XRD graphitization degrees: a review of the published data and new calculations, correlations, and applications

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Abstract. A system for transformation, correlation, and unification of subordinations between d_{002} (Å) of semi-graphite and graphite, graphitization degrees and metamorphic temperature was created. The existing equations in the literature were analyzed and new equations, which determine correlation relationships between these parameters, were formulated. The effect of factors that control graphitization processes (temperature, general pressure and tectonic stress, structure and origin of primary carbon matter, orientation of carbon formations, fluids, mineral and chemical composition, and duration of processes) was also considered. It was concluded that the structural state of semi-graphite and graphite is reversible, and this can be used for facies diagnostics and studying of metamorphic history of graphite-bearing metamorphic rocks. A new scale for graphitization degrees was proposed.

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INTRODUCTION

Determining the ideal structure of hexagonal (2H) graphite allows monitoring of the deviations from it. The structural variations of graphite and semi-graphite dispersed in metamorphic rocks have been used by a number of authors to determine the conditions of metamorphism. The P-T conditions of graphitized carbon formation and the tectonic evolution of graphite-bearing metamorphites are directly related to its structural order. It is one of the factors controlling the properties of this mineral, its significance as a raw material, its application, and price. The industrial significance of graphite as a valuable and expensive raw material has been highlighted by many authors (Faizullin, 1984; Nikolaev *et al.*,

1985; Mitchell, 1992; Trashliev, 1989; Pierson, 1993; Chung, 2002; Beyssac and Rumble, 2014; Luque *et al.*, 2014). Graphite has been defined as a strategic and critical raw material for the European Union since 2010 (Catinat *et al.*, 2010).

Graphite and carbon substances with a lower degree of structural order (degree of graphitization) have been the subject of research for nearly 100 years. Authors have used different XRD characteristics to determine the degree of structural ordering of natural carbon substances. Different schemes for arranging carbon formations according to their degree of graphitization have been created. Researchers relate the structural order of the carbon substance with its chemical composition, particle size, and with the mineral and chemical composition of the graphite-

bearing metamorphites. The combination of XRD and DTA of semi-graphite and graphite, and their relationships with other rock-forming minerals, is often used for facies diagnostics of metamorphic rocks.

The purpose of the present study is to establish correlations between the results of different researchers, which will allow unification of the XRD data on the degree of structural order/disorder, temperature, and other factors for the formation of graphite-containing rocks with subsequent proof of new correlations. This facilitates the study of the metamorphic evolution of carbonaceous rocks and the qualitative assessment of graphite raw materials.

PROBLEM STATUS

Determining the ideal structure of hexagonal (2H) graphite allows the deviations from it to be taken into account (Hassel and Mark, 1924; Bernal, 1924) (Fig. 1a, b).

Emergence of additional peaks in the XRD patterns of graphite indicates the presence of the rhombohedral (3R) modification of graphite (Taylor and Laidler, 1940; Lipson and Stokes, 1942) (Fig. 1c).

The degree of structural disorder of graphite (ρ) is determined by the unit cell volume of the structure consisting of randomly oriented layers of covalently bonded carbon atoms. Carbon materials with d_{002} spacing between 3.440 Å and 3.350 Å have been defined as graphitized carbon (Ergun, 1968). These materials always have a heterogeneous structure, retaining some characteristics of both the crystalline graphite and non-graphitic carbon. This heterogeneous structure can be calculated, using the structural differences between crystalline graphite and non-graphitic carbon. Contamination with various components affects structural characteristics (Franklin, 1951a; Ergun, 1968). The magnitude of the structural disorder (ρ) is related to the value of the interplanar distance d_{002} (Å). The change in ρ from 0 to 1 corresponds to the change in d_{002} from 3.354 Å (fully ordered graphite) to 3.440 Å (completely disordered graphite). Franklin (1951a) formulated the following relationship between d_{002} (Å) and ρ :

$$(1) d_{002} (\text{Å}) = 3.440 - 0.086 (1 - \rho^2).$$

The degree of structural order (u) is determined by the following equation (2):

$$(2) u = 1 - \rho.$$

A structural order of the carbon matter from practically amorphous to fully crystalline graphite ex-

ists. The increase in the degree of structural organization of the carbon material in the rocks associates with the increase in the degree of metamorphism, as temperature is the major factor controlling the processes of graphitization. All authors from 1951 to 2020 defined pressure, duration, origin and structure of the primary carbon substance, the mineral composition of the carbon-bearing rocks, the fluid activity of the medium, the orientation of the carbon particles and the graphite crystals with respect to tectonic stress as secondary factors of graphitization. They can act simultaneously or sequentially over time and can have different effects on graphitization processes. Their effect on graphitization processes are discussed in detail below.

Kwiecinska (1980) and Kwiecinska and Petersen (2004) used the degrees of graphitization (u) of Franklin (1951a) and classified natural carbon into four groups: anthracite ($u = 0.06-0.27$); meta-anthracite ($u = 0.27-0.45$); semi-graphite ($u = 0.45-0.57$); and graphite ($u = 0.57-1.00$). The content of 3R polytype varies from 3% to 10% in single graphite crystals with a structure close to ideal. In microcrystalline and cryptocrystalline graphite, it reaches 27%, and in semi-graphite – up to 35% (Kwiecinska, 1980).

Based on the results from experiments on graphite synthesis at 0.5–5.0 kbar and 300–600 °C, and depending on the values of d_{002} (Å) and the size of the crystallites L_{c002} (Å), the following types of carbon substance have been distinguished: carbon material, disordered graphite, graphite, and completely ordered graphite (Tagiri and Oba, 1986).

Seehra and Pavlovic (1993) formulated the following equation (3) for calculating the degree of graphitization (DOG), which is still used today (Li *et al.*, 2018):

$$(3) \text{DOG} = (3.440 - d_{002}, \text{Å}) / (3.440 - 3.354).$$

Ivashita *et al.* (2004) modified the equation (3) of Seehra and Pavlovic (1993) and determined the degree of graphitization (D.G%) as:

$$(4) \text{D.G\%} = [(3.440 - d_{002}, \text{Å}) / (3.440 - 3.354)] \times 100.$$

The decrease in d_{002} (Å) of graphite structure is significantly accelerated at temperatures above 400 °C. The relationship between the degree of graphitization (DG) and temperature is determined (Wada *et al.*, 1994) by equations (5) and (5a):

$$(5) T \text{ °C} = 3.2 \times \text{DG} + 280;$$

$$(5a) \text{DG} = (T \text{ °C} - 280) / 3.2.$$

Fig. 1. Crystal structure of graphite: a, b) graphite 2H (after Hassel and Mark, 1924; Bernal, 1924); c) graphite 3R (after Taylor and Laidler, 1940; Lipson and Stokes, 1942).

The dependence (5 and 5a) of Wada *et al.* (1994) has also been widely used in later studies (*e.g.*, Martinez *et al.*, 2003; Baiju *et al.*, 2005; Rawat and Sharma, 2011).

The correlation between the temperature of metamorphism (T °C), d_{002} (Å), and the degree of graphitization (GD) was calculated directly (Vlahov, 2015, 2018, 2019, 2020) using the following equations (6, 7, 8, and 8a):

$$(6) T \text{ °C} = 300 + (3.371 - d_{002}, \text{ Å}) \times 24000;$$

$$(7) \text{GD} = (3.371 - d_{002}, \text{ Å}) \times 8000;$$

$$(8) T \text{ °C} = 3 \times \text{GD} + 300;$$

$$(8a) \text{GD} = (T \text{ °C} - 300)/3.$$

RESULTS. NEW CALCULATIONS

All solutions of the cited equations from (1) to (8a) have been calculated. The direct correlation between d_{002} (Å), graphitization degrees (GD), and temperature of metamorphism (T °C) are expressed

by equations (6), (7), (8), and (8a). They allow quantitative comparison and conversion of the correlations formulated by different authors. The combination of equations (6), (7), (8), and (8a) with the other cited above equations allows to derive new correlations (Vlahov, 2020):

$$(9) T \text{ °C} = (3.380 - d_{002}, \text{ Å}) \times 24000 + 84;$$

$$(10) T \text{ °C} = [(DOG - 0.69767)/0.01163] \times 24 + 84;$$

$$(11) T \text{ °C} = [(D.G\% - 69.767)/1.163] \times 24 + 84.$$

All possible solutions of equations (1) to (11) in the interval $d_{002} = 3.440 - 3.350$ Å are shown in Table 1. The analysis of the facts had led to the formulation of six new regularities:

$$(12) \text{DOG} = (3.440 - d_{002}, \text{ Å})/0.086;$$

$$(13) \text{DOG} = 1 - \rho^2;$$

$$(14) \text{D.G\%} = [(3.440 - d_{002}, \text{ Å})/0.086] \times 100;$$

$$(15) \text{D.G\%} = (1 - \rho^2) \times 100;$$

$$(16) \text{GD}_{(0-30)} = (T \text{ °C} - 84)/24;$$

Table 1

Correlation between d_{002} (Å), graphitization degrees (u , DOG, D.G%, DG, and GD) and temperature of metamorphism ($T^{\circ}\text{C}$) for the range semi-graphite–graphite after equations of different authors. Numbers of equations in parentheses are the same as in the text

