Padrť Stock (Teplá–Barrandian Unit, Bohemian Massif): petrology, geochemistry, U–Pb zircon dating of granodiorite, and Re–Os age and origin of related molybdenite mineralization

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The Padrť Stock is a small (~5 km²) intrusion located near the SE margin of the Teplá–Barrandian Unit, Bohemian Massif, several kilometers away from the NW periphery of the Central Bohemian Plutonic Complex. On outcrops, which are all located close to the contact of the stock with Neoproterozoic sedimentary rocks, two types of granitoids were detected, fine- to medium-grained hornblende–biotite Padrť granodiorite, and, along its SW margin, fine- to medium-grained partly porphyritic biotite Teslíny leucogranite. The U–Pb zircon dating of the more voluminous Padrť granodiorite by laser ablation ICP-MS yielded a magmatic age of 342.8 ± 1.1 Ma, which is slightly lower than are the published age data for the nearby Blatná suite granitoids of the Central Bohemian Plutonic Complex. The Re–Os dating of molybdenite occurring in quartz veins within a quartzite lens in close exocontact yielded ages of 337.2 ± 2.4 Ma and 339.8 ± 2.5 Ma (two samples). The data indicate that the formation of molybdenite postdated that of the magmatic rock. This is in agreement with relatively low-temperature deposition of quartz related to formation of the molybdenite, as indicated by the fluid inclusions (280 to 300°C).

Keywords: Teplá–Barrandian Unit, Variscan granitoids, petrology, geochemistry, U–Pb zircon dating, Re–Os molybdenite dating

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1. Introduction

Several small stock-like granitoid intrusions occur at the SE rim of the Teplá–Barrandian Unit (TBU). The Bohutín Stock (~3.4 km² at the surface; Dudek and Fediuk 1956; Vlašímský 1982; Bambas 1990) is dominated by quartz diorite and granodiorite. It is, thanks to underground mining of Ag–Pb–Zn–Sb vein-type ores of the Bohutín Deposit (Piša 1966; main operation 1841–1979), documented down to a depth of 1.350 m below the surface. Another intrusive stock in this area is represented by the poorly known Padrť Stock, located farther to the W (see Fig. 1).

All these small intrusions belong to the NW peripheral part of the Příbram Ore Region, an area exploited for vein-type ores and geologically studied for centuries (e.g., Bambas 1990; Žák K and Doběš 1991). These small stocks intruded almost unmetamorphosed Neoproterozoic and Cambrian sedimentary rocks at a distance of several km away from the Central Bohemian Plutonic Complex (CBPC). The CBPC is a voluminous multiphase intrusive complex (c. 3.200 km²; Holub et al. 1997b), which is well characterized with respect to petrology, geochemistry and ages of individual intrusions (e.g., Janoušek et al. 1995; Holub et al. 1995, 1997a; Janoušek et al. 2000a, 2009, 2010; Žák J et al. 2005a, b, 2009). The ages of the main-phase plutons within the CBPC range from 354 ± 4 Ma to 337 ± 1 Ma. Deeper within the TBU and another 25 km to the W, small early-Variscan Štěnovice Pluton (~27 km², granodiorite–tonalite) occurs, for which zircon U–Pb dating yielded an age of 375 ± 2 Ma (Žák J et al. 2010).

The Padrť Stock is little known due to its location inside the Brdy Military Training Area with restricted access (1927–recent) and because it is largely concealed beneath Quaternary cover. Rather controversial views regarding the petrology and extent of the Padrť Stock were presented in the geological maps and short papers (e.g., Fediuk 2008). The purpose of this study is not only to bring new petrological and geochemical insights, but also provide U–Pb age for the Padrť Stock. The research focused also on sub-economic molybdenite mineralization in quartz veins within a thermally-metamorphosed quartzite at its exocontact. Lastly, in order to improve the
understanding of relationships between the Padrť Stock and the molybdenite mineralization, fluid inclusions from three quartz types were studied and molybdenite dated by the Re–Os method.

2. Geological setting

2.1. Regional position of the Padrť Stock and studied samples

The Padrť Stock (Fig. 1a–b) is located close to the SE margin of the TBU, where several sets of regional faults intersect. Into the area south of the Padrť, there is directed the SW continuation of the NE–SW oriented, regionally important fault system of the so-called Clay Fault. The Clay Fault is, at the current exposure level, responsible for repetition of belts of Neoproterozoic and Cambrian rocks, and it also controls the extent of the Ag–Pb–Zn veins in the Pribram Ore Region. Younger phases of movement on this tectonic zone are visible as faults inside the Bohutín Stock, but the displacement was small, on the order of 20 m at maximum (Bambas 1990). The main phases of movements on this fault system therefore pre-dated the intrusion of the Bohutín Stock and the formation of vein sulfidic mineralizations. Minor movements probably continued until the Tertiary (see Knížek 2013).

South of the Padrť area is located the Rožmitál Block, a relic of the contact-metamorphosed roof of the CBPC. It contains Cambrian to Devonian metasedimentary rocks intruded by granitoids with Au mineralization (Yazdi 1997; Yazdi et al. 1997; Zachariáš et al. 2001). The Rožmitál Block is surrounded by granite intrusions of the Blatná suite; its boundaries are locally modified by faults. The faults of NW–SE direction partly limiting the Rožmitál Block on its eastern side are also directed into the Padrť area, where they can be responsible for the boundary between the Neoproterozoic and Cambrian sediments.

The Padrť depression is limited on its eastern and northern sides by steep slopes with outcropping Cambrian continental clastic sedimentary rocks – predominating quartz-rich conglomerate with minor greywackes, quartz sandstones to quartzites. The Padrť Stock itself intruded shale and greywacke with lenses of silicates and bodies of submarine basalts, i.e. a rock sequence typical of the Blovice Complex of the TBU (Hajná et al. 2011).

