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Re-Os and U-Th-Pb dating of the Rochovce granite and its mineralization (Western Carpathians, Slovakia)

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Abstract: The subsurface Rochovce granite intrusion was emplaced into the contact zone between two principal tectonic units (the Veporic Unit and the Gemeric Unit) of the Central Western Carpathians (CWC), Slovakia. The Cretaceous age of this granite and its Mo-W mineralization is shown using two independent methods: U-Pb on zircon and Re-Os on molybdenite. The studied zircons have a typical homogeneous character with oscillatory zoning and scarce restite cores. SHRIMP U-Pb data provide an age of 81.5 ± 0.7 Ma, whereas restite cores suggest a latest Neoproterozoic–Ediacaran age (~565 Ma) source. Zircon $\varepsilon Hf_{(81)}$ values –5.2 to +0.2 suggest a lower crustal source, whereas one from the Neoproterozoic core $\varepsilon Hf_{(565)}$ = +7.4 call for the mantle influenced old precursor. Two molybdenite-bearing samples of very different character affirm a genetic relation between W-Mo mineralization and the Rochovce granite. One sample, a quartz-molybdenite vein from the exocontact (altered quartz-sericite schist of the Ochtiná Formation), provides a Re-Os age of 81.4 ± 0.3 Ma. The second molybdenite occurs as 1–2 mm disseminations in fine-grained granite, and provides an age of 81.6 ± 0.3 Ma. Both Re-Os ages are identical within their 2-sigma analytical uncertainty and suggest rapid exhumation as a consequence of post-collisional, orogen-parallel extension and unroofing. The Rochovce granite represents the northernmost occurrence of Cretaceous calc-alkaline magmatism with Mo-W mineralization associated with the Alpine-Balkan-Carpathian-Dinaride metallogenic belt.

Key words: Western Carpathians, Cretaceous granitic rocks, SHRIMP zircon dating, Re-Os molybdenite dating, Mo-W mineralization.

Introduction

The Western Carpathians metallogenic province is a division of the Alpine-Balkan-Carpathian-Dinaride (ABCD) metallogenic belt, one of the word's oldest mining areas, playing a major role in the history of European civilizations. The Carpathians form part of an extensive, equatorial, orogenic belt extending from the Moroccan Atlas, through the Alps, Dinarides, Pontides, Zagros, Hindukush to the Himalayas and China. The Western Carpathians are the northernmost, E–W trending branch of this Alpine belt, linked to the Eastern Alps in the west and to the Eastern Carpathians in the east, continuing farther to the Apuseni Mountains and the Southern Carpathians (Săndulescu 1984). The recent structure of the Alps, Carpathians and Dinarides originated from the subduction–collision (convergence) processes of the African plate fragments (Adria-Apulia) with Eurasia mainly from the Cretaceous to the present. The timing and duration of geological events that produce economic concentrations of mineral wealth in the earth's crust are of crucial importance in understanding ore deposits. However, unravelling ore-forming episodes in the ore deposits is practically impossible without precise dating, as spatial-structural relations are frequently ambiguous. There are several radioactive isotope tracers commonly used for dating metalliferous events (K-Ar, $^{40}Ar/^{39}Ar$, Rb-Sr, Sm-Nd, and U-Pb), although often can fail to date mineralization because of alteration processes and/or not consanguineous origin. In the last decade the ^{187}Re–^{187}Os chronometer applied to molybdenite (MoS_2) and/or other sulphide and oxide minerals has shown that the timing of mineralization can be directly determined (Stein et al. 1997, 2001; Selby & Creaser 2001; Selby et al. 2007). Since its discovery, the Rochovce granite and its Mo-W mineralization has provided the possibility to determine both the age of mineralization and the granite magmatism thereby providing improved knowledge of the geologic evolution of the Veporic and Gemeric Units contact zone. Because a modern single-grain cathodoluminescence controlled (CLC) zircon dating (Poller et al. 2001) brings different result than a conventional zircon U-Pb dating (Hraško et al. 1999) we decided to test this uncertainty with additional methods. We present a new SHRIMP zircon U-Th-Pb dating and high-precision Re-Os ages for molybdenite from the Rochovce granite and its host rock occurrences to determine synchronous magmatic/mineralization process in the contact zone between the Gemeric and the Veporic Superunits, Central Western Carpathians, Slovakia.

Geological setting

The Western Carpathians as a part of the extensive Alpine–Himalayan orogenic system represent a typical collisional orogen. They are divided into two belts: the Outer Western Carpathians, consisting mostly of Neo-Alpine nappes and the Inner Western Carpathians with essentially a Paleo-Alpine structure overlain by Tertiary post-nappe deposits. The Inner Western Carpathians consist of three main crustal-scale superunits which are, from north to south (Fig. 1A): the Tatric, Veporic and Gemeric and several cover-nappe systems: the Fatric, Hronic and Silicic (Plašienka et al. 1997). The basement units together with the Mesozoic cover and nappe complexes were tectonically juxtaposed through north-directed thrusting during the Late Cretaceous. The Rochovce granite is a not exposed intrusion in the south-eastern part of the Veporic Unit near the contact with overlying Gemeric Unit (Fig. 1B,C). The hidden granite body was discovered by the drill-hole KV-3 (Klinec et al. 1979, 1980), situated in the centre of a magnetic anomaly (Filo et al.

