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# Duration of Variscan granitic magmatism inferred from Re–Os dating of molybdenite in the Tatric Unit of the Western Carpathians

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**Abstract:** In the Tatric Unit (Western Carpathians, Slovakia), high-temperature molybdenite mineralisation was formed contemporaneously with Variscan granitic rocks hosting economically important Au–Sb mineralisation. In this work, four molybdenite separates were taken from representative samples of mineralised granite at the Pezinok – Trojárová and Dúbrava deposits. Re–Os ages of 368.6±1.4 and 356.7±2.6 Ma (Trojárová) together with Re–Os ages of 349.2±1.3 and 348.3±1.3 Ma (Dúbrava) suggest a long-lived mineralisation processes. Our Re–Os molybdenite ages are in agreement with recently published U–Th–Pb single-grains zircon and/or electron-microprobe monazite magmatic ages from hosting granite intrusions. These Re–Os ages mirror the principal periods of granite-forming processes connected with Variscan subduction-collision in the Tatric Unit of the Western Carpathians, that are: subduction stage (369–360 Ma), collision peak (357–349 Ma), and post-collisional extension (345–332 Ma).

**Keywords:** Re–Os molybdenite dating, Variscan ore mineralisation, granitic rocks, Western Carpathians, Malé Karpaty Mts., Nízke Tatry Mts.

## Introduction

Magmatism and mineralisation are intimately linked and controlled by the thermal structure and fluid dynamics in magma chambers and their host rocks. Mineralised igneous rocks are affected by hydrothermal fluids exsolved from the later co-genetically evolved magmas. Unravelling ore-forming and/or mineralisation episodes in the ore deposits or magmatic bodies is practically impossible without precise dating, as the classical spatial structural relations of the ore veins are frequently ambiguous. The determination of the age and timescale based on the selection of dating method in the granitic system is a challenging and critical issue to understand the complex magmatic–hydrothermal evolution processes and related mineralisation. The Re–Os system ($^{187}Re \rightarrow {}^{187}Os$) represents a long-lived isotopic system with direct application to the study of sulfides, oxide minerals, highly siderophile elements, and related ores (e.g., Stein et al. 1997, 2001; Ackerman et al. 2017; Rooney et al. 2024, and citations therein). Molybdenum sulfide ($MoS_2$) or molybdenite is a relatively common high-temperature hydrothermal mineral, often genetically associated with granitic rocks, and now frequently used for dating of ore mineralisations and related magmatism. Complex molybdenite and granite radiometric dating can better track granite source nature and evolution processes.

The Tatric Unit of the Central Western Carpathians (CWC) hosts many ore deposits and occurrences related to the Variscan granite magmatism (e.g., Chovan et al. 1992, 1995, 1996, 2002; Majzlan et al. 2020a, 2020b, and references therein). Previous studies have reported a relatively wide range of the Variscan granite intrusion U–Th–Pb zircon and monazite ages (367–332 Ma) within the Tatric Unit (Poller et al. 2000; Finger et al. 2003; Kohút et al. 2009; Broska et al. 2013, 2022; Kohút & Larionov 2021; Catlos et al. 2022). On the other hand, scarce Re–Os molybdenite data indicated somewhat shorter high-temperature mineralisation period of ca. 352–343 Ma related to granite magmatism in the Tatric Unit of the CWC (Mikulski et al. 2011; Chovan et al. 2013; Majzlan et al. 2020b). The aim of this contribution is to present new results of precise Re–Os molybdenite dating from the Pezinok – Trojárová and Dúbrava localities, and to discuss granite-related genesis of a high-temperature mineralisation in the Tatric Unit in general.

## Geological setting

The pre-Alpine crystalline basement is cropping out mainly in the Central Western Carpathians, heart of the Western Carpathians. The CWC represent a pile of the Cretaceous

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thick- and thin-skinned thrust sheets consisting of three principal crustal-scale superunits. They are, from bottom (north) to top (south): Tatric Unit, Veporic Unit and Gemeric Unit (Fig. 1). The Tatric Unit (TU) includes so-called core mountains in western and northern Slovakia where Variscan granitic rocks form a backbone of their crystalline basement. The Malé Karpaty Mountains (MKM) represent a typical core mountain of the TU, situated in the SW part of the Central Western Carpathians, linking the Western Carpathians with the Eastern Alps (Fig. 1a, b). The Bratislava and the Modra granitic massifs are the dominant parts of the Malé Karpaty Mts., forming their pre-Alpine basement between Bratislava and Modra town. The granitic rocks of the MKM consist of the Variscan peraluminous granitic suite with S-type (Bratislava Massif) and calc-alkaline I-type (Modra Massif) geochemical affinity (Cambel & Vilinovič 1987; Petrík et al. 2001). They both exhibit a distinct intrusive and thermal metamorphic contact with the adjacent Lower Paleozoic (Silurian to Devonian) metapelites to metapsammites and amphibolitic metabasic rocks whose metamorphic grade reached only the greenschist facies (below 350 MPa and 550 °C; Korikovsky et al. 1984; Krist et al. 1992; Polák et al. 2011, 2012). The dominant rocks of the Bratislava Massif are biotite to muscovite-biotite granodiorites, monzogranites to leucocratic syenogranites, and widespread pegmatite–aplite dykes. The typical rocks of the Modra Massif, on the other hand, are biotite (leuco)tonalites and granodiorites; granites and pegmatites are subordinate to lacking (Cambel & Vilinovič 1987; Petrík et al. 2001; Kohút et al. 2009; Uher et al. 2014). The metamorphic host rocks form typical volcano-sedimentary sequences (*Pezinok/Pernek*

