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THERMOANALYTICAL STUDY OF THE METAMORPHISM GRADE IN MALÉ KARPATY MTS. REGION

(Figs. 6)

A b s t r a c t: The paper deals with the problem of temperature and pressure conditions of the metamorphism in the productive zones of Pezinok-Pernek crystalline complex and in the black slates of Harmónia Group in Malé Karpaty Mts. using the results of thermal analysis of the rocks and the extracted organic matter (DTA in the controlled atmosphere of oxygen, nitrogen and static air). In conclusion the possibility in differentiation of these series is suggested.

Р е з ю м е: В статье решена проблема условий температуры и давления метаморфического процесса в продуктивных зонах Пезинок-Пернекского кристалликикума и в черных сланцах гармонской серии в Малых Карпатах на основе результатов термического анализа пород и химически отделенного органического вещества (измерения были проведены в контролированной атмосфере O_2, инертной атмосфере N_2 и в атмосфере статического воздуха). Внимание обращено на возможность дифференциации обоих толщ.

The geological structure of Pezinok-Pernek crystalline complex

Pezinok-Pernek crystalline complex represents bulky (4—8 km broad) zone of crystalline schists extending in NW-SE direction oriented approximately perpendicular to the range of mountains (C a m b e l, 1958). The specific conditions of the geological evolution in geosynclinal region of Lower Paleozoic formation in this series were described by C a m b e l (1958). This magmatogenic-sedimetary complex is bordered on its NE and SW side with granitoid rocks of Bratislava and Modra massifs (Fig. 1).

The part of Pezinok-Pernek crystalline complex consists of so called productive zones defined by C a m b e l (1959), (Fig. 1).

To the opinion of C a m b e l (1959) in these series are situated all antimonite deposits which are in essence analogous to the positions of synsedimentary submarine-volcanic-pyrrhotite lenses of the paleozoic age (C a m b e l, 1956; P o l á k, 1956).

The crystalline schists in the productive zones of Pezinok-Pernek crystalline complex consist of metamorphosed derivatives formed by combined metamorphism: at first by progressive periplutonic-regional metamorphism in Variscan orogeny, or by means of the contact metamorphism connected with the intrusion of granitoid magma followed by retrograde tectonometamorphic younger Alpine-Carpathian orogeny affecting not uniformly the schists of Malé Karpaty crystalline complex (B e c k — V e t t e r s, 1904; K o u t e k — Z o u b e k, 1936; C a m b e l, 1962).

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The slaty strata group in Pezinok-Pernek crystalline complex occurs in its NE edge in the subgrade of the independent lithological-facial, stratigraphic younger series of Harmónia Group (Low Devonian — Carboniferous) (Cambel — Čorná, 1974), defined between Modra and Častá by Cambel (1954).

The exploration by boring has revealed that series of Pezinok-Pernek crystalline unit overlies the younger rocks of the Harmónia Group. It cannot be

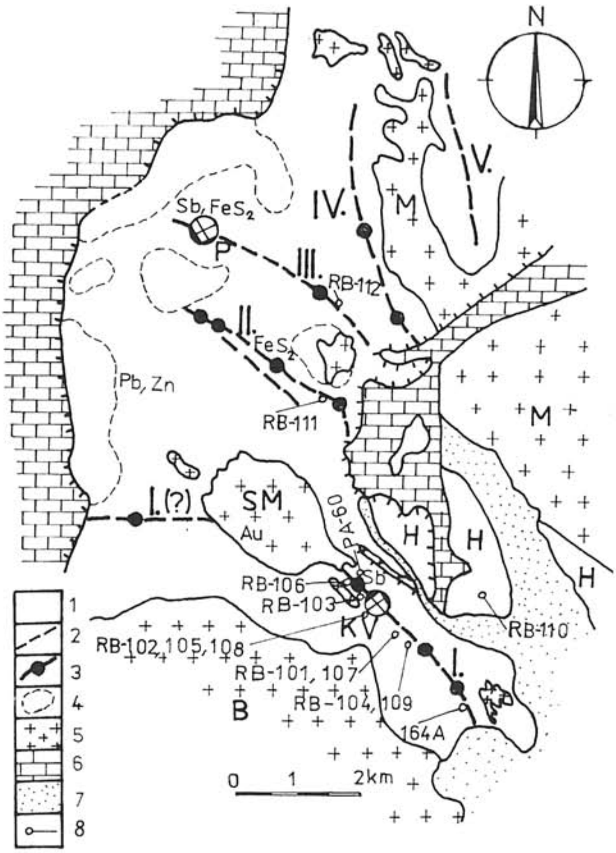


Fig. 1. Schematic geological map of the Pezinok-Pernek crystalline complex in Malé Karpaty region (Polák — Rak, 1980), inclusive the localization of the samples.