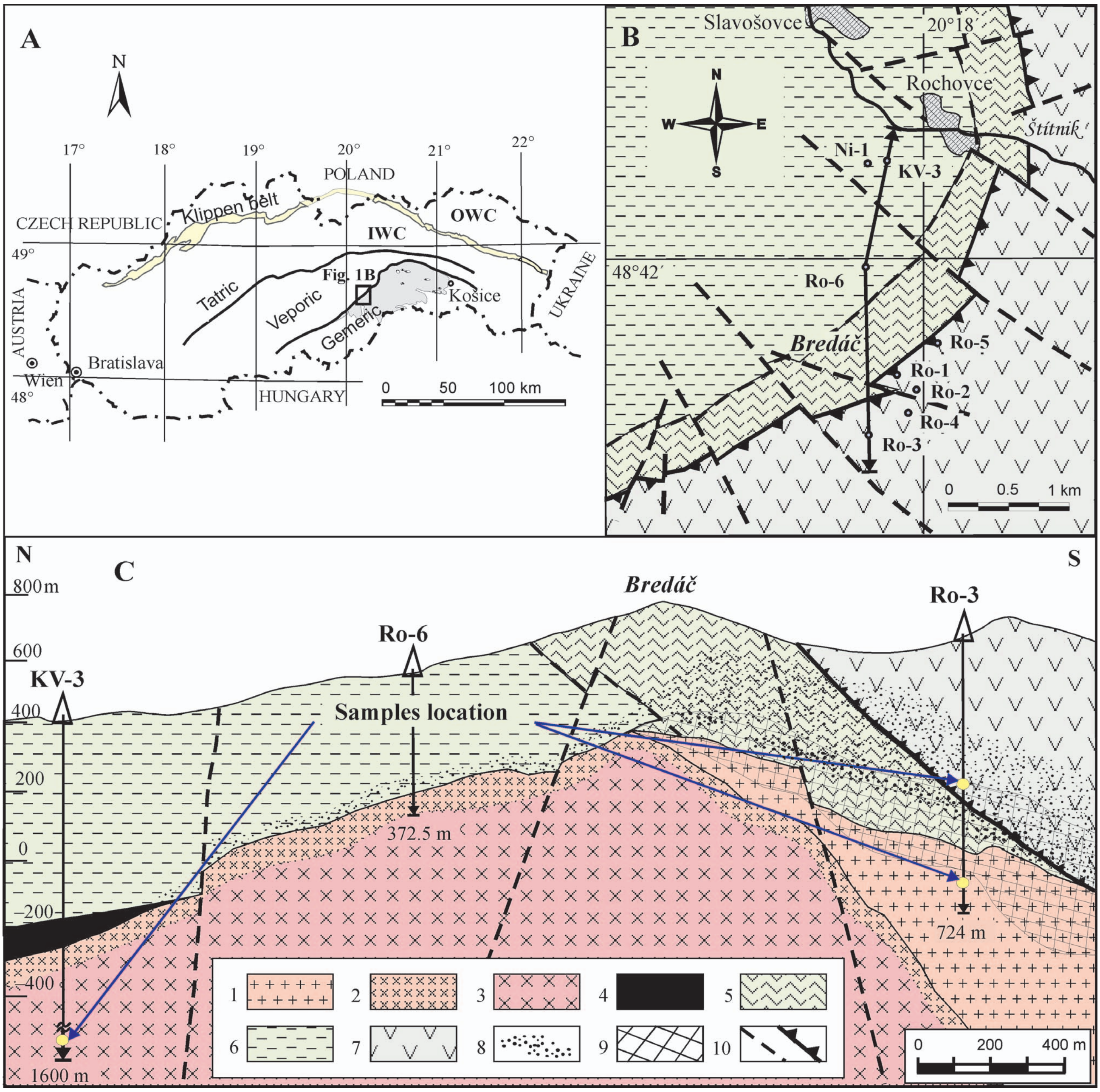

Fig. 1. A — Simplified tectonic-geological sketch of the Western Carpathians (Slovak part), displaying the principal tectonic units of the IWC and position of the study area. **Explanations:** OWC — Outer Western Carpathians, IWC — Inner Western Carpathians. **B** — Detailed geological sketch of the study area with the positions of principal exploration boreholes. Rocks symbols are identical as in Fig. 1C. **C** — Idealized geological profile across Rochovce granite body, with location of dated samples Ro-3/398.5 and Ro-3/676.6 m. **Explanations:** 1 — granite of the 2nd intrusive phase, 2 — marginal fine-grained granite of the 1st intrusive phase, 3 — coarse-grained porphyric granite — 1st phase, 4 — metagabbro, 5 — Rimava Formation, 6 — Slatviná Formation, 7 — Ochtiná Formation, 8 — mineralized zone with sulphides and tungsten [W-zone], 9 — mineralized zone with molybdenite [Mo-zone], 10 — tectonic lines — fault and thrust.

