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GRAPHITE IN SHALES AND SANDSTONES OF THE COAL-BEARING CARBONIFEROUS IN THE "ANNA" MINE (UPPER SILESIA COAL BASIN) POLAND

Abstract. Small amounts of graphite of three types occur in sandstones and shales (marls) from the coal beds of the Anna mine:

- i) graphite forming intergrowths with carbonates. The carbonates formed through replacement of organic matter and are pseudomorphous after this matter. Graphite appears as intercalations on the crystallographic planes with hexagonal symmetry of calcite and Fe dolomite;
- ii) graphite forming intercalations in highly coalified organic substance of the kerogen type;
- iii) graphite from carbonaceous marls, forming intergrowths with aluminosilicates of mica type. Probably epitaxial graphite layers form on the 001 plane of mica.

The formation of the graphite in question did not presumably require high temperature and involved:

- i) the oxidation of organic matter. As a result of this, the readily oxidable aliphatic hydrocarbons were removed, and the remaining organic matter was enriched in aromatic hydrocarbons, highly resistant to oxidation. Aromatic hydrocarbons (benzene rings) are the principal constituent of graphite;
- ii) benzene rings were formed into graphite layers on the planes with hexagonal symmetry of mica and carbonates.

INTRODUCTION

Low-temperature graphites owing their origin to catalytic oxidation of organic matter, with the ions of transition metals and γ radiation acting as catalysts, have been described from the copper-bearing shales of the Lubin mine (Kucha 1981, 1982). Transition metals and, above all, γ radiation are powerful catalysts of oxidation of organic matter (Waters 1963). As a result of such processes, the mixture of various organic compounds undergoes selective oxidation. The most resistant to oxidation are aromatic hydrocarbons (Waters 1963), which are the principal constituent of graphite. It seems, therefore, that oxidation is a prerequisite for the formation of fine graphite flakes. However, oxidation alone is not enough as it usually leads to the formation of kerogen, a graphite-like substance in which the graphitic ordering of the lattice (graphite domains) is less than 1000 Å (Kucha 1982). At this size, the graphitic ordering is generally undetectable with X-rays.

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Electron diffraction studies of kerogen (Kucha 1982) have shown that it consists of three types of graphitic planes: i) of a thickness typical of graphite, i.e. 6.72 Å, ii) of a thickness of Van der Waals layer (benzene ring), i.e. 7.40 Å, and iii) of a greater thickness for these rings to which short substituent groups of CO, CH₃ or OH type are linked. In spite of the different thickness of the benzene ring, the linked rings, owing to the lattice discontinuities, form a structure in which the planes of the benzene ring are parallel to one another, though displaced by discontinuity jogs. As a result of this, kerogen shows strong optical anisotropy in reflected light.

In order that graphite may form at low temperatures, it is necessary for the benzene rings to be ordered into layers extending to microscopic scale. This may be effected by the epitaxial growth of graphite layers on:

- i) the 001 plane of mica, whose identity period is nearly identical with that of graphite;
- ii) probably on the planes of carbonates with hexagonal symmetry close to the identity period of graphite.

EXPERIMENTAL AND RESULTS

Microscopic studies in reflected light were carried out on both bituminous coal and sandstones and shales from the coal-bearing horizon of the Anna mine. The mine is located in the south-western part of the Upper Silesian Coal Basin. The samples were taken at a depth of 700 m.

Electron diffraction patterns were recorded with a JEOL JEM 100C microscope operated at an accelerating voltage of 100 kV. The particles to be investigated were taken under the microscope from the selected microareas. Carbon foil coated with gold and placed next to the carbon foil with the investigated particles was used as standard.

Petrographic studies

The samples of black coal do not contain graphite. The component with the highest *R*% is vitrinite, which is accompanied by three other components showing a lower *R*%. All these constituents of bituminous coal are amorphous and do not display electron diffraction patterns.

The principal component of sandstones is quartz. It is accompanied by feldspars, clasts of igneous rocks, heavy minerals such as the TiO₂ group, and garnets showing a zonal structure. A fairly common phenomenon is the filling of the intergranular space with organic substance. A part of this substance has got into the sediment as clastic material. The organic matter with higher reflectance is, as a rule, strongly anisotropic and has the optical features of kerogen thucholite (Kucha 1982). Such kerogen contains streaks of graphite exhibiting typical optical features in reflected light (Phot. 1).