Explanations: 1 — metamorphosed rocks on the whole; 2 — productive zones (I—V); 3 — the occurence of the Sb mineralization in productive zones; 4 — the regions with the insufficient defined course of the productive zones; 5 — bigger bodies of granitoid rocks; 6 — Mesozoic rocks of the covering and higher tectonic units; 7 — Neogene rocks — Quaternary; 8 — localization and indicating of the sample; KV — Sb-deposit Pezinok-Kolársky vrch; P — Sb-deposit Pernek-Jahodnisko; B — Bratislava granitoid massif; M — Modra granitoid massif; SM — granitoid massif Staré mesto; H — Harmónia Group; Au, Pb, Zn, FeS — the occurence of the corresponding mineralization.

decided whether a thrust fault is involved or whether the crystalline complex is allochtonous as is presumed by M a h eľ (1980, 1983).

The important part in Pezinok-Pernek and Harmónia Groups are the black slates. According to C a m b e l et al. (1980, 1981), C a m b e l — K h u n (1979), K h u n (1980) the black slates in productive zones of Pezinok-Pernek crystalline complex contain syngenetic (synsedimentary) acummulations of the sulphide ores (pyrite-pyrrhotite). Antimonite ores represent acummulation which were mobilized during metamorphic and hydrothermal processes and then epigenetically deposited. The black slates were in Alpine-Carpathian orogeny partly affected by remobilization again and they were locally tectonically overworked. The black slates of Harmónia Group are not ore bearing.

The pressure and temperature conditions in the origin of the metamorphic rocks in Malé Karpaty region (concise review)

The first data on the pressure and temperature conditions (p, T conditions) in the origin of the metamorphic rocks in Malé Karpaty region were given by D y d a (1980 a, b; 1981, 1982) and C a m b e l et al. (1981, 1983). These authors have presumed for regional-periplutonic metamorphic process the temperature interval 450—610 °C and pressure 3.0—3.5 kbar.

K o r i k o v s k i j et al. (1984) in the study of mineralogical paragenesis of metamorphism in Malé Karpaty region distinguished two stages:

1. The regional-periplutonic stage defined by temperatures 500—550 °C and pressures 300—350 MPa reaching maximum (the highest P—T values) during intrusion of Bratislava granitoid magma. K o r i k o v s k i j et al. (1984) have divided the metamorphosed rocks in the crystalline complex of Malé Karpaty into four zones: biotitic, garnetic, staurolite-chloritic and staurolite-sillimanitic.

2. Metamorphism connected with the crystallization of Modra massif is characterized by pressure conditions 100—150 MPa and under its influence andalusite and cordierite cherts and spotted shales are formed.

Localization of the samples analyzed

The samples of the black slates represent first of all the productive zone in which the sole exploited deposit of the antimonite ores in Malé Karpaty region (Pezinok) is situated (Fig. 1). The prevailing part of the samples was collected from the geological bores performed by the group directed by S. P o l á k (Geological Survey, Spišská Nová Ves). The samples collected from the workings (antimonite gallery, PA—60) and exposures (RB—110, 164 A) were studied to compare the results.

Thermoanalytical measurements

Powder samples (bellow 0.05 mm) were studied using Duppont 990 Thermoanalyzer by means of DTA method (the sample weight: 15—20 mg, heating rate 20 °C min^{-1}) in dynamic oxygen and inert (N_2) atmosphere (the rate of gas flow was 1 cm^3 s^{-1}).

The starting temperature "T_0" (the initiation of the oxidation of the organic matter) and peak temperature were derived from DTA curves obtained in

