FORMATION OF THE MALÉ KARPATY PALEOZOIC CRYSTALLINE BASEMENT: A VIEWPOINT OF GENETIC MINERALOGY
Excursion guide MinWien 2023 conference

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Abstract

The Malé Karpaty crystalline basement is the westernmost occurrence of the Variscan basement in the Alpine structure of the Western Carpathians. The Bratislava and Modra granite massifs are principal structural elements with particular evolution reflected by differences in their accessory mineral assemblage. The accessory assemblage of the Bratislava granite massif with S-type affinity contains abundant monazite, xenotime, and garnet. Bratislava granite massif has been emplaced at an age span range of 358-355 Myr earlier and to the deeper crustal position in comparison to the Modra granite massif. The Modra granite massif showing abundant accessory apatite and allanite is typical for I-type affinity intruded in a time span of ca 353-347 Myr. The emplacement of the Bratislava granite massif was accompanied by periplutonic contact metamorphism, forming sillimanite and garnet facies in metapelites on granite contact (P ~ 350-500 MPa, T ≤ 500-550 °C). The Modra granite massif formed the contact mineral assemblage in Devonian limestones and associated metasediments point to the emplacement to upper-crustal granite position at T = 300 °C and P = 150-200 MPa. Both granite massifs intruded the Pezinok and Pernek Paleozoic crystalline basements which have been formed in the back-arc basin. The Pernek back-arc metaophiolite complex is lithologically rich in organic carbon and volcanic admixtures forming crystallization of unique V-Cr phases, mainly goldmanite. Initial sedimentation on exposed Variscan granitic rocks during the Permian period is represented by Lower Triassic quartzite (Lužná Formation), where the occurrence of tourmalinites contributes to solving of quartzite provenance and paleogeography.

Introduction

The present evolutionary knowledge of the crystalline basement in the Paleozoic Malé Karpaty mountains has been obtained from long-term, mineralogical investigations and bulk rock chemistry. In other words, the genesis of various mineral phases became a starting point for the geotectonic interpretation of the structure and evolution of the recent Malé Karpaty crystalline complex. The present Alpine edifice of the Malé Karpaty mountain range, just like in the entire Western Carpathians, results from the Late Jurassic to Tertiary subduction-collision Alpine orogeny along the belt between the stable North European Platform and Africa-related Apulian (Adria) continental fragments (PLAŠIENKA et al., 1997). The Malé Karpaty crystalline basement is part of the Alpine thick-skinned Tatric Unit, or the part of the lowermost nappe structure – the main Alpine Slovakian tectonic units are generally formed from bottom to top by the Tatric, Veporic, and Gemeric nappes. This excursion guide briefly introduces the important mineralogical features of the Malé Karpaty crystalline basement from mineralization in the Lower Paleozoic metamorphic rocks to the Variscan granite composition up to the beginning of the Triassic sedimentation on these granites.

Granitic rocks in the Malé Karpaty Mountains

Variscan granitic rocks are exposed in the core of the Alpine horst tectonic structure of the Malé Karpaty mountains. According to the geodynamic model of STAMPFLI & BOREL (2002), the Variscan granites of the Western Carpathians originated in the Galatian volcanic-arc setting during the northward Upper Devonian/Lower Carboniferous subduction of the Paleotethys ocean (BROSKA et al., 2013). The subduction arc system was terminated by continental collision and the break-off of a subducted slab (BROSKA et al., 2022) based on the model introduced by DAVIES & VON BLANCKENBURG (1995). The slab break-off during the subduction became an important factor in triggering the granite formation with some adakitic features that are commonly found in the granites of the Western Carpathians. The slab break-off triggered the melting of the deep, crustal part due to the increased heat and fluid transfer from the ascending asthenosphere. This process was accompanied by exhumation and subsequent melting of the crust during decompression within the high-grade metamorphic complexes, where diatexites of the Upper Devonian age were formed; they marked the beginning of the large granite formation (BROSKA et al., 2022; MARASZEWSKA et al., 2022). Therefore, on this basis, the main granitic masses in the Western Carpathians, including those known from the Malé Karpaty Mts., have been emplaced as (post)-collisional granites (BROSKA et al., 2022).

In the Malé Karpaty Mts., two Variscan granite massifs (1) Bratislava and (2) Modra were distinguished, and the following description shows some of their different geodynamic evolutionary features (Fig. 1a). The intrusion of the Bratislava granitic massif contains abundant pegmatite dykes and paragneiss xenoliths. The granite intrusion into former low-grade Lower Paleozoic metapelitic-metapsammitic lithologies generated metamorphic aureole in amphibolite facies ($P \sim 300$-350 MPa, $T \leq 500$-550 °C), which correspond to ca. 12 to 14 km depth for the granite emplacement (CAMBEL & VILINOVIČ, 1987). The following metamorphic isogrades can be recognized as stemming outward from granites: staurolite-sillimanite zone (St-Sill), staurolite-chlorite zone (St-Chl), garnet zone (Gr) and biotite zone (Bt) (KORIKOVSKY et al., 1984) (Fig. 1b). Locally, staurolite forms

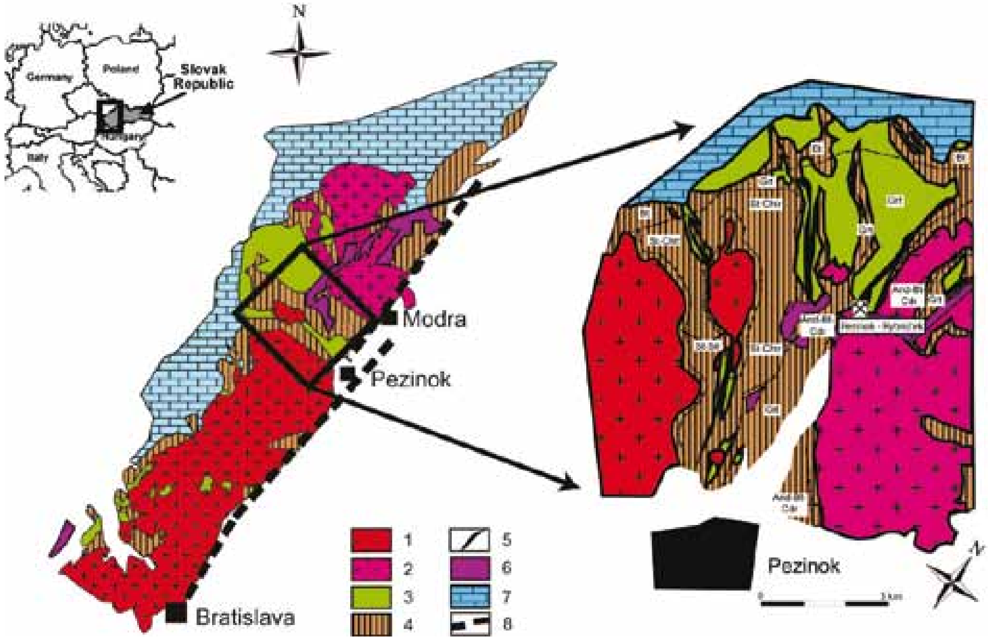

Fig. 1: Simplified geological map of the crystalline basement of the Malé Karpaty Mountains (according to POLÁK et al. 2011). Left: Location of the Bratislava and Modra Granite Massifs; Right: mineral isograds in metamorphic rocks around the granite massifs and the Rybníček mine with metamorphic V-Cr mineralization. 1: Bratislava Granite Massif, 2: Modra Granite Massif, 3: Devonian ophiolite metabasites 4: Devonian metasediments 5: Carbon- and pyrite/pyrrhotite-rich mafic metapyroclastic rocks (3 to 5: Pernek Group), 6: Lower Triassic quartzites and conglomerates of the Lúžna Formation, 7: other Mesozoic sedimentary rocks, undistinguished, 8: tectonic faults.

large crystals, and CT tomography revealed rotation of staurolite during granite emplacement. Thermodynamic modelling of metapelite from the locality of Hrubá Pleš (Bratislava) with mineral association St–Grt-Bt-Ms-Chl-Qtz by pseudosection calculation showed PT conditions, even 580-610 °C at a pressure of 500 (700) MPa (DYDA, 2000; VOJTKO et al., 2011).

Bratislava Granite Massif

An example of granites from the early magmatic phase of the Bratislava granite massif is represented by the locality along the Hlboká cesta in Bratislava ("Deep road") with outcrops of biotite granodiorites and diorites (Fig. 2a). In general, the Variscan Bratislava granite massif is formed mainly by granodiorite/granite intrusions with peraluminous, calc-alkaline, and S-type characteristics (CAMBEL & VILINOVIČ, 1987; PETRÍK & BROSKA, 1994). The rock-forming minerals of the granitic rocks comprise anhedral quartz, subhedral plagioclase (An_{24}-An_{06}) 2-4 mm in size, but in a more basic form, almost like in the I-type granites found at the Hlboká cesta site, where plagioclases with An_{34} are present. Two types of K-feldspars can be distinguished. K-feldspars of the first type are represented by large crystals, 6-8 mm in length, with elevated BaO contents in the range of 1.2-2.7 wt.%, and Na_2O up to 1.3 wt.%. This type contains numerous inclusions of biotite and plagioclase. The second type of K-feldspar forms small (up to 1.0 mm), unzoned to patchy-zoned, interstitial grains. Biotite is strongly pleochroic and its colours range from pale-yellow (np) to dark red-brown (ng). It forms crystal clusters 0.5 to 1.0 mm in size and contains abundant inclusions of apatite and zircon, which often form pleochroic halloes. Biotite shows Mg/(Mg+Fe) ratios of 0.36 to 0.40 and up to 3.8 wt.% TiO_2. Primary muscovite associates with biotite. Secondary biotite contains high FeO (4.4-5.0 wt.%) and low MgO (1.2-2.3 wt.%) contents — Mg/(Fe+Mg) = 0.33-0.45.

Typical accessory minerals of the Bratislava Massif granitic rocks are zircon, fluorapatite, monazite-(Ce), xenotime-(Y), ilmenite, pyrite, and garnet with almandine>spessartine (VESELSKÝ & GBELSKÝ, 1978). Zircon forms low L and S morphological subtypes according to PUPIN (1980), and these L_1, S_1, S_2, S_6, and Q zircon subtypes indicate a low alkaline level during precipitation. Many zircons have been formed in at least two evolutionary stages, forming zircon rims in later fluid activity (Fig. 2b). To the best of our knowledge from the other Western Carpathians core mountains, this could be an effect of a Visean thermal overprint caused by intruded later granite pulses (BROSKA & SVOJTKA, 2020). Zircon saturation temperature according to WATSON & HARRISON (1983) indicates temperature $T \sim 750$ to 700 °C as a main interval for the magmatic crystallization of zircon, and it is lower in comparison to the Modra granite massif. Except for common primary magmatic monazite, which crystallized in the entire magmatic process (Fig. 2c), allanite was observed in accessory paragenesis as a product of the early crystallization phase before mainly monazite became a predominant carrier of rare earth elements (Fig. 2d).

