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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

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Abstract: Representative granitic rock samples from the Malé Karpaty Mountains of the Western Carpathians (Slovakia) were dated by the SHRIMP U-Th-Pb isotope method on zircons. Oscillatory zoned zircons revealed concordant Mississippian magmatic ages: 355 ± 5 Ma in Bratislava granodiorite, and 347 ± 4 Ma in Modra tonalite. The results document nearly synchronous, successive Meso-Hercynian plutonic events from S-type to I-type granites. The Neo-Proterozoic inherited zircon cores (590 ± 13 Ma) were identified in the Bratislava S-type granitic rocks whereas scarce Paleo-Proterozoic inherited zircons (1984 ± 36 Ma) were detected within the Modra I-type tonalites.

Key words: Western Carpathians, Malé Karpaty Mts, Bratislava Massif, Modra Massif, granitic rocks, zircon, SHRIMP dating.

Introduction

A typical feature of the Hercynian orogeny in Europe is production of voluminous felsic igneous rocks during the subduction-collisional processes. The granitic rocks form an important constituent of the Western Carpathians basement (WCB). Geodynamic evolution of the WCB is comparable to the other Hercynides of Western and Central Europe, such as the Iberian Massif, Massif Central, Bohemian Massif. Peraluminous S-type, calk-alkaline I-type, post-orogenic subalkaline A-type and ore specialized S_s-type of granitic rocks were identified in the Western Carpathians (see review of Petrík et al. 2001). However, Carboniferous S-type granodiorites — granites and I-type tonalites — granodiorites dominate in the WCB at the present erosion level and their distribution is associated with distinct thermal and tectonic events. Available isotopic datings (Rb-Sr WR isochrons, conventional U-Pb zircon data) suggest a time gap (30–40 Ma) in the genesis of the two types of granitic rocks (Petrík et al. 2001). However, there is still a general lack of modern isotope data within the WCB.

The aim of our study is to present the new age relationship and discuss the evolution of both S- and I-type granitic rocks from the Malé Karpaty Mts using the SHRIMP U-Th-Pb dating on zircon.

Geological setting

The Malé Karpaty Mountains represent a typical core mountain of the Tatric Unit situated in Western Slovakia, a SW part of the Central Western Carpathians. The Bratislava and the Modra granitic massifs are dominant parts of the Malé Karpaty Mts forming their pre-Alpine basement between Bratislava and Modra towns (Fig. 1), and in the Hundsheimer Berge on the right side of the Danube river near Hainburg town, NE Austria.

The granitic rocks of the Malé Karpaty Mountains consist of a Hercynian orogeny related plutonic peraluminous granitic suite with S-type (Bratislava Massif) and calc-alkaline I-type (Modra Massif) geochemical affinity (e.g. Cambel & Vilinovič 1987; Petrík et al. 2001). They exhibit a distinct intrusive and thermal metamorphic contact with adjacent Lower Paleozoic (Silurian to Devonian) metapelites to metapsammites and amphibolitic metabasic rocks (Korikovsky et al. 1984; Korikovsky in Krist et al. 1992). The dominant rocks of the Bratislava Massif are biotite to muscovite-biotite granodiorites, monzogranites to leucocratic syenogranites and widespread pegmatite-aplite dikes, whereas biotite (leuco)tonalites and granodiorites and subordinate to lacking granites and pegmatites are typical features of the Modra Massif (Cambel & Vilinovič 1987; Petrík et al. 2001). Small bodies of biotite-amphibole diorites occur in both massifs. The first K-Ar isotopic geochronological data for K-feldspar and micas from the Bratislava Massif indicated mainly Upper Paleozoic, Carboniferous to Permian ages (348~281 Ma, Kantor 1959; Bagdasaryan et al. 1977), which were later also confirmed by the whole-rock Rb-Sr isochrone age (347 ± 4 Ma, Bagdasaryan et al. 1982), and Th-U-Pb electron-microprobe monazite dating (355 ± 18 Ma, Finger et al. 2003; 353 ± 2 Ma, Uher et al. submitted). Geochronological

