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THERMODYNAMIC MEASUREMENTS OF ORIGIN OF MINERALS
IN METAMORPHITES IN THE AREA OF CRYSTALLINE OF MALÉ
KARPATY MTS.

(Tab. 1, Figs. 10)



Abstract: The authors analysed the metamorphic processes, by which crystalline rocks of the Low Carpathians were affected. The metamorphism was taking place here under thermodynamic conditions of lower and medium grade of the amphibolite facies, where the temperature of metamorphism 500 — 600 °C and lower is supposed, according to the distance from the granitoid intrusion. Cooling of minerals of the granitoid magma probably took place at temperatures between 900 and 600 °C (in feldspars somewhat lower), was of unequable discontinuous course depending on tectonic processes of the Variscan orogene and on the velocities of the movements of melts. The authors point to the discrepancy of some thermodynamical data in comparison with geological knowledge and state that especially determination of depths of endogenic processes in orogenic regions has rather a normative than real value.

Резюме: Авторы резюмируют знания касающиеся метаморфических процессов в области Малых Карпат; характеризуют их термодинамические условия на основе анализ разных типов метаморфических процессов которые здесь взаимно комбинируются и перекрываются. Авторы оценивают знания и данные касающиеся определений термодинамических параметров метаморфоза, полученные разными методами. Метаморфоз в области Малых Карпат проходил при термодинамических условиях низшей и средней степени амфиболовой фации и предполагаемая температура метаморфоза является 500—600 °C или низшая, согласно расстояний от гранитоидной интрузии от которой был в зависимости метаморфический эффект. Застывание отдельных минералов гранитоидной магмы проходило приблизительно при температурах с 900 до 600 °C и у полевых шпатов немножко ниже, и оно имело неравномерный прерывистый ход зависящий от тектонических процессов варийского опогена, от скорости движений выплавов и эманаций происходящих из них. Авторы показывают на противоречия некоторых полученных термодинамических данных, вместе с геологическими знаниями и устанавливают, что главным образом определение глубин эндогенных процессов в орогенных областях имеет скорее нормативную как реальную величину, что вытекает из того что в орогенных областях фактор, давления не имеет характер только гидростатического, а также выпрямленного давления. Поэтому авторы считают приведенные расчеты глубины эндогенных процессов меньше реальными чем были вычислены.

Introduction and approach to interpretations

The present state of the geochemical, mineralogical and petrological investigation provides the possibilities to determine by exact methods the thermodynamic conditions of the origin of the geological objects. It is self-evident, that all these establishings are dependent on fulfilment of certain pre-

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conditions, which the geochemist-geologist sets as the basis for the validity of calculation. The measure of correctness of determination of thermobarometric conditions of the origin is the conformity of determination of these values with geological knowledge, which the field or other laboratory geological investigation provides. It happens, that when we want to put the results of thermobarometric conditions of origin e.g. of metamorphosed rocks into conformity with geological conditions, disproportions occur, which are caused by the circumstance, that the obtained calculation cannot be applied to the given area and genesis of the studied object without correction factors. Sometimes there can be also an erroneous geological interpretation of field observations, which is necessary to verify and consider again just because it is not in agreement with the calculated thermobarometric data. The cause of discrepancy is usually caused by the fact that all conditions of the natural process are not known to us and cannot be substituted into the calculation formula or graph. Each method of determination of conditions of origin is based on presumptions, which need not be fulfilled in natural environment. Therefore in our calculations we often are getting data, which are only of some normative importance and correspond to the criterii of the applied method, because each method of calculation is based on certain simplification and takes into regard only a part of the factors, which are acting in real natural environment.

For determination of thermodynamic conditions on the basis of the study of minerals or pair of minerals, the most advantageous are the environments which are formed by long-lasting equable metamorphic processes in areas of platformic metamorphism, in which is a suitable situation for manifestation of geochemical balance among minerals of the rock. For calculation are much more unsuitable the conditions of determination of origin of metamorphosed rocks, which are formed by orogenic processes, mainly in the phase of intrusive penetration of granitoid magmas into the supercrustal schistose series. The orogene could have caused repeated uplifting and sinking of complexes as well as various rate of cooling of the melted masses or rock masses affected by metamorphism. Such conditions existed also in formation of metamorphites of the concrete Low Carpathian region and similarly also in other regions of crystalline rocks of the West Carpathians. In the ascent of magma an intensive periplutonic metamorphic influence of granitoids on rocks of the sedimentary mantle is shown under overheated conditions of the amphibolite metamorphic facies.

The narrow isometamorphic zones around granitoid bodies (from the zone of gneisses and migmatites to the zone of biotite phyllites, thickness is not greater than 800—1000 m), which are characteristic of the Low Carpathians, indicate that the equilibrium states in forming of minerals of metamorphic facies are dependent on rapidly changing thermodynamic and physical-chemical factors as are the hydrostatic and unilateral pressure called forth by the orogene and temperature, which is dependent not only on the geothermic gradient but also on active, often local supply of thermal energy. Important is also the supply of material, connected with the intrusive process and ascending granitoid magma.

These facts should be taken into consideration in interpretations of the results, mainly in determination of the depth of processes, which were usually

calculated only on the basis of suppositions of the existence of hydrostatic pressure and not taking into regard the unidirectional pressure originating with folding of the mountains. Also the content of water in processes of the metamorphism is a changing and supposed (not exactly determinable) factor, but often of much influence on the endogenic processes. We also know that some methods [e.g. Barth's two-feldspar method] can lead to incorrect conclusions, because fulfilment of the required conditions of calculation is too much complicated. Similarly also the methods of gas-fluid inclusions require care in paleothermometric interpretations.

So far several investigations of metamorphites in the Low Carpathian region, concerning the thermobarometric measurements of minerals, were carried out. The thermodynamic conditions of origin of clay-quartz metamorphites (gneisses and migmatites, Dyda, 1980 a, 1980 b, 1981) were determined. The determination of the temperature of metamorphism of basic rocks at the Hlboká cesta way considered as the products of the anatexis of metabasites (Pitoňák, 1980; Cambel — Medved — Pitoňák, 1981). Particularly from viewpoint of the geochemical criterii Spišiak paid attention to the thermodynamic conditions of basic metamorphites of the Low Carpathians (presented work) and Hovorka — Spišiak to those of the West Carpathians (in press). We have also the results of measurements of gas-fluid inclusions occurring in pyrite ores, which are of syngenetic character and can indicate metamorphic conditions, which the whole sequence containing ore layers underwent (Žukov — Savčenko, in Cambel — Žukov — Savčenko, 1980).

