THE ORIGIN OF GRAPHITE IN THE CRYSTALLINE BASEMENT OF THE WESTERN TATRA MTS. (WESTERN CARPATHIANS, S-POLAND)

ALEKSANDRA GAWĘDA[*] and STEFAN CEBULAK

University of Silesia, Faculty of Earth Sciences, Dept. of Geochemistry, Mineralogy and Petrography, Będzińska st. 60, 41-200 Sosnowiec, Poland; *gaweda@us.edu.pl

Abstract: Metamorphic rocks with graphite contents from 0.1 wt. % to 4 wt. % were analysed using Oxyreactive Thermal Analysis as a main tool with supporting X-ray and optical methods. Two generations of graphite were found in these rocks: 1. predominant graphite *Gph*$_1$ of organic origin (graphitized petroleum coke); 2. hydrothermal graphite *Gph*$_2$, in association with postmagmatic muscovite, albite and quartz. The *P-T* conditions of final graphitization for Gph$_1$ were assumed as 7.5-10 kbar and 700-780 °C. The hydrothermal graphite precipitation took place at the temperature of 700-730 °C and pressure about 6 kbar and continued during cooling up to 400 °C and 2 kbar of pressure.

Introduction

Graphite present in metamorphic rocks in thought to be a product of two geological processes: 1. transformation of organic matter of different origin, related mainly to heat; 2. precipitation from fluid saturated with respect to C, with the typical association with hydrous silicates (muscovite) and Fe-Ti oxides (Wopenka & Pasteris 1993; Connolly 1995). The type of graphite we observe in natural circumstances in the result of the following factors: A. temperature; B. pressure (stress and hydrostatic pressure); C. type of organic precursors; D. catalytic properties of inorganic host-minerals; E. fluid composition (by means of oxidizing/reduction conditions); F. porosity/compaction and permeability of the host rocks; G. geological time.

Temperature is thought to be the most important factor in graphite formation, but graphitization in nature could be caused by all the above mentioned geological factors, promoting or inhibiting the process of carbon transformation (Bonijoly et al. 1982; Wilks et al. 1993). Strain — in addition to temperature — is needed not only to initiate the graphitization process but it significantly lowers the critical temperature, at which the transformation of organic matter into graphite could occur. The critical *P-T* conditions of syn-kinematic metamorphism, documented in many natural occurrences show at least greenschist or lower amphibolite metamorphism (300–500 °C and 4–5 kbar of pressure) as well as much higher — upper amphibolite to granulite facies conditions (Landis 1971; Diessel & Offler 1975; Wilks et al. 1993). The polytype of graphite (3R or 2H) depends on the kind of pressure: stress facilitates the **2H** polytype formation, while hydrostatic pressure dominated conditions could — in some cases — facilitate **3R** polytype crystallization. The significance of oxygen fugacity in graphite bearing assemblages was demonstrated in detail by Connolly (1995). Low oxygen fugacity (f_{02}) is indispensably required for the graphitization of organic matter, regardless of the type of the actual process.

In the case of high oxygen fugacity (oxidizing conditions) all carbon present in rocks would be transformed into CO_2 (gas) and possibly removed from the system. The removal of the gaseous products of carbon transformation is important for the *P-T* conditions of graphitization: under conditions preventing the escape of gaseous product graphitization would take place slowly and would require higher temperatures and pressures (Diessel et al. 1978).

The aim of this paper is to describe graphites present in metamorphic rocks of the Western Tatra Mts. and to determine their origin as well the relative time of graphitization. An additional, but not the least, aim is to check the usefulness of the oxyreactive thermal analysis for graphite investigations.

Geology

The crystalline basement of the Western Tatra Mts. is composed of metamorphic rocks, intruded by the Variscan Roháče granitoid pluton. In the metamorphic complex both metasedimentary rocks (paragneisses, migmatites and mica schists) and orthoamphibolites and orthogneisses can be distinguished (Fig. 1a). The metasedimentary (metapelitic-metapsamitic) origin of most of the gneisses, migmatites and micaschists was confirmed by mineralogical investigations (Gawęda & Burda 1995) and geochemical analyses of major and trace elements (Gawęda et al. 1996). The coarse-grained orthogneisses, found both on the Polish and Slovak sides of the metamorphic cover in question, were recently dated by the U-Pb method to 380 Ma (Poller et al. 1997). The main tectono-metamorphic event, which formed the peak metamorphic conditions is assumed to have occurred at 340–350 Ma (Poller et al. 1997). The Main Tatra Granite cooling ages

were calculated as 305–327 Ma (Janák & Onstott 1993). In the Polish (northern) part of the crystalline basement one can distinguish several parallel shear zones, running NE–SW and dipping gently (5–15°) to SE–SSE intruded by alaskitic leucogranites and their pegmatites (Gawęda 1995). Graphite-bearing rocks were found in the shear zones, mainly in the westernmost part of the investigated area (Fig. 1b).

Different origins have been presumed for the so-called graphitoid schists: a biogenic-tuffogenic origin of these rocks was considered by Bober et al. (1966); later on, a pneumatolytic or hydrothermal origin was assumed (Skupinski 1975; Kapera & Michalik 1995). The latter authors suggested metamorphic conditions in the sillimanite zone of the amphibolite facies and — using the "graphite geothermometer" of Shengelia et al. (1978) calculated the temperature of graphite crystal-

lization as 500 °C (for graphite from schists) and 600 °C (for graphite from quartzites).