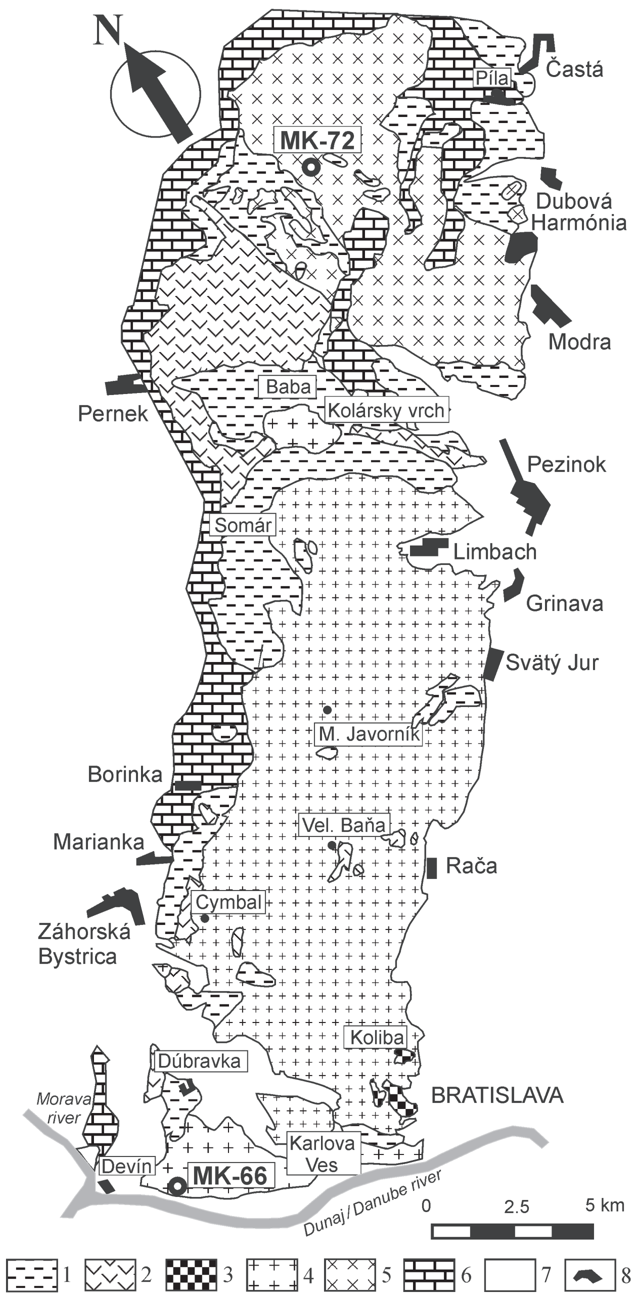

Fig. 1. Position of the studied granitic rocks in the Bratislava and Modra Massifs of the Malé Karpaty Mts [simplified geological sketch modified from Cambel & Vilinovič (1987)]. Explanations: **1** — Lower Paleozoic metasedimentary rocks en bloc, **2** — metabasic rocks, **3** — diorites, **4** — granitic rocks of the Bratislava Massif, **5** — granitic rocks of the Modra Massif, **6** — Mesozoic rocks en bloc, **7** — Cenozoic sedimentary rocks en bloc, **8** — settlement.

data from the Modra Massif revealed slightly younger Hercynian ages: 326±22 Ma by the whole-rock Rb-Sr isochron method (Bagdasaryan et al. 1982), ~320 Ma by the zircon U-Pb dating (Scherbak et al. 1988), and 345±22 Ma by the Th-U-Pb electron-microprobe dating of monazite (Finger et al. 2003), respectively 355±18 Ma from identical sample MK-72 (Kohút, unpublished data). However, some K-Ar data from both the Bratislava and Modra Massifs also gave younger, Paleo-Alpine Jurassic to Cretaceous ages (190 to ~80 Ma, Bagdasaryan et al. 1977; Bagdasaryan in Cambel et al. 1990).