The zircon U-Pb SHRIMP dating indicates a Mississippian (Lower Carboniferous) age of crystallization for the Bratislava Massif (355 ± 5 Ma; KOHÚT et al., 2009). However, the dating of the Bratislava Massif from Bratislava, Hlboká road site, which is located on the excursion route, indicates a somewhat older formation age (358 Ma, BROSKA et al., in preparation). The older granite age is closer to the ages of diatexites formed during decompression after Variscan collision; therefore, the granitic rocks from Hlboká cesta with S-(I)-type affinity belong to the earliest West-Carpathians post-collisional granites, which formed soon after the slab break-off or after the main Variscan collisional stage.

Diorites in the Bratislava Granite Massif

The dioritic body included in the Bratislava granite massif is observable at the Bratislava, Hlboká cesta (Hlboká road) site and shows a slightly older age than host granodiorite (ca. 359 Ma, paper in prep.). Dioritic rocks from the Hlboká cesta site have been investigated since the 19th century (see CAMBEL et al., 1981 and references therein, such as Kornhuber, 1857, Andrian and Paul, 1864). The former diorite descriptions considered diorite and the associated gabbroic rocks from the Hlboká cesta location as a basic magmatic differentiates of the Bratislava granite massif. Moreover, a wide hybrid (mixing) zone in the host granitic rocks around diorite bodies has been at that time described (see also KOUTEK & ZOUBEK, 1936; ZOUBEK, 1936). Later, diorites were suggested as the products of basic magmatism preceding felsic granodiorite/granite magmatic activities (CAMBEL et

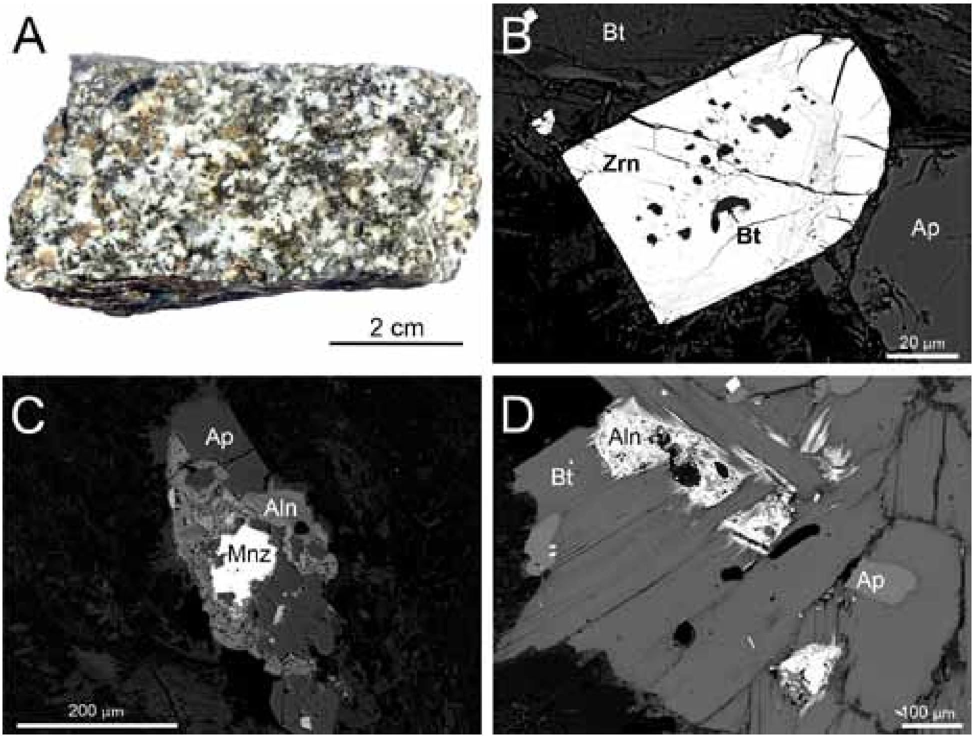

Fig. 2: Biotite granodiorite (a) and their accessory minerals on BSE images (b–d) from Bratislava, Hlboká cesta (the Bratislava granite massif); (b) zircon; (c) monazite-(Ce); (d) allanite-(Ce). Photo: A, B,D –Sergii Kurylo; C – Ivan Holický.

al., 1981; CAMBEL & VILINOVIČ, 1987) and it supports diorite age close to host granodiorite and features of its assimilation.

The diorite from Bratislava, Hlboká cesta is dark-grey, equigranular, and medium-grained, which indicates rapid cooling or rapid emplacement (Fig. 3a). It consists of (in vol%) plagioclase (20 to 50), amphibole (8 to 55), biotite (3 to 24), quartz (5 to 26), titanite (0.1 to 2.0), pyroxene (diopside) (0 to 1.5), and secondary chlorite and epidote (Fig. 3b). Zircon, fluorapatite, and allanite-(Ce) are the most common accessory minerals (Fig. 3c, d). Mixing with the host granite indicates its metaluminous/subaluminous character (ASI ~ 0.9). The diorite is enriched in Sr = 410-1660 ppm and Ba = 980-2340 ppm, pointing to its adakitic character (CAMBEL et al., 1981; CAMBEL & VILINOVIČ, 1987).

Plagioclase (An_{36-40}) is subhedral to euhedral and contains numerous apatite inclusions. A strong alteration towards albite + clinozoisite + albite aggregate is evident. The amphiboles are light-yellow to blue-green and have a composition ranging from magnesiohornblende to tschermakite ($Mg/(Mg+Fe^{2+})$ = 0.51–0.60). They form columnar and euhedral crystals with sizes ranging from 0.5 to 2.0 mm, but locally up to 4 mm. Euhedral biotite (up to 3 mm in size) shows intermediate annite to phlogopite a composition with Mg/(Mg+Fe) = 0.50-0.52 and 2-3 wt.% TiO_2. Zircon and fluorapatite inclusions are widespread in biotite. Zircon in diorite

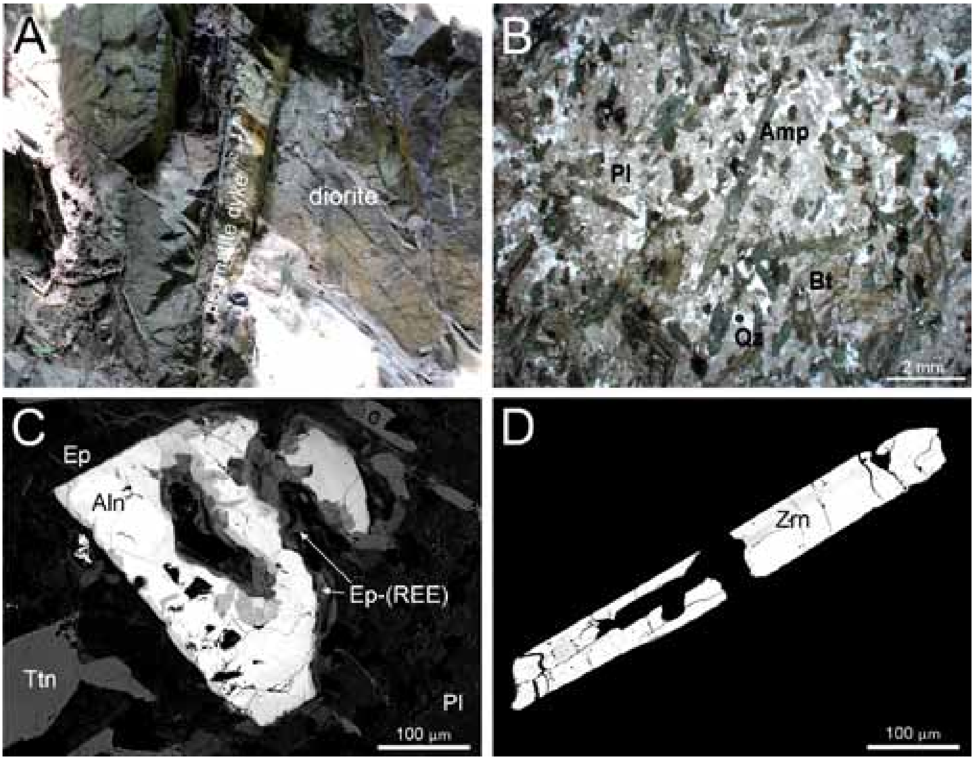

Fig. 3: Dioritic rocks of the Bratislava Massif (Bratislava, Hlboká cesta); (a) diorite with granitic pegmatite dyke (b): diorite in plane polarized light, green magnesiohornblende dominates; (c) allanite-(Ce); BSE; (d) zircon; BSE. Photo: Sergii Kurylo.

is acicular in comparison to zircons from the host granite, thereby indicating rapid growth due to the likely re-precipitation during the uplift and final emplacement. This is supported by the presence of acicular apatite as well. The zircon typology (according to PUPIN, 1980) shows the prevalence of subtypes L_1, S_1, S_2, S_6, Q_1, and Q_2; the zircon morphology is identical to the surrounding host (I-)S-type granites of the Bratislava granite massif (Fig. 3d).

