Contr. Mineral. and Petrol. 30, 34–45 (1971)

Graphitization of Dispersed Carbonaceous Material in Metamorphic Rocks

C. A. Landis
Department of Geology, University of Otago, Dunedin

Received October 1, 1970

Abstract. Dispersed carbonaceous material concentrated from some New Zealand and Japanese metamorphic rocks has been analysed by X-ray and electron diffraction methods. A classification to describe sub-graphitic material (graphite-d) is proposed. Progressive graphitization is related to metamorphic grade as conventionally defined by mineral assemblages. Thus carbonaceous material in zeolite facies rocks as well as some lawsonite-albite-chlorite facies rocks is nearly amorphous (graphite-d_3); material from slightly higher grade rocks of the lawsonite-albite-chlorite, pumpellyite-actinolite, greenschist, and blueschist facies show a more advanced degree of crystallinity (graphite-d_2, -d_1). Fully-ordered graphite is first recognized in albite-epidote amphibolite and amphibolite facies rocks.

X-ray diffraction data are also presented for New Zealand coals of known rank. Lignite and high volatile bituminous coal samples yield graphite-d_3 patterns. A low volatile bituminous sample is transitional between graphite-d_2 and -d_3, while a semi-anthracite sample is graphite-d_2.

Analysis of X-ray and electron diffraction data permits some understanding of the structure of sub-graphitic materials. It is shown that peak broadening may be produced by structural variations within a given sample, and for this reason the estimation of crystallite size solely on the basis of diffractograms should be regarded with caution.

The controls of graphitization are discussed and it is tentatively concluded that graphitization is primarily dependent upon metamorphic temperature; pressure and variation in starting material presumably constitute secondary controls. Under metamorphic conditions, true graphite probably forms above 400° C.

Introduction

Graphite and fine-grained dispersed carbonaceous material have long been recognized as components of metamorphic rocks. Progressive graphitization of carbonaceous debris has an inherent interest and the importance of such carbon to metamorphic petrology has become increasingly recognized during recent years. The structure of carbonaceous material ranges from virtually amorphous to fully crystalline graphite, perfection of crystallinity increasing with grade of metamorphism (Quinn and Glass, 1958; French, 1964; Kato and Nakai, 1966; Griffin, 1967; Izawa, 1968). Degree of graphitization may influence chemical activity of carbon and hence redox potential during metamorphism (Zen, 1963; Miyashiro, 1964; French, 1965; Izawa, 1966). The relationship between mineralogy of burial metamorphic rocks and rank of associated coals has been described (Kisch, 1966, 1968, 1969), but few data relating structural perfection of carbon to mineralogically defined metamorphic facies have been published.

Samples were collected from numerous localities in the Wakatipu and Tasman metamorphic belts of New Zealand (Landis and Coombs, 1967) and from the Sanbagawa Belt of Japan (e.g. Miyashiro, 1961). Sanbagawa rocks were collected from the Shiratake area, Kochi Pref., Shikoku by Prof. D. S. Coombs. All specimens are housed in the Geology Museum, University of Otago.

Mineral facies terminology follows usage of Hashimoto (1966), Fyfe and Turner (1966) and Coombs (1968). Petrology of the Wakatipu belt zeolite and prehnite-pumpellyite facies rocks is described by Coombs (e.g. 1954, 1960) and by Coombs, Ellis, Fyfe and Taylor (1959); lawsonite-albite-chlorite facies rocks are described by the writer (Landis, 1969); higher grade rocks of the Wakatipu Belt have been studied by numerous workers (e.g. Hutton, 1940; Mason, 1956; Reed, 1958; Brown, 1967). Petrology of Sanbagawa rocks of central Shikoku has been described by Banno (1964) and by Ernst and Seki (1967).

Sample Preparation

Most samples were chosen from metagreywackes, meta-argillites, metatuffs, semi-schists and schists in which carbonaceous material was recognized in thin section, often widely dispersed and less than 1% by volume. Rock samples were crushed 4 to 10 seconds in a N.V. Tema Laborscheibenschwingmühle and sieved to less than 0.066 or 0.053 mm. Carbonaceous material was concentrated from the powder by treatment with hot HF and HCl (cf. French, 1964, p. 917). In some cases, purification was not achieved even after six repetitions of this treatment, relatively insoluble minerals such as zircon, pyrite, tourmaline, and a synthetic phase comparable to ralstonite (Pauly, 1965) surviving along with carbonaceous material.