Analytical methods

Preliminary investigations on all samples of graphite-bearing rocks were conducted in transmitted light and in reflected light. From the samples with graphite content of 2–4 wt. % concentrates of different grain sizes were prepared for X-ray investigations. Minor changes in structural state of graphite were observed after the demineralization with HCl-HF mixtures. After the set of experiments on the separated pure graphites we stated that the mixture of HCl+HF (5:1) had the smallest infuence on both X-ray characteristics and the
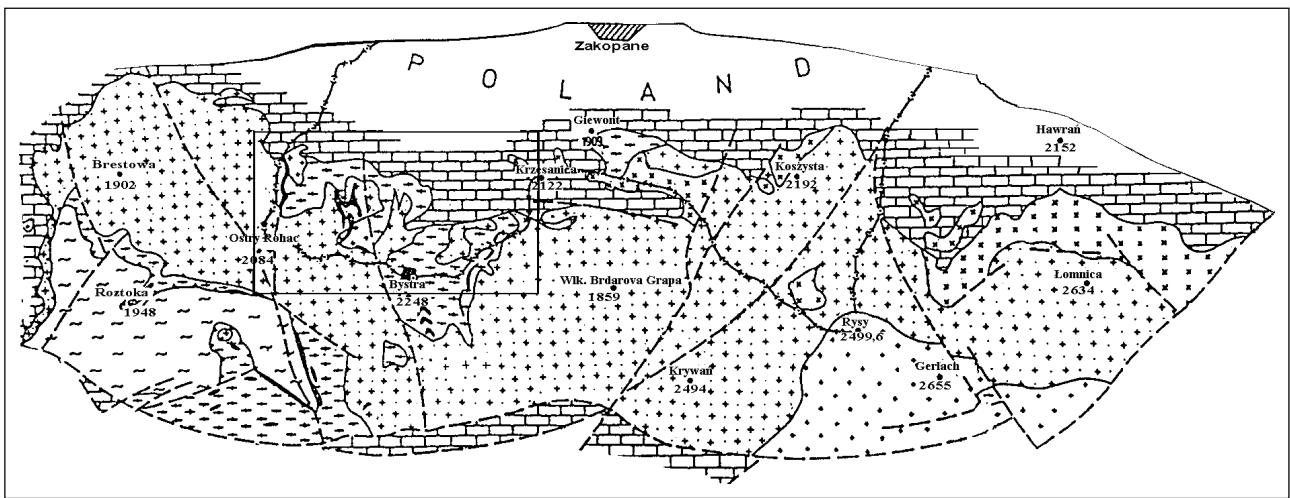

Fig. 1a. Simplified geological sketch of the Tatra Mts. (after Kohút & Janák 1994; all symbols according to these authors).
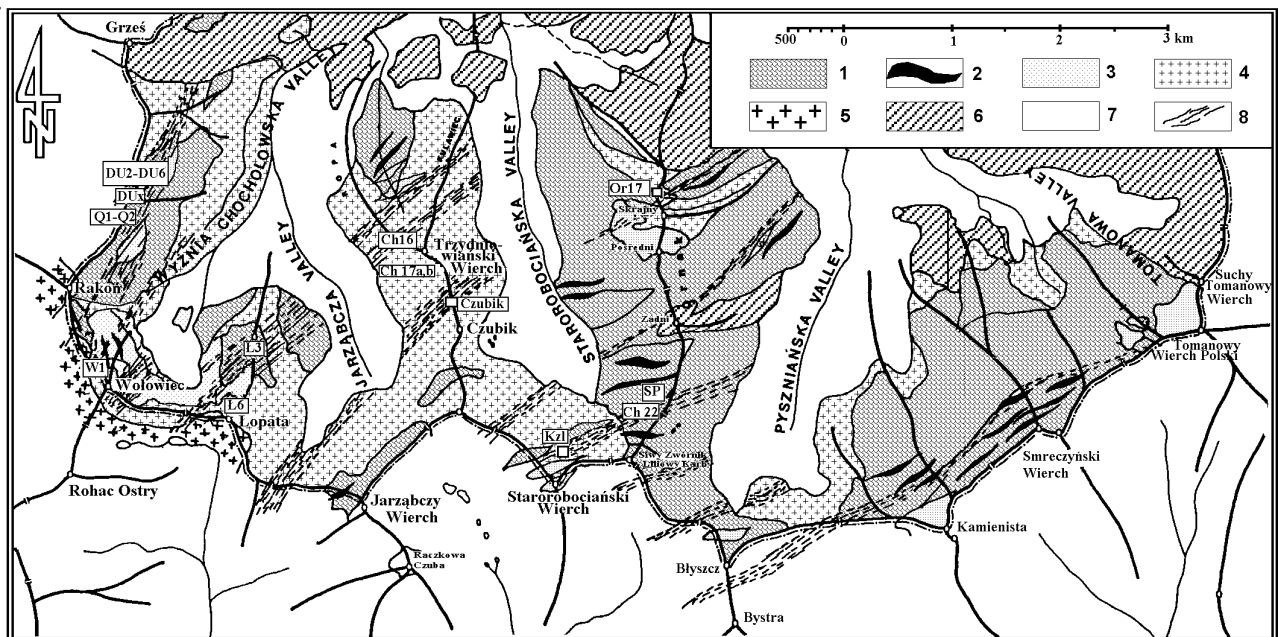

Fig. 1b. Simplified geological map of the Polish Western Tatra Mts. and sampling places. Explanations: 1 — metasedimentary rocks; 2 — amphibolites; 3 — alaskites; 4 — mylonitized orthogneiss; 5 — Roháče Granite; 6 — sedimentary cover (T+J); 7 — Quaternary deposits; 8 — shear zones.

thermal analysis pattern of graphite under investigations. X-ray analyses were carried out at the Dept. of Geochemistry, Mineralogy and Petrography, Univ. of Silesia (Rigaku Denki; CoKα) and — for comparison — at the Dept. of Geochemistry, Mineralogy and Petrography, University of Mining and Metallurgy (Philips X'Pert; CuKα).