1974). As revealed by the borehole KV-3, the granitic rocks intruded mostly into the metapelitic to psammitic mica-schists and phyllites of the so-called Slatviná Formation (Vozárová & Vozár 1982). Direct contact forms a layer of metagabbro 100 m thick (607–702 m). Subsequent drilling exploration revealed that in the SE part this granite intruded into the quartz-sericite schists of the Ochtiná Formation (Gemeric Unit) (Fig. 1C), and the southern part intruded into the Permian psammitic to psephitic rocks of the Rimava Formation as well as. The Alpine contact metamorphism is bound exclusively to these Carboniferous and Permian metasedimentary rocks. The Rochovce magmatic body is formed by two intrusive phases (Határ et al. 1989). *The first phase* comprises two petrographic varieties: (i) coarse-grained biotite monzogranites with the pink K-feldspars phenocrysts, locally with mafic microgranular enclaves (central part of the body); and (ii) granite porphyries (marginal part). *The second phase*, forming mainly the S to SE part of the magmatic body, is more evolved type represented by medium- to fine-grained biotite leucogranites and leucogranitic porphyries. Narrow veins of leucogranite randomly penetrate coarse-grained granites of the 1st phase (Fig. 2A). When the first granite samples from drill-core KV-3 appeared on surface they were attracted attention not only for their fresh pinkish colour, but also for their undeformed character, rather unusual for the Western Carpathians basement granites. The Rochovce granites have normal to elevated SiO_2 values (66–77 wt. %), a typical calc-alkaline, subaluminous to peraluminous character (Shand's index — A/CNK = 0.9–1.4), high concentrations of Ba, Rb, Li, Cs, Mo, Nb, Y, V, W, Cr, F, Th, U and low concentrations of Sr, Zr and Be (Határ et al. 1989). The low to moderate initial Sr isotope ratios (I_{Sr} = 0.7083–0.7126), together with negative $\varepsilon Nd_{(81)} = -3.0$ to -2.4, and stable isotopes values ($\delta^{18}O_{(VSMOW)} = 8.0$ to 8.3 ‰; $\delta^{34}S_{(CDT)} = -2.1$ ‰; $\delta^{7}Li_{(SVEC)} = 4.7$ ‰) suggest a lower crustal meta-igneous protolith (Hraško et al. 1998; Kohút et al. 2001; Magna et al. 2010). Although the first K/Ar cooling ages on biotites 88–75 Ma (Kantor & Rybár 1979) indicated the Alpine–Cretaceous age of the Rochovce granite, Cambel et al. (1989) still supposed its Permian age by means of Rb/Sr isochron