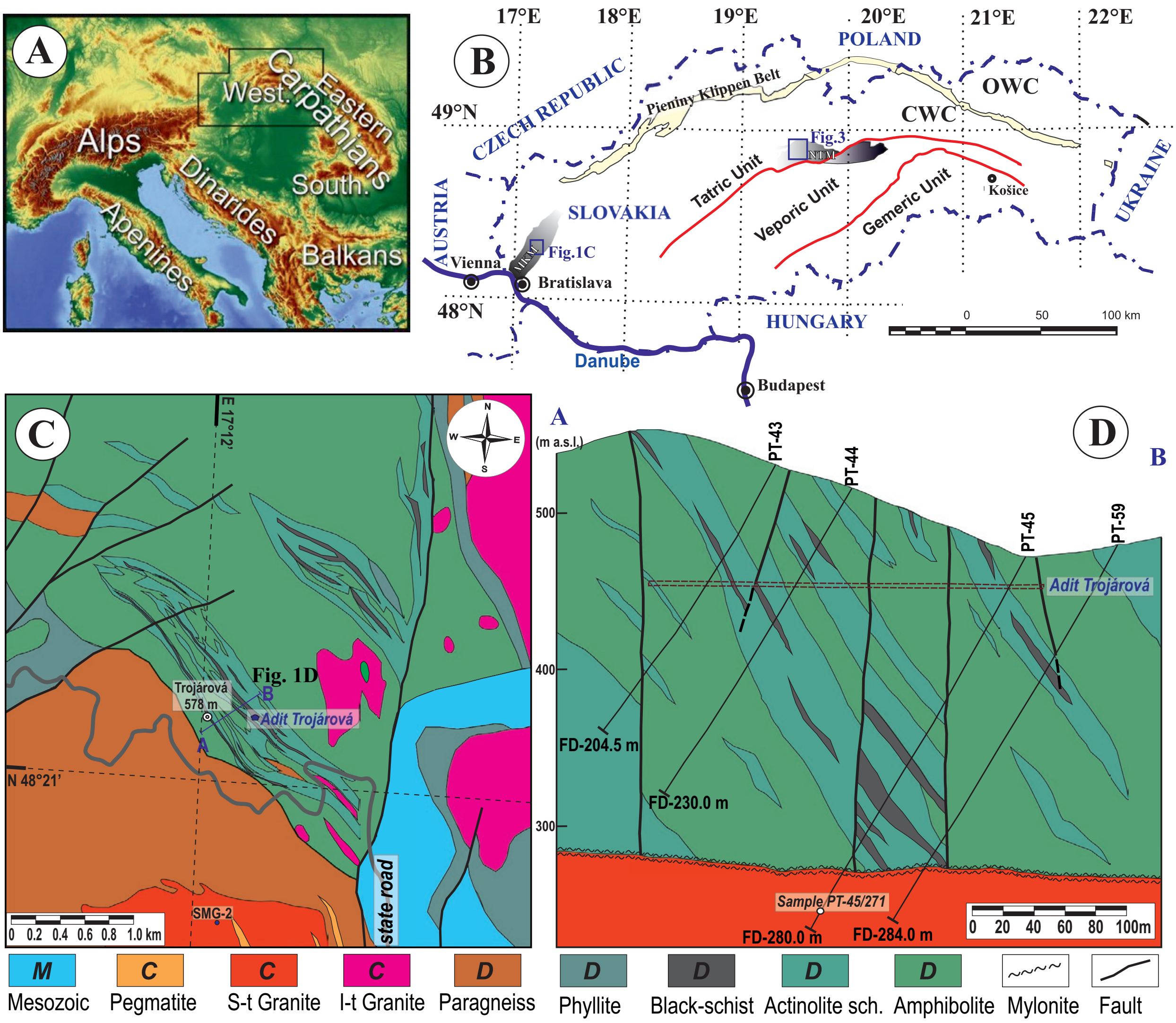


**Fig. 1. A** — Digital Elevation Model (DEM) with position of the Western Carpathians within Europe. **B** — Tectonic scheme of the Western Carpathians with situation of the Malé Karpaty Mts. and Nízke Tatry Mts. *Abbreviations*: CWC – the Central Western Carpathians, OWC – the Outer Western Carpathians, MKM – the Malé Karpaty Mts., NTM – the Nízke Tatry Mts. **C** — Simplified geological map of the Pezinok – Trojárová area according Polák et al. (2011). **D** — Geological profile across Trojárová ore body after Hanas et al. (1989) with position of the molybdenite sample PT-45/271. Relative stratigraphy in legend abbreviations: ***D*** – Devonian; ***C*** – Carboniferous; ***M*** – Mesozoic en bloc.

*ophiolites*) composed of metagreywackes, phyllites, metabasites (epidote–actinolite amphibolites), black shales, lenses of calc-silicates, and polymetallic mineralisation (Cambel 1954; Cambel in Buday et al. 1962; Ivan et al. 2001, 2007; Méres 2005; Kohút et al. 2022). However, we cannot exclude that these "*Pezinok/Pernek ophiolites*" relics belong to a belt of Devonian magmatites (ophiolite remnants and island arc granitoids) that are presumably hidden under the northern front of the Alps in Austria (Finger & Riegler 2022). The ore mineralisations in the Malé Karpaty Mts. were the subject of numerous studies (Cambel 1959; Chovan et al. 1992, 2002; Uher et al. 2000). The following mineralisation types were distinguished in the Malé Karpaty Mts. crystalline basement (Chovan et al. 1992, 2002):

***I*** *– Metamorphosed exhalation-sedimentary mineralisation with pyrite*;

***II*** *– Hydrothermal mineralisation*, with following subtypes:

(a) molybdenite in granitic rocks;

(b) copper–base-metal with silver: *(i)* Cu–Pb, Ag ± Ni, *(ii)* Pb–Zn, *(iii)* Pb–Ag;

(c) antimony–gold: *(i)* gold–sulfidic, *(ii)* gold–quartz; *(iii)* stibnite.

Generally, the exhalation-sedimentary mineralisation is Devonian in age, and is related to oceanic basaltic volcanism (*Pezinok/Pernek ophiolites*) that interacted with the deep-water oceanic sediments. The exhalation-sedimentary mineralisation experienced Variscan metamorphism which caused conversion of a substantial part of pyrite to pyrrhotite. There is no evidence of such metamorphic overprint in the molybdenite/scheelite mineralisation, rendering them younger than the pyrite–pyrrhotite, originally exhalation-sedimentary mineralisation.

However, in the Malé Karpaty Mts., molybdenite was found in a drill core and the relationship with the younger stibnite and base-metal mineralisation is more or less ambiguous, and can be inferred only by correlation with the mineralisations in the Nízke Tatry Mts. Similar relationship was observed at the Dúbrava deposit (Nízke Tatry Mts.) where quartz veins and veinlets with molybdenite, scheelite, and Bi–Te minerals are clearly cut by the younger stibnite mineralisation. This is also supported by fluid inclusion studies which show that quartz hosting molybdenite and scheelite was formed from much higher-thermal fluids than the later Sb mineralisation (Chovan et al. 1995).

