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ARTICLE

Temporal evolution of mineralization events in the Bohemian Massif inferred from the Re–Os geochronology of molybdenite

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Abstract Molybdenite is a common mineral accompanying Sn–W, Au, and base metal mineralizations located in different geotectonic units of the Bohemian Massif, but it is also widespread in granitoids and/or related quartz veins/pegmatites forming disseminated Mo mineralization. Thirty Re–Os ages were obtained for molybdenite samples from the Bohemian Massif to provide constraints on the timing and duration of mineralization event(s) within the framework of previously published geochronological data for the host and/or associated rocks. The obtained data for Sn–W–(Li) deposits in the Erzgebirge metallogenetic province indicate the predominance of one and/or multiple short-time mineralization events taking place between ~319 and 323 Ma, with the exception of the Krupka deposit associated with the Altenberg–Teplice caldera where the data may suggest prolonged activity until ~315 Ma. The ages of the Pb–Zn–(Au–Mo) Hůrky u Rakovníka and Fe–Cu–As Obří důl mineralizations from the exocontacts of the Čistá pluton and Krkonoše-Jizera Plutonic Complex, respectively, provide evidence for synchronous emplacement of the ore and the associated granitic rocks. In contrast, the Padrť Fe–As–Mo mineralization postdates the age of the associated Padrť granite. Disseminated Mo mineralization in Cadomian and Variscan granitoids and/or related to quartz veins/pegmatites provides Re–Os ages that overlap with the previously published geochronological data for the host rocks, suggesting coeval evolution. Molybdenite samples from the Sázava suite granites of the Central Bohemian Plutonic Complex (CBPC) have resolvable younger ages than their host granites, but similar to the age of spatially related Au mineralization which is associated with the latest evolution of the CBPC.

Keywords Re–Os · Geochronology · Molybdenite · Bohemian Massif · Granite

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Introduction

The Re–Os system ($^{187}Re \rightarrow {}^{187}Os$) represents a long-lived isotopic system with direct application to the study of sulfides, highly siderophile elements, and related ores (e.g., Stein et al. 2000; Morgan et al. 2002; Morelli et al. 2010). Molybdenite (MoS_2) is a very common mineral in many hydrothermal ore-bearing systems (e.g., Au–Mo, Cu–Mo, Sn–W, and Pb–Zn). Compared to other sulfides, it has high concentrations of Re (typically parts per million levels) due to similar valence and ionic radii as Mo, but contains no or very little common Os, resulting in very high Re/Os (typically 10,000 or higher). Therefore, it offers the possibility of its direct dating by the Re–Os system through single analyses and calculation of a model age (Selby and Creaser 2001; Stein et al. 2001; Markey et al. 2007; Lawley and Selby 2012). In spite of well-discussed problems including the possible heterogeneity of the molybdenite separates or decoupling of ^{187}Re and ^{187}Os after crystallization and during metamorphism (Stein et al.

2001; Košler et al. 2003; Selby and Creaser 2004; Aleinikoff et al. 2012), the reliability of Re–Os molybdenite ages has been demonstrated many times through a consistency between the Re–Os and U–Pb ages for related rocks (e.g., Stein et al. 2001; Porter and Selby 2010; Xia et al. 2015).

The Bohemian Massif hosts a substantial number of Au, Sn–W, U, and base metal deposits/mineralizations located in different geotectonic positions. Some of them represent an important resource of precious and/or strategic metals (e.g., Au or U), but most deposits and even whole mineralization types lack precise dating, and thus the temporal evolution of ore formation in the Bohemian Massif remains a matter of debate. Such information is highly demanding as the metallogenic and geodynamic evolution of the Bohemian Massif shares many common features with the rest of the Variscides (e.g., Massif Central in France and Iberian Belt in Spain). Molybdenite is a mineral commonly accompanying several deposits occurring in the Bohemian Massif, but it is also widespread in the granitic intrusions of Cadomian (~600–550 Ma) and Variscan to post-Variscan (~370–290 Ma) ages in different geotectonic units (Drábek et al. 1993). In spite of this fact, there are few molybdenite Re–Os ages available, and most are reported from Au deposits (Žák et al. 1998a; Zachariáš et al. 2001; Zachariáš and Stein 2001), with the results sometimes being a matter of debate. Only a few data were reported for other mineralization styles such as Sn–W deposits (Romer et al. 2007) or Mo–Th–Nb–REE mineralized marbles (Drábek and Stein 2015).

In this study, we report an extensive dataset of Re–Os ages for 30 molybdenite samples from the Bohemian Massif, associated with Sn–W, base metal (Fe–Cu–As, Pb–Zn, and Fe–As), or Au mineralization, as well as data for disseminated molybdenite occurring in granitic intrusions and/or related quartz veins/pegmatites. These data are discussed with respect to previously published geochronological data derived from zircon (U–Pb), whole-rock and silicate minerals (Rb–Sr, K–Ar, and Ar–Ar), or thorianite–monazite–uraninite–columbite (Th–U–Pb) from associated and/or host rocks.

Geology of the Bohemian Massif

The Bohemian Massif is the easternmost remnant of the Middle to Late Paleozoic Variscan belt in Europe usually interpreted as a result of collision of the Laurussia-Baltica and Gondwana continents with the intervening Avalonia and Armorica microplates (Franke 1989; Matte 2001; Cháb et al. 2010) or just two-plate convergence of Laurussia and Gondwana in the Paleozoic (Kroner and Romer 2013). The massif itself represents a tectonic collage of continental terranes with different compositional and temporal tectonostratigraphic evolution, and its assembly during the Variscan orogeny is a matter of debate (e.g., Franke 1989; Matte et al. 1990; Schulmann et al. 2009, 2014; Kroner and Romer 2013, 2014). Nevertheless, it has been traditionally divided into four major tectonic units (Kosmatt 1927; Matte et al. 1990; Schulmann et al. 2009): Teplá–Barrandia, Saxothuringia, Moldanubia, and Moravo-Silesia (Fig. 1). All these units have been intruded by voluminous granitic plutons forming large batholiths and complexes such as the Central Bohemian Plutonic Complex or the Moldanubian Batholith (Fig. 1).