Thermal analyses were carried out using an oxyreactive variety of this method at the Dept. of Geochemistry, Mineralogy and Petrography, University of Silesia. The oxyreactive modification of the thermal anylysis is based on the maximum accesibility of oxygen to reacting particles during heating at the time of analysis. The size of particles of the analysed substance should enable such a run of reaction, that the stoichiometry of the reagents is maintained in minute time intervals. During the carbonization process the size of reacting particles should guarantee that the reaction takes place in the whole particle, and avoid the formation of lag of reaction products. To fulfill these conditions we need: thin layers of substance, particle sizes below 0.1 μm and their dispersion in a neutral medium (Al_2O_3) as well as a dynamic atmosphere. All analyses were performed on a MOM Derivatograph (Hungary) in an air atmosphere. The analytical conditions were as follows: dynamic conditions for air suction of 1.9 cm^3min^{-1} and inflations rate of 1 cm^3min^{-1}; multiple sample holders (3–10 Pt plates) [3]. The weight of each sample depended on the carbon content and is in the range of 40 mg to 1500 mg. Samples with high carbon content were ground with Al_2O_3 powder in proportions of 1:2 to 1:3 to increase porosity of the samples and to enable the reactions between the oxygen and the sample components.

The Oxyreactive Thermal Analysis (OTA) was successfully used for examination of unmetamorphosed and weakly metamorphosed organic matter by means of its origin and temperature or metamorphism (Cebulak & Langier-Kuźniarowa 1997; Cebulak et al. 1997a). The preliminary results, obtained from the rocks of different metamorphic degree and different organic matter contents (Cebulak et al. 1997b, 1998) encouraged us to use OTA as the main tool for graphite investigations and description. This is in agreement with previous studies (Kwiecińska & Parachoniak 1976; Kwiecińska 1980) establishing a correlation between metamorphic degree and the peak temperature of DTA for graphites and related materials, as well as a correlation between DTA maximum and interlayered spacing d_{002}.

For Oxyreactive Thermal Analysis we used a collection of graphite standards (both natural and synthetic ones) with different degrees of crystallinity, different origins and different parent organic materials, obtained from A. Szymanski (Technical University, Warsaw, Poland), Carbon Electrode Plants (Racibórz, Poland) Museum of Earth (Univ. of Silesia, Sosnowiec, Poland).

The chemistry of associated minerals were investigated by electron microprobe at the Dept. of Mineralogy and Petrography, University of Wroclaw (Cambridge Microscan M9 electron microprobe, donation of the Vrije Universiteit Amsterdam). Analytical conditions: 15 kV accelerating voltage, 20 s counting time, ZAF correction procedure with sets of internationally recognized natural and synthetic mineral standards. The associated ore minerals were investigated in the

Dept. of Geochemistry, Mineralogy and Petrography, University of Silesia.

Abbreviations and phase notations used here:

Q — quartz, Kfs — K-feldspar, Ab — albite, An — anorthite, Mt — magnetite, Ilm — ilmenite, Bt — biotite, Ms — muscovite, Gph — graphite, AS — Al_2SiO_5 polymorphs, V — vapour phase.

Petrography of graphite-bearing rocks

Graphite was found in quartzites, quartz-rich gneisses (sample Nos.: Q2, Q3, DUx, DU1–DU6, Or.17, SP1, Ł3), mica schists (W1, Kżl), mylonitic orthogneisses with S-C structures (Ł6) and blastomylonites (Ch22, Ch17a) present in the shear zones (Fig. lb). In quartzites and quartz-rich gneisses the graphite content ranges from 2 to 4 wt. % (Table 1). Most of the graphite is concentrated in micro-laminae 0.2–0.3 mm thick (Fig. 2), subordinate amounts of graphite flakes are scattered among the quartz grains. In the sample Or.17 one can observe both graphite scattered in the quartz matrix and graphite inclusions in the muscovite flakes (Fig. 3). Blastomylonites and mica schists contain 0.1–1.0 wt. % of graphite. In the S-C mylonitic orthogneisses graphite is a component of the black "impregnant" (1.5 wt. % of graphite) found on the S and C surfaces (Fig. 4) and associated with the large muscovite flakes. The phengitic muscovite (Table 2A) and almost pure albite (Table 2B) are the products of sillimanite + alkali feldspar decomposition (Fig. 5).

Table 1: Modal analyses of representative graphite-bearing rocks (in vol. %).

Sample No	Quartz	Feldspars	Mica	Graphite	O.M.[**]
Or.17	84.8	1.8	8.6	4.0	0.8 (H+M)
SP1	84.5	3.05 (An$_{3-4}$)	7.55	4.0	0.9 (H)
DU2	84.4	2.6	9.6	2.1	1.3 (I+M)
DU3	84.4	8.5 (An$_{20}$)	2.8	2.8(.)	1.5 (I+H)
W1	9.0	5.0 (An$_{14-18}$)	84.0	0.2	1.8 (G+H)
Ł6	51.8	35.14 (An$_{0.1-0.3}$)	9.06	1.5[*]	2.5 (M+G)

[*] *percent of graphite in the black "impregnant" (2.5 vol. % of the rock) counted from thermal analysis of the separated impregnant;*
[**] *O.M. = ore minerals: ilmenite (I), hematite (H), magnetite (M), goethite (G).*
(In brackets − the anorthite content in plagioclase)
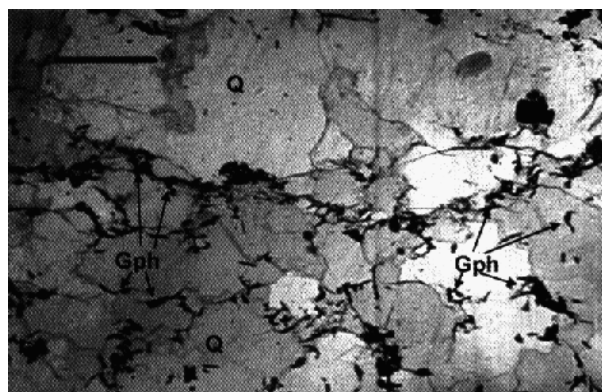
Fig. 2. Graphitic quartzite (DU4) from Dlhý Uplaz. Graphite flakes (Gph) concentrate in thin lamellae among the quartz grains (Q). Scale bar = 0.5 mm.