Kotlensky and Walker (1960, p. 427) have noted an increase in d_{002} of Ceylon graphite from 3.35 to 3.63 Å with prolonged grinding. In order to ensure that grinding in the Tema was not producing a similar effect, samples of a graphitic slate (23678) were prepared by hand grinding, five-second Tema grinding and 150 second Tema grinding. Diffractograms of graphite concentrates from the three powders were indistinguishable.

Concentrates for electron microscope study were placed in distilled water to which a small quantity of detergent had been added, and dispersed by agitation in an ultrasonic bath (300 watts, 24.1 kc/sec). Diffractograms of samples so treated 2 to 30 minutes did not differ significantly from a split of the same sample which had not been ultrasonically dispersed.

Analytical Methods

Samples were sedimented from distilled water onto glass slides and analysed with a Philips X-ray diffractometer using Ni-filtered CuKα radiation. Diffractograms were run at scanning speeds of 1° 2 Θ/min, chart speed 800 mm/h. At least two patterns were obtained from all samples. Powder photographs were obtained with a 114.83 mm diameter Philips Debye-Scherrer powder camera. Concentrates were mounted in Lindemann capillary tubes and exposed to CuKα radiation for four to ten hours.

Ultrasonically dispersed concentrates from two specimens sedimented onto copper grids were examined with an Hitachi HU 11A electron microscope. Selected area electron diffraction patterns were obtained with the microscope operating at 75 KV with double condenser lenses.

Description and Classification of the Graphitization Series

On the basis of visual comparison of X-ray diffractograms French (1964) proposed a four-fold subdivision of carbonaceous material in metamorphic rocks, reflecting increasing perfection of crystallinity, viz.:

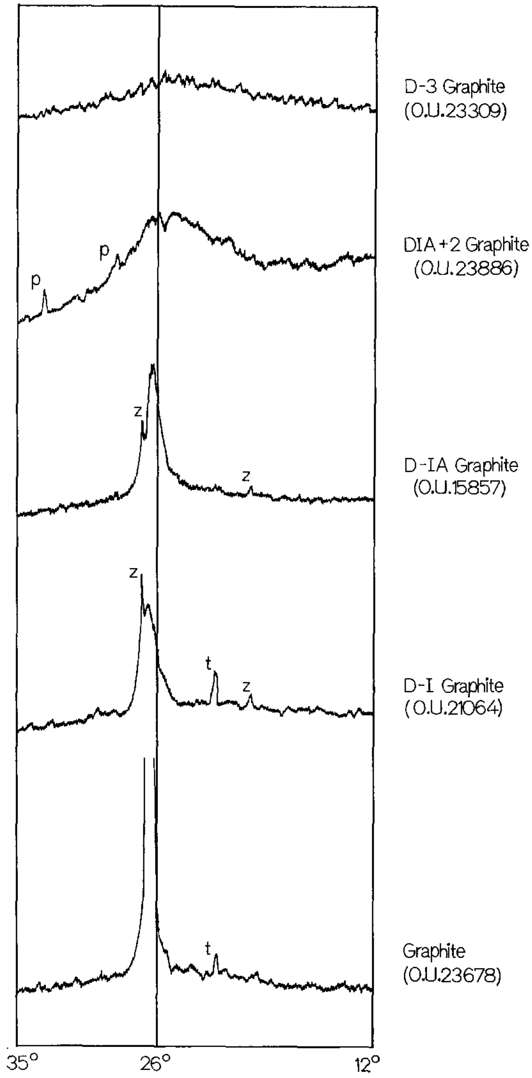

Fig. 1

Fig. 1. X-ray diffractograms illustrating the various stages of progressive graphitization of acid-insoluble residues from metamorphosed sedimentary rocks. Note the gradual increase in degree of crystallinity from graphite-d_3 (a nearly amorphous hydrocarbon), through ill-defined and assymetrical reflections in the range 20–26° 2Θ (Cu-radiation), to an intense and symmetrical 002 reflection characteristic of fully ordered graphite. Non-carbonaceous insoluble residues include pyrite (*p*), zircon (*z*) and turmaline (*t*)

Fig. 2A–C. Electron micrographs of carbonaceous particles concentrated from metamorphic rocks. A and B sample 15857, graphite-d_{1A}. Note variation in size and shape of particles; some particles from this sample were more than twice the size of the largest particle shown here; smallest grain size difficult to determine. Well-formed hexagonal crystallite evident in centre of B. Scale: A ×24500, B ×36325. C From sample 23678, fully ordered graphite. Note one well-formed hexagonal crystallite and portions of several others. ×46500. Electron diffraction patterns from selected crystallites in samples 15857 and 23678 shown in Fig. 5

