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# GEOTHERMOBAROMETRY OF METAMORPHIC ROCKS FROM THE ZEMPLINICUM (WESTERN CARPATHIANS, SLOVAKIA)

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**Abstract:** The pre-Alpine crystalline rocks of the Zemplinicum, occurring in the eastern part of Slovakia, has been subject of mineralogical and petrological investigation. In addition to the most common paragneisses, locally intercalated by amphibolites, they are represented by acidic- to intermediate orthogneisses, migmatites and granitoids. The index minerals of the paragneisses are biotite, muscovite (Si = 6.0 - 6.2 a./f.u), plagioclase ($An_{10-23}$), garnet ($Alm_{60-70}$, $Prp_{10-20}$, $Grs_{8-20}$, $Sps_{2-20}$), occasionally sillimanite, kyanite and staurolite. Apart from hornblende and plagioclase, some amphibolites also contain garnet. The metamorphic conditions, estimated using the dataset of Berman (1988) and standard geothermobarometers were 600–700 °C at 550–850 MPa. Metamorphism culminated by granitoid magmatism. All metamorphic rock types and granitoids underwent varying degree of mylonitization (up to greenschist facies conditions).

**Key words:** Western Carpathians, Zemplinicum, pre-Alpine rocks, petrology, phase relations, geothermobarometry, metamorphic conditions.

## Introduction

The Zemplinicum is a tectonic unit situated in the eastern part of Slovakia, on the frontier with Hungary (Fig. 1). The geological position of this unit in the content of the Carpathian Belt has been subject of several works (e.g. Pantó et al. 1967; Slávik 1976; Grecula et al. 1981a). The pre-Alpine rocks of the Zemplinicum occurring in the Hungarian territory were studied by Pantó (1965). Two Proterozoic ages corresponding to 962±39 and 984±108 Ma were obtained by the whole rock Rb/Sr method for two kyanite-bearing and kyanite-free samples, respectively (Pantó et al. 1967). Rb/Sr data in muscovite from these two samples however gave 394±52 and 450±130 Ma (l.c.). A 260±10 Ma K/Ar age was obtained for the first sample. Pantó et al. (1967) consider the presence of high-grade/medium pressure Proterozoic and low-grade Paleozoic in this area. The low-grade rocks found by them were correlated with the greenschist facies rocks of the Gemericum (Fig. 1). According to Kisházi & Ivancsics (1988) the rocks supposed by previous authors to be low-grade Paleozoic, are actually mylonites.

Following Slávik (1976), Rudinec & Slávik (1971), Mahel' (1967, 1986) and Fusán et al. (1971), the Zemplinicum represents a continuation of the Western Carpathian crystalline basement units to the east. After Grecula et al. (1981a) the eastern border of the West Carpathians is limited by a fault zone, representing continuation of the Darnó line (Fig. 1), and the Zemplinicum is considered as a part of the Pannonian block. The difference between the Western Carpathian and the Zemplinicum crystalline rocks is partly based on geochronological data, since the Western Carpathians pre-Alpine units gave mostly Early Paleozoic age (300-450 Ma, Bagdasaryan et al. 1977; Burchart 1968; Kantor et al. 1980). The presence of kyanite, supposed to represent a medium- to high-pressure metamorphism, and the lack of granitoids in this unit, were the additional arguments for distinguishing the Zemplinicum from the Western Carpathian crystalline complex. Although some petrological studies have been done, concerning the metamorphic rocks of the Zemplinicum (Lelkes-Felvári & Sassi 1981; Vozárová 1989), the questions outlined above remain open. Vozárová (1991) subdivided the rocks occurring in the borehole BB-1 (Fig. 1) into three types, representing biotite (sillimanite/amphibole) gneisses, amphibolites and migmatites. In contrast to the assumption of previous authors, Vozárová considers a lower pressure metamorphism (350–500 MPa at 650–720 °C) for this unit.

This paper summarizes the results of petrographical study performed on the rocks exposed on the surface, occurring in the deep boreholes and present as pebbles in overlying Late Paleozoic and Neogene conglomerates. Particular attention is paid to the rocks which have not been reported before from this area. Metamorphic conditions are estimated using different geothermobarometers as well as some equilibrium reactions among coexisting minerals.

## Geology

The crystalline basement of the Zemplinicum occurs in the eastern part of Slovakia and forms a small (6 km × 2 km) window exposed between Slovakia and Hungary (Fig. 1). The presence of crystalline rocks under the Late Paleozoic and Neogene sediments has been confirmed by several boreholes in Slovak as well as in Hungarian territory (Tr-59, 1615 m; Tr-61, 1686 m; Rbcs, 1040 m etc.). Following Slávik (1976) and Fusán et al. (1981), the crystalline basement between Zemplinicum and West-Carpathian crystalline complex to the West is covered by thick Neogene volcanic and sedimentary sequences.

Although the crystalline basement is tectonically overlain by Late Paleozoic (Grecula et al. 1981) and Neogene rocks, conglomerates containing pebbles of underlying metamorphic rocks suggest their autochthonous position. The most common rocks exposed

