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Petrological and mineral-chemical variations in blueschist facies metasedimentary rocks from a single outcrop in the lower complex of the Bôrka Nappe (Meliata Unit, Western Carpathians, Slovak Republic)

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A detailed petrographic and mineral-chemical study on metapelites from the Meliatic accretionary wedge complex (Bôrka Nappe, Western Carpathians, Slovak Republic) reveals the HP character of the samples using quantitative phase diagrams contoured with mineral composition,  $H_2O$  mode isopleths and garnet-phengite thermometry. The presented PT pseudosections prove that small-scale differences in bulk rock composition are responsible for the variations in the mineral assemblages formed at the same PT conditions. The peak conditions indicate blueschist facies metamorphism (520–620 °C, 11–14 kbar) and are correlated with the 150–165 Ma subduction of the Mesozoic Meliata Oceanic branch of the Neotethys. Continuous decrease of P and T from peak conditions enabled the metapelitic rocks to preserve their HP assemblages. The presented HP conditions and retrograde PT path with decreasing P and T are characteristic of subduction zone tectonic settings which are in agreement with most of the geodynamic and tectonic reconstructions for the area.

Key words: metapelites, blueschist facies, pseudosections, accretionary wedge complex, Western Carpathians, Slovak Republic

## Introduction

Accretionary wedges often contain high-pressure metamorphic blocks and slices tectonically emplaced in non- or low-grade metamorphosed sedimentary matrix. Metapelites associated with HP rocks (eclogite, blueschist) rarely record peak PT conditions similar to those of the metabasic rocks. Recent works on petrogenetic grids (e.g. Proyer 2003a, b; Wei and Powell 2003, 2004, 2006)

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considerably helped the investigation of high-pressure metapelites. These grids helped to settle the long-standing debate whether the metapelites experienced the same HP conditions as the metabasites or were involved in late-stage tectonic juxtaposition.

The Bôrka Nappe is one of the most intensely discussed tectonic units of the Western Carpathians (e.g. Faryad 1995a, b; Mello et al. 1998). It represents the deeply buried and HP/LT metamorphosed parts of the Jurassic Meliatic accretionary wedge formed by the subduction of the Meliata Ocean. The wedge is built up by a Lower to Upper Jurassic (mostly very low- to low-grade) shaley matrix which incorporates remnants of the subducted oceanic crust and the most subsided parts of the shelf, both Triassic and Jurassic in age.

However, not all of the HP rocks of the unit have their protoliths in the Mesozoic Meliata Basin. As was shown in numerous works (Mello et al. 1996; Ivan and Kronome 1998), the protolith of the basal parts of the HP unit originates partly from the Permian cover sequences of the underlying Gemeric units forced into the subduction zone, as well as from an enigmatic volcano-sedimentary source which was already metamorphosed, probably as early as in the Devonian (Faryad and Henjes-Kunst 1997).

The discussed polymetamorphosed basal complex of the Bôrka Nappe is exposed only rarely: 1) it forms the topmost parts of the Cilakovský Vrch Hill at the end of the Cremošná Valley near the village of Bôrka, and 2) it builds some hills between the villages of Nizná Slaná and Roštár (our study area). In addition, although not yet proved, we propose that probably 3) some badly exposed phyllite in the Teplica Valley near the village of Jasov and possibly also 4) some of the metabasites on the northern slopes of the Sivá Skala Massif could represent the discussed Lower Paleozoic polymetamorphic complex. However, 5) the metabasites in the higher parts of Repisko Hill south of the study area does not appear to consist of "ordinary Meliatic matter", e.g. Triassic basites; their assignment to the discussed basal polymetamorphic volcano-sedimentary complex requires further investigation.

The aim of this paper is to provide some new mineralogical and petrological data concerning the metamorphism of this problematic part of the Bôrka Nappe. We present petrographic and mineral-chemical data forming the basis of the quantitative phase diagrams (PT pseudosections) calculated for selected samples. All these data are used to establish a PT path paying special attention to the preservation of high-pressure metamorphism in metapelitic assemblages formed in a Mesozoic subduction zone.

# Geologic setting

The innermost Western Carpathians are built up by several nappe systems (Fig. 1b). In the tectonic map of Mello et al. (1996) five tectonic units were distinguished (from bottom to top):



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Fig. 1 a) Main tectonostratigraphic units of the Pannonian Basin and neighboring areas. Box indicates the study area enlarged in b b) Geologic map of the study area, star indicates the sample locality. 1. metarhyolite tuff (Permian), 2. metasandstone (Permian), 3. "sericite phyllite" (Lower and Middle Triassic), 4. crystalline limestone (Middle and Upper Triassic), 5. "sericite-chlorite phyllite" with abundant metabasic tuffs (Middle and Upper Triassic), 6. serpentinite (Triassic-Jurassic) c) Schematic sketch of the studied section (sample localities indicated)





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1. Early Paleozoic rocks of the Gemericum (greenschist facies) with Late Paleozoic cover sequences;

2. Bôrka Nappe, represented only by blueschist facies rocks (focus of the present study);

3. Meliata Unit, containing metabasalt, serpentinite, and radiolarite embedded in Triassic-Jurassic slate, sandstone, and marl;

4. Torna (Turna Nappe): Upper Carboniferous-Triassic metasedimentary rocks;

5. Silica Unit: non-metamorphic Permian evaporites, Triassic and (rare) Jurassic carbonates.

In addition to the metabasic rocks, tectonic blocks of the Silica and Turna Units are also found in the Meliata Unit. In the field the separation of the Meliata Unit and Bôrka Nappe is not easy due to the lack of good exposures. Blueschist blocks were found in the sedimentary series of the Meliata Unit (Faryad and Dianiska 1999; Horváth 2000; Horváth and Árkai 2005); thus the separation of the highpressure rocks from the Meliata Unit into a separate tectonic unit (Bôrka Nappe) is controversial. This was argued by Faryad (1997) who supported the earlier interpretation of the Meliata Unit as an accretionary mélange complex (Plašienka et al. 1997). We include the Bôrka Nappe into the Meliata Unit in this study.