Sampling and methods

For the SHRIMP dating, the following samples were selected:

MK-66: *medium-grained, slightly porphyric biotite granodiorite. Bratislava-Devín, large operating quarry, [48°09′47.54″ N; 17°00′17.81″ E, alt. 226 m]. This sample consists of 34.4 vol. % of quartz, 37.8 vol. % of plagioclase, 18.5 vol. % of K-feldspar, 8.1 vol. % of biotite, 0.3 vol. % of muscovite, and 1.0 vol. % of accessories (zircon, apatite, monazite, ilmenite); Eltinor point count = 2173.*

MK-72: *medium-grained biotite tonalite. Modra-Piesok, natural outcrops in the Krištofka area, [48°23′45.12″ N; 17°14′37.06″ E, alt. 548 m]. Mineral content is: 32.6 vol. % of quartz, 49.1 vol. % of plagioclase, 5.2 vol. % of K-feldspar, 11.4 vol. % of biotite, and 1.7 vol. % of accessories (apatite, zircon, allanite, epidote, monazite, magnetite); Eltinor point count = 2254.*

The heavy-mineral separation of accessory zircon was performed at the Comenius University and Geological Institute, Slovak Academy of Sciences in Bratislava, using a common separation procedure (crushing, sieving, gravitation separation by using Wilfley table, heavy liquid — bromophorm, and electro-magnetic separation). Euhedral transparent crystals of zircon, usually 150 to 450 μm in size, were selected for dating. The zircon sample preparation and the SHRIMP dating were done at the All-Russian Geological Research Institute (VSEGEI) in St.-Petersburg; the procedure includes BSE, CL (using CamScan MX 2500S with detector CLI/QUA 2) and optical imaging of the polished mounts with zircon crystals for the choice of the measured spots. The age measurements were performed using the SHRIMP II apparatus, the high-resolution five-collector secondary ion mass-spectrometer (ion microprobe) of ASI (Australian Scientific Instruments) zircon TEMORA was used as the standard (Black et al. 2003). The ion beam on the dating area was 25 μm in diameter. Nearly all the measured spots provided concordant ages, which fall on calculated concordia curves. Reproducibility of concordant zircon U-Pb analyses (10 measurements) is 1.5 % or better. Error in standard calibration was 0.54 %. In both measured samples, 10 spots from 5 or 6 different zircon crystals have been measured per rock sample. Detailed methodics concerning measurement and age calculations can be found in the works of Larionov et al. (2004) and/or Putiš et al. (2008). The measured isotope data are summarized in Tables 1 and 2.

Results

The SHRIMP dating reveals three distinct concordant to nearly concordant age populations in the Bratislava Massif: (1) Neo-Proterozoic to Cambrian, (2) Mississippian Meso-Hercynian, and (3) Jurassic Paleo-Alpine (Table 1, Fig. 2A–B).

Table 1: SHRIMP U-Th-Pb zircon data of the Bratislava-Devín biotite granodiorite (MK-66 sample).