The Pezinok ore area is the main mine district in the MKM with a long history from the Eneolithic – Bronze Age (copper seams), through the Middle Ages in the 14th to 16th centuries (gold ±silver), later continued by pyrite mining at the end of the 19th to 20th centuries, and terminated by exploitation of the antimony ores at the end of 20th century. Nearly 50 mineral species are currently known from the Pezinok area with the world's finest kermesite, valentinite, stibnite, goldmanite, and rare species such as chapmanite and garavellite (Uher et al. 2000; Števko et al. 2021). The last ore-deposit survey was carried out in the 1980's and early 1990's in the area of Pezinok – Kolársky vrch and Pezinok – Trojárová (Hanas et al. 1989, 1995). On the basis of technical and economic evaluation and mining options, the Pezinok – Trojárová deposit was classified as one with low predicted profitability, with the estimated reserves of 831 kt of ore with a metal content of 5.645 % Sb and 0.676 g/t Au.

The Pezinok – Trojárová deposit is situated about 7 km NNW of downtown Pezinok at the south-eastern slope of the MKM. Currently, the ore zone in the NW–SE direction is verified in a length of approx. 2 km. The deposit is located in a complex of actinolite schists, amphibolites, and layers of black schists. The Sb-mineralisation is bound to the black schists which are strongly tectonically deformed and cut by quartz–carbonate veins. The whole complex is inclined to NE 45–55° (Fig. 1c, d). Antimony ore is found in the form of impregnations, small veins, and lenses. The main mineral in the deposit is stibnite that occurs as coatings, irregular aggregates, veins and nests in the black schists. The second most common Sb mineral in the deposit is berthierite, which forms coatings, veins and small nests or needle-like occurrence in calcite veins. Gudmundite and tetrahedrite are rare, microscopic, almost always present as isolated grains or granular aggregates in stibnite. Native antimony is usually associated with stibnite. Hydrothermal kermesite, valentinite, and senarmontite are typical minerals for this deposit (Cambel 1959; Hanas et al. 1989, 1995; Chovan et al. 1992, 2002; Polák et al. 2012; Kaufmann et al. 2024).

A molybdenite crystal was found in greisenized leucocratic S-type granite (the Bratislava massif) in the PT-45 diamond drill core, drilled during the exploration of the Pezinok – Trojárová deposit (Hanas et al. 1989). So far, it is the only known *in situ* molybdenite occurrence within the granitic rocks in the MKM. The molybdenite mineralisation was found in the footwall of the metavolcanic complex, within the granitic rocks (see Fig. 1d). Molybdenite was found within the so-called Staré Mesto granite – medium grained, peraluminous, biotite–muscovite leucogranite, having elevated values of silica and alkali's ($SiO_2$=73.4–75.6 wt.%, $Na_2O$= 3.6–4.1 wt.%, $K_2O$=3.7–4.3 wt.%); moderate $Al_2O_3$=14.4–14.8 wt.%; along with lower values of iron and magnesium ($FeO^t$=0.8–1.4 wt.%, MgO=0.10–0.25 wt.%) see Cambel & Vilinovič (1987). Nevertheless, small granitoid lenses (dykes) north of Trojárová are mainly biotite-bearing granodiorites/tonalites having an affinity to the Modra I-type massif. The studied borehole sample PT-45/271 (Fig. 2) shows sign of fluid alteration with increased volume of quartz and white micas due to decomposition of Fe-micas and feldspars what resemble a greisenization process when large volume of mineralizing fluids attacks granitic rocks (Štemprok 1987; Pirajno 1992). Molybdenite is present in the form of coatings, flakes or more massive clusters on a foliation shear plane, and fine-grained inclusions within the greisenized granite endo-contact (Fig. 2). This finding confirmed the presence of high-temperature mineralisation in the MKM (Chovan et al. 1992). On the basis of the electron probe micro-analysis (EPMA), the studied molybdenite is chemically pure $MoS_2$ (Chovan et al. 2002).

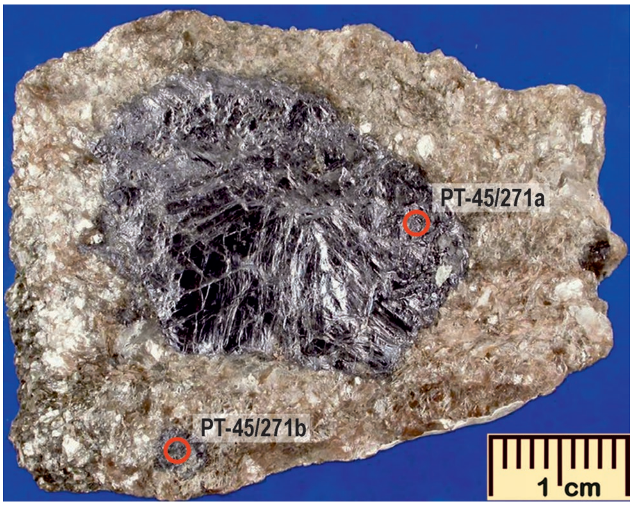


**Fig. 2.** Molybdenite crystals from greisenized granite, borehole sample PT-45/271 with indication of location of both analysed samples.

The Nízke Tatry Mountains (NTM) are situated in the northern sector of the central Slovakia and represent a typical multicomplex and polyorogenic part of the CWC (Fig. 1b). Gold-bearing, antimony mineralisations have been intensively exploited in numerous vein deposits of the Nízke Tatry Mts. (e.g., Magurka, Lom, Medzibrod) since the Medieval period. The Magurka deposit was an important producer of gold in the former Austrian–Hungarian Empire during the 16–17$^{th}$ century. In the middle of the 19$^{th}$ century, Magurka was considered as the largest deposit of antimony in Europe. During the second half of the 20$^{th}$ century, mining activity was concentrated on the Dúbrava deposit (Fig. 3) and terminated in 1992, while there was produced around 15,000 metric tons of antimony during this period. The Dúbrava deposit is the most systematically studied antimony deposit of the Western Carpathians. The deposit is hosted by granitoid rocks, migmatites and amphibolic gneisses, the latter occurring as xenoliths in the granitoids. The Dúbrava ore field consist of a swarm of quartz-sulfide veins, veinlets and impregnations developed in mylonite zones and open fractures in the granodiorite–tonalite massif, less frequently in gneisses and migmatites. Since, these veins do not penetrate the Mesozoic sedimentary cover, their Variscan origin is obvious. Mineralised zones follow the NNW–SSE direction and their total length attains more than 4 km. The veins have been mined up to 350 m deep (Chovan et al. 1995). Following mineralisation has been formed during five spatially and temporally separated stages in the Dúbrava deposit (Chovan 1990; Chovan et al. 1995):