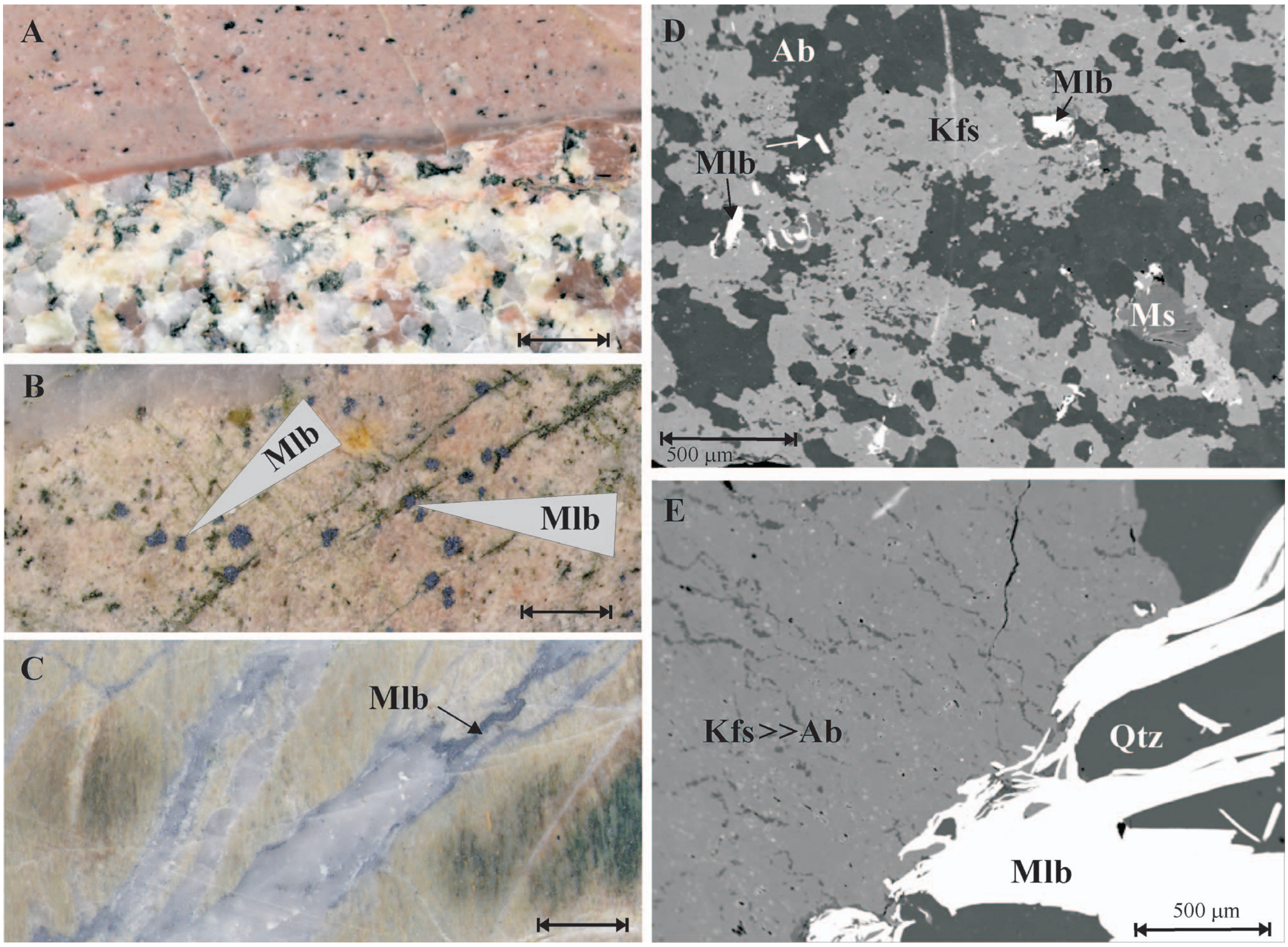

Fig. 2. A — Sharp contact of the narrow vein of fine-grained granite — 2nd intrusive phase to coarse-grained granite of the 1st phase with chilled margin. Sample taken from borehole KV-3 depth 1379.8 m. Scale bar 1 cm. **B** — Molybdenite-bearing (Mlb) veinlets structure in the fine-grained granite-porphyry of the 2nd intrusive phase — sample Ro-3/676.6 m. Natural size (scale bar 1 cm). **C** — Quartz-molybdenite veinlet structure in host rock quartz phyllite of the Ochtiná Formation — sample Ro-3/398.5 m. Scale bar 1 cm. **D** — Tiny inclusions of molybdenite (Mlb) in medium-grained porphyry — sample Ro-2/532.3 m. **Abbreviations:** Ab — albite, Kfs — K-feldspar, Ms — muscovite. Back-scattered electron image (BSEI). **E** — Quartz-molybdenite (Qtz-Mlb) veinlet in phyllite rock (Ochtiná Formation); sample Ro-5/549.5 m; BSEI.

(WR) — 253±2 Ma. However, a Cretaceous magmatic age for the Rochovce granite was already proved by U-Pb zircon dating — conventional method 82±1 Ma (Hraško et al. 1999) and cathodoluminescence controlled single zircon method 75.6±1.1 Ma (Poller et al. 2001).

Sample description

We selected for zircon dating purpose a representative sample of coarse-grained biotite porphyric granite of the 1st intrusive phase (sample KV-3/1360) and two representative molybdenite samples for the time comparison of the granite porphyry-type mineralization to stockwork mineralization in the host rocks. Sample RO-3/676.6 — was typical fine-grained granite of the 2nd intrusive phase with disseminated flakes of molybdenite (Fig. 2B), taken from a depth of 676.6 m in the borehole RO-3, whereas the next sample RO-3/398.5 was taken from the depth of 398.5 m in the same borehole. It is a quartz-molybdenite veinlet from exocontact of the Rochovce granite body in the Gemeric — hydrothermally altered quartz-sericite schists of the Ochtiná Formation (Fig. 2C).

Analytical methods

The heavy-mineral separation of accessory zircon was done using a common separation procedure (crushing, sieving, gravitation separation by Wilfley table, heavy liquid — bromophorm, and electro-magnetic separation). Euhedral transparent and semitransparent 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) at St. Petersburg; including the CL, BSE and optical images of the polished mounts with zircon crystals for the choice of the measured spots. The U-Th-Pb analyses were done using SHRIMP II, using the SQUID Excel Macro of Ludwig (2000). Data for each spot were collected in sets of five scans through the mass range. The probe spot diameter was 25 μm and primary beam intensity was about 4 nA. The Pb/U ratios have been normalized relative to a value of 0.0668 for the $^{206}Pb/^{238}U$ ratio of the TEMORA reference zircons, equivalent to an age of 416.75 Ma (Black et al. 2003). Uncertainties given for individual analyses (ratios and ages) are at the one σ level; however the uncertainties in calculated concordia ages are reported at two σ levels. The measured U-Th-Pb isotope data are summarized in Table 1.

Lu-Hf-isotope analyses were carried out with a New Wave DUV 193 nm. Laser-ablation system based on 193 nm COMPex-102 ArF excimer laser and a multi-collector ICPMS Neptune at the Centre of Isotopic Research of the All-Russian Geological Research Institute in St. Petersburg. Faraday cups configuration allowed simultaneous registration of ^{172}Yb, $^{174}(Yb+Hf)$, ^{175}Lu, $^{176}(Hf+Yb+Lu)$, ^{177}Hf, ^{178}Hf, ^{179}Hf, ^{180}Hf. ^{175}Lu and ^{172}Yb were used for interference correction of ^{176}Lu and ^{176}Yb on ^{176}Hf. The laser spot size was ~50 μm in diameter and ~30 μm depth. The repetition rate was 5–7 Hz, laser energies of ~120 mJ/pulse; helium

Table 1: SHRIMP U-Th-Pb zircon data of the Rochovce biotite granite (KV-3/1360 m sample).

Spot	% $^{206}Pb_c$	ppm U	ppm Th	$^{232}Th/^{238}U$	ppm $^{206}Pb^*$	(1) $^{206}Pb/^{238}U$ Age		(2) $^{206}Pb/^{238}U$ Age		(3) $^{206}Pb/^{238}U$ Age		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
KV-3/1.1	0.00	2482	1455	0.61	195	564.2	±4.5	564.1	±4.60	563.0	±5.10	10.935	0.83	0.05898	0.65	10.934	0.83	0.05904	0.7	0.7446	1.1	0.09146	0.83	.790
KV-3/1.2	0.37	1410	516	0.38	15.7	82.6	±0.90	82.6	±0.88	82.5	±0.94	77.29	1.10	0.0505	2.3	77.58	1.10	0.0476	5.7	0.0846	5.8	0.01289	1.10	.189
KV-3/2.1	0.23	2186	1016	0.48	23.9	81.3	±0.8	81.2	±0.80	81.4	±0.87	78.58	0.98	0.05071	1.9	78.76	0.99	0.0489	3.0	0.0856	3.1	0.01270	0.99	.314
KV-3/3.1	0.51	1581	515	0.34	17.3	81.3	±0.86	81.3	±0.86	81.4	±0.91	78.40	1.00	0.0514	2.2	78.81	1.10	0.0473	4.3	0.0827	4.4	0.01269	1.10	.243
KV-3/4.1	0.37	1638	533	0.34	18.0	81.6	±0.86	81.5	±0.86	81.6	±0.91	78.22	1.00	0.0518	2.1	78.51	1.10	0.0489	3.8	0.0858	3.9	0.01274	1.10	.270
KV-3/4.2	0.27	1267	335	0.27	13.8	81.0	±0.90	81.0	±0.90	80.7	±0.94	78.83	1.10	0.0501	2.5	79.04	1.10	0.0480	4.1	0.0837	4.3	0.01265	1.10	.260
KV-3/5.1	1.33	340	196	0.59	3.74	80.9	±1.60	80.8	±1.50	80.9	±1.80	78.20	1.80	0.0588	4.9	79.2	2.00	0.0482	15.0	0.0840	15	0.01262	2.00	.128
KV-3/5.2	0.52	1531	683	0.46	16.8	81.2	±0.88	81.3	±0.86	81.1	±0.94	78.46	1.10	0.0511	2.2	78.87	1.10	0.0469	5.1	0.0820	5.2	0.01268	1.10	.209