Table 2: A. chemical analyses and crystall-chemical formulae of muscovites (22 O^{2-}). **B**. Chemical analyses and crystall-chemical formulae of albites (8 O^{2-}).

A

Sample	Msl(C)	Msl(M)	Ms2(C)	Ms2(M)
SiO$_2$	47.01	46.34	46.29	45.56
TiO$_2$	0.89	0.95	1.19	1.45
Al$_2$O$_3$	34.88	36.02	35.56	34.84
FeO	0.95	0.92	1.00	0.92
MnO	0.02	0.00	0.05	0.03
MgO	0.64	0.45	0.60	0.63
Na$_2$O	0.40	0.51	0.67	0.49
K$_2$O	10.48	10.90	10.48	10.81
Total	95.27	96.09	95.84	94.73
formula				
Si	6.234	6.115	6.120	6.111
Al^{IV}	1.766	1.885	1.880	1.889
Al^{VI}	3.685	3.717	3.662	3.620
Ti	0.089	0.094	0.118	0.146
Fe	0.110	0.102	0.111	0.104
Mg	0.127	0.088	0.118	0.126
Mn	0.002	0.000	0.005	0.004
K	1.774	1.835	1.767	1.850
Na	0.102	0.131	0.171	0.126

C – core; M – margin

B

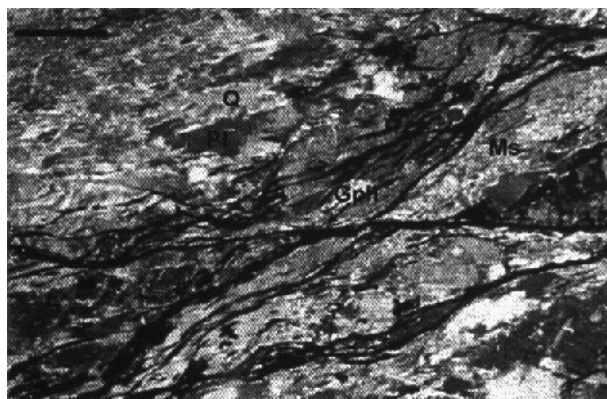| Sample	Ab1(C)	Ab1(M)	Ab2(C)	Ab2(M)
SiO$_2$	69.91	70.75	70.53	69.73
Al$_2$O$_3$	19.96	19.77	20.28	19.90
FeO	0.08	0.07	0.05	0.01
CaO	0.04	0.03	0.07	0.06
Na$_2$O	11.55	11.82	11.87	11.80
K$_2$O	0.06	0.11	0.06	0.06
An	**0.2**	**0.1**	**0.3**	**0.3**
Ab	**99.5**	**99.3**	**99.4**	**99.4**
Or	**0.3**	**0.6**	**0.3**	**0.3**

C – core; M – margin
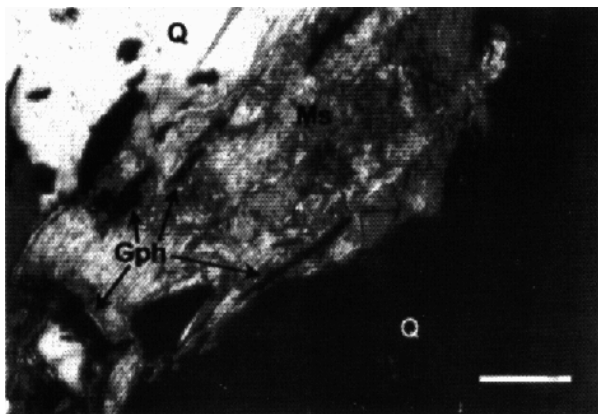
Fig. 3. Grain of postmagmatic muscovite (Ms) among the quartz grains (Q) in the graphitic quartzite from Ornak (Or.17) enclosing the graphite flakes (Gph). Scale bar = 0.5 mm.

Fig. 4. S-C structure of orthogneiss from Łopata (Ł6). The post-magmatic muscovite (Ms) and graphite (Gph) crystallized on the S-C planes. Pl = albitic plagioclase. Scale bar = 0.3 mm.
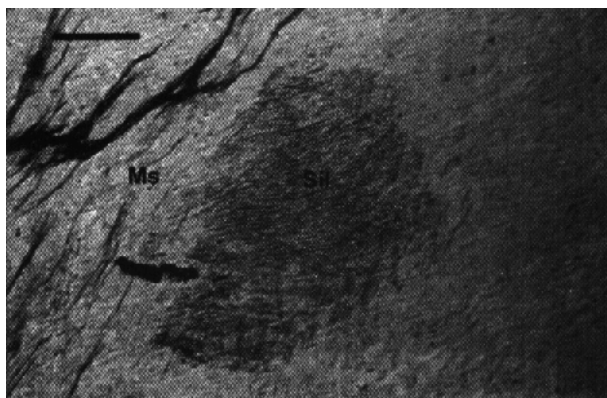
Fig. 5. Sillimanitic nodule (Sil) in the core of the postmagmatic muscovite (Ms). Sample Ł6. Scale bar = 0.1 mm.