Because in the Low Carpathians is periplutonic metamorphism closely linked with intrusions and the proximity of granitoids, the study of metamorphism of the schistose sequence requires also knowledge of the thermodynamic conditions, under which cooling of the granitoid magma takes place. Several data to this problem, concerning granitoids of the West Carpathians, are published in the work by Kľomňnsky et al. (in press) and in the work by Vilínovič (in press). Similar data concerning the conditions of crystallization of biotite in granitoid rocks were already published by Petrík (1980). Also the specialists studying K-feldspars and other minerals (zircon) in Variscan granitoids of the West Carpathians contemporaneously with this contribution give into press the results of investigations, which clear up the thermodynamic conditions of K-feldspar origin and so also cooling of granitoids. There are, for instance, the works of Macek (in press), Dávidová (in press), Krist (in press).

When we have to present a brief characterization of metamorphism of schistose rocks in the region of the Low Carpathians still before beginning with evaluation of the thermobarometric analysis of the results, then the following survey can be mentioned:

The characteristic of metamorphism in the Low Carpathians

The metamorphic processes in the region of the Low Carpathians are complicated and mutually combined. Before the intrusion of the Variscan granitoids we suppose a relative low-grade metamorphism of schistose facies of green schists. Therefore the Variscan granitoid plutonism could form distinct

isometamorphic zones around intrusions, which are characterized by gradual and continuous, or also more or less discontinuous transition of phyllites into gneisses. The discontinuity is caused by younger tectonics. This transition of decreasing intensity of metamorphism is variously rapid and in the area of the Bratislava massif the distance between phyllites and gneisses varies from 800 to 1000 m, the gneisses begin to form only several 100 m from the contact with the granitoids. On the basis of mineral associations we can differ four isometamorphic zones around granitoids (Janák, 1980). They are the chlorite, biotite-garnet, staurolite and sillimanite zones. The individual zones can be characterized mineralogically as follows:

The chlorite zone is characteristic of metapelites by the association: chlorite, light-coloured mica (sericite), quartz, \pm biotite. It is the lowest grade of metamorphism with dominating manifestations of pre-granite metamorphism.

The biotite-garnet zone is characterized by the presence of biotite, garnet, muscovite, quartz, \pm chlorite. Garnet and biotites are porphyroblastic and originated under the metamorphic effect of granitoids.

The staurolite zone has clayey-quartz metamorphites with the content of staurolite, biotite, muscovite, garnet, chlorite and quartz (chlorite can be also secondary). This association is an indicator of medium-grade metamorphism.

The sillimanite zone is characterized by rocks with the content of fibrolitic sillimanite, muscovite, biotite, garnet and quartz. This association is of unbalanced character and transitional from the staurolite zone into the sillimanite zone. The sillimanite zone as the highest metamorphic grade of periplutonic metamorphism is, besides the above-mentioned minerals, also characterized by plagioclase.

It is necessary to remark, that in the area of Júr near-contact migmatites of injection character and hybrid granitoids arose. Otherwise the granitoid intrusions have sharp contacts with the sedimentary rocks and at the direct contact no more intensive granitization of sediments is evident, which retain the gneiss character. From the geochemical viewpoint we can consider the metamorphism essentially as isochemical (Cambel — Kupčo, 1965; Cambel — Veselský, in press).

The facial alterations of sediments influence the grade of metamorphic recrystallization. Mainly the higher content of quartz, basic tuffogenic material and organic substance reduces the metamorphic crystallinity of metapelites in contrast to common metapelites, where the size of biotite and garnets depends on the grade of metamorphism, e.g. on the proximity of the rock to the contact with granitoids.

It is necessary to call attention to the fact that a lowered metamorphic recrystallization is observed in the schists of the Harmónia Group (Middle Devonian to Lower Carboniferous), which are of microflyschoid character (alternating pelitic interjacent beds with the content of organic substance with thin psammitic-pelitic beds with clastogenic feldspars). So lithologically inhomogeneous rocks of the Harmónia Group reduce the metamorphic effect caused by granitoid magma. The second factor of reduction of the metamorphic effect in the area of the Harmónia Group is, that the biotite granodiorite of the Modra massif is petrochemically more basic in comparison with granitoids of the Bratislava massif and intrudes more or less interjacent, also

reducing the metamorphic effect of the Modra granitoids. At the contact of granitoids with schists of the Harmónia Group metamorphic phenomena are evident, which are close to caustic (thermic) metamorphism and hornfels biotite schists, calcareous-silicate hornfelses (where are layers of limestones) and spotted schists with andalusite and biotite etc. formed here. An essential factor of reduction of the grade of metamorphism is gradual alteration of the periplutonic deep contact metamorphism into near-surface caustic contact metamorphism in the Harmónia Group area. This fading out of deep metamorphism into shallow-subsurface is caused by the fact, that the Harmónia Group is post-Middle Devonian to pre-Middle Carboniferous and the granitoid intrusions were emplaced into the little overheated stratigraphically relatively young horizons in comparison with the underlying Pezinok—Pernek schistose complex and Bratislava crystalline rocks, the age of which is estimated on the basis of palynological results, as Lower Devonian, Cambro—Silurian and in the lower parts possibly also Upper Proterozoic.

Just this reduced metamorphic effect and near-surface character of the contact metamorphism of the Harmónia Group by granitoid rocks can serve as an example of controversy of field investigations with some calculated thermobarometric results, which indicate greater depths mainly on the basis of calculations, carried out by feldspar—quartz eutectic. These results cannot be interpreted directly, but it is necessary to consider them as normative, which must be adjusted with regard to the real geological situation.

Methods of determination of P. T. conditions

A more detailed division of the grade of metamorphism belong always to the topical objectives of petrology of metamorphosed rocks. Using of some index minerals e.g. staurolite, cordierite etc. is often limited by chemical composition of rocks. The thermodynamic approach of the evaluation of physical conditions of the recrystallization sets out from the chemical composition of balanced coexisting minerals.

In rocks, in which are not present index minerals, neither diagnostic mineral pairs suitable to the thermodynamic analysis of paragenesis (garnet—biotite, garnet—cordierite, plagioclase—amphibole), however, difficulties with their ranging into a closer metamorphic scale arise.

Minerals with little variable chemical composition and delimited extent of stability, as e.g. the modifications of Al_2SiO_5 , belong to reliable indicators of the metamorphic grade. Suitable are also minerals in which solid solutions controlled by chemical composition of rocks, mineral paragenesis and the grade of metamorphism are forming. In tracing of the grade of metamorphism these methods are shown as most reliable, which evaluate contemporaneously the mineral paragenesis, chemical composition of rock, also of the coexisting phases. This approach with supposed chemical equilibrium in rock, using suitable calibration of distribution coefficients (K_D) in thermodynamic conversions, is often getting nearer to the theoretical model and is in combination with the microscopic-structural study of thin sections usually reliable.