The Teplá–Barrandian Unit consists of Cadomian basement (~550–500 Ma) metamorphosed at low grade, intruded by Cambro–Ordovician plutons, and finally covered by Late Cambrian to Devonian sedimentary and volcanic rocks (e.g., Franke 1989; Zulauf et al. 1997; Sláma et al. 2008; Hajná et al. 2011). Later, the unit was intruded by a large number of Late Devonian–Early Carboniferous (~370–337 Ma) calc-alkaline granitic plutons (e.g., Central Bohemian Plutonic Complex, Štěnovice and Čistá plutons) along the Teplá–Barrandian–Moldanubian boundary. The plutons have variable compositions, suggesting different melt sources and processes during magma emplacement (e.g., Janoušek et al. 1995, 2000, 2010; Žák et al. 2011a, 2014a, b, and references therein).

The Saxothuringian Unit comprises Neoproterozoic volcano-sedimentary sequences (e.g., Linnemann et al. 2008) intruded by the Lusatian Granitoid Complex of Late Neoproterozoic to Cambrian age (~590–500 Ma; Kröner et al. 1994; Tichomirova 2002; Białek et al. 2014) and overlain by Paleozoic volcano-sedimentary rocks (McCann 2008, and references therein). During the Variscan orogeny, the high-strain domain of the Saxothuringian Unit (Kroner and Romer 2010), presented essentially in the Krušné Hory/Erzgebirge, has undergone extensive (U)HP–HT metamorphism and reworking followed by the intrusion of evolved, mildly to strongly peraluminous granitic bodies hosting Sn–W mineralization in the Erzgebirge (e.g., Breiter et al. 1999; Förster et al. 1999; Förster and Romer 2010; Breiter 2012). The northeastern part of the Saxothuringian Unit, represented by the low-strain domain (Kroner and Romer 2010) in the Lusatia/West Sudetes area, was intruded by Early Carboniferous (~330–305 Ma) granitic plutons such as the peraluminous Krkonoše-Jizera Plutonic Complex (Slaby and Martin 2008; Žák et al. 2013; Kryza et al. 2014) or the Königshain granite (Förster et al. 2012).

The Moldanubian Unit is a middle-lower crustal unit with variable metamorphic grades recorded by LP/HT paragneiss to (U)HP–HT eclogite-granulite and peridotite (e.g., Fiala 1995; Vrána et al. 1995; Medaris et al. 2005; Faryad 2009; Lexa et al. 2011). Two major suites of granitic rocks ranging in age from ~340 to 300 Ma can be distinguished in the Moldanubian Unit: (1) I/S-type to peraluminous S-type granitoids forming together the composite and large Moldanubian Batholith (e.g., Finger et al. 1997; Breiter 2010; Žák et al. 2011b) and (2) ultrapotassic granitoids/syenites