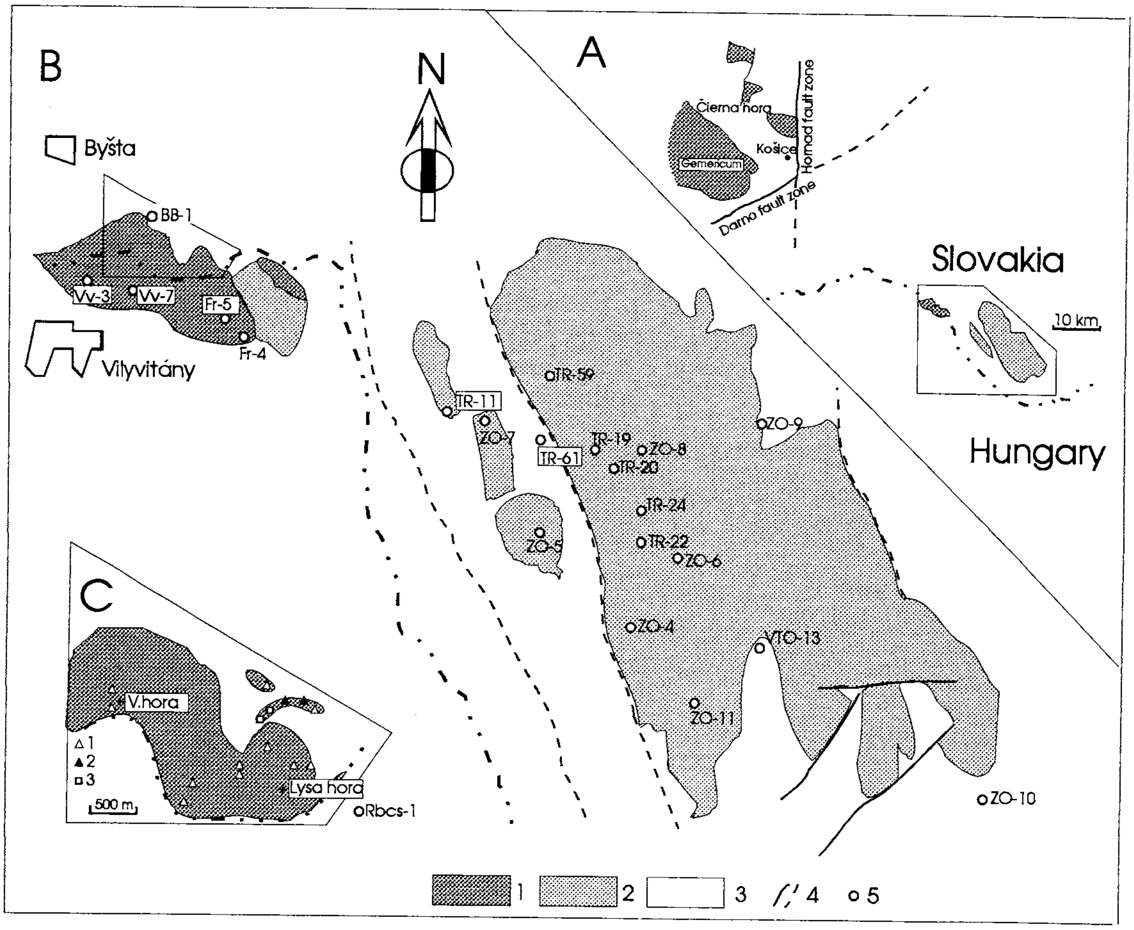


Fig. 1. A - Geological setting of the Zemplinicum in the content of the Western Carpathians. B - Geological map of the Zemplinic Unit (Baňacký et al. 1988; Pantó 1965): 1 - Crystalline basement, 2 - Late Paleozoic, 3 - Mesozoic and Cainozoic, 4 - Major faults and overthrust lines, 5 - Location of boreholes. C - Detail: sample locations: 1 - muscovite-quartz gneisses (strongly mylonitized), 2 - biotite- plagioclase gneisses, 3 - amphibolites.

on the surface are quartz-muscovite gneisses forming the Lysá Hora as well as Veľká Hora Hills (Fig. 1). They are usually mylonitized and sporadically outcropped. Amphibolites and some biotite gneiss are present on the north-western flank of the Lysá Hora.

## Petrography

More than 250 thin-sections of pre-Upper Carboniferous metamorphic rocks from boreholes and from the surface have been petrographically investigated. The locations of the boreholes, indicated by symbols of ZO, TR and VTO, as well as of some samples are shown in Fig. 1. With respect to lithology and metamorphic mineral assemblages, the rocks studied here are classified as quartz-rich muscovite/biotite gneisses (paragneisses), orthogneisses, amphibolites, migmatites and granitoids. The presence of the latter rocks was also reported Grecula et al. (1981b).

*1* - Muscovite gneisses represent one of the most common rock types exposed on the surface. Representative modes of these rocks are shown in Tab. 1. Some graphitic gneisses with plagioclase occur along the tectonic zone between Lysá and Velká Hora. Muscovite gneisses without aluminium silicate minerals were found in several boreholes (TR-61, VTK-24, VTK-25, TR-59), as well as pebbles in the Late Paleozoic conglomerates (boreholes ZO-5, ZO-6, ZO-8, ZO-9, ZO-10, TR-18 a VTO-13). All these gneisses reveal varying degrees of mylonitization. Feldspars and staurolite are replaced by fine-grained white mica and chlorite. Kyanite from muscovite gneiss was reported by Pantó et al. (1965), Kisházi & Ivancsics (1988) from boreholes and by Magyar (1969) from the Lysá Hora.

*2* - Biotite gneisses are present on the northern flank of Lysá Hora and have been found also as pebbles in Late Paleozoic and Badenian (borehole Hj-2) conglomerates. Similar to muscovite gneisses, they underwent mylonitization; garnet, biotite, feldspars are replaced by chlorite and fine-grained mica. In some plagioclase gneisses, epidote-quartz veins are present. After Vozárová (1991), garnet, sillimanite, plagioclase and K-feldspar are the most common phases in these gneisses.

*3* - Orthogneisses underlay muscovite and muscovite-biotite paragneisses in the boreholes TR-59 (1860-1998 m) and TR-61. They are distinguished from the paragneisses by textural characteristics (the lack of intercalations of different rock composition) as well as by mineral mode, mainly small amount of quartz and white mica, and the presence of biotite, occasionally also amphibole. Considering a volcanic origin for the protolith, chemically they correspond to dacite and rhyodacite (Faryad 1989). K-feldspar usually forms large crystals (up to 10 mm in diameter). The fine-grained, green- to brown-colour biotite follows schistosity in the rock. Apatite, titanite, zircon and occasionally allanite occur as accessory phases. The rocks are mylonitized to varying degrees.

*4* - In addition to a few occurrences of amphibolites in the

**Table 1:** Mineral assemblages from crystalline rocks of the Zemplinicum.

| | Q | Ms | Bt | Sil | St | Ky | Gr | Hbl | Pl | Kf |
|---|---|---|---|---|---|---|---|---|---|---|
| Ms-paragneisses | xxx | xxx | | (x) | (x) | (x) | | | (xx) | (x) |
| Bt-paragneisses | xxx | x | xxx | | | | (xx) | | xx | (xx) |
| orthogneisses | xx | | x | | | | | | xx | (xx) |
| amphibolites | x | | (x) | | | | (xx) | xxx | xx | |
| migmatites | xxx | xx | (x) | (x) | | | (x) | | xx | xx |
| granitoids | xx | xx | | | | | | | xxx | xx |

Symbols represent mineral modes: xxx > 20 %, xx > 5 %, x < 5 %, ( ) uncommon minerals