The sandstones also contain carbonates up to 0.6 mm in size, with common graphite intergrowths (Phot. 2). The distribution of graphite streaks in calcite suggests that calcite and graphite are pseudomorphous after oxidized organic matter.

Abundant fine graphite flakes have also been noted in marls (coal shales) (Phot. 3). This graphite is generally intercalated by a dark mineral which has been identified as mica on the electron microscope. The co-existence of graphite and mica intercalations suggests a genetic relation between these two minerals. The

occurrence of carbonates in coal shales is also positively correlated with the presence of graphite.

Electron diffraction studies

Both kerogen and the three distinguished types of graphite were subjected to electron diffraction investigation.

Kerogen. Three types of ordering were detected in kerogen: i) amorphous, ii) of a thickness of Van der Waals graphite layer - $c_0 = 7.40 \pm 0.07$ Å, and iii) typical graphite of a layer thickness $c_0 = 6.72 \pm 0.06$ Å. The latter type of order can be presumably assigned to the graphite streaks observed in kerogen (Phot. 1).

Graphite in carbonates. Graphite found in carbonates (Phot. 2) has the lattice parameters typical of this mineral: $a_0 = 2.45 \pm 0.03$ and $c_0 = 6.73 \pm 0.07$ Å. It seems that graphite forms, or may form, epitaxial layers on those planes of calcite whose identity period is close to that of graphite. The attempts to determine the crystallographic orientation of graphite with respect to the calcite ground-mass failed to give unequivocal results, and further studies are required to answer this question.

It is worth noting that graphite growing on both the external and internal surfaces of siderite has been reported from the Krzemianka deposit (Kucha *et al.* 1979).

Graphite in shales. Graphite forms intergrowths with minerals of the mica type. Such intergrowths produce a complex diffraction pattern (Phot. 4). Two lattices can be distinguished: one of a mica-type mineral, with the unit cell close to that of muscovite, and the other of typical graphite. A feature deserving note is the splitting of diffraction points in places where the graphite and mica lattices coincide (Phot. 4). One of such subpoints can be identified as arising from graphite, and the other can be attributed to the mica-type lattice. At high magnification, such coinciding reflections show a far more complex structure, presumably resulting from double diffraction on the plane of epitaxial intergrowth.

ORIGIN OF GRAPHITE

The petrographic and electron microscope studies suggest that graphite from the Anna mine owes its origin to oxidation of organic matter. This hypothesis accounts for the fact that graphite occurs in carbonate shales (marls), sandstones and in calcite and Fe-dolomite pseudomorphs after organic matter but has not been found in pure coal in which the Eh was very low, inhibiting oxidation. The organic matter of natural origin is a mixture of aliphatic and aromatic compounds differing markedly in oxidability (Waters 1963). The most resistant to oxidation are aromatic hydrocarbons. When the Eh is high enough, aliphatic derivatives are oxidized whereas aromatic compounds may remain intact. The organic matter after oxidation may be subject to conjugation (linking of benzene rings) on the hexagonal matrix of mica- or carbonate-type minerals. This may lead to the formation of epitaxial layers of graphite, which may subsequently become a matrix controlling the growth of successive graphite layers. This process may eventually give rise to microscopic graphite flakes (Photos. 1, 2, 3). If the intergrown minerals have similar or identical crystal symmetry, the epitaxial layer forms quickly and efficiently (Schneider 1976). This applies to graphite-mica intergrowths, in which the hexagonal symmetry on the 001 plane of graphite and mica is nearly identical

(Theng 1974). A similar system carbonate-graphite requires further studies, as the investigations carried out to-date failed to determine the graphite-carbonate orientation.

The growth of microscopic graphite may proceed according to the "concept of stage" (Herold 1979). In the first stage, all the spaces between coal (graphite) layers are occupied by non-graphitic intergrowths. The next stages consist in the successive removal of the intergrowths either through a physical process or through chemical reactions (Herold 1979). In consequence the degree of ordering increases and its range may attain microscopic scale, as was observed in the samples studied.

It is worth noting that the growth of graphite on siderite has been reported from the Krzemianka deposit (Kucha *et al.* 1979), and graphite-montmorillonite intergrowths have been noted in copper-bearing shales. These observations imply that the suggested mechanism of graphite formation, involving the oxidation of organic matter combined with the ordering of benzene rings on the hexagonal matrix of carbonates and clay minerals, is widespread in nature. Such a process would not require high temperatures.

