CARBONACEOUS MATTER IN SOME METAMORPHIC ROCKS IN JAPAN

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INTRODUCTION

Many pelitic metamorphic rocks contain widely-scattered black material or "graphite". Recently the role of graphite has been emphasized in relation to the problem of oxidation and reduction in metamorphism (MIYASHIRO, 1964). Up to the present, however, there is little knowledge on the nature of such black material itself.

In the present paper isolation procedures of black material are described and it is shown that most of the black material or so-called graphite in various metamorphic rocks in Japan are not graphitized but have nature of anthracite. The possibility of zonal mapping by the carbonaceous matter is also suggested.

MATERIALS STUDIED

The materials studied were pelitic schists from the Sanbagawa and other metamorphic belts in Japan. Coaly materials in younger sedimentary rocks were also examined for comparison.

No attempt was made to know exact contents of carbonaceous matter in these rocks. Yet approximate contents were assumed from the amounts of carbonaceous matter which were obtained by the isolation procedures. Thus the content of carbonaceous matter ranges from 0.1 to 2.0 per cent by weight, except 12 per cent of the sample no. 11 (Table 1).

Carbonaceous matter in these metamorphic rocks can readily be seen in a thin section. It is black and opaque under the microscope and is intimately associated with muscovite or sericite and often co-exists with fine grained pyrite. Mode of occurrences of carbonaceous matter are shown in Plates 1 and 2.

ISOLATION PROCEDURES

Carbonaceous matter in metamorphic rocks was concentrated by combinations of froth flotation and acid treatments.

Coal and graphite are hydrophobic and possess natural floatability. They float very well in the neutral or acid aqueous solution even without any reagent.

A rock specimen, 100-200 g, was pulverized to the size less than 0.15 mm (-100 mesh). Then 1 l of

distilled water was added to the pulverized rock in a flotation cell. About 20 mg of α -terpineol was added as a frother, and froth flotation was performed.

Though the content of carbonaceous matter in the concentrate varied for each specimen, an average was about 30 per cent by weight. The amount of quartz, plagioclase and chlorite were distinctly diminished by the procedure but the appreciable amount of muscovite entered in the concentrate. The existence of these minerals precludes to obtain the X-ray diffraction patterns of carbonaceous matter. The concentrates obtained were then treated with hot acid.

Though the effect of acid to carbonaceous matter is not wholly investigated, coaly materials are known to be nearly inert to hydrochloric acid without oxidizing agent. At low temperature hydrofluoric acid also does not react with most of the carbonaceous matters, except charcoal and oil-soot. Nitric acid and sulfuric acid, however, react with carbonaceous matter. Thus hydrofluoric and hydrochloric acids were used to remove the ash from the carbonaceous matter.

The carbonaceous concentrate was put in to a platinum crucible. Then hydrochloric acid and hydrofluoric acid were added to it. The mixture was heated on the water bath for few days. Carbonate and silicate minerals were decomposed almost completely by this method. After washing with distilled water, aluminum fluoride and fluosilicate, which in some cases formed in the procedure, were dissolved by hydrochloric acid. The acid treatment was repeated when large amount of inorganic minerals was contained in the concentrate.

The concentrate obtained by these methods was very fine black powder resembling to coal dust. The ash content of the concentrates ranges from 1 to 9 per cent by weight, with an average of 4 per cent by weight.

Most of the inorganic minerals were removed by acid treatments but pyrite and zircon were remained. Usually zircon was small in quantity and can be neglected. Pyrite, however, prevent obtaining the good X-ray diffraction pattern if even a small amount of it is present.

An attempt to remove the pyrite by the zinc-hydrochloric acid digestion method (FORSMAN and HUNT, 1958) was unsuccessful. Separation by a centrifuge with a heavy liquid also failed. The removal of pyrite is an important problem especially for dealing with

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Table 1. Samples and contents of carbonaceous matter.