Spot	% $^{206}Pb_c$	ppm U	ppm Th	$^{232}Th/^{238}U$	ppm $^{206}Pb^*$	(1) $^{206}Pb/^{238}U$ Age (Ma)	Total $^{238}U/^{206}Pb$	± %	Total $^{207}Pb/^{206}Pb$	± %	(1) $^{238}U/^{206}Pb^*$	± %	(1) $^{207}Pb^*/^{206}Pb^*$	± %	(1) $^{207}Pb^*/^{235}U$	± %	(1) $^{206}Pb^*/^{238}U$	± %	err corr
MK-66.1.1	0.44	566	109	0.20	27.4	351.7 ± 4.9	17.75	1.4	0.0556	2.3	17.83	1.4	0.052	4.0	0.402	4.2	0.05608	1.4	0.340
MK-66.1.2	1.14	181	37	0.21	8.8	350.2 ± 7.0	17.70	1.8	0.0608	3.5	17.91	2.0	0.0516	15	0.397	15	0.0558	2.0	0.135
MK-66.2.1	2.83	4104	821	0.21	101	177.4 ± 2.3	34.82	1.3	0.0717	0.95	35.83	1.3	0.0491	6.2	0.189	6.4	0.0279	1.3	0.211
MK-66.3.1	0.09	1109	90	0.08	54.6	359.0 ± 4.6	17.45	1.3	0.05545	1.4	17.46	1.3	0.05475	1.8	0.4323	2.2	0.05727	1.3	0.601
MK-66.4.1	0.59	1085	778	0.74	81.0	533.9 ± 6.9	11.51	1.3	0.06443	1.3	11.58	1.3	0.0596	2.9	0.710	3.2	0.0864	1.3	0.418
MK-66.4.2	2.28	2967	169	0.06	75.3	183.3 ± 2.7	33.87	1.3	0.06914	1.3	34.66	1.5	0.051	12	0.203	12	0.02884	1.5	0.124
MK-66.5.1	0.56	159	63	0.41	13.1	588.2 ± 9.6	10.40	1.7	0.063	3.2	10.46	1.7	0.0584	5.7	0.769	6.0	0.0955	1.7	0.284
MK-66.5.2	0.01	268	163	0.63	22.1	591.4 ± 8.4	10.41	1.5	0.0601	2.5	10.41	1.5	0.0601	2.5	0.796	2.9	0.0961	1.5	0.518
MK-66.6.1	0.66	3012	118	0.04	148	356.6 ± 4.4	17.46	1.3	0.05826	0.98	17.58	1.3	0.0529	2.3	0.415	2.6	0.05688	1.3	0.484
MK-66.7.1	0.37	157	77	0.50	7.7	356.1 ± 6.5	17.54	1.8	0.0595	6.0	17.6	1.9	0.0565	8.3	0.443	8.5	0.0568	1.9	0.220

Errors are 1-σ; Pb_c and Pb* indicate the common and radiogenic portions, respectively; (1) common Pb corrected using measured ^{204}Pb.

Table 2: SHRIMP U-Th-Pb zircon data of the Modra-Piesok biotite tonalite (MK-72 sample).

Spot	% $^{206}Pb_c$	ppm U	ppm Th	$^{232}Th/^{238}U$	ppm $^{206}Pb^*$	(1) $^{206}Pb/^{238}U$ Age (Ma)	Total $^{238}U/^{206}Pb$	± %	Total $^{207}Pb/^{206}Pb$	± %	(1) $^{238}U/^{206}Pb^*$	± %	(1) $^{207}Pb^*/^{206}Pb^*$	± %	(1) $^{207}Pb^*/^{235}U$	± %	(1) $^{206}Pb^*/^{238}U$	± %	err corr
MK-72.1.1	0.63	501	131	0.27	23.4	340.1 ± 4.9	18.34	1.4	0.0583	2.0	18.46	1.5	0.0532	4.8	0.397	5.1	0.05417	1.5	0.292
MK-72.2.1	0.21	149	100	0.69	41.5	1802 ± 24	3.092	1.5	0.1247	2.8	3.098	1.5	0.1228	3.1	5.46	3.4	0.3226	1.5	0.445
MK-72.2.2	0.01	228	94	0.42	72.6	2029 ± 25	2.703	1.4	0.1218	1.1	2.703	1.4	0.1218	1.1	6.21	1.8	0.37	1.4	0.786
MK-72.3.1	0.33	717	369	0.53	35.6	361.0 ± 5.0	17.30	1.4	0.055	2.1	17.36	1.4	0.0524	5.6	0.416	5.7	0.0576	1.4	0.248
MK-72.3.2	0.33	446	151	0.35	20.8	339.8 ± 4.9	18.41	1.5	0.0566	2.7	18.47	1.5	0.0539	4.0	0.402	4.3	0.05413	1.5	0.348
MK-72.4.1	0.48	593	223	0.39	28.2	346.0 ± 4.8	18.05	1.4	0.0571	2.3	18.14	1.4	0.0532	3.9	0.404	4.1	0.05513	1.4	0.346
MK-72.5.1	8.12	545	250	0.47	26.0	320.4 ± 5.8	17.99	1.4	0.1183	3.2	19.58	1.9	0.053	19	0.372	19	0.05096	1.9	0.095
MK-72.5.2	2.68	403	191	0.49	21.7	381.6 ± 6.7	15.95	1.5	0.0711	2.7	16.39	1.8	0.0497	16	0.418	16	0.061	1.8	0.113
MK-72.6.1	0.01	378	179	0.49	18.1	350.0 ± 5.2	17.93	1.5	0.0538	3.0	17.93	1.5	0.0539	3.0	0.415	3.3	0.05579	1.5	0.456
MK-72.6.2	3.19	515	219	0.44	25.1	344.2 ± 5.4	17.62	1.4	0.0851	2.0	18.2	1.6	0.0591	10	0.447	10	0.05484	1.6	0.157