Table 1. *Descriptive parameters (under experimental conditions described in text) characterizing different stages in the graphite-d-graphite series with respect to the 002 peak and its structural precursors (peaks not corrected for instrumental broadening)*

	Height/width at $^1/_2$ height	d_{002} Å (at I_{maximum})	d_{002} Å ($^1/_2$ width at $^1/_3$ height)
graphite (fully ordered)	30	3.35–3.36	3.35–3.36
graphite-d_1	3–15	3.35–3.36	3.38–3.41
graphite-d_{1A}	3–15	3.37–3.44	ca. 3.40
graphite-d_2	0.5–1	3.45–3.55	3.75–3.85
graphite-d_3	0.5	3.50–3.75	ca. 3.8

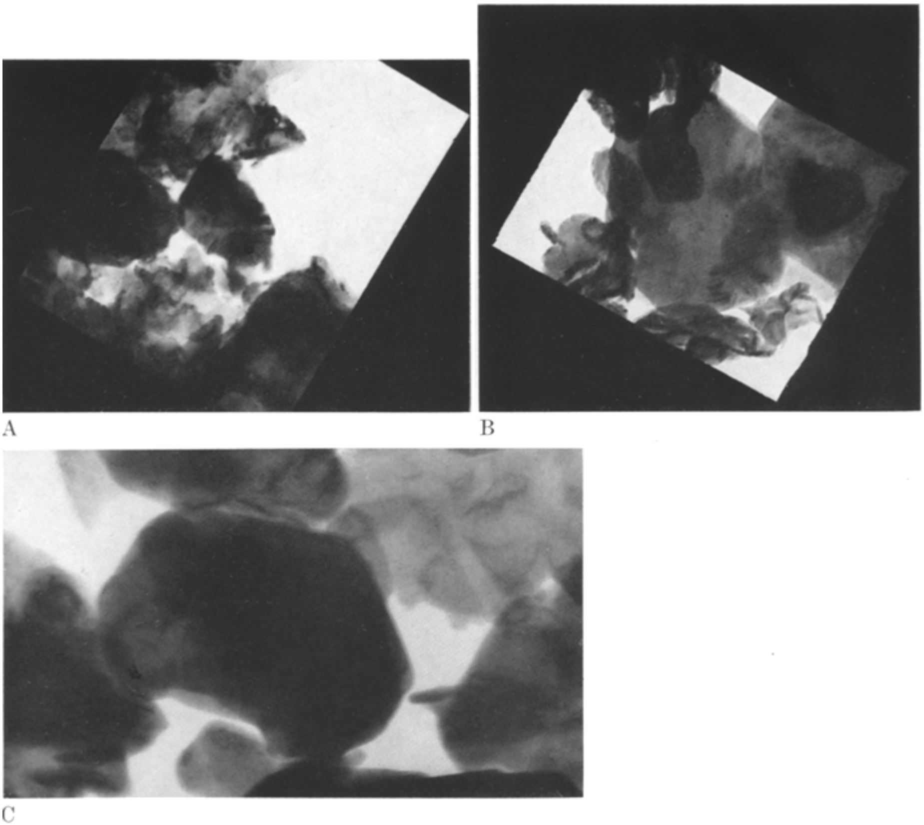

Fig. 2A–C (for caption see p. 36)

1) amorphous carbonaceous material,
2) asphaltic carbonaceous material,
3) d-graphite (i.e. "disordered" graphite), and
4) graphite.

Several factors suggest that a revision of the above classification scheme is desirable:

1. The categories proposed by French are all part of a graphitization series, a fact not suggested by the names.

2. *Asphalt*, as generally used (e.g. Am. Geol. Institute *Glossary of Geology and Related Sciences*, 1960) carries no connotation of crystallinity or position in the graphitization series.

3. Some samples of natural asphalt from Trinidad and Venezuela (20102, 20105) analysed by the writer produce patterns which more closely resemble amorphous substances than the "type" asphaltic carbonaceous material described by French.

4. Numerous patterns obtained by the writer from carbonaceous material in schists are unlike any described by French.

The writer proposes to describe sub-graphitic carbonaceous material in metamorphic rocks in terms of different "degrees of disorder". By extending the usage proposed by French (1965), all sub-graphitic carbon can be designated graphite-d, and increase in degree of disorder can be expressed in terms of subscript values (d_1, d_2, d_3).