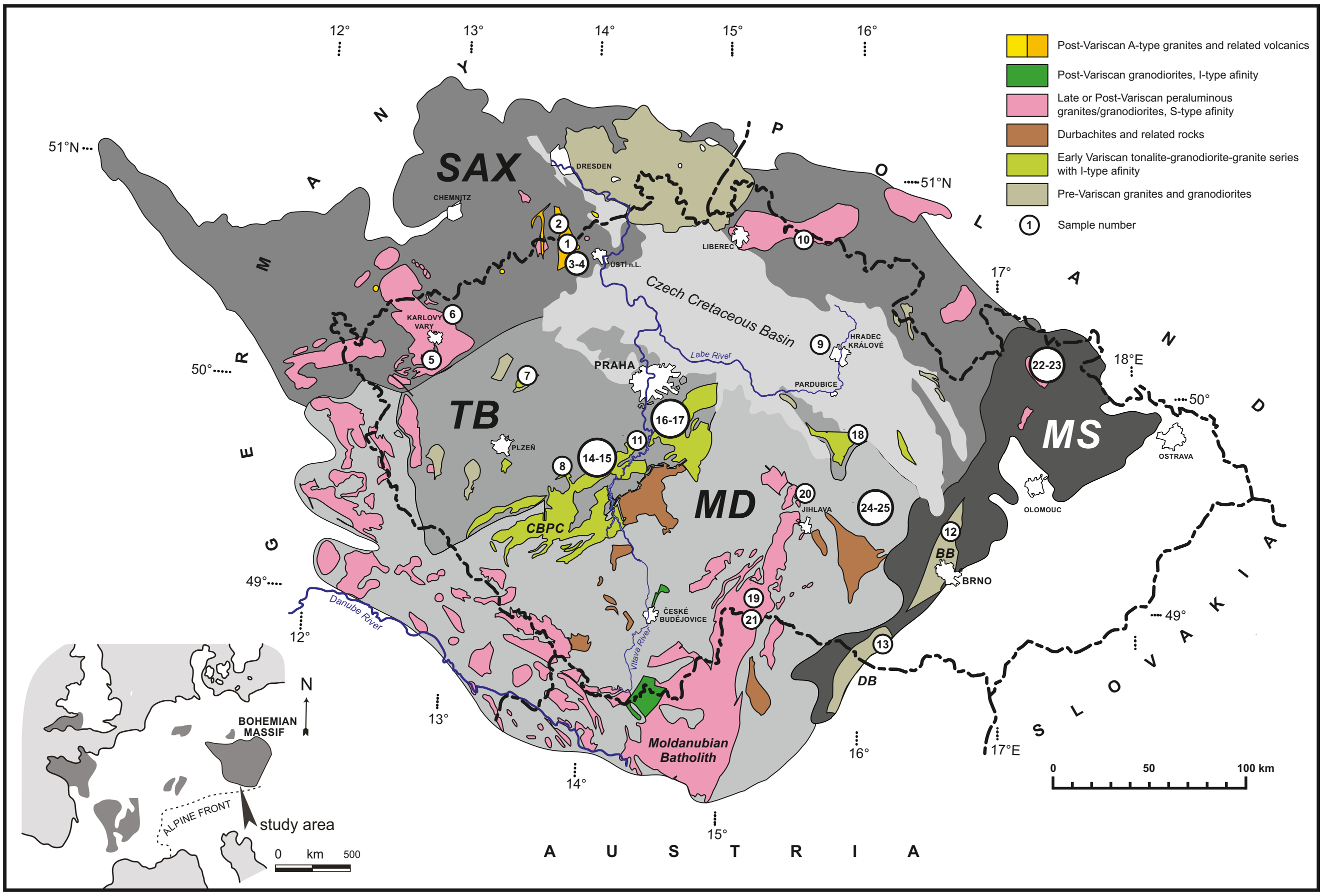

Fig. 1 Geological map of the Bohemian Massif with emphasis on granitic intrusions. Numbers of the studied molybdenite localities correspond to those given in Table 1. *TB* Teplá-Barrandian Unit, *SAX* Saxothuringian Unit, *MD* Moldanubian Unit, *MB* Moravo-Silesian Unit, *CBPC* Central Bohemian Plutonic Complex, *DB* Dyje Batholith, *BB* Brno Batholith

("durbachites") such as the Třebíč and/or Tábor pluton (Holub 1997) representing the melts derived from a metasomatized and heterogeneous mantle source mixed with anatectic melts (e.g., Janoušek et al. 2000).

The Moravo-Silesian (Brunovistulian) unit consists of a Cadomian basement (~600–570 Ma) composed of metamorphosed volcano-sedimentary rocks (schist and phyllite), I-type granitoids forming the Brno and Thaya/Dyje Batholiths, migmatites, metabasites, and gneisses (Dudek 1980; Finger et al. 2000; Kröner et al. 2000; Linnemann et al. 2008). During ~345–340 Ma, an extensive sequence of flysch sediments was deposited on the eastern side of the Brunovistulian Unit (Maluski et al. 1995; Schneider et al. 2006).

Molybdenite occurrences, their relationship to ore mineralizations, and studied samples

Molybdenite is a widespread mineral associated with different types of rocks and mineralization styles occurring in the Bohemian Massif (e.g., Drábek et al. 1993; Pašava et al. 2015, 2016). Four different molybdenite groups can be distinguished with respect to mineralization type, host rock, trace element chemistry, and associated ore minerals: (1) molybdenite associated with Sn/W-bearing greisenized granite and related quartz veins; (2) molybdenite related to Au mineralization; (3) molybdenite from base metal mineralization; and (4) disseminated molybdenite in granitoids and/or related quartz and pegmatite veins. Altogether, 30 molybdenite samples from these groups were sampled and analyzed for their Re–Os ages. Their location is shown in Fig. 1.

The Sn–W–(Li) deposits of greisen type represented by cassiterite, wolframite, and zinnwaldite are related to strongly fractionated granites of S and A types within the Saxothuringian Unit along the Czech–German boundary (Erzgebirge). Several deposits such as Cínovec/Zinnwald, Krupka, Krásno, and/or Sadisdorf belong to the Krušné Hory/Erzgebirge metallogenetic province (Hösel et al. 1995, 1997). In these deposits, molybdenite is a trace mineral within greisens and/or related quartz veins where it forms larger grains (e.g., at Krupka up to 1 cm in diameter) or, more commonly, small (<2 mm) grains dispersed in the greisen matrix. The trace element chemistry reveals that greisen-related molybdenite has a unique chemistry with very low Re contents (0.4 ppm, on average) paralleled by high Cu, As, and Zn

(Pašava et al. 2016). The studied molybdenite samples form up to 1 cm large grains located in quartz veins in granites and greisens (Krupka and Cínovec, respectively) or dispersed in greisen (Krásno, Jáchymov, and Sadisdorf).

The Au mineralizations of the Bohemian Massif are predominantly located within quartz veins associated with granitoids of the Central Bohemian Plutonic Complex (Fig. 1) forming a large gold district which includes important deposits such as Mokrsko-Čelina, Jílové, Kasejovice, or Petráčkova hora (Morávek 1996; Zachariáš et al. 2001, 2013, 2014). Other mineralization styles include individual localities of Au-bearing quartz veins in the metamorphic rocks of the Moldanubian Unit (e.g., Kašperské Hory: Strnad et al. 2012; Roudný: Zachariáš et al. 2009) and polymetallic Zn–Pb–Cu–Au (Zlaté Hory) and Fe–Au–Mo (Vidly) mineralizations in the Moravo-Silesian Unit. With the exception of the Vidly deposit, molybdenite is restricted to Au-bearing quartz veins at several localities related to the Central Bohemian Plutonic Complex and Kašperské Hory where it forms an accessory, mostly finely disseminated (<1 mm) mineral together with other sulfides such as pyrite, pyrrhotite, and arsenopyrite. The analyzed sample of molybdenite was collected at the Mokrsko-West deposit (Josef adit) at the contact of a barren quartz vein with surrounding granodiorite.