Errors are 1-sigma; Pb_c and Pb^* indicate the common and radiogenic portions respectively.
Error in Standard calibration was 0.48 % (not included in above errors but required when comparing data from different mounts).
(1) Common Pb corrected using measured ^{204}Pb.
(2) Common Pb corrected by assuming $^{206}Pb/^{238}U$– $^{207}Pb/^{235}U$ age-concordance.
(3) Common Pb corrected by assuming $^{206}Pb/^{238}U$– $^{208}Pb/^{232}Th$ age-concordance.

Table 2: Lu-Hf isotopic results from studied zircons of the Rochovce biotite granite.

Sample	Age	$^{176}Yb/^{177}Hf$	$^{176}Lu/^{177}Hf$	$^{176}Hf/^{177}Hf$	$\varepsilon Hf_{(0)}$	$\varepsilon Hf_{(t)}$	$t_{(DM)}$	$t_{(DM2st)}$
KV–3/1.1	564	0.032587 ± 2118	0.001562 ± 56	0.282632 ± 38	–8.1	7.4	899	992
KV–3/2.1	81	0.026890 ± 1159	0.001123 ± 11	0.282639 ± 30	–7.8	–2.9	877	1105
KV–3/3.1	81	0.058380 ± 1529	0.002497 ± 09	0.282575 ± 51	–10.1	–5.2	1007	1226
KV–3/4.1	82	0.019412 ± 2191	0.000848 ± 48	0.282726 ± 47	–4.7	0.2	747	945
KV–3/4.2	81	0.044856 ± 2019	0.001833 ± 39	0.282615 ± 37	–8.6	–3.8	929	1151

Table 3: Re-Os data for molybdenites from the Rochovce samples Ro-3/398.5 m and Ro-3/676.6 m.

Re-Os data and ages for two molybdenite samples from the Rochovce granite, east-central Slovakia

AIRIE Run	Sample Name	Re, ppm	^{187}Os, ppb	Age, Ma
MDID-222	RO-3 676.6 m, schist host, mylonitic fabric	43.67 (1)	37.24 (2)	81.4 ± 0.3
MDID-228	RO-3 398.5 m, granite host, 2nd intrusive phase	5.203 (2)	4.447 (2)	81.6 ± 0.3

Assumed initial $^{187}Os/^{188}Os$ for age calculation = 0.2 ± 0.1
Absolute uncertainties shown, all at 2-sigma level, for last digit indicated
Decay constant used for ^{187}Re is 1.666×10^{-11} yr^{-1} (Smoliar et al. 1996)
Re blank = 1.16±0.03 pg, Os blank = 1.9±0.1 pg with $^{187}Os/^{188}Os$ = 0.245±0.01
Two-sigma ages calculated using $^{187}Os = ^{187}Re\,(e^{\lambda t}-1)$ include all analytical and ^{187}Re decay constant uncertainties

was used as a carrier gas (1 l/min He through the ablation chamber and then, after ablation chamber add +1 l/min of Ar to sample line). The standard zircons Temora, Mud Tank and GJ-1 (Morel et al. 2008; Yuan et al. 2008) were used in analytical session to confirm a normal ^{176}Lu and ^{176}Yb interferences correction. The typical LA-MC-ICPMS analytical procedure was included: 40 seconds of blank (zero lines of Faraday cups amplifiers) measurements, preablation time ~9 seconds, ablation (integrations) time ~32 seconds. This time is sufficient to obtain the internal standard errors of $^{176}Hf/^{177}Hf$ ratios about 0.01 % for references zircons, with weighted mean $^{176}Hf/^{177}Hf$ of 0.282488±12 (2 σ) for Temora (n=20) and 0.282005±9 (2 σ) for GJ-1 (n=26). The evolution line was calculated using the decay constant of ^{176}Lu: $\lambda = 1.867*10^{-11}$ per year and Primordial composition $^{176}Hf/^{177}Hf = 0.27978$. The εHf(t) values were calculated using the chondritic Hf data of $^{176}Hf/^{177}Hf = 0.28286$ and $^{176}Lu/^{177}Hf = 0.0334$. The Hf model ages [$Hf_{t(DM)}$] were calculated to depleted mantle composition with value $^{176}Hf/^{177}Hf = 0.28325$; whereas two-stage [$Hf_{t(DM2st)}$] model ages were calculated to DM with crustal correction $^{176}Lu/^{177}Hf = 0.0093$. The measured Hf isotope data are given in Table 2.