Thus "graphite" is used here to describe only that mineral whose diffraction pattern is essentially identical to fully ordered graphite (Smith, 1969). All other material is graphite-d. The number of categories is arbitrary; on the basis of diffractograms, the writer recognizes four fairly distinctive stages in the graphitization series (Table 1 and Fig. 1). Fully ordered graphite is characterized by a diffractometer trace with an intense, sharp and symmetrical 002 reflection at 3.35–3.36 Å as well as other considerably weaker reflections at higher angles (e.g. 100, 101, 004). Graphite-d_1 is characterized by a relatively intense 002 peak at approximately 3.35–3.36 Å, which however is noticeably broadened and markedly skewed toward lower angles. Reflections other than 002 are absent. Other material (d_{1A}) produces very similar diffraction patterns which differ in having less marked skewness but slightly larger spacing (ca. 3.4 Å) of the "002" peak.

In less well-ordered samples (d_2), the single peak is broader and has a conspicuously larger spacing (ca. 3.5 Å) than fully ordered graphite or graphite-d_1. Such samples are uncommon and occur in mixtures with d_{1A}-graphite. Diffractograms of graphite-d_3 range from featureless charts which can be considered amorphous (French, 1965) to patterns with very broad, low-intensity peaks with mean spacing of 3.50–3.75 Å. Similar (d_3) patterns are obtained from lamp-black and natural asphalt.

A series of X-ray powder photographs was prepared including at least one for each stage in the graphitization series. Diffractograms and powder photos of fully ordered graphite were found to be closely comparable, although the powder photos contain high-angle and back-reflections which are not evident on diffractograms. In contrast, graphite-d_1 photos contain numerous relatively low-angle graphite lines (100, 101, 110, 112) which are not evident in diffractograms. The cause of this difference is probably two-fold: (1) preferred orientation in diffractometer samples would cause suppression of $h\ k\ l$ reflections, (2) long exposure times of powder photos (5–10 hours) allows detection of peaks produced by minor amounts of intermixed material in which interlayer orientation has developed. Powder photographs of graphite-d_3 and of an impure d_2 sample reveal a broad 002 band and a very weak and diffuse band at the graphite 100–101 position.

Several samples appear to consist of mixtures of carbonaceous material belonging to two categories. In such samples, two distinct peaks are evident both in powder photographs and diffractograms (Fig. 1); thus two d-values must be used to describe such materials (e.g. $d_1 + d_2$). Probably many cases of mixtures have not been recognized. For example, the skewed graphite-d_1 peak may be a mixture of fully ordered graphite and slightly disordered graphite.

Electron Microscopy and Diffraction

Grain size, shape and crystallinity of selected samples (d_{1A}, 15857; fully ordered, 23678) were studied with an Hitachi electron microscope. Particle size was found

Fig. 3. Electron diffraction patterns obtained from two graphite crystallites in sample 23678 (fully ordered graphite). Several other diffraction patterns were obtained from particles in this sample; all were closely similar. Patterns represent a portion of the graphite lattice; visible lattice points are 100 and 110 (002 lattice points visible on some other patterns). Figure B produced by more than one superimposed co-planar crystallites

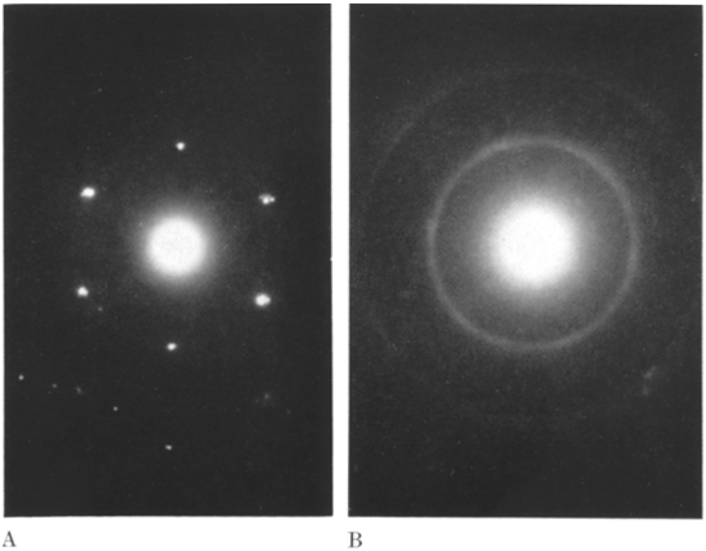

Fig. 4. Electron diffraction patterns obtained from a sample of graphite-d_{1A} (15857). Two distinctive types of pattern were obtained from this sample: A) characterised by sharp reciprocal lattice points similar to those produced by fully ordered graphite (cf. Fig. 3), and B) characterised by rings which possess spacings corresponding to 100 ($d = 2.13$ Å) and 110 ($d = 1.23$ Å), and in addition a diffuse 002 ring (containing two bright nodes). Patterns of type B suggest turbostratic structure (see text)