Errors are 1-σ; Pb_c and Pb* indicate the common and radiogenic portions, respectively; (1) common Pb corrected using measured ^{204}Pb.

Bratislava Massif

Zircons of the oldest (1) population show apparent regular oscillatory zoning crystals or cores; they give Neo-Proterozoic ages of 591±8, 588±10 and 534±7 Ma (Table 1, Fig. 3A). The Meso-Hercynian zircon population (2) is dominant; the zircons form cores or long prismatic crystals with fine oscillatory zoning (Fig. 3A). They yield a relatively narrow age interval of 359±5 to 350±7 Ma (5 spots; Table 1, Fig. 2B). The two Paleo-Alpine ages (177±2 and 183±3 Ma) of population (3) were obtained from oscillatory zoned zircon overgrowths on probably older crystals with different crystal morphology, U and common Pb concentrations and low CL signal (Table 1, Figs. 2A, 3A).

Modra Massif

Zircons from the Modra Massif show two age populations: (1) Paleo-Proterozoic and (2) Mississippian Meso-Hercynian (Table 2, Fig. 2C–D).

Two spot datings from a large oval shaped inherited zircon with irregular zoning revealed ages between 1802±24 and 2029±25 Ma (Fig. 3B). However, their projections are discordant with an upper intercept of 1984±36 Ma and 0 Ma at a lower intercept (Fig. 2C).

Short prismatic zircon with distinct oscillatory zoning show Hercynian ages, six of them exhibit a narrow interval between 340±5 and 350±5 Ma, with an average nearly concordant age of 347±4 Ma (Table 2, Figs. 2D, 3B).

Discussion and conclusion

The SHRIMP U-Th-Pb dating of zircon represents a sensitive isotopic method with a large advantage for the dating of zircons from orogen-related S- and I-type granitic rocks with a complex crystallization history. The Bratislava and Modra Massifs are typical examples of the West-Carpathian Hercynian intrusive suites incorporated in the younger Alpine terranes. Zircons from both massifs revealed the presence of older inherited Paleo-Proterozoic (Modra) cores or Neo-Proterozoic to Cambrian (Bratislava) cores. Similarly, old Precambrian (Archean to Proterozoic) ages have been reported from several Paleozoic (meta)granitic suites of the Western Carpathians (Cambel et al. 1990; Poller et al. 2001; Putiš et al. 2008). However, most data from zircons indicate Meso-Hercynian, Mississippian ages for both massifs: 355±5 Ma and 347±4 Ma, for Bratislava and Modra, respectively. The results obtained are in accordance with older whole-rock Rb-Sr and electron-microprobe Th-U-Pb monazite datings of the Bratislava Massif (Bagdasaryan et al. 1982; Finger et al. 2003; Uher et al. submitted). However, our new data for the Modra Massif ruled out the possibility