d_{002} (Å)	Structural state of carbon matter (Kwiecinska, 1980)	u eq. (1), (2)	DOG eq. (3)	D.G% eq. (4)	DG eq. (5a)	GD eq. (7)	GD eq. (8a)	GD eq. (16)	$T^{\circ}\text{C}$ eq. (6)	$T^{\circ}\text{C}$ eq. (8)	$T^{\circ}\text{C}$ eq. (9), (17)	$T^{\circ}\text{C}$ eq. (10), eq. (11)
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.
3.380	meta-anthracite, semi-graphite	0.45	0.69767	69.767	0	0	0	0	–	–	84	84
3.379	semi-graphite	0.46	0.70930	70.930	0	0	0	1	–	–	108	108
3.378	semi-graphite	0.47	0.72093	72.093	0	0	0	2	–	–	132	132
3.377	semi-graphite	0.48	0.73256	73.256	0	0	0	3	–	–	156	156
3.376	semi-graphite	0.49	0.74419	74.419	0	0	0	4	–	–	180	180
3.375	semi-graphite	0.51	0.75581	75.581	0	0	0	5	–	–	204	204
3.374	semi-graphite	0.52	0.76744	76.744	0	0	0	6	–	–	228	228
3.373	semi-graphite	0.53	0.77907	77.907	0	0	0	7	–	–	252	252
3.372	semi-graphite	0.54	0.79070	79.070	0	0	0	8	–	–	276	276
3.371	semi-graphite	0.56	0.80232	80.232	6	0	0	9	300	300	300	300
3.370	semi-graphite, graphite	0.57	0.81395	81.395	14	8	8	10	324	324	324	324
3.369	graphite	0.58	0.82558	82.558	21	16	16	11	348	348	348	348
3.368	graphite	0.60	0.83721	83.721	29	24	24	12	372	372	372	372
3.367	graphite	0.61	0.84884	84.884	36	32	32	13	396	396	396	396
3.366	graphite	0.63	0.86046	86.046	44	40	40	14	420	420	420	420
3.365	graphite	0.64	0.87209	87.209	51	48	48	15	444	444	444	444
3.364	graphite	0.66	0.88372	88.372	59	56	56	16	468	468	468	468
3.363	graphite	0.68	0.89535	89.535	66	64	64	17	492	492	492	492
3.362	graphite	0.70	0.90698	90.698	74	72	72	18	516	516	516	516
3.361	graphite	0.72	0.91860	91.860	81	80	80	19	540	540	540	540
3.360	graphite	0.74	0.93023	93.023	89	88	88	20	564	564	564	564
3.359	graphite	0.76	0.94186	94.186	96	96	96	21	588	588	588	588
3.358	graphite	0.78	0.95349	95.349	104	104	104	22	612	612	612	612
3.357	graphite	0.81	0.96512	96.512	111	112	112	23	636	636	636	636
3.356	graphite	0.85	0.97674	97.674	119	120	120	24	660	660	660	660
3.355	graphite	0.89	0.98837	98.837	126	128	128	25	684	684	684	684
3.354	graphite	1.00	1.00000	100.000	134	136	136	26	708	708	708	708
3.353	graphite	–	–	–	141	144	144	27	732	732	732	–
3.352	graphite	–	–	–	149	152	152	28	756	756	756	–
3.351	graphite	–	–	–	156	160	160	29	780	780	780	–
3.350	graphite	–	–	–	164	168	168	30	804	804	804	–

$$(17) T\text{ }^{\circ}\text{C} = \text{GD}_{(0-30)} \times 24 + 84.$$

The results of the calculations of these equations are shown in Table 1. Their derivations are discussed below.

DISCUSSION

Direct use of the parameter d_{002} (Å)

The X-ray diffraction parameter d_{002} (Å) has been used as an indicator to establish the structural state of natural carbon, as well as to determine the temperature, the course of metamorphism, and for facies diagnostics of graphite-containing rocks, for 70 years.

Some authors directly use the value of d_{002} (Å) to determine the degree of crystallinity (degree of graphitization) of natural carbon and the temperature of metamorphism.

French (1964) distinguished four structural states of carbon substance by the appearance, shape, and position of the diffraction peak 002 in the powder XRD patterns: 1) amorphous carbon substance – peak 002 is missing; 2) coal and asphalt – very wide and diffuse peak at about 3.5 Å; 3) structurally disordered graphite – diffuse peak at about 3.43 Å; 4) well-crystallized graphite – a sharp peak at 3.36 Å.

Landis (1971) classified carbon in metamorphic rocks by the position and ratio between the height and width of the 002 peak, respectively (Table 2). The system of Landis (1971) is also used in later publications (e.g., Šinkovec and Krkalo, 1994).

Grew (1974) studied the structural state of carbon in rocks with varying degrees of metamorphism from different parts of the world. He found that, with the increase of the metamorphic impact, the width of peak 002 and the value of d_{002} (Å) decrease. He

pointed out that the first stage in the arrangement of the layers of the graphite structure under the conditions of regional metamorphism corresponds to a temperature of 300–500 °C and a pressure of 3 kbar (or more) and to 1000 °C and 1 kbar in contact metamorphism conditions. The complete arrangement of the graphite structure is performed at 660–690 °C and 4.5–5 kbar.

Shengelia *et al.* (1979) conducted an experiment with carbon-graphite substance and crystalline graphite in the temperature range 300–850 °C and pressure from 1 bar to 6000 bar. The unit cell parameter c (Å) = $2d_{002}$ (Å) of graphite is a sensitive indicator of the temperature of mineral formation under the conditions of regional metamorphism. The authors suggest that variations in the parameter c (Å) of the carbon-graphite substance can be used as a geothermometer.

Yanchuk and Laz'ko (1980) determined the degree of structural ordering of graphite, using the values of d_{002} (Å). Graphite with high structural order ($d_{002} = 3.350\text{--}3.355$ Å) is characteristic of rocks of high-temperature facies.

Based on studies of natural graphite and semi-graphite, it has been established (Kwiecinska, 1980; Kwiecinska *et al.*, 2010) that cryptocrystalline carbon aggregates have $d_{002} = 3.400$ Å, and those with $d_{002} = 3.371$ Å were characterized as cryptocrystalline and microcrystalline semi-graphites. The carbon substance with $d_{002} = 3.364\text{--}3.354$ Å was defined as graphite.

Biske (1982) studied graphite in rocks metamorphosed from greenschist to granulite facies by XRD methods, with d_{002} (Å) used as the main indicative XRD parameter. The temperature conditions of rock formation were 500 °C and lower for the greenschist facies and up to 750–800 °C for the granulite facies at a total pressure of 4.5 kbar. Low-temperature and high-temperature zones were

Table 2
Powder XRD parameters and stages of structural order in the series graphite – disordered graphite (*d*-graphite) with respect to the 002 peak and values of d_{002} (Å), temperature and pressure of the metamorphism (Landis, 1971)

Stage	FWHM	d_{002} (Å) at I max	d_{002} (Å) (½ width at ½ height)
Fully ordered graphite	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	~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	~3.80

separated. It was established that graphite from the low-temperature biotite and staurolite zones had a lower structural order. In the biotite zone, d_{002} of graphite is in the range of 3.356–3.370 Å, and in the staurolite zone – in the range of 3.355–3.358 Å. The carbon substance from the zones of high-temperature metamorphism shows XRD characteristics of graphite with a structure close to the ideal ($d_{002} = 3.350\text{--}3.360$ Å). Upon reaching these values, the parameter d_{002} (Å) ceases to be a function of the temperature of the metamorphism (Biske, 1982).

Rietmeier and McKinnon (1985) confirmed the conclusion of Shengelia *et al.* (1979) and Biske (1982) that the structural characteristics of carbon materials based on d_{002} (Å) can be used as a geothermometer.

Wada *et al.* (1994) found that the decrease in graphite d_{002} (Å) values is significantly accelerated at temperatures above 400 °C.

Sharma *et al.* (1998), Howe *et al.* (2003), and Parthasarathy *et al.* (2003) claimed that graphite preparations for powder XRD analysis are always textured to a great extent, leading to intensity lowering or disappearance of peaks other than 001 series. Such peaks should be used with caution in calculating the structural order of natural carbon. For this reason, many authors work only with well-textured preparations and use the parameter d_{002} (Å) and the characteristics based on it as an indicator for studying the processes of graphitization and metamorphic evolution of rocks.

Rodas *et al.* (2000) identified four graphite associations in the low-pressure and high-temperature metamorphic belts of Sierra de Aracena (southern Spain). Graphite of all types shows a high degree of structural order, with unit cell parameter $c \approx 6.70$ Å = $2d_{002}$ (Å). These values are in accordance with the conditions of metamorphism in the area.