Apart from the HP metabasic and metasedimentary rocks (Faryad 1995a, b; Horváth 2000; Horváth and Árkai 2005), the Meliata Unit contains very low to low-grade metamorphic rocks of magmatic and sedimentary origin as well. Árkai et al. (2003) described the petrological and metamorphic features of the metasedimentary rocks focusing on the phyllosilicate characteristics. They revealed that the low-T prograde metamorphism was synchronous with the retrograde metamorphism of the blueschist (between 150 and 120 Ma; Faryad and Henjes-Kunst 1997). So far, only limited work has been carried out on the metapelitic series of the Bôrka Nappe. Faryad (1995b) investigated the blueschistfacies metapelites and estimated the PT conditions for several localities. He indicated 400–460 °C and 10–12 kbar for glaucophane and/or pyroxene-bearing rocks, and 360–400 °C and 8–10 kbar for chloritoid-bearing rocks. Faryad (1995a) calculated 380–460 °C and 10–13 kbar for mafic blueschist of the Meliata Unit.

## Methodology

Major element composition of the bulk rock samples was determined using a Perkin Elmer 5000 atomic absorption spectrophotometer (AAS), after digestion with lithium metaborate, in the Institute for Geochemical Research, Hungarian Academy of Sciences. In addition to the AAS technique, permanganometric (FeO), gravimetric (SiO<sub>2</sub>, TiO<sub>2</sub>, H<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub>) and volumetric (CO<sub>2</sub>) methods were applied.

EMP analyses were performed on selected rock samples in the same institute using a JEOL JCXA-733 electron microprobe equipped with an Oxford INCA 200 EDS. Operating conditions were 20 keV accelerating voltage, 4 nA sample

current, and 100 s counting time. The PAP correction procedure was applied for data preparation. The following standards were used: albite for Na, quartz for Si, corundum for Al, MgO for Mg, orthoclase for K, apatite for Ca, hematite for Fe, spessartine for Mn and rutile for Ti.

## Petrography and mineral chemistry

The road cut between the villages of Nizná Slaná and Roštár is probably the best-preserved outcrop of the metasedimentary part of the Meliata accretionary wedge. The outcrop is about 13 m long and on average about 2.5–3 m high (Fig. 1c). For all practical purposes the sequence is continuously exposed. Due to its coherent and tectonically undisturbed appearance we assume the same metamorphic history for the entire outcrop, providing a good background for modeling the phase relations in HP metapelitic rocks. For the present study 8 samples were chosen, of which 4 (GND-47, -48, -51 and -54) contained HP mineral assemblages. These samples were investigated in detail, paying special attention to the mineralogical differences originating from the variations in bulk rock chemistries. All samples apart from GND-54 have garnet, glaucophane, phengite clinozoisite/epidote, and quartz as indicators of blueschist facies, whereas albite, chlorite and paragonite are not always present. Biotite, minor carbonate (mostly calcite) and some chlorite and albite are retrograde phases. Neither chloritoid nor Na-pyroxene was found in the samples studied. Sample GND-54 has no glaucophane but garnet, biotite, phengite, quartz and albite are present as major rock-forming minerals. The foliation is marked by aligned phengite and quartz in all samples (Fig. 2a). Biotite is also parallel to the foliation where present. Large glaucophane grains (up to 3 mm) are usually part of the matrix assemblage forming foliation, but in some cases they occur as pre-tectonic, bent crystals (Fig. 2b and c). Large (1–2 mm) muscovites together with minor chlorite and calcite rarely overgrow the foliation-forming phengite. Epidote/clinozoisite when present is part of the matrix assemblage and occurs as small (50–100  $\mu$ m) grains. Garnet grains are small (100–200  $\mu$ m) in all samples (Fig. 2a) apart from GND-48, where it forms large (up to  $500 \,\mu$ m), pre- or syn-tectonic porphyroblasts (Fig. 2d). Inclusions in garnet are clinozoisite, chlorite and quartz; glaucophane contains albite, paragonite (only in sample GND-48), chlorite and clinozoisite. Paragonite does not appear as a discrete phase in the other studied samples, but white mica (phengite, muscovite) has an elevated Na content (see later). The retrograde assemblage is chlorite, biotite, muscovite, epidote/clinozoisite and calcite; locally albite and calcite are also present. Matrix rutile is replaced by titanite. Retrogressed samples not used in this study contain chlorite, muscovite, epidote, calcite and quartz as major phases. We found relic glaucophane and phengite in sample GND-49. The presence of secondary calcite indicates that retrogression was triggered by the infiltration of CO<sub>2</sub>-bearing fluids. The distribution of HP rocks in the studied section (Fig. 1) cannot be connected to any preferred orientation (e.g. tectonic zone).

