	24	320-340
	711	3.37	72	29	320-340
	3-15	3.36	642	177	400
Western Otago	35-21	3.36	108	35	400

metamorphic district by Grew (1974); the Western Otago metamorphic district by Brown and O'Neil (1982); the Sanbagawa metamorphic belt by Ernst *et al.* (1970), Toriumi (1975 and 1977) and Wada *et al.* (1984); the Shuksan metamorphic district by Brown and O'Neil (1982); the Kamuikotan metamorphic district by Hervé (1975) and Gouchi (1983); the Franciscan metamorphic district by Ernst *et al.* (1970); the New Caledonia metamorphic district by Diessel *et al.* (1978) and Brown and O'Neil (1982). Moreover, we estimated metamorphic temperatures of pelitic schists employing oxygen isotope geothermometry in the metamorphic terrain of Shuksan, Western Otago and New Caledonia (Brown and O'Neil, 1982; Brown, unpublished data; Diessel *et al.*, 1978). The degrees of graphitization listed in Table 4 were of the carbonaceous materials in the pelitic schists which were collected from the same or nearby outcrops as the samples employed in the oxygen isotope geothermometry. Temperatures indicated in Table 4 were calculated by E.H. Brown using the calibration curves of Bottinga and Javoy (1973).

Comparing the experimental results at

above 1 kbar with the graphitizing-degrees of carbonaceous rocks from various metamorphic districts, the graphite-formation boundary obtained from the experiments is located at a lower temperature than estimated from natural data (Fig. 6). Graphite crystallizes at higher temperatures in metamorphic rocks than in experimental products. This disagreement may be due to the previously noted experimental condition in which hydrogen gas could easily escape from a capsule so that fo_2 was incompletely controlled by carbonaceous material and water. Experiments presented in this paper indicate that temperature, oxygen fugacity and fluid composition in rocks must strongly controlled the progress of graphitization in nature. Total pressure conditions, however, may not give any significant effect to the graphitization of carbonaceous material in rocks.

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References

- Baird, T. (1977), Carbon formation on Ni foils by pyrolysis of propene (290°–800°C). In *Reactivity of Solid* (Wood, J., Lindqvist, O., Helgesson, C., and Vannerberg, Nils-Gosta Ed.). Plenum Press, New York, 143–147.
- Bottinga, Y. and Javoy, M. (1973), Comments on oxygen isotope geothermometry. *Earth Planet. Sci. Lett.*, **20**, 250–265.
- Brown, E.H. and O'Neil, J.R. (1982), Oxygen isotope geothermometry and stability of lawsonite and pumpellyite in the Shuksan Suite, North Cascades, Washington. *Contrib. Mineral. Petrol.*, **80**, 240–244.
- Buseck, P.R. and Bo-Jun, H. (1985), Conversion of carbonaceous material to graphite during metamorphism. *Geochim. Cosmochim. Acta*, **49**, 2003–2016.
- Diessel, C.F.K., Brothers, R.N. and Black, P.M. (1978), Coalification and graphitization in high-pressure schists in New Caledonia. *Contrib. Mineral. Petrol.*, **68**, 63–78.
- Ernst, W.G. (1972), CO₂-poor composition of the fluid attending Franciscan and Sanbagawa low-grade metamorphism. *Geochim. Cosmochim. Acta*, **36**, 497–504.
- Ernst, W.G. (1976), *Petrologic phase equilibria*. pp. 333, W.H. Freeman and Company Press, San Francisco.
- Ernst, W.G., Seki, Y., Onuki, H. and Gilbert, M.C. (1970), Comparative study of low-grade metamorphism in the California Coast Ranges and the Outer Metamorphic Belt of Japan. *Geol. Soc. Amer. Memoir*, **124**, 109–122.
- French, B.M. (1964), Graphitization of organic material in a progressively metamorphosed Precambrian iron formation. *Science*, **146**, 917–918.
- French, B.M. and Eugster, H.P. (1965), Experimental control of oxygen fugacities by graphite-gas equilibria. *J. Geophys. Res.*, **70**, 1529–1539.
- French, B.M. and Rosenberg, P.E. (1965), Siderite (FeCO₃): Thermal decomposition in equilibrium with graphite. *Science*, **147**, 1283–1284.
- Gouchi, N. (1983), Kamuikotan metamorphic rocks in the Kamuikotan gorge area, west of Asahikawa, Hokkaido. *J. Japan. Assoc. Min. Petr. Econ. Geol.*, **78**, 383–393.
- Grew, E.S. (1974), Carbonaceous material in some metamorphic rocks of New England and other areas. *J. Geol.*, **82**, 50–73.
- Griffin, G.M. (1967), X-ray diffraction techniques applicable to studies of diagenesis and low rank metamorphism in humic sediments. *J. Sed. Petrol.*, **37**, 1006–1011.
- Hariya, Y., Oba, T. and Terada S. (1974), Stability relation of some hydro-silicate minerals at high pressure. In *Proceedings of the 4th International Conference on high pressure*, Kyoto, 206–210.
- Hervé, F. (1975), Petrology of the Kamuikotan metamorphic belt at the Uzun-Orowan cross section, central Hokkaido, Japan. *J. Fac. Sci. Hokkaido Univ., Ser. IV*, **16**, 453–470.
- Hirai, T. and Yajima, S. (1967), Structural features of pyrolytic graphite. *J. Mater. Sci.*, **2**, 18–27.
- Hirt, T.J. and Palmer, H.B. (1963), Kinetics of decomposition of pyrolytic carbon films from methane and carbon suboxide. *Carbon*, **1**, 65–70.
- Honda, H., Kobayashi, K. and Sugawara, S. (1968), X-ray characteristics of non-graphitizing-type carbon. *Carbon*, **6**, 517–523.
- Hood, A., Gutjahr, C.C. and Heacock, R.L. (1975), Organic metamorphism and the generation of petroleum. *Amer. Assoc. Petrol. Geol. Bull.*, **59**, 986–996.
- Itaya, T. (1981), Carbonaceous material in pelitic schists of the Sanbagawa metamorphic belt in central Shikoku, Japan. *Lithos*, **14**, 215–224.
- Itaya, T. and Banno, S. (1980), Paragenesis of titanium-bearing accessories in pelitic schists of the Sanbagawa Metamorphic Belt, Central Shikoku, Japan. *Contrib. Mineral. Petrol.*, **73**, 267–276.
- Izawa, Z. (1968), Carbonaceous matter in some metamorphic rocks in Japan. *J. Geol. Soc. Japan*, **74**, 427–432.
- Krauskopf, K.B. (1967), *Introduction to Geochemistry*. pp. 721, McGraw-Hill, New York.
- Landis, C.A. (1971), Graphitization of dispersed carbonaceous material in metamorphic rocks. *Contrib. Mineral. Petrol.*, **30**, 34–45.
- Macak, J., Knizek, P. and Malecha, J. (1978), Formation of carbonaceous deposits on metallic Ni from methane-water vapor mixtures. *Carbon*, **16**, 111–114.
- Mckee, D.W. (1974), Effect of metallic impurities on the gasification of graphite in water vapor