The carbon matter from the Hidaka metamorphic belt in Hokkaido (Japan) is a dispersed organic material with a turbostatic structure with $d_{002} = 3.431 \pm 0.007$ Å, and the carbon matter from the Shimanto Cretaceous complex is amorphous with $d_{002} = 3.505 \pm 0.013$ Å (Nakamura *et al.*, 2015, 2019, 2020). The results of these authors correspond to the classification of French (1964), where structurally disordered graphite has $d_{002} = 3.43$ Å, but carbon matter that has $d_{002} = 3.50$ Å was defined as coals and asphalt. The change in d_{002} (Å) of natural carbon is a more sensitive indicator of graphitization processes than the ratio [(Area D1 + D4 bands)/(Area G + D2 + D3 bands)] obtained by Raman spectroscopy and FWHM of peak 002 (Nakamura *et al.*, 2020).

Equations

Vlahov (2015, 2017, 2018, 2019, 2020) determined the temperature of metamorphism and the degree of graphitization, using only the values of d_{002} (Å) of graphite and semi-graphite (equation 6) based on the results of the experiment of Shengelia *et al.* (1979). According to the latter authors, the insufficient duration of their experiment affects the correlation between the T °C values and the parameter c (Å) = $2 d_{002}$ (Å) of the graphite. Vlahov (2015) used the data of Shengelia *et al.* (1979) only for pressure of 1 atm (1.013 bar) in the range $d_{002} = 3.371\text{--}3.350$ Å, which corresponds to an increase in temperature from 300 °C to 800 °C and constructed a new dependence curve. The value of c (Å) at 300 °C is constant in all experiments with or without changes in pressure and heating duration. The temperature of 300 °C corresponds to carbon matter with $c = 6.742$ (Å) at the beginning of the experiment. As temperature increases, the parameter c (Å) = $2d_{002}$ (Å) decreases regularly up to the end of the experiment: T = 700 °C, $c = 6.708$ (Å); and T = 800 °C, $c = 6.700$ (Å). These are the three points, where the results are not skewed due to the short duration of the experiment, and they form a straight line of correlation between c (Å) of the carbon substance and the temperature. This fact justifies the derivation of equation (6), which is of the type $y = a + bx$ (Vlahov, 2015). Equation (6) calculates the change in d_{002} (Å) with increasing temperature from 300 °C to 800 °C. The calculations showed (Vlahov, 2015) that, with the increase of the temperature by 24 °C, the value of d_{002} (Å) of the semi-graphite and graphite decreases by 0.001 (Å). Equation (6) is the basis for the unification of the different published data on the change of the values of d_{002} (Å) and the degrees of graphitization as a function of temperature (Table 1). This equation calculates the temperature of the metamorphism from 300 °C to 804 °C. The degree of structural order $u = 0.45$ is the lower limit of semi-graphite (Kwiecinska, 1980). This fact and the decrease of d_{002} by 0.001 Å with increasing temperature by 24 °C allow the formulation of equation (9). It has solutions in the range of $d_{002} = 3.380\text{--}3.350$ Å with increasing temperature from 84 °C to 804 °C (Vlahov, 2020). The formation of disordered accumulations of graphene layers at the initial temperature (84 °C) is possible only with the overall process-supporting effect of the secondary graphitization factors.

The XRD evaluation of the degrees of graphitization can be divided into two groups depending on how they are calculated: 1) degrees of graphitiza-

tion showing the relationship between structural order and disorder in the volume of the carbon material (Franklin, 1951a; Seehra and Pavlovic, 1993; Ivashita *et al.*, 2004); 2) degrees of graphitization expressed in integers (Wada *et al.*, 1994; Vlahov, 2015).

Franklin (1951a) determined the structural disorder (ρ) and the structural order (u) of carbon substances according to the change of d_{002} from 3.440 Å to 3.350 Å by equations (1) and (2). The same values of u very often correspond to different values of d_{002} (Å) at the beginning of the graphitization process ($d_{002} = 3.440\text{--}3.391$ Å). The values of u increase regularly with the decrease of d_{002} (Å) in the interval $d_{002} = 3.390\text{--}3.377$ Å. Equation (1) has no solution for a large number of graphitization degrees (u) at $d_{002} = 3.376\text{--}3.354$ Å, when semi-

graphite and graphite with a structure close to the ideal are formed (Table 3, Fig. 2). These facts can be interpreted as indicating a delay in graphitization in the initial and middle stages of the process due to the release of volatile components: nitrogen, sulfur and carbon oxides, hydrocarbons, water, and others (Izawa, 1968). The lack of values (1 to 10, Table 3) of u when reducing d_{002} by 0.001 Å can be explained by the acceleration of the process in the final stage due to the high temperature. Its energy reduces the possible negative effects of secondary factors of graphitization. Another possible explanation is the relatively low accuracy (0.01) of the calculation of the structural order (u) after Franklin (1951a) of the carbon substance, because the degrees of graphitization (DOG, DG%, DG, and GD) increase naturally with the decrease of d_{002} (Å) in the range

Table 3
Structural parameter d_{002} in the range 3.440–3.354 Å and graphitization degrees (u) of graphitized natural carbon substances (after Franklin, 1951a)

d_{002} (Å)	u	d_{002} (Å)	u	d_{002} (Å)	u
3.440	0.00	3.410	0.19*	3.380	0.45
3.439	0.01*	3.409	0.20	3.379	0.46
3.438	0.01*	3.408	0.21	3.378	0.47
3.437	0.02*	3.407	0.22*	3.377	0.48
3.436	0.02*	3.406	0.22*	3.376	0.49***
3.435	0.03	3.405	0.23	3.375	0.51***
3.434	0.04*	3.404	0.24	3.374	0.52
3.433	0.04*	3.403	0.25*	3.373	0.53
3.432	0.05*	3.402	0.25*	3.372	0.54***
3.431	0.05*	3.401	0.26	3.371	0.56***
3.430	0.06	3.400	0.27	3.370	0.57
3.429	0.07*	3.399	0.28*	3.369	0.58***
3.428	0.07*	3.398	0.28*	3.368	0.60***
3.427	0.08	3.397	0.29	3.367	0.61***
3.426	0.09*	3.396	0.30	3.366	0.63***
3.425	0.09*	3.395	0.31	3.365	0.64***
3.424	0.10*	3.394	0.32	3.364	0.66***
3.423	0.10*	3.393	0.33	3.363	0.68***
3.422	0.11	3.392	0.34*	3.362	0.70***
3.421	0.12*	3.391	0.34*	3.361	0.72***
3.420	0.12*	3.390	0.35	3.360	0.74***
3.419	0.13	3.389	0.36	3.359	0.76***
3.418	0.14*	3.388	0.37	3.358	0.78***
3.417	0.14*	3.387	0.38	3.357	0.81***
3.416	0.15	3.386	0.39	3.356	0.85***
3.415	0.16	3.385	0.40	3.355	0.89***
3.414	0.17*	3.384	0.41	3.354	1.00***
3.413	0.17*	3.383	0.42		
3.412	0.18	3.382	0.43		
3.411	0.19*	3.381	0.44		

* the same (u) values at different d_{002} (Å) values;

*** missing (u) values by decrease in d_{002} with 0.001 Å

Fig. 2. Graphitization degree (u) values (after Franklin, 1951a) vs d_{002} (Å) values of carbon matter and its structural state (after French, 1964).

of $d_{002} = 3.380\text{--}3.354$ Å. The degree of graphitization (u) reaches its maximum 1.00, corresponding to $d_{002} = 3.354$ Å (Table 1). Many authors point out that graphite with a well-ordered structure has $d_{002} = 3.350$ (Landis, 1971; Shengelia *et al.*, 1979; Yanchuk and Laz'ko, 1980; Biske, 1982; Tagiri and Oba, 1986; Wada *et al.*, 1994; Beyssac *et al.*, 2002a; Baiju *et al.*, 2005; Rawat and Sharma, 2011). The calculation of equations (1) and (2) when $d_{002} < 3.354$ Å gives incorrect results for u (Table 4).

Franklin (1951a) used the constant 0.086 in her equation (1) to determine the disorder degree ρ . Part of equation (3) for determining the degree of graphitization DOG (Seehra and Pavlovic, 1993) contains the expression $(3.440 - 3.354) = 0.086$. The numerical value of DOG is obtained as an intermediate result before the calculation of ρ by equation (1). This makes it possible to formulate two new dependencies, based on connecting (1) and (3):

$$(12) \text{DOG} = (3.440 - d_{002}, \text{Å})/0.086;$$

$$(13) \text{DOG} = 1 - \rho^2.$$

The degree of graphitization (DOG), calculated by equation (3) of Seehra and Pavlovic (1993), is still used today (*e.g.*, Li *et al.*, 2018).

Ivashita *et al.* (2004) launched the standardized version of (3) as a new regularity (4), which calculates the degree of graphitization D.G%. This allows the following modifications to be made, combining equations (1), (2), (3), and (4):

$$(14) \text{D.G\%} = [(3.440 - d_{002}, \text{Å})/0.086] \times 100;$$

$$(15) \text{D.G\%} = (1 - \rho^2) \times 100.$$

The standardized variant of the graphitization degree D.G% (Ivashita *et al.*, 2004) was used in the studies of Touzain *et al.* (2010). Hewathilake *et al.* (2018) reported an increase in D.G% with increasing depth.