For the region of the Low Carpathians one of the co-authors (M. Dýda) carried out numerous thermobarometric investigations of the origin of clayey-quartz metamorphites (metapelites) and the results are published in several

works (Dyda, 1980 a, 1980 b, 1981) and the author informs about the conclusions in the following text.

With the purpose to establish the temperatures and pressures on the basis of distribution of Mg and Fe among the coexisting phases in geological conditions, many experimental and field works were carried out.

Table 1

P—T conditions of metamorphism of the Low Carpathian metapelites

Sample	$X_{Mg}^{Bt^{XX}}$	$X_{Mg}^{Grt^{XX}}$	T (°C)*	P (MPa)*	$\ln X_{Grt}/X_{An}$	P ₂	P ₃
4Y.	0.517	0.122	353	440	-2.035	430	390
7Y.	0.468	0.118	555	450	-1.907	510	460
17Y.	0.494	0.108	510	410	-2.137	360	310
KB—1Y.	0.350	0.099	545	480	-2.437	300	250
KB—2Y.	0.463	0.130	560	470	-2.484	300	260
KB—5Y.	0.362	0.116	575	520	-1.798	580	540

* According to calibration of Perčuk (1973). P₂ — on the basis of thermodynamic data Robie — Waldbaum (1968). P₃ — Ghent (1973).

** Data adopted from the work of Dyda (1980)

Further explanations in Fig. 1.

Frost (1962) pointed out the systematically rising coefficient of distribution (K_D) with rising temperature of rock recrystallization. Albee (1965) established on the basis of evaluation of 70 garnet and biotite pairs that $D K_D^{Mg-Fe}$ systematically alters into rocks metamorphosed in the garnet zone to rocks of the sillimanite zone. Sen and Chakraborty (1968) have come to the conclusion, that K_D is a systematic function of the grade of metamorphism. An important moment in valuation of K_D is establishing of the mineral homogeneity. The inhomogeneity can as a rule exclude the evaluation of physical properties and render more difficult the conversion of K_D . It is necessary to take into regard the disturbing factors as e.g. are unbalanced state of rocks, the zonality of some minerals, analytical errors, mistakes in separation, also of crystallo-chemical conversion.

When we avoid these mistakes in experimental work, it is possible to foresee from the knowledge of Fe/Mg distribution among almost ideal isomorphous mixtures, the change of the mineral association as a function of changing temperature, pressure and activity of H₂O (Thompson, 1976).

Setting out from the methodic approach in the works of Thompson (1955); Perčuk (1970, 1973); Saxena (1973) and Thompson (1975), the conditions of metamorphism of some Low Carpathian metamorphosed rocks were obtained by thermodynamic approach. These results are mentioned in Tab. 1.

From these data, which should clear up more in detail the grades of metamorphism, several statements result.

In the majority of the mentioned samples the temperature of 510—520 °C (Fig. 1) was surpassed, which is considered as the lower boundary of the medium grade of metamorphism. This is in metapelitic rocks connected with

the presence of diagnostic minerals characterized by their field of stability. These obtained temperatures are in the majority of samples confirmed by the occurrence of staurolite, usually testifying to surpassing of 510 °C in metapelites. It determines the higher achieved temperatures of staurolite with its disappearance, however, its occurrence and disappearance is also caused by chemical composition of rocks. Higher temperatures in the samples

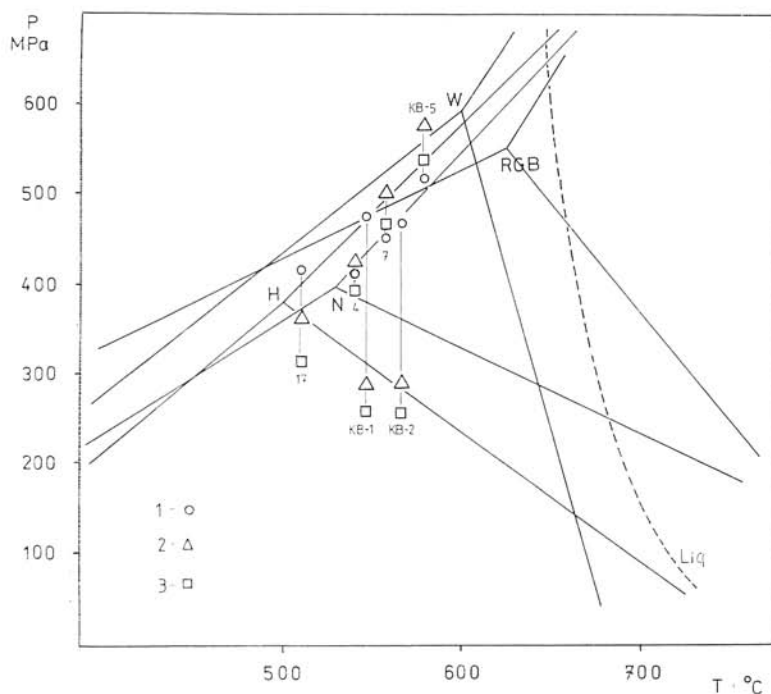


Fig. 1. Thermodynamically determined temperature and pressure conditions of recrystallization of some Low Carpathian metapelitic rocks. 1 — according to calibration of Perčuk (1973), 2 — on the basis of temperature according to Perčuk and thermodynamic data of Robie and Waldbaum (1968), 3 — Ghent et al. (1976). The triple points of polymorphic alterations of Al_2SiO_5 are designated N — Newton (1966), RGB — Richardson et al (1969), H. Holdaway (1971).

are connected with the presence of fibrolitic sillimanite, the occurrence of which is often placed into the area of triple point of polymorphic modifications of Al_2SiO_5 . Achieving of these temperatures, however, need not exclude the presence of staurolite in the traced rocks.

The mentioned pressures in Tab. 1 are from the geological viewpoint of considerable importance because they indicate the depth of metamorphism, which so far cannot be determined independently on the pressures. The control of calculated pressures is rendered more difficult by the factor, that the mutual reactions of minerals and formation of new mineral associations are more influenced by temperature than by pressure.

In some samples of Low Carpathians metapelites with the mineral association



in which garnet, sillimanite, plagioclase and quartz coexist, the reaction was used.



for calculation of metamorphic pressures.

The values of changes of enthalpy (H), entropy (S) and molar volume (V) for this reaction were obtained from the data of Robie and Waldbaum (1968) and taken over from the work of Ghent (1976). The molar fraction of grossularite in garnet was ($X_{\text{Gros}}^{\text{Gar}}$) obtained by combination of the physical properties of garnet and its chemical composition. The molar fraction of anorthite in plagioclase ($X_{\text{An}}^{\text{Plag}}$) was determined from approximative chemical composition of plagioclase.