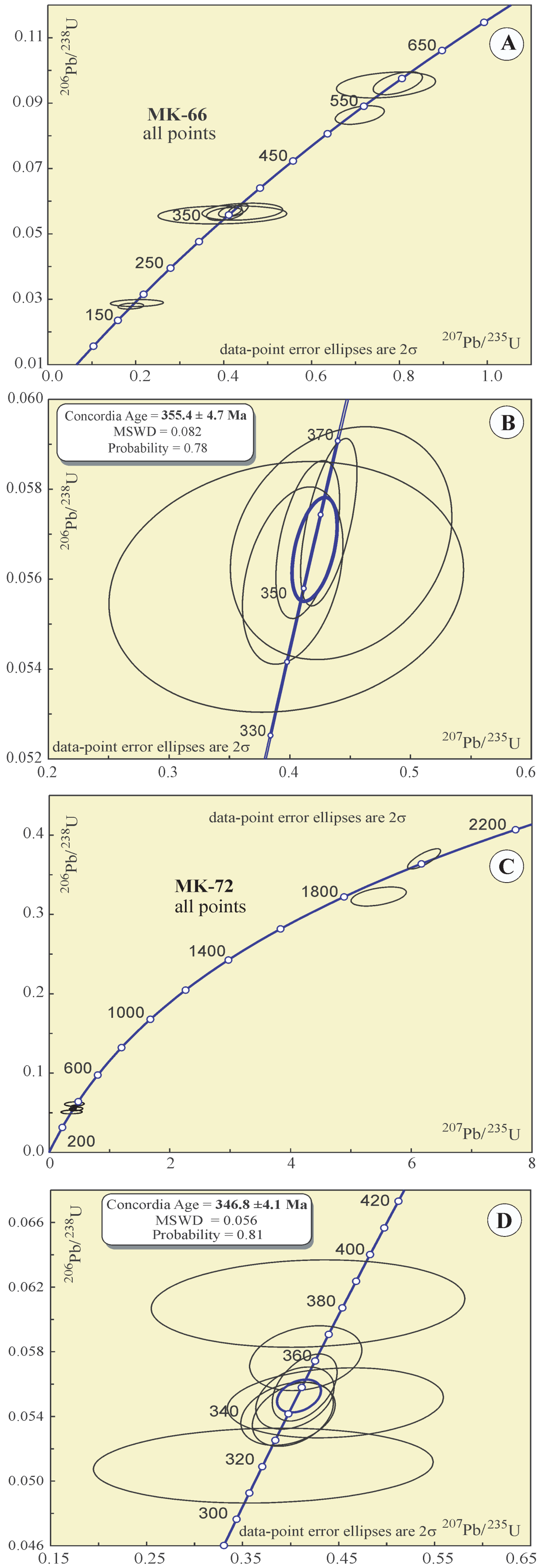

Fig. 2. U-Pb isotope concordia diagrams of the Malé Karpaty Mts granitic rocks: **A** — Bratislava Massif — all measurements; **B** — Bratislava Massif — the Hercynian population; **C** — Modra Massif — all measurements; **D** — Modra Massif — the Hercynian population.