The real extent of the Padrť Stock is not precisely known. There are only a few drillings (two of them were discussed by Fediuk 2008) and the rest of knowledge comes from rare outcrops and/or loose granodiorite blocks. Figure 1b shows the extent of the Padrť Stock in geological map 1:200 000 (Čepek and Zoubek 1961). In the granodiorite area shown on this map, the current authors were able to find only several weathered granodiorite blocks contained in the Quaternary cover and grus in the dumps of an abandoned 19th century Fe mine.

2.2. Contact-metamorphosed rocks and ore mineralizations

Manifestations of contact metamorphism by both Bohutín and Padrť stocks can be typically found up to several hundred meters from the contact, but never more than 1 km away (Bambas 1990). Apart from the common types of Neoproterozoic contact-metamorphosed rocks, several others can be found at the exocontact of the Padrť Stock. One of them is a graphite-rich chiastolite slate (with ~4.2 wt. % C), which was found in now inaccessible draining gallery of the Fe mine located near the eastern contact of the Padrť Stock. The chiastolite slate probably represents a tectonic segment within the fault zone bordering also the Cambrian sediments. This rock was identified by Slavík (1915), who, based on similarities to other contact-metamorphosed rocks in the area of CBPC, considered its precursor to be Ordovician shale.

Two lenses of light-gray to almost white, fine-grained quartzite occur very close to the contact of the Padrť Stock SW of the former village of Přední Záběhlá (Ambrož 1865). They are not shown properly on the published geological maps. Except for abundant arsenopyrite both contain also other interesting ore minerals; in one of the lenses molybdenite occurs as large flakes (up to 5 mm across) in quartz veins and partly also in the host quartzite. The second quartzite lens was described to contain antimonite mineralization (Ambrož 1865), which the authors have not been able to confirm.

3. Analytical methods

3.1. Sampling

All sites where granitoids were sampled are located outside of the extent of the Padrť Stock shown on the
published geological map of Čepek and Zoubek (1961). The best outcrops, described in detail already by Ambrož (1865), are located proximally north of the ruins of the former Teslín Monastery (samples PAD-GR1, PAD-GR2; Teslín means always the ruins of the former small monastery in this paper, not the village of the same name located more to the south). These outcrops became later forgotten and are not shown on any modern geological maps. The drillings described by Fediuk (2008) are located close to this area. The second sampled site is represented by blocky outcrops close to the former village Přední Záběhlá (PAD-GR3). The third site where granitic rocks were sampled is an outcrop of a very small, probably isolated stock (~60 m in diameter) in an abandoned pit for quarrying granodiorite grus in the former village Kolvin (PAD-GR4). This granodiorite body, outcropping as large blocks at the bottom of this pit, was never mentioned or mapped before. Therefore, this site represents a new field discovery (first identified by J. Litochleb), located deeper inside the TBU at a distance of 4 km away from the earlier known outcrops of granitoids. All samples of granitoids were taken in the field from internal parts of large (0.5 to 1.0 m) blocks.

The quartz veins containing molybdenite were sampled for Re–Os dating and for fluid inclusion study. Positions of samples are shown in Fig. 1b.

### 3.2. Whole-rock and mineral chemistry

After homogenization, whole-rock major- and trace-element analyses were carried out in laboratories of the Czech Geological Survey (V. Janovská and R. Kašičková analysts). Silica was determined using titration method. Other major oxides were measured using Flame Atomic Absorption Spectroscopy on an AAnalyst 100 instrument. Analytical errors for major-element analyses in this laboratory were discussed in detail by Dempirová (2010) and Dempirová et al. (2010). Carbon and sulfur were determined on an element analyzer ELTRA CS-500, which measures the C and S content of the gasses produced by sample combustion using infrared absorption. Trace elements were determined by the X-ray fluorescence method on an ARL9400 Advant’XP instrument. The precision of the analyses varied between 1 and 5 %, depending on the elemental concentration (detection limits were 1–2 ppm).

Rock-forming silicate minerals were analyzed using a CAMECA SX100 electron microprobe at the Institute of Geology of the Academy of Sciences of the Czech Republic (AS CR), Prague, in wavelength dispersive mode, using an accelerating voltage of 15 kV, beam current of 10 nA, and a beam diameter of 2 µm. The following standards and X-ray K$_\alpha$ lines were used: Na, Al – jadeite, Mg, Si, Ca – diopside, K – leucite, Ti – rutile, Ba – baryte, P – apatite, Mn – MnCr$_2$O$_4$, Fe – magnetite, and F – fluorite.

The peak counting times were (in seconds), F 30, Na 20, Si 10, Mg 10, Al 10, K 10, Ca 10, Ti 20, Mn 30, Fe 30, Rb 30, Ba 10, Cr 30, Cs 30, Zn 6. The raw data obtained from electron microprobe were reduced using X-Phi(ZAF) procedure (Merlet 1994).

### 3.3. U–Pb dating of zircons

Zircon grains were separated from the fresh rock sample using conventional techniques: crushing, Wilfley concentration table, and finally, magnetic and heavy liquid separations (tetrabromoethane, density of c. 3 g cm$^{-3}$, and diiodomethane). After that, zircon concentrates were handpicked for morphological types and mounted in an one-inch epoxy disc and polished. Before analysis in the mass spectrometer, the internal zircon structures and inclusions were characterized by backscattered electron (BSE) and cathodoluminescence (CL) imaging using a Tescan scanning electron microscope at the Institute of Geology AS CR, Prague.