Several base metal (Fe–Cu–As–Zn) mineralizations located in the Teplá–Barrandian (Padrť, Hůrky u Rakovníka, and Všestary), Moldanubian (Ransko), and Saxothuringian (Obří důl) Units are accompanied by molybdenite (Fig. 1). At Padrť, molybdenite occurs as isolated flakes (up to 5 mm) within quartz veins and host quartzite together with abundant arsenopyrite (Fe–As–Mo mineralization; Žák et al. 2014a, b). The Hůrky Pb–Zn–(Au–Mo) mineralization (sphalerite, galenite, and molybdenite) is developed within quartz veins associated with fenitized (alkaline metasomatic) zones of the Čistá granodiorite (Klomínský 1962; Žáček et al. 2008). The studied fine-grained (<1 mm) molybdenite grains were separated from quartz. The Obří důl base metal deposit is formed by pyroxene-garnet skarn hosting polymetallic mineralization represented by pyrrhotite, chalcopyrite, and arsenopyrite (Fe–Cu–As association) with minor pyrite, sphalerite, molybdenite, cassiterite, scheelite, and other ore minerals (Pašava et al. 2016). The molybdenite for this study was separated from garnet-rich skarn where it forms 2- to 6-mm crystals dispersed in the matrix. Molybdenite from Všestary was obtained from the deep Vy-1 borehole penetrating the Cretaceous Basin. At level 634.5 m, very abundant molybdenite associated with pyrite forms crystals and spherical aggregates with dimensions up to 1 mm dispersed in quartz veins cross-cutting felsic porphyries (Malkovský et al. 1974).

Disseminated molybdenite mineralization is widespread in the granitoids of Cadomian (e.g., Brno and Dyje Batholiths) and Variscan (e.g., Central Bohemian Plutonic Complex or Moldanubian Batholith) ages and/or related quartz vein and pegmatites (Fig. 1). In granitoids, the sampled molybdenite forms grains, aggregates up to 8 mm in size mostly filling cracks, or fissures, whereas quartz veins and pegmatite from Dolní Bory contain disseminated molybdenite within the matrix or enclosed in quartz. The Skalsko pegmatite veins represent an anomalous type of molybdenite-rich pegmatite with average contents of about 0.19 wt% Mo (Morávek et al. 2010). Molybdenite from the Dolní Rožínka pegmatite (barren type) was sampled underground in the Rožná uranium mine.

Methods

Larger (>5 mm) molybdenite grains were separated from the matrix by rock crushing and handpicking. However, about half of the samples are represented by fine-grained molybdenite, and their separates were obtained using the protocol of Lawley and Selby (2012) as follows. Larger pieces (several grams) of quartz containing molybdenite were placed in a polyethylene beaker and up to 15 ml of concentrated HF (Romil UpA) was added. The mixture was stirred occasionally and left for 48 h to reach complete quartz dissolution. The remaining molybdenite fraction was rinsed several times by deionized water and finally dried at room temperature. The final separate was checked optically and cleaned manually where necessary.

The rhenium and osmium concentrations and isotopic determinations of molybdenite were obtained in two different laboratories: the joint Re–Os geochronology lab of the Institute of Geology of the Czech Academy of Sciences and the Czech Geological Survey (GLU/CGS lab) and the Crustal Re–Os geochronology laboratory of the Canadian Centre for Isotopic Microanalysis at the University of Alberta (UofA lab).

The GLU/CGS lab utilizes the Re spike–Os normal method (Selby and Creaser 2001) following the analytical protocol described in detail previously (Kohút et al. 2013). In brief, an aliquot of molybdenite separate was weighted into a Carius tube, mixed with the ^{185}Re spike–Os normal solution, and decomposed using 2 ml of concentrated HCl and 4 ml concentrated HNO_3 at 220 °C for 2 days (Shirey and Walker 1995). Osmium was extracted from reversed aqua regia by a mixture of $CHCl_3$ and HBr (Cohen and Waters 1996), and the final fraction was purified by microdistillation (Birck et al. 1997). Rhenium was separated by anion exchange chromatography using AG 1×8 resin (Eichrom) and its isotopic composition was determined by sector field inductively coupled plasma mass spectrometry (SF-ICP-MS) using the Element 2 (Thermo) instrument at the Institute of Geology of the Czech Academy of Sciences or the multi-collector ICP MS Neptune at the Czech Geological Survey (see Žák et al. 2014a, b for details on the latter method). In-run precision of rhenium isotopic ratio measurements was always better than ±0.4 % (2σ). Osmium was loaded onto Pt filaments and its isotopic composition was obtained by negative thermal ionization spectrometry (Creaser et al. 1991; Völkening et al. 1991) using the Finnigan MAT 262 at the Czech Geological Survey. Internal precision of the analyses was always better than ±0.1 % ($2\sigma_m$), whereas external precision was monitored on the UMCP standard solution (Johnson-Matthey), yielding $^{187}Os/^{188}Os$ value of 0.11380 ± 20 (2σ). The accuracy of the whole analytical protocol was checked by repeated analyses ($n = 3$) of Henderson mine molybdenite reference material (NIST RM 8599), which yielded an average age of 27.6 ± 0.2 Ma, similar to the reference values of Markey et al. (2007).

At the UofA lab, the ^{187}Re and ^{187}Os concentrations in molybdenite were determined by isotope dilution mass spectrometry using Carius tube, solvent extraction, anion chromatography, and negative thermal ionization mass spectrometry techniques (Selby and Creaser 2004). A mixed double spike containing known amounts of isotopically enriched ^{185}Re, ^{190}Os, and ^{188}Os analysis is used (Markey et al. 2007). Isotopic analysis used a ThermoScientific Triton mass spectrometer with Faraday collectors. Total blanks for Re and Os are less than <3 and 2 pg, respectively, which are insignificant for the Re and Os concentrations in molybdenite. The age determined for NIST RM 8599 during the course of this work (November 2015) was 27.73 ± 0.13 Ma, in accord with the recommended age.

Results

The Re–Os concentrations and model ages of the studied molybdenite samples are summarized in Table 1.