Molybdenite is exceptionally suitable for the Re-Os dating because it usually contains ppm level Re and essentially no initial or common Os, making it a single mineral chronometer. General principles and methodology for molybdenite dating are outlined in Stein et al. (2001, 2003) and Stein (2006). Mineral separates were prepared and Re and Os concentrations were determined at AIRIE, Colorado State University. A Carius-tube digestion was used, whereby molybdenite is dissolved and equilibrated with a Re-double Os spike (Markey et al. 2003) in HNO_3–HCl (*aqua regia*) by sealing in a thick-walled glass ampoule and heating for 12 hours at 230 °C. The Os is recovered by distilling directly from the Carius tube aqua regia into HBr, and is subsequently purified by micro-distillation. The Re is recovered by anion exchange. The Re and Os are loaded onto Pt filaments and isotopic compositions are determined using NTIMS on NBS 12-inch radius, 68° and 90° sector mass spectrometers at Colorado State University. Two in-house molybdenite standards, calibrated at AIRIE, are run routinely as an internal check (Markey et al. 1998). The Re-Os data, analytical details, and blank information are given as footnotes in the data table (Table 3).

Results

The euhedral transparent and semitransparent zircon crystals of 0.15 to 0.45 mm in size are enclosed mainly by biotites, whereas in feldspars and quartz they were observed in a lesser amount in the Rochovce granite. The studied zircons according to zircon typology (Pupin 1980) correspond mainly to P_1–P_3, G_1 and S_4–S_5 subtypes with medium temperature and a high (Na+K)/Al ratio in magma during zircon crystallization typical for the alkaline type of magma. Cathodoluminescence (CL) and back-scattered electron (BSE) images of zircon crystals reveal their magmatic oscillatory zoning partly with several luminescent areas and local presence of old, inherited cores (Fig. 3). SHRIMP analysed spot ages vary in the narrow interval from 82.6±0.9 Ma to 80.9±1.6 Ma (Table 1), forming the concordia intercept point age of 81.5±0.7 Ma (Fig. 4). The inherited cores indicate partial contribution of the Neoproterozoic–Ediacaran (564 Ma) source material at the genesis of the Rochovce granite.

LA-ICPMS Lu-Hf-isotope analyses realized close SHRIMP spot ones show little variation in Hf isotopic composition. The $^{176}Hf/^{177}Hf$ ratio ranges from 0.282575 to 0.282726 (Table 2), while recent εHf values range from –4.7 to –10.1. This indicates a crustal origin of the magma, and the $t_{(DM)}$ ages give a minimum age for the source material of

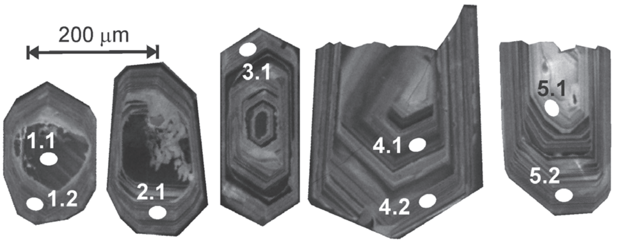

Fig. 3. Zircon CL images of the Rochovce granite sample KV-3/1360 m with location of the SHRIMP dating spots.

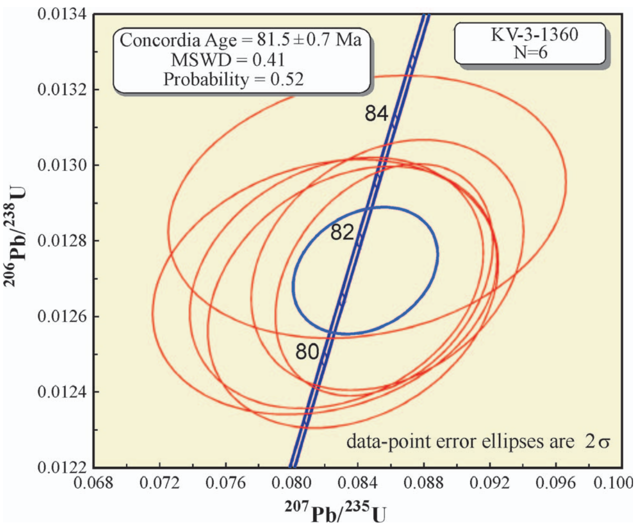

Fig. 4. SHRIMP U-Th-Pb zircon data of the Rochovce biotite granite (KV-3/1360 m sample).

about 747–1007 Ma. The crustal model ages $t_{(DM2st)}$ range from 945 to 1105 Ma. However, an inherited core in a zircon grain from the Rochovce granite shows much more radiogenic Hf isotope signature with $\varepsilon Hf_{(t)} = +7.4$ indicating former mantle character of the source, whereas the majority of analyses from the Upper Cretaceous homogenized parts of zircons (t = 82–81 Ma) have $\varepsilon Hf_{(t)} = -5.2$ to $+0.2$ indicating rather a lower crustal origin.

Detailed microscopy and electron microprobe studies reveal that molybdenites occurred not only as visually observed (1–3 mm) disseminated inclusions in the second intrusive phase, but they were spotted as minute grains in both petrographic varieties (coarse-grained monzogranites and medium-grained porphyries) of the 1st intrusive phase (Fig. 2D). Other ore minerals like magnetite, pyrite, chalcopyrite, galena, sphalerite, and fluorite were also identified. These minerals occur in small quantities even though the first intrusive phase is not regarded as ore-bearing. The rocks of the 2nd intrusive phase contain increased contents of hydrothermal-stage minerals (molybdenite, chalcopyrite, pyrite, galena, sphalerite, and fluorite). The molybdenite and pyrite also constitute disseminated and veinlet mineralization (veins to several cm ±dm) exclusively associated with exocontact of the fine-grained leucogranites and porphyries in the host rock phyllites (Fig. 2E). Due to their fractionated-evolved character, the granites of the second phase have decreasing contents or absence of accessory magnetite, allanite and titanite, what are typical for the first intrusive phase. Generally, the Rochovce granite related Mo-W deposit consists of two individual zones (Mo- and W-zone) that partly overlap (Fig. 1C). In the Mo-zone the main mineral is molybdenite, distinctively associated to exocontact of the granite body and/or disseminated inclusions directly in the granite-porphyry. Molybdenite-quartz veinlets are of cm scale rarely of dm scale, and this mineralization can be defined as stockwork type. The contents in the distinctively mineralized veinlets are in the range 0.1–0.7 wt. % Mo, rarely up to 1 or 2 wt. % Mo. The main economic mineral of the W-zone is scheelite, in less amount ferberite. A characteristic feature of the W-zone is the intensive pyritization in the stockwork. The highest content found was 0.4–0.7 wt. % W.