***Ia*** – scheelite, pyrite, quartz
***Ib*** – molybdenite, pyrite, quartz
***II*** – arsenopyrite, pyrite, quartz
***IIIa*** – sphalerite, zinckenite, Pb–Sb sulfosalts, quartz, Fe-dolomite
***IIIb*** – stibnite, pyrite, quartz, Fe-dolomite
***IV*** – tetrahedrite, bournonite, chalcostibite, Pb–Sb–Bi sulfosalts, quartz, Fe-dolomite
***V*** – barite, Fe-dolomite, calcite, strontianite, quartz

The high temperature assemblages: scheelite, molybdenite, arsenopyrite with gold, and most likely also substantial part of stibnite are linked to the Variscan magmatic and/or metamorphic processes. These veins contain economically important lenses dominated by stibnite, accompanied by the abundant Fe-dolomite and quartz. Pyrite and arsenopyrite host Au; in Dúbrava, only as invisible gold in the crystal structure of the sulfides, whereas the ores in Magurka are known for rich aggregates of metallic gold. At both deposits, a varied assemblage of sulfosalts (zinkenite, boulangerite, robinsonite, geocronite, and others) occurs together with stibnite (Majzlan et al. 2020a). However, the Alpine rejuvenation of hydrothermal sulfidic mineralization in the Variscan crystalline basement has an important role in the NTM (see Majzlan et al. 2020b). The analysed sample D-602 (Fig. 4) comes from the Lukač adit, ca. 50 m to south of measuring point 333. The host rock of studied quartz vein with molybdenite in the Lukač adit is biotite granodiorite/tonalite (Lubela block on the north side of the Dúbrava deposit). More details about the Nízke Tatry Mts. granitic rocks, their mineralisations and Dúbrava deposit can be found in Maraszewska et al. (2022), Chovan et al. (1995) and Majzlan et al. (2020a, b).

## Analytical methods

### *Re–Os geochronology*

Molybdenite is particularly 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 (Stein et al. 2001). Rhenium–osmium geochronology was carried out by the AIRIE Program in Fort Collins, USA. Molybdenite separates were obtained using a handheld drill and/or by hand crushing and picking molybdenite grains under a binocular microscope. Molybdenite separates were weighed and then combined with a mixed Re-double Os spike. Samples and spike were digested and equilibrated in $HNO_3$ using the Carius tube method (Shirey & Walker 1995). Once Re and Os were chemically isolated and purified by micro-distillation, the clean fractions of each were separately loaded onto Pt filaments, and Re and Os isotope ratios were measured by negative thermal ionization mass spectrometry (NTIMS) on Triton™ machines. When employed on molybdenite or low-level, high-radiogenic (LLHR) sulfides (Stein et al. 2000), the method yields highly accurate and precise ages (e.g., Stein et al. 1997, 2001). Age calculations used the decay constant for $^{187}$Re determined by Smoliar et al. (1996). Together with NIST, AIRIE developed a reference material for molybdenite (RM8599, Henderson Molybdenite) which is routinely analyzed. The Re–Os data, analytical details, and blank information are provided in Table 1.

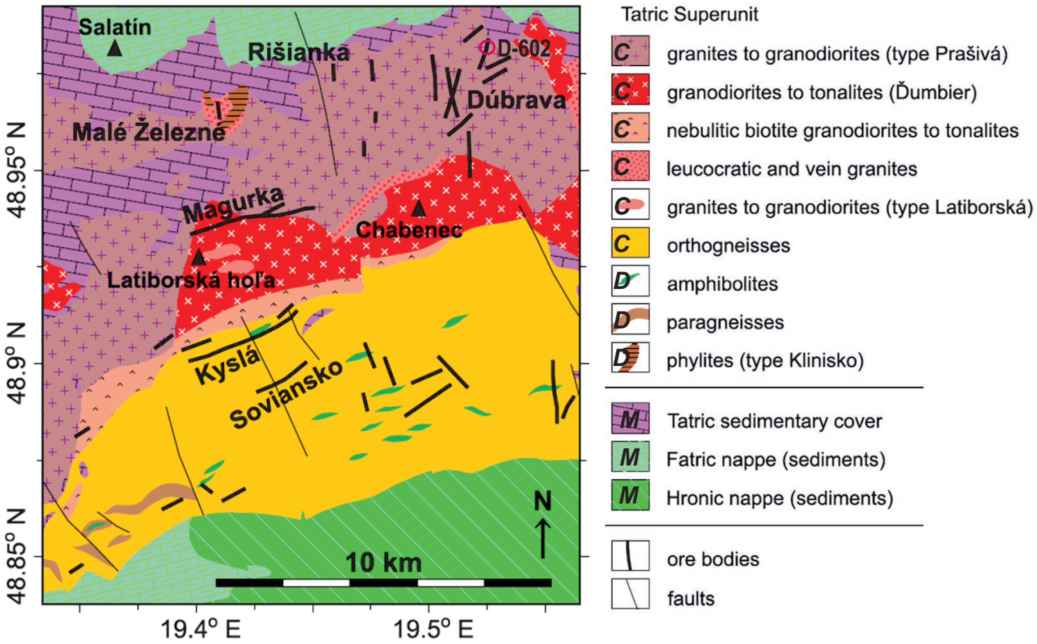


**Fig. 3.** Simplified and modified geological map of the central part of the Nízke Tatry Mts. (Biely et al. 1992) with location of the Dúbrava ore field. Relative stratigraphy in legend abbreviations: ***D*** – Devonian; ***C*** – Carboniferous; ***M*** – Mesozoic en bloc.