**Table 2:** Representative analyses of garnets.

| Sample | HJ-2 | | | T3-8 | | | T3-7 | | T3-6 |
|---|---|---|---|---|---|---|---|---|---|
| | c | cr | r | c | cr | r | c | r | |
| $SiO_2$ | 36.66 | 36.71 | 36.77 | 38.26 | 38.13 | 38.00 | 38.09 | 38.13 | 38.28 |
| $TiO_2$ | 0.02 | 0.00 | 0.02 | 0.03 | 0.02 | 0.04 | 0.03 | 0.03 | 0.05 |
| $Al_2O_3$ | 20.52 | 20.76 | 20.46 | 22.25 | 22.17 | 22.02 | 21.78 | 21.96 | 22.12 |
| $Cr_2O_3$ | 0.02 | 0.02 | 0.00 | 0.06 | 0.05 | 0.02 | 0.00 | 0.05 | 0.05 |
| $Fe_2O_3$ | 1.36 | 0.89 | 0.79 | 0.50 | 0.52 | 0.60 | 0.56 | 0.43 | 0.57 |
| FeO | 31.47 | 31.55 | 31.91 | 26.39 | 26.11 | 25.88 | 26.74 | 26.32 | 26.73 |
| MnO | 0.71 | 0.80 | 1.19 | 0.61 | 0.85 | 0.90 | 1.84 | 1.02 | 0.88 |
| MgO | 4.75 | 4.54 | 4.09 | 5.00 | 4.93 | 4.25 | 2.80 | 2.61 | 4.59 |
| CaO | 3.14 | 3.12 | 2.90 | 7.80 | 7.58 | 7.30 | 7.69 | 8.68 | 6.97 |
| Total | 98.68 | 98.51 | 98.28 | 100.40 | 100.32 | 99.01 | 99.43 | 99.23 | 100.23 |
| Oxygen basis | | | | 12 | | | | | |
| Si | 2.961 | 2.968 | 2.989 | 2.794 | 2.967 | 2.998 | 3.018 | 3.018 | 3.003 |
| $Al^{IV}$ | 0.038 | 0.031 | 0.010 | 0.026 | 0.032 | 0.001 | 0.000 | 0.000 | 0.000 |
| $Al^{VI}$ | 1.915 | 1.949 | 1.950 | 2.013 | 2.009 | 2.046 | 2.034 | 2.048 | 2.036 |
| Cr | 0.001 | 0.001 | 0.000 | 0.003 | 0.003 | 0.001 | 0.000 | 0.003 | 0.003 |
| $Fe^{3+}$ | 0.082 | 0.054 | 0.048 | 0.000 | 0.042 | 0.043 | 0.042 | 0.039 | 0.043 |
| Ti | 0.001 | 0.000 | 0.001 | 0.002 | 0.001 | 0.002 | 0.001 | 0.001 | 0.002 |
| Mg | 0.572 | 0.547 | 0.495 | 0.579 | 0.571 | 0.499 | 0.328 | 0.307 | 0.528 |
| $Fe^{2+}$ | 2.126 | 2.135 | 2.169 | 1.715 | 1.731 | 1.747 | 1.802 | 1.770 | 1.763 |
| Mn | 0.048 | 0.054 | 0.081 | 0.040 | 0.056 | 0.060 | 0.123 | 0.068 | 0.057 |
| Ca | 0.271 | 0.270 | 0.252 | 0.649 | 0.631 | 0.617 | 0.652 | 0.736 | 0.576 |
| Alm | 0.70 | 0.71 | 0.72 | 0.57 | 0.58 | 0.60 | 0.62 | 0.61 | 0.66 |
| Prp | 0.19 | 0.18 | 0.17 | 0.19 | 0.19 | 0.17 | 0.12 | 0.11 | 0.18 |
| Grs | 0.09 | 0.09 | 0.08 | 0.22 | 0.21 | 0.21 | 0.22 | 0.26 | 0.20 |
| Sps | 0.01 | 0.02 | 0.03 | 0.01 | 0.02 | 0.02 | 0.04 | 0.02 | 0.02 |

HJ-2 - paragneiss: Pl+Bt+Ms+Gr+Q+Rt; T3-8 - amphibolite: Pl+Hbl+Gr+Q+Rt+Tur; T3-7 - paragneiss: Pl+Bt+Gr+Q+Rt; T3-6 - paragneiss: Pl+Gr+Bt+Q, c - core, r - rim

Table 3: Amphibole composition from amphibolites and orthogneisses.

| Sample | T3-8 | | T2-9 | | TR-59 | |
|---|---|---|---|---|---|---|
| | 1 | 2 | | | c | r |
| $SiO_2$ | 41.76 | 41.74 | 42.74 | 41.98 | 46.99 | 47.43 |
| $TiO_2$ | 0.83 | 0.83 | 0.74 | 0.88 | 0.71 | 0.52 |
| $Al_2O_3$ | 16.37 | 15.65 | 13.57 | 12.72 | 8.03 | 7.63 |
| $Cr_2O_3$ | 0.11 | 0.06 | 0.00 | 0.05 | 0.00 | 0.00 |
| $Fe_2O_3$ | 5.80 | 6.64 | 6.93 | 7.11 | 2.72 | 0.79 |
| FeO | 9.21 | 8.91 | 11.08 | 12.30 | 11.91 | 13.86 |
| MnO | 0.04 | 0.15 | 0.42 | 0.11 | 0.54 | 0.50 |
| MgO | 9.71 | 9.67 | 9.26 | 8.98 | 12.38 | 11.90 |
| CaO | 11.15 | 10.98 | 11.16 | 11.45 | 11.86 | 11.86 |
| $Na_2O$ | 1.26 | 1.37 | 1.73 | 1.54 | 1.12 | 1.26 |
| $K_2O$ | 0.83 | 0.58 | 0.26 | 0.26 | 0.86 | 0.79 |
| Total | 96.49 | 95.91 | 96.93 | 96.67 | 96.85 | 96.46 |
| Oxygen basis | | | 23 | | | |
| Si | 6.145 | 6.177 | 6.298 | 6.288 | 6.949 | 7.074 |
| $Al^{IV}$ | 1.854 | 1.822 | 1.701 | 1.711 | 1.050 | 0.925 |
| $Al^{VI}$ | 0.984 | 0.907 | 0.670 | 0.533 | 0.348 | 0.415 |
| Ti | 0.091 | 0.092 | 0.082 | 0.099 | 0.079 | 0.058 |
| Cr | 0.012 | 0.007 | 0.000 | 0.005 | 0.000 | 0.000 |
| $Fe^{3+}$ | 0.642 | 0.739 | 0.773 | 0.802 | 0.302 | 0.088 |
| $Fe^{2+}$ | 1.133 | 1.102 | 1.374 | 1.540 | 1.473 | 1.729 |
| Mn | 0.005 | 0.018 | 0.052 | 0.014 | 0.067 | 0.063 |
| Mg | 2.129 | 2.133 | 2.046 | 2.004 | 2.728 | 2.645 |
| Ca | 1.758 | 1.741 | 1.773 | 1.837 | 1.879 | 1.895 |
| Na | 0.359 | 0.393 | 0.497 | 0.447 | 0.321 | 0.364 |
| K | 0.155 | 0.109 | 0.049 | 0.049 | 0.162 | 0.150 |

T3-8 - amphibolite: Pl+Hbl+Gr+Q+Rt+Tur; T2-9 - amphibolite: Hbl+Pl+Gr+Q+Tnt; TR-59 - orthogneiss: Pl+Kf+Bt+Hbl+Tnt+Ep+Q

eastern part of Lysá Hora, they were also reported from borehole BB-1 (Vozárová 1991), and Fr-5 (Kisházi & Ivancsics 1988). In the latter case, amphibolites form up to 10 m thick layers. They are massive, weakly foliated rocks and contain amphibole, plagioclase, small amount of biotite and accessory tourmaline, biotite, apatite, zircon, titanite, rutile, calcite, chlorite and epidote. Some coarse tourmaline grains enclosing plagioclase and apatite are parallel to the schistosity. Chlorite, epidote and calcite replace one or more of the minerals plagioclase, biotite, garnet and hornblende.