- and hydrogen. *Carbon*, **12**, 453-464.
- McKee, D.W. and Chatterji, D. (1978), The catalyzed reaction of graphite with water vapor. *Carbon*, **16**, 53-57.
- Murphy, D.B., Palmer, H.B. and Kinney, C.R. (1958), *Industrial Carbon and Graphite*. pp. 77, Society of Chemical Industry, London.
- Osetzky, D. (1974), Macrocristalline graphite from magnesium carbide. *Carbon*, **12**, 517-523.
- Seki, Y. (1973), Temperature and pressure scale of low-grade metamorphism. *J. Geol. Soc. Japan*, **79**, 735-743.
- Seki, Y., Oki, Y., Matsuda, T., Mikami, K. and Okumura, K. (1969), Metamorphism in the Tanzawa Mountains, central Japan. *J. Japan. Assoc. Min. Petr. Econ. Geol.*, **61**, 1-25.
- Tagiri, M. (1973), Metamorphism of Paleozoic rocks in the Hitachi district, southern Abukuma Plateau, Japan. *Sci. Rep. Tohoku Univ., Ser. III*, **12**, 1-67.
- Tagiri, M. (1981), A measurement of the graphitizing-degree by the X-ray powder diffractometer. *J. Japan. Assoc. Min. Petr. Econ. Geol.*, **76**, 345-352.
- Tagiri, M. and Tsuboi, S. (1979), Mixed carbonaceous material in Mesozoic shales and sandstones from Yamizo Mountain-system, Japan. *J. Japan. Assoc. Min. Petr. Econ. Geol.*, **74**, 47-56.
- Tensner, P.A. and Rafal'kes, I.S. (1952), The study on the formation process of carbon on surface by the thermal decomposition of hydrocarbon. *Doklady Akademii Nauk SSSR*, **87**, 821-824.
- Tomita, A. and Tamai, Y. (1972), Hydrogenation of carbons catalyzed by transition metals. *J. Catalysis*, **27**, 293-300.
- Tomita, A., Sato, N. and Tamai, Y. (1974), Hydrogenation of carbons catalyzed by nickel, platinum and rhodium. *Carbon*, **12**, 143-149.
- Toriumi, M. (1975), Petrological study of the Sanbagawa metamorphic rocks. The Kanto Mountains, central Japan. pp. 99, University of Tokyo Press.
- Toriumi, M. (1977), Metamorphism of the southern Kanto Mountains-Its pressure condition. In the Sanbagawa Belt (Hide, K. Ed.). pp. 440, Hiroshima University Press, 217-221.
- Wada, H., Enami, M. and Yanagi, T. (1984), Isotopic studies of marbles in the Sanbagawa metamorphic terrain, central Shikoku, Japan. *Geochem. J.*, **18**, 61-73.
- Yui, S. (1968), Results of equilibrium calculation on the reaction between graphite and a H_2O - CO_2 fluid. *J. Mineral. Coll. Akita Univ., Ser. A.*, **4**, 29-39.

300~600°C, 0.5~5 kbar での瀝青炭からの石墨の熱水合成

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表題の条件下で瀝青炭を出発物質として石墨の熱水合成を行った。触媒として 1% Li_2CO_3 又は 2% Ni 金属を用いた。酸素をバッファーしない実験では 375°C-0.5 kbar, 405°C-1 kbar, 390°C-2 kbar, 320°C-5 kbar で石墨が生成した。HM, NNO, QFM を用いて酸素をバッファーした 1 kbar での実験では, NNO バッファーの時, 420°C で石墨が生成した。しかし, 生成物の石墨化度は極めて高く, 天然物に見られるような石墨化度の果進的増加は認められなかった。炭質物から石墨が生成する境界は, 反応物を特定できないため, 自由度 1 の曲線ではない。石墨化作用の加熱時間依存性は低温では認められるが, 410°C 以上では認められない。

実験結果を變成岩中の石墨化作用や酸素同位体温度計と比較すると, 石墨生成の圧力依存性は実験結果ほど大きくないことが示された。石墨化作用は, 圧力に対する依存性は小さく, 温度と酸素分圧に対しては極めて大きい。