to vary widely (Fig. 2). Numerous hexagonal graphite crystals occur in both samples but these are much less common in the graphite-d_{1A}. Electron diffraction patterns were obtained from numerous particles in each sample. Particles of fully ordered graphite (23678) invariably yield sharp spot patterns (Fig. 3) containing reciprocal lattice points 100 and 110. Kikuchi lines were evident in some patterns. Numerous flakes from the d_{1A} sample (15857) produced virtually identical spot patterns; however, numerous other flakes in the same sample produced ring patterns with weak superimposed spots corresponding to 100 and 110 (Fig. 4).

Structural Evolution of Graphite in Metamorphic Rocks

Carbonaceous material (graphite-d_3) from the lowest grade rocks ranges from virtually amorphous to material possessing a rudimentary graphite structure. Such material appears to consist of variably spaced (mean 3.5 to 3.75 Å) carbon layers which are crudely parallel to one another and unoriented about the layer normal. Evidence for incipient two-dimensional order in graphite-d_3 is provided by a diffuse 2.13 Å band in powder photographs. A similar diffuse band has been observed in experimentally heat-treated carbon (Franklin, 1951). This band is the precursor for the graphite 100 line (2.12 Å).

From graphite-d_3, graphitization is effected in three ways:

1) perfecting of the layer lattice structure;
2) reduction of interlayer spacing;
3) ordering of carbon layers with respect to one another.

Thus with decrease in d-value, kurtosis of the 002 peak increases, skewness decreases, and interlayer spacing decreases toward an ultimate value of 3.35 Å.

The transition from graphite-d_3 to -d_2 is gradational, whereas available data suggest that more crystalline types may be separated by natural breaks. Pervasive three-dimensional ordering and uniform graphite interlayer spacing are generally developed concomitantly. However, in material such as graphite-d_{1A}, the interlayer *orientation* of true graphite may be acquired before the interlayer *spacing* is reduced to 3.35 Å.

The structure of graphite and of products of incomplete experimental graphitization have been studied in some detail. An early stage in the graphitization of industrial carbon is characterized by perfect hexagonal planar layers of carbon atoms which, though parallel, show no ordered stacking sequence (Bacon, 1950; Franklin, 1950, 1951; Ubbelohde and Lewis, 1960). These are termed *turbostratic structures*. French (1965) has suggested that some natural material which he calls "d-graphite" may have turbostratic structure. The diffractogram of French's type d-graphite is virtually identical with those of graphite-d_{1A} described in the present study. Thus it is important to note that although diffractograms of such material suggest a turbostratic structure, powder photos and electron diffraction photos reveal the presence of well-developed three-dimensional order of at least a portion of the sample studied by the writer (see also Franklin, 1951). Reference to turbostratic structure should therefore be regarded with caution in the classification of natural graphite-d.

The diffractogram typical of graphite-d_1 is unlike patterns described in previous studies of natural graphitization. Such material apparently consists of true graphite intermixed (?interlayered) with graphite-*d*. Three-dimensional order is present but discontinuous in such material. A similar stage in the graphitization of carbon black was recognized by Houska and Warren (1954).

The recognition of numerous samples comprising mixed graphite-$d_{1+1\mathrm{A}}$ and graphite-$d_{1\mathrm{A}+2}$ suggests that the estimation of crystallite size in carbonaceous materials from diffractogram peak widths (van Krevelen, 1961; Izawa, 1968; Griffin, 1967) should only be attempted in conjunction with other methods, notably X-ray powder photography, electron microscopy, and electron diffraction.