Pegmatites in the Bratislava Granite Massif

Pegmatites are widespread in the Bratislava Massif. They occur as dykes (usually up to 5 m wide) placed either directly in the parental granite and diorite rocks (Fig. 3a) or in the adjacent metapelites-metapsammites and amphibolites. The pegmatites commonly form networks of several dykes, over 20 m long (e.g., on the nearby Bratislava castle hill, MADARÁS et al., 2014). Crossing of pegmatite dykes are typical as well: the pegmatites were emplaced in the cooling batholite that formed cracks with a-c perpendicular orientation. In general, the granite pegmatites show a zoning exhibiting a dominant coarse-grained alkali-feldspar + quartz + muscovite ± biotite unit (Fig. 4a), a graphic to blocky K-feldspar (grey microcline) unit (Fig. 4b,c) and a quartz core. Fine-crystalline aplite forms a wall

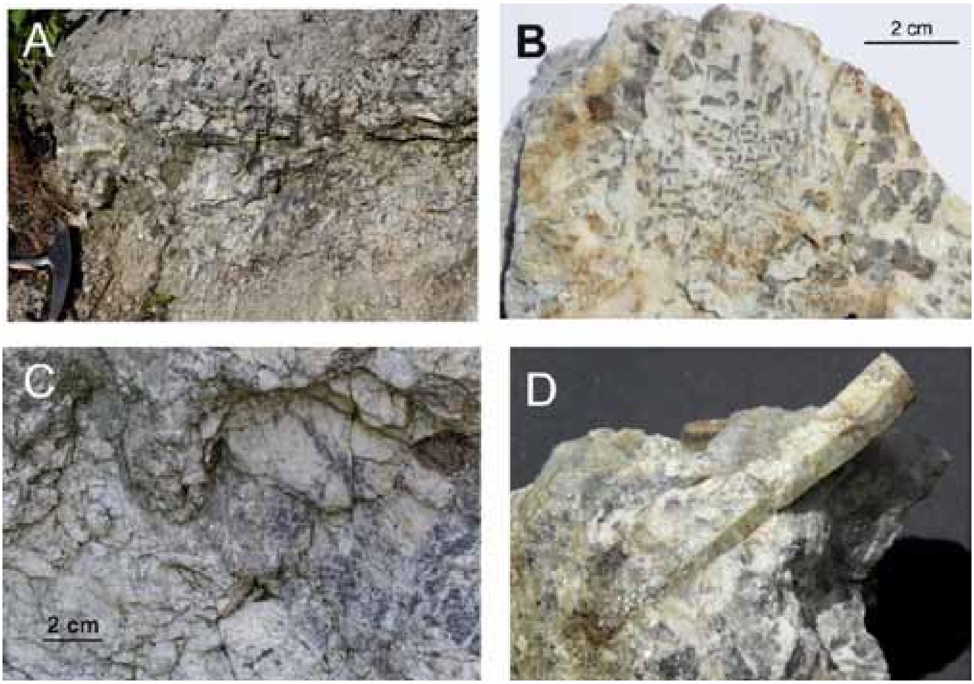

Fig. 4: Granitic pegmatites of the Bratislava massif; (a) blocky K-feldspar (microcline) and quartz zones; (b) graphic K-feldspar + quartz zone; (c) grey blocky K-feldspar (microcline) and late plumose mica; (a–c: Bratislava, Zuckermandel); Photo: Sergii Kurylo (d) beryl, 8 cm long crystal in quartz and K-feldspar (Bratislava, Hlboká Road, photo: J. Uhrová-Kernová).

zone of many pegmatites, whereas saccharoidal albite and fan-shaped muscovite aggregates form irregular replacement domains within the former coarse-crystalline pegmatite parts. Black, thin, tabular crystals of biotite (annite with 1.60-1.75 Al apfu (atoms per formula unit) and Fe/(Fe+Mg) = 0.66-0.71) extend up to 40 cm in length; they associate with pseudohexagonal platy muscovite crystals. The biotite composition corresponds to crystallization temperatures of 580-630 °C and 300-400 MPa pressure (according to the biotite geothermometer from HENRY et al., 2005 and the geobarometer according to UCHIDA et al., 2007). Garnet (almandine 50-60, spessartine 35-40, pyrope + grossular ≤ 5 mol. %) forms dark red, up to 8 cm-large euhedral crystals or crystal clusters, which are commonly corroded. Small pink crystals (0.1 to 2 mm in size) in thin garnet-rich layers in the saccharoidal albite aplite are typical. Accessory metamict zircon shows elevated contents of Hf (generally from 2 to 10, but rarely up to 22 wt. % HfO_2), P, and Y + HREE (UHER & ČERNÝ, 1998).

Rare columnar, pale-green beryl crystals (1 to 5, exceptionally up to 20 cm long) are associated with coarse-grained quartz, muscovite, and K-feldspar (Fig. 4d). The beryl is simple in its composition and exhibits moderately elevated contents of Na, Fe, and Mg, and is rarely enriched in Cs (UHER et al., 2010). Some highly fractionated pegmatite dykes of the Bratislava Massif contain accessory gahnite and Nb-Ta oxide minerals: columbite-(Fe) to tantalite-(Mn), rarely tapiolite-(Fe),

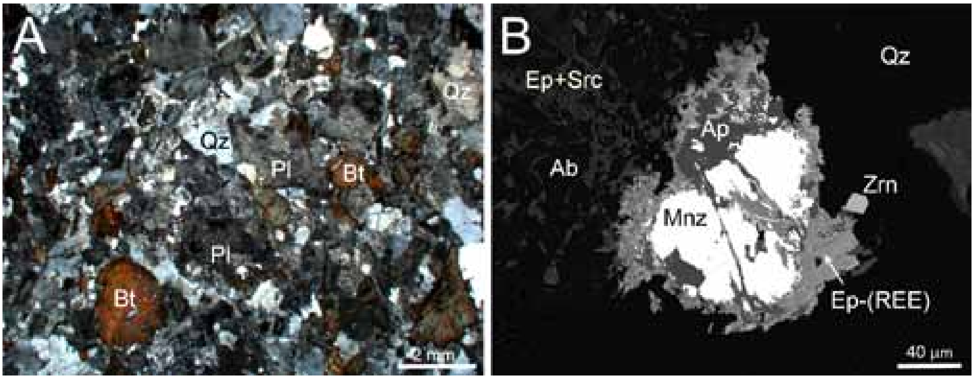

Fig. 5: Biotite granodiorite from Modra, Harmónia site (Modra massif); (a) photomicrograph of the rock; (b) monazite-(Ce) in association with REE-rich epidote and fluorapatite; BSE. photo: Sergii Kurylo.

ferrowodginite, and secondary microlite-group minerals (CHUDÍK et al., 2011). Consequently, the granitic pegmatites of the Bratislava granite massif are classified as rare-element, LCT family, and beryl-columbite subtype (according to ČERNÝ & ERCIT, 2005). Subsolidus fluid-driven hydrothermal alteration of beryl led to the formation of secondary phenakite, bertrandite, muscovite, and quartz (UHER et al., 2022), Moreover, hydrothermally formed native bismuth with oxidation rims of bismutite and bismite were found in Bratislava, Švábsky Hill pegmatite (ŠTEVKO et al., 2012). The radiometric dating of pegmatite minerals (muscovite Rb-Sr, monazite EMPA U-Th-Pb, columbite-tantalite in-situ U-Pb isotope; results obtained from the Bulgarian Academy of Sciences, Sofia) reveal an age of 350 to 360 Ma, similar or coeval to the parental Bratislava granite massif (UHER et al., 2014; unpublished data).

Modra Granite Massif

The representative locality of the Modra Granite Massif is situated in the Modra-Harmónia abandoned quarry. Modra granitic massif are mainly tonalites to granodiorites, less frequently granites, generally lower in SiO_2, and K_2O, but higher in TiO_2, FeO, MgO, and CaO in comparison with the Bratislava Granite Massif. The modal compositions of the Modra granitic rocks indicate the dominance of granodiorites and tonalites with (in vol. %) quartz (26-31), plagioclase (53-60), K-feldspar (0-5), and biotite (7-12) (Fig. 5a). Zircon dating by the U-Pb SHRIMP method shows solidification age of 347 ± 4 Ma (KOHÚT et al., 2009); however, other SHRIMP age shows slightly older magmatic formation age of ca. 353 Ma (BROSKA et al., in preparation). The presence of inherited zircon crystals indicates the Cambrian age of melted protolith. The biotite granodiorite from the Modra, Harmónia quarry is medium-grained (1.5 to 3.0 mm) rock with subhedral plagioclase, quartz, K-feldspar, and biotite; zircon, fluorapatite, monazite-(Ce), allanite-(Ce), and ilmenite are the predominant accessory minerals. Chlorite, epidote, titanite, and rutile belong to late secondary minerals.

Plagioclase is 1 to 3 mm in size, and it is strongly altered to clinozoisite + muscovite (sericite) + albite aggregates; the primary shape of the former plagioclase is locally defined only by secondary saussurite. The highest content of anorthite molecule

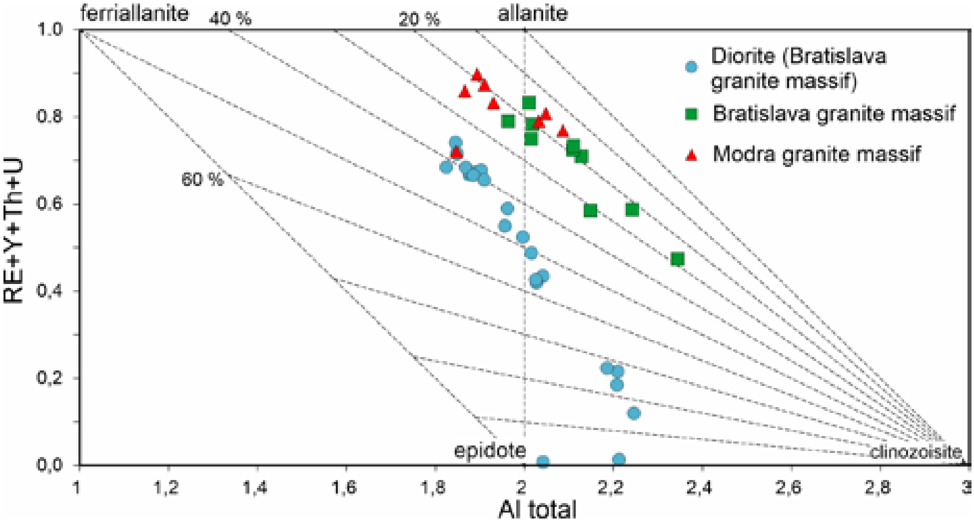

Fig. 6: Composition of allanite-(Ce) from diorites (BMD-1) and granodiorites (BMG-1) of the Bratislava granite massif and granodiorites of the Modra granite massif (MM-2).

($An_{22\text{-}25}$) was found in plagioclase with biotite inclusions, while plagioclase in the groundmass is more albitic (<An_{17}). K-feldspar is perthitic and anhedral, and occurs mainly as small interstitial grains (<0.5 mm), while larger individual crystals (0.8 to 1.0 mm) are rare. Compositional zoning is not observed due to the late hydrothermal equilibration. The BaO content ranges from 0.3 to 1.7 wt.% and locally up to 3.4 wt.%, while the Na_2O content is low (up to 0.5 wt.%). Biotite is represented by pale-yellow to red-brown, subhedral flakes (0.5 to 2.2 mm across) with low TiO_2 contents (ca. 1 wt.%).