The Pb/U isotopic ratios were acquired using an Element 2 (Thermo Scientific) high-resolution sector field mass spectrometer coupled with a 213-nm NdYAG UP-213 laser ablation system (New Wave Research), housed at the Institute of Geology AS CR, Prague. Samples were ablated in an original New Wave Research large format ablation cell. The laser was fired at a repetition rate of 5 Hz, using a spot size of 30 µm and a fluence of c. 9 J cm$^{-2}$. Acquisitions for all measured samples consisted of a 35 s measurement of blank followed by acquisition of U and Pb signals from zircons for another 60 s. Data were collected for masses 204, 206, 207, 208, 232 and 238 using both analogue and ion counting modes of the SEM detector, one point per mass peak and relevant dwell times per mass of 10, 15, 30, 10, 10 and 15 ms. The sample introduction system was modified using Y-piece tube attached to the back end of the plasma torch and connected to the helium gas line carrying the sample from the laser cell. The Hg impurity in the carrier He gas, which can cause isobaric interference of 204Hg on 204Pb, was reduced by using in-house made gold-coated sand trap. The relative contribution of common Pb to total Pb was less than 0.1 % and, therefore, no common Pb correction was applied to the data. Elemental fractionation and instrumental mass bias were corrected by normalization of internal U–Pb calibration zircon standard 91500 (1065 Ma, Wiedenbeck et al. 1995) and reference natural zircon standard GJ-1 (609 Ma, Jackson et al. 2004) periodically analyzed during the measurement for quality control. The obtained concordia ages of these standards 1062 ± 5 and 610 ± 3 Ma (2σ) correspond well within the errors to published zircon standards ages. Raw data reduction and age calculations, including corrections for baseline, instru-
3.4. Re–Os molybdenite geochronology

The Re–Os molybdenite dating was also performed at the Institute of Geology AS CR, Prague, using the Re spike–Os normal method (Selby and Creaser 2001). A detailed description of the analytical procedure (sample decomposition, Re–Os separation), including preparation and calibration of the $^{185}$Re–Os normal solution, was given elsewhere (Kohút et al. 2013). Rhenium concentrations were determined using multi-collector inductively-coupled plasma mass spectrometry (MC-ICPMS) on Neptune (Thermo Scientific) at the Czech Geological Survey, Prague. The instrument was coupled with a de-solvation nebulizer Aridus II (CETAC) to achieve a more stable signal. The isotopic fractionation was corrected on-line using exponential law and Ir as an internal standard.

3.5. Fluid-inclusion study

Fluid inclusions were studied at the Faculty of Science, Charles University in Prague, using Leica DMPL and Olympus BX-40 microscopes and a Linkam THMSG 600 heating–freezing stage. Salinity of aqueous-only inclusions was calculated using the equation of Bodnar (1993). Salinity of aqueous–carbonic inclusions was estimated using software of Bakker (1997). Bulk composition and fluid inclusions were computed using equation of state (Bakker 1999) implemented in the software FLUIDS (Bakker 2003).

4. Results

4.1. Petrology and geochemistry

Samples of granitoids from the studied Padrť area include two distinctly different facies: hornblende–biotite granodiorite and biotite leucogranite (Fig. 2).

Dark gray fine-grained weakly porphyritic hornblende–biotite granodiorite was found in blocky outcrops near the former Teslíny Monastery (PAD-GR2) and near the former village of Přední Zaběhlá (PAD-GR3). A non-porphyritic, very fine-grained variety of the same granodiorite crops out in a small abandoned sandpit in the former village of Kolvín (PAD-GR4). Both varieties of the granodiorite are composed of about 30–31 vol. % quartz, 33–37 % plagioclase, 8–11 % K-feldspar, 14–15 % biotite and 8–11 % actinolitic hornblende. Apatite, zircon and pyrite are accessory phases.

Mostly subhedral plagioclase is zoned with cores of An$_{0.35-0.40}$ (andesine) and rims An$_{20-30}$ (oligoclase). Younger anhedral and perthitic K-feldspar contains 0.3 to 1.1 wt. % BaO (0.005 to 0.020 apfu Ba). Abundant subhedral hornblende (Mg-hornblende to actinolite) forms clots together with biotite. Hornblende is homogeneous or only insignificantly zoned with Mg# (Mg/(Mg + Fe)) in the range 0.50–0.55. At Kolvín, the Mg# reaches up to 0.72. Hornblende is generally Si-rich (mostly in the range 7.4–7.9 Si apfu; Fig. 3; Electronic Supplement 1). Biotite (anne) which was later than hornblende, is chemically homogeneous (Mg# = 0.40–0.45: Fig. 4; Electronic Supplement 2).

Light gray to whitish fine-grained weakly porphyritic biotite leucogranite has been found in several blocks near the former Teslíny Monastery (PAD-GR1). It is composed of approximately 37 vol. % quartz, 30 % oligoclase–andesine (An$_{18-34}$), 28 % K-feldspar, and 5 % biotite. Apatite and zircon represent accessory phases. Perthitic cores of the K-feldspar grains are enriched in Ba (up to 0.65 wt. % BaO) compared to the rims (<0.1 wt. % BaO). Annette (Mg# = 40–41) is the only mafic mineral.

The chemical compositions of both rock types are summarized in Tab. 1 and the relationships between some chemical elements plotted in Fig. 2. Comparisons of the chemistry of hornblende and biotite from the studied rocks to the compositions of the same minerals in granitoids of the CBPC are made in Figs 3 and 4.
Fig. 2 Comparison of chemical composition of Padrť granitoids with selected intrusions of the CBPC. Data are from Holub et al. (1995, 1997b), René (1999), Sokol et al. (2000) and unpublished data of the authors.
Hornblende–biotite granodiorite is, based on the three studied samples, chemically homogeneous (63.2–64.3 wt. % SiO$_2$). It is characterized by relatively high contents of mafic elements (5.3–5.7 wt. % Fe$_{O3tot}$, 2.2–2.4 wt. % MgO) and low alkalis with a predominance of Na over K (3.1–3.4 wt. % Na$_2$O and 2.6–3.0 wt. % K$_2$O). Among trace elements, Rb reaches 102–127 ppm, Sr 207–232 ppm and Zr 120–139 ppm. Low contents of radioactive and ore elements (< 2–6 ppm U, 11–14 ppm Th, 7–8 ppm Nb and < 2 ppm Sn) indicate low degree of fractionation of this rock.