*5* - The presence of migmatites was reported from the lower part of the borehole BB-1 (500-645 m, Vozárová 1991) and they were found also in pebbles of the Late Paleozoic conglomerates. In addition to stromatitic and nebulitic migmatites, some augen gneisses are also present. A pebble of augen gneiss from the borehole VTO-13 (982.3 m) contains plan-parallel, fine-flaky biotite (up to 0.1 mm in size ). Together with quartz, it is partly enclosed by randomly oriented porphyroblasts of muscovite (0.3-0.7 mm). The mineral fabrics, especially the presence of some spots comprising fine-grained white mica (pseudomorphs after cordierite ?) suggests a possible thermal overprint on this rock.

*6* - Pebbles of granitoids were found in the Late Paleozoic conglomerates from the boreholes ZO-9, ZO-10 TR-11, TR-18, TR-20 and VTO-13. Besides fine- to medium-grained types, containing hypidiomorphic plagioclase, some porphyric varieties with perthitic K-feldspar also occur. According to modal contents of the present phases, they correspond to granite and granodiorite. Plagioclase, determined optically, corresponds to albite and oligoclase in granite, and to acid andesine in granodiorite. It is partly sowed with epidote and white mica. Tabular hypidiomorphic biotite is usually replaced by muscovite and chlorite.

**Table 4:** Microprobe analyses of biotite.

| Sample | HJ-2 | | T3-7 | | T3-8 | T3-6 | TR-59 |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | | | | | |
| $SiO_2$ | 35.64 | 35.86 | 35.82 | 35.91 | 35.54 | 36.39 | 36.79 |
| $TiO_2$ | 1.62 | 1.63 | 3.02 | 3.69 | 2.59 | 3.24 | 2.22 |
| $Al_2O_3$ | 19.14 | 19.42 | 17.84 | 17.29 | 15.80 | 16.09 | 16.10 |
| FeO | 17.76 | 17.52 | 20.19 | 20.28 | 18.38 | 18.05 | 18.05 |
| MnO | 0.06 | 0.10 | 0.00 | 0.14 | .09 | 0.27 | 0.22 |
| MgO | 9.63 | 10.20 | 9.59 | 9.38 | 11.59 | 10.69 | 12.23 |
| BaO | 0.14 | 0.12 | 0.00 | 0.00 | 0.10 | 0.02 | 0.00 |
| $Na_2O$ | 0.24 | 0.31 | 0.43 | 0.20 | 0.14 | 0.25 | 0.00 |
| $K_2O$ | 9.43 | 9.40 | 9.54 | 9.44 | 8.42 | 9.73 | 9.81 |
| Cl | 0.02 | 0.02 | - | - | - | - | - |
| F | 0.37 | 0.51 | - | - | - | - | - |
| Total | 94.05 | 95.09 | 96.53 | 96.37 | 92.89 | 94.78 | 95.42 |
| Oxygen basis | 22 | | | | | | |
| Si | 5.479 | 5.450 | 5.416 | 5.439 | 5.525 | 5.565 | 5.646 |
| $Al^{IV}$ | 2.520 | 2.550 | 2.583 | 2.560 | 2.474 | 2.434 | 2.353 |
| $Al^{VI}$ | 0.948 | 0.928 | 0.595 | 0.526 | 0.420 | 0.465 | 0.477 |
| Ti | 0.187 | 0.186 | 0.343 | 0.420 | 0.302 | 0.372 | 0.256 |
| $Fe^{2+}$ | 2.283 | 2.226 | 2.553 | 2.569 | 2.389 | 2.308 | 2.316 |
| Mn | 0.007 | 0.012 | 0.000 | 0.018 | 0.011 | 0.035 | 0.028 |
| Mg | 2.206 | 2.310 | 2.161 | 2.117 | 2.685 | 2.436 | 2.797 |
| Ba | 0.008 | 0.007 | 0.000 | 0.000 | 0.016 | 0.003 | 0.000 |
| Na | 0.071 | 0.091 | 0.126 | 0.058 | 0.042 | 0.074 | 0.000 |
| K | 1.849 | 1.822 | 1.840 | 1.824 | 1.669 | 1.898 | 1.920 |
| Cl | 0.005 | 0.005 | - | - | - | - | - |
| F | 0.179 | 0.245 | - | - | - | - | - |

HJ-2 - paragneiss: Pl+Bt+Ms+Gr+Q+Rt; T3-7 - paragneiss: Pl+Bt+Gr+Q+Rt; T3-8 - amphibolite: Pl+Hbl+Gr+Q+Rt+Tur; T3-6 - paragneiss: Pl+Gr+Bt+Q; TR-59 - orthogneiss: Pl+Kf+Bt+Hbl+Tnt+Ep+Q

## Mineral compositions

*Garnet:* Representative analyses of garnet are given in Tab. 2. Structural formulae and ferrous/ferric iron ratios were calculated on the basis of 12 oxygens and using the charge balance $Al^{VI} + Cr + Ti + Fe^{3+} = 2$. All garnet patterns reveal a weak zonation. The $Fe^{2+}$ content increases and Mg decreases towards the rim. In garnet from amphibolite the Ca content also decreases towards the rim. Almandine-rich ($Alm_{70-74}$) and spessartine- and grossulare-poor garnet ($Sps_{2-3}$, $Grs_{8-9}$) occurs in plagioclase gneiss (sample HJ-2). The pyrope content in garnet ranges between 17 and 19 mol %. Garnet relatively rich in Ca and poor in Mg occurs in muscovite-free biotite gneisses.