The equations, in which the degree of disorder of the structure of natural carbon matter (ρ) is present with an accuracy of 0.01 (Franklin, 1951a), show insignificant deviations in the results for DOG and D.G%, which are of no practical significance.

The analysis and interpretation of the data in Table 1 allows the formulation of two more regularities:

$$(16) \text{GD}_{(0-30)} = (T \text{ °C} - 84)/24;$$

$$(17) T \text{ °C} = \text{GD}_{(0-30)} \times 24 + 84.$$

The calculated degrees of graphitization (0–30), using equation (16), are valid for the field of semi-graphite and graphite in the range $d_{002} = 3.380\text{--}3.350$ Å and $T \text{ °C} = 84\text{--}804$ °C. This is the only system in which the degrees of graphitization follow one after the other without missing values. GDs from 0 to 30 cover the entire temperature range of graphite XRD geothermometry. Each subsequent step corresponds to a decrease in d_{002} by 0.001 Å and an increase in metamorphic temperature by 24 °C. Another advantage is that the values of the degrees of graphitization calculated by equation (16) are integers and correspond exactly to the values of the parameter d_{002} (Å). This means that the values of d_{002} (Å) can

Table 4
Doubled ρ and u values for different values of d_{002} (Å)

$d_{002} > 3.354$ Å	ρ	u	$d_{002} < 3.354$ Å	ρ	u
3.355	0.11	0.89	3.353	0.11	0.89
3.356	0.15	0.85	3.352	0.15	0.85
3.357	0.19	0.81	3.351	0.19	0.81
3.358	0.22	0.78	3.350	0.22	0.78

also be used independently as degrees of structural order of semi-graphite and graphite. The number of degrees of graphitization is limited and they cannot exceed 30.

Tagiri (1981) determines the degree of graphitization (DG) by introducing the formula:

$$DG = [(d_{002} - 3.7) / (\log Lc_{(002)} / 1000)] \times 100,$$

where Lc is size of the crystallites in the direction of accumulation of layers (Å) and is directly calculated by the equation:

$$Lc_{(002)} = K\lambda/(\beta_{(002)} \cos\theta),$$

where: K – shape constant set to 0.9 (Griffin, 1967; Tagiri and Tsuboi, 1979); $\beta_{(002)}$ – the full width of the peak at half the maximum; λ – wavelength of X-ray radiation in Å; θ – diffraction angle in radians.

Tagiri and Oba (1986) conducted experiments for the synthesis of graphite at 0.5–5.0 kbar and 300–600 °C. They take into account the values of d_{002} (Å) and the size of the crystallites Lc_{002} (Å) and the following types of carbon were differentiated based on the results of the experiments: coal material; disordered graphite; graphite; and completely ordered graphite.

Laggoun-Défarge *et al.* (1994) determined the number of structural layers ($\langle N \rangle$) in Lc (Å) crystallites when studying the changes of relatively weakly graphitized substances under thermal influences. The dependence of Laggoun-Défarge *et al.* (1994) is expressed by the following equation: $\langle N \rangle = Lc (\text{Å}) / d_{002} (\text{Å})$.

Wada *et al.* (1994) used the results of Tagiri's (1981) DG and found a relationship between the degree of graphitization (DG) and temperature. The mathematical expression of this regularity is calculated by equation (5) and its variant (5a). Due to the convenience and simplicity of this equation, it is also widely used (*e.g.*, Martinez *et al.*, 2003; Baiju *et al.*, 2005; Rawat and Sharma, 2011).

The use of XRD characteristics based on the widths of half of the peak maximum (FWHM) should be limited to the area of the greenschist facies. XRD methods are not sufficiently correct for Lc and La sizes above 1000 Å, which is characteristic of amphibolite and granulite facies (Biske, 1982). Grinding the samples for analysis with X-ray diffraction methods will cause a reduction in the size of the crystallites. This means that the use of these characteristics can affect the reliability of the results.

Vlahov (2015, 2020) avoids the use of $\beta_{(002)}$ (FWHM of peak 002), the size of the crystallites

Lc (Å) and Lc (Å), and the number of structural layers $\langle N \rangle$ to determine the degree of graphitization GD. Equations (7), (8), and (8a) are formulated by calculating the variation of d_{002} (Å) by equation (6) in the range 300–804 °C with increasing temperature by 1 °C. Comparing the results with those obtained using (5) and (5a) by Wada *et al.* (1994) shows: 1) the increase of GD by 8 degrees corresponds to an increase in the temperature by 24 °C and a decrease of d_{002} by 0.001 Å; 2) the increase of GD by 1 degree corresponds to an increase in the temperature of 3 °C. The degrees of graphitization DG (Wada *et al.*, 1994) and GD (Vlahov, 2015) show slight deviations. This is due to the different starting values of temperature and d_{002} (Å) used by these authors. The similarity and compatibility of the two systems is shown in Table 1.

Graphitization factors

Effect of temperature

Temperature is the most important factor causing the graphitization processes of natural carbon and carbon-containing substances. This is the conclusion of all authors in hundreds of publications from the period 1951–2020.

Anthracites readily convert to graphite when heated above 2000 °C (Franklin, 1951b; Oberlin and Terriere, 1975). There is a relationship between the rank of coal and the metamorphism of rocks caused by temperature (Quinn and Glass, 1958). Graphite with a degree of disorder d_3 is formed at $T < 300$ °C, disordered graphite $d_{1,2}$ – at $T = 300$ –480 °C, and completely ordered graphite – at $T > 480$ °C (Landis, 1971). The first stage in the arrangement of the layers of the graphite structure corresponds to a temperature of 300–500 °C and a pressure of 3 kbar or more, and to 1000 °C and 1 kbar in contact metamorphism. The complete ordering of the graphite structure is performed at 660–690 °C and 4.5–5 kbar (Grew, 1974). Temperature is the only factor that causes graphitization processes and the pressure between 1.0 bar and 6.0 kbar has no effect (Shengelia *et al.*, 1979). Natural hard bitumens are dehydrated and converted to almost pure carbon when heated (high degree of metamorphism). They also contain a graphite-like component but are amorphous when studied by X-ray diffraction methods (Cornelius, 1987; Jacob, 1993; Massman and Nagy, 1996). Sequential heating (2000 °C and 2500 °C) of graphite-like carbon particles shows a decrease in d_{002} (Å) with increasing temperature. The lowest achieved value is $d_{002} = 3.375$ Å when heated to 2500 °C.

The natural semi-graphite–graphite substance that has not been thermally treated has $d_{002} = 3.371 \text{ \AA}$ (Rodrigues *et al.*, 2011). These values of d_{002} (Å) correspond to 204 °C and 300 °C, respectively, and were calculated (Table 1) by Vlahov (2015, 2019, 2020), using equations (6) and (9). Natural carbon substances reach a high degree of structural order at $T > 650 \text{ °C}$. All organic precursors were partially transformed into graphite at 500 °C and completely graphitized at 700 °C (Beyssac *et al.*, 2002a, 2002b). Graphite with a high degree of structural order ($c = 6.7084 \pm 0.0002 \text{ \AA}$; $d_{002} = 3.35347 \text{ \AA}$) is formed at temperatures above 720 °C (Shengelia *et al.*, 1979; Luque *et al.*, 1993; Safonov *et al.*, 2018). The indicated value of d_{002} (Å) corresponds to 732 °C according to Vlahov (2015, 2019, 2020). Graphitization processes are accelerated at temperatures above 400 °C (Wada *et al.*, 1994) under natural conditions. The industrial synthesis of graphite takes place at 2700–2800 °C (Rouzaud and Oberlin, 1989; Beyssac *et al.*, 2002b). Graphitization of organic matter is achieved at temperatures far higher than the conditions in Earth's crust (Wang, 1989; Rellick *et al.*, 1992; Zeng *et al.*, 1995). All the cited facts show that the effect of temperature is combined with the effect of other physicochemical parameters of the natural environment like metamorphism.

Effect of the general pressure and tectonic stress

Graphitization of carbon substances has been studied mainly as an effect of temperature at atmospheric pressure until the 1980s (Oberlin, 1989; Rouzaud and Oberlin, 1989).

The content of the polytype 3R increases with prolonged grinding of graphite samples (Bacon, 1950, 1952). Graphite 3R (25–30%) is formed in the 2H polytype by unilateral pressure combined with significant lateral shifting (Laves and Baskin, 1956), which is characteristic of semi-graphite (Kwiecinska, 1980).