The Re-Os data are shown in Table 3. Two molybdenite separates from the distinct representative samples of the Rochovce Mo-W mineralization (granite-porphyry and host rock stockwork mineralization) yield Re-Os ages of 81.6±0.3 and 81.4±0.3 Ma respectively. Analytical uncertainties are given at the 2-sigma level and include the error in the ^{187}Re decay constant, thereby permitting direct comparison with ages based on other isotopic methods, as cited in this paper.

Discussion

The Late Cretaceous age of the Rochovce granite magmatism was determined by Hraško et al. (1999) using U-Pb zircon conventional (multi-grains) dating with the lower intercept (LI) concordia age 82±1 Ma. The discordant U-Pb isotope results of analysed zircons and their BSE images document participation of an old source material forming the upper intercept (UI) age 2123±89 Ma. Poller et al. (2001) using the U-Pb zircon single-grain method, when checked each grain by CL and BSE before its dissolutions and measurements in mass spectrometry, obtained LI age 75.6±1.1 Ma and UI age 1203±500 Ma. Although Poller et al. (l.c.) selected only homogeneous zircon grains for TIMS analysis, to obtain concordant age, which can reflect a time of real magmatic crystallization, acquired age (75.6 Ma) is slightly younger than published Hraško et al. (1999) and results presented in this paper. This age is surprisingly younger than the age of 81.3±3 Ma (weighted mean age) from four biotite K/Ar cooling ages in Kantor & Rybár (1979). Comparison of all zircon U-Pb data from various laboratories and methodics used for determination the Rochovce granite magmatic age is presented in Fig. 5. Previous datings (Hraško et al. 1999; Poller et al. 2001) brought discordant results with a large scatter in UI, which can indicate absence of larger inherited components. Our recent dating employing two independent methods (SHRIMP zircon U-Th-Pb & molybdenite Re-Os) proved the Campanian (81.5 Ma) age of the Rochovce granite magmatism and mineralization. Participation of the Neoproterozoic source material (t = 564 Ma; Table 1) is very common for the Western Carpathians (e.g. Kohút et al. 2009; Putiš et al. 2009). It is noteworthy that our limited study did not confirm the ef-

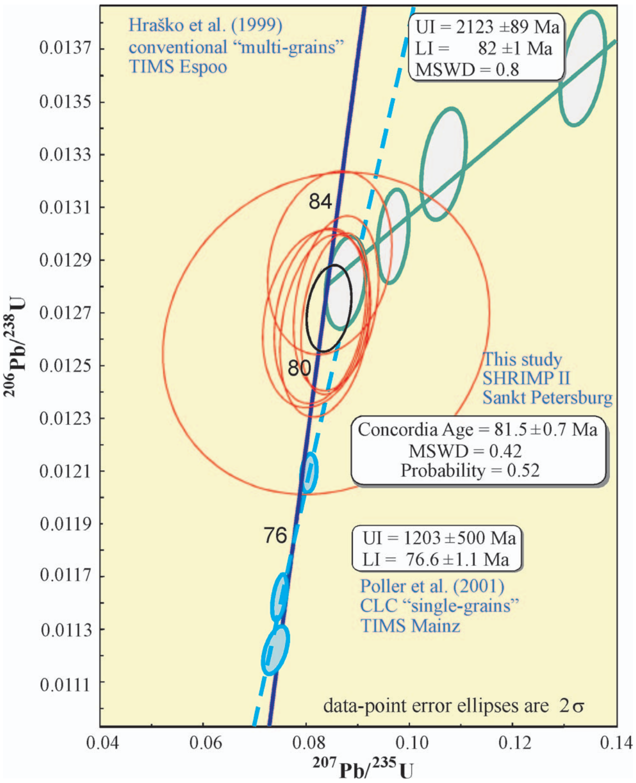

Fig. 5. Comparison of the Rochovce U-Pb zircon data from all published sources.

fect of the Variscan metamorphic/magmatic processes on the studied zircons, whereas the Variscan granitic and meta-igneous rocks are common in the south Veporic Zone (Putiš et al. 2009; Kohút et al. 2010; Broska et al. 2011). This could be explain in two ways: ***i)*** the source of the Rochovce granite was from the deeper part of the lower crust not significantly influenced by the Variscan orogenesis or ***ii)*** due to limited study from three analysed zircon cores, only one was older than Cretaceous, but not Variscan, and a random feature is a matter of statistics, therefore this question remains open for future study. The Hf isotope signature (Table 2) of the studied zircons with $\varepsilon Hf_{(81)} = -5.2$ to $+0.2$ call for lower crustal meta-igneous source provenance of the Rochovce granite magma, whereas the inherited core with $\varepsilon Hf_{(564)} = +7.4$ indicates a former mantle contribution to its source. This is in accordance with negative values $\varepsilon Nd_{(81)} = -3.0$ to -2.4 (Hraško et al. 1998), which suggests that a lower crustal protolith is more probable than an upper crustal metasedimentary or mantle source. There are comparable Hf model ages $t_{(DM2st)}$ ranging from 945 to 1105 Ma, whereas the Nd model ages $t_{(DM2st)}$ are 994~1115 Ma.