Biotite leucogranite sample is significantly more acid (74.7 wt. % SiO$_2$), poor in mafic components (1.55 wt. % Fe$_{O3tot}$, 0.44 wt. % MgO) and slightly enriched in potassium (4.94 wt. % K$_2$O). The contents of Rb and Sr are low (127 and 79 ppm, respectively) while U is slightly enriched (13 ppm).

### 4.2. Zircon U–Pb dating

Most of the studied zircons are clear to brownish and the morphological zircon populations present are equant to prismatic (stubby) grains, and euhedral needles. Using CL imaging (Fig. 5), internal zircon structures revealed common oscillatory zoning, typical of igneous zircon (e.g., Vavra 1990). Despite the morphological differences mentioned above, dominant feature of the studied zircons is recrystallization around the dark inclusions or cracks (often filled with SiO$_2$). In a few images, CL revealed sector zoning, characteristic of slowly grown zircons in plutonic environments (Hanchar and Miller 1993). The U–Pb measurements of 29 zircons yielded concordant ages between 337 Ma and 351 Ma, with a mean concordia age of 342.8 ± 1.1 Ma (2σ; Fig. 6; Electronic Supplement 3). The concordia zircon age is interpreted as the age of the crystallization of the Padrť Stock granodiorite.

### 4.3. Molybdenite Re–Os dating

The results of the Re–Os dating of molybdenite from Padrť are given in Tab. 2. The analyses of NIST 8599 molybdenite reference material yielded an age of 27.5 ± 0.2 Ma (2σ), which is well within given uncertainty of certified value (27.66 ± 0.1 Ma) and also similar to the ages of Porter and Selby (2010) and Lawley and Selby (2012). The studied molybdenite samples from Padrť (two independent molybdenite separations and analyses) have very high rhenium contents of 602 and 542 ppm as well as a high $^{187}$Os contents of 2133 and 1934 ppb, yielding two Re–Os ages of 337.2 ± 2.4 and 339.8 ± 2.5 Ma.
4.4. Fluid-inclusion study

4.4.1. Studied samples

Fluid inclusions were studied in six samples of quartz veins from the locality PAD-Q1 (Fig. 1b). Texturally they represent two principal types of quartz gangue: (1) massive quartz, and (2) drusy vugs with euhedral quartz crystals. Quartz veins composed of massive quartz are up to 15 cm wide and represent the most common type in the studied area. Those with sparse vugs and euhedral crystals are much less frequent and usually less than 5 cm thick. Drusy vugs are related either to younger veins that crosscut the massive veins, or they locally develop in the core of massive veins.

Three generations of quartz were identified based on microscopic study: Q1 – the oldest, anhedral quartz grains, size of which may slightly increase from the vein rim towards the core. Individual grains are nearly opaque in their cores, mostly due to the presence of numerous small and/or decrepitated fluid inclusions, and become more transparent near their rims. Notably Q1 quartz exhibits a moderate degree of ductile deformation and several phases of brittle deformation. The latter is recorded by numerous trails of secondary fluid inclusions, frequently occurring as parallel sets. Q2 – massive quartz (Q2a), it usually shows marked progressive grain-size gradation along the vein rim-to-core profile. Locally, in the core zone, vugs with subhedral quartz crystals (Q2b) are present. It is significantly less deformed than Q1. The amount of fluid inclusions in Q2 also decreases from grain core to grain rim. Q3 – forms sparse thin rims on the Q2 crystals. It differs from Q2, however, by having radial internal structure.

4.4.2. Fluid inclusions

Two types of fluids were identified in the Q1 trough Q3, with respect to major components: aqueous–carbonic (H₂O–CO₂ ± CH₄-salts) and aqueous-only (H₂O-salts).

| Tab. 1 Whole-rock chemical compositions of granitoids (wt. %; trace elements in ppm) |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| Locality | PAD-GR1 | PAD-GR2 | PAD-GR3 | PAD-GR4 |
| Teslíny Monastery | Teslíny Monastery | Přední Záběhlá | Kolín |
| Latitude | 49.63956 | 49.63931 | 49.65908 | 49.66535 |
| SiO₂ | 74.70 | 64.26 | 63.17 | 63.26 |
| TiO₂ | 0.12 | 0.55 | 0.65 | 0.59 |
| Al₂O₃ | 13.31 | 16.50 | 16.26 | 16.80 |
| Fe₂O₃ (tot.) | 1.55 | 5.27 | 5.68 | 5.32 |
| MgO | 0.44 | 2.16 | 2.37 | 2.17 |
| MnO | 0.030 | 0.101 | 0.101 | 0.103 |
| CaO | 1.47 | 4.32 | 4.22 | 4.17 |
| Li₂O | 0.004 | 0.005 | 0.006 | 0.004 |
| Na₂O | 2.78 | 3.45 | 3.14 | 3.38 |
| K₂O | 4.94 | 2.64 | 2.98 | 2.81 |
| P₂O₅ | 0.02 | 0.11 | 0.13 | 0.11 |
| CO₂ | < 0.01 | < 0.01 | < 0.01 | < 0.01 |
| S (tot.) | 0.15 | < 0.010 | < 0.010 | 0.32 |
| LOI | 0.38 | 0.49 | 0.83 | 0.80 |
| H₂O | 0.09 | 0.07 | 0.14 | 0.12 |
| S (equiv.) | −0.04 | 0.00 | 0.00 | −0.08 |
| Total | 100.00 | 99.95 | 99.69 | 99.97 |