The parameter d_{002} (Å) was used to determine the temperature according to the pressure limits of the metamorphic facies (Landis and Coombs, 1967; Landis, 1971). Grew (1974) drew the following conclusions: 1) the first stage in the arrangement of the layers of the graphite structure under conditions of regional metamorphism corresponds to a temperature of 300–500 °C and a pressure of 3 kbar or more, and to 1000 °C and 1 kbar for contact metamorphism; 2) the complete arrangement of the graphite structure is carried out at 660–690 °C and 4.5–5 kbar. Dissel *et al.* (1978) concluded that the

high pressure caused by the entrainment processes accelerates graphitization. Tectonic stress contributes to the structural arrangement of the atomic layers of carbon (Blanche *et al.*, 1995; Mählmann *et al.*, 2002). Large-flake ($>150 \text{ }\mu\text{m}$) and, less frequently, fine-flake ($<150 \text{ }\mu\text{m}$) graphite is formed under conditions of high-grade metamorphism at high temperature and pressure (Tamashauskys, 1998). Lateral pressure contributes to the increase in the intensity of the XRD peak 002 of vitrinite due to the increase in the structural order of the carbon material (Nishimura *et al.*, 2000).

Graphite was obtained within 5 min from unstructured carbon glass at 2500 °C and 1 GPa local transverse stress, which increased graphitization by inductive local friction of microscopic grains (Noda and Kato, 1965; Kamiya *et al.*, 1973). Inagaki *et al.* (1977) and De Fonton *et al.* (1980) described the appearance of three-dimensional graphite in vitreous carbon at 1700 °C and 0.5 GPa. Pyrolytic graphitization is the result of molecular orientation, which increases with increasing of the stress. It also causes the orientation of the structural layers. Semi-graphite is obtained from anthracite at a temperature of 1000 °C and a pressure of 5 kbar, and at a required temperature of 2000 °C without pressure (Oberlin and Terriere, 1975; Bonijoly Roussel, 1980; Bonijoly *et al.*, 1982). Carbon precursors that do not have a lamellar structure cannot be graphitized only under the influence of temperature. They can be graphitized only with the added effect of hydrostatic pressure or oriented stress (De Fonton *et al.*, 1980; Bustin *et al.*, 1995; Beyssac *et al.*, 2000).

The combined effects of temperature, quasi-hydrostatic pressure, and stress cause the transformation of structurally disorganized carbon material into graphite (Teichmüller and Teichmüller, 1982; Castro-Reis and Canto-Machado, 1992; Zeng *et al.*, 1995).

The structural state of meta-anthracite and semi-graphite is associated with low-grade metamorphism of rocks, but temperatures of 350 °C to 600 °C can lead to the transformation of organic matter into graphite in the presence of high pressure (Teichmüller, 1987).

Ross and Bustin (1990) and Bustin *et al.* (1995) came to the following conclusions: 1) the presence of some anisotropy in the volume of the starting material and the hydrostatic pressure add additional compression energy, supporting and increasing the microtextural organization, which temperature cannot achieve on its own; 2) the compression energy causes adhesion of the pore walls and a sharp increase in the homogeneity and propagation of these

two phenomena perpendicular to the *c*-axis of the unit cell; 3) in experiments with the application of lateral pressure, it results in rotation of small uniform areas and tearing of the pore walls. This causes the formation of graphite lamellae. Wilks *et al.* (1993) transformed anthracite into graphite in a stress experiment at a temperature of 900 °C and pressure of 1.0 GPa. Natural graphitization is controlled by temperature, but pressure and process duration are important. The influence of these two parameters has not yet been studied precisely (Beyssac *et al.*, 2002a, 2002b, 2004). Wang *et al.* (2003) graphitized glassy carbon at high temperatures and pressures. The overall effect of temperature, pressure, lateral pressure, and sufficient duration of the process leads to an increase in the order and degree of interconnection of carbon layers (Nover *et al.*, 2005). Wheeler (2014) defines the effect of stress on metamorphic reactions as dramatic. Schmalholz and Podladchikov (2014) discuss the relationship between stress, minerals, and the depth at which they are formed. Golubev *et al.* (2019) investigated the structural and chemical transformations of natural bitumens at heating (400–1000 °C) under the conditions of low vacuum (8 kPa). Particle sizes are reduced. The samples become electrically conductive after elimination of the hydrocarbon component. Nakamura *et al.* (2020) conducted an HPHT experiment ($T = 1200$ °C and $P = 0.5\text{--}8$ GPa), showing that the morphological and structural characteristics of the carbon substance change completely at the end of the experiment (8 GPa). Flakes with a diameter of 1–10 μm with a planar structure and the peaks 110 and 112 appear in the XRD analysis. Their presence is an indicator of completely ordered graphite with ABAB... structure (Bluman *et al.*, 1974; Biske, 1982; Wada *et al.*, 1994; Nakamura *et al.*, 2020). The crystallinity of natural carbon is a function of the peak temperature, but the rapid increase in the degree of graphitization is due to the effect of pressure (Nakamura *et al.*, 2020).

Effect of the structure of primary carbon matter

Comprehensive studies prove that in addition to temperature, quasi-hydrostatic pressure and stress, there are other factors that control graphitization. One of them is the structure of the primary carbon substance.

Franklin (1951b) studied the growth of carbon crystallites from graphitized and non-graphitized natural substances. Forsman (1963) and Landis (1971) considered that graphitization processes are con-

trolled by complex characteristics resulting from the nature of primary carbon substance. Oberlin and Terriere (1975), Bonijoly Roussel (1980) and Blanche *et al.* (1995) reported pores located in parallel planes in anthracite and metaanthracite samples. De Fonton *et al.* (1989) found that graphitization of a microporous carbon substance is possible when transforming it into an intermediate stable phase. It is microporous at temperatures above 1100 °C, and complete graphitization takes place at 1700 °C and 0.5 GPa. Starting materials that do not have a lamellar structure cannot be graphitized under the influence of temperature only. Completing the process requires exposure to hydrostatic pressure or stress (De Fonton *et al.*, 1980; Oberlin, 1989; Rouzaud and Oberlin, 1989; Bustin *et al.*, 1995; Beyssac *et al.*, 2000). Graphitization of bituminous (hard) coal requires a temperature of about 2200 °C. Lignite and subbituminous coal are classified as non-graphitized carbon and are not graphitized before heating to about 3000 °C (Oberlin, 1984). Other authors conclude that the degree of graphitization strongly depends on the structural organization of the starting material (Beny-Bassez and Rouzaud, 1985; Oberlin, 1989; Kríbek *et al.*, 1994; Large *et al.*, 1994; Bustin *et al.*, 1995; Beyssac *et al.*, 2000). Graphitization is made possible by the formation of a transitional microtexture when the carbon material contains cross-linked carbon and sulfur atoms. The pore diameter increases and the precursor is transformed into graphite. The adhesion of the pores increases the homogeneity of the carbon material perpendicular to the *c*-axis of graphite-like structure, and their subsequent rupture leads to the formation of graphite lamellae (Ross and Bustin, 1990; Bustin *et al.*, 1995). Poorly crystallized carbon material was diagnosed both in the chlorite and silymanite metamorphic zones. The low degree of graphitization in the silymanite zone is a consequence of the presence of micropores that internally “buffer” the effect of high pressure during metamorphism (Large *et al.*, 1994). Graphitization of coke increases the degree of molecular order and the bonding between carbon layers. This is expressed in the parallel orientation of the polyaromatic base structural units (BSUs) at a greater distance. These formations (several nm in size) are characteristic of carbon substances with a turbostatic structure (Blanche *et al.*, 1995; Blanche and Rouzaud, 1997). The use of unsuitable precursors leads to a random orientation of the polyaromatic BSUs, and an isotropic microtexture with the same disorder is formed. The construction of a structure that can be graphitized requires the achievement of lamellar orientation of BSUs. Precursors with pores causing mechanical pressure that support the formation of two-dimensional microtex-

turing of polyaromatic BSUs are suitable (Blanche *et al.*, 1995; Blanche and Rouzaud, 1997). As the temperature and pressure increase, the turbostatic form of carbon disappears and partial graphitization begins. Graphite is formed when a three-dimensional arrangement of the layers is reached with an increase in their thickness to about 5000 μm . The orientation, crystallinity, and degree of interlayer bonding determine the properties of synthesized graphite (Nover *et al.*, 2005). Beyssac *et al.* (2002b, 2004) found that, in the XRD study of different carbon starting materials, they could show the same structures. However, their microtextures will be different. The structural order of carbon substances corresponds directly to the degree of metamorphism. Natural carbon substances can be graphitized to varying degrees, depending on their initial characteristics (Oberlin, 1989; Rouzaud and Oberlin, 1989). Differences between the amorphous state and the turbostatic structure of primary carbon substances play an important role in the processes of natural graphitization in low-pressure conditions (Wada *et al.*, 1994; Beyssac *et al.*, 2019; Nakamura *et al.*, 2020).