Sample No.	Rock	Cont. of C Mat.
1	Shimoyamada	Silicified wood (Paleogene)
2	Tsuyazaki 14	Silicified wood (Paleogene)
3	Amakusa 2-4	Semi-anthracite (Paleogene)
4	Makimine 2-6	Sandy black phyllite (Shimanto belt)
5	Chichibu N 88	Black schist (Sanbagawa met. belt)
6	Kune K-4	Black schist (Sanbagawa met. belt)
7	Iimori I-1	Spotted black schist (Sanbagawa met. belt)
8	Iimori I-2	Spotted black schist (Sanbagawa met. belt)
9	Ōgushi	Spotted black schist (Snoki met. district)
10	Shirataki	Spotted black schist (Sanbagawa met. belt)
11	Amō	Biotite gneiss (Hida met. belt)

Key: 1 the Shimoyamada coal-mine, Fukuoka Pref. (ASANO, 1964), 2 Tsuyazaki, Fukuoka Pref. (ASANO, 1964), 3 the Horinosako coal-mine, Amakusa, Kumamoto Pref. (ASANO & TANAKA, 1963), 4-11 (This study), 4 10-level of the Makimine mine, Miyazaki Pref., 5 Nagatoro, Saitama Pref., 6 Kamihirayama path near the Nakō mine, Shizuoka Pref., 7 Shinshakō cross cut of the Iimori mine, Wakayama Pref., 8 Kamiji cross cut of the Iimori mine, Wakayama Pref., 9 Ōgushi, Nishisonoki Pref., 10 Genkō adit of the Shirataki mine, Kōchi Pref., 11 the Amō mine, Gifu Pref.

Table 2. Atomic compositions and crystallite dimensions of carbonaceous matter.
(Analyses were made by Nobuya TANAKA)

Sample No.	Ultimate analysis*			Atomic H/C ratio	d (002) Å	L (002) Å
	H	C	(O+N+S)			
Bituminous coal						
1	5.29	79.2	5.5	0.80		
2	4.75	75.4	9.8	0.75		
Semi-anthracite						
3		85.9**			3.59	21
4	1.76	84.6	13.6	0.25	3.48	29
5	1.46	90.2	8.3	0.192	3.49	29
Anthracite						
6	1.03	95.3	3.6	0.128	3.40	58
7	0.99	94.3	4.7	0.125	3.41	68
8	0.67	93.2	6.1	0.085	3.41	68
9	0.63	96.3	3.1	0.077	3.39	102
10	0.44	95.7	3.8	0.054	3.39	102
Meta-anthracite or graphite						
11					3.37	164

* Data are given in weight per cent on a dry, ash-free basis. $(O+N+S) = 100 - (H+C)$

** Value of fixed carbon by proximate analysis.

low grade metamorphic rocks, in which carbonaceous matter often associates intimately with fine grained pyrite.

ATOMIC COMPOSITION AND X-RAY PATTERN

The carbon content is usually used as an index of metamorphic rank of coal. For example, ASTM

classification is based upon the value of fixed carbon. The value of fixed carbon is 86—92 per cent by weight for semi-anthracite, 92—98 per cent for anthracite and 98 per cent or more for meta-anthracite. The hydrogen content or atomic H/C ratio may also be useful in evaluation of metamorphism for the higher rank carbonaceous matter. Ultimate analyses of the purified carbonaceous matter are given in Table 2. Data are

Fig. 1 Compositions of anthracitic coal and carbonaceous matter in metamorphic rocks. Numbers refer to those in the text.

● 1 and 2, coaly material; ● 4-10, carbonaceous matter in metamorphic rocks; ○ and +, anthracite and meta-anthracite.

Fig. 2 X-ray diffraction patterns of coaly materials and carbonaceous matter in low grade metamorphic rocks. (Data were obtained with diffractometer, Geigerflex, using nickel filtered Cu K α radiation. Scanning speed was 2° per minute, receiving slit of 0.2 mm was used). H= the hydrogen content (weight per cent).

arranged in order of the hydrogen content.

The accuracy of the ultimate analyses is difficult to estimate. For the standard material, saccharose, the standard deviations were 0.69 per cent by weight for carbon and 0.09 per cent by weight for hydrogen.

Fig. 1 represents the compositions of anthracitic coals and carbonaceous matter in metamorphic rocks. From the aspect of chemical composition, most analysed carbonaceous matter in metamorphic rocks are essentially identical with anthracite.

X-ray diffraction patterns for coal were reported by MENTSER *et al.* (1962), and ASANO and TANAKA (1963). These studies show that the degree of anthracitization and graphitization can be estimated by X-ray diffraction patterns. A distinction of semi-anthracite from bituminous coal can be made on the basis of the disappearance of the γ -band and the appearance of the (002) band. Anthracite can be recognized by the existence of the two-dimensional (10) (11) reflections. Meta-anthracite and graphite have the three-dimensional (hkl) reflections.