From the above studies it appears that three types of evolution of organic matter are feasible. This evolution is controlled by the Eh (oxidation) and the quantitative proportion between the contents of organic matter and clay or carbonate minerals.

- i) Coalification: Organic matter prevails quantitatively over clay minerals. The low Eh does not promote oxidation. Under these conditions graphite cannot form without the action of heat.
- ii) Oxidation of organic matter at the marked prevalence of clay over organic substance. The Eh is relatively high. This, together with the matrix effect produced by the hexagonal lattice of clay and carbonate minerals, may lead to the formation of fairly large amounts of fine-dispersed graphite (Photos 1, 2, 3).
- iii) Thucholitization (Kucha 1982) occurs when organic matter prevails quantitatively over clay minerals. The oxidation process is controlled catalytically by γ radiation and transition metals, leading to specific polymerization and dimerization of the oxidation products high in aromatic hydrocarbons, and eventually to graphitization.

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WYSTĘPOWANIE GRAFITU W ŁUPKACH I PIASKOWCACH KARBONU PRODUKTYWNEGO KOP. ANNA, GÓRNOŚLĄSKIE ZAGŁĘBIE WĘGLOWE, POLSKA

Streszczenie

W piaskowcach i łupkach (marglach) z warstw węglowych kop. Anna występują niewielkie ilości grafitu trzech typów:

i) grafit jako przerosty z węglanami. Węglany powstały przez zastąpienie substancji organicznej i tworzą pseudomorfozy po materiale organicznym. Grafit występuje jako przewarstwienia na płaszczyznach krystalograficznych o symetrii heksagonalnej kalcytu i dolomitu Fe.

ii) grafit jako przerosty w wysokowęglowej substancji organicznej typu kerogenu.

iii) grafit tworzący przerosty z glinokrzemianami typu miki. Na płaszczyźnie 001 miki tworzą się przypuszczalnie epitaksjalne warstwy grafitu.

Opisywany w pracy grafit powstał prawdopodobnie bez udziału wysokiej temperatury w rezultacie:

i) utlenienia substancji organicznej. Wskutek tego węglowodory alifatyczne jako łatwiej utleniające się uległy usunięciu, a pozostały materiał organiczny wzbogacił się w węglowodory aromatyczne bardzo odporne na utlenianie. Węglowodory aromatyczne (pierścien benzenowy) stanowią podstawowy składnik grafitu.

ii) pierścienie benzenowe (aromatyczne) zostały uformowane w warstwy grafitowe na płaszczyźnie o symetrii heksagonalnej miki i węglanów.

OBJAŚNIENIA FOTOGRAFII

PLANSZA I

Fot. 1. Kerogen (K) zawierający przerosty grafitu (G) w piaskowcu węglowym. Preparat 9, skala 50 μm , światło odbite

Fot. 2. Przerosty grafitu (G) w ziarnie węglanowym z piaskowca węglowego. Grafit lokuje się prawdopodobnie w sposób uporządkowany na heksagonalnej matrycy węglanowej. Węglan powstał prawdopodobnie przez zastąpienie bioklastu lub klastu substancji organicznej. Preparat 9, skala 70 μm , światło odbite

PLANSZA II

Fot. 3. Grafit z przerostami minerału typu miki (M) występujący w marglu węglowym. Badania dyfrakcyjne wykazują istnienie epitaksjalnych warstw grafitu na micy (Fot. 4). Preparat 31, skala 70 μm , światło odbite

Fot. 4. Elektronowy obraz dyfrakcyjny naturalnie utworzonych epitaksjalnych warstw grafitu na płaszczyźnie 001 minerału typu miki ($uvw = 001$). Punkty dyfrakcyjne mają złożoną strukturę wskutek niepełnej równości odpowiednich wartości d_{hkl} dla grafitu i minerału typu miki. Z reguły wskaźnikowane refleksy składają się co najmniej z dwu punktów z których jeden może być zidentyfikowany jako odpowiedni refleks grafitu (w nawiasie) a drugi jako odpowiedni refleks pochodzący od minerału typu miki (bez nawiasu)

НАХОЖДЕНИЕ ГРАФИТА В СЛАНЦАХ И ПЕСЧАНИКАХ ПРОДУКТИВНОГО КАРБОНА ШАХТЫ „АННА”, ВЕРХНЕСИЛЕЗСКИЙ УГОЛЬНЫЙ БАСЕЙН, ПОЛЬША

Резюме

В песчаниках и сланцах (мергелах) с угольных пластов шахты „Анна” встречаются небольшие количества графита трех типов:

а) графит срastaющийся с карбонатами. Карбонаты возникли путем замещения органического вещества и образуют псевдоморфозы по органическому веществу. Графит развит в виде прослоев на кристаллографических плоскостях гексагональной симметрии кальцита и Fe-доломита,

б) графит, образующий срastания с высокоуглефицированным органическим веществом типа керогена,

в) графит, образующий срastания с алюмосиликатами типа слюды. На плоскости 001 слюды образуются предположительно эпитаксиальные слои графита.

Описываемый в работе графит вероятно образовался без участия высокой температуры в результате:

а) окисления органического вещества. В следствие этого алифатические углеводороды, как легче окисляющиеся, были удалены, а остальной органический материал обогатился ароматическими углеводородами очень стойкими на окисление. Ароматические углеводороды (бензолные кольца) являются основным компонентом графита,

б) бензолные (ароматические) кольца сформировались в графитовые прослойки на гексагональной симметрии плоскостях слюды и карбонатов.

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

ТАБЛИЦА I

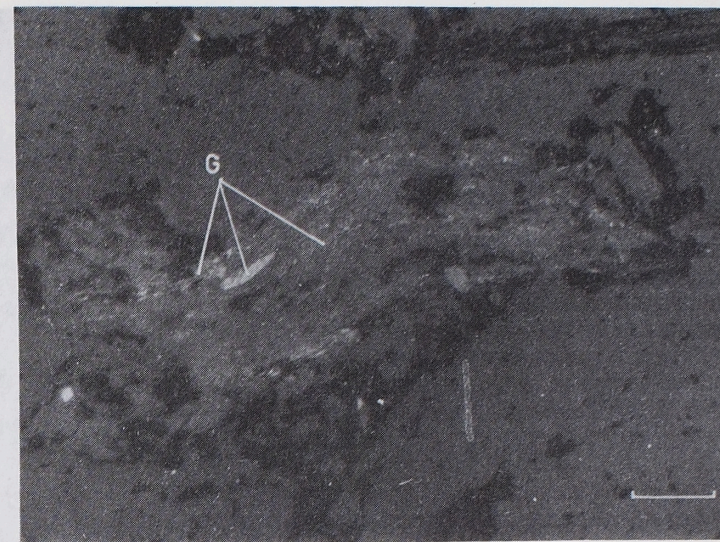
Фото 1. Кероген (K) в угольном песчанике, содержащий включения графита (G). Образец № 9, масштаб 50 мкм; отраженный свет.

Фото 2. Включения графита (G) в зерне карбоната из угольного песчаника. Графит вероятно занимает упорядоченное положение на гексагональной карбонатной матрице. Карбонат, по-видимому, образовался путем замещения биокласта, или класта органического вещества. Образец № 9, масштаб 70 мкм, отраженный свет.

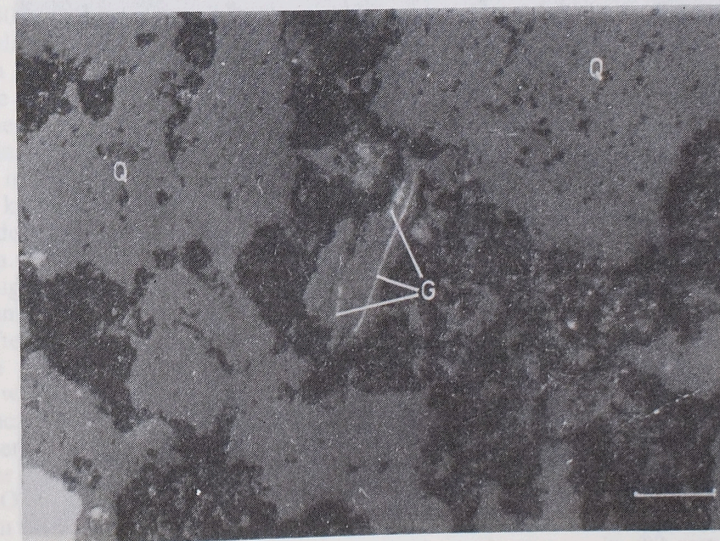
ТАБЛИЦА II

Фото 3. Графит в угольном мергеле, срastaющийся с минералом типа слюды (M). Дифракционные исследования обнаруживают присутствие эпитаксиальных слоев графита на слюде (фото 4). Образец № 31, масштаб 70 мкм, отраженный свет.