Effect of orientation of carbon formations

The orientation of graphite crystals and aggregates towards the direction of tectonic stress affects the processes and degrees of graphitization in different ways. The coincidence of directed pressure with the direction of the *c*-axis of crystals supports the action of the temperature, and thus graphitization occurs at lower temperatures in the conditions of progressive regional metamorphism. Small deviations of the directed pressure from the direction of the *c*-axis of graphite structure can have different effect on the degree of structural order of the carbon substance. The large angles between the *c*-axis and the direction of stress to some extent prevent the arrangement of the graphite structure in accordance with the temperature of the metamorphism. Tectonic impacts can lead to a partial reduction in the structural order of graphite under conditions of regressive metamorphism (Vlahov, 2017, 2019). The coexistence of lonsdaleite, diamond, and single graphite crystals in a certain volume is due to the different orientation of the graphite basal atomic planes relative to the direction of the impact stress (Afanasyev *et al.*, 2019).

Effect of the origin of primary carbon matter

Clarification of the origin of carbon (organic, inorganic, mantle, or mixed) is important in the study

of the genesis and industrial potential of graphite deposits.

Graphite in Greenland is of inorganic origin, and carbon-containing fluids are likely of mantle origin (Naraoka *et al.*, 1996). According to Ueno *et al.*, (2002), graphite in Greenland is of primary biogenic origin. Zuilen *et al.* (2003) do not categorically deny the possibility of the formation of biogenic graphite in metamorphites in Greenland with an age of 3.8 Ga. Graphite deposits in Norway were formed during the conversion of organic matter to graphite during metamorphism (Harben and Kuzvart, 1996). The rich graphite mineralizations in the Ukrainian Shield are spatially and genetically related to carbonate-free gneisses. They are made of isotopically light carbon. The values of $\delta^{13}\text{C}$ are in the range typical for solid organic matter and liquid hydrocarbons. The graphite found in calciphires and marbles are enriched in the heavy isotope of carbon compared to graphite from gneisses. The values of $\delta^{13}\text{C}$ are within the range of variations in marine carbonates (Korzhinsky and Mamchur, 1978). Grenville graphite deposits (Canada) were formed by the destruction of organic material and the deposition of graphite by metamorphic fluids (Taner *et al.*, 2017). The gneiss-dispersed flaky graphite from the Aracoyaba-Baturite region of Brazil was formed by the metamorphism of carbon substance of sedimentary origin. The $\delta^{13}\text{C}$ values indicate that the primary carbon substance is of biogenic origin (Weis *et al.*, 1981). Graphite deposits in South India, Sri Lanka, and Madagascar are of the most common genetic types: 1) formed during the metamorphism of biogenic carbon; 2) epigenetic deposits formed during the deposition of graphite by fluids (Landis, 1971; Wada *et al.*, 1994; Luque *et al.*, 1998, 2014; Pasteris, 1999; Galvez *et al.*, 2013). Acharya and Dash (1984) launched the idea that graphite in the Eastern Ghats Mobile Belt (EGMB), Orissa, India, is abiogenic. It was probably formed by the dissociation of methane from the decarbonatization of carbonate-silicate granulites. However, a large number of graphite bodies do not associate with carbonate-silicate granulite. Other graphite deposits are formed by the mixing of carbon from organic matter and carbon separated from carbonates and/or mantle sources. EGMB graphite has three probable carbon sources, but the $\delta^{13}\text{C}$ values indicate that the majority of graphite bodies were formed during the transformation of organic matter during metamorphism (Sanyal *et al.*, 2009). The isotopic composition of carbon in the dominant type of graphite from Chinese deposits indicates the biogenic origin of the primary carbon substance (Yang *et al.*, 2014).

The metamorphosed natural carbon from the Hida-ka metamorphic belt and the Shimanto Cretaceous Complex in Japan is of biological origin according to isotope analysis data (Nakamura *et al.*, 2015, 2019, 2020).

The cited data show that graphite in regionally metamorphosed rocks has a predominantly biogenic origin. Large amounts of volatiles are released during the recrystallization of organic matter (Oberlin *et al.*, 1999). Hayes and Waldbauer (2006) argue that dispersed organic matter in rocks and subduction processes play a major role in the deep carbon cycle. The carbon fluids released are an important source of light carbon in the carbon cycle. This is important for estimating the duration of metamorphic devolatilization and the recrystallization and recycling of carbon material (Nakamura *et al.*, 2020).

The influence of the origin and isotopic composition of graphitized carbon on the processes and degrees of graphitization is still unclear.

Effect of fluids

The fluid regime also affects the course and efficiency of graphitization processes.

The origin of vein graphite in Sri Lanka is explained by the export of carbon from metamorphic rocks and its deposition in cracks and tectonic zones under conditions of high-grade regional metamorphism (Wadia, 1943).

Massive polycrystalline vein graphite, as well as well-crystallized graphite crystals and spherulites formed as deposits of epigenetic C-O-H fluids in metamorphic or magmatic rocks, have been described by a number of authors in different parts of the world. High temperature fluids with high activity can partially or completely dissolve the various carbon formations and graphite. These hydrocarbon fluids transport and redeposit the carbon that recrystallizes (French, 1964; Rumble *et al.*, 1986; 2014; Frost *et al.*, 1989; Křibek *et al.*, 1994; Yui *et al.*, 1996; Luque *et al.*, 1998; Pasteris, 1999; Beyssac *et al.*, 2002a; Mählman *et al.*, 2002). Tagiri and Oba (1986) suggested that graphitization depends mainly on metamorphic temperature and fugitive oxygen and to a lesser extent on pressure.

The veined graphite bodies crossing the metamorphosed in granulite facies rocks of the metamorphic belt of the Sierra de Aracena, Spain, are defined as epigenetic (Rodas *et al.*, 2000; Crespo *et al.*, 2004, 2005). Fluids have mobilized graphite particles from metamorphites and deposited them mechanically in tectonic collapsed areas (Crespo

et al., 2005). Such processes have been described and documented in graphite-containing marbles and gneisses from the Madan lithotectonic unit in the Central Rhodopes, Bulgaria (Vlahov, 2017, 2019). The released carbon fluids are an important source of light carbon within the carbon cycle (Nakamura *et al.*, 2020). The vein graphite deposits are of great informational significance for the study of the processes of regional metamorphism. The high content of graphite in them is of economic interest. For this reason, they are described as a separate industrial genetic group (Mitchell, 1992; Acharya *et al.*, 1996; Luque *et al.*, 1998; Galves, 2013; Chehreh *et al.*, 2016).

Graphite vein bodies are deposited by C-O-H fluids or by mechanically mobilized, transported, and deposited graphite particles in zones affected by tectonic disturbances (Rumble *et al.*, 1986; Luque *et al.*, 1993, 1998; Frost *et al.*, 1989; Pasteris, 1999; Crespo *et al.*, 2005; Rumble, 2014). This genesis illustrates the accumulative role of fluids in metamorphic processes. However, their destructive activity is manifested in the removal and partial dissolution of carbon from the rocks. These processes reduce the degree of structural order of the residual undissolved or partially dissolved or crushed graphite (Vlahov, 2006, 2017, 2019).

Increased contents of volatile components, such as S, CO₂, etc., are found in rocks that have undergone regressive metamorphism. Another indicator of the participation of fluids in the processes of regressive changes of metamorphites is the association of graphite with pyrite. Graphite is mainly associated with pyrrhotite in rocks not affected by regression changes. Graphite particles in regressively metamorphosed rocks are smaller than those in rocks that have not undergone such changes. The graphite parameter d_{002} (Å) varies from 3.355 Å to 3.350 Å in rocks of the amphibolite and granulite facies. In regressively modified rocks, graphite has $d_{002} = 3.356\text{--}3.358$ Å. Regressive metamorphism leads to a partial structural disorder of graphite, caused by fluids saturated with volatile substances (Yanchuk and Laz'ko, 1980).

Effects of mineral and chemical composition

The mineral and chemical composition of the primary carbon substance, as well as that of the hosting sedimentary rocks, have a significant influence on the degree of graphitization. The mineral phases in anthracites act as a catalyst for processes that increase the structural order of the starting carbon material (Evans *et al.*, 1972; Oberlin and Terri-

ere, 1975; Oya and Otani, 1979; Oya *et al.*, 1983; González *et al.*, 2004, 2005; Pappano and Schobert, 2009). Increase in the crystallinity of carbon matter is achieved by the addition of minerals or metals during the catalytic graphitization process (Fitzer *et al.*, 1995; Zeng *et al.*, 1995). The main non-organic elements in the mineral components of coal (Al, Fe, Mg, Mn, Si, and Ti) are used as catalysts for graphitization in the production of various carbon materials. Clay minerals (illite, kaolinite) also catalyze the graphitization process. Their catalytic effect is particularly effective in the presence of iron (Marsh and Warburton, 1970; Oberlin and Terriere, 1975; Bonijoly *et al.*, 1982; Oya and Marsh, 1982; Dhakate *et al.*, 1997; Wang *et al.*, 2001; González *et al.*, 2005; Rodrigues *et al.*, 2012).

Effect of the processes' duration

Some authors also pay attention to the duration of the effect of the listed factors on dispersed carbon in rocks. The duration of the process is important for the course of graphitization, but its influence has not yet been studied precisely (Beyssac *et al.*, 2002b). The combined effect of temperature, pressure, and sufficient duration leads to an increase in the order and degree of cohesion of earlier randomly oriented carbon layers (Nover *et al.*, 2005).