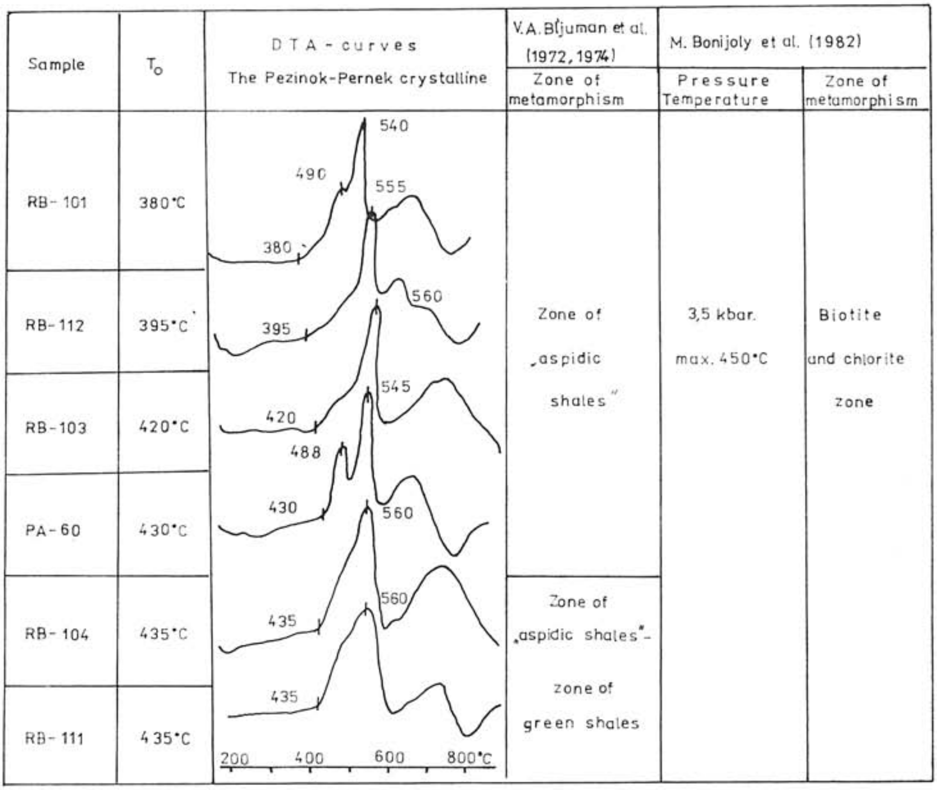


Fig. 2. Thermograms for the black states of Pezinok-Pernek crystalline complex, T_0 — the initiation of the oxidation reaction.

oxygen atmosphere (Figs. 2, 3). The same data were extracted from endothermic and exothermic effects from DTA curves obtained in nitrogen atmosphere (Fig. 5, 6).

Organic matter extracted from the black slates by means of the flotation in toluene according to the method by Bonijoly et al. (1982) was analyzed in the static air using Derivatograph MOM Q—1500 D (the sample weight: 0.5—1.0 g, heating rate 10 °C min^{-1}). The results are shown in Fig. 4. The initiation of the exothermal peak occurs at temperatures 360—435 °C, peak temperature occurs at 468—485 °C.

Determination of the metamorphism grade in productive zones of Pezinok-Pernek crystalline complex

Bljumen et al. (1972, 1974) have characterized various metamorphic rocks containing the admixture of organic matter by means of the starting temperature of oxidation reaction using the thermoanalytical method. This temperature increases with increasing of metamorphosis and progressive graphi-

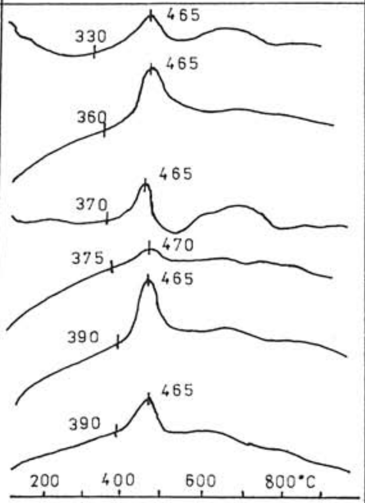
Sample	T_o	DTA – curves The Harmónia Group	V.A. Bljuman et al. (1972) Zone of metamorphism	M. Bonijoly et al. (1982) Pressure Temperature	M. Bonijoly et al. (1982) Zone of metamorphism
RB-106	330 °C		Zone of „aspidic shales"	3 kbar. max. 350 °C	Chlorite zone
RB-108	360 °C				
RB-107	370 °C				
RB-109	375 °C				
RB-105	390 °C				
RB-110	390 °C				

Fig. 3. Thermograms for the black states of Harmónia Group, T_o — as in Fig. 2.

tization of carbonaceous matter in the rock. Bljumen et al., (1972, 1974) stated that the starting temperature of oxidation reaction does not depend upon the initial composition of the rock as well as upon amount of organic matter. The initial temperature of oxidation is about 100 °C higher for every next facia. Bljumen et al., have also found that the graphite structure formed at higher temperature does not change in heating at lower temperature.