The so calculated pressures are mentioned in Tab. 1 and have simultaneously a comparing value with pressures obtained on the basis of $X_{\text{DMg-Fe}}^{\text{Gar-Bio}}$ with using of calibration of Perčuk (1973).

Taking into regard these values thus it remains to explain the processes of tectonics which have exposed these rocks at the earth surface. The measure of these determined values was possible to confirm only by available methods and accessible control of results. We consider, however, these results as sufficiently reliable for interpretation of metamorphic processes.

The obtained values of pressures would serve then as an argument, that metamorphic recrystallization of the Low Carpathian metapelites in the periplutonic zones was taking place at the depth of 10—20 km.

In evaluation of these relevant geological phenomena it is necessary to take into consideration that these data are only an approximation to the real thermodynamic state. The real values of temperature and pressure create the dynamic conditions of intrusions in orogenic regions, and therefore the values of pressure need not unequivocally indicate the depth of crystallization and the measure of the chemical equilibrium between the minerals in the rock can be suppressed by kinetic factors acting in recrystallization. The decisive importance of determination of the thermobarometric conditions falls on the study of the character of the whole mineral association in the rock chosen for these investigations.

Determination of P, T, conditions of metabasites formation

Determination of formation of basic metamorphites of gabbroid rocks, diorites, amphibolites was tried by P. Pitoňák (1980) in his diploma work. He used here the isotherms mentioned by Perčuk (1970). The original graphs, after new analysis of biotites we revised, completed and compiled the graph 3 according to the isotherms of Perčuk et al. (1976) and the result is mentioned in Figs. 2 a, 2 b and 3. The determination of temperature of formation of metabasites lies in the supposition, that at certain temperature

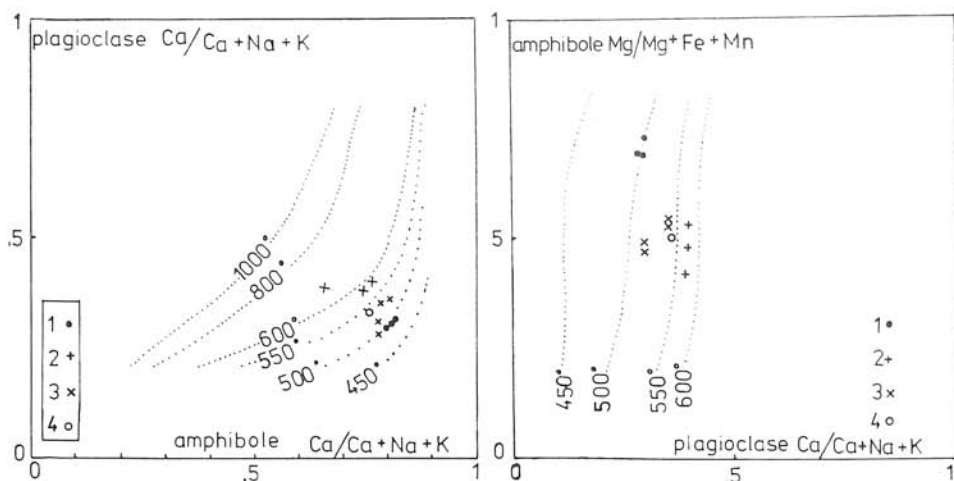


Fig. 2 a. Relation of ratio $\text{Ca}/\text{Ca}+\text{Na}+\text{K}$ in plagioclase and amphibole.

Fig. 2 b. Relation of ratio $\text{Ca}/\text{Ca}+\text{Na}+\text{K}$ in plagioclase to $\text{Mg}/\text{Mg}+\text{Fe}+\text{Mn}$ in amphibole with indicated isotherms according to Perčuk (1970). 1 — gabbroids from the Hlboká cesta way, 2 — diorites from the Hlboká cesta way, 3 — diorites from Peterklín, 4 — diorites from Hlboká cesta way (microprobe analysis).

the coexisting minerals of the given composition are in equilibrium. The work of Cambel — Medved — Pitoňák (1981) brings evidence that diorites, which are situated in granitoids and other amphibolic rocks from the Hlboká cesta way (Bratislava) and amphibolic rocks of granitoids from Peterklín and the area of the Sb deposit Pezinok are of metamorphic anatectic origin. Therefore the data about the temperature of origin of amphiboles and biotite of these rocks are contemporaneously data about the temperature of metamorphic processes, because the temperature of granite and basic magma should be higher as it results from Fig. 2 and 3. As amphibole is in some of the mentioned rocks corroded by plagioclase, no equilibrium state occurred between the minerals and therefore also the real estimation of temperatures must be taken with reserve. The chemical analysis of plagioclase was not carried out, but was calculated by Pitoňák from optical determination of plagioclase basicity. From this data conversion to chemical analysis was carried out and graphs 2 a, b were compiled.

The mentioned thermobarometric investigations indicate that the interpretation of the obtained data is not unequivocal and that the application of various methods of determination and of various dependences and graphs gives in details different results. With all these circumstances, however, all calculations approach to one another and are varying between 500 and 600 °C. It is interesting that the gabbroids from the Hlboká cesta way give the lowest temperatures of origin 500 °C, what may confirm that these rare rocks from the Hlboká cesta way are a product of metamorphic alteration. The amphiboles are more calcareous and perhaps originated with assimilation

of layers with a higher content of carbonates. A higher metamorphic temperature show diorites from Peterklín (north—east of Pezinok) 500 to 550 °C and the highest between 550—600 °C diorites from the Hlboká cesta way and amphibole granitoids from the area of Sb-deposit of Pezinok. This valuation of the temperature of origin 600 °C is low for the magmatic process and high for the metamorphic process. There are, however, rocks of transitional