With only two exceptions (Krupka-Knetl and Krásno), molybdenite related to Sn–W mineralization is characterized by very low Re contents, below 1 ppm, in agreement with in situ LA-ICP-MS results published recently by Pašava et al. (2016) and, consequently, low ^{187}Os values. In contrast, the Krupka-Knetl and Krásno molybdenite samples contain ~9.9 and 3.06 ppm Re, respectively. Nevertheless, all molybdenite samples related to Sn–W mineralization display similar Re–Os ages in the narrow interval between ~315 and ~323 Ma, with the youngest age found at the Krupka deposit (~315–319 Ma).

Two molybdenite samples from the Mokrsko-West Au deposit yield undistinguishable Re–Os ages of 342.6 ± 2.2 and 343.6 ± 2.2 Ma, similar to the previously published Re–Os age for molybdenite from the Mokrsko-East Au deposit (342.9 ± 1.4 Ma; Zachariáš and Stein 2001).

Molybdenite related to base metal mineralization is characterized by elevated to very high Re contents (up to 602 ppm at Padrť; Žák et al. 2014a, b), and the ages vary from 312.7 ± 1.4 Ma for the Obří důl Fe–Cu–As skarn mineralization to 376.9 ± 2.4 Ma in molybdenite from the Hůrky u Rakovníka Pb–Zn–Mo–Au deposit within the Čistá pluton.

Disseminated molybdenite mineralization related to granitoids and/or associated quartz veins and pegmatites shows highly variable ages reflecting the age of the host rock. The molybdenite samples from Cadomian granitoids of the Brunovistulian Unit at Černá Hora (Brno Batholith) and Derflice (Dyje Batholith) yield the oldest ages of 596.9 ± 2.7 and 583.8 ± 3.7 Ma, respectively. In comparison, molybdenite related to Variscan and/or post-Variscan granitoids returned ages in the range between 345.9 ± 1.5 and 341.3 ± 2.2 Ma for the Central Bohemian Plutonic Complex, 320.4 ± 1.5 and 317.3 ± 1.4 Ma for the Moldanubian Batholith, and 303.2 ± 1.9 and 297.7 ± 2.1 Ma for the youngest Žulová pluton. A single molybdenite sample from the Nasavrky/Železné Hory Plutonic Complex yielded an age of 341.5 ± 2.2 Ma.

Two molybdenite samples from pegmatites occurring close to each other within the metamorphic rocks of the Moravian part of the Moldanubian Unit (Dolní Bory and Rožná) yield undistinguishable ages of 335.4 ± 1.6 and 333.7 ± 1.5 Ma, respectively.

Discussion

Constraints on the age of Sn–W mineralization

The medium-sized composite S-type plutons with greisen-type Sn–W deposits in cupolas of the youngest sub-intrusions appear in the western (Krásno deposit in the Slavkovský lea area) and central (Geyer and Ehrenfriedersdorf deposits in the German Erzgebirge) parts of the province, accompanied by small intrusions of A-type granites disseminated throughout the whole Erzgebirge. The style of mineralization varies from pervasive greisenization (Cínovec and Sadisdorf deposits) through magmatic-hydrothermal quartz (±feldspar) veins (Krupka) to pervasive hydrothermal alteration of rhyolite in the exocontact (Altenberg).

In spite of numerous studies, the exact timing of the Sn–W mineralization in the Erzgebirge metallogenetic province has been a matter of debate for a long time (e.g., Kempe 2003; Kempe et al. 2004; Romer et al. 2007, 2010, and others). This is especially due to a complex evolution of these granite- and volcanic-related mineralized systems including multiple magmatic pulses with different melt sources, large-scale hydrothermal overprint, metamorphic and tectonic effects, and specific chemical conditions. This results in the disturbance of typically used geochronological systems such as Rb–Sr, U–Pb, or K–Ar/Ar–Ar. For example, there are virtually no reliable zircon U–Pb data due to extremely high U contents (up to ~15 wt% UO_2; Förster et al. 1999; Breiter et al. 2006) detected in zircon resulting in its metamict nature, whereas U–Pb