The initiation of the first exothermal peak for the samples of Pezinok-Pernek series occurs in temperature interval 380—435 °C corresponding to the phase of the low metamorphosed "aspide-slates" (Bljumen et al., 1972, 1974) beyond the boundary of the green slates in the biotite-chlorite metamorphic zone with pressure conditions up to 3.5 kbar and maximum temperature up to 450 °C (Bonijoly et al., 1982). It concerns the rocks of low grade metamorphosis according to Winkler's classification (Winkler, 1974). Exothermal effect proceeds in the narrow temperature interval and exhibits a sharp maximum. The oxidation reaction finishes at the temperature lower than 900 °C which is typical for the paleozoic rocks as described by Bljumen et al. (1972).

DTA curves of the black slates of Harmónia Group show the initiation of the first exothermic peak at temperatures 330—390 °C what indicates likewise the black slates of Pezinok-Pernek Group the stage of low metamorphosed "aspide-slates". The pressure and temperature conditions were, according to calculations and comparisons of Bonijoly et al. (1982), slightly lower (less than 3 kbar) therefore the slates of Harmónia Group may be classified

Sample	T_o	$T_{max.}$		DTA-curves	Zone of metamorphism (Diessel— Offler, 1975)
164 A	380 °C	470 °C	The Pezinok-Pernek crystalline		Chlorite zone
RB-104	435 °C	470 °C			
RB-102	395 °C	480 °C			Biotite zone
RB-101	380 °C	485 °C			
RB-105	360 °C	468 °C	The Harmónia Group		Chlorite zone
RB-106	360 °C	470 °C			
RB-107	360 °C	470 °C			

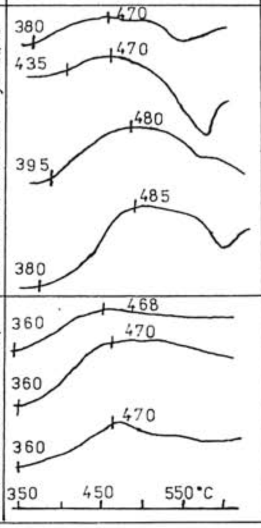


Fig. 4. Thermograms for the organic matter separated from the black states of Pezinok-Pernek and Harmónia Groups.
Explanations: T_o — as in Fig. 2; $T_{max.}$ — DTA peak temperature.

as the slates of chlorite zone. According to Winkler (1974) and to the thermoanalytical data represent the slates of Harmónia Group the rocks of very low and low grade metamorphism. They can be classified one grade lower than the slates of Pezinok-Pernek Group which were metamorphosed in the conditions of the biotite-chlorite zone.

The DTA curves of organic matter extracted from the black slates by means of toluene (Fig. 4) confirmed the results obtained from the samples of the rocks.

The samples of Pezinok-Pernek Group on the basis of the maximum of the first exothermal peak represent the rocks of chlorite and biotite metamorphic zone (Diesel — Offler, 1975). Characterization of the metamorphism grade according to the methods by Bljumen et al. (1972, 1974) and Bonijoly et al. (1982) is the same as in the case of the samples of the rocks.

The possibility of differentiation of the slates from Pezinok-Pernek and Harmónia Groups on the basis of thermoanalytical results

The importance of the differentiation of the black slates from Pezinok--Pernek Group comprising a part of the productive zones form the Harmónia

Group has been suggested by Cambel — Khun (1979), Khun (1980), Cambel — Khun (1983) from the lithological point of view as well as from the standpoint of the genesis of the mineralization.

The samples of Pezinok-Pernek Group, analyzed in oxygen atmosphere, exhibit the exothermal peak in the temperature region 540—560 °C (Fig. 2). Less developed exothermal effect (with the exception of the samples PA-60 and RB-101) occurs at temperatures 470—490 °C. Intensive exothermal peak at 540—560 °C is typical for Pezinok-Pernek Group.

In temperature interval 600—800 °C occurs next exotherm. The initial and peak temperatures of this effect do change in the broad temperature interval.

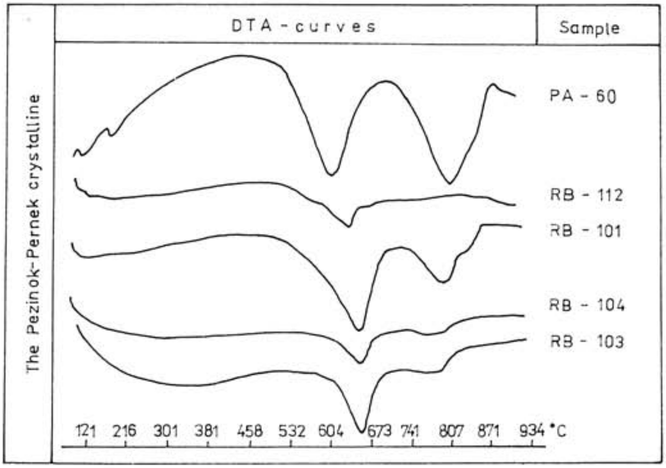


Fig. 5. Thermograms for the black slates of Pezinok-Pernek Group (DTA in inert atmosphere — N_2).