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Fig. 2a, b

Photomicrographs of the observed mineral assemblages. a) Phengite (Phn) and quartz (Qtz) form the foliation with minor retrograde biotite (Bt). Small garnets (Grt) occur both in phengite- and quartz-rich microdomains, sample GND-47. b) Large glaucophane (Gln) grains are part of the foliation-forming matrix with phengite and quartz, or occur as pre-tectonic grains, sample GND-48



### Fig. 2c, d

Photomicrographs of the observed mineral assemblages. c) Bended glaucophane crystal in phengiterich matrix, sample GND-47. d) Garnet, glaucophane, phengite and quartz form the equilibrium HP assemblage. Note that garnet is more frequent in the phengite-rich part than in quartz-dominant areas. The zoning profile of the garnet grain in the lower middle part is shown in Fig. 3, sample GND-48

Garnets are zoned in all samples (Fig. 3). The absolute values vary from sample to sample, but the overall zoning trend is the same with decreasing XFe [Fe/(Fe+Mg)], Grs and Sps and increasing Alm and Prp values from core to rim. XFe is 0.92–0.98 in the cores and 0.87–0.89 in the rims. Grs rims show relatively



uniform compositions with 0.18–0.26, while the cores have a wider range of 0.31–0.48. Sps is generally 0.18 in the cores except sample GND-54 where it is up to 0.37, while the rim compositions are down to 0.02–0.05 in all samples. The Prp content is steadily increasing from 0.01 to 0.08 from core to rim in all samples. All these compositional features point to prograde crystallization conditions to garnet. Matrix phases are compositionally homogeneous as opposed to garnet. XFe in glaucophane (XFe<sup>2+</sup> in  $M_{1-3}$  position) varies from sample to sample: 0.21–0.29 in GND-47, 0.27–0.37 in GND-48 and 0.20–0.28 in GND-51. Biotite has a relatively narrow compositional range in all samples; its XFe varies between 0.45 and 0.52. Phengite compositions show some differences relative to their textural positions. In sample GND-47 matrix phengites have 3.15–3.2 Si a.p.f.u while inclusions are Si-richer (3.45–3.5). The same can be observed in sample GND-48 (matrix phengite has 3.1-3.2 Si, inclusion has 3.43–3.45). In samples GND-51 and -54 phengite has 3.2–3.5 and 3.13–3.4, respectively. The Na<sub>2</sub>O content of phengite is usually between 0.1 and 0.5 wt%, but in some cases it reaches up to 1.5 wt%, showing a relatively high paragonite component of phengite in the samples where no discrete paragonite was found. Mineral compositional features for the studied samples are in Table 1.

Table 1

Mineral-chemical data for the selected samples

	GND-47 Garnet core	rim	Glaucophane	Phengite	Biotite	GND-48 Garnet core	rim	Glaucophane	Phengite	Biotite
xFe*	0.95	0.89	0.21-0.29		0.52	0.98	0.90	0.27-0.37		-
XCa	0.48	0.22				0.35	0.23			
xFe*	0.92	0.88				0.95	0.87			
XCa	0.28	0.24				0.21	0.18			
Si				3.15-3.45					3.1-3.2	
				3.5 (i)					3.43 <b>–</b> 3.45 (i)	

	GND-51 Garnet		Glaucophane	Phengite	Biotite	GND-54 Garnet		Glaucophane	Phengite	Biotite
	core	rim				core	rim			
xFe*	0.92	0.88	0.20-0.28		0.47-0.48	0.98	0.89	-		0.45-0.48
XCa	0.33	0.26				0.31	0.20			
xFe*						0.94	0.88			
XCa						0.31	0.22			
Si				3.2-3.5					3.13-3.3	

\*XFe in garnet and biotite is  $Fe^{2+}/(Fe^{2+}+Mg)$ , while in glaucophane XFe is  $XFe^{2+}$  in  $M_{1-3}$  position, i: inclusion

#### Whole-rock geochemistry

In the investigated samples  $SiO_2$  varies between 41 and 70 wt% (Table 2). Samples with low  $SiO_2$  (less than 60) are more retrogressed and have higher CaO and  $CO_2$  due to the presence of secondary calcite and other carbonate phases (FeO and MgO are also higher). The samples with high  $SiO_2$  contents are used for detailed mineral chemical and thermobarometric studies. The above-