Experimentals and results

X-ray analyses of both raw pure graphites and samples after acidification showed that the graphite represents 2H polytype, with high ordering degree (G.D.= 0.83; method after Tagiri 1981, updated by Barrenechea et al. 1992). In the classification of Landis (1971) it represents *d1* type with high crystallinity. The a_0 and c_0 parameters were calculated for raw concentrates and for samples after acidification during 48 and 120 hours. Their values change a little with the time of acid treatment which influenced the calculated temperatures of graphite crystallization (Table 3a). The temperatures obtained from curves presented by Demeny (1989) are significantly lower than those obtained by Shengelia (1978) and temperatures obtained in our experiments. We should remember that all curves presented in the paper of Demeny (1989) are almost parallel to the temperature axis in the interval over 500 °C, that is for graphite samples with good structural ordering, which can result in inprecise temperature estimations.

Oxyreactive thermal analysis (OTA) was carried out for raw samples, to calculate the amount of graphitic carbon and then for homogenized samples, ground for 30' with Al$_2$O$_3$. The ground samples showed lowering of the peak temperature (approx. 100 °C; Fig. 6a), but the grinding allowed us to distinguish the peaks from organic matter of different origin and/or metamorphic degree, and to avoid the influence of crystal-size on the temperature of the graphite decomposition. The large graphite flakes (Ø > 0.2 mm) usually show a higher degree of ordering and higher temperatures of crystallization, observed both in X-ray and OTA methods (Table 3b; Fig. 6a).

Table 3: A. Unit cell parameters of graphites (raw and after acidification — time of treatment in brakets) and estimated temperatures of crystallization. **B.** Unit cell parameters and estimated temperatures of crystallization of raw graphites. (Ts = according to Sengelia et al. 1978; Td = Demeny 1989).

A

Sample	a_o	c_o	Ts [°C]	Td [°C]
Or.17 (raw)	2.4570(0.0015)	6.7075(0.0038)	730	600
Or.17 (48 h)	2.4601(0.0002)	6.7111(0.0005)	680	590
Or.17 (120 h)	2.4613(0.0003)	6.7124(0.0006)	660	570

B

Sample	a_o	c_o	Ts [°C]	Td [°C]
SP_{XL}	2.4612(0.0007)	6.7127(0.0008)	666	575
SP_L	2.4611(0.0008)	6.7151(0.0008)	630	560
SP_M	2.4630(0.0008)	6.7164(0.0007)	625	530

*XL–crystal size > 0.2 mm; L– crystal size 0.01-0.2 mm; M–crystal size < 0.01 mm*

Samples after treatment with (HCL + HF) mixture were analysed in the same conditions as raw samples. During the experiments we observed a decrease of peak temperatures after acidification (Fig. 6b), and the effect was comparable with the shift observed for X-ray analysis. The acid treatment didn't influence the shape of the exothermal peak. The experiments carried out previously allowed us to determine the typical features of metamorphosed organic matter of different origin. Two thermal points are important in the OTA characteristics of graphites: 1. the beginning of reaction marks the lowest temperature threshold at which the organic matter was transformed and carbonized; 2. the peak of exothermal reaction marks the maximum thermal stability of the carbon structure. The beginning temperature of the exothermal reaction for the analysed graphites is quite stable and occurs in the range of 570–590 °C. The peaks of reactions for raw samples can be grouped into two intervals: 640–650 °C and 698–780 °C (Table 4). One exception is the sample Ł3 with the first peak about 450 °C. This could be evidence for the possible presence of weakly metamorphosed (antracithic) carbon.