Complex effect of all factors

The data and conclusions of the cited authors show a complex influence of temperature and secondary factors on the processes of transition from amorphous carbon to graphite with different structural order. Graphitization is the transformation of unordered or partially ordered non-crystalline carbon material into pure carbon with an end member of crystalline graphite. Incomplete graphitization is most common and is expressed in the formation of carbon substances with varying degrees of structural organization. This phenomenon is a result of the different combination of temperature, pressure, kinetics, and in some cases fluid activity. The stable form of carbon in the Earth's crust and on the Earth's surface is graphite. Well-crystallized graphite, however, is relatively rare. Poorly crystallized and structurally disordered material (graphite carbon) occurs in a variety of geological conditions (Beyssac *et al.*, 2002a; Buseck and Beyssac, 2014). Glassy carbon resembles graphite carbon and is a typical disordered substance. It contains sparsely distributed curved graphene layers, also called disordered multilayer graphenes (DMLG). Their frag-

ments are dispersed in the amorphous matrix (Hu *et al.*, 2017).

The factors controlling graphitization can be divided into: 1) characteristics of the carbon precursor; 2) factors, including the changing parameters of the environment during metamorphism. The characteristics (factors) of the carbon precursor are its structure, chemical and isotopic composition. The characteristics (factors) of metamorphism are: temperature, total pressure and tectonic stress, the orientation of carbon particles relative to the direction of stress, the mineral and chemical composition of rocks, the action of fluids, and the duration of graphitization processes. The characteristics of the primary carbon material come into balance with the change of the factors of the environment. Some of the parameters of metamorphism can have only a positive effect on the graphitization processes: temperature and total pressure. All other factors can affect the structural order of the carbon substance in different ways, depending on their combined simultaneous or sequential impact (Vlahov, 2006, 2007, 2017, 2019). The sequence of factors controlling the graphitization influences the final degree of graphitization of the carbon material in the rocks.

Irreversibility and reversibility of the structural state

Irreversibility

The use of a structural graphite geothermometer to measure the peak temperature of metamorphism and the corresponding structural state of the carbon substance is based on the irreversibility of graphitization processes. The structural state of the dispersed in rocks carbon substance is determined as a consequence only of the processes of progressive metamorphism, and the degree of graphitization is irreversible and corresponds to reaching the highest degree of metamorphism (French, 1964, 1965; Landis, 1971; Grew, 1974; Shengelia *et al.*, 1979; Teichmüller and Teichmüller, 1982; Rietmeijer and Mackinnon, 1985; Firsova *et al.*, 1986; Teichmüller, 1987; Oberlin, 1989; Luque *et al.*, 1993; Beyssac *et al.*, 2002b, 2004; Baiju *et al.*, 2005; Rawat and Sharma, 2011; Buseck and Beissac, 2014; Kuo *et al.*, 2017; Beyssac *et al.*, 2019; Tamiati *et al.*, 2020). Ivanova *et al.* (1974) argued that, due to the irreversibility of the structural state of graphite, the determination of structural changes caused by regressive metamorphism is impossible with X-ray powder diffraction methods. They can only be detected using DTA. Sparkes *et al.* (2020) suggested

that similar to zircon graphite flakes can be used to track extreme tectonic events. According to these authors, this is possible due to the resistance of graphite to physical, chemical, and biological degradation.

Reversibility

The data of some authors contradict the thesis about the irreversibility of the structural state of the graphitized carbon substance, reflecting the peak of progressive metamorphism.

According to Bacon (1950, 1952), prolonged grinding of graphite increases the content of 3R polytype in the samples.

Under directed displacement pressure on graphite crystals consisting mainly of 2H polytype, a 3R phase is formed, the content of which can reach 25–30% (Laves and Baskin, 1956). These values of the 3R polytype are characteristic of semi-graphite (Kwiecinska, 1980). After heating at high temperatures, the 2H modification is completely restored (Laves and Baskin, 1956).

Regressive metamorphic effects cause a partial structural disorder of graphite due to the action of fluids saturated with volatile components. Regressive structural changes are more pronounced in smaller-scale graphite formations and are expressed by an increase in the value of d_{002} (Å) compared to the values of this parameter in unchanged rocks (Yanchuk and Laz'ko, 1980).

The carbon matter in the Carboniferous metasediments of the Eastern Alps is a mixture of vitrinite and granular or lamellar carbon particles. Two types of carbon with different degrees of graphitization are defined by HRTEM. The first type is characterized by elongated round outlines. The second type is represented by graphite lamellae and polygonal flakes, whose structure is composed of long and arranged aromatic layers. Tectonic movements during the Late Cretaceous led to the turbostatic arrangement of the aromatic layers (Rantitsch *et al.*, 2004). The established fact can be explained by the combined effect of the structure, chemical and mineral composition of the primary carbon material, and the subsequent tectonic stress.

An experiment was performed to determine the dependence of the parameter d_{002} (Å) on the duration of grinding of graphite samples using pure calcite as an abrasive substance (Vlahov, 2017). The results show that the values of d_{002} (Å) do not change until 30 min of manual grinding. The value of d_{002} (Å) increases by 0.001 Å with every additional 15 min above the indicated duration (Vlahov, 2017). The

experiment proves that the degree of graphitization of a structurally well-ordered graphite decreases under mechanical impact over a certain period of time. Kirilova *et al.* (2018) found that crushing processes cause mechanical modifications in the crystallinity of graphite aggregates. They concluded that the calibrated Raman spectroscopy graphite thermometer is ambiguous in active tectonic zones.

Another experiment shows that the thermal effect on graphite has a different impact on its structural order in the air (Vlahov, 2017). The degree of graphitization decreases when the graphite material is partially oxidized and the values of d_{002} (Å) increase. This result is obtained when the temperature of graphite formation is significantly lower than the heating temperature (700–800 °C) and with a sufficient heating duration of 6 h (Vlahov, 2017).

The summary of all the above cited facts shows that the values of temperature, degrees of graphitization, and d_{002} (Å) include the integrated effect of all other factors that control graphitization. The most significant comparisons, correspondences, and correlations between the data of the different authors are illustrated in Figs 2–5.

Chemical and physical changes in carbon matter

The analysis of the results for the degree of graphitization (u) according to Franklin (1951a), presented in Table 3, and their comparison (Izawa, 1968) with the data of other authors (Table 1) show that:

Fig. 3. Graphitization degree (u) values (after Franklin, 1951a) vs d_{002} (Å) values of carbon matter and its structural state (after Kwiecinska, 1980).

Fig. 4. Graphitization degree (u) values (after Franklin, 1951a) vs d_{002} (Å) values of carbon matter and its structural state (after Grew, 1974; Kwiecinska, 1980) with metamorphic temperature (T °C) data.

1) The chemical changes of the carbonaceous precursor dominate at the beginning of the graphitization, and different successive values of d_{002} (Å), correspond to the same degree of graphitization (u). The release of a large amount of volatile components during this stage cools the system and temporarily slows down the reduction of d_{002} (Å) and its entry into equilibrium with the temperature;

2) The progress of the graphitization processes leads to intensification of the effect at the physical level, which is expressed in a regular decrease in the values of d_{002} (Å) with the proportional increase in the values of u , temperature, and pressure;

3) The last stage of the graphitization process is characterized by the dominance of physical changes in the structural state of graphite, because the volatile components are removed from its volume. The third stage of graphitization is realized by the rapid increase of the degree of structural order of the graphite, as the increase in the values of u precedes the decrease of d_{002} (Å), as shown in Table 3. Equations (1) and (2) of Franklin (1951a) have a rational solution only up to $d_{002} = 3.354$ Å, which corresponds to a temperature of 708 °C (Table 4). The structural evolution of graphite continues to $d_{002} = 3.350$ Å according to all authors cited above. The calculated temperature corresponding to $d_{002} = 3.350$ Å is 804 °C (Table 1). The improvement of the graphite structure is only at the physical level in

the range of 708 °C and 804 °C, which is expressed in the reduction of the d_{002} parameter from 3.354 Å to 3.350 Å;

4) The system for the degrees of graphitization (GD from 0 to 30) calculated by equation (16) shows regular proportional increase in GD with the decrease in d_{002} by 0.001 Å, which corresponds to the increase in the temperature by 24 °C. Only this system takes into account the general change in the structural state of the carbon substance in the range 84–804 °C, which makes it convenient to work;

5) The ways of calculating the temperature and the degrees of graphitization by different authors can be combined and complemented.