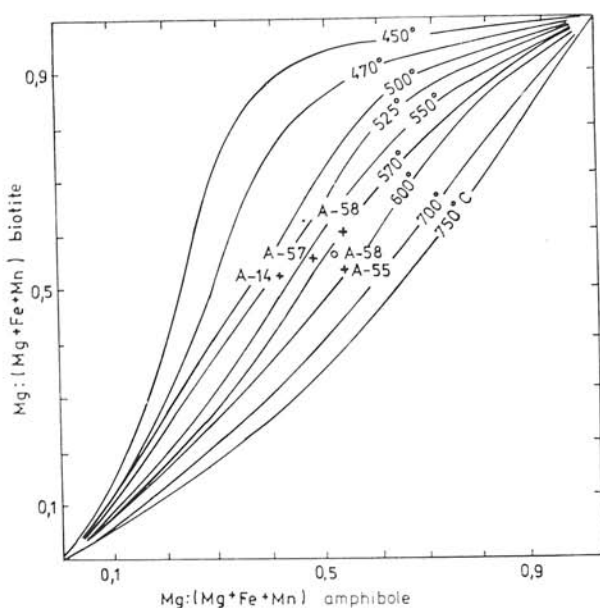


Fig. 3. Relation of ratio $Mg/(Mg+Fe+Mn)$ in biotite and amphibole with indicated isotherms according to Perčuk (1970). A-58 — biotite — amphibole quartz metariorite, Hlboká cesta way, A-55 — biotite — quartz diorite with amphibole, Pezinok, borehole KV 2 (73—75 m), A-57 — amphibole quartz diorite, Peterklín (Pezinok), A-14 — biotite tonalite with amphibole near Kalvária, Hlboká cesta way Bratislava.

magmatic-metamorphic character and therefore the result of measurement can be accepted. The mentioned succession of temperatures can be accepted because diorites from the Hlboká cesta way have essentially already magmatic structures and represent anatectic palingenic magmatic types. Further, it will be necessary to carry out similar measurements in amphibolites and metabasites less affected by metamorphism, which do not occur directly as bodies in granitoids, but are a part of the schistose sequence. Here the confrontation of measurements obtained in metapelites and metabasites should lead to analogical results.

Further thermobarometric methods of the investigation of metabasites

In the last time metabasites from crystalline rocks of the Low Carpathians were very intensely studied, (B. Cambel — L. Kamenický monograph

in press and B. Cambel — J. Medved, 1981). Attention was paid mainly to metabasites higher-grade metamorphosed, corresponding to the conditions of amphibolite metamorphic facies or metamorphosed in the sense of Winkler (1975) in conditions of „low grade and medium grade“ metamorphism. In the presented part of the work we mention the results of the investigation of metamorphism of basic rocks, carried out in the last time by J. Spišiak

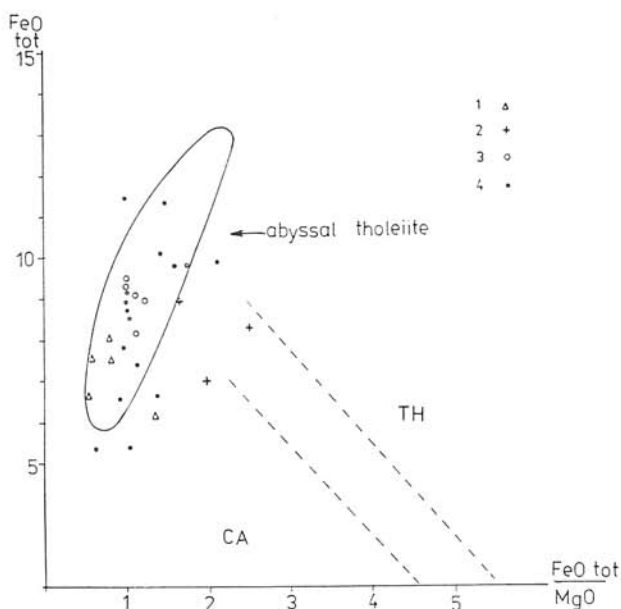


Fig. 4. Diagram of content dependence of FeO_{tot} on $\text{FeO}_{\text{tot}}/\text{MgO}$ [A. Miyashiro — H. Shido, 1975]. 1 — gabbroamphibolites, 2 — diorites, 3 — gabbrodiorites, 4 — amphibolites.

and concerning the thermobarometric conditions of their origin. We use also some data of amphiboles published in the work of B. Cambel — P. Pitoňák [1980].

On the basis of various petrochemical and geochemical classifications, mainly on the basis of elements of the iron groups and contents of rare earths [B. Cambel — J. Spišiak, 1979; B. Cambel — J. Kamenický — in press] the metabasites of the Low Carpathians correspond to rocks of the tholeiite association and closer to tholeiites of the ocean floor (Fig. 4). Similar results showed also the studies of metabasites of the other mountains of the West Carpathians [Hovorka — Spišiak, in press, Hovorka — Bajanič — Spišiak, in press]. The conditions of metamorphism of metabasites in the Low Carpathians were determined on the basis of several methods, with regard to several determinations and working procedures making possible the thermobarometric valuation.

Concerned are the determinations: a) of the grade of basicity of the plagioclases, b) study of pleochroical colouring of amphiboles according to γ ,

c) study of mineral parageneses, d) study of composition of coexisting pairs of minerals, e) study of chemical composition of some rock-forming minerals, mainly amphiboles and biotites.

In the following one of the authors (Spišiak) presents following analysis of results with application of the individual methods and applies them to conditions of the origin of metabasites (amphibolites) in the Low Carpathian region.

For determination of thermodynamics of amphibolite origin can be used the step-like change in composition of plagioclases (composition of plagioclases with basicity from An_5 to An_{17} is missing in the order of plagioclases of various rock types). For the occurrence of plagioclases in metamorphites this characteristic step in their composition is used for thermometric investigations, because it has been established to proceed as to the temperature of feldspar origin 20 to 40 °C, below the limit between the low and medium grade of metamorphism „low grade, medium grade“ (H. Winkler, 1975). It should be remarked that in investigations a big problem in amphibolites and other amphibolic rocks of the Low Carpathians is to determine the basicity of feldspars, mainly because they are influenced by younger processes, which caused their alterations or dimming.

The changes of Ti, Al contents or other cations are also shown in the change of pleochroism of amphiboles originated at various temperature or also pressure conditions. Generally the following change of pleochroic colours of amphibolites of metabasites with rising temperature is accepted: bluishgreen, green, greenish-brown, brown. As in metabasites of the Low Carpathians relatively often also several types of amphiboles originated with later processes are present (concerned is mainly disintegration of larger individuals into smaller), we were directed to the study of amphiboles of green to greenish-brown pleochroism, which we consider as primary and from the viewpoint of determination as most suitable. The pleochronic shades of amphiboles in the individual types of amphibolic rocks are various: green in amphibolites, from greenish-blue to green in gabbroamphibolites, from green through greenish-brown and sometimes to brown in diorites. These properties are depending also on the intensity of overheating, e.g. on the distance of metabasites from granitoid bodies and also on the supply of alkali in metamorphism, etc.

The study of thermodynamic conditions of metamorphism on the basis of coexisting pairs of minerals was valuated and expressed already in this work, in graphs 2 a, 2 b and 3. But also the chemical characteristics themselves can be used for approximate determination of thermality of mineral origin.