Table 1 Re-Os data for molybdenites from the Bohemian Massif

Sample	No.	Locality	Type of mineralization	Host rock	Age of related intrusion	Re (ppm)	2σ	^{187}Os (ppb)	2σ	Common Os (pg)	Model Age (Ma)	2σ
Cin-9	1*	Cínovec	Sn-W	Qtz vein in greisen	316–331 Ma (*1–3*)	0.169	0.001	0.57	0.01	2.1	322.4	5.5
Sad-6	2*	Sadisdorf	Sn-W	Greisen	316–331 Ma (*1–3*)	0.0898	0.00026	0.303	0.003	3.1	321.4	3.8
51/M	3	Krupka-Knetl	Sn-W	Qtz vein in greisen	316–331 Ma (*1–3*)	9.82	0.02	32.9	0.2	n.d.	319.2	2.0
						9.89	0.02	33.0	0.2	n.d.	317.7	2.0
Kru-2	4*	Krupka-Preiselberg	Sn-W	Qtz vein in greisen	316–331 Ma (*1–3*)	0.385	0.001	1.27	0.01	3.0	315.3	2.3
Kra-2	5*	Krásno	Sn-W	Greisen	320–330 Ma (*4–6*)	3.063	0.009	10.40	0.03	5.3	323.3	1.6
Jach-30	6*	Jáchymov	Sn-W	Greisen	320–330 Ma (*4–6*)	0.870	0.003	2.91	0.01	2.0	319.0	1.7
46/M	7	Hůrky u Rakovníka	Base metal	Fenite, Čistá pluton	373 ± 1 Ma (*7*)	9.79	0.02	38.8	0.23	n.d.	376.9	2.4
Pad-1#	8	Padrť	Base metal	Qtz vein	343 ± 1 Ma (*8*)	542.0	2.0	1934	12	n.d.	339.8	2.5
						602.4	1.3	2133	13	n.d.	337.2	2.2
VSE-41	9*	Všestary	Base metal	Qtz vein	?	52.00	0.15	183.07	0.17	3.1	335.3	1.5
OBR-38	10*	Obří Důl	Base metal	Skarn	312–313 Ma (*9*)	14.57	0.04	47.83	0.05	19	312.7	1.4
Mokr-1	11	Mokrsko-West	Au	Qtz vein	345–358 Ma (*10–11*)	60.24	0.13	216.7	1.3	n.d.	342.6	2.2
						61.76	0.14	222.8	1.3	n.d.	343.6	2.2
CH26	12*	Černá Hora	Disseminated Mo	Qtz vein, Brno Batholith	579–600 Ma (*12–13*)	145.1	0.4	911.6	1.3	8.1	596.9	2.7
14/M	13	Derflice	Disseminated Mo	Granodiorite, Dyje Batholith	560–596 Ma (*14–15*)	73.8	0.2	453.1	2.7	n.d.	583.8	3.7
Vra-40	14*	Vrančice	Disseminated Mo	Granite, CBPC	345–348 Ma (*11*)	13.50	0.04	49.03	0.07	1.3	345.9	1.5
PRI-33	15*	Příbram	Disseminated Mo	Granite, CBPC	345–348 Ma (*11*)	26.09	0.08	94.49	0.15	34	344.9	1.6
Kamen-1	16	Kamenný Přívoz	Disseminated Mo	Granodiorite, CBPC	354 ± 4 Ma (*10*)	46.13	0.12	165.4	1.0	n.d.	341.5	2.2
Skal-1	17	Skalsko	Disseminated Mo	Pegmatite, CBPC	354 ± 4 Ma (*10*)	133.5	0.3	478.0	3.0	n.d.	341.3	2.2
SKU-36	18*	Skuteč	Disseminated Mo	Granite, Železné Hory/ Nasavrky Pluton	?	205.1	0.7	733.4	3.8	2.0	340.5	2.3
HUR-37	19*	Hůrky u Nové Bystřice	Disseminated Mo	Qtz vein, Moldanubian Batholith	320–330 Ma (*16–18*)	2.50	0.01	8.4	0.01	2.3	320.4	1.5
POHL-42	20*	Pohled	Disseminated Mo	Granite, Moldanubian Batholith	320–330 Ma (*16–18*)	3.114	0.009	10.37	0.01	2.8	317.3	1.4
52/M	21	Kozí Hora	Disseminated Mo	Qtz vein, Moldanubian Batholith	~316 Ma (*17,19*)	0.486	0.002	1.62	0.01	n.d.	317.2	2.2
						0.499	0.002	1.65	0.01	n.d.	314.8	2.3
8/95	22	Černá Voda	Disseminated Mo	Granodiorite, Žulová Pluton	292–300 Ma (*20*)	33.64	0.08	106.5	0.6	n.d.	301.7	1.9
						31.38	0.07	99.9	0.6	n.d.	303.2	1.9
10/M	23	Štachlovice	Disseminated Mo	Granodiorite, Žulová Pluton	292–300 Ma (*20*)	3.37	0.01	10.5	0.1	n.d.	297.7	2.1
Bor-27	24*	Dolní Bory	Disseminated Mo	Pegmatite	?	74.6	0.2	262.7	0.4	2.8	335.4	1.6
Roz-35	25*	Rožná	Disseminated Mo	Pegmatite	?	513.7	1.5	1799.9	1.7	41	333.7	1.5

Numbers of the studied molybdenite samples are the same as in Fig. 1

Sources of data for related intrusions: (1) Romer et al. (2007); (2) Romer et al. (2010); (3) Hoffmann et al. (2013); (4) Tichomirova (1997); (5) Förster et al. (1999); (6) Förster et al. (2009); (7) Venera et al. (2000); (8) Žák et al. (2004b); (9) Kryza et al. (2014); (10) Janoušek et al. (2004); (11) Janoušek et al. (2010); (12) Fritz et al. (1996); (13) van Breemen et al. (1982); (14) Finger et al. (2000); (15) Friedl et al. (2004); (16) Friedl (1997); (17) Gerdes et al. (2003); (18) Žák et al. (2011a, b); (19) Chen and Siebel (2004); (20) Laurent et al. (2014)

CBPC Central Bohemian Plutonic Complex, *n.d.* not determined

[a] Data from Žák et al. (2014a, b)

[b] Analyses performed at the University of Alberta (UofA)

dating of monazite is complicated due to its possibly multiple overprint by several magmatic and metamorphic events. Consequently, the reported ages for Sn–W mineralization and related granites/volcanic rocks in the Erzgebirge so far span an age range from ~290 to ~330 Ma (Gerstenberger et al. 1995; Förster 1998; Kempe et al. 1999, 2004; Romer et al. 2007, and references therein). On the other hand, as noted by Romer et al. (2007), the most reliable conventional U–Pb analyses of uraninite, monazite, and apatite paralleled by two Re–Os molybdenite ages from Altenberg yield a more narrow age interval between ~313 and 331 Ma. Chemical composition (peak concentrations of Ag, As, Bi, Cu, Nb, Pb, Te, Zn, and W) and the presence of nano- to microscale inclusions (including native Bi and locally accompanied by a Pb–Bi–Cu phase, bismuthinite, galena, wolframite, and scheelite) in molybdenite from greisen-type occurrences reflect the close relationship to Sn–W mineralizing events (Pašava et al. 2016). Our new Re–Os data for molybdenite samples from four different Sn–W deposits clearly show that the mineralization events on the western (323.3 ± 1.6 Ma at #5 Krásno and 319.0 ± 1.7 Ma at #6 Jáchymov) and eastern (322.4 ± 5.5 Ma at #1 Cínovec and 321.4 ± 3.8 Ma at #2 Sadisdorf) sides of the Erzgebirge are contemporaneous. This indicates the predominance of one and/or multiple short-time Sn–W mineralization event(s) in the Erzgebirge metallogenetic province, which occurred around ~320 Ma. At the Krásno and Jáchymov deposits, this age is identical to the age of related granites of the Eibenstock–Nejdek pluton (Table 1), indicating the close temporal relationship. Similarly, the Re–Os molybdenite ages determined at Cínovec and Sadisdorf overlap with the Altenberg–Teplice caldera rocks represented by the Mikulov Rhyolitic Ignimbrite, Altenberg greisen and related quartz veins, and the Teplický vrch granite porphyry cross-cutting Altenberg–Teplice rocks (Table 1). Therefore, our new data demonstrate that Sn–W mineralization in the Erzebirge is closely related to the granites and does not postdate granitic magmatism. Nevertheless, resolvable younger Re–Os ages determined for molybdenite from the Krupka deposit (#4 with 315.3 ± 2.3 Ma and #3 with 317.7 ± 2.0 Ma/319.2 ± 2.0 Ma) may indicate a prolonged mineralizing activity at the Altenberg–Teplice caldera until ~315 Ma.