*Amphibole:* Structural formulae and $Fe^{2+}$/ $Fe^{3+}$ contents were calculated on the basis of 23 oxygens and 13 cation charges (Tab. 3). Amphiboles from garnet-amphibole gneiss are tschermakitic hornblende, tschermakite and aluminium-tschermakite with $Al_2O_3$ content up to 16 wt. % ($Al^{VI}$ >1). In orthogneisses (Tr-59) a magnesio-hornblende occurs. It is usually zoned with Al decreasing towards the rim. The $Na^{M4}$ content in amphiboles ranges between 0.11 and 0.25 a/f.u., the latter value refers to amphibolites.

*Biotite:* The structural formulae of biotite as well as of muscovite were calculated on a 22 oxygen basis (Tab. 4 and 5). The $Mg/Mg+Fe^{2+}$ ratios in biotite range between 0.45 and 0.52. Biotite with higher annite content occurs in muscovite-free gneisses. In muscovite-bearing rocks, biotite is relatively rich in Al.

*Muscovite:* Microprobe analyses of muscovites are presented in Tab. 5. They come from garnet-biotite gneisses (HJ-2) as well as from diaphtorized quartz-rich gneiss from Byšta (samples T3-3 and T2-2) and from the borehole TR-59 (Tab. 5).

In all samples muscovite has low Si contents ranging between 6.0 - 6.2 a/f.u.

*Plagioclase:* Representative analyses of some Ca-rich plagioclase are given in Tab. 6. In all the studied samples plagioclase is partly replaced by albite. Plagioclase with anorthite content of about 34 mol % occurs in some amphibole-bearing orthogneisses. Many analysed plagioclases correspond to oligoclase.

*Other minerals:* The accessory tourmaline occurring in amphibolite (sample T3-8) is near to schorl end-member $(Na_{0.58}Ca_{0.29})(Mg_{1.95}Ti_{0.34}Fe_{0.82})Al_{6.28}B_3Si_{5.95}O_{30}(OH)_2$ in composition. Epidote rimming allanite from the sample Tr-59 has a composition $Fe_{0.7}Al_{2.3}Ca_2Si_3O_{12}(OH)$ with a pistacite content of about 12 %.

## Phase relations between minerals

To describe the chemographic relations between the studied minerals, the 11 component system $SiO_2$-$Al_2O_3$-MgO-FeO-MnO-$Fe_2O_3$-CaO-$K_2O$-$Na_2O$-$H_2O$ has been considered. The assemblages involving garnet, biotite, plagioclase, muscovite and quartz are plotted in the diagrams $(Al_2O_3+Fe_2O_3-Na_2O)$: CaO: (Fe+Mg+Mn)O (Fig. 2) and $(Al_2O_3+Fe_2O_3-Na_2O)$: $K_2O$: (Fe+Mg+Mn)O (Fig. 3). In Fig. 2, the phases are projected from $SiO_2$, $H_2O$ and K-feldspar. The tie-lines connecting mineral phases in Fig. 2 suggest the appearance of garnet and muscovite/K-feldspar after reactions:

(1) Pl + Bt = Ms + Gr

(2) Pl + Bt + Q = Gr + Kf + $H_2O$

Both reactions result in a decrease of Ca in plagioclase. The first reaction studied by Ghent & Stout (1981) was used as a geobarometer.

In Fig. 3 mineral phases are projected from $SiO_2$, $H_2O$ and plagioclase ($An_{22}$), analysed in this assemblage. The mineral reaction linking minerals in Fig. 3 is the reaction resulting in the appearance of garnet and K-feldspar:

(3) Ms + Bt + Q = Gr + Kf + $H_2O$

The phase relations of the assemblage containing hornblende, biotite, plagioclase, K-feldspar, quartz and accessory epidote from sample Tr-59 are presented in Fig. 4. Compared to Fig. 2, biotite having relatively high Al content is shifted to the FM side.

The phase relations in this diagram suggest possible formation of hornblende, K-feldspar and plagioclase after reaction:

(4) Bt + Ep + Q = Hbl + Kf + Pl

## Metamorphic conditions

P-T conditions of metamorphism were calculated using computer program Geo-Calc (Brown et al. 1989) The activity models were adapted from the following authors: garnet (Guiraud et al. 1991), biotite, muscovite and feldspars (Massonne 1991), amphibole (Will & Powell 1992), epidote (Frey et al. 1991). The temperatures and pressures obtained, using the sliding reactions in the KCMASH system, for garnet-biotite-muscovite gneisses, hornblende orthogneisses and garnet amphibolites are shown in Fig. 5 and 6. The equilibrium curves of reactions (1-3) (sample HG-2) form an invariant point at 665 °C at 770 MPa (Fig. 5). Supposing a constant pressure of 700 MPa, similar temperatures for this assemblage were obtained following the Gr-Bt geothermometer of Perchuk & Lavrentjeva (1983) as well as of Ganguly & Saxena (1984) (Tab. 7). Higher temperatures scattered in a large interval were calculated by the methods of Ferry & Spear (1978) and Hodges & Spear (1986). All calculations reveal a decrease of crystallization temperature from the core to the rim of garnet. The pressure conditions obtained using the garnet-muscovite-plagioclase-quartz geobarometer

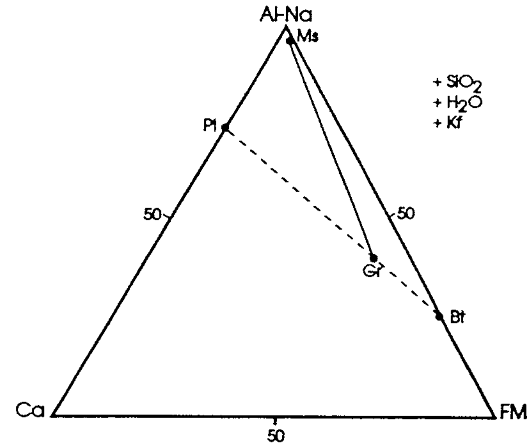


**Fig. 2.** $(Al_2O_3+Fe_2O_3-Na_2O)$ : CaO : (Fe+Mg+Mn)O diagram for garnet-biotite-muscovite gneisses (sample HJ-2). The mineral phases are projected from $SiO_2$, $H_2O$ and K-feldspar.

