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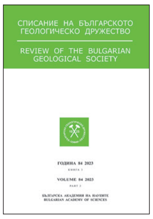

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Different graphitization degrees of carbon matter in rocks of a same metamorphic evolution

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Различни степени на графитизация на въглеродното вещество в скали с еднаква метаморфна еволюция

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Abstract. Two X-ray diffraction methods were chosen to determine the degree of structural order (degree of graphitization) of natural carbonaceous matter. Factors influencing the graphitization processes during the progressive and regressive stages of metamorphism are examined. The correlation of the degrees of structural order of the carbonaceous material with the sequence of mineral growth allows the metamorphic history of the graphite-bearing rocks to be traced. The obtained data can be used for the evaluation of graphite as a raw material.

Keywords: graphitization degree, graphite, regional metamorphism, critical raw-materials.

Introduction

Graphite is a critical raw material for the EU. Its importance is growing greatly due to the increasing use of electric transport worldwide. The high-quality graphite raw material has a high content of graphite carbon with flake sizes (> 0.1 mm). The high degree of structural order of graphite crystals together with other criteria determines its use in new high-tech productions. The price of medium flake graphite with 95% carbon content is around 1000 USD/t, and medium flake graphite with 99.9% carbon content used for battery production reaches 20000 USD/t (Gautneb et al., 2020).

The structural variations of graphite and carbon substances with a lower degree of structural order (degree of graphitization) dispersed in metamorphic rocks have been used by many authors to determine the conditions of metamorphism. Different schemes for arranging carbon formations according to their degree of graphitization, determined with XRD analysis have been created. They are based on the relationship between the increase of the temperature of metamorphism, the decrease of the interplanar distance d_{002} (Å) and increasing of the graphitization degree of semi-graphite and graphite and have been summarized and converted into one system (Vlahov, 2021 and references therein). Two of the scales are used to substantiate the thesis in this work:

1) DOG = (3.440 – d_{002}, Å) / (3.440 – 3.354), where DOG is degree of graphitization after Seehra and Pavlovic (1993);

2) T °C = (3.380 – d_{002}, Å) × 24000 + 84; $GD_{(0–30)}$ = (T °C – 84) / 24;

T °C = $GD_{(0–30)}$ × 24 + 84, where $DG_{(0–30)}$ is graphitization degree scale from 0 to 30 after Vlahov (2021).

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State of the problem: graphitization factors

All authors from the period 1951–2020 concluded that temperature is the most important factor causing the graphitization of natural carbon. 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 during regional metamorphism, and to 1000 °C and 1 kbar under the conditions of contact metamorphism. The complete ordering of the graphite structure is performed at 660–690 °C and 4.5–5 kbar (Grew, 1974). All organic precursors are partially transformed into graphite at 500 °C and completely graphitized at 700 °C. The industrial synthesis of graphite is possible at 2700–2800 °C (Beyssac et al., 2002a, 2002b). These facts show that the effect of temperature is combined with the effect of other physicochemical parameters of the natural environment during the metamorphism.

The high pressure accelerates graphitization (Dissel et al., 1978; Beyssac et al., 2000). Tectonic stress contributes to the structural arrangement of the atomic layers of carbon (Mählmann et al., 2002). The orientation of graphite crystals and aggregates towards the direction of the tectonic stress affects the processes and degrees of graphitization in different ways. The coincidence of the direction of the tectonic stress with the direction of the c-axis of graphite crystals supports the action of the temperature, and thus graphitization occurs at lower temperatures in the conditions of progressive regional metamorphism. Tectonic impacts with large angles between the c-axis of graphite crystals and the direction of the tectonic stress can lead to a partial reduction in the structural order of graphite under conditions of progressive and especially during regressive metamorphism (Vlahov, 2019).

The degree of graphitization depends on the structural organization of the starting material. Graphitization is made possible by the formation of a transitional microtexture when the carbon material contains cross-linked carbon and sulfur atoms. 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 (Beyssac et al., 2000). The low degree of graphitization in the sillimanite metamorphic zone is a consequence of the presence of micropores that internally "buffer" the effect of high pressure (Large et al., 1994).

The fluids mobilized graphite particles from granulites and deposited them mechanically in tectonic affected areas during regressive metamorphism of the metamorphic belt of the Sierra de Aracena, Spain (Crespo et al., 2005). Such processes have been documented in graphite-bearing marbles from the Madan lithotectonic unit in the Central Rhodopes, Bulgaria (Vlahov, 2019).

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} = 3.356–3.358 Å. Regressive metamorphism leads to a partial structural disorder of graphite, caused by fluids saturated with volatile substances (Yanchuk, Laz'ko, 1980).

The combined effect of temperature, pressure, and sufficient duration leads to an increase in the arrangement of earlier randomly oriented carbon layers (Nover et al., 2005). As the duration of mechanical grinding of graphite increases, its structural order decreases (Vlahov, 2019).