Table 2	
Whole-rock analyses	of selected metapelitic rocks

	GND-45	GND-47	GND-48	GND-49	GND-51	GND-52	GND-53	GND-54
SiO <sub>2</sub>	41.66	69.03	61.10	50.57	66.03	42.44	45.32	64.79
TiO <sub>2</sub>	0.83	0.56	0.90	0.85	0.56	0.70	1.04	0.79
$AI_2O_3$	16.76	11.78	18.38	18.95	13.26	16.70	17.58	15.91
$Fe_2O_3$	2.67	2.63	4.19	1.92	3.56	2.96	2.11	3.35
FeO	5.28	3.71	2.14	6.96	3.74	5.75	7.56	2.05
MnO	0.15	0.20	0.32	0.14	0.36	0.15	0.16	0.26
MgO	9.74	3.44	1.96	5.10	2.27	7.82	8.94	1.82
CaO	9.71	1.86	1.85	5.91	3.02	10.99	7.07	1.76
K <sub>2</sub> O	2.02	1.88	3.46	2.96	1.44	1.52	1.38	3.44
Na <sub>2</sub> O	2.22	1.17	1.74	1.94	3.36	2.66	2.62	1.60
$-H_2O$	0.08	0.05	0.06	0.02	0.01	0.01	0.05	0.04
+ H <sub>2</sub> O	4.73	3.06	3.49	3.88	2.22	3.52	4.63	3.20
CO <sub>2</sub>	3.81	-	-	-	-	3.72	0.61	-
$P_2O_5$	0.04	0.11	0.11	0.17	0.10	0.06	0.06	0.11
LOI	7.95	2.65	3.25	3.11	1.80	6.60	4.40	2.97
Total	99.70	99.48	99.70	99.37	99.93	99.00	99.13	99.12

Samples in italics are used for mineral-chemical studies and pseudosection modeling

mentioned shift does not correlate with the  $Al_2O_3$  contents which vary between 11 and 19 wt%. Both  $Na_2O$  and  $K_2O$  are between 1 and 3.5 weight%.  $P_2O_5$  content is low and is represented by accessory apatite. TiO<sub>2</sub> is less than 1 wt% in most samples (apart from GND-53) and is present as rutile or ilmenite. The analyzed samples are similar to the ones in Faryad (1995b). According to his results the samples correspond to greywacke and shale, and plot into the field covering common sedimentary rocks.

## PT calculations

Phase relations are best illustrated and understood using pseudosections (quantitative phase diagrams) where the bulk composition of a rock is incorporated into the calculations. The pseudosection modeling was undertaken with Version 3.25 of the THERMOCALC software (Powell et al. 1998) and the internally-consistent thermodynamic dataset 5.5 (August 2004 upgrade). The data file coding of the activity-composition relationships of the minerals used in the NCKFMASH system follow the coding of White et al. (2001) and Wei and Powell (2006). All the constructed pseudosections are in the 5–15 kbar and 400–650 °C PT range with quartz and  $H_2O$  in excess. As was previously discussed, garnet and phengite were formed in equilibrium so the garnet-phengite thermometer of Green and Hellman (1982) was applied. As biotite is a retrograde phase, mostly after glaucophane, the garnet-biotite thermometer is not applicable for the determination of peak temperatures in our samples.

The studied samples show different peak mineral assemblages: in sample GND-47 garnet-glaucophane-phengite-clinozoisite-chlorite; in sample GND-48 garnet-glaucophane-phengite-clinozoisite-paragonite; in sample GND-51 garnet-glaucophane-phengite-clinozoisite-albite; in sample GND-54 garnet-phengite-clinozoisite-albite; in sample GND-54 garnet-phengite-clinozoisite-albite). In the following chapter we present PT pseudosections for the studied samples to prove that bulk rock composition differences are responsible for these variations.

#### PT pseudosections

## Sample GND-47

The pseudosection calculated for sample GND-47 shows that albite is not stable over 8 kbar and plagioclase breaks down to paragonite in narrow divariant fields (Fig. 4a). At ca. 9 kbar and 580 °C a change occurs when garnet joins the assemblage. The divariant field responsible for plagioclase disappearance is replaced by univariant reactions. There is a wedge-shaped area in the pseudosection from ca. 8.5 kbar and 570 °C to 11 kbar and 620 °C where muscovite is not stable. It reappears again and the same happens with paragonite at higher P (the paragonite-absent window is at ca. 11.5 kbar). Al<sub>2</sub>SiO<sub>5</sub> polymorphs (kyanite and sillimanite) are present only at high temperatures (over 600 °C for kyanite). They replace muscovite at low P. Chlorite is stable over nearly the entire PT range and only reacts out at temperatures over 620-630 °C. The glaucophane-in line has a shallow positive slope apart from the transition from chl-bi-mu-pa-cz to chl-bimu-pa-gl-cz (9–11 kbar). Biotite appears in the PT pseudosection as a replacement phase for phengite. Garnet enters the assemblage over 500 °C at high-P with a steep negative slope. The garnet-in line has very shallow slope when the chl-bi-mu-pa-gl-cz assemblage disappears to form the g-chl-mu-pa-glcz peak assemblage. This assemblage is stable over 11 kbar and between 520 and 600 °C. At higher T cz, then chl reacts out and ky joins the assemblage. Garnetphengite thermometry yields 540-565 °C at 11 kbar and 550-575 °C at 13 kbar, restricting peak temperatures to this range in g-chl-mu-pa-gl-cz.

### Sample GND-48

There are some similarities in the pseudosection of this sample with GND-47. Garnet is not stable under 500 °C and  $Al_2SiO_5$  minerals appear at ca. 600 °C (Fig. 4b). The garnet-in line usually has a steep negative slope, but it has a shallow positive slope at 10–11 kbar and 515–575 °C. Apart from the above-mentioned similarities, striking differences are observed in the pseudosection. Albite and plagioclase are stable to higher pressures; plagioclase is even stable over the entire P range. At low pressures (5–6 kbar) albite and plagioclase appear together. Chlorite stability is restricted; it reacts out to form ky or sill at high T in chl-mupl-ky or chl-mu-pl-sill. At high P the chl-out line has a steep negative slope.