Fluorapatite with very low Mn, Fe, and light REEs commonly forms prismatic, slightly zoned crystals with numerous zircon and ilmenite inclusions. Monazite-(Ce) occurs at Modra-Harmónia site in association with fluorapatite as an allanite-(Ce) precursor and contains very low ThO_2 content unsuitable for U-Th-Pb dating (up to 2.1 wt.%) (Fig. 5b). U-Th-Pb dating of monazite from other sites shows primary magmatic age of ca. 350 Ma.

Zircon usually forms transparent euhedral prismatic-dipyramidal crystals in biotite or quartz with dominant S_7 subtypes (ca. 55 %), but also a noticeable presence of a P_1 subtype (18 %), which indicates a peraluminous lower temperature and higher alkaline evolution trend of the parental magma (mean I.A = 393 and I.T = 358). Zircon crystals show 1.2 to 2.0 wt.% HfO_2 ($Zr/Hf_{wt.}$ = 28-50), ≤0.3 wt.% Y_2O_3, and ≤0.1 wt.% ThO_2 and UO_2.

Individual allanite-(Ce) crystals form subhedral and skeletal-zoned grains (up to 100 μm in size) included in plagioclase and close to fluorapatite–monazite-(Ce) clusters. Allanite-(Ce) is poor on Th; total REE is between 0.7 and 0.85 apfu. In the compositional diagrams Al_{tot} vs REE + Th + U (PETRÍK et al., 1995), allanite-(Ce) is generally similar to peraluminous granitic rocks and also similar to allanite-(Ce) from the Bratislava Massif, but it differs from allanite-(Ce) of the previously mentioned diorites (Fig. 6). Textural and compositional data indicate the following crystallization succession of REE-rich accessory minerals from the Modra, Harmonia quarry: primary allanite-(Ce) (magmatic) → primary monazite-(Ce) (late-magmatic) → secondary allanite-(Ce) to ferriallanite-(Ce) ± cheralite to huttonite or thorite phase (post-magmatic) → REE-bearing clinozoisite to epidote (post-magmatic).

Calc-silicate skarns in contact with Modra granodiorite

Intrusion of the Modra granites formed contact metamorphic aureole with local occurrences of calc-silicate skarns. The skarns, as well as metamorphosed marly limestones, form lens-shaped bodies within the phyllites, black shales, and basaltic metavolcanic rocks of the Dubová Formation (the Harmónia Group). The stratigraphic position and the rare fossils in metacarbonate rocks indicates Middle Devonian age of their formation (CAMBEL & PLANDEROVÁ, 1985).

Grossular, diopside, vesuvianite, wollastonite, epidote, titanite, and calcite have been previously described from the calc-silicate hornfels (CAMBEL, 1954; ČAJKOVÁ & ŠAMAJOVÁ, 1960; ŠÍMOVÁ & ŠAMAJOVÁ, 1979; KORIKOVSKIJ et al., 1985; CAMBEL et al., 1989) (Fig. 7a). Garnet (79-94 mol. % grossular, 5-19 mol. % andradite, 1-2 mol. % pyrope + spessartine; CAMBEL et al., 1989) forms up to 1 cm large porphyroblasts in calcite-quartz-diopside or vesuvianite-diopside-(wollastonite) groundmass. Zoning in the garnet composition is expressed by a decrease in Fe and Ti from the core to the rim. Titanium-rich vesuvianite (2.5-5.5 wt. % TiO_2, ~1-2 Ti apfu) show fine oscillatory zoning; some zones in vesuvianite contain up to 5.3 wt. % REEs (0.96 REE apfu; Ce>La,Nd,Pr>>Y,HREE), and 0.3-1.8 wt. % ThO_2 (0.03-0.21 Th apfu). Barium-rich K-feldspar (hyalophane variety) to celsian form 20-40 μm large subhedral to euhedral inclusions in vesuvianite; the barian K-feldspar contains 6-28 wt. % BaO or 12-59 mol. % of celsian, 29-79 mol. % orthoclase, 6-10 mol. % albite and 2-4 mol. % anorthite (UHER et al., in prep.). The REE-bearing vesuvianite was partially replaced by secondary allanite-(Ce) or REE-rich epidote along the fractures and rims (the composition is now being prepared for a new vesuvianite classification, UHER in preparation, Fig. 7b). Barium-poor K-feldspar and albite form intergranular anhedral grains in association with vesuvianite, grossular, and diopside; K-feldspar contains 0.6-0.9 wt. % BaO and shows an $Or_{94-97}Ab_{02-04}Cn_{01-02}An_{00}$ composition, while albite displays $Ab_{98-99}An_{01}$. Diopside inclusions in garnet are homogenous. In contrast, diopside in groundmass shows a zoning with a Fe enrichment in the rim of the grains. The peak metamorphic assemblage indicates pressure of ~150-200 MPa and temperature of ~550-650 °C with XCO_2 ~0.05-0.10 (KORIKOVSKY et al., 1985; CAMBEL et al., 1989).

Lower Paleozoic Pernek ophiolite complex and metamorphic V-Cr mineralization

The Modra Granite Massif intruded into the Devonian (meta)-ophiolite Pernek complex (Pernek Group), which is located NW of the town of Pezinok in the Hrubá Valley (Fig. 1b). The Pernek Group belongs to the Paleozoic basement of the Tatric Unit. It is formed mainly by metabasites with ocean-pelitic metasediments that

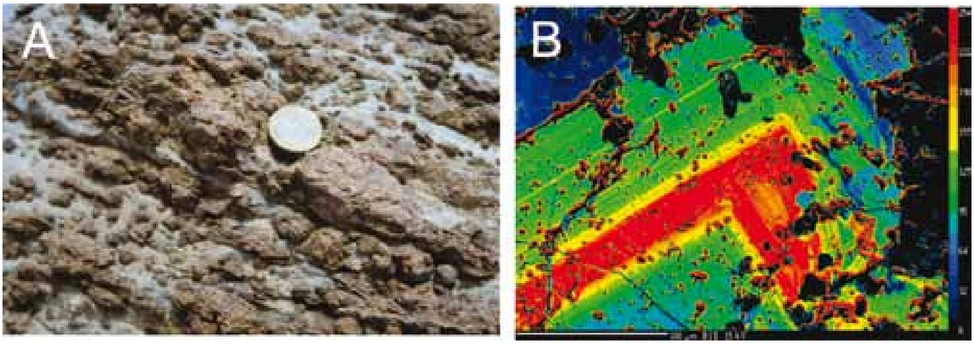

Fig. 7: Minerals of Ca-skarn in the contact-metamorphic aureole of the Modra Massif, Dubová, Horné Trávniky vineyards; (a) grossular (brownish red) in calcite. Photo: I. Broska; (b) BSE image of oscillatory zoned vesuvianite from Dubová Horné Trávniky, REE-Th rich zones in red. Photo: V. Kollárová.

are rich in organic carbon and volcanic admixtures (black schists; CAMBEL & KHUN, 1983; IVAN et al., 2001).

Several pyrrhotite-pyrite bearing horizons and small pyrite-pyrrhotite and Sb deposits occur in the Pernek complex. The Rybniček pyrite-pyrrhotite mine with its unique metamorphic minerals that are a result of overprinting by the regional Variscan metamorphism of the Pernek meta-ophiolite complex. Amphibole-pyrrhotite-pyrite metabastic rocks found in the Rybníček mine represent a special lithological type showing high concentrations of S, Corg, V, Cr, Ni, Cu, and other metallic elements (CAMBEL & KHUN, 1983). Here, a unique silicate mineralization with V and Cr-rich silicate phases is found. In the Rybníček mine, the amphibole-pyrrhotite-pyrite metabasic rocks contain 1150 ppm V and 760 ppm Cr (UHER et al., 2008), which resulted in the formation of V and Cr-bearing members of garnet, epidote, and mica-group minerals. The presence and evolution of accessory minerals in the black shales revealed three metamorphic stages forming distinct mineral assemblages. V-Cr metamorphic mineralization occurs in several pyrite-pyrrhotite enriched horizons in amphibole-rich metavolcanic-metasedimentary rocks within ophiolite sequences of the Pernek Group. These unusual metamorphic rocks contain Ca-rich silicate minerals (dominant amphiboles, less frequent pyroxene (diopside), garnet, albite, epidote-group minerals, micas, titanite, as well as common pyrite and/or pyrrhotite. The V-Cr garnets from the Rybníček mine form euhedral to subhedral emerald-green crystals (up to 3 mm in size; Fig. 8a, b) or aggregates with anomalous birefringence. Moreover, they associate with amphibole, albite, diopside, epidote-group minerals, pyrite, and pyrrhotite. The garnets exhibit a goldmanite-uvarovite-grossular composition (Fig. 8c) with V_2O_3 (5 to 22 wt. %), Cr_2O_3 (5 to 11 wt. %), and Al_2O_3 (1 to 13 wt. %); the molar end-member composition is following: goldmanite (16 to 72 mol. %), uvarovite (19 to 36 mol. %), and grossular (4 to 59 mol. %), cf. UHER et al. (1994, 2008 unpublished data).

Epidote-group minerals form euhedral to anhedral porphyroblasts (up to 0.5 mm in size) or fine-grained aggregates. Central parts of the porphyroblasts consist of V- and Cr-rich dissakissite-(La) with V ≤0.33 apfu, Cr ≤0.44 apfu, which continually alters to REE-rich mukhinite with REE ≤0.46 apfu and 0.13-0.43 Cr apfu (BAČÍK

& UHER, 2010). To date, the Rybníček mine is the second-known occurrence of dissakisite-(La) worldwide (Fig. 8d). Two generations of clinozoisite are present at the rim of dissakisite-(La)-mukhinite crystals. Clinozoisite I is V- and Cr-rich (V ≤0.40 apfu, Cr ≤0.42 apfu) forming overgrowths of the dissakisite-(La)-mukhinite cores. The second generation of V-, Cr-, and REE-poor clinozoisite II replaces mukhinite and clinozoisite I at the rim, as well as in the fissures of crystals (BAČÍK & UHER, 2010).