Progressive Graphitization in Metamorphic Rocks

Table 2. *Relationship between metamorphic grade and relative crystallinity of carbonaceous material; for comparative purposes, subfacies is treated as interchangeable with zone*

Metamorphic grade	Specimen number	Degree of disorder
Wakatipu Metamorphic Belt, New Zealand		
Zeolite Facies:		
Heulandite subfacies	8766	d_3
Laumontite subfacies	8784, 23961	d_3
Prehnite-pumpellyite-laumontite subfacies	23813, 23878	d_3
Lawsonite-Albite-Chlorite Facies:		
Lawsonite-prehnite-pumpellyite subfacies	23309	d_3
Lawsonite-epidote-pumpellyite subfacies	23665, 23769	$d_{1\mathrm{A}+2}$
	23295	$d_{1+1\mathrm{A}}$
Pumpellyite-actinolite Facies:	23886	$d_{1\mathrm{A}+2}$
	4502, 22289	d_1
	23873	$d_{1+1\mathrm{A}}$
Greenschist Facies:		
Chlorite subfacies	15857	$d_{1\mathrm{A}}$
	23874	$d_{1+1\mathrm{A}}$
	23824, 23968, 21097	d_1
Biotite subfacies	21064, 23823, 23968	d_1
Amphibolite Facies:		
Garnet-oligoclase subfacies	14796, 23034	fully ordered
Tasman Metamorphic Belt, New Zealand		
Above biotite isograd	23678, 23972	fully ordered
Amphibolite Facies	14796	fully ordered
Sanbagawa Metamorphic Belt, Central Shikoku, Japan		
Blueschist Facies:		
Pumpellyite-actinolite-glaucophane subfacies	22251, 22216	$d_{1+1\mathrm{A}}$
Epidote-actinolite-glaucophane subfacies	22249	$d_{1+1\mathrm{A}}$
	22221	$d_{1\mathrm{A}}$
Epidote-actinolite-glaucophane subfacies transitional to albite epidote amphibolite facies	22223	$d_{1+1\mathrm{A}}$
	22247	d_1
Albite-epidote Amphibolite Facies:	22246	fully ordered
Albite-epidote Amphibolite Transitional to Amphibolite Facies:	22253, 22256	fully ordered

The degree of crystallinity of carbonaceous materials from metamorphic rocks of the Wakatipu and Sambagawa metamorphic belts (low ratio $t{:}p$) and the Tasman Metamorphic Belt (high ratio $t{:}p$) is described in Table 2. Progressive graphitization is clearly related to increase in metamorphic grade.

X-Ray Diffraction of New Zealand Coals

The degree of crystallinity of some New Zealand Upper Cretaceous coals has also been investigated. Rank, coal field and X-ray data are listed in Table 3. The 002 graphite precursor, although quite weak and broad, reveals a distinct decrease in degree of disorder with increase in coal rank (cf. Quinn and Glass, 1958; Griffin, 1967).

Table 3. *Relationship between rank and degree of graphitization of some New Zealand coals. Rank determinations after Suggate (1959, Table 6)*

Sample number	Description	Rank	Description of structural precursor of graphite 002 reflection as determined under experimental conditions described in text		Approximate position in d-graphite-graphite series as described in Table 1
			Height/width at $^1/_2$ height	d, Å (at $I_{max.}$)	
23696	Fern Hill Lignite (cf. Willowbank Lignite)	6.6	0.25–0.50	4.1–4.4	d_3
23925	Strongman Coal; High volatile; Bituminous	11.3	0.25–0.50	3.8–3.9	d_3
23926	Liverpool Coal; High volatile; Bituminous	13.2	0.25–0.50	3.8–3.9	d_3
23927	Paparoa Coal; Low volatile; Bituminous	15.5	0.50	3.5–3.6	d_{2-3}
23966	Fox River semianthracite	18.0	0.75–1.0	3.5–3.6	d_2

Controls of Graphitization

Recent advances in metamorphic geology, experimental petrology and isotope studies have permitted increased understanding of the p-t fields occupied by the various metamorphic facies. Several recently proposed diagrams relating metamorphic facies and isograds to pressure and temperature of metamorphism have shown broad agreement (e.g. Fyfe and Turner, 1966; Hietanen, 1967; Landis and Coombs, 1967); and these, revised in light of recent data pertaining to the alumino-silicate triple point (e.g. Richardson *et al.*, 1969; Althaus, 1969) and lawsonite-laumontite equilibria (Liou, in press) are tentatively accepted for the purpose of estimating geologic conditions of graphite formation (Fig. 5). Data of Quinn and Glass (1958), French (1964) and the present study, indicate that fully ordered graphite first appears in uppermost grade greenschist facies to lower amphibolite facies rocks. Extremes of total pressure probably ranged between less