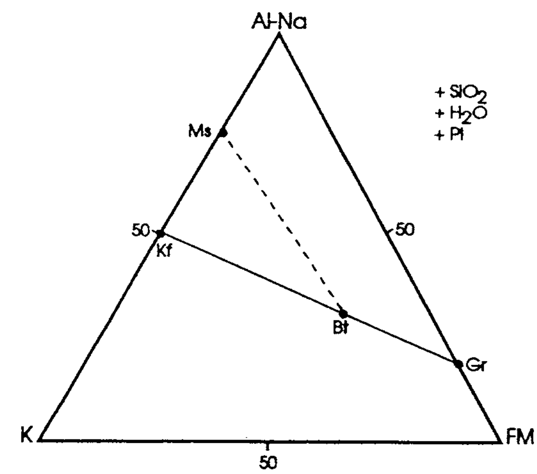


**Fig. 3.** $(Al_2O_3+Fe_2O_3-Na_2O)$ : $K_2O$: (Fe+Mg+Mn)O diagram for garnet-biotite-muscovite gneisses (sample HJ-2).

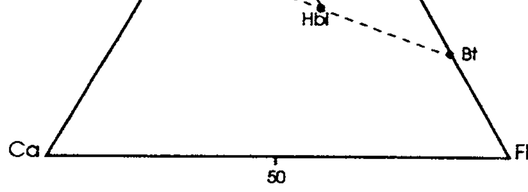


**Fig. 4.** $(Al_2O_3+Fe_2O_3-Na_2O)$ : CaO : (Fe+Mg+Mn)O diagram for amphibole-bearing orthogneisses (sample TR-59). The mineral phases are projected from $SiO_2$, $H_2O$ and epidote.

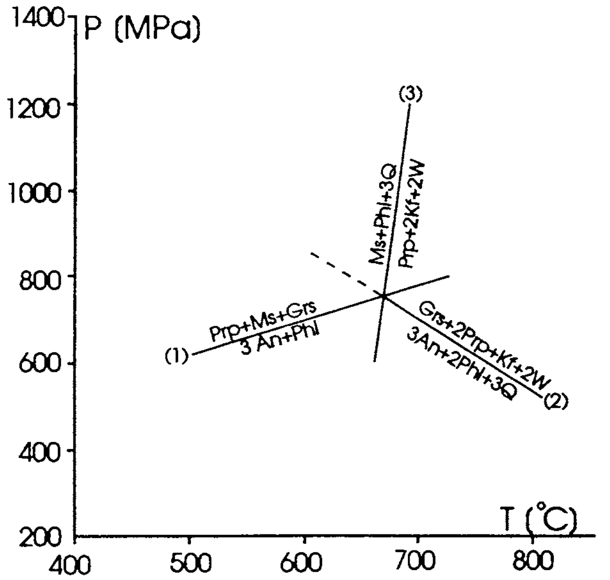


**Fig. 5.** The equilibrium curves of reactions (1-3), obtained for garnet-biotite-muscovite gneisses.

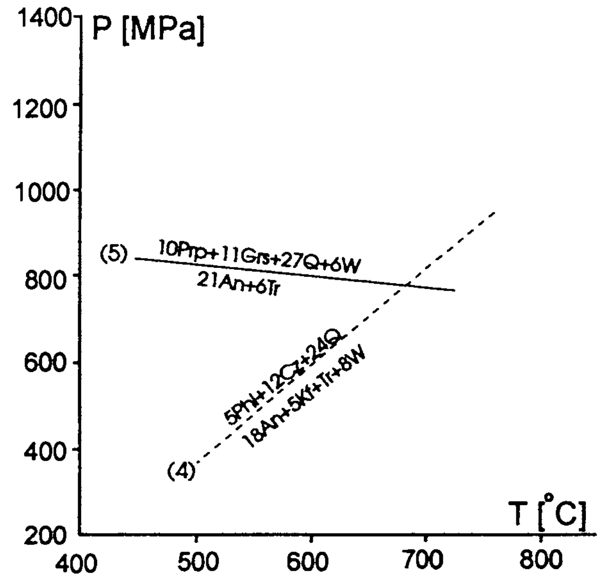


**Fig. 6.** The equilibrium curves of reactions (4, 5), calculated for garnet amphibolites (solid line) and amphibole orthogneisses (dashed line).

of Ghent & Stout (1981) at 670 °C are given in Tab. 7. The calculated pressures using the KCMASH system ($P_{Mg}$) are consistent with the position of invariant point of reactions (1–3, Fig. 5). Higher pressures ($P_{Fe}$), obtained using the activity model CFASH, probably resulted because of poorly known thermodynamic data in the iron subsystem (Holland & Powell 1990b). Similarly to the temperatures, the pressures calculated for the cores of the garnets are higher than those for the rims.

Metamorphic pressures and temperatures for garnet-bearing amphibolite were estimated using the Gr–Hbl geothermometer and Gr–Hbl–Pl–Q geobarometer (Tab. 7) with combination of the equilibrium curve of reaction:

(5) Hbl + Pl = Gr + Q

(Fig. 6). The Hbl-Gr thermometer of Graham & Powell (1984) gave 686 °C for the core and 650 °C for the rim of garnet from amphibolite. Assuming temperatures of 650–680 °C, the corresponding pressures for equilibrium curve (5) are 760–800 MPa. Using the Gr–Hbl–Pl–Q barometry of Khon & Spear (1989) two different pressure conditions for sample T3-8 are obtained (Tab. 7). Pressures similar to those for the equilibrium curve of reaction (5) were obtained using the activity model in the CMASH system. Low pressures (400–690 MPa) calculated using the activity model $P_{Fe}$ (the CFASH system) are due to the uncertainty of thermodynamic data in the iron subsystem.

The equilibrium curve of reaction (4), obtained for orthogneisses (TR-59) is shown in Fig. 6. It was calculated for $An_{34}$ (representing maximum anorthite content in the analysed plagioclase). The biotite–amphibole thermometry of Perchuk & Ryabchikov (1978), based on the Fe/(Fe+Mg): (Mg/(Mg+Fe+Mn)) contents in these two minerals, gave a temperature of about 650 °C. Assuming these temperatures, the equilibrium curve of reaction (4) shown in Fig. 6 gave a pressure value of about 700 MPa for these rocks.

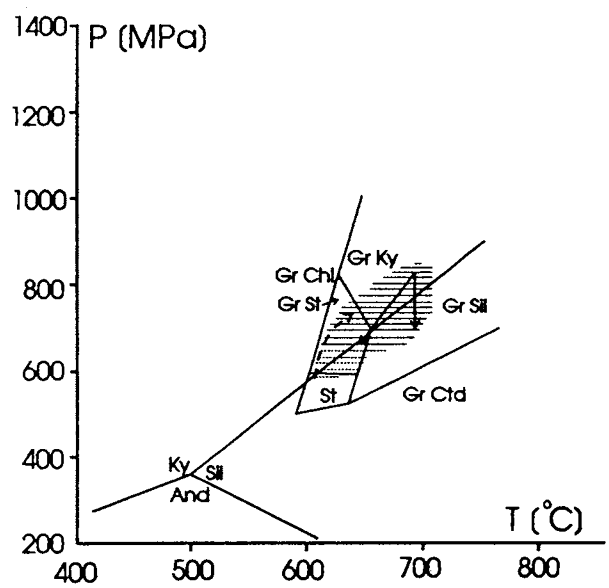


**Fig. 7.** P-T conditions of metamorphism for the crystalline rocks of the Zemplinicum. Dashed field corresponds to staurolite gneisses. Arrows indicate probable prograde (dashed) and retrograde (solid) paths of metamorphism. Triple point of $Al_2SiO_5$ polymorphs after Holdaway (1971). Stability fields of the assemblages St–Gr, Gr–Ctd, Gr–Sil, Gr–Ky are from Powell & Holland (1990a).