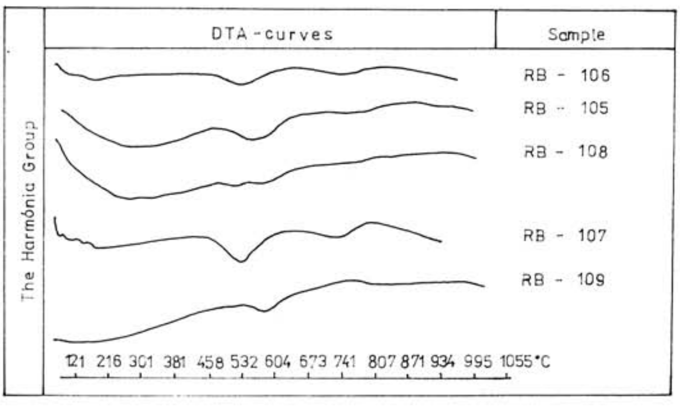


Fig. 6. Thermograms for the black states of Harmónia Group (DTA in inert atmosphere — N_2).

The occurence of this exotherm is also typical for all samples of Pezinok-Pernek Group. Endothermal effect at 800 °C which can be observed in DTA curves of the samples PA-60 and RB-101 represent the heat consumption during decarbonization reaction.

DTA curves obtained from the samples of Harmónia Group distinguish from the former significantly (Fig. 3). They are characteristic by lower intensity of the exothermal effects and do not exhibit maximum at 540—550 °C. The common for these curves is exotherm at 465—470 °C and less developed maximum in the region of 700 °C. The starting temperature of the first exothermal reaction occurs at 330—390 °C (Fig. 3).

Thermograms of the samples from Pezinok-Pernek Group analyzed in inert nitrogen atmosphere show two significant endotherms (in the exception of the sample RB-102) at 600—650 °C and 800 °C. The first endotherm indicates the process of the evolution of organic matter by destillation, the second one the decarbonization (Fig. 5).

The samples of Harmónia Group analyzed in nitrogen atmosphere distinguish from the former by morphology and temperature characteristics of the effects in DTA curves (Fig. 6).

Conclusion

On the basis of graphite geothermometer was studied the grade of metamorphism for the rocks of productive zones in Pezinok-Pernek crystalline complex and Harmónia Group by means of thermal analysis.

According to the results of thermal analysis the rocks of Pezinok-Pernek Group were metamorphosed in the stage of biotite-chlorite zone corresponding to the pressure 3.5 kbar and the maximum temperature 450 °C (B o n i j o l y et al., 1982). According to the classification of W i n k l e r (1974) it concerns the rocks with low stage of metamorphosis. The data of thermal analysis show, that the highest temperature of the metamorphosis was 435 °C.

These results would evidence that the rocks of Harmónia Group were metamorphosed in the contitions of the chlorite zone at the temperatures 330—390 °C. The schists of the Harmónia Group belong to the slates on the boundary between very low and low grade metamorphosis according to the classification of W i n k l e r (1974) and to the results of the thermal analysis.

The temperatures and pressures determined by the method of graphite thermometer are lower compared with data given by D y d a (1980 a, b, 1981, 1982), C a m b e l et al. (1981) and K o r i k o v s k i j (1984).

The highest temperatures and pressures stated the papers by D y d a (1980 a, b; 1981; 1982) and C a m b e l et al. (1981). These works are based an the study of index minerals (they have determined the temperature interval 450—610 °C and pressures 300—350 MPa). K o r i k o v s k i j et al. (1984) studying the mineral paragenesis have found lower parameters (500—550 °C, 100—350 MPa).

The thermoanalytical study of the black slates showed, that the lowest p, T conditions are given by the method of graphite geothermometer (330—435 °C, 300—350 MPa) when comparying with other methods.

This fact must be taken into consideration in the thermobarometric studies. Diversity of methods used in determination of p, T conditions of metamorphism of slates in the Malé Karpaty Mts. enabled such comparison.

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