The Alpine-Balkan-Carpathians-Dinaride (ABCD) orogenic belt and/or metallogenic province is part of the Alpine-Himalayan orogenic system that resulted from convergence of the African, Arabian and Indian plates and their collision with Eurasia, mainly from the Cretaceous to the recent (Heinrich & Neubauer 2002; Neubauer 2002). Major ore deposits within the ABCD are mostly related to calc-alkaline magmatism, which was associated with transitional subduction-collision processes followed by extension during the Late Cretaceous and Oligocene to Neogene periods. Late Cretaceous magmatism/volcanism dominates mostly in the eastern part of the ABCD metallogenic belt, often denoted as the Banatitic Magmatic and Metallogenetic Belt (BMMB — Berza et al. 1998; Ciobanu et al. 2002 and citation therein) or Apuseni-Banat-Timok-Srednogorie belt (ABTS — Popov & Popov 2000; von Quadt et al. 2005 and citation therein) occurred in Romania, Serbia and Bulgaria. Although granitic rocks — "banatites" and their characteristics are similar within this belt, there are mutual differences in type of mineralization, for example, the porphyry-type Cu±Au±Mo deposits, associated epithermal massive sulphides, and Fe-Cu skarn. The Late Cretaceous ore-bearing magmatism lasted over 25 Ma (from ca. 92 to 65 Ma) and more than 50 important deposits and occurrences are genetically and spatially associated with "banatites" (see reviews: Ciobanu et al. 2002; von Quadt et al. 2005; Zimmerman et al. 2008). However, Late Cretaceous magmatism is scarce within the western part of the ABCD belt where only minor aplite and pegmatite veins are reported to accompany Cretaceous metamorphism in the Alps and mineral deposits contrast with contemporaneous metamorphogenic siderite/magnesite/talc and hydrothermal Cu vein deposits exposed in the Eastern Alps and Western Carpathians (Neubauer 2002). It is noteworthy that the Rochovce granite (81.5 Ma in age) together with its porphyry and stockwork mineralization forms the northernmost continuation of the BMMB or ABTS belt.

The Rochovce granite was intruded to a relative shallow level. The ultimate depth of the granite emplacement estimated on the basis of contact metamorphism should be between 200–100 MPa (Korikovsky et al. 1986; Vozárová 1990). Our Re-Os molybdenite data confirm shallow granite emplacement with rapid cooling because granite-porphyry mineralization shows identical age to stockwork mineralization in host rock schists and phyllites, and/or K/Ar cooling ages on the granite biotites (Kantor & Rybár 1979) are comparable to our results from both isotope systems. Albeit second-boiling reaction and hydrothermal processes at the granite exocontact are limited by granite body dimension, the diameter of the intrusion is less than 3 km. However, apart from the contact metamorphism, regional metamorphism is known in connection with the development of a metamorphic core complex during Cretaceous orogenic events (Janák et al. 2001). Recent $^{40}Ar/^{39}Ar$ laser-probe dating of white micas from metapelites of the SE part of the Veporic Unit 77–72 Ma (Janák et al. l.c.) indicates that cooling below the blocking temperature in different parts of the SE Veporic territory was not instantaneous. On the other hand Dallmeyer et al. (1996) published a muscovite plateau age (86.9±0.2 Ma) from the Late Paleozoic/Triassic Veporic cover sequence from the contact zone between the Veporic and Gemeric Units. This in part higher age can be affected by excess argon, as the authors supposed termination of regional compressional tectonics at 82 Ma. Late Cretaceous exhumation of these metamorphic terrains is interpreted in terms of post-collisional, orogen-parallel extension and unroofing along low-angle detachment faults (Plašienka et al. 1999). The following scenario for the generation and emplacement of the Rochovce granite was inferred (Poller et al. 2001): in the Late Jurassic–Early Cretaceous, continental collision and crustal stacking followed the closure of the Meliata Ocean. Crustal thickening together with some heat input from the mantle triggered partial melting and generation of granite in the lower crust. During the middle Cretaceous period, shortening and crustal stacking continued and prograded outwards. Shortening in the rear of the Veporic wedge triggered its exhumation and orogen-parallel extension. During the final stages of exhumation, the Rochovce granite was emplaced into the extensional shear zones. The sources of the Rochovce granitic melts can be seen in the lower crustal meta-igneous root, not exposed on the surface.

Conclusion

New SHRIMP zircon U-Pb and Re-Os molybdenite ages presented in this paper bring detailed information concerning the age of granite related mineralization from the contact zone between the Gemeric and Veporic Units in the Rochovce area. It is obvious that calc-alkaline granite magmatism and associated porphyry-type and stockwork mineralization from this locality are Late Cretaceous in age and were formed 81.5 Ma. Our data attest instantaneous cooling of a shallow level granite intrusion due to rapid exhumation as a consequence of post-collisional, orogen-parallel extension and unroofing. The Cretaceous Rochovce granite with typical Mo-W mineralization is unique in the Western Carpathians and represents the northernmost continuation of mineralization associated with the Cretaceous calc-alkaline magmatism within the Alpine-Balkan-Carpathians-Dinaride metallogenic belt. The Hf isotope study from zircons confirmed the lower crustal source material of the Rochovce granite.

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