ASI – alumina saturation index, defined as the molar ratio Al₂O₃/(CaO + K₂O + Na₂O).

| Tab. 2 Re–Os data for the studied Padř’ molybdenite and Henderson Mine reference material NIST 8599 |
|---------------------------------|-----------------|-----------------|-----------------|
| Sample | Description | Re (ppm) | ⁱ⁸⁷Os (ppb) | Age (Ma) |
| Os 296 (PAD-Q1/1) | Molybdenite sample PAD-Q1/1 | 602 (1) | 2133 (13) | 337.2 ± 2.4 |
| Os 381 (PAD-Q1/2) | Molybdenite sample PAD-Q1/2 | 542 (2) | 1934 (12) | 339.8 ± 2.5 |
| NIST 8599 | Molybdenite reference material (Henderson Mine) | 12.04 (3) | 3.47 (3) | 27.5 ± 0.2 |

Model Age was calculated assuming no presence of common Os. Total uncertainties shown are at 2-sigma level.
These form primary, pseudosecondary and secondary fluid inclusions (e.g., Roedder 1984). A relatively large number of totally or partially decrepitated fluid inclusions is observed in many of the studied samples. These are located not only in the anhedral and ductile/deformed Q1, but also in the undeformed and euhedral Q2. There seems to be a relation between the size, shape and composition of fluid inclusions and their ability to decrepitate naturally: the largest, mostly aqueous–carbonic and irregularly-shaped inclusions are frequently leaked.

4.4.3. Aqueous–carbonic inclusions 
\((H_2O–CO_2 ± CH_4-salts)\)

The aqueous–carbonic fluid inclusions were identified mostly in the Q1 quartz, but also in older growth zones of Q2. They form both primary and secondary inclusions. Degree of fill is mostly homogeneous, reaching values 0.9 to 0.8. Temperatures of melting of solid CO\(_2\) \((Tm-CO_2)\) varied from –66.6 to –58.4 °C (with a subtle maximum from –61 to –59 °C) and together with melting of clathrate above 10 °C (from 10.6 to 13.8 °C), suggest low-salinity fluids (~ 2 wt. % eq. NaCl) and an admixture of CH\(_4\) in the gaseous phase. Homogenization of the carbonic phase (Th-car) occurred from –20.0 to +27.7 °C (always to vapor; most data lie between 3 and 17 °C). In the absence of microRaman data we used the general relation between Th-car and Tm-CO\(_2\) (van den Kerkhof and Thiéry 2001) in order to quantify the composition of the gaseous phase (10–30 mol. % CH\(_4\), 90–70 mol. % CO\(_2\); and 85–185 cm\(^3\)/mol). Final homogenization to the liquid phase occurred between 231 °C and 340 °C with a single maximum at 290–310 °C (Fig. 7). A few inclusions homogenized to vapor from 270 to 320 °C.

Fig. 6 U–Pb concordia diagram for zircons from the Padrť granodiorite (29 analyses). All data are plotted with 2σ uncertainties.

Fig. 7 Summary of measured microthermometric data for primary, pseudosecondary and secondary fluid inclusions. Corresponding fields of most representative data for Q1, Q2 and Q3 quartz are highlighted by shaded boxes. Summary histogram of final homogenization temperatures is plotted on the right side of the figure.
In addition to fluid-inclusion assemblages with homogeneous degree of fill, we noted also that of secondary fluid inclusions hosted by euhedrall crystal (Q2b) that contained a mixture of monophase vapor (CO\textsubscript{2}) inclusions, two-phase vapor- and liquid-rich inclusions and of rare monophase liquid (H\textsubscript{2}O) inclusions. The following data were measured: Tm-\textsubscript{CO\textsubscript{2}} (--59.0 to --59.2 °C), Th-car (17.0 to 27.7 °C for two-phase inclusions and 3.6 °C for the monophase vapor inclusion; always to vapor state). Final homogenization of two-phase inclusions occurred from 230 to 280 °C; those representing end-members homogenized from 230 to 240 °C. We believe that this assemblage was trapped from an unmixed fluid and the measured 230–240 °C correspond therefore to the actual temperatures of Q2b formation.

4.4.4. Aqueous-only inclusions (H\textsubscript{2}O-salts)

**Q1 quartz** All aqueous-only fluid inclusions in Q1 are clearly of secondary origin. They are related to trails (fractures) that crosscut more than two quartz grains and frequently are parallel with margins of the studied Q1 vein (pointing thus to their formation under approximately NE–SW oriented extension). They homogenize to liquid between 155 and 257 °C, with a marked maximum at 210 to 220 °C; salinity varies from 2.9 to 7.0 wt. % eq. NaCl.

**Q2 quartz** At least three generations of aqueous-only fluids can be identified in Q2: the oldest one is represented by three-dimensional clusters of primary liquid-rich fluid inclusions in the “dark” cores of anhedral quartz grains. They display mostly homogeneous degree of fill (0.9). They gradually pass into the next inclusion generation that is hosted by transparent outer rims/zones of Q2. Inclusions here are similar to those from cores, except for slightly lower degree of fill (0.85–0.80) and increasing abundance of vapor-rich and vapor-only fluid inclusions (both types indicate that boiling of fluid locally occurred). Third (and fourth) generation of inclusions is represented by well-defined secondary trails, some of which contain a heterogeneous mixture of boiled fluids (highly variable degree of fill).