Facial diagnostics of graphite-bearing rocks and forecasting of graphite industrial properties

The values of d_{002} (Å) and the degrees of graphitization will not reflect the absolute temperature peak from the progressive metamorphic stage in rocks that have undergone regressive regional metamorphism. However, they will be close enough to the peaks of the progressive regional metamorphism in some parts of the graphite scale, because the retrograde effects cannot be manifested with the same intensity in its entire volume. Such graphite “relics”, having the structural characteristics of the

Fig. 5. Graphitization degree (GD), calculated with eq. (16), vs d_{002} (Å) values of carbon matter, its structural state according to graphitization degree (u) values (after Franklin, 1951a) and classification of Kwiecinska (1980) with metamorphic temperature (T °C) data.

previous prograde stage, are located at a greater distance from the fault zones and the tectonically reworked areas around them. The finding of such graphite formations is one of the probable reasons for substantiating the thesis about the irreversibility of the structural state of graphite, reached in the conditions of the progressive regional metamorphic stage. The reversibility of the structural order, the values of d_{002} (Å), the degrees of graphitization of natural carbon formations, and the sequence of mineral formation in metamorphites can be used for facial diagnosis and tracking the metamorphic evolution of graphite-bearing rocks.

Landis (1971) empirically determined the variations in the values of d_{002} (Å) of the carbon phases for the facies of progressive regional metamorphism (Table 5) according to the scheme of Landis

and Coombs (1967). The zeolite, lawsonite-albite-chlorite, and pumpellyite-actinolite facies were combined into subgreenschist facies in a later officially recommended scheme (Smulikowski *et al.*, 2007). The values of d_{002} (Å) corresponding to a temperature change of 100 °C (Vlahov, 2018) are plotted on this facial scheme (Fig. 6). Graphite with a well-ordered structure is formed at a temperature above 480 °C (Landis, 1971), which corresponds to $d_{002} = 3.363$ – 3.362 Å (Table 1) and falls in the field of the epidote-amphibolite facies (Fig. 6). The initial ordering of the graphite structure begins between 300 °C and 500 °C (Grew, 1974). The d_{002} values corresponding to these temperatures are 3.371–3.362 Å (Table 1), and they fall into the fields of the greenschist and epidote-amphibolite facies (Fig. 6). Other facial schemes have been published in the recent

Table 5
Values of d_{002} (Å) of the carbonaceous matter in rocks of different facies of the regional metamorphism (Landis, 1971)

Facies of regional metamorphism	d_{002} (Å) of carbonaceous matter
Zeolite	3.50–3.75
Lawsonite-albite-chlorite	3.45–3.55; 3.50–3.75
Pumpellyite-actinolite	3.37–3.44; 3.45–3.55
Epidote-amphibolite and Amphibolite	3.35–3.36

Fig. 6. Modified diagram after Smulikowski *et al.* (2007) showing relative positions of metamorphic facies in the P-T field and their corresponding d_{002} (Å) values of carbon matter (PX-HPLS, pyroxene hornfelses).

literature, where the epidote-amphibolite facies of regional metamorphism has been dropped because the field of the greenschist facies has been expanded (Bucher, 2005; Stephenson *et al.*, 2013). The data of Landis (1971) and Grew (1974) fall entirely into the field of the greenschist facies on the second facial scheme (*e.g.*, Bucher, 2005; Stephenson *et al.*, 2013).

The proposed system for correlation, transformation, and unification of the values of d_{002} (Å), temperature and degrees of graphitization of the different authors was tested, the graphite-bearing marble from the Central Rhodopes (Byalata skala quarry) having been used as a model. The results obtained are reported in Table 6. As the parameter

Table 6
Decrease of d_{002} (Å), T °C, and graphitization degrees of graphite from the Byalata Skala quarry, Central Rhodopes (S Bulgaria), during regressive regional metamorphism from amphibolite to greenschist facies

d_{002} (Å)	3.356	3.359	3.364
Temperature of regional metamorphism (T °C)	660 Calculated with equations (5), (6), (8), (9), (10), (11), (17)	588 Calculated with equations (5), (6), (8), (9), (10), (11), (17)	468 Calculated with equations (5), (6), (8), (9), (10), (11), (17)
Graphitization degrees after different authors	$u = 0.85$ – equations (1), (2); DOG = 0.97674 – equations (3), (12); DOG = 0.9775 – eq. (13); D.G% = 97.674 – equations (4), (14); D.G% = 97.750 – eq. (15); DG = 119 – eq. (5a); GD = 120 – equations (7), (8a); GD ₍₀₋₃₀₎ = 24 – eq. (16)	$u = 0.76$ – equations (1), (2); DOG = 0.94186 – equations (3), (12), DOG = 0.9424 – eq. (13); D.G% = 94.186 – equations (4), (14); D.G% = 94.240 – eq. (15); DG = 96 – eq. (5a); GD = 96 – equations (7), (8a); GD ₍₀₋₃₀₎ = 21 – eq. (16)	$u = 0.66$ – equations (1), (2); DOG = 0.88372 – equations (3), (12); DOG = 0.88440 – eq. (13); D.G% = 88.372 – equations (4), (14); D.G% = 88.440 – eq. (15); DG = 59 – eq. (5a); GD = 56 – equations (7), (8a); GD ₍₀₋₃₀₎ = 16 – eq. (16)

d_{002} (Å) increases, the values of the temperature and the degrees of graphitization decrease as a result of the transition from amphibolite to greenschist facies. The check was performed by calculating the temperature and the degrees of graphitization with different equations (Table 6). The results of the powder XRD analysis were confirmed by data from DTA and the formation of lower-temperature minerals over high-temperature ones. The sequence of the mineral formation and the increase in d_{002} (Å) of graphite corresponds to the regressive transition from the upper limit of the amphibolite to the lower limit of the greenschist facies (Vlahov, 2006, 2007, 2017, 2019).

The high degree of structural order of graphite means that its carbon content is high, the presence of heteroatoms is minimal, and its useful properties as an industrial mineral are fully expressed. The regular relationship between the conditions of genesis, the values of d_{002} (Å), and the degree of graphitization can be used as one of the ways to assess the properties of graphite and to select the most appropriate areas of its application in industry.

CONCLUSIONS

The powder XRD measured parameter d_{002} (Å) of semi-graphite and graphite is a sensitive indicator for determining the structural state of these natural forms of carbon. Carbon matter has been affected by a number of factors during progressive and regressive regional metamorphism for millions of years. Structural, spectroscopic, thermal, and other methods of research determine the structural state of carbon as a total result of the action of all factors controlling the processes of graphitization. The data obtained from laboratory synthesis of graphite in a controlled environment should be used with caution. Their absolutization and mechanical transfer to natural objects can lead to misinterpretations and inaccurate conclusions. The reversibility of the structural state of graphite allows tracing the metamorphic evolution of graphite-bearing rocks. Specimens from places located far enough from the fault tectonic, processed and hydrothermally altered, zones contain “relics” of graphite with structural characteristics approximately corresponding to the peak of the progressive metamorphism. The structural characteristics of graphite from the regressively changed parts of the rocks are underestimated and correspond to the conditions of the retrograde metamorphic stage. All structural, spectroscopic, thermal, and other data must be confirmed by the

mineral composition and the order of mineral formation in the rocks. The study of the contradictions between the instrumental data of the carbon material and the mineral composition of the host rocks leads to the discovery of new facts about the metamorphic history of carbon-bearing rocks. The dependence of graphitization processes on many factors and on long period of time proves that the use of d_{002} (Å) with an accuracy of 0.001 Å is completely sufficient for the facial diagnosis of graphite-bearing rocks and for the approximation of the industrial properties of graphite.

The degrees of graphitization depend on the same factors as the values of d_{002} (Å). The numbers of the degrees of graphitization (u , DOG, D.G%, DG, GD, and $GD_{(0-30)}$) are different, but they change proportionally to the change of temperature and the degree of metamorphism. The formulated equations are combined in one system for correlation, transformation and unification of the data for d_{002} (Å), the temperature of the metamorphism, and the numerical values of the degrees of graphitization proposed by different authors. This allows the comparison of these data for different graphite deposits and mineralizations, regardless of how the numerical values of the degrees of graphitization are determined. The proposed scale $GD_{(0-30)}$ for the degrees of graphitization of the semi-graphite/graphite structural order is convenient to operate because: 1) the degrees of graphitization form a regular continuous numerical order from 0 to 30; 2) the change with one degree of graphitization corresponds to a change in the temperature of metamorphism by 24 °C and by 0.001 Å of the structural parameter d_{002} (Å) of the semi-graphite and graphite. This accuracy is sufficient for the purposes of mineralogical research, facial diagnostics of metamorphic rocks, and forecasting the industrial properties of graphite; 3) the GD system (0–30) is based on equations (16) and (17), which can be easily transformed for another initial temperature, without changing the calculation principle.

The values of the calculated metamorphism temperature also include the influence of secondary factors controlling the graphitization. Literature data and those from the system test on a real object (Byalata Skala quarry in the Central Rhodopes, Bulgaria), as well as the results of other geothermometers for the same area, show that the graphite geothermometer gives indications close to the real temperature of metamorphism (Vlahov, 2019, and references therein). XRD-graphite geothermometry data are applicable for the purposes of facial diag-

nostics and the establishment of the metamorphic history of graphite-bearing rocks. The most reliable results for the temperature of metamorphism are in the range of 280–300 °C to 800 °C. The accuracy of the calculations probably decreases with the decrease in temperature from 300–280 °C to 84 °C due to the stronger negative influence of the secondary graphitization factors in the field of low and very low metamorphism.

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