The thermal characteristics of the graphites under investigation are typical for bituminous precursor material: petroleum cokes originated from metamorphosed pyrobitumins, such as: asphalts, ozokerite or heavy fractions of rock-oil. The high degree of metamorphism of the graphitized organic substance is shown in Fig. 7. Different and high temperature oxyreactive patterns of graphites are results of both degree of metamorphism and the genetic diversification of the parent organic substance. Graphites originated from bituminous substances metamorphosed in amphibolite facies conditions usually show oxyreactive effects at high temperatures — i.e. above 700 °C.
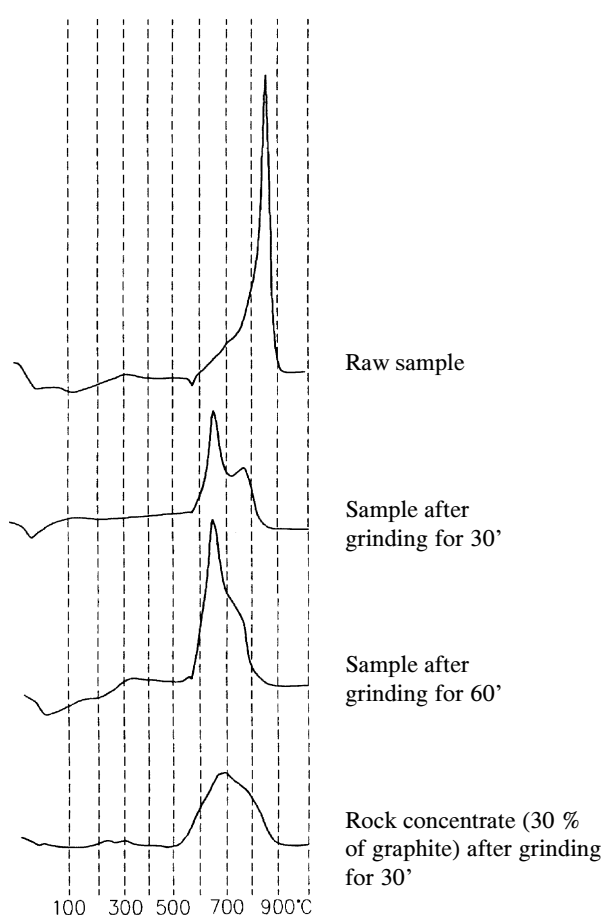
Fig. 6a. Oxyreactive thermal patterns of graphite (sample Or.17) raw and after grinding.
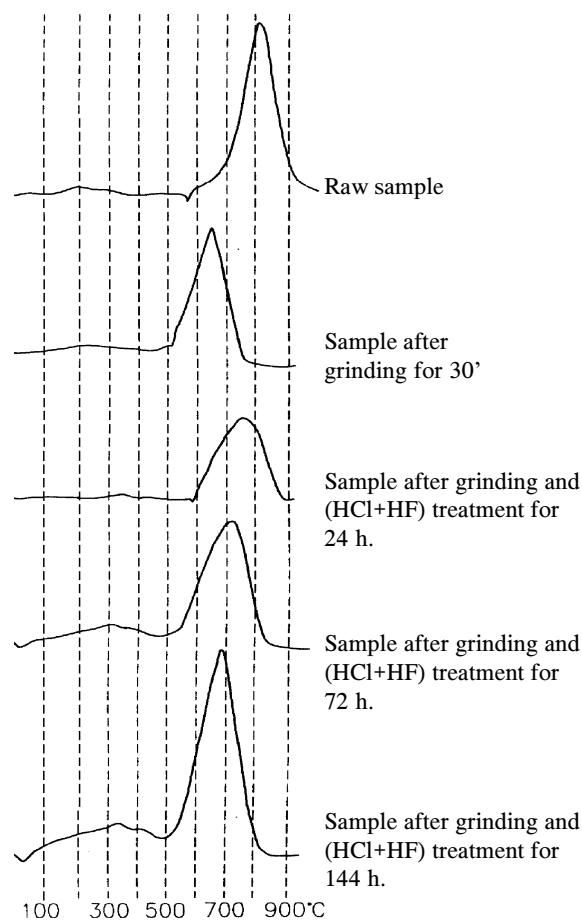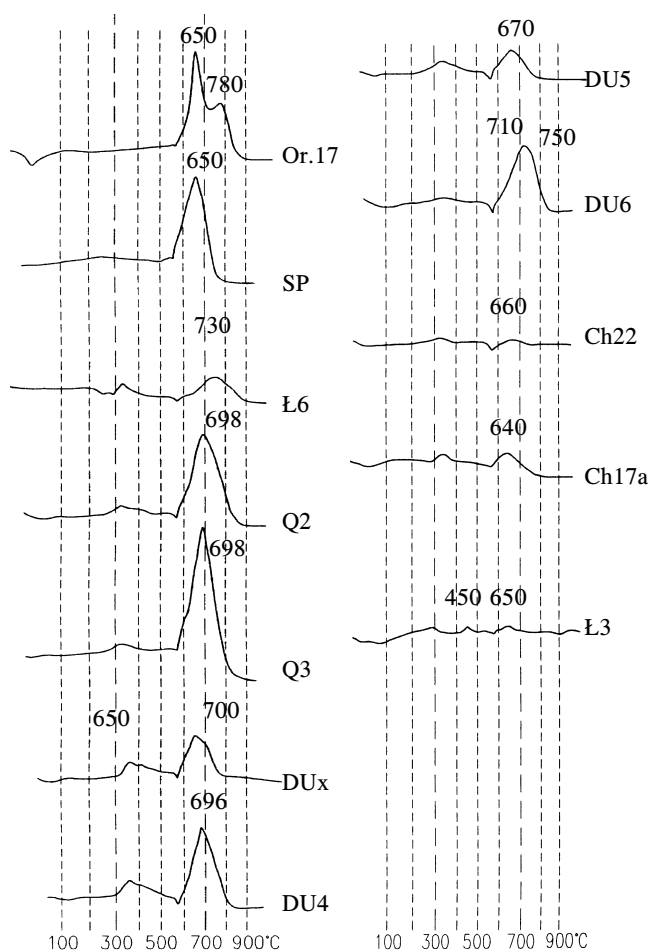

Fig. 6b. Oxyreactive thermal patterns of graphite (sample SP) raw and after acid treatment.

Table 4: Thermal characteristic of graphites from the W-Tatra Mts.

Sample No	beginning of reaction [°C]	peak of reaction [°C]
Or.17	570	650
	660	780
SP1	570	650
Ł6	590	730
Q2	580	698
Q3	580	698
DUx	590	650
		700
DU5	580	670
DU6	590	720
Ch22	590	660
Ch17a	590	640
Ł3	420	450
	590	650

The oxyreactive peaks in the temperature range of 600–700 °C are typical of humolitic precursor material (metamorphosed in the same conditions in amphibolite facies). Such a conclusion is supported by a series of OTA experiments led for the carbonization products of antracites and pitches of different origin as well as petroleum coke carbonization products obtained from Carbon Electrode Plants — Racibórz (Poland).

Fig. 7. Oxyreactive thermal analyses of graphites from the Western Tatra Mts.
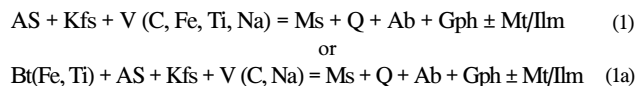
Discussion

The origin of graphite

The high concentration of graphite in rocks that have undergone significant polymetamorphic changes as well as locations of graphite-rich rocks in the shear-zones and the unequivocal mineral relations raise the question if all the graphite is of organic or hydrothermal origin in the Western Tatras crystalline basement. To solve the problem of its origin we considered both hydrothermal and organic hypotheses, taking into account the geological and thermodynamic aspects of graphite occurrence as well.