Inclusions representing the early fluids characterize broadly variable homogenization temperatures of 160–226 °C (to liquid) and a narrow range of salinities (5.0 to 5.9 wt. % eq. NaCl). Primary inclusions of the next generation (grain rims) show slightly higher homogenization temperatures (223.7 to 234 °C; to liquid), but more variable and generally lower salinities (1.9 to 4.6 wt. % eq. NaCl). Pseudosecondary inclusions from the same zone yielded even lower temperatures (172 to 210 °C; to liquid) and salinities (0.7–2.9 wt. % eq. NaCl) and the same holds for clearly secondary inclusions (188–190 °C, 0.5–1.6 wt. % eq. NaCl). A few vapor-rich secondary fluid inclusions homogenized to vapor at c. 200–215 °C. Conditions of late boiling can bet thus set at about 200 °C.

**Q3 quartz** Sparse, likely primary fluid inclusions homogenized from 165 to 186 °C (to liquid); salinity is estimated to be 0.9–1.2 wt. % eq. NaCl.

5. Discussion

5.1. Comparison of the Padřt Stock with granitoids of the CBPC

Granitoids of the CBPC are classified into several major suites: normal calc-alkaline Sázava suite (e.g., gabbrons, Sázava tonalite, Marginal granite), high-K calc-alkaline Blatná suite (e.g., Blatná granodiorite, Kozárovce granodiorite, Červená granodiorite, Milín granite), K- and Mg-rich Čertovo Břemeno suite (e.g., Sedlčany granite, durbachites), and peraluminous Maršovice suite (e.g., Kozlovice and Maršovice granodioritites) (Janoušek et al. 1995; Holub et al. 1997b; Janoušek and Skála 2011 and references therein). Published geological maps and papers (Čepek and Zoubek eds. 1961; Holub et al. 1997b; Mašek ed. 1990) assigned the granitoids from Padřt to the types later included into Sázava or the Blatná suites. However, all mentioned authors classified the granitoids probably only on the basis of macroscopic and microscopic observations; whole-rock chemical data were not available, except for an average of two analyses in an unpublished report by Vlašímský (1976).

But even on the basis of our new chemical analyses of rocks and minerals, the Padřt granitoids cannot be classified unequivocally. Figure 2 compares the Padřt granitoids with selected granitoid types of the CBPC with similar SiO\textsubscript{2} contents: the Sázava tonalite, Blatná granodiorite, Červená granodiorite, Milín granite, and the Marginal granite. The contents of MgO, CaO and K\textsubscript{2}O in Padřt granodiorite vary between values typical of the Sázava and Blatná suites (Fig. 2). In addition, K\textsubscript{2}O vs. Rb and Rb vs. Sr diagrams further highlight the intermediate nature of the Padřt granodiorite between the typical compositions of the Sázava and Blatná suites. The chemical composition of the Teslíny leucogranite is close to the Marginal granite according to Holub et al. (1997b) and granites from the area of Underground Gas Storage Facility near Příbram (Sokol et al. 2000). Two samples from the Padřt Stock analyzed by Vlašímský (1976) were of a more basic composition (SiO\textsubscript{2}~57.7 wt. %) but their exact location in the field is unknown.

Regarding the amphibole composition, analyses from Padřt are richer in silica than early magmatic hornblende from the Sázava and Blatná intrusions (mostly in the range 7.4–7.9 apfu Si, Fig. 3). Such composition is typi-
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The age of the Padrť Stock, Bohemian Massif, is in the range obtained for younger small isolated apophysis at Kolvín, and (ii) Teslíny leucogranite cropping out between Teslíny and Přední Záběhlá, with a small isolated apophysis at Kolvin, and (ii) Teslíny leucogranite forming a mostly hidden body between Teslíny (including two drilling sites described by Fedíuk 2008) and the southern end of the Upper Padrť Pond.

The Teslíny leucogranite intrusion includes tourmaline- and locally also garnet-bearing pegmatite-like rock described by Ambrož (1865), and again briefly by Fedíuk (2008), which we found as blocks between Teslíny and the southern Padrť Pond. The relationship between leucogranite and granodiorite cannot be resolved. The leucogranite is most similar to the Marginal granite (sensu Janoušek and Skála 2011), whereas correlation between the hornblende–biotite granodiorite and the other intrusions remains unclear.

5.2. Geochronology

Morphology, internal zoning, and Th/U ratios can be used in the interpretation of zircon origins (Pupin 1980; Hoskin and Schaltegger 2003). Constant Th/U ratios through time are interpreted to reflect closed-system behavior, whereas higher Th/U in overgrowths can indicate the occurrence of Th-rich inclusions (monazite, allanite etc.; Harley et al. 2007). All Padrť zircons show Th/U values below 0.5 (c. 0.50–0.60 ppm Th, 0.12–0.45 ppm U; see Electronic Supplement 3), and the majority of them yield a mean value at 0.3. This uniform, intermediate Th/U ratio suggests an origin from a single magmatic source and it appears that the Th/U is more variable than the U–Pb age of the studied Padrť granodiorite of 342.8 ± 1.1 Ma in the range obtained for younger types of the CBPC by U–Pb or Pb–Pb zircon dating. In spite of the chemical contrasts between intrusions within the CBPC (see Holub et al. 1997b; Janoušek et al. 1995, 2000b), the age span of main-phase plutons is restricted with c. 15–20 My, between 354 ± 4 and 337 ± 1 Ma. Individual published ages are as follows (all errors are 2σ): (i) calc-alkaline rocks of the Sázava suite, 354 ± 4 Ma (Janoušek et al. 2004) and 346 ± 10 Ma (Holub et al. 1997a); (ii) high-K calc-alkaline rocks, Blatná and Kozárovice granodiorites, 347 ± 2 Ma and 346 ± 2 Ma, (Janoušek et al. 2010), Klatovy granodiorite, 347 ± 1 Ma (Dörr and Zulauf 2010); Nýrsko granite, 339 ± 2 Ma (Dörr and Zulauf 2010). The youngest ages within the CBPC were obtained for (iii) potassic to ultrapotassic rocks, Cerovto brémeno durbachite (343 ± 6 Ma; Holub et al. 1997a) and Tábor quartz syenite (337 ± 1 Ma; Janoušek and Gerdes 2003).