Muscovite forms subhedral, lamellar, greenish crystals up to 1 mm in size, in association with amphibole, quartz, and pyrite/pyrrhotite or tiny, up to 0.1 mm, subhedral to anhedral, colourless crystals in the groundmass. Two muscovite generations are recognized: V,(Cr)-rich muscovite I with 2.5–8 wt. % V_2O_3 and up to 7 wt. % Cr_2O_3 (0.12 to 0.45 and up to 0.39 apfu V and Cr, respectively) and V,Cr-free muscovite II with ≤0.4 wt. % V_2O_3 and Cr_2O_3 (UHER et al., 2008).

Amphiboles are the most common minerals, forming aggregates or individual euhedral to subhedral crystals. The amphiboles are classified as magnesiohornblende, actinolite, tremolite, and rarely edenite with a high Mg/(Mg+Fe) ratio of 0.84 to – 0.99. In some places, elevated V and Cr contents of up to 2.6 wt. % V_2O_3 (0.3 V apfu) and up to 0.9 wt. % Cr_2O_3 (0.1 Cr apfu) occur in the amphiboles; diopside contains up to 1.7 wt. % V_2O_3 and 0.4 wt. % Cr_2O_3 (UHER et al., 2008).

The V-Cr-rich mineral association in the amphibole-pyrrhotite-pyrite metabasic rocks indicates three main metamorphic stages.

(1) Early Variscan, low-grade greenschist-facies metamorphism (M1) resulted in a fine-grained silicate + carbonaceous matter + pyrite mineral assemblage in the mafic tuffitic rocks and formed metamorphic foliation.

(2) Intrusion of the Modra tonalites and granodiorites into the folded Lower Paleozoic volcano-sedimentary rocks caused the late Variscan, low-pressure contact metamorphism (M2) at P ≤200 MPa and T ≤580 °C (KORIKOVSKY et al., 1985; CAMBEL et al., 1989). This dominant metamorphic event (M2) overprinted the regional M1 metamorphism. The peak of the M2 metamorphism resulted in the crystallization of silicate minerals enriched in V and Cr (garnet, dissakisite-mukhinite, amphibole, diopside, muscovite I), the recrystallization of pyrite, and the formation of pyrrhotite. The U-Th-Pb electron-microprobe dating of accessory uraninite gave an age of 345-350 Ma (UHER, unpublished data), which is consistent with the known ages of the Modra granite massif. In other words, the V-Cr mineralization originated as a product of high-T and low-P skarn-like Variscan contact-metamorphism by the intrusion of the Modra Granite Massif, which overprinted V-Cr and Corg enriched mixed metabasite and sedimentary (black shale) oceanic protolith of the Pernek Group.

(3) The youngest M3 metamorphic event clearly shows a retrograde character in comparison to the M2 stage. During M3, a metamorphic association formed under prehnite-pumpellite facies conditions, which formed phases low in V and Cr (i.e., pumpellyite-(Mg), muscovite II, clinozoisite II, and prehnite, and possibly albite II and clinochlore II). Thin hydrothermal quartz + siderite veinlets, also associated with clinozoisite II, points to a remobilization during this latest post-kinematic event. This event is related to the thermal decline of M2 or more likely to the Alpine (Cretaceous) tectonometamorphic processes.

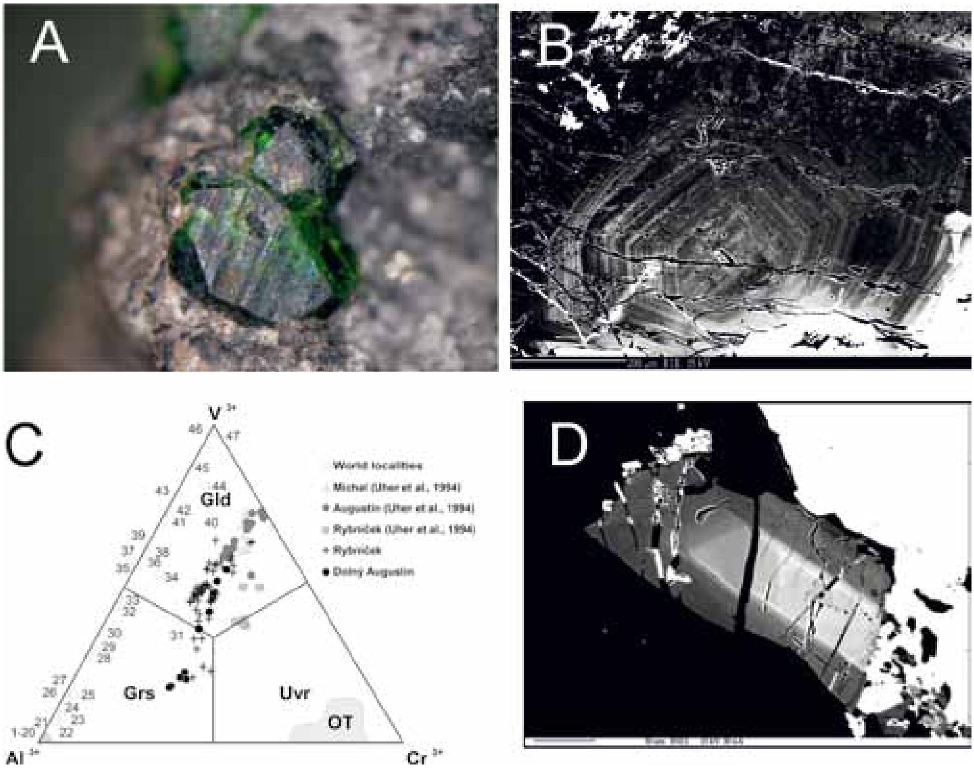

Fig. 8: Minerals of V-Cr metamorphic assemblage in black schists (amphibole-dominant metapyroclastic rocks enriched in C, V and Cr), the Pezinok, Rybníček mine; (a) emerald-green crystals of goldmanite garnet (up to 2 mm across), photo: A. Russ; (b) fine oscillatory zoning of goldmanite crystal, BSE, photo: V. Kollárová; (c) Compositional variations of garnet in the goldmanite (Gld) – grossular (Grs) – uvarovite (Uvr) triangular diagram (atomic proportions). Analyses of samples from the Pezinok area (Pernek Group) are compared with other world occurrences of V-Cr-rich garnets (OG: Ogcheon belt, South Korea, PB: Poblet area, Spain, OT: Outokumpu, Finland, numbers: other localities; UHER et al., 2008); (d) Zonal crystal of dissakisite-(La) to mukhinite in contact with pyrite (white), BSE; photo: P. Konečný.

Post-Variscan sedimentary record in the Malé Karpaty Mountains.: Lower Triassic quartzites with tourmalinite clasts

During the Permian period due to a long-termed uplift, the crystalline basement of the Malé Karpaty Mountains was exposed to weathering. New sedimentation was important for deciphering of geomorphology at that time. After Permian exposure of the Tatric basement, Triassic sedimentation started with the formation of Upper Permian (?) to Lower Triassic quartzites as the base of the Lúžna Formation. The Lúžna Formation (type locality Liptovská Lúžna, Central Slovakia) is composed of medium- to coarse-grained quartzites, quartzite to arkose sandstones, siltstones, and silty sandstones with intercalations of nearly monomict quartz conglomerates. The Lúžna Formation is widespread in the Tatric, Fatric, and Veporic Superunites (SAMUEL, 1985). Accumulations of conglomerates are locally found in quartzites, which are located only in the western part of the Tatric Unit, that is, the Malé Karpaty, the Považský Inovec, and the Tribeč Mountains (Figs. 9a,b, 10).

Fig. 9: Quartzites of the Lúžna Formation (Lower Triassic) with occurrences of tourmalinite clasts, Modra, Traja Jazdci outcrop; (a) quartzite rock; (b) conglomerate accumulation. Photo: P. Bačík.

The Lower Triassic quartzites are interpreted as continental deposits in a (semi-) arid climate, in which aeolian sediment transport prevailed with occasional flows, bringing coarse clastic detritus. The conglomerate intercalations are dispersed in the entire quartz mass. The clasts are concentrated in the middle of the layers and/or on their upper surface. The lateral decline of the pebble facies in quartzite is observable. Therefore, conglomerates do not form continuous, larger bodies (MIŠÍK & JABLONSKÝ, 1978).

There have been several hypotheses on the sedimentary environment during the formation of Lower Triassic quartzites, of which two are the most prominent. The first one was presented by FEJDIOVÁ (1971), who was inclined to the origin in a shallow-marine environment up to beach facies. She believed that a significant influence of long-flowing rivers for the transport of exotic materials. In contrast, MIŠÍK & JABLONSKÝ (1978; 2000) assumed a continental environment with an arid to semi-arid climate with a major influence of aeolian activity and the contribution of material by occasional flows. The transport directions of Lower Triassic quartzite material were evaluated based on the directions of crossbedding. The data correlate with the Eastern Alps (EISBACHER, 1963; MIŠÍK & JABLONSKÝ, 2000). More than 80 % of all crossbedding stratifications indicate paleotransport from N to NW, outside of the Carpathian Arc (Fig. 10). Dispersion can be caused by the influence of occasional flows, surface irregularities, later tectonic factors (rotation of some areas of the Western Carpathians), and especially by the presence of aeolian lamination. There are two theories about the source: MIŠÍK & JABLONSKÝ (2000) believed it to be on the eastern edge of the Czech Massif. MICHALÍK (1994) assumed the source of the Tatric Unit on the southeast of the Armorican Massif and consequently the French Massif Central could be acceptable as the source of clastic material (UHER, 1999). Later on, the entire Western Carpathians were shifted in the northeast direction. The absence of granitic pebbles may indicate a mechanical break-up in an arid desert climate where the granite clasts disaggregate into a monomineralic psammitic fraction. However, the clasts also come from metamorphic rocks (graphite schists, tourmalinites, lydites