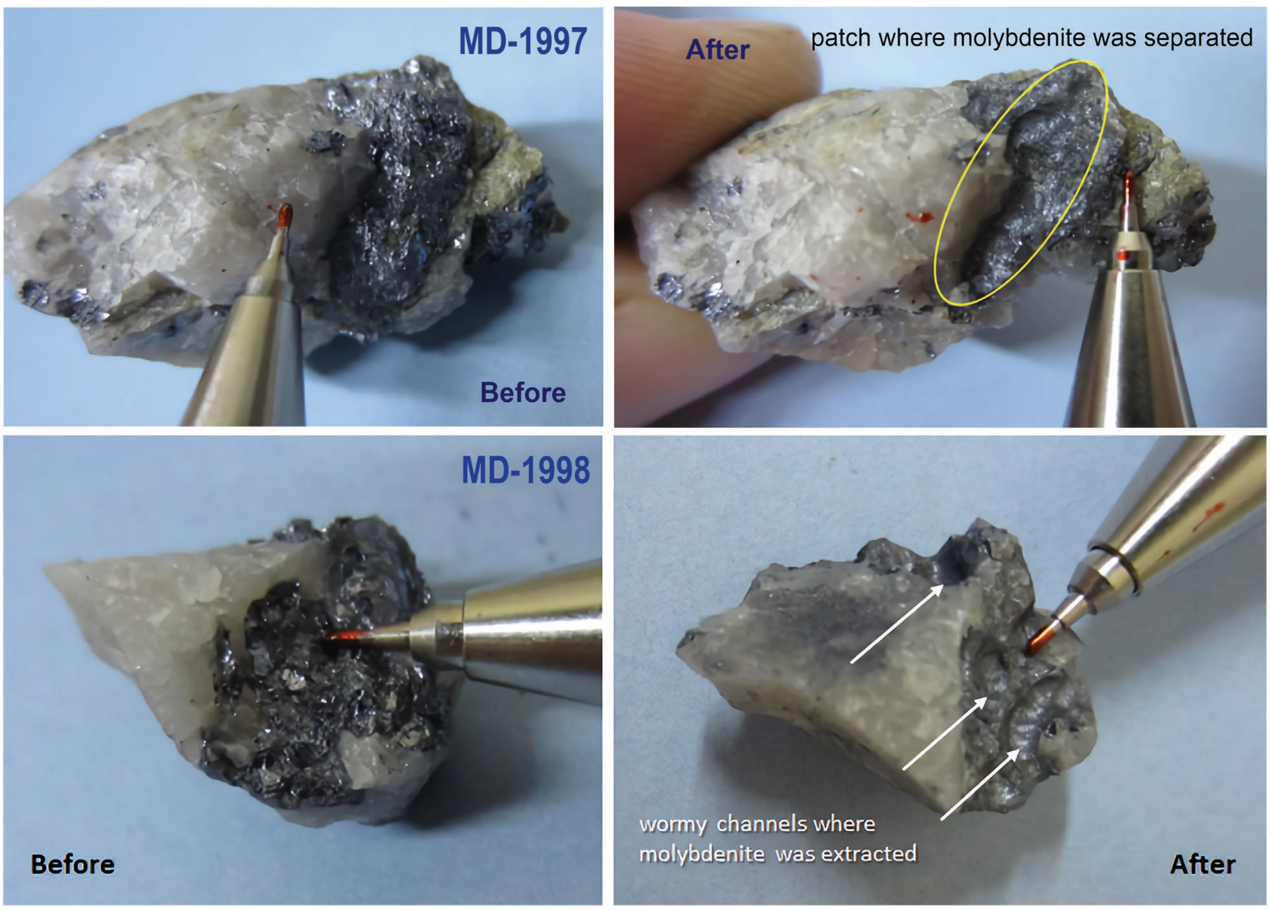


**Fig. 4.** Molybdenite in quartz from Dúbrava; samples D-602 N-1 (MD-1998) and D-602 N-2 (MD-1999). Pen tip and finger-thumb for scale.

## Results

The Re–Os data are shown in Table 1. Two mineral separates from a single drill-core hand specimen (PT-45/271) representative of Pezinok–Trojárová high-temperature granite-related mineralisation yielded Re–Os ages of 368.6±1.4 Ma (fine-grained molybdenite aggregates from greisenized granite endo-contact, Fig. 2, Supplementary Fig. S1) and 356.7 ±2.6 Ma (coarse-grained molybdenite, Fig. 2, Supplementary Fig. S2). 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.

Since previous Re–Os dating of molybdenite from the Dúbrava deposit of the Nízke Tatry Mountains by two different laboratories yielded different ages, i.e., 342.5±3.8 Ma (Chovan et al. 2013) and 351.8±2.6 Ma (Majzlan et al. 2020b), we decided to further explore this apparent difference working through a third laboratory. In this study, two molybdenite separates from samples collected very close to the previous sampling site D-602 at the Dúbrava deposit yield Re–Os ages in excellent agreement at 348.3±1.3 and 349.2±1.3 Ma (Table 1).

## Discussion

High precision Re–Os dating of molybdenite sample PT-45/271 provides two different ages for the high-temperature granite-related molybdenite mineralisation of the Pezinok –Trojárová greisenized granites: (a) the Upper Devonian–Famennian age of ca. 369 Ma, and (b) Lower Carboniferous – Tournaisian age of 357 Ma (Table 1). The younger Mississippian (357 Ma) molybdenite age is consistent with previously reported magmatic age of the Bratislava granitic pluton. These rocks were dated to 355±5 Ma and 352.3±1.8 Ma by sensitive high-resolution ion microprobe (SHRIMP) zircon U–Th–Pb method (Kohút et al. 2009), and the EPMA monazite Th–U–Pb dating with an isochron age of 355±18 Ma (Finger et al. 2003) or of 353±2 Ma (Uher et al. 2014). It is noteworthy that the Re–Os molybdenite age determined in this work is consistent with the most recent LA−ICP–MS U–Pb dating of columbite–tantalite showing a Concordia age of 354.5±4.5 Ma, obtained from the Jezuitské Lesy pegmatite of the Bratislava granite Massif (Uher et al. 2024). This congruency suggests a temporal and genetic link between the Variscan granite magmatism and molybdenite mineralisation in the MKM.

The older, Late Devonian Re–Os age (369 Ma) from this site does not match any precise dating of granitic magmatism in the MKM, although the best indication of this Early Variscan granite magmatism comes directly from the granite that hosts the molybdenite mineralisation. Uher et al. (2014) dated this granite from outcrops at Staré Mesto (sample SMG-2) by means of the EPMA monazite Th–U–Pb method. A quick inspection of the primary data points out a slightly older age with several spot ages between 375 and 360 Ma. Curiously, almost half of the data (19 out of 42 in total) have spot ages