X-ray powder diffraction patterns of the purified carbonaceous matter are shown in Fig. 2 and Fig. 3. The patterns are arranged in decreasing order of the

Fig. 3 X-ray diffraction patterns of carbonaceous matter in high grade metamorphic rocks. H= the hydrogen content (weight per cent); Cp, chalcopryite; Py, pyrite; Z, zircon.

hydrogen content.

Carbonaceous matter in high rank has a random layer structure. The layer dimension of crystallite can be estimated from the line broadening of the (002) reflection. Equation in its simple form is

$$L(hkl) = k\lambda / \beta \cos \theta$$

where $L(hkl)$ is the crystallite dimension in a direction perpendicular to the reflection plane (hkl) in Å unit, k is a shape factor and its customary value is 0.9, λ is the wave length of X-ray in Å unit, β is the half-value breadth of the diffraction peak in radian and θ is the diffraction angle. Results obtained are given in Table 2.

The interlayer spacing, $d(002)$, decreases from 3.6 Å to 3.4 Å* with increase in the layer dimension of crystallites, i. e., increase in ordering of the layer structure. This progressive change of X-ray diffraction patterns is corresponding with increasing rank of carbonaceous matter.

In view of the above facts it may be concluded that carbonaceous matter in pelitic metamorphic rocks is equivalent to coal in various rank regarding its atomic composition and the structure of crystallites. Thus the terms "semi-anthracite, anthracite, meta-anthracite and graphite" may be applied to such carbonaceous matter.

CARBONACEOUS MATTER IN METAMORPHISM

Carbonaceous matters in sedimentary rocks have various chemical compositions as shown by FORSMAN (1962). This is due to the differences of original materials and depositional environments such as pH and Eh.

Relationships between rank of coal or carbonaceous matter and the metamorphic grade of associated rocks were studied by QUINN and GLASS (1958) and FRENCH (1964). QUINN and GLASS (1958) reported on the coal in regional metamorphic rocks of the greenschist facies in Rhode Island. From their data all of the coals studied seem to belong to rank of anthracite. Carbon contents of these anthracites increase from 92 per cent by weight in the muscovite-chlorite zone to 95 per cent by weight in the biotite-chlorite zone.

FRENCH (1964) studied carbonaceous matter in a Precambrian iron formation intruded by gabbro. "Amorphous" carbonaceous matter occurs in the unmetamorphosed rock. The X-ray diffraction pattern of carbonaceous matter in the moderately metamorphosed formation shows the " γ -band", then it can be assumed to be the bituminous stage. In the highly metamorphosed formation adjacent to the gabbro carbonaceous matter changes from semi-anthracite,

$d(002)=3.43$ Å, to nearly graphite, $d(002)=3.36$ Å. This suggests the existence of the appreciable temperature gradient in the contact zone during metamorphism.

In the Sanbagawa metamorphic belt carbonaceous matter ranges from semi-anthracite in low-grade metamorphic rocks of the glaucophane schist facies to anthracite or nearly meta-anthracite in the zone of the epidote-amphibolite facies. In this study graphite was not found in the rocks from the Sanbagawa metamorphic belt. Carbonaceous matter in the Hida gneiss is nearly graphitized.

All of the results described indicates a general increase of rank of carbonaceous matter with increasing metamorphic grade of associated rocks. Accordingly, zonal mapping on the basis of carbonaceous matter may be possible.

Carbonaceous matter mainly consists of carbon, hydrogen and oxygen and it liberates gases in the forms of methane, water or carbon dioxide during the process of metamorphism. According to MORT (1943), methane with a little water and no carbon dioxide is component of the reaction products in the stage of anthracitization. This is supported by the fact that considerable concentration of methane is often detected in the bore holes at some metal mines in the Sanbagawa metamorphic belt, for example, the Besshi mine and the Sazare mine. Thus it seems reasonable that methane as well as organic carbon itself may be significant as reducing agent in metamorphism.

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* The value of $d(002)$ is 3.354 Å for Ceylon graphite.