The hydrothermal hypothesis

Hydrothermal graphite precipitation can occur from C-O-H ($\pm$ Fe, Ti, Si, Na) fluids saturated with respect to carbon, during cooling and exhumation of metamorphic terranes (Cesare 1995). The most important feature which determine if graphite would precipitate is the composition of the fluid, expressed by X_0 (atomic fraction of oxygen relative to oxygen plus hydrogen — Fig. 8). The mineral devolatilization reactions or the C-O-H $\pm$ Fe fluid influx are factors determining the redox conditions in natural systems (Connolly 1995). In the first case siderite decarbonization and oxidation can lead to graphite + magnetite precipitation. The next possibility can result in hydration of the K-feldspar + Al_2SiO_5 system to produce muscovite, graphite and quartz. The general reaction can be written as:

$$AS + Kfs + V (C, Fe, Ti, Na) = Ms + Q + Ab + Gph \pm Mt/Ilm \qquad (1)$$
$$\text{or}$$
$$Bt(Fe, Ti) + AS + Kfs + V (C, Na) = Ms + Q + Ab + Gph \pm Mt/Ilm \quad (1a)$$

In that case the amount of graphite precipitated can be correlated with the amount of muscovite (as the hydrated phase) so that the production of 1 cm^3 muscovite involve the precipitation of 0.0002 cm^3 graphite (Connolly 1995).

The sample adequate to that model is the S-C orthogneiss (Ł6). In that sample graphite is a component (1.5 wt. %) of the black "impregnant" found on the S-C surfaces (Fig. 4). In the whole sample muscovite content is 9.06 vol. %, and the "impregnant" content is 2.5 vol. %, what makes the real graphite content 0.0004 wt.% (for simplification we recalculate every number as wt. % taking specific gravities as: for muscovite = 2.79 g/cm^3; for graphite = 2.2 g/cm^3; for the whole rock = 2.7 g/cm^3; for the black "impregnant" = 4 g/cm^3). Taking into account that the graphite in the Ł6 sample occurs only as mineralization on cleavage (C) and schistosity (S) planes it seems to be possible that in this particular case graphite could precipitate from the carbon-saturated vapour phase. The same interpretation can be assumed for the mica schists with very small graphite content (i.e. W1) or for the graphite cogenetic with muscovite flakes found in the quartzite sample Or.17 (Fig. 3). The above intrepretation can support the suggestion of Kapera & Michalik (1996) about the hydrothermal precipitation of graphite in the so called "chlorite" schists (in fact mica schists, with no chlorite present).
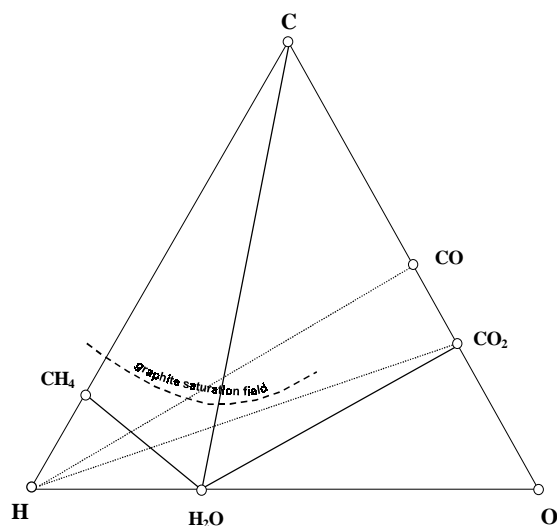
Fig. 8. C-H-O phase diagram with the graphite growth limits in CH_4-CO-CO_2-H_2O fluids (combined from Connolly 1995; Bachmann et al. 1991).

The organic hypothesis

If we consider the graphitic quartzites (2–4 wt. % of graphite) with only 2.8 vol. % of sericite/muscovite such a hypothesis looks improbably. Hydrothermal precipitation cannot produce the laminar structures characteristic for graphite-rich rocks. Both the rock fabric and the thermal characteristics of the graphites point to the organic origin of the graphite in question. Their geological position — xenoliths inside the sheared orthogneiss — suggests that they were fragments of the metasediments emplaced in the older granite (possibly 380–400 Ma ago) and their metamorphism was much older than the Roháče granite intrusion. Such interpretation is in agreement with the high crystallinity index of graphite, the type of organic matter (the Early Paleozoic rocks could not contain more evolved organic matter) and the high temperatures of decomposition.

The problem to consider is the amount of primary organic matter (possibly bitumins from Lower Paleozoic algae), present in the rocks before metamorphism. To obtain the presently observed 2–4 wt. % of graphite we need the primary bitumins concentration in the range of 15–20 wt. %. Such a concentration can be found in the Early Paleozoic rocks from the Baltic area. The fingerprints of the oxyreactive features of the organic matter from the Baltic area is shown on the Fig. 9 and was discussed in a recent paper (Cebulak & Langier-Kuźniarowa 1997). The present host-rocks — quartzites, previously sandstones, cannot be considered as favourable oil-bearing host rocks for primary bitumins but they could serve as good collectors for migrating bitumins. In such an interpretation in the described rocks we can observe the bitumin deposits, conserved during metamorphism.

Special attention should be paid to sample Or.17. It shows two-peak characteristics and two modes of graphite occurrence: both the disseminated graphite and graphite flakes growing together with muscovite. Such a situation could suggest the presence of both types of graphite in this sample.

P-T conditions and time relations of graphitization

The conditions of post-magmatic graphite (***Gph2***) crystallization are quite easy to estimate. This type of graphite is associated with the mineral reaction 1a: AS + Kfs + Bt + V (C, Na) = Ms + Q + Ab + Gph + Mt/Ilm. Applying the phengite-in-muscovite geobarometer (Massonne & Schreyer 1987), the critical curve of the reaction and the muscovite stability field, we can assume the maximum temperature and pressure of precipitation as 700–730 °C and 6 kbar. The minimum conditions are as low as 450 °C and approx. 2 kbar (Fig. 10). We can observe the similarity of peak temperature obtained from OTA (Fig. 7 — sample Ł6) and maximum temperature estimated from mineral reactions. The origin of hydrothermal fluids could be related to the Roháče granite emplacement and fluid migration along the cracks, cleavage and schistosity — best developed in the shear zones.