Fig. 4a

PT pseudosections of samples GND-47. Dashed lines indicate the T ranges calculated from garnetphengite thermometry

Paragonite appears at pressures above 8 kbar. The peak assemblage garnet-glaucophane-phengite-clinozoisite-paragonite is stable over 11 kbar at 540–640 °C. Temperatures of 530–610 °C (at 11 kbar) and 540–620 °C (at 13 kbar) were calculated using the garnet-phengite thermometer.

# Sample GND-51

The calculated pseudosection for sample GND-51 has albite and plagioclase over the entire PT range, but Al<sub>2</sub>SiO<sub>5</sub> minerals are not stable (Fig. 4c). The garnet-



Fig. 4b

PT pseudosections of samples GND-48. Dashed lines indicate the T ranges calculated from garnetphengite thermometry

in line at high P is almost vertical with a very steep positive slope. At lower P it has a steep negative slope, similar to those of other PT pseudosections. Muscovite disappears from the mineral assemblage to form paragonite and biotite at ca. 8 kbar and 500 °C, and muscovite-free assemblages are present at low P from 500 °C (chl-bi-pl-cz, chl-bi-pl, g-chl-bi-pl and g-bi-pl). Muscovite is not stable at medium P and T. It reappears again (as phengite) at 9 kbar and 600 °C with a shallow positive slope to higher temperatures. It forms from paragonite at 9 kbar and 600 °C, marking the high T end of this mineral. The pa-out line has a very steep positive slope until it meets the gl-in line over 10 kbar. From this point the pa-out



Fig. 4c

PT pseudosections of samples GND-51. Dashed lines indicate the T ranges calculated from garnetphengite thermometry

line has a very shallow positive slope (almost horizontal) in biotite-bearing fields. In the bi-free part of the pseudosection at high P (over 10 kbar), the pa-out line has a positive slope marking the low T end of the garnet-glaucophane-phengiteclinozoisite-albite peak assemblage. The garnet-phengite thermometer yields 520–560 °C at 11–13 kbar. The high T end of the peak assemblage is the pl-in line. In a very narrow divariant field ab, pl and cz are all stable. With increasing T, first cz then ab breaks down. Biotite joins in at high T.



Fig. 4d

PT pseudosections of samples GND-54. Dashed lines indicate the T ranges calculated from garnetphengite thermometry

## Sample GND-54

The calculated pseudosection shows that paragonite forms at the expense of chlorite and no chlorite is stable over medium P and T (over 8 kbar and 600 °C). The garnet-in line has the same slope as in the other samples, but it has the smallest stability field amongst the studied samples similar to the Al<sub>2</sub>SiO<sub>5</sub> minerals (Fig. 4d). Albite/plagioclase is stable over the whole PT range apart from the high P / low T end. The sample has no glaucophane and has the highest

modal content of biotite. From textural similarities to the other ones we propose that the sample had previously contained glaucophane. PT pseudosection calculations indicate that garnet and biotite are stable together in plagioclasebearing fields only. No plagioclase, only albite was found in the sample. The nonequilibrium state of garnet and biotite is supported by garnet-phengite thermometry data which indicate 545–600 °C, plotting mostly outside the biotite stability field. There is only a small area with stable garnet, glaucophane and biotite and textural observations in the other samples show that biotite formed after glaucophane. From these we presume that the peak assemblage was garnetglaucophane-phengite-clinozoisite-albite-paragonite and biotite is a retrograde phase.

## Mineral composition isopleths

Mineral composition isopleths were performed to compare the measured and observed compositional features as well to put tighter constraints on the peak PT conditions. All mineral compositions were recalculated in the NCKFMASH system. This causes no problem for glaucophane, biotite or phengite, but does with garnet. The latter is strongly zoned indicating fractional crystallization (Marmo et al. 2002), and has a high Mn content; therefore the NCKFMASH system is probably not modeling the garnet properly. The Mn-free system was used instead because: 1. garnets are relatively small and the rims have low Sps content (usually 1–3); 2. the other phases have very low MnO, mostly beneath the EMP detection limit, so the MnNCKFMASH calculations resulted in garnet-bearing fields in the entire pseudosection ranges. This is not in accordance with the petrographic observations. The calculated garnet compositions in NCKFMASH have higher Grs than measured ones (see below), but this feature is still present in the Mn-bearing ones as well. We will address this question later.

# Sample GND-47

XFe [Fe/(Fe+Mg)] isopleths of garnet have a steep negative slope and decrease with increasing T (Fig. 5a). The measured values for XFe in the sample were 0.92–0.95 in the core and 0.88–0.89 in the rim. This corresponds to a small T increase during garnet formation in the g-chl-mu-pa-gl-cz peak assemblage and is in good agreement with data from garnet-phengite thermometry. The corresponding XCa values [Ca/(Fe+Mg+Ca)] are higher than the measured ones. The XFe values of glaucophane (XFe<sup>2+</sup> in M<sub>1-3</sub> position) have a steep negative slope in g-chl-mu-pa-gl-cz and in g-chl-mu-pa-gl; they decrease with increasing T (Fig. 5b). The slopes change to positive in g-mu-pa-gl after the breakdown of chlorite. The measured values are 0.21–0.29. They are in good accordance with XFe data of garnet and garnet-phengite thermometry. In the garnet-free fields XFe of glaucophane has a positive slope, its values decreasing with increasing T



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Fig. 5c Mineral composition isopleths for sample GND-47, phengite

The trend changes in chl-mu-pa-gl-cz, where the isopleths have the same slope but they increase with decreasing T until the 0.3 isopleth is reached again. The Si isopleths of phengite (muscovite) have a very steep positive slope, decreasing with increasing T (Fig. 5c). This trend changes in g-mu-pa-gl and in chl-mu-gl-abcz, where the isopleths have a shallow negative slope. The measured values of 3.15-3.2 in matrix phengites yield pressures over 11 kbar in the peak assemblage and are in good agreement with other mineral composition isopleths.