**Table 1:** Re–Os data for molybdenites from the Pezinok – Trojárová and Dúbrava samples analysed in this study.

| AIRIE Run # | Sample Name | Re, ppm | Re err, abs (ppm) | Re err, percent | $^{187}$Os, ppb | $^{187}$Os err, abs (ppb) | $^{187}$Os err, percent | OsC, ppb | OsC err, abs (ppb) | Age, Ma | abs err, w/λ (Ma) | Age err, percent w/λ | Analytical err, abs (Ma) | Age err, percent | Sample weight (g) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MD-1997 | Pezinok – Trojárová molybdenite, PT-45/271a | **5.303** | 0.034 | 0.65 | **19.8682** | 0.0075 | 0.038 | **0.966** | 0.023 | **356.7** | 2.6 | 0.72 | 2.3 | 0.65 | 0.01743 |
| MD-2009 | Pezinok – Trojárová molybdenite, PT-45/271b | **3.2851** | 0.0032 | 0.097 | **12.718** | 0.022 | 0.17 | **0.3753** | 0.0011 | **368.6** | 1.4 | 0.38 | 0.72 | 0.20 | 0.02188 |
| MD-1998 | Dúbrava molybdenite, smaller piece, D-602 N1 | **27.025** | 0.047 | 0.17 | **99.100** | 0.038 | 0.038 | **0.2412** | 0.0058 | **349.2** | 1.3 | 0.37 | 0.62 | 0.18 | 0.0379 |
| MD-1999 | Dúbrava molybdenite, larger piece, D-602 N2 | **36.315** | 0.061 | 0.17 | **132.830** | 0.048 | 0.036 | **0.01051** | 0.00094 | **348.3** | 1.3 | 0.36 | 0.60 | 0.17 | 0.03872 |

Sample-spike equilibration with a double Os spike was carried out by Carius tube and nitric acid for molybdenite dissolution; all mineral separates essentially 100% molybdenite.

Re-Os isotopic ratios measured by NTIMS on a Triton machine at the AIRIE Program, Fort Collins, CO; lambda (λ) is the decay constant for $^{187}$Re, and reports error on the age should always include lambda.

Model age calculation assumes $^{187}$Os/$^{188}$Os initial = 0.2; OsC stands for common (initial) Os; all data reported at two-sigma uncertainty; uncertainties reported both as absolute (abs) and percent (%).

For MD-1997, MD-1998, MD-1999, Re blank = 1.31 ± 0.26 pg, Os = 0.0219 ± 0.0064 pg with $^{187}$Os/$^{188}$Os = 0.34 ± 0.11

For MD-2009, Re blank = 3.732 ± 0.010 pg, Os = 0.2966 ± 0.0015 pg with $^{187}$Os/$^{188}$Os = 0.8500 ± 0.0026

Run MD-1997 was slightly overspiked for Re (propagates into a larger uncertainty in age); spiking was still within the realm of acceptable; age should not be compromised.

For MD-2009, (b) refers to second separate created from multiple grains from multiple vials, combined to create enough for a second Re–Os analysis.

that yield a weighted mean age of 365.9±6.5 Ma, overlapping with the molybdenite age of 368.6±1.4 Ma (Fig. 5). Since the principal age of the granitic Bratislava Massif magmatic age was already anchored to 355±5 Ma (Kohút et al. 2009), these authors interpreted the obtained isochron age of 353±2 Ma (based on robust dating with $n$=290 spot data) in the same way. The older monazite spot data (375–360 Ma) were linked to the Variscan metamorphism, showing an age of 359±11 Ma in the adjacent paragneisses, or as xenocrystic, detrital grains (505–400 Ma) from the metasedimentary source rocks (Uher et al. 2014). However, we cannot exclude the possibility that the Staré Mesto granite represents a product of water saturated partial melting (Sawyer 1999), passing to the genesis of diatexites, and the first "immature" unhomogenised granitic rocks during the Famennian subduction period of the Variscan orogeny. Later, in the course of Mississippian (Tournaisian) emplacement of the main masses of the Bratislava Massif, this portion of the older Devonian granite was sheared and invaded by younger granite melts. Nevertheless, it was not entirely amalgamated and/or homogenised, but remained as a roof pendant on the top of the Bratislava massif.

The increasing volume of the EPMA monazite Th–U–Pb data revealed bi-modal or multi-modal distribution of the monazite ages from various core mountains granitic rocks of the Tatric Unit. Based on these observations, Kohút (2017) suggested a long-term, multi-pulse evolution of the Variscan granitic magmatism in the TU. Interestingly, the pegmatites of the CWC Variscan granites show a relatively long evolution as well, as evidenced by recently published columbite LA−ICP–MS U–Pb ages (360–350 Ma, Uher et al. 2024), as well as the new EPMA uraninite U–Th–Pb data (~370–330 Ma, F. Finger, personal communication). A sum of these facts gradually confirms the original conclusion of Finger et al. (2003) that the formation of Variscan granites was a long-lasting process between 367 and 333 Ma in the CWC. Noteworthy, an identical granite evolution time scale was determined from

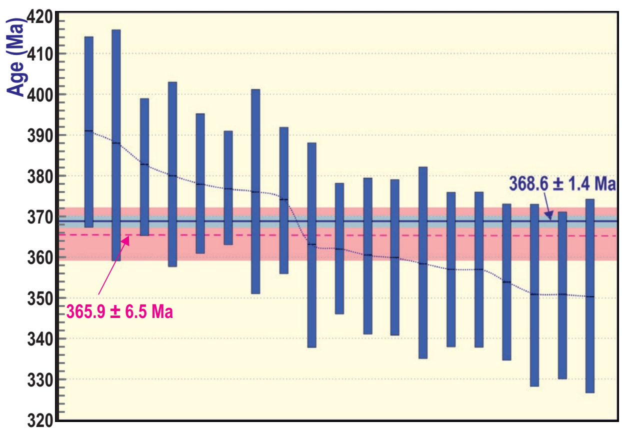


**Fig. 5**. Probability plot using selected individual monazite spot U–Th–Pb ages from sample SMG-2 from Staré Mesto (Uher et al. 2014) forming a weighted mean age of 365.9±6.5 Ma, which are overlapping within the error with the molybdenite age of 368.6 ±1.4 Ma from Pezinok–Trojárová (this study).

the results of the SHRIMP zircon U–Th–Pb dating (Kohút & Larionov 2021).

On the other hand, the Famennian age of ca. 369 Ma is equal within the error to the age of gabbro-dolerite (371±4 Ma, Putiš et al. 2009) which intruded into the Lower Paleozoic metamorphic series forming a host-rock of the MKM granites. It is known that the metamorphosis of the crystalline basement predated the intrusion of the Variscan granites in the MKM. This notion is supported by an age of 387±19 Ma from the Rb/Sr whole-rock isochron on gneisses from the Malé Karpaty Mts. basement (Bagdasaryan et al. 1983) and the EPMA monazite Th–U–Pb age of 359±11 Ma from the same rocks (Uher et al. 2014).