Relationship between molybdenite and base metal mineralization

The Hůrky u Rakovníka Pb–Zn–(Au–Mo) mineralization is related to fenitized parts of the Čistá granodiorite pluton with a reported Pb–Pb zircon age of 371 Ma, with an over-optimistically small uncertainty of only 1 Ma (Venera et al. 2000). The obtained molybdenite Re–Os age of 376.9 ± 2.4 Ma for molybdenite (#7) is slightly older than the zircon age, but within the range of Ar–Ar ages on muscovite and whole rock (~375–380 Ma) from the nearby Tis granite interpreted as Early Variscan tectonothermal overprint (Dallmeyer and Urban 1994). Together, these ages indicate a coeval age of mineralization and host rocks.

The Obří důl Fe–Cu–As mineralization is associated with skarn in the exocontact of the composite granitic Krkonoše-Jizera Plutonic Complex which has been recently dated by the high-precision CA-ID-TIMS U–Pb zircon method, providing identical ages of 312.5 ± 0.3 and 312.2 ± 0.3 Ma for two different granite facies (Kryza et al. 2014). Our Re–Os age of molybdenite from the Obří důl (#10) skarn base metal mineralization of 312.7 ± 1.4 Ma is in excellent agreement with the granite U–Pb zircon ages, providing evidence for the simultaneous formation of skarn with its base metal mineralization and the Krkonoše-Jizera Plutonic Complex.

At Padrť (#8), the age of Fe–As–Mo base metal mineralization obtained from the Re–Os age for molybdenite (337.2 ± 2.2 and 339.8 ± 2.5 Ma) postdates the age of the associated Padrť granite (Table 1), which is in agreement with the low-temperature character (~300 °C) of quartz related to molybdenite formation (Žák et al. 2014a, b).

The position of the Vy-1 borehole (Všestary #9 molybdenite) with respect to the tectonic units of the Bohemian Massif is hard to constrain due to extensive cover by the Czech Cretaceous Basin. Nevertheless, the obtained Re–Os age of 335.3 ± 1.5 Ma implies a Variscan age of the molybdenite mineralization and perhaps also of the hosting volcano-sedimentary sequence.

Temporal relationship between molybdenite, related granitoids, and Au mineralization

Cadomian intrusions

Two Cadomian batholiths on the eastern side of the Bohemian Massif host molybdenite mineralization (Fig. 1). The Brno Batholith is formed by the Western and Eastern Granitoid Complexes separated by the Central Metabasite Zone (e.g., Leichmann and Höck 2008). Geochronological data obtained so far indicate an older age of the Eastern Complex (599 ± 1 Ma; Fritz et al. 1996) in comparison to the Western Complex (~579–588 Ma; Van Breemen et al. 1982; Fritz et al. 1996). Our molybdenite from Černá Hora (#12) in the Eastern Complex yields a Re–Os age of 596.9 ± 2.7 Ma. The Dyje/Thaya Batholith has a poorly constrained age, with data for (meta)granitoids spanning a wide range between ~560 and ~596 Ma (Table 1). A single Re–Os age derived from molybdenite enclosed in granodiorite at the locality Derflice (#13) shows an intermediate age (583.8 ± 3.7 Ma), and therefore, further chronological interpretations are difficult without additional data.

Variscan and post-Variscan intrusions

The Central Bohemian Plutonic Complex forms a large body along the boundary between the Teplá-Barrandian and Moldanubian Units (Fig. 1). It consists of three major magmatic suites: (1) Sázava suite with an age of 354.1 ± 3.5 Ma (Janoušek et al. 2004); (2) Blatná suite yielding ages of 346.1 ± 1.6 and 346.7 ± 1.6 Ma (Janoušek et al. 2010); and (3) Čertovo břemeno (durbachite) suite with an age of 343 ± 6 Ma (Holub et al. 1997). Two molybdenite samples (#14 Vrančice and #15 Příbram) from the Blatná suite granodiorites return ages of 345.9 ± 1.5 and 344.9 ± 1.6 Ma, undistinguishable from U–Pb zircon ages and suggesting contemporaneous emplacement of molybdenite mineralization and host granitoids. On the other hand, two molybdenite samples related to the Sázava suite (#16 Kamenný Přívoz and #17 Skalsko) show almost identical Re–Os ages of 341.5 ± 2.2 and 341.3 ± 2.2 Ma, respectively, resolvably younger than the host granitoids. However, they are similar to the Re–Os ages of molybdenite from Au mineralizations related to the Central Bohemian Plutonic Complex (#11 Mokrsko-West, 342.6 ± 2.2 and 343.6 ± 2.2 Ma; this study; Bělčice, Mokrsko-East, and Petráčkova Hora, 339–346 Ma; Zachariáš et al. 2001; Zachariáš and Stein 2001). Taking these molybdenite ages together, they overlap with the reported Ar–Ar cooling ages of the Central Bohemian Plutonic Complex (336–343 Ma; Matte et al. 1990; Dörr et al. 1998; Žák et al. 1998b) and the Jílové gold deposit (339.0 ± 1.5 Ma; Zachariáš et al. 2013). This implies a close relationship of molybdenite and Au mineralization with the latest evolutionary stages of the Central Bohemian Plutonic Complex. This is also supported by the chemical composition of molybdenite (highest average Au values—24 ppm in molybdenite from different types of mineralization in the Bohemian Massif) and distribution of microinclusions in molybdenite (native Au, Au(Ag), Bi–Au–Te phase, Bi–Te–Ag phase, Ag–Se phase, and Ag–Te phase; Pašava et al. 2016).