Besides the classical chemical analyses, the chemical analyses were obtained by X-ray microanalyser. The amphiboles represent one of the fundamental mineral phases of metabasites, which underwent various grade of metamorphic recrystallization and subsequent influences were reflected in the properties of these minerals. Already the amphiboles alone are thus an important indicator of thermodynamic conditions of the origin of amphibolites. The present-day statements permit to find out the general regularities of their chemical composition. For example, it has been established that with rising temperature of metamorphic recrystallization in amphiboles the content of alkalic metals and titanium increases and simultaneously aluminium in four-fold coordination increases to the detriment of aluminium in six-fold

coordination, also a gradually sinking silicon content with increasing of metamorphism was established. It is also necessary to call attention, that in the work of Cambel (1952) are considerations and deductions, on basis of which the thermodynamic conditions of metamorphic processes or their mutual combination can be determined also according to forms of amphibole individuals (needles, lath development, splintery development, columns and

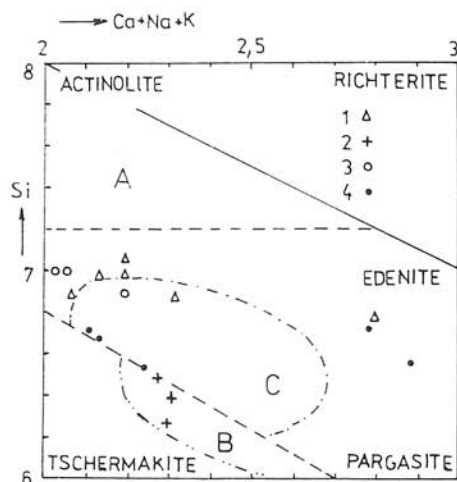


Fig. 5. Diagram of dependence of Si content on $\text{Ca}+\text{Na}+\text{K}$ [A. Miyashiro, 1973]. Fields according to gamma pleochroism of amphiboles: A — field of actinolite, B — bluishgreen, C — greenish-brown. The other as in Fig. 4.

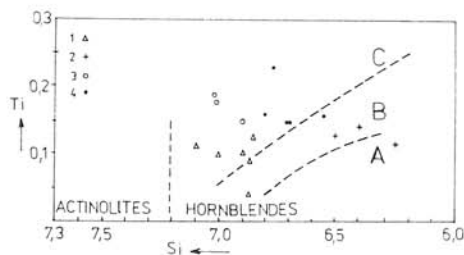


Fig. 6. Diagram of dependence of Ti content on Si [Vejnar, 1977]. A — field of bluishgreen amphiboles, B — field of green and brownishgreen amphiboles, C — field of brown amphiboles. The other as in Fig. 4.

isometric grains]. Higher thermal amphiboles have more isometric forms than amphiboles, which were metamorphosed in zones more remote from the source of metamorphism of granitoids or were subsequently affected by pressure or other effects. Similarly also the forms of relict (more isometric, more elongated) eyes of feldspars in spotted amphibolites are indicators of the thermodynamic conditions of metamorphism derived mainly from coarse-grained or porphyric gabbroid metabasites.

Genetic conclusions on the conditions of origin of metabasites in the region of the Low Carpathians can be drawn on the basis of the enclosed graphs. They are Figs. 5 and 6.

The projection points of all analyses in Fig. 5 and 6 are lying in the field of common amphiboles, no one analysis falls into the field lower thermal actinolites.

The analyses of gabbroamphibolites form a relatively independent field and with shifting to higher values of Si and lower values of Ti, i.e. to higher temperatures. Such observations are common also from other regions of the West Carpathians and determination of lower thermality of these rocks on the contrary to amphibolites or diorites is a certain surprise, because these

rocks could be considered as magmatic types and thus high-thermal according to numerous marks. It will be necessary to pay more attention to these rocks and to take this fact into consideration appropriately in clearing up of the genesis.

Amphiboles from diorites in both cases (Figs. 5 and 6) fall into the field B. The relatively reduced content of titanium and alkalis can be caused by preferential entering of these components into biotite or into biotites forming with later biotitization of amphiboles.

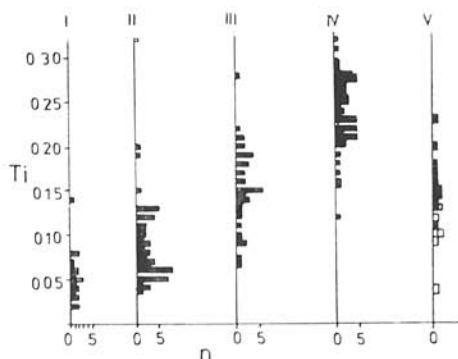


Fig. 7. Diagram of Ti distribution in amphiboles from metabasites of various grade of the metamorphic recrystallization (Raase, 1974). I — facies of green schists, II — low-temperature part of amphibole facies, III — high-temperature part of amphibolite facies, IV — amphibole-granulite facies, V — amphiboles from metabasites of the Low Carpathians, empty squares — amphiboles from gabbroamphibolites, full squares — amphiboles from diorites and amphibolites s.s.

The amphiboles from amphibolites are lying at the boundary of fields B and C, what corresponds to their pleochroic colouring (Figs. 5, 6).

In the diagram of Ti distribution in amphiboles from metabasites of various grade of metamorphic recrystallization (Fig. 7) amphiboles from amphibolites and gabbrodiorites fall into the lower part of the lower-temperature amphibolite facies and amphiboles from amphibolites and diorites into the higher-temperature part of amphibolite facies.

On the basis of amphibole classification according to Leake (1978) we can the studied amphiboles from metabasites of the Low Carpathians range among calcareous ones belonging to the subgroup of magnesium common amphiboles [Mg-hornblende]. (Figs. 8, 9). Of similar composition are also amphiboles from metabasites from the other mountains of the West Carpathians (Hovorka — Spišiak, in press; Hovorka — Bajaník — Spišiak, in press). This fact could testify to metamorphic and genetic similarity of metabasites in the extent of the whole West Carpathians.

On the basis of preliminary results of the investigation metabasites of the Low Carpathians, as it follows from the above mentioned analysis, were metamorphosed in conditions of amphibolite facies corresponding to the higher part of „low grade and medium grade“ metamorphism in sense of Winkler (1975). The baric conditions of metamorphism on the basis of the presented results were 400 to 600 MPa. It is necessary to point out, that, however, in dynamic comprehension of development of the given region the supposed pressure cannot be related only to the depth, in which the metamorphic conditions exist.