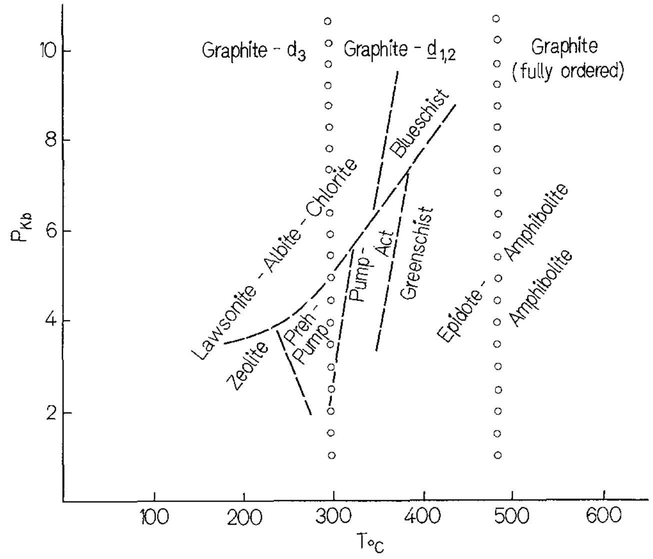

Fig. 5. *p*-*t*-facies metamorphic grid, showing estimated conditions at which graphite and disordered graphite occur in nature. Facies boundaries after Landis and Coombs (1967, Fig. 4) with modifications after Althaus (1967), Richardson *et al.* (1968), Landis (1969) and Liou (in press). Estimated field boundaries of graphite and graphite-*d* indicated by open circles

than two kb and more than six kb while temperature probably exceeded 400°, and it is concluded that of the pressure and temperature variables, the crystallization of graphite is primarily dependent upon temperature. Other factors such as nature of original detritus (e.g. Forsman, 1962; Franklin, 1951) may also influence graphitization.

Acknowledgments. Several present and former colleagues at the University of Otago have assisted me by providing materials and discussing various aspects of this investigation: D. S. Coombs, A. F. Cooper, A. E. Grady, Y. Kawachi, P. B. Read, A. Reay and J. Rogers. Dr. T. Muckerjee, Electron Microscope Laboratory, University of Otago, assisted greatly with the electron microscopy and electron diffraction studies. The manuscript has been reviewed by Professor D. S. Coombs.

I am also grateful for financial assistance from the U.S. National Science Foundation (G/18700) and from the New Zealand University Grants Committee.

References

Althaus, E.: The triple point andalusite-sillimanite-kyanite. Contr. Mineral. and Petrol. **16**, 29–44 (1967).

Bacon, G. E.: Unit-cell dimensions of graphite. Acta Cryst. **3**, 137–139 (1950).

Banno, S.: Petrologic studies on Sanbagawa crystalline schists in the Bessi-Ino District, Central Sikoku, Japan. J. Fac. Sci. Univ. Tokyo **15**, 203–319 (1964).

Brown, E. H.: The greenschist facies in part of Eastern Otago, New Zealand. Contr. Mineral. and Petrol. **14**, 259–292 (1967).

Coombs, D. S.: The nature and alteration of some Triassic sediments from Southland, New Zealand. Trans. Roy. Soc. New Zealand **82**, 65–109 (1954).

Coombs, D. S.: Lower grade mineral facies in New Zealand. Rept. Intern. Geol. Congr., 21st, Copenhagen, Norden 1960, Part XIII, 339–351 (1960).

— Lower grade mineral facies. Trans. Amer. Geophys. Un. **49**, 344 (1968).

— Ellis, A. J., Fyfe, W. S., Taylor, A. M.: The zeolite facies with comments on the interpretation of hydrothermal syntheses. Geochim. Cosmochim. Acta **17**, 53–107 (1959).

Ernst, W. G., Seki, Y.: Petrologic comparison of the Franciscan and Sanbagawa metamorphic terranes. Tectonophysics **4**, 463–478 (1967).

Forsman, J. P.: Geochemistry of kerogen. In: Organic geochemistry, p. 148–182. Oxford: Pergamon Press 1962.

Franklin, R. E.: The interpretation of diffuse X-ray diagrams of carbon. Acta Cryst. **3**, 107–121 (1950).

— Graphitizable and non-graphitizable carbons. Compt. Rend. **232**, 232–234 (1951).

French, B. M.: Graphitization of organic material in a progressively metamorphosed Precambrian iron formation. Science **146**, 917–918 (1964).