The granodiorite–tonalite intrusive bodies of the Stěnovice and Čistá plutons, located within the TBU, are significantly older than granitoids of the CBPC. These plutons were dated using zircon U–Pb laser ablation ICP-MS (Žák J et al. 2010) and the Pb–Pb evaporation technique (Venera et al. 2000), which yielded mutually comparable ages (375 ± 2 Ma and 373 ± 1 Ma, respectively).

Zircon U–Pb ages for the Bohutín Stock are lacking. There are some old K–Ar ages which were clearly influenced by excess argon and thus yielded unrealistically high Silurian ages (e.g., Vlašimský 1982). Žák K et al. (1998) dated hornblende from the Bohutín Stock by the Ar–Ar method. The argon released during the low-temperature steps indicated older ages up to 370 Ma, while the plateau age (argon released at 1150–1600 °C) was 348.5 ± 0.5 Ma (Žák K et al. 1998). Nevertheless, it was clear that this plateau age was also affected by excess argon, which was probably inherited when this narrow intrusive stock intruded Neoproterozoic rocks. When we use only the data from the 9 highest temperature steps (1275–1600 °C), the calculated isochron age is 342 ± 0.3 Ma, which is similar to the zircon U–Pb age of the Padrť Stock. It is therefore possible that intrusion of Bohutín and Padrť magmas could have been roughly coeval. However, zircon ages from the Bohutín Stock are needed.

The newly obtained Re–Os ages of molybdenite mineralization spatially related to the Padrť Stock (337.2 ± 2.4 and 339.8 ± 2.5 Ma) are somewhat younger than the Re–Os age of molybdenite from the Petročkova hora gold deposit in the Rožmitál Block (344.4 ± 2.8 Ma; Zachariáš et al. 2001). The Rožmitál Block is surrounded mostly by granitoids belonging to the Blatná suite (347 ± 2 Ma; Janoušek et al. 2010). For small porphyritic granitoid bodies located within the Rožmitál Block, rather controversial age results of c. 343–355 Ma have been obtained (see review in Zachariáš et al. 2001). In case of the Padrť Stock, the zircon age on the one hand, and the two molybdenite ages on the other, are within the error different. Therefore, estimating the temperature of molybdenite formation is crucial for the explanation of this possible age gap (see below in Section 5.3).

Detailed study of the age relationships between small intrusive stocks and related mineralization can
improve our understanding of the chronology of individual pulses of hydrothermal vein mineralizations in the Příbram Ore Region. Cross-cutting relations show that both quartz veins with molybdenite and quartz veins with gold postdated the intrusion of the Bohutín Stock (Piša 1966; Bambas 1990). The Bohutín intrusive body and the quartz–molybdenite as well as quartz–gold veins were later cross-cut by the younger Ag–Pb–Zn ± Sb veins (Piša 1966). Similar types of mineralizations occur around the Padrť Stock – molybdenite and antimonite occurrences (Ambrož 1865). Indications of Pb–Zn and Au mineralizations were found by regional ore prospection (Piša et al. 1976; Studničná 1989).

The largest difference with respect to hydrothermal ore mineralizations can be viewed in the abundance of arsenopyrite in the surroundings of the Padrť Stock, ore mineralizations can be viewed in the abundance of arsenopyrite in the surroundings of the Padrť Stock, which is uncommon in the Bohutín area.

Were the molybdenite mineralization at Padrť and Bohutín contemporaneous, the obtained molybdenite ages define the older age limit for the Ag–Pb–Zn ± Sb veins. Field evidence, and evaluation of stable isotope data, fluid types and temperatures of deposition show that the Ag–Pb–Zn ± Sb veins were older than the U mineralization of the Příbram Ore Region (e.g., Vlašimský et al. 1995; Žák K and Dobeš 1991; Škácha et al. 2009). The U mineralization of the main uranium ore district in the southern part of the Příbram Ore Region was repeatedly dated by the U–Pb method on uraninite. Probably the most concordant and reliable age data of 275 ± 4 to 278 ± 4 Ma have been obtained by Anderson (1987), which set the younger age limit for the Ag–Pb–Zn ± Sb veins. Škácha et al. (2009) attempted to date uraninite postdating the Ag–Pb–Zn veins directly at the Příbram – Březové Hory deposit in the polymetallic part of the Příbram Ore Region. The uraninite contained high levels of common lead and the mathematical regression of the data gave only a rough age estimate of 269.8 ± 20.3 Ma. Chemical (electron-microprobe) dating using the only uraninite grain without galena inclusions (supposing no common lead in uraninite) yielded an age of 263.2 ± 8.9 Ma. These data probably indicate that the U mineralizations in both parts of the Příbram Ore Region could have been roughly synchronous. The large interval between the magmatic processes and formation of U mineralization was probably related to the time necessary for erosion of the overlying rocks, opening of brittle faults, and activation of the circulation of shallow-crustal fluids, as evidenced by fluid-inclusion and stable-isotope studies (Žák K and Dobeš 1991).

The formation of economically and historically important Ag–Pb–Zn ± Sb mineralization (production of 3.500 t Ag, 480.000 t Pb, 260.000 t Zn; Bambas 1990) is therefore still chronologically poorly constrained within an age interval of c. 60 My (337 to c. 275 Ma). With respect to the presence of Sn and W minerals in the deep part of the Březové Hory deposit (Bambas 1990), and relatively high temperatures of deposition inferred from fluid inclusions (Žák K and Dobeš 1991), the formation of the Ag–Pb–Zn ± Sb veins was probably closer to 337 than to 275 Ma.