Discussion: different graphitization degrees of the carbon substance in rocks of the same metamorphic evolution

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 with a sharp peak at 3.36 Å. The classification of French (1964) shows that in the stage of coal and asphalt there are clusters of disordered graphene layers, which corresponds with the established interplanar distance d_{002} = 3.5 Å. Coal and graphite can coexist in the P–T interval 3 kbar/255 °C – 5.5 kbar/335 °C (Dissel et al., 1978).

Shungite forms amorphous or nanocrystalline masses consisting of carbon with traces of N, O, S and H. The determined interplanar spacing of carbon in Onega shungite is d_{002} = 3.48 Å and it is compared with the same structural parameter of anthracite (d_{002} = 3.52 Å) and well-crystallized graphite – d_{002} = 3.35 Å (Kwiecinska, Petersen, 2007).

The flaky graphite occurrence at Piippumäki (Eastern Finland) is embedded in quartz-feldspar gneisses and amphibolites. The granulite-facies level metamorphism of the rocks from the Piippumäki area is evidenced by the garnet-cordierite-sillimanite + melt paragenesis and the absence of orthopyroxene in the samples. This indicates a temperature at about 750 °C and a pressure at about 5 kbar. Epidote, chlorite and white mica (pyrophyllite) were formed next. This mineral composition is typical for metamorphism at the level of greenschist facies at temperatures not exceeding 400 °C. The flaky graphite is of good quality and with a high degree of structural order (d_{002} = 3.35 Å) despite the followed regressive metamorphism. All these

Table 1. XRD data summary of graphite from the Central Rhodopes (samples BS-1–5) and Eastern Rhodopes (samples 890, 898, 899 and 8911), Bulgaria: values of d_{002} (Å), graphitization degrees of carbon matter and temperature of the regional metamorphism

Samples from the Byalata Skala quarry №	BS-1–3	BS-4	BS-5
Analytical system	HUBER Imaging Plate Camera G670	powder diffractometer Siemens 500	powder diffractometer Siemens 500
d_{002} (Å)	3.356	3.359	3.364
Graphitization degree DOG (Seehra, Pavlovic, 1993)	0.97674	0.94186	0.88372
Graphitization degree $GD_{(0–30)}$ after Vlahov (2021)	24	21	16
T °C of regional metamorphism (Vlahov, 2021)	660 upper boundary conditions of amphibolite facies	588 upper boundary conditions of greenschist facies	468 greenschist facies
Samples from Ardino-Nedelino area №	**890**	**898 and 899**	**8911**
Analytical system	HUBER Imaging Plate Camera G670	DRON 1.5 M	DRON 1.5 M
d_{002} (Å)	3.356	3.356	3.360
Graphitization degree DOG (Seehra, Pavlovic, 1993)	0.97674	0.97674	0.93023
Graphitization degree $GD_{(0–30)}$ after Vlahov (2021)	24	24	20
T °C of regional metamorphism (Vlahov, 2021)	660 upper boundary conditions of amphibolite facies	660 upper boundary conditions of amphibolite facies	564 upper boundary conditions of greenschist facies

facts confirm the presence of high-quality graphite deposits in terrains with regressive metamorphism (Palosaari et al., 2020 and references therein).

The degrees of structural ordering of flaky graphite from the Central and Eastern Rhodopes, Bulgaria show that the progressive regional metamorphism at the amphibolite facies metamorphic conditions was followed by regressive metamorphic changes at the greenschist facies (Table 1). This thesis is supported by the DTA data of the graphite and by the partial or complete replacement of the high-temperature minerals by those specific to the greenschist facies conditions (Vlahov, 2019, 2021).

Conclusions

Temperature and quasi-hydrostatic pressure favor the graphitization processes of natural carbonaceous substances. All other factors can speed up or slow down the transformation of the primary carbonaceous matter into graphite during the stage of progressive regional metamorphism.

During the regressive metamorphic stage, the high-temperature minerals of the first stage are partially or completely replaced by the characteristic minerals of the lower facies. Depending on the intensity and duration of action of the listed factors, the graphite and the mineral composition of the rocks can show different facies of metamorphism. Furthermore, graphite can show different values of graphitization degree in samples collected at one site. Therefore, the results of all equations showing the relationship between the structural parameter d_{002} (Å), GD of carbonaceous matter and T °C of metamorphism should be combined with data on the mineral composition of graphite-bearing rocks and also compared with the results of other research methods. Only in this way, the evolution of graphite-bearing rocks can be traced. Flaky graphite from the Rhodopes has a high degree of structural order, although the graphite-bearing rocks have undergone regressive metamorphism at the greenschist facies. Determining the degree of graphitization has not only scientific, but also practical significance.

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