— Some geologic implications of equilibrium between graphite and a C-H-O fluid phase at high temperatures and pressures (abst). Geol. Soc. Am. Spec. Papers **87**, 59–60 (1965).

Fyfe, W. S., Turner, F. J.: Reappraisal of the metamorphic facies concept. Contr. Mineral. and Petrol. **12**, 354–364 (1966).

Griffin, G. M.: X-ray diffraction techniques applicable to studies of diagenesis and low rank metamorphism in humic sediments. J. Sediment. Petrol. **37**, 1006–1011 (1967).

Hashimoto, M.: On the prehnite-pumpellyite metagreywacke facies. J. Geol. Soc. Japan **72**, 253–265 (1966).

Hietanen, A.: On the facies series in various types of metamorphism. J. Geol. **75**, 187–214 (1967).

Hutton, C. O.: Metamorphism in the Lake Wakatipu region, western Otago, New Zealand. N. Z. Dep. Scient. Ind. Res. Geol. Mem. **5**, 90p. (1940).

Izawa, E.: Carbonaceous matter in some metamorphic rocks in Japan. J. Geol. Soc. Japan **74**, 427–432 (1968).

Kato, K., Nakai, N.: Carbon in metamorphic rocks (Abst.). Geochem. Soc. Japan, Program Annual Meeting 1966, 78–79 (*fide* Y. Kawachi) (1966).

Kisch, H. J.: Zeolite facies and regional rank of bituminous coals. Geol. Mag. **103**, 414–422 (1966).

— Coal rank and lowest-grade regional metamorphism in the southern Bowen Basin, Queensland, Australia. Geologie Mijnbouw **47**, 28–36 (1968).

— Coal-rank and burial-metamorphism mineral facies. In: Advances in organic geochemistry 1968, p. 407–425. Oxford: Pergamon 1969.

Kotlenski, W. V., Walker, P. L., Jr.: Crystallographic and physical changes of some carbons upon oxidation and heat treatment, 4th Conf. Carbon Proc., p. 423–442. New York: Pergamon 1960.

Krevelen, D. W. van: Coal: typology, chemistry, physics, constitution, p. 514. Amsterdam: Elsevier 1961.

Landis, C. A.: Upper Permian rocks of South Island New Zealand—lithology, stratigraphy, structure, metamorphism and tectonics. Ph. D. thesis, Univ. of Otago, Dunedin, New Zealand (1969).

— Coombs, D. S.: Metamorphic belts and orogenesis in southern New Zealand. Tectonophysics **4**, 501–518 (1967).

Liou, J. G.: P-T stabilities of laumontite, wairakite, lawsonite and related minerals in the system $CaO \cdot Al_2O_3 \cdot 2SiO_2$—$SiO_2$—$H_2O$. (In press).

Mason, B.: Metamorphism in the Southern Alps of New Zealand. Bull. Amer. Mus. Nat. Hist. **123**, 211–248 (1962).

Miyashiro, A.: Evolution of metamorphic belts. J. Petrol. **2**, 277–311 (1961).

— Oxidation and reduction in the Earth's crust with special reference to the role of graphite. Geochim. Cosmochim. Acta **28**, 717–729 (1964).

Pauly, H.: Ralstonite from Ivigtut, South Greenland. Am. Mineralogist. **50**, 1851–1864 (1965).

Quinn, A. W., Glass, H. D.: Rank of coal and metamorphic grade of rocks of the Narragansett Basin of Rhode Island. Econ. Geol. **53**, 563–576 (1958).

Reed, J. J.: Regional metamorphism in Southeast Nelson. N. Z. Geol. Surv. Bull., N. S. **60**, 64p. (1958).

Richardson, S. W., Bell, P. M., Gilbert, M. C.: Kyanite-sillimanite equilibrium between 700° and 1500° C. Am. J. Sci. **266**, 513–541 (1968).

Smith, J. V. (ed.): Index (Inorganic) to the powder diffraction file 1969. American Society for Testing and Materials, Publication PD1S-19i (1969).

Suggate, R.. P.: New Zealand coals. N.Z. Dept. Sci. Ind. Res. Bull. **134**, 113 (1959).

Ubbelohde, A. R., Lewis, F. A.: Graphite and its crystal compounds, 217p. Oxford: Claredon 1960.

Zen, E-an: Components, phases, and criteria of chemical equilibrium in rocks. Am. J. Sci. **261**, 929–942 (1963).

Dr. C. A. Landis
Department of Geology
University of Otago
Dunedin, New Zealand