## Sample GND-48

The XFe isopleths of garnet have a steep negative slope in g-chl-mu-pa-gl-cz and in g-mu-pa-gl-cz (peak assemblage), but they become positive when pl enters the assemblage (Fig. 6a). They decrease with increasing T. The measured values (0.95–0.98 in the core, 0.87–0.9 in the rim) point to T increase during garnet formation. The XCa isopleths decrease with increasing T, with a steep negative slope in g-chl-mu-pa-gl-cz and with a moderate positive slope in g-mu-pa-gl-plcz. They show an increasing trend in between the two fields in the g-mu-pa-glcz peak assemblage. The measured values (0.32–0.35 in the core and 0.18–0.23 in the rim) are lower compared to the calculated ones in the peak field. The XFe isopleths of glaucophane decrease with increasing T in g-chl-mu-pa-gl-cz and in g-mu-pa-gl-pl-cz, with the slopes similar to the XCa of garnet (Fig. 6b). They



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Fig. 6c Mineral composition isopleths for sample GND-48, phengite

decrease with increasing P in the peak assemblage (g-mu-pa-gl-cz). The measured values of 0.27–0.37 are comparable with the calculated ones in pl-free fields. The Si isopleths of phengite have steep positive slopes in most of the fields; the values decrease with increasing T. The differences to this trend are in g-mu-pa-gl-cz (shallow slope) and in g-bi-mu-pa-gl-cz, where isopleths have a negative slope and values decrease with increasing P (Fig. 6c).

#### Sample GND-51

The calculated garnet XFe isopleths decrease with increasing T, while the XCa values increase with increasing P (Fig. 7a). The measured XFe values for garnet are 0.92 (rim) and 0.88 (rim). According to the composition isopleths these values are indicative of T increase during garnet growth. The corresponding XCa values are higher than the measured ones. XFe of glaucophane decreases with increasing T and the measured values of 0.20–0.28 yield temperatures above 550 °C (Fig. 7b). The XFe isopleths have very steep positive slopes in garnetbearing fields and more gentle ones in garnet-free assemblages. Retrograde biotite has 0.47.048 XFe [Fe/(Fe+Mg)], indicating temperatures not in excess of 550 °C (Fig. 7c). The isopleths have a positive slope at low-medium-T, but in g-chl-bi-pl and g-chl-bi-pa-pl-cz fields isopleths run parallel with the g-in and chl-out lines with a negative slope. The Si isopleths of phengite have a positive slope and



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Fig. 7c, d Mineral composition isopleths for sample GND-51, c) biotite, d) phengite

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the measured values of 3.2-3.5 correspond to pressures above 11 kbar in the gmu-gl-ab-cz peak assemblage. An overturn of the mentioned trend is visible at high PT in g-mu-gl-pl and g-bi-mu-gl-pl fields, where the 3.25 Si isopleth reappears again (Fig. 7d).

## Sample GND-54

The calculated XCa isopleths show decrease from 0.55 to 0.13; the measured values are 0.31 (core) and 0.20-0.22 (rim), respectively (Fig. 8a). Such low values are not recognized in glaucophane- and albite-bearing fields. The measured decreasing XFe trend from core to rim yields a T increase from g-mu-pa-gl-ab-cz to g-mu-gl-ab-cz and is good agreement with the calculated 545-600 °C temperature range. No glaucophane was found in the sample. Biotite has XFe values between 0.45 and 0.48 corresponding to bi formation in the bi-mu-pa-glab-cz field outside garnet stability, highlighting the retrograde nature of the mineral in question (Fig. 8b). The measured Si values (3.13-3.4) yield pressures above 10 kbar in garnet-bearing assemblages (Fig. 8c). The Si isopleths decrease with increasing T and have a steep positive slope.





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Fig. 8b, c Mineral composition isopleths for sample GND-54, b) biotite, c) phengite

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### H<sub>2</sub>O mode isopleths

The PT pseudosections of the studied blueschist-facies metapelites are also contoured for  $H_2O$  content, that is, the sum of  $H_2O$  in the minerals under  $H_2O$ -saturated conditions. The calculation procedure follows Yang and Powell (2006). These mode isopleths are useful for considering the closed-system behavior of rocks because those that are  $H_2O$ -saturated will remain  $H_2O$ -saturated while their PT path crosses contours of decreasing value, but will tend to become fluid-absent when crossing contours of increasing value, according to Guiraud et al. (2001). Their suggestion is that preservation of mineral assemblages tends to occur from the point where a rock becomes devoid of fluid.