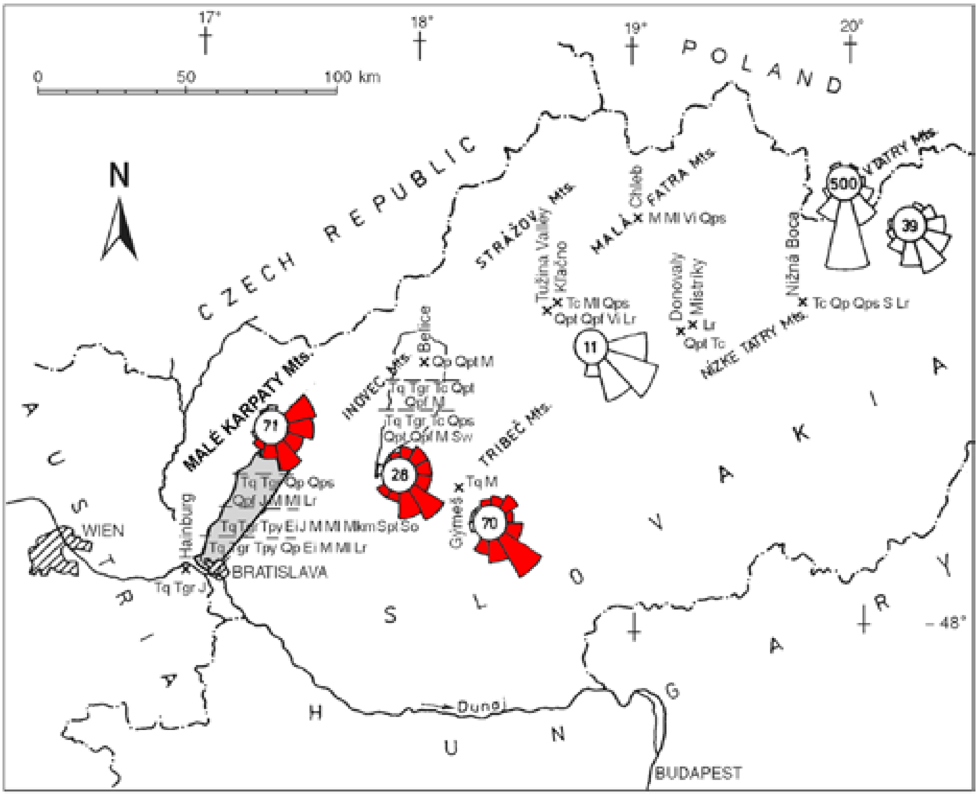

Fig. 10: Direction of crossbedding stratifications indicating the paleotransport from outside the Carpathian Arc (after MIŠÍK & JABLONSKÝ, 2000). Tourmalinites occur only in areas highlighted in red.

with radiolaria). Basic and acidic to intermediate volcanic rocks were not preserved due to their lower stability.

The conglomerate material consists of strongly dominant crystalline quartz; in general, other rocks are rare. They include tourmaline-rich rocks (tourmalinites), acidic, intermediate to basic volcanic rocks, red silicites (hematitic jaspers and metaquartzites), black silicites with organic remnants (silicified wood, silicites with ostracodes, radiolarite lydites, black and grey limnoquartzites), and graphitic metaquartzites (MIŠÍK & JABLONSKÝ, 2000).

Tourmalinites are the most remarkable component in the clast material of conglomerate accumulations found in the Lower Triassic quartzites of the western part of the Tatric Unit (Malé Karpaty, Považský Inovec, Tríbeč Mts). MIŠÍK & JABLONSKÝ (1978). The black quartz-tourmalinites are macroscopically fine-grained with sharp-edged white fragments. Pebbles with milky-white quartz and only dispersed tourmaline rarely occur. Cataclasis occurs quite frequently (Fig. 11). Microscopically, tourmalines frequently form zoned spherulites (Fig. 12). Prismatic crystals of tourmaline are often broken and healed with quartz; in contrast, the second generation of tourmaline fills cracks across the rock, which gives evidence for repeated cataclasis. Accessory zircon is present and sometimes muscovite, rutile, titanite, and epidote as well (MIŠÍK & JABLONSKÝ, 1978;

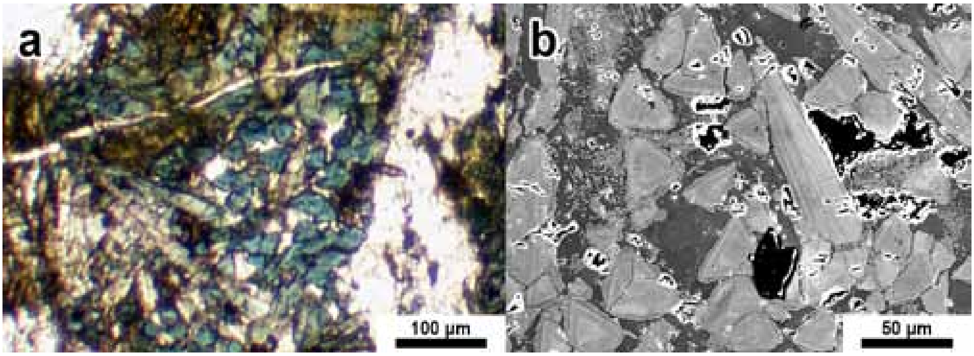

Fig. 11 Tourmalinite rock from Modra, Traja Jazdci; (a) image in transmitted light at parallel nicols Photo: P. Bačík; (b) BSE. Photo: D. Ozdín.

BAČÍK & UHER, 2007). Tourmalinized phyllites with distinct foliation were described by MIŠÍK & JABLONSKÝ (1978). Quartz aggregates form angular fragments elongated along the direction of foliation. Tourmaline forms bands of aggregates, but rarely spherulites. Light mica and baueritized biotite are commonly present. Titanite, accessory zircon, and hematite can also be found (MIŠÍK & JABLONSKÝ, 1978). Tourmalinized phyllites are (i) acid pyroclastic rocks forming black rock pebbles with a fine breccia structure and (ii) quartzites - two pebbles from Jablonové. Tourmaline spherulites are independent of the quartz aggregates (MIŠÍK & JABLONSKÝ, 1978). Tourmalinite clasts reach a size of up to 8 cm. Tourmaline is often zonal and blue on the rim of green or brown crystals. The second generation fills the cracks throughout the entire rock. The boron content in the rock was determined in three analyses to be 0.7 to 1.2 wt %, which corresponds to an approximate content of 40 % tourmaline in the rock.

A wide range of tourmaline compositions was described in the tourmalinite samples from Lower Triassic quartzites in the Western Carpathians (Fig. 13). Compositions corresponding to the schorl-dravite series occur most often. Less common are *X*-site vacant tourmalines – foitite and magnesio-foitite (BAČÍK & UHER, 2007). Low-Al tourmalines – low-Al schorl, low-Al dravite, and bosiite (described as povondraite – BAČÍK et al., 2008) are unique in the Bratislava – Devínska Kobyla area.

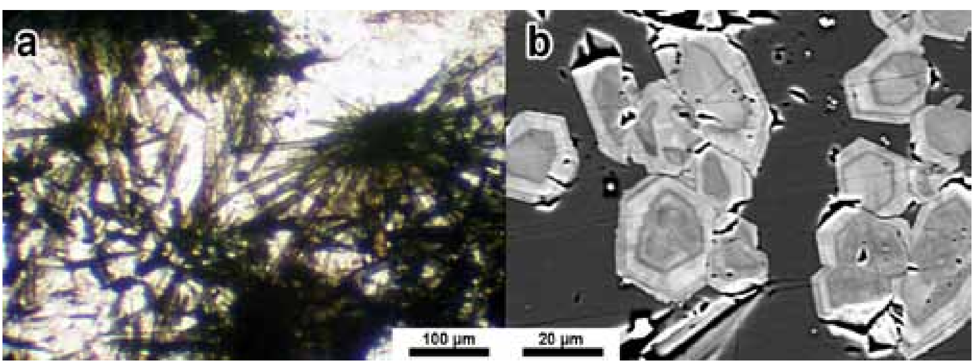

Fig. 12 Tourmalinite rock from Bratislava, Devínska Kobyla locality; (a) image in transmitted light at parallel nicols; (b) BSE Photo: P. Bačík; (b) BSE. Photo: D. Ozdín.

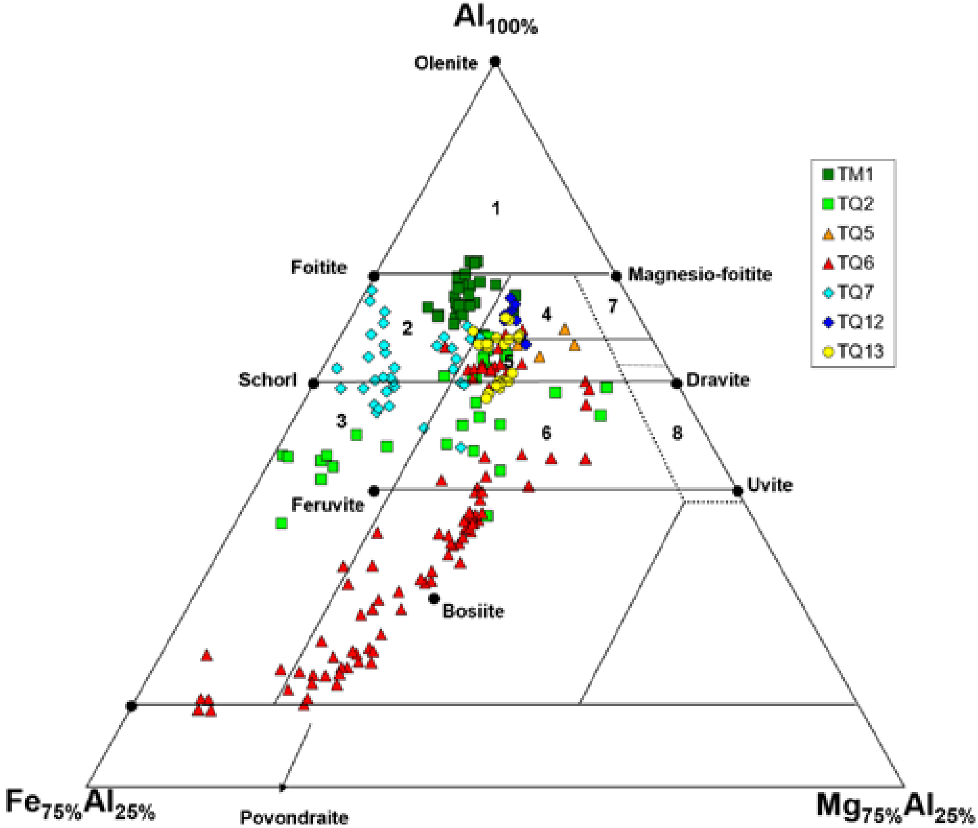

Fig. 13. Chemical composition of tourmaline from tourmalinite pebbles in Lower Triassic quartzites in triangular Al vs. Fe vs. Mg plot (in total molecular proportions). The fields represent distinct rock types: 1 – Li-rich granitic pegmatites and aplites; 2 – Li-poor granites and their associated pegmatites and aplites; 3 – Fe3+-rich quartz-tourmaline rocks (hydrothermally altered granites); 4 – Metapelites and metapsammites coexisting with an Al-saturating phase; 5 – Metapelites and metapsammites not coexisting with an Al-saturating phase. 6 – Fe3+-rich quartz-tourmaline rocks, calc-silicate rocks, and metapelites; 7 – Low-Ca metaultramafics and Cr,V-rich metasediments; 8 – Metacarbonates and meta-pyroxenites (HENRY & GUIDOTTI, 1985, modified).