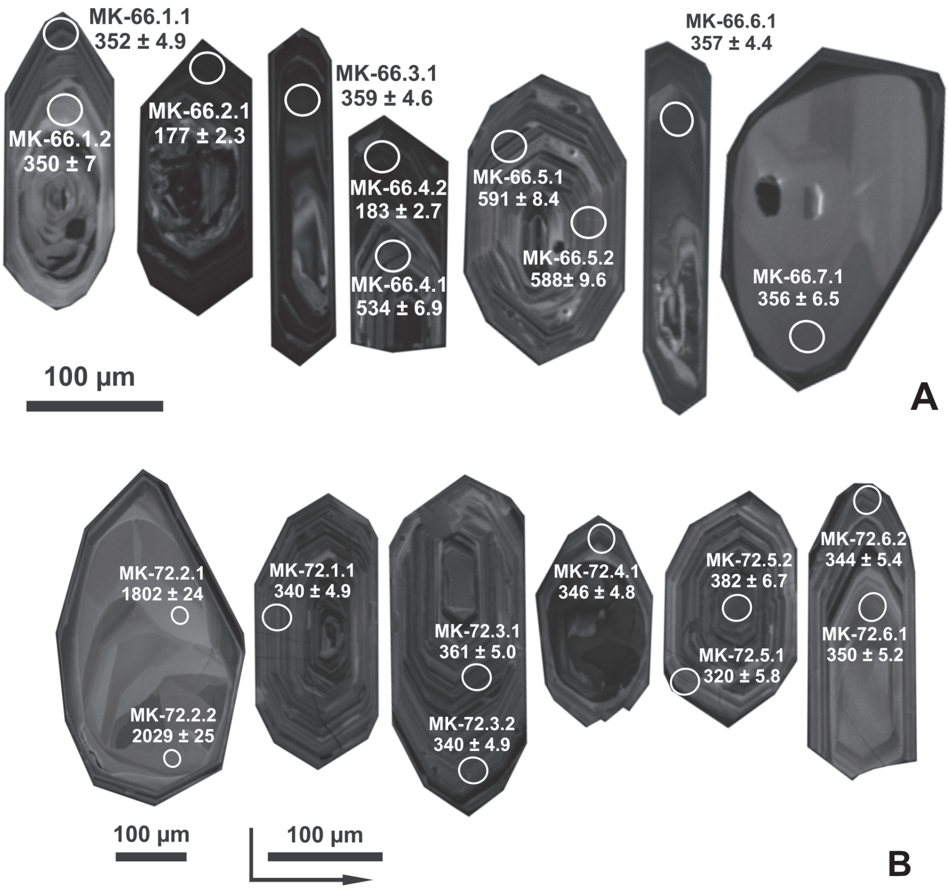

Fig. 3. Zircon CL images of the Malé Karpaty Mts granitic rocks with location and results of the SHRIMP dating (in Ma): **A** — Bratislava Massif; **B** — Modra Massif.

of a significant time gap between magmatic crystallization of the two massifs suggested by Bagdasaryan et al. (1982) and Scherbak et al. (1988) and support their nearly coeval origin. It is noteworthy, that equal age was recently determined for other I-type tonalites including the Sihla (s.s.) tonalite from the Tlstý Javor quarry 349.9 ± 4.4 Ma (Kohút et al. 2008). The Bratislava and Modra Massifs represent the products of Meso-Hercynian orogen-related granitic S- to I-type magmatism, probably caused by the same collisional event and resulting in succeeding partial melting of somewhat different sedimentary/igneous sources. The Meso-Hercynian 350 ± 10 Ma age belongs to the strongest collisional metamorphic/magmatic event recorded in the pre-Alpine basement of the Western Carpathians as well as in the broader Central European area (e.g. Cambel et al. 1990; Finger et al. 1997, 2003; Petrík et al. 2001, 2006; Putiš et al. 2008). The Mississippian age of S-type suite of the granitic rocks is common for the Western Carpathians (Petrík & Kohút 1997; Finger et al. 2003), as is shown by zircon U-Pb datings from the Tatric Unit: the Strážovské vrchy Mountains 356 ± 9 Ma (Kráľ et al. 1997), the Malá Fatra Mountains 353 ± 11 Ma (Scherbak et al. 1990), the Tatry Mountains 347 ± 14 Ma (Poller & Todt 2000; Poller et al. 2000), the Veľká Fatra Mountains 356 ± 25 Ma (Kohút et al. 1997), as well as from the Veporic Unit: the Sinec type 350 ± 5 Ma (Bibikova et al. 1988) and the Kráľova Hoľa type 345 ± 11 Ma (Gaab et al. 2005). However, the I-type suite of the Western Carpathians granodioritic-tonalitic rocks was characterized by the Pennsylvanian magmatic ages up to now as is shown by the Sihla tonalite 303 ± 2 Ma (Bibikova et al. 1990), the Tribeč tonalite 306 ± 10 Ma (Broska et al. 1990), the High Tatra tonalite 314 ± 4 Ma (Poller & Todt 2000), and the Smrekovica tonalite 307 ± 10 Ma (Poller et al. 2005). Interestingly, the first SHRIMP zircon data from the WCB shows concordant ~350 Ma age (Poller et al. 2001) for I-type granodiorite of the High Tatra Mts. comparable to our results. Naturally, more data from the I-type granite suite are needed to date zircons U-Pb parallel by SHRIMP and by TIMS (thermal ionization mass spectrometry) to solve this problem properly. Although the youngest, Jurassic (~180 Ma) obtained zircon data suggest rather a recent lead loss, we cannot exclude that it might be connected with a still poorly known Paleo-Alpine thermal event, which also seems to be supported by some older K-Ar data (Bagdasaryan et al. 1977; Bagdasaryan in Cambel et al. 1990).

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