## Discussion

Considering the mineral assemblages and calculated P-T data, discussed above, the crystalline rocks of the Zemplinicum exposed in Slovak territory can be classified into two metamorphic types. The first type represented by gneisses, containing layers of amphibolite, is mostly exposed in Lysá Hora and the second type corresponding to mylonitized muscovite gneisses and graphitic gneisses, is present between Lysá and Veľká Hora. The pressures and temperatures of 650–850 MPa and 650–700 °C calculated for the first type are consistent with the petrogenetic grid of pelitic rock (Powell & Holland 1990a). Such pressure conditions can also be considered from the presence of garnet in amphibolite (Ghent & Stout 1985). Following Powell & Holland (l.c.) the low-stability field of the assemblage involving

**Table 5:** Some representative analyses of muscovite.

| Sample | HJ-2 | | TR-59 / 2 | T3-3 | T2-2 |
|---|---|---|---|---|---|
| | 1 | 2 | | | |
| $SiO_2$ | 46.81 | 46.74 | 46.45 | 47.41 | 47.33 |
| $TiO_2$ | 0.73 | 0.55 | 0.96 | 0.75 | 0.48 |
| $Al_2O_3$ | 35.07 | 34.72 | 35.94 | 35.83 | 35.51 |
| FeO | 1.08 | 1.09 | 0.85 | 0.93 | 1.04 |
| MnO | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 |
| MgO | 1.12 | 1.20 | 0.77 | 0.51 | 0.75 |
| BaO | 0.22 | 0.29 | | | |
| $Na_2O$ | 0.83 | 0.95 | 0.00 | 0.55 | 0.56 |
| $K_2O$ | 9.42 | 9.33 | 10.32 | 9.67 | 9.74 |
| F | 0.17 | 0.00 | | | |
| Total | 95.5 | 94.87 | 95.29 | 95.81 | 95.41 |
| Oxygen basis | | | 22 | | |
| Si | 6.169 | 6.197 | 6.106 | 6.189 | 6.206 |
| $Al^{IV}$ | 1.831 | 1.802 | 1.893 | 1.810 | 1.793 |
| $Al^{VI}$ | 3.615 | 3.622 | 3.675 | 3.710 | 3.694 |
| Ti | 0.072 | 0.055 | 0.094 | 0.072 | 0.047 |
| $Te^{2+}$ | 0.119 | 0.121 | 0.093 | 0.100 | 0.114 |
| Mn | 0.002 | 0.000 | 0.000 | 0.000 | 0.000 |
| Mg | 0.220 | 0.236 | 0.000 | 0.000 | 0.000 |
| Ba | 0.011 | 0.015 | 0.150 | 0.098 | 0.146 |
| Na | 0.211 | 0.245 | 0.000 | 0.000 | 0.000 |
| K | 1.582 | 1.578 | 1.730 | 1.594 | 1.629 |
| F | 0.070 | 0.000 | 0.000 | 0.137 | 0.142 |

HJ-2 - paragneiss: Pl+Bt+Ms+Gr+Q+Rt; TR-59 / 2 - mylonite: Ms+Q+Pl+Rt; T3-3, T2-2 - mylonite: Ms+Q+Ab+Rt

Gr-Sil and Gr-Ky corresponds to 600 and 750 MPa, respectively (Fig. 7). Disregarding higher temperatures obtained using the Gr-Bt geothermometer of Ferry & Spear (1978) and Hodges & Spear (1982), the temperatures calculated by different methods are in good agreement. The $Fe^{2+}$/Mg content in the core and rim of garnet suggests decrease of temperatures as well as pressures (Fig. 7) during metamorphism. An increase of temperatures resulting in the appearance of muscovite gneisses and migmatites can be related to a possible granitoid magmatism during lates metamorphic history. Metamorphic conditions similar to the first type of rocks are assumed for the amphibole-bearing orthogneiss as well as for the paragneisses pebbles.

The mylonitized gneisses and small amount of graphitic gneiss are present between the Lysá and Veľká Hora. According to the geological situation on the surface, they are in tectonic contact with the first type of rocks. The mylonitized gneisses contain relic plagioclase, biotite and occasionally also staurolite. In the borehole BB-1, such rocks forming a 120 m thick sequence (between 80 and 200 m) overlain by the Badenian sediments, were described by Vozárová (1991). The presence of staurolite in these rocks, consistently with its stability field (Fig. 7), indicate temperatures lower than 660 °C. Following Holdaway et al. (1988) staurolite in such assemblage disappears at temperature lower than 570-610 °C). With respect to the mineral phases, mainly the presence of staurolite, a similar pressure series of metamorphism can be considered for both types of rock.

Although the question of Proterozoic age doubted by many authors (Slávik 1976; Rudinec & Slávik 1971; Maheľ 1967) remains open, there are several analogies in lithology and metamorphic conditions between the Zemplinicum and Western Carpathian crystalline basements. Regarding to the tectonic division of the Central Western Carpathians into Tatricum, Veporicum and Gemericum, the eastern Čierna Hora Unit (Fig. 1) is considered to be an analogue of the Veporicum (Jacko 1985; Maheľ 1986; Krist et al. 1992). It consists of paragneisses, migmatites, granitoids and locally garnet-bearing amphibolites. Apart from quartz, micas, feldspars, the paragneisses contain sillimanite, garnet and staurolite. Orthogneisses have not been reported from the Čierna Hora Unit yet, however they are known from the Veporicum (Kamenický 1982; Hovorka et al. 1987). In addition