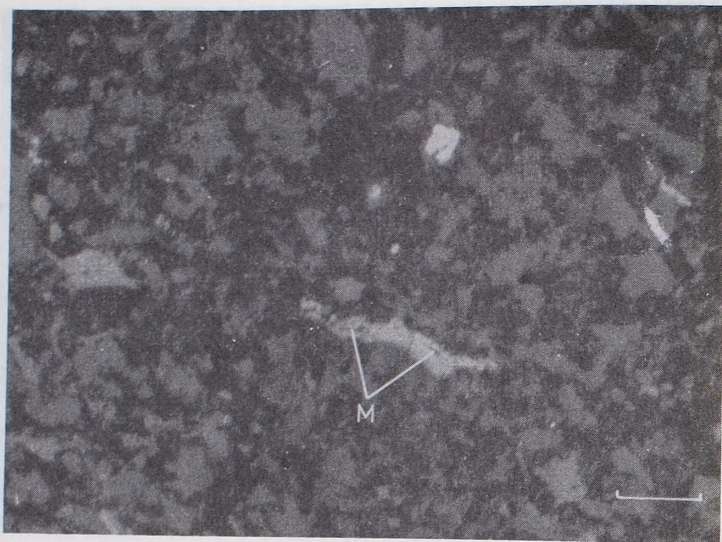
Фото 4. Электронное дифракционное изображение естественных образований эпитаксиальных слоев графита на плоскости 001 минерала типа слюды ($uvw = 001$). Дифракционные точки сложной структуры в следствие неполного равенства соответствующих значений d_{hk} графита и минерала типа слюды. Как правило, индикаторные отражения состоят по крайней мере из двух точек, одна из которых может быть отождествлена как соответствующее отражение графита (в скобках), а второе как соответствующее отражение, происходящее от минерала типа слюды (без скобок).



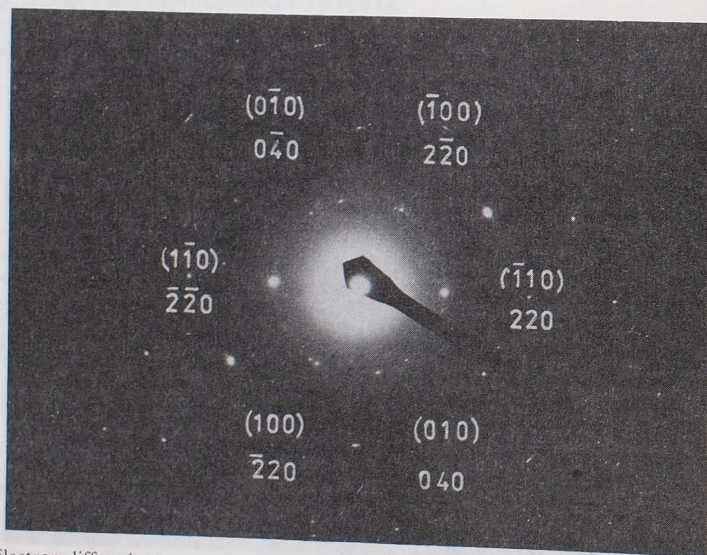
Phot. 1. Kerogen (K) containing graphite intergrowths (G) in coal sandstone. Sample 9, scale 50 μ m, reflected light



Phot. 2. Graphite intercalations (G) in a carbonate grain from coal sandstone. Graphite presumably grows in an orderly manner on the hexagonal carbonate matrix. The carbonate formed probably through replacement of a bioclast or clast of organic matter. Sample 9, scale 70 μ m, reflected light



Phot. 3. Graphite with intercalations of a mica-type mineral (*M*) in coal marl. Electron diffraction studies have revealed the presence of epitaxial graphite layers on mica (Phot. 4). Sample 31, scale 70 μm , reflected light



Phot. 4. Electron diffraction pattern of natural epitaxial graphite layers on the 001 plane of a mica-type mineral ($uvw = 001$). The diffraction points have a complex structure due to misfit equality of the respective d_{hkl} values for graphite and mica-type mineral. The indexed reflections consist, as a rule, of at least two points, one of which can be attributed to graphite (in brackets), and the other to mica-type mineral (without brackets)

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