Two new molybdenite ages of 349 Ma from the Dúbrava Sb–Au deposit of the Nízke Tatry Mts. are in excellent agreement with one another (Table 2), and agree with the previous Re–Os molybdenite dates of 351.8±2.6 Ma (Majzlan et al. 2020b), but are older than the first molybdenite age at this deposit of 342.5±3.8 Ma (Chovan et al. 2013). However, the Tournaisian age of the NTM granite magmatism is well documented by the secondary-ion mass spectrometry (SIMS) U–Th–Pb zircon analyses with a Concordia age of 353±3 Ma (Broska et al. 2013) and the SHRIMP zircon U–Th–Pb dating showing ages of 352±3 Ma and 351.9±2.9 Ma (Maraszewska et al. 2022). Conversely, there are radiometric dates pointing to a Visean age of granitic magmatism in the NTM obtained from a conventional multigrain zircon U–Th–Pb dating by thermal ionisation mass spectrometry (TIMS) with an age of 343±3 Ma (Putiš et al. 2003). A similar Visean melting event was also recorded in the Nízke Tatry Mts. by monazite Th–U–Pb EPMA dating of 346±7 Ma (Petrík & Konečný 2009) and of 345.0±2.0 Ma (Chovan et al. 2013). Interestingly, an identical age of 342.9±2.6 Ma (Kohút & Ackerman, unpublished Re–Os data) gave the molybdenite from Ťahanovce (Veporic Unit). Noteworthy, the single-grain zircon U–Th–Pb dating by SHRIMP from zircon rims, showing an age of 340±3 Ma (Kohút & Larionov 2021) from the NTM, indicate rejuvenation melting and pervasive melt flow due to a collapse of the Variscan collisional thickened orogeny and exhumation of the continental subduction wedge from eclogite-facies to mid-crustal conditions. Such decompression melting (around 345 Ma) connected with exhumation of eclogitized lower crust (at 354.5±1.2 Ma) was recently documented in the Tatry Mts. (Janák et al. 2022; Kohút et al. 2023). Generally, obtained Tournaisian age of granite magmatism and mineralisation clearly postdates the Variscan metamorphism, since this granite intrusion reflected the main phase of Variscan deformation (see Kriváňová et al. 2023), whereas the Visean reactivation was caused by changed strain forces due to extension and decompression.

It is not common to have two different Re–Os molybdenite ages from one presumed high-temperature mineralisation event, and therefore the two differing ages may indicate a long-lived granite-related mineralisation process. Indeed, we cannot exclude local molybdenite rejuvenation at the present-day state of knowledge. An interesting long-lived granite-related molybdenite mineralisation was described at Connemara (Western Irish Caledonides), where Re–Os molybdenite chronometry indicates that molybdenite mineralisation extended from 423 to 380 Ma. This mineralisation is overlapping with the Galway Granite Complex multi-pulse emplacement history determined by U–Pb zircon chronometry (Feely et al. 2010).

An overview of the high-temperature granite-related molybdenite mineralisation within the Tatric Unit would be incomplete without mention of the Wołovec molybdenite dating (Mikulski et al. 2011; Gawęda et al. 2013) from the Západné Tatry Mts. (Table 2). The Re–Os age of 350.5±1.2 Ma of this pegmatite Mo mineralisation is in a good agreement with the age of the host granites (i.e., 347±14 Ma, Poller et al. 2000; 350.5±4.7 Ma, Burda et al. 2013; 355.2±8.2 Ma, Gawęda et al. 2016; 350.1±2.6 Ma, Broska et al. 2022; 349.3±2.9/−1.5 Ma, Catlos et al. 2022).

At present, several Re–Os ages of molybdenite are available from various granite-related high-temperature ore deposits and occurrences within the Tatric Unit of the CWC. The data are summarized in Table 2 and Fig. 6. They show rather a wide age range from 368.8±1.4 to 342.5±3.8 Ma; but nevertheless, these mineralisation ages are in excellent agreement with the magmatic ages of the host rocks. The vast majority of the data are spreading over the 350 Ma reference line, confirming the main granite-forming and mineralisation process during the peak of the Variscan orogeny. However, there are two outliers. One of them could be linked to an initial stage of the molybdenite mobilisation from the source during Variscan primary granite melting at ca. 369 Ma. Whereas, the other one can indicate a possible rejuvenation of the molybdenite mineralisation connected with subsequent partial melting at ca. 343 Ma (Chovan et al. 2013; Kohút & Ackerman unpublished) during the post-collisional period.

On the basis of existing data (e.g., Kohút et al. 2009; Putiš et al. 2009; Broska et al. 2013, 2022, 2024; Kohút & Larionov 2021; Catlos et al. 2022; Janák et al. 2022; Maraszewska et al. 2022; Kohút et al. 2023 and citations therein) we can divide the following Variscan geodynamic stages in the Central Western Carpathians (CWC): (a) subduction stage (ca. 374–367 Ma), (b) collision stage (ca. 367–332 Ma). However, after initial subduction period between 367–360 Ma (b1), oceanic lithosphere detached from continental lithosphere during continental collision in a slab breakoff period (e.g., Davies & von Blanckenburg 1995; Broska et al. 2022) before ca. 360–357 Ma (b2). The continental crust was sufficiently thickened for syn-collisional metamorphism. Although the heat from the underplated mantle magma did not only overheat the lower crust, but generally softened the continental crust with an increased partial melting, decreased density of crustal rocks triggered gravitational instabilities, what caused a collapse of the collisional thickened orogeny. Oblique collision with dominating transpression formed space for plutonism and led to the flare-up of granitic late-collisional magmatism 357–345 Ma (b3) see Fig. 7. However, when the character of the Variscan Orogen changed from convergent to divergent due to extensional crustal thinning, decompression