The fluid composition is a result of the interaction of magmatic vapour phase and the envelope rocks. Taking into account that the hydrothermal graphite isn't very common phase in the metamorphic rocks we can assume that the presence of graphite-saturated CH_4-CO-CO_2-H_2O fluid (Fig. 8) originated as the result of assimilation of organic components present in some metasedimentary rocks.

The graphite with organic precursors (***Gph1***), metamorphosed in situ, is more difficult to investigate. The richest graphite occurrences are situated rather close to the tonalite-granodiorite Roháče intrusion. This granitoid was characterized by the high oxygen fugacity, manifested by the oxidation of Fe-minerals (Kohút & Janák 1994) and the temperatures of emplacement as high as 850 °C, thus in the contact aureole the temperature could exceed 700 °C (Ludhová & Janák 1996). In such a situation the carbon present in any unmetamorphosed form in country rocks should be oxi-
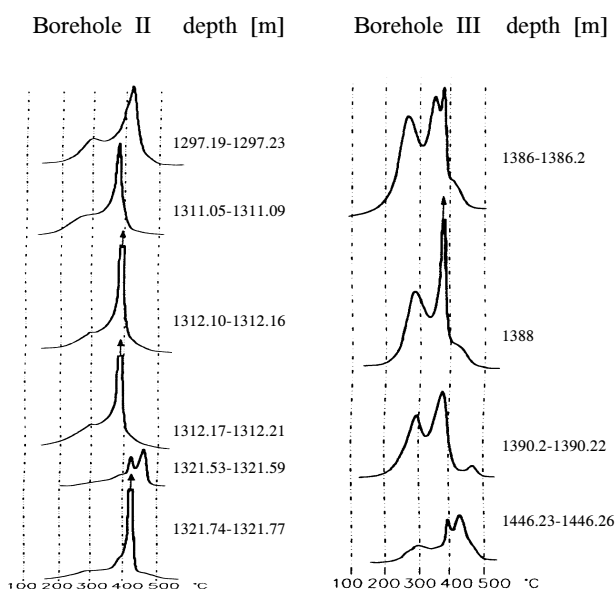

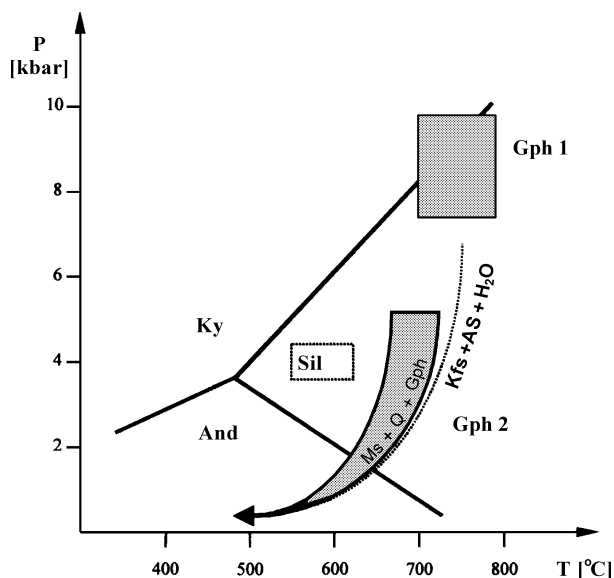**Fig. 9.** Examples of the Early Paleozoic kerogens from the Baltic area (after Cebulak & Langier-Kuźniarowa 1997).

Fig. 10. *P-T* diagram with the suggested graphitization conditions. Explanations: Gph₁—graphitization conditions of the primary organic matter; Gph₂—post-magmatic graphite precipitation.

dized to CO_2. The only solution is to assume that carbon was present as graphite before the Roháče granite intrusion, meaning that its transformation to the mineralogically stable form took place during an older metamorphic event.

The graphite polytype 2H is thought to be typical of stress conditions. That fact, together with the location points — in the shear zones — could suggest that the Old Variscan shearing episode, which occurred at about 345 Ma (Gawęda et al. 1998), had formed the graphitic structure. The *P-T* conditions in the sheared complex were estimated at 710–780 °C and 7.5–10 kbar (Gawęda & Burda 1995; Gawęda & Kozlowski 1997). It is possible, that in the rocks outside the shear zones the form of carbon was more weakly metamorphosed and was oxidized during or after granite intrusion. That could be the explanation for the graphite presence only in shear zones. A further consequence of the carbon oxidation could be that the CO_2 enrichment in postmagmatic fluids resulted in carbonate mineralization — very rich in that part of the Tatra crystalline basement (Paulo 1970, 1979; Wątocki 1950).

Conclusions

We can conclude that in the investigated area it is possible to distinguish two genetic types of graphite:

1. Most of the graphite (= *Ghp₁*), present in the Western Tatra metamorphic rocks was formed as the result of polymetamorphism of the older organic matter (possibly bitumins such as: ozokerite, asphalt, heavy fractions of rock-oil, etc.). Final graphitization took place before the Roháče granitoid intrusion and was possibly the result of the shearing event (345 Ma).

2. A minor amount of graphite (= *Gph₂*) was precipitated from the post-magmatic CO_2-CH_4-H_2O fluids and is syngenetic with secondary muscovite and albite. The origin of this type of graphite is connected with the postmagmatic fluids circulation in the vicinity of the Roháče granitoid pluton.

3. The remobilization of carbon (not as resistant as the graphite) to the volatile phase as CO_2 is a possible source of carbonate mineralization in the Western Tatra Mts.

4. The shear zones in the crystalline basement preserved graphite *G₁* and contain younger graphite *G₂* precipitated from the hydrothermal fluid phase.

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