#### Sample GND-47

The pseudosection contoured for H<sub>2</sub>O mode isopleths (in mol %) is shown in Fig. 9a. The mode isopleths decrease with increasing T, but the slopes are variable. The calculated peak temperatures of 540–575 °C correspond to 13–14 mol%. The narrow divariant fields responsible for the formation of paragonite or kyanite (i.e. chl-bi-mu-pl-ky) have very dense contours while fields with higher variance experience smaller-scale variations in H<sub>2</sub>O content.

#### Sample GND-48

The  $H_2O$  contours of the sample follow the same trend as GND-47, but the absolute values are different (Fig. 9b). The 530–620 °C peak temperature range is at ca. 15.5–16 mol%, corresponding to max. 2 mol % of fluid-loss during prograde metamorphism. The overall trend for the isopleths is to decrease with T increase, but in some cases perturbations occur mostly in divariant fields like chl-bi-mu-pa-ab-cz or chl-bi-mu-pa-pl-cz.

#### Sample GND-51

The sample has the lowest  $H_2O$  content in the studied sample set (Fig. 9c). The  $H_2O$  mol% is 8.5–9.5 for the peak temperature range (520–560 °C). The lowest calculated isopleth (7 mol%) runs parallel to the chl-out line at low P, then to the cz-out line and at high-P it corresponds to the gl-out line. The ab to pl transition line at low P (max. 8 kbar) is described as a major  $H_2O$ -release area with contours from 9 to 9.7 all running there.

## Sample GND-54

The  $H_2O$  mode isopleths show similar trends to the other samples (Fig. 9d). Values decrease with increasing T. The calculated temperatures of 545–600 °C correspond to 13.5–14 mol % of  $H_2O$ . The diagram shows that  $H_2O$  addition was

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Fig. 9a, b  $H_2O$  mode isopleths for sample GND-47 (a), GND-48 (b)

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not necessary for biotite formation under retrograde conditions, because the field where measured and calculated bi XFe values meet (see above) has slightly higher  $H_2O$  mol % values (14–14.5 mol %).

### Discussion

#### Garnet compositional features

All garnet grains regardless of their size or textural position in the studied samples show increasing values for Alm and Prp while exhibiting decreasing XFe, Grs and Sps, indicating garnet growth during prograde metamorphic conditions (increasing T). No retrograde zoning features can be found. Usually, measured XFe are higher than the calculated ones at peak PT conditions caused by compositional modification during cooling, and Grs is unchanged due to its slower diffusion compared to Fe or Mg. This is not the case in our samples. Comparison of the measured and calculated garnet compositions showed that XFe values match each other quite well, but measured Grs values tend to be lower than the calculated ones. We propose two interpretations to solve the problem:

1. The garnet XFe values were modified and Grs values show the true formation conditions. In this case, if we choose sample GND-47, garnets were formed at 8–10 kbar and over 600 °C in the g-chl-bi-mu-pl field outside the stability field of glaucophane and albite. As no Ca-bearing plagioclase was found in the samples and textural studies indicate that glaucophane is part of the peak assemblage instead of biotite this assumption is questionable. The same shift to lower P and higher T is visible in the other samples.

2. The garnet XFe values show the peak conditions and Grs values do not. This interpretation is supported by the fact that garnets have prograde zoning patterns not modified by later diffusional processes, and the other mineral compositions (glaucophane, phengite) are comparable to garnet XFe. The observed "underestimation" of Grs may be caused by the separation of Ca-rich minerals (e.g. clinozoisite) from the rock matrix as inclusions in garnet (Yang and Powell 2006) or the application of a Mn-free system for phase diagram calculations. As the previously published grids for HP metapelites are produced in NCKFMASH (e.g. Marmo et al. 2002; Wei and Powell 2006; Yang and Powell 2006), no comparison for Mn-bearing systems is available at the moment. Adding Mn to the system in our case resulted in that garnet became part of every assemblage, since the other phases have no significant MnO content over the EMP detection limit. Textural studies do not support this either. A tentative calculation for the peak conditions in sample GND-47 using the MnNCKFMASH system (not shown) resulted in the same Grs "underestimation" still being present. Taking the above-mentioned facts into consideration we presume that the calculated PT pseudosections, coupled with the mineral composition and mode isopleths, model quite well the PT evolution of the studied samples.

# Variations in peak mineral assemblages

All blueschist facies samples (GND-47, -48 and -51) contain garnet, glaucophane, phengite and clinozoisite. Samples GND-47 has chlorite in the peak assemblage, while in the other samples it appears as a retrograde phase. This is clearly demonstrated in Fig. 10c. Chlorite is stable in GND-47 and -48 up to 630–650 °C, but in sample GND-48 it is not present at high P in this T range. Chlorite stability is restricted to pressures lower than 9–10 kbar in samples GND-51 and -54. Sample GND-51 has albite as a peak phase, which is not found in samples GND-47 and -48 (Fig. 10a). Albite is present in all assemblages in samples GND-51 and -54, and the Ab/Pl transition has a very steep positive slope. In samples GND-47 and -48, albite breaks down to paragonite and/or glaucophane and has a limited stability range. Biotite and glaucophane stability lines run parallel to each other, especially at temperatures over 500 °C (Fig. 10b and e). Glaucophane forms from biotite during P increase; in other words biotite is the breakdown product of glaucophane (and garnet) during decompression. Garnetin reaction in all samples has a strong T dependence, except for the 500–600 °C range, where it forms from biotite (Fig. 10d). At high P (over 10 kbar) the garnetin line has a steep positive slope in samples GND-48 and -54 and a steep negative slope in samples GND-47 and -51. Muscovite has a strange stability in samples GND-47 and -51, while it is stable in the whole PT range in the other samples (Fig. 10f). There is a muscovite-free "island" in sample GND-47 from ca. 8.5 kbar and 570 °C to 11 kbar and 620 °C. A muscovite-free "bulge" is present in sample GND-51 from ca. 500 °C and 9 kbar to 600 °C and 11 kbar, shifting the muscovite-out line to lower temperatures.