It is necessary also to mention, that in thermobarometric determinations on the basis of the investigation of metabasites it is necessary to take into

regard the combination of several types of metamorphism in the region of the Low Carpathians, where preintrusive metamorphism is manifested combined with the metamorphic effects taking place with penetration of the granitoid magma in the orogenic and late-orogenic phases. This process of unequal and local overheating was also not always continuous, but in places also discontinuous. Similarly with regression of metamorphic conditions, which followed after culmination of progressive metamorphism during gradual cooling of the environment, tectonic processes still belonging to the

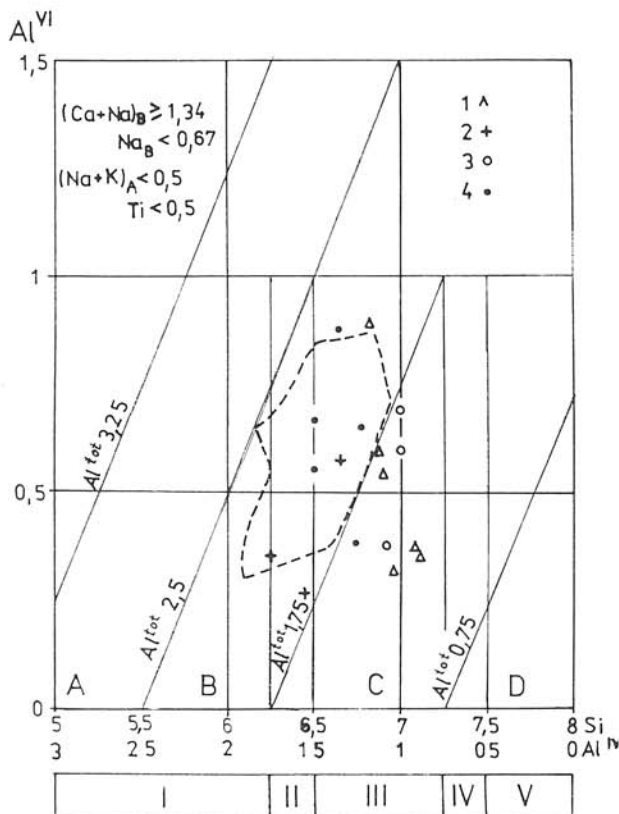


Fig. 8. Classification diagram of amphiboles modified by Wenk et al. (1974). A — field of tschermakite common amphibole, B — field of Mg-Fe of common amphibole, C — field of actinolite common amphibole, D — field of actinolite and tremolite, dashed is the field of amphiboles from the amphiboles of the Lepontine Alps.

Variscan orogene were taking place and later the rocks were influenced by the Alpine orogeny, as testified by radiometric datings by K/Ar method (Cambel — Veselský, 1981).

So retrograde metamorphism of metabasites took place. All these processes had influence on formation of forms of amphibole individuals and on further

changes of the properties of individual amphibole grains, as well as on their chemical composition. The formation of needle-like, columnar and splintery forms of amphiboles could have taken place in the progressive or regressive part of development of metamorphism. A strong progressive metamorphism led to gradual shortening of elongated forms of amphiboles and formation of isometric grains.

The above mentioned facts support the importance of metamorphic conditions, which render determination of thermobarometric data of amphibole origin very difficult.

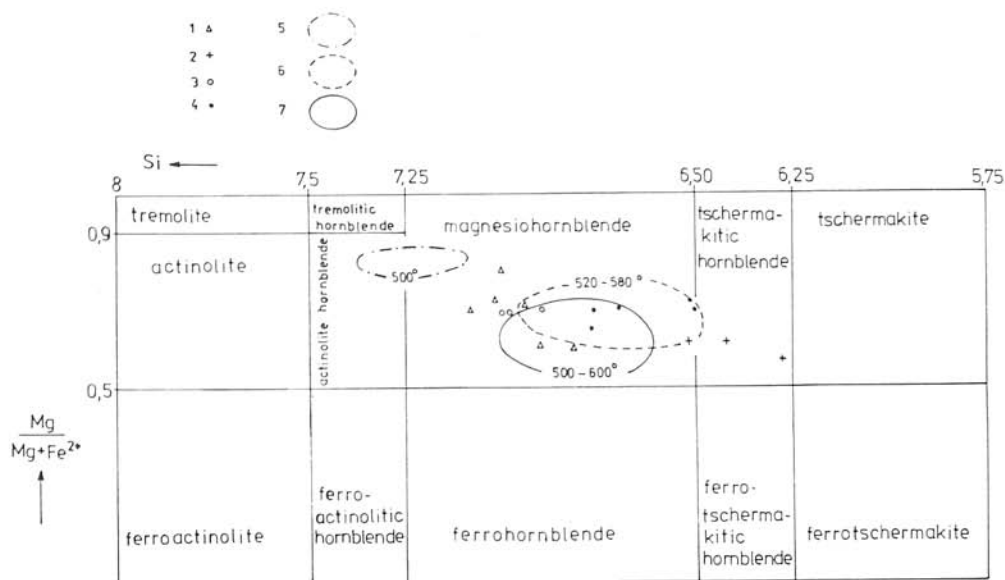


Fig. 9. Classification diagram of amphiboles according to Leake (1978) 1 to 4 as in Fig. 4 (I—IV), 5 — field of amphiboles from gabbroid rocks, 6 — field of amphiboles from diorite rocks with plotting of the calculated temperatures according to Pitoňák (1980), 7 — field of amphiboles from metabasites of the Rudňany area (Hovorka — Spišiak, in press).

Thermobarometry of ores and granitoids

We remind that paleothermometric measurements were also carried out on pyrite ores of the Low Carpathian region. (Žukov — Savčenko in Cambel — Žukov — Savčenko, 1980). The results of research provided considerably lower paleothermometric values against expectation, which do not exceed the temperature of 350 °C. A part of younger calcite fillings of joints in ores indicates the temperatures of 100 to 200 °C. From these data results, that although there are syngenetic ores, metamorphosed together with rocks in which they are found, the established paleothermometric data cannot be considered as decisive from the standpoint of determination of the

formed in the regressive and not progressive phase of metamorphic process. maximum grade of metamorphism. Perhaps they are inclusions, which already This is attested also by low-temperature calcites and quartz found in veins of primary pyrite ores.