Peraluminous (S-type) granites forming two major granite plutons—Weinsberg and Eisgarn—predominantly compose the Moldanubian Batholith. The age of both plutons overlap in the range of ~320–330 Ma (Table 1). Molybdenite from Hůrky (#19) and Pohled (#20) in the Eisgarn granite yield Re–Os ages of 320.4 ± 1.5 and 317.3 ± 1.4 Ma, respectively, suggesting molybdenite crystallization coeval with the host granites. In addition to the predominant Eisgarn and Weinsberg plutons, several small intrusions accompanying these two types yield much younger ages down to ~316 Ma (e.g., Mauthausen type; Table 1), and some of them are characterized by high Sr contents and common molybdenite mineralization (Breiter 2010). The studied molybdenite samples from Kozí Hora (#21) with ages of 317.2 ± 2.2 and 314.8 ± 2.3 Ma occur within quartz veins related to greisenized parts of the Mauthausen-type granitoids, and the Re–Os ages are in excellent agreement with the U–Pb zircon ages. However, it should be kept in mind that molybdenite from Kozí Hora is characterized by very low Re contents (~0.5 ppm) and the absence of determined common Os for this particular sample may possibly alter the accuracy of the obtained age (e.g., Zimmerman and Stein 2010). The close relationship between greisenization and molybdenite mineralization at Kozí Hora is also evidenced by the anomalous molybdenite chemistry with As (up to 505 ppm), W (up to 499 ppm), Cu (up to 469 ppm), Zn (up to 482 ppm), and Sn (up to 53 ppm; Pašava et al. 2016).

The Žulová pluton belongs to the so-called Sudetic Granitic Belt (Finger et al. 2009) in the Saxothuringian Unit, which consists of several granitic massifs (Krkonoše-Jizera, Strzegom-Sobótka, Strzelin, Klodzsko-Zlaty Stok, and Žulová) intruded between ~312 and 283 Ma (U–Pb zircon: Turniak and Bröcker 2002; Turniak et al. 2005a, b; Oberc-Dziedzic et al. 2013; Kryza et al. 2014; Laurent et al. 2014; Re–Os molybdenite: Mikulski and Stein 2012). The granites of the Žulová pluton have a prolonged magmatic history from melting to emplacement at ~300–292 Ma (Laurent et al. 2014). This would be in agreement with three Re–Os ages obtained for molybdenite from the Žulová granodiorite (#22 and #23) spanning the range from ~298 to ~303 Ma.

The age of the Železné Hory/Nasavrky pluton is poorly constrained by a whole-rock Rb–Sr age of ~320 Ma (Scharbert 1987). However, the similar I-type calc-alkaline composition may indicate its close connection to the Central Bohemian Plutonic Complex (Cháb et al. 2010). The molybdenite from Skuteč (#18) located in the eastern periphery of the pluton returns a Re–Os age of 340.5 ± 2.3 Ma. This is much older than the previous Rb–Sr age, but identical to the nearby (ultra)basic Ransko intrusion with a Re–Os age of 341.5 ± 7.9 Ma (Ackerman et al. 2013), suggesting possibly contemporaneous mafic–felsic magmatism in this area.

Disseminated molybdenite mineralization related to pegmatites within the Moldanubian Unit

The Moldanubian Unit of the Bohemian Massif hosts abundant pegmatite bodies with common rare metal mineralizations (e.g., Novák and Povondra 1995; Novák et al. 2012). Their age was previously investigated by U–Pb dating of columbite/tantalite (Melleton et al. 2012) and monazite (Novák et al. 1998). Considering both studies, two ages of pegmatite emplacement can be distinguished (~333 ± 3 and ~325 ± 4 Ma), with the former event being predominant and related to HT–HP melting events during exhumation of the lower crust. Two pegmatites from Dolní Bory (#24) and Dolní Rožínka (#25), which belong to the Strážek pegmatite field, yield undistinguishable Re–Os ages of 335.4 ± 1.6 and 333.7 ± 1.5 Ma, providing evidence for their relationship to the older pegmatite event.

Conclusions

The Bohemian Massif represents a complex terrane collage assembled during the Variscan orogeny and hosting a variety of ore deposits (e.g., Sn–W, Au, U, and base metals). Molybdenite is a common mineral accompanying some of these mineralization styles, but it is also widespread in the granitic intrusions and/or related quartz veins/pegmatites occurring throughout all geotectonic units. The Re–Os geochronology of molybdenite from four Sn–W deposits in the Erzgebirge metallogenetic province (Krásno, Jáchymov, Cínovec, and Sadisdorf) yields a narrow age interval of 319–323 Ma, indicating one and/or multiple short-time mineralization events closely associated with the felsic host rocks. However, resolvable younger Re–Os ages (315–319 Ma) of molybdenite from the Krupka Sn–W deposit within the Altenberg–Teplice caldera may indicate a prolonged mineralization activity until ~315 Ma. The molybdenite Re–Os ages for base metal deposits developed at the fenitized parts of the Čistá pluton (Hůrky) and skarn in the exocontact of the granitoids of the Krkonoše-Jizera Plutonic Complex (Obří důl) suggest coeval age of mineralization and associated granitic