## Peak PT conditions

Variations in bulk rock composition resulted in various peak mineral assemblages in the studied sample set collected from a single outcrop, where uniform peak PT conditions were supposed. The variations are small-scale, e.g. chlorite is part of the peak assemblage in GND-47, or albite is in GND-51. These variations were justified by the calculated PT pseudosections. Using mineral composition isopleths together with garnet-phengite thermometry the peak PT conditions were estimated at 520–620 °C, 11–14 kbar. These values are higher than previously published for the Meliata blueschist by Faryad (1995a, b) who applied different methods for samples originating from different outcrops than the ones used in this study. Mazzoli and Vozárová (1998) calculated ca. 500 °C and 13 kbar as peak conditions for the Bôrka Nappe followed by rapid decompression to 400 °C and 5 kbar. These values are still somewhat lower than ours. The age of the HP metamorphism is quite well known from the works of Maluski et al. (1993) and Faryad and Henjes-Kunst (1997), who estimated 150–165 Ma using Ar-Ar and K-Ar methods on micas.



Fig. 10a, b Mineral stabilities for the studied samples, a) albite, b) biotite

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Fig. 10e, f Mineral stabilities for the studied samples, e) glaucophane, f) phengite

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## Retrograde PT path

The preservation of high-pressure metapelitic assemblages is mostly related to changes in their modal H<sub>2</sub>O content during their PT evolution path (e.g. Guiraud et al. 2001), but other factors play important roles as well (e.g. Proyer 2003a, b). During prograde metamorphism the rock crosses decreasing H<sub>2</sub>O contours, dehydrates and loses fluid. The metamorphic peak corresponds to the conditions where dehydration ends. During retrogression this peak assemblage is preserved when the necessary H<sub>2</sub>O is not available for the retrograde reactions. The main consequence of drawing the H<sub>2</sub>O contours in a PT pseudosection is that without any infiltration of H<sub>2</sub>O into the rock, the H<sub>2</sub>O content can only decrease (Guiraud et al. 2001). In the investigated samples the peak conditions are at 520-620 °C, 11-14 kbar corresponding to blueschist facies conditions. These peak assemblages are quite well preserved in some of the samples, and completely overprinted by retrograde phases in others from the studied section. In order to preserve of the high-pressure assemblages the temperature had to decrease simultaneously with pressure during the retrograde PT path (Fig. 11). If decompression is accompanied by T increase (Barrow-type metamorphism) or is in an isothermal decompressional setting, the assemblages cross contours of decreasing H<sub>2</sub>O content and the rocks will begin to rehydrate and lose their HP assemblages. The most common retrograde phase is biotite, forming from garnet and/or glaucophane. It is clear from the pseudosections that no external H<sub>2</sub>O is required for biotite growth during retrogression; biotite will appear in the mineral assemblages during cooling. Another argument for the simultaneous P and T decrease is the complete absence of (Ca-bearing) plagioclase; only albite was found. A path without cooling in the early retrograde stages must enter the plagioclase-bearing fields in all samples. A PT path with decreasing P and T is a feature of rocks in subduction zones which is the tectonic setting for the studied rocks according to many geodynamic and tectonic reconstructions (e.g. Plašienka et al. 1997).

## Conclusions

A detailed petrographic and mineral chemical study was performed on selected metapelitic samples originating from a single outcrop of the Bôrka Nappe (Western Carpathians, Slovak Republic). The HP character of the samples was confirmed using quantitative phase diagrams contoured with mineral composition and  $H_2O$  mode isopleths and garnet-phengite thermometry. The peak conditions are at 520–620 °C, 11–14 kbar, corresponding to blueschist facies conditions and are correlated with the 150–165 Ma blueschist facies event representing the subduction of the Mesozoic Meliata °Cean. Retrograde metamorphism after peak conditions was highlighted by continuous decrease of pressure and temperature, enabling the metapelitic rocks to preserve their HP assemblages. Non-metamorphosed, LT–LP metamorphosed and HP meta-



Fig. 11 PT path for sample GND-51

morphosed sedimentary and magmatic rocks are part of the accretionary complex forming the Meliata Unit (including the Bôrka Nappe). Various PT paths during the tectonic evolution of the accretionary wedge were experienced by parts of the dismembered sequence, which originally formed a coherent unit, and were brought back into close spatial relationship only during the postmetamorphic exhumation processes. This metamorphic heterogeneity was verified by extensive work on metabasites (e.g. Faryad 1995a; Horváth 2000; Horváth and Árkai 2005), but only sporadic data are present from the metasedimentary rocks. Future work on other localities will improve our knowledge on the effect and range of Alpine (Jurassic) subduction of similar lithologies in the Western Carpathians.

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