On the basis of paleothermometric investigations of granitoid rocks in the Low Carpathian and West Carpathian regions it may be stated, that the temperature of mineral crystallization mostly varied above 600 °C, in feldspars mainly between 600 — 700 °C. However, also lower temperatures, mainly in K-feldspars were established. Macek (in press) determined by the two-

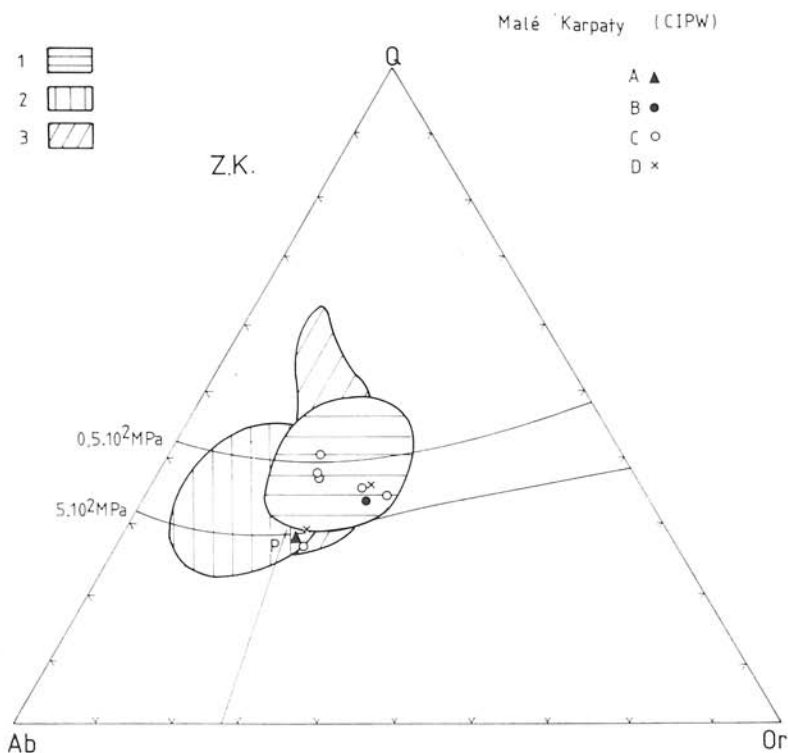


Fig. 10. Three-bed A-Ab-Or graph with indication of distribution of the fields of fundamental West Carpathian granitoid rock types. The individual points represent rocks from the Low Carpathian region, of the group of granitoids „ZK“.

Explanations: 1 — two-mica granitoids and biotite granites, 2 — biotite granodiorites, 3 — biotite and biotite-amphibole tonalites; A — tonalites, B — biotite granodiorites, C — two-mica granitoids, D — leucocratic granitoids.

feldspar method according to Barth (Barth, 1962) also very low temperatures of crystallization of a certain generation of K-feldspars in granitoids of the West Carpathians (420 °C). It is necessary to remark that with crystallization of K-feldspars under such a low temperature the surrounding

minerals must have recorded the changes caused by hydrothermal solutions, mainly when there are superimposed younger regeneration processes, which the author supposes. Therefore genetic interpretations cannot be based on this paleothermometric determination.

In our article we mention the graph Q-Ab-Or of thermodynamic conditions of crystallization of granitoids, which is quoted in Fig. 10. From the graph is to be seen, that a part of two-mica granitoids is of subsurface character when we apply the data of pressure to the geological profile. On the other hand, more basic types of rocks (biotite granitoids) should be derived from 17 km depth on the basis of pressure. As just the granitoids of the Modra massif, which are biotite granodiorites, metamorphose the Harmónia Group, it is not possible to accept this data of depth from the geological viewpoint. Against such an interpretation also the character and grade of metamorphism, caused by the granodiorite of the Harmónia Group, testify. On the contrary, some two-mica granitoids of the Bratislava massif, which originated and also intruded into greater depths, as is also testified by the data on thermobarometric investigation of metapelites, must have originated and also intruded in greater depths, as indicated in the graph. It is necessary to mention, that our graph Q-Ab-Or does not take into regard the presence of An component in eutectic mixture. According to such an assumption the thermobarometric data would have changed mainly in the sense of growing depth parameter. These facts are taken into regard in the graph compiled by Viliňovič (in press), whose analyses are recalculated according to mesonorm. According to the results of the investigation of Petřík (1980) the paleothermality of biotites took place in the interval of 700–900 °C and Macek (in press), on the basis of scandium contents, determined the temperatures of biotite crystallization to 650–730 °C. From these data results that the lowest temperature of feldspar crystallization from melt was essentially above 600 °C and in some K-feldspars also lower. On the whole, it may be stated that the process of cooling of granitoid magma took place between 600–900 °C when we are not including the anomalous data of formation mainly of potassium feldspars, which sometimes crystallized also below the value of 600 °C.

Conclusion

The authors summarized the knowledge about metamorphic processes in the Low Carpathian region, characterized their thermodynamic effects and analysed various types of metamorphic processes, which are mutually combining and overlapping here. They valued the knowledge and data concerning determination of thermodynamic parameters of metamorphism obtained by various methods. The metamorphism in the Low Carpathian region was taking place in thermodynamic conditions of the lower and medium grade of amphibolite facies and the supposed temperature of metamorphism is 500–600 °C and lower, depending on the distance from the granitoid intrusion, which largely controlled the metamorphic effect. Cooling of individual minerals of the granitoid magma took place probably at temperatures between 900–600 °C and at feldspars somewhat lower and was of unequal discontinuous course, depending on tectonic processes of the Variscan oro-

geny, on the velocity of the movement of melts and emanations escaping from them. The authors point to the contradiction of some obtained thermodynamic data with geological knowledge and state, that mainly the determination of depths of endogenous processes in orogenic regions has rather a normative than a real value, resulting mainly from the fact that in orogenic regions the pressure factor is not only of the character of hydrostatic but also of uni-directional pressure. Therefore the authors consider the mentioned calculations of the depth of endogenous processes as less real.

Translated by J. Pevný

Explanations to location and description of the studied samples in Tab. 1, and Fig. 1.

- 4Y: Sillimanite—staurolite—biotitic paragneiss (p), fine-grained, Bratislava, na Hrebienku.
 7Y: Garnet—sillimanite—biotite paragneiss (p), fine-grained, Limbach, Slnecné údolie valley, (p), elev. p. 306.
 17Y: Biotite paragneiss (p), fine-grained, Road from Bratislava to Devín, Lištie diery, mouth of Mokrý jarok.
 KB — 1Y: Sillimanite—garnet—biotite paragneiss (p), fine-grained, Bratislava, Železná studnička, at the left side of the brook 100 m from the concrete bridge.
 KB — 2Y: Garnet—biotite paragneiss (p), fine-grained, Bratislava, Železná studnička, Cesta mládeže way, 150 m from the houses at the left side of the brook.
 KB — 5Y: Garnet—sillimanite—biotite paragneiss (p), fine-grained, Bratislava—Lamač, cottage area, 200 m from the last cottage in the narrowed valley of the brook.

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