Tourmalines of the schorl-dravite–povondraite series composition were studied in two samples of tourmalinite pebbles from Bratislava, Devínska Kobyla (BAČÍK et al., 2008). The investigated tourmalines belong to the schorl-dravite subgroup and they attain a bosiite composition by virtue of a visible schorl–dravite–povondraite trend that is partially overlapped by the schorl–feruvite trend. A significant portion of Fe^{3+} (at least 59 % of the total Fe) in the tourmaline was experimentally determined by Mössbauer spectroscopy; this result compares well with the cation-charge deficiency (Fe^{3+} up to 3.7 apfu). The Al content is usually lower than 5.0 apfu, locally reaching as little as 2.86 apfu. Moreover, the expansion of the structure in Fe^{3+}-rich tourmalines enables occupation of the *X* site by K atoms up to 0.03 apfu (BAČÍK et al., 2008).

The genesis of the tourmalinites is derived mainly from petrographic observations and the chemical composition of the tourmalines. By comparing the chemical composition and the textural appearance of tourmalines and tourmalinites, approximately three possibly genetically different groups of tourmalinites can be distinguished: (i) tourmalines with a higher Al content and vacancies at the *X*-site as compared to the schorl-foitite series. (ii) tourmalinites with low-Al tourmalines close to the schorl(dravite)-(feruvite)-bosiite-povondraite series. (iii) tourmalines with an intermediate schorl-dravite composition.

Samples from group (i) fall into the field of granites, associated pegmatites, and aplites (HENRY & GUIDOTTI, 1985). Any direct granitic or pegmatitic formation of the tourmalines is not necessarily evident; however, tourmalines generated fluids derived from granitic magmas, that is, from a melt that was geochemically related to granite (SMITH & YARDLEY, 1996) or leucocratic metamorphic rocks (TORRES-RUIZ et al., 2003). A similar chemical composition is also found for tourmalines from Gemeric granites (Western Carpathians), whose marginal zones were formed during late magmatic or hydrothermal processes; they have an increased Al content and an increased number of vacancies (BROSKA et al., 1999; KUBIŠ & BROSKA, 2005). Therefore, it is likely that the first type is connected to contact-metasomatic processes related to the granite intrusion.

The group (ii) tourmalinites with low-Al tourmalines could form in metasomatic processes in iron-rich environments with relatively high O_2 fugacities. The presence of Fe^{3+} confirms the increased oxidation potential of the environment, which was likely caused by the contribution of meteoric fluids (i.e., seawater). From the zoning of these samples, their probable volcanic-exhalative origin can be assumed, going along with a change in the oxidation-reduction potential of the environment caused by the contribution of meteoric (marine, possibly evaporitic) fluids.

Most analyses of the group (iii) tourmalinites from the Lower Triassic quartzites range between schorl and dravite, with a predominance of dravite. The analyses correspond to the composition of metapelites; however, coexistence with an Al-saturation phase is not verified. This composition is typical of most metasomatic tourmalinites associated with volcanic-exhalation deposits (HELLINGWERF et al., 1994; FRIETSCH et al., 1997); tourmalinites from such deposits are usually Mg-rich (SLACK, 1996).

It is also worth mentioning the spatial distribution of individual genetic types. The type (iii) tourmalinites (most likely sedimentary or exhalative) are the most widely distributed in the entire area of the Malé Karpaty and the Považský Inovec mountains. Tourmalinites that have formed by contact metasomatism occupy a small spatial extension in the area of the Modra part of the Malé Karpaty Mts. (TM1 - Traja Jazdci, TQ7 - Kamenná brána). This could have been influenced by the small size of the primary rocks, since the metasomatic aureoles were small and derived from the granitic intrusion. Tourmaline samples likely connected to volcanic-exhalative Fe deposits are geographically bound to the area of Bratislava, Devínská Kobyla. They may have resulted from the small spatial extent of this deposit type and the deposition of detrital tourmaline only in a rare bed of a wild stream. However, any interpretation of the spatial distribution with respect to the source area requires further investigation in combination with arguments from other minerals, e.g., zircon (BAČÍK & UHER, 2007; BAČÍK et al., 2008).

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Description of excursion stops in brief:

<u>Saturday 16/9/2023</u>

Bratislava, Hlboká cesta (Hlboká Road)

Large outcrop in granodiorites, diorites to gabbroic rocks and dykes of granitic pegmatites (the Bratislava granite massif).

Bratislava, outcrop along staircase to Slavín monument

Paleozoic metapelites-metapsammites (paragneisses) originated by periplutonic contact metamorphism during emplacement of the Bratislava granite massif.

Pezinok, Hrubá Valley

Introduction to geology of the Pezinok and Pernek groups, recumbent fold in abandoned quarry.

Pezinok, Rybníček

V-Cr metamorphic mineralization in black schists of the Pernek Group (Devonian ophiolite complex).

Modra-Harmónia (abandoned quarry in granites)

I-type Modra granodiorite with contact metamorphic low-grade skarn.

Modra- Harmónia (abandoned quarry in skarns)

Calc-silicate skarns were formed in contact with Devonian limestone and Modra granodiorite.

<u>Sunday 17/9/2023</u>

Bratislava castle

Outcrop in the S-type granite; pegmatite textures of the Bratislava granite massif (observation on castle wall).

Bratislava-Zuckermandel

Pegmatites and aplites in the Bratislava granite massif outcrops.

Bratislava, Devín castle hill

Paleozoic phyllites, Upper Permian conglomerates, Lower Triassic quartzites and Lower Jurassic breccias, confluence of Danube and Morava rivers, views to Hainburg (Hundsheim) Hills in Austria.

References

BAČÍK, P. & UHER, P. (2007): Tourmaline group minerals from redeposited tourmalinites in Lower Triassic quartzites, Tatric Unit, Western Carpathians. – Mineralia Slovaca 29:185–196 (In Slovak, English summary).

BAČÍK, P. UHER, P, SÝKORA, M. & LIPKA, J. (2008): Low-Al tourmalines of the schorl-dravite - povondraite series in redeposited tourmalinites from the Western Carpathians, Slovakia. - Canadian Mineralogist, 46:1117–1129.

BAČÍK, P. & UHER, P. (2010): Dissakisite-(La), mukhinite, and clinozoisite: (V,Cr,REE)-rich members of the epidote group in amphibole - pyrite - pyrrhotite metabasic rocks from Pezinok, Rybníček mine, Western Carpathians, Slovakia. - Canadian Mineralogist 48: 523–536.

BROSKA, I., UHER, P. & SIMAN, P. (1999): Na sodík chudobný skoryl a foitit v spišsko-gemerských granitoch. - Mineralia Slovaca 31:507–512.

BROSKA, I., PETRÍK, I., BE`ERI-SHLEVIN, Y., MAJKA, J., & BEZÁK, V. (2013): Devonian/Missisipian I-type granitoids in the Western Carpathians: a subduction-related hybrid magmatism. - Lithos 162–163: 27–36.

BROSKA, I. & SVOJKA, M. (2020): Early Carboniferous successive I/S granite magmatism recorded in the Malá Fatra Mountains by LA-ICP-MS zircon dating (Western Carpathians). - Geologica Carpathica 71: 391-401.

BROSKA, I., JANÁK, M., SVOJTKA, M., YI, K., KONEČNÝ, P., KUBIŠ, M., KURYLO, S., HRDLIČKA, M. & MARASZEWSKA, M. (2022): Variscan granitic magmatism in the Western Carpathians with linkage to slab break-off. - Lithos 412: 106589.

DAVIES, J.H. & von BLANCKENBURG, F. (1995): Slab breakoff: A model of lithosphere detachment and its test in the magmatism and deformation of collisional orogens. - Earth and Planetary Science Letters 129, 85-102.

CAMBEL, B., MEDVEĎ, J. & PITOŇÁK, P. (1981): Geochemie und Petrogenese dioritischer Gesteine der Kleinen Karpaten. - Geologický Zborník Geologica Carpathica 32:189–220.

CAMBEL, B. & KHUN, M. (1983): Geochemical characterisation of black shales from the ore bearing complex of strata of the Male Karpaty Mts. - Geologický Zborník Geologica Carpathica 34: 255–382.

CAMBEL, B. & PLANDEROVÁ, E. (1985): Biostratigraphic evaluation of metasediments in the Malé Karpaty Mts. region. - Geologický Zborník Geologica Carpathica 36: 683–701.

CAMBEL, B. & VILINOVIČ, V. (1987): Geochemistry and petrology of the granitic rocks of the Male Karpaty Mts. - Veda, Bratislava 1-247 (in Slovak with English resume).

CAMBEL, B. KORIKOVSKY, S.P., MIKLOS, J. & BORONICHIN, V. (1989): Calc-silicate hornfelses (erlans and Ca-skarns) in the Male Karpaty Mts. region. - Geologický Zborník Geologica Carpathica 40: 281–304.

ČAJKOVÁ, M. & ŠAMAJOVÁ, E. (1960): Contribution to topographic mineralogy of the Malé Karpaty Mountains. - Acta Geologica Geographica Universitatis Comenianae, Geologica 4:51–67 (in Slovak).

ČERNÝ, P. & ERCIT, T.S. (2005) Some recent advances in the mineralogy and geochemistry of Nb and Ta in rare-element granitic pegmatites. - Bull Mineral 108:499-532.

CHUDÍK, P., UHER, P., GADAS, P., ŠKODA, R. & PRŠEK J. (2011): Niobium-tantalum oxide minerals in the Jezuitské Lesy granitic pegmatite, Bratislava Massif, Slovakia: Ta to Nb and Fe to Mn evolutionary trends in a narrow Be,Cs-rich and Li,B-poor dike. - Mineralogy and Petrology 102:15–27.

EISBACHER, H. (1963): Primäre gerichtete Gefüge und Paläogeographie des alpinen Buntsandstein im Raume Innsbruck - Saalfelden. Veröff. Ferdinandeum Innsbruck, 43:113–141

FEJDIOVÁ, O. (1971): Sedimentary petrology of the Lower Triassic quartzites from the Vysoké Tatry and Malé Karpaty envelope units. – Geologický Zborník - Geologica Carpathica 22: 49–77.