**Table 2:** Summary of all available Re–Os molybdenite data from the Tatric Unit of the Central Western Carpathians.

| Original № | Location | Laboratory | AIRIE № | Weight (g) | Re (ppm) | ±2σ (abs, ppm) | $^{187}$Re (ppm) | $^{187}$Re (ppb) | ±2σ (ppb) | $^{187}$Os (ppb) | ±2σ (ppb) | Age ±2σ (Ma) | Source |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ta3-Moly | Wołovec | AIRIE | MD-1155 | 0.02983 | 16.584 | 0.012 | 10.436 | 10436 | 8 | 61.038 | 0.051 | **350.5 ±1.2** | Mikulski et al. (2011) |
| S-602 | Dúbrava | China | - | 0.05765 | 35.696 | 0.384 | 22.436 | 22436 | 241 | 128.39 | 0.347 | **342.5 ±3.8** | Chovan et al. (2013) |
| D-602 | Dúbrava | Prague | - | | 30.670 | 0.070 | 19.301 | 19301 | 44 | 113.30 | 0.700 | **351.8 ±2.6** | Majzlan et al. (2020b) |
| MZ-1 | Malé Železné | Prague | - | | 40.580 | 0.090 | 25.537 | 25537 | 57 | 149.40 | 0.900 | **350.5 ±2.5** | Majzlan et al. (2020b) |
| PT-45/271a | Trojárová | AIRIE | MD-1997 | 0.01743 | 5.303 | 0.034 | 3.337 | 3337 | 21 | 19.8682 | 0.0075 | **356.7 ±2.6** | This study |
| PT-45/271b | Trojárová | AIRIE | MD-2009 | 0.02188 | 3.2851 | 0.0032 | 2.067 | 2067 | 2 | 12.718 | 0.022 | **368.6 ±1.4** | This study |
| D-602_N1 | Dúbrava | AIRIE | MD-1998 | 0.03790 | 27.025 | 0.047 | 17.007 | 17007 | 30 | 99.100 | 0.038 | **349.2 ±1.3** | This study |
| D-602_N2 | Dúbrava | AIRIE | MD-1999 | 0.03872 | 36.315 | 0.061 | 22.853 | 22853 | 38 | 132.830 | 0.048 | **348.3 ±1.3** | This study |

melting occurred during rapid uplift and exhumation in the post-collisional period at ca. 345–332 Ma (b4).

Generally, the Tournaisian age interval of ca. 357–349 Ma represents the maximum peak of the Variscan granitic rocks generation in the Tatric Unit (Kohút & Larionov 2021; Broska et al. 2022, 2024; Catlos et al. 2022). Obviously, the granite-forming process had a multi-pulse character, reflecting a gradual transition from subduction in a volcanic arc, through continental collisional thickening, slab breakoff followed by asthenospheric mantle upwelling which caused thermal weakening of thickened crust as was suggested for the Malá Fatra Mts. in the CWC by Broska et al. (2022), and final extensional, gravitational collapse of the Variscan orogeny. On the basis of available Re–Os molybdenite data, it is evident that magmatism and mineralisation did not occur as a single episode in the CWC. The granite-related high-temperature molybdenite mineralisation was associated mainly with the maximum of crustal thickening and peak of the HP metamorphism directly followed by slab break-off when a significant part of the granites was produced in the Tatric Unit. The older age of 369 Ma may indicate an initial granite melting/mineralisation episode related to the subduction process. However, possible younger molybdenite rejuvenation of ca. 343 Ma can be connected with new decompression melting due to exhumation of the collision-induced thickened crust as a younger portion of relatively long-lived multi-phase granitic magmatism evolution in the Tatric Unit of the CWC.

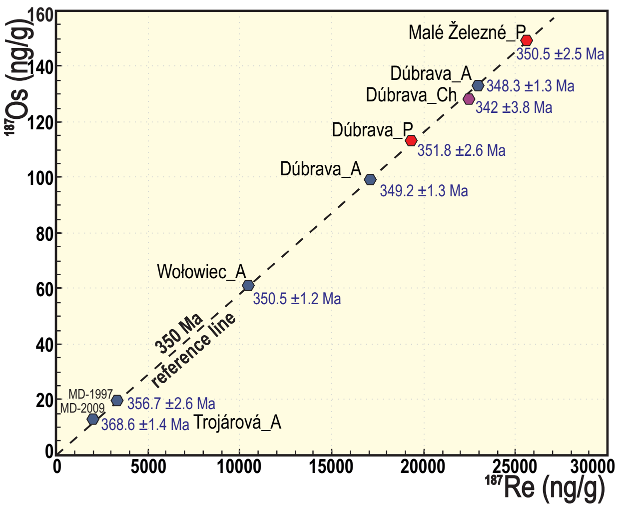


**Fig. 6**. Re–Os plot summarising all individual data of molybdenites from the Tatric Unit of the CWC. Errors are smaller than the size of the used symbols. *Abbreviations*: A capital letter after the location designation indicates the laboratory where the dating was done: **A** – AIRIE lab Fort Collins; **Ch** – China, Nanjing University; **P** – Prague, Institute of Geology of the Czech Academy of Sciences. (Data source – see Table 2).

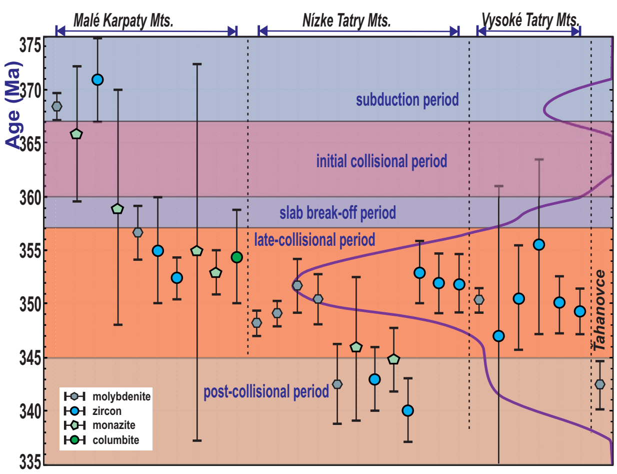


**Fig. 7.** Summary plot of the molybdenite Re–Os data in comparison with dating of the host granitic rocks (cited in Discussion) in relation to the Variscan subduction/collision geodynamic stages in the CWC. Noteworthy, the Ťahanovce molybdenite mineralisation is from the Veporic Unit. Violet colour line reflects Probability plot.

## Conclusions

High-precision Re–Os dating of molybdenite was employed to obtain ages for high-temperature mineralisation associated with Variscan granitic magmatism in the Western Carpathians. The obtained results of ca. 369 and 357 Ma for the Pezinok–Trojárová Sb deposit and of ca. 349 Ma for the Dúbrava Sb–Au deposit, integrated with previously reported magmatic ages, confirm a temporal and genetic link between the Variscan granitic rocks and molybdenite mineralisation in the Tatric Unit of the CWC. Genesis of the high-temperature ore mineralisation and the granitic host rocks was a consequence of melting within collisionally-thickened crust, assimilation/fractionation of magma, and emplacement of fertile granitic rocks in the middle/upper crust during the Variscan orogeny.

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**Electronic supplementary material** is available online:
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