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本邦変成岩中の炭質物

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(要 旨)

日本各地の泥質変成岩に含まれる、いわゆる石墨について、その化学組成および結晶子の構造を調べた。

試料は主として三波川変成帯の黒色片岩を使用した。比較のため古第三紀層の石炭質物についてもふれた。

炭質物の分離濃集には、浮選と酸処理を併用して、よい結果が得られた。

元素分析の結果、三波川変成帯の場合、藍閃石片岩相の岩石に含まれる炭質物は、亜無煙炭に相当する組成 (C: 90%, H: 1.5%) であり、緑簾石角閃岩相の岩石中では、変無煙炭に近い無煙炭に相当する組成 (C: 96%, H: 0.4%) であった。X線回折図形による考察によっても同様の結論が得られた。

石墨化が完了したと思われる炭質物は、飛驒変成帯の片麻岩に含まれていたが、今回用いた三波川変成帯の岩石からは見いだされなかった。

炭質物の無煙炭化、石墨化は、周囲の岩石の変成の程

度に対応して進行していることが考えられるので、炭質物を用いて、変成地域の分帯を行なうことが出来ると思われる。

また変成作用における酸化還元のプロセスで、有機炭素の存在と同時にメタンガスが重要な役割を果たすと考えられる。

地名

Akanda	赤沼田	Makimine	槇峰
Amō	天生	Nakō	名合
Funashiro	船代	Nishisonoki	西彼杵
Genkō	源坑	Ōgushi	大串
Horinosako	堀ノ迫	Shimoyamada	下山田
Kamihirayama	上平山	Shinshakō	新斜坑
Kamiji	神路	Tsuyazaki	津屋崎

Explanation of Plate 1

A. No. 4 Makimine 2-6: Sandy black phyllite from the Makimine mine where the weak thermal metamorphism is recognized in sulfide beds. Quartz-chlorite-sericite-albite-calcite-carbonaceous matter. Among quartz grains there are fine grained sericite and chlorite. Coalescence of fine fragmental carbonaceous matter with sericite shows banding in parallel with fissility plane. (All of the thin sections shown in Pl. 1 and 2 are cut normal to the fissility or schistosity plane).

B. No. 5 Chichibu N88: Black schist in the zone of the glaucophane-schist facies (zone V; SEKI, 1958). Quartz-chlorite - sericite - albite - calcite - garnet - carbonaceous matter. Fine grained stilpnomelane is widely distributed. Banded carbonaceous matter exist in the sericite rich layer.

C. No. 6 Kune K-4: Black schist of the Funashiro formation. Quartz-chlorite-sericite-albite-calcite-garnet-carbonaceous matter. There are two kinds of thin layers. One of them is rich in quartz and the other is rich in sericite with carbonaceous matter.

D. No. 7 Iimori I-1: Spotted black schist of the Akanda black schist formation. Metamorphic grade of associated green rocks is the glaucophane-schist facies or green schist facies (KAMIYAMA *et al.*, 1964). Quartz-muscovite-albite-chlorite-garnet-carbonate-pyrite-carbonaceous matter. Bands of carbonaceous matter cross albite porphyroblasts. Greenish brown biotite occurs sparsely.

Explanation of Plate 2

A. No. 8 Iimori I-2: Spotted black schist in the zone of the epidote amphibolite facies of the Upper formation of the Iimori greenschist group (KAMIYAMA *et al.*, 1964). Quartz-muscovite-albite-garnet-chlorite-carbonate-pyrite-carbonaceous matter. Carbonaceous matter occurs intimately with muscovite. Greenish brown biotite occurs in small amounts.

B. No. 9 Ōgushi: Spotted black schist from the Sonoki metamorphic district. Quartz-albite-muscovite-garnet-chlorite-pyrite-carbonaceous matter. Carbonaceous matter occurs with sericite and in albite porphyroblasts.

C. No. 10 Shirataki: Spotted black schist in the zone of the epidote amphibolite facies (zone IIIb; Hide, 1961). Quartz-albite-muscovite-chlorite-garnet-pyrite-carbonaceous matter. Bands of carbonaceous matter show micro-folding. Carbonaceous matter coexists muscovite, chlorite and pyrite and occurs in and around the grains of albite and garnet.

D. No. 11 Amō: Biotite gneiss. Quartz-plagioclase-biotite-carbonaceous matter. In this sample most of the biotite is altered to chlorite.