FRIETSCH, R., TUISKU, P., MARTINSSON, O. & PERDAHL, J.A. (1997): Early Proterozoic Cu-(Au) and Fe ore deposits associated with regional Na-Cl metasomatism in northern Fennoscandia.- Ore Geology Review 12:1–34

IVAN, P., MÉRES, Š., PUTIŠ, M. & KOHÚT, M. (2001): Early Paleozoic metabasalts and metasedimentarz rocks from the Malé Karpaty (Western Carpathians): Evidence for rift basin and ancient oceanic crust . – Geologica Carpathica 52: 67–78.

HELLINGWERF, R.H., GATEDAL, K., GALLAGHER, V. & BAKER, J.H. (1994): Tourmaline in the central Swedish ore district. - Mineralium Deposita 29:189–205.

HENRY, D.J., GUIDOTTI, C.V. & THOMSON, J.A. (2005): The Ti-saturation surface for low-to-medium pressure metapelitic biotites: Implications for geothermometry and Ti-substitution mechanisms. - American Mineralogist 90: 316–328.

HENRY, D,J., GUIDOTTI, C.V. & THOMSON, J.A. (2005): The Ti-saturation surface for low-to-medium pressure metapelitic biotites: Implications for geothermometry and Ti-substitution mechanisms. - American Mineralogist 90: 316–328.

KOHÚT, M., UHER, P., PUTIŠ, M., ONDREJKA, M., SERGEEV, S., LARIONOV, A. & PADERIN, I. (2009): SHRIMP U-Th-Pb zircon dating of the granitoid massifs in the Malé Karpaty Mountains (Western Carpathians): evidence of Meso-Hercynian successive S- to I-type granitic magmatism. - Geologica Carpathica 60: 345–350.

KORIKOVSKY, S.P., CAMBEL, B., MIKLÓŠ, J. & JANÁK, M. (1984): Metamorphism of Malé Karpaty crystallinikum: Stages, zoning, connection to granites. - Geologický Zborník – Geologica Carpathica 35: 437–462 (in Russian).

KORIKOVSKY, S.P., CAMBEL, B., BORONIKHIN, V.A., PUTIŠ, M. & MIKLÓŠ, J. (1985): Phase equilibria and geothermometry of metapelite hornfels adjacent of the Modra granite massif (Malé Karpaty). - Geologický Zborník – Geologica Carpathica 36: 51–74 (in Russian).

KOUTEK, J. & ZOUBEK, V. (1936): Explanation to the geological map in a scale 1:75 000, sheet Bratislava 4758. - Knihovna Státního geologického ústavu ČSR 18:1–150 (In Czech with French summary)

KUBIŠ, M. & BROSKA, I. (2005): Role of boron and fluorine in evolved granitic rock systems (on example Hnilec area, Western Carpathians). - Geologica Carpathica 56:193–204.

MADARÁS, J., BUČOVÁ, J., BROSKA, I. & PETRÍK, I. (2014): Petrography and tectonics of medieval quarry on the northern terrace of the Bratislava Castle. - (In: Bratislavský hrad: dejiny, výskum a obnova), 277–284, (Mestský ústav ochrany pamiatok v Bratislave: Slovenské národné múzeum - Historické múzeum), Bratislava (in Slovak, English resume).

MARASZEWSKA M., BROSKA, I., KOHÚT, M., YI, K., KONEČNÝ P. & KURYLO, S. (2022): The Ďumbier-Prašivá high K calc- alkaline granite suite (Low Tatra Mts., Western Carpathians): Insights into their evolution from geochemistry and geochronology. - Geologica Carpathica 73: 273–291.

MICHALÍK, J. (1994): Notes on the paleogeography and paleotectonics of the Western Carpathian Area during the Mesozoic. - Mitteilungen der Österreischen Geologischen Gessellschaft 86:101–110

MIŠÍK, M. & JABLONSKÝ, J. (1978): Lower Triassic quartzites and conglomerates in Malé Karpaty Mts. (pebble analysis, transport directions, genesis). - Acta Geologica Geographica University Comenianae 33: 5–36 (in Slovak, German summary).

MIŠÍK, M. & JABLONSKÝ, J. (2000): Lower Triassic quartzites of the Western Carpathians: source of clastics, transport directions. - Geologica Carpathica 51:251–264.

PETRÍK, I. & BROSKA, I. (1994): Petrology of two granite types from the Tribeč Mountains, Western Carpathians: an example of allanite (+magnetite) versus monazite dichotomy. - Geological Journal 29: 59–78.

PETRÍK, I., BROSKA, I., LIPKA, J. & SIMAN, P. (1995): Granitoid allanite-(Ce): substitution relations redox conditions and REE distributions (on example of I-type granitoids, Western Carpathians, Slovakia). - Geologica Carpathica 46: 79–94.

PLAŠIENKA, D, GRECULA, P, PUTIŠ, M, KOVÁČ M. & HOVORKA, D. (1997): Evolution and structure of the Western Carpathians: an overview. – (In: Grecula, P., Hovorka, D., Putiš, M. (eds) Geological evolution of the Western Carpathians), 1-24 (Mineralia Slovaca – Monograph), Bratislava.

POLÁK M., PLAŠIENKA D., KOHÚT M., PUTIŠ M., BEZÁK V., FILO I., OLŠAVSKÝ M., HAVRILA M., BUČEK S., MAGLAY J., ELEČKO M., FORDINÁL K., NAGY A., HRAŠKO Ľ., NÉMETH Z., IVANIČKA J. &

BROSKA, I. (2011): The Malé Karpaty Mts. Geological map in a scale M = 1:50 000. - Dionýz Štúr State Institute of Geology.

PUPIN, J.P. (1980): Zircon and granite petrology. - Contributions to Mineralogy and Petrology 73: 207–220.

SAMUEL, O. (1985): Lúžňanské súvrstvie. (In: Andrusov D and Samuel O (eds): Stratigrafický slovník Západných Karpát), 40–41, (Geol. Ústav. D. Štúra), Bratislava.

SLACK, J.F. (1996): Tourmaline associations with hydrothermal ore deposits. – Review in Mineralogy 33:559–643.

SMITH, M.P. & Yardley, B.W.D. (1996): The boron isotopic composition of tourmaline as a guide to fluid processes in the southwestern England orefield: An ion microprobe study. - Geochimica at Cosmochimica Acta 60:1415–1427.

STAMPFLI, G.M. & BOREL, G.D. (2002): A plate tectonic model for the Paleozoic and Mesozoic constrained by dynamic plate boundaries and restored synthetic oceanic isochrons. - Earth and Planetary Science Letters 196: 17–33.

ŠÍMOVÁ M. & ŠAMAJOVÁ, E (1979): Indications of the contact metamorphism in the Dolinkovský hill area, Malé Karpaty Mountains. - (In: Cambel B (ed.) Petrogenesis and geochemistry of geological processes symposium), 223–229, (Veda), Bratislava (in Slovak).

ŠTEVKO, M., UHER, P. & OZDÍN, D. (2012): Bismuth and its alteration products: accessory minerals of beryl type granitic pegmatite from Bratislava, Švábsky Hill (Malé Karpaty Mts., Slovakia). - Bull Mineral-Petrol Odd. Nár Muz (Praha) 20: 226–229 (in Slovak, English abstract).

TORRES-RUIZ, J, PESQUERA, A, Gil-CRESPO, P.P. & VELILLA, N. (2003): Origin and petrogenetic implications of tourmaline-rich rocks in the Sierra Nevada (Betic Cordillera, southeastern Spain). - Chemical Geology 197: 55–86.

UCHIDA, E, ENDO, S. & MAKINO, M. (2007): Relationship between solidification depth of granitic rocks and formation of hydrothermal ore deposits. - Resource Geology 57: 47–56.

UHER, P., CHOVAN, M. & MAJZLAN, J. (1994): Vanadian-chromian garnet in mafic pyroclastic rocks of the Malé Karpaty Mts., Western Carpathians, Slovakia. - Canadian Mineralalogist 32: 319–326

UHER, P. (1999): Clasts of tourmaline-rich rocks in Lower Triassic quartzites, the Tatric unit, Central Western Carpathians: tourmaline composition and problem of source areas. - Geologica Carpathica 50:140–141.

UHER, P. & ČERNÝ, P. (1998): Accessory zircon in Hercynian granitic pegmatites of the Western Carpathians, Slovakia. - Geologica Carpathica 49: 261–270

UHER, P., KOVÁČIK, M., KUBIŠ, M., SHTUKENBERG, A. & OZDÍN, D. (2008): Metamorphic vanadian-chromian silicate mineralization in carbon-rich amphibole schists from the Malé Karpaty Mountains, Western Carpathians, Slovakia. – American Mineralogist 93: 63–73

UHER, P., CHUDÍK, P., BAČÍK, P., VACULOVIČ, T. & GALIOVÁ, M (2010): Beryl composition and evolution trends: an example from granitic pegmatites of the beryl-columbite subtype, Western Carpathians, Slovakia. - Journal of Geosciences 55: 69–80

UHER, P, KOHÚT, M., ONDREJKA, M., KONEČNÝ, P., & SIMAN, P. (2014): Monazite-(Ce) in Hercynian granites and pegmatites of the Bratislava Massif, Western Carpathians: compositional variations and Th-U-Pb electron-microprobe dating. - Acta Geologica Slovaca 6: 215–231

UHER, P., OZDÍN, D., BAČÍK, P., ŠTEVKO, M., ONDREJKA, M., RYBNIKOVA, O., CHLÁDEK, Š., FRIDRICHOVÁ, J., PRŠEK, J. & PUŠKELOVÁ, Ľ. (2022): Phenakite and bertrandite: products of post-magmatic alteration of beryl in granitic pegmatites (Tatric Superunit, Western Carpathians, Slovakia). - Mineralogical Magazine 86: 715–729

VESELSKÝ, J. & GBELSKÝ J. (1978): Results of accessory mineral investigation from granitoids and pegmatites of the Malé Karpaty. Acta Geoologica Geographica Universita Comeniannae 33, 91–112 (in Slovak).

WATSON, E.B. & HARRISON, T.M. (1983): Zircon saturation revisited: temperature and composition effects in a variety of crustal magma types. - Earth and Planetary Science Letters, 64:295–304

ZOUBEK, V. (1936): Diorites from the vicinity of Bratislava as an example of magma differentiation in situ. - Věda Přírodní 17: 222–225 (In Czech, French abstract).