5.3. Conditions of quartz and molybdenite formation at Padrť

Optical microscopy and fluid-inclusion microthermometry revealed the presence of at least three generations of quartz gangue at Padrť, at the locality with occurrence of molybdenite. Early quartz (Q1) corresponds to formation of the most common quartz veins dominated by massive “saccharoidal” quartz gangue. It precipitated from aqueous carbonic fluids that were relatively rich in CH$_4$ (10–30 mol. % in gaseous phase), were of low-salinity (c. 2 wt. eq. NaCl) and had homogenization temperatures clustered around 300 °C.

Younger quartz (Q2), that forms euhedral crystals in the vugs in the Q1, or its own late veins, exhibits higher salinities (6–7 wt. % eq. NaCl) and lower homogenization temperatures (230–260 °C; Fig. 8). The Q2 gradually evolved through the time to slightly lower salinities (4–5 wt. % eq. NaCl) and temperatures (c. 190–220 °C).

Significantly lower salinity (c. 1 wt. % eq. NaCl) of fluids associated with the Q3 indicate their later hydrothermal origin, most probably unrelated to the formation of Q1 and Q2. It differs from Q2 by having radial internal structure, that might indicate its precipitation from silica-saturated solutions and/or original presence of chalcedony that later recrystallized with time to α-quartz.

It is uncertain whether the Q1 and Q2 represented two genetically and chronologically unrelated events, or whether they were the products of a single, more or less, continuous process. Apparent optical transition of Q1 into Q2 in some samples, as well as existence of both aqueous–carbonic and aqueous-only fluids in the older growth zones of Q2 seem to support the later hypothesis. This is further supported by similar slopes of fluid isochores for fluids in the Q3 zones of Q2 seem to support the later hypothesis. This is further supported by similar slopes of fluid isochores for both aqueous–carbonic and aqueous-only fluids (Fig. 8). An argument that supports the former hypothesis is, however, the difference in fluid salinities.

Likely P–T conditions of the Q1, Q2, and Q3 formation are summarized in Fig 8. As already mentioned above, the final stages of Q2 evolution are well-constrained by the heterogeneous fluid assemblage unmixed at c. 230–240 °C and c. 60 MPa. This corresponds to a depth of about 2.2 km, if a fully lithostatic regime is considered. Formation of Q1 is restricted to a P–T range delimited by steep isochores of aqueous–carbonic fluids; they approach the solidus of water-saturated granite melt.
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at > 500 MPa, i.e. at a depth greater than 15 km. This is, in light of the practically unmetamorphosed character of the Neoproterozoic and Cambrian sediments (except in contact zone of the stock) an unrealistically great depth. Therefore we may conclude that fluids precipitating Q1 did not exsolve from the Padrť granodiorite melt, despite the fact that they are spatially closely related. This also explains well the age difference between the magmatism and molybdenite mineralization. We consider 5 km (130 MPa) as a reasonable estimate of maximum depth of the Padrť Stock emplacement. Thus, we may conclude that Q1 formed at temperature not higher than c. 320 °C. Formation of molybdenite, that is younger than most of Q1, but older than Q2b, can therefore be estimated at 280–300 °C. Finally, the widespread presence of decrepitated aqueous–carbonic inclusions in the Q1 may have resulted from thermal and pressure stresses associated with the intrusion of the Padrť Stock. In this case, Q1 quartz veins would be even older than the Padrť intrusion.

The present study, and earlier conclusions of Vlašínský (1982) and Žák K and Dobeš (1991), show that with respect to regional position, time span, fluid types and mineralization conditions, the source of the economically most important Ag–Pb–Zn ± Sb hydrothermal vein deposits could not have been fluids derived during crystallization of CBPC granitoids and satellite stocks. The source of fluid components of this mineralization type had to be in a deeper crust, probably related to clastic metasedimentary rocks (see Beaudoin et al. 1999).

6. Conclusions

The present geochemical and geochronological study leads to the following conclusions:

1. At least two types of granitoids crop out in the Padrť area, fine- to medium-grained hornblende–biotite Padrť granodiorite, and fine- to medium-grained partly porphyritic biotite Teslíny leucogranite accompanied by pegmatoid rock with tourmaline ± garnet.

2. The whole-rock contents of MgO, CaO and K₂O in the Padrť granodiorite vary between values typical of the Sázava and Blatná suites of the CBPC. Furthermore, variations in K₂O, Rb and Sr highlight the intermediate compositions of the Padrť granodiorite between the typical values of the Sázava and Blatná suites. In contrast, chemical composition of the Teslíny leucogranite is close to the Marginal granite (probably part of the Sázava suite) of the CBPC. Amphibole compositions from Padrť differ from early magmatic amphiboles of both the Sázava and Blatná suites. The studied amphiboles are more siliceous (often actinolitic), which is otherwise more typical of the Čertovo břemeno suite of the CBPC or some late amphiboles in the Sázava and Blatná suites. Biotite compositions from Padrť fill the gap between those from typical Blatná granodiorite and Milín granite of the CBPC.

3. Oscillatory-zoned zircons from the Padrť granodiorite yielded a concordant age of 342.8 ± 1.1 Ma (2σ), which is interpreted as the intrusive age.

4. Two Re–Os datings of molybdenite from quartz veins within a quartzite lens in close exo-contact of the...
Padrť granodiorite yielded ages of 337.2 ± 2.4 and 339.8 ± 2.5 Ma.

5. Several generations of quartz were identified in the quartz veins. The molybdenite mineralization was younger than Q1, but older than Q2b quartz. Quartz fluid-inclusion data indicate deposition of molybdenite at 280–300°C at depths between 2.2 and 5 km below the original surface.

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Electronic supplementary material. Supplementary data for this paper, including hornblende and biotite mineral analyses as well as results of zircon U–Pb dating by the LA ICP-MS method, are available online at the Journal web site (http://dx.doi.org/10.3190/jgeosci.177).

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