**Table 6:** Composition of plagioclase in gneisses and amphibolite.

| Sample | HJ-2 | | T3-7 | T3-8 | T2-9 | TR-59 |
|---|---|---|---|---|---|---|
| $SiO_2$ | 62.40 | 62.63 | 60.86 | 60.98 | 64.45 | 59.90 |
| $Al_2O_3$ | 23.78 | 23.21 | 24.74 | 24.85 | 22.69 | 25.87 |
| $Fe_2O_3$ | 0.01 | 0.00 | 0.00 | 0.03 | 0.05 | 0.00 |
| CaO | 4.90 | 4.83 | 5.82 | 6.32 | 3.05 | 6.75 |
| $Na_2O$ | 8.68 | 8.58 | 8.01 | 8.10 | 10.08 | 6.98 |
| $K_2O$ | 0.18 | 0.16 | 0.15 | 0.03 | 0.07 | 0.15 |
| Total | 100.01 | 100.04 | 99.64 | 100.03 | 100.43 | 99.65 |
| Oxygen basis | | | 8 | | | |
| Si | 2.762 | 2.778 | 2.710 | 2.702 | 2.834 | 2.668 |
| Al | 1.241 | 1.213 | 1.299 | 1.297 | 1.169 | 1.358 |
| $Fe^{3+}$ | 0.000 | 0.000 | 0.000 | 0.000 | 0.002 | 0.000 |
| Ca | 0.232 | 0.229 | 0.278 | 0.300 | 0.143 | 0.322 |
| Na | 0.744 | 0.737 | 0.692 | 0.696 | 0.854 | 0.603 |
| K | 0.009 | 0.009 | 0.009 | 0.001 | 0.004 | 0.009 |

HJ-2 - paragneiss: Pl+Bt+Ms+Gr+Q+Rt; T3-7 - paragneiss: Pl+Bt+Gr+Q+Rt; T3-8 - amphibolite: Pl+Hbl+Gr+Q+Rt+Tur; T2-9 - amphibolite: Hbl+Pl+Gr+Q+Tnt; TR-50 - orthogneiss: Pl+Kf+Bt+Hbl+Tnt+Ep+Q

**Table 7:** Calculated metamorphic temperatures (°C) and pressures (MPa) for metamorphic rocks of the Zemplinicum.

Gr-Bt-Ms-Pl barometer (Ghent & Stout 1981) at 670 °C for muscovite-bearing garnet biotite gneiss (sample HJ-2).

| No. analyse | $P_{Mg}$ | $P_{Fe}$ |
|---|---|---|
| Gr(r)-Ms(1)-Bt(1) | 760 | 1220 |
| Gr(cr)-Ms(1)-Bt(1) | 830 | 1230 |
| Gr(c)-Ms(2)-Bt(2) | 820 | 1230 |
| Gr(c)-Ms(2)-Bt(2) | 820 | 1230 |

Garnet-biotite thermometers, calculated at 700 MPa for muscovite-bearing garnet biotite gneiss (sample HJ-2).

| No. analyse | FS | PL | HS | GS |
|---|---|---|---|---|
| Gr(r)-Bt(1) | 695 | 651 | 729 | 632 |
| Gr(c)-Bt(1) | 768 | 688 | 792 | 673 |
| Gr(c)-Bt(2) | 738 | 672 | 774 | 642 |
| Gr(r)-Bt(2) | 665 | 636 | 699 | 604 |

FS (Ferry & Spear 1978), PL (Perchuk & Lavrentjeva 1983), HS (Hodges & Spear 1982), GS (Ganguly & Saxena 1984).

Hbl-Gr thermometer (Graham & Powell 1984) and Hbl-Gr-Pl-Q barometer (Khon & Spear 1989) for garnet-bearing amphibolite (sample T3-8)

| No. analyse | T | $P1_{Mg}$ | $P2_{Mg}$ | $P1_{Fe}$ | $P2_{Fe}$ |
|---|---|---|---|---|---|
| Gr(r)-Hbl(1) | 650 | 740 | 680 | 410 | 510 |
| Gr(c)-Hbl(1) | 686 | 740 | 700 | 400 | 540 |
| Gr(c)-Hbl(2) | 685 | 820 | 850 | 520 | 690 |
| Gr(r)-Hbl(2) | 649 | 810 | 830 | 510 | 640 |

P1 and P2 correspond to models 1 and 2, respectively.

to some Tatric units (the Western High Tatras and Považský Inovec), kyanite also occurs in some metapelites from the Čierny Balog series of the Veporicum. Metamorphic conditions, relatively lower but close to the Zemplinicum are considered for the Čierna Hora (Miklošovce, 570-610 °C at 530-600 MPa, Krist et al. 1992; Bujanová, 620-625 °C at 400-450 MPa, Jacko et al. 1990) as well as for the Hron (560-570°C at 600-620 MPa, Krist et al. 1992) and Čierny Balog (500-560 °C at 420-700 MPa, l.c.). Higher metamorphic pressures were reported from the Western High Tatras (1000-1200 MPa at 750 °C, Janák 1993) and from the

Gneiss-amphibolite complex of the Gemericum (700-900 MPa at 700 °C, Faryad, submitted to print). Variations in metamorphic conditions among the above mentioned units are mostly a result of different erosion level as well as of the Variscan nappe tectonics. Following Putiš et al. (1993) and Bezák (1994) two or three (lower/middle and upper) Variscan lithotectonic levels, different in metamorphic conditions, are distinguished in the Central Western Carpathian crystalline basement. In most cases, the upper lithotectonic level corresponds to high-grade and the lower level to medium- or low-grade rocks. The Zemplinicum, especially the gneisses and amphibolites, can be correlated to the high-grade rocks of the upper unit. Similarly to the Western Carpathians, the metamorphism in the Zemplinicum probably culminated in granitoid magmatism which locally resulted in the migmatization.

## Conclusions

- The crystalline rocks of the Zemplinicum exposed on the surface and found in boreholes or as pebbles in the Late Paleozoic conglomerates are represented by paragneisses, orthogneisses, amphibolites, migmatites and granitoids.
- Temperatures and pressures of 650-700 °C and 650-850 MPa were obtained for gneisses and amphibolites exposed in the eastern part of the crystalline unit. Mineral zonation, mainly in garnet suggests a decrease of P-T conditions during metamorphism.
- Temperatures of 600-650 °C at 550-650 MPa are estimated for mylonitized gneisses occurring in the central and western parts of the crystalline unit. The two types of rocks showing different metamorphic conditions are in tectonic contact.
- The amphibolite facies metamorphism was probably followed by granitoid magmatism which resulted in migmatization and granitization of metamorphic rocks.
- All metamorphic rocks including granitoids underwent mylonitization which locally reached the greenschist facies conditions.
- With respect to metamorphic evolution and lithology, the crystalline rocks of the Zemplinicum can be compared with those from the Central Western Carpathians.

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**Appendix:** Mineral abbreviations.

| | | | |
|---|---|---|---|
| An | anorthite | Ky | kyanite |
| And | andalusite | Ms | muscovite |
| Bt | biotite | Phl | phlogopite |
| Chl | chlorite | Pl | plagioclase |
| Ctd | chloritoid | Prp | pyrope |
| Cz | clinozoisite | Q | quartz |
| Gr | garnet | Sil | sillimanite |
| Hbl | hornblende | St | staurolite |
| Grs | grossularite | Tr | tremolite |
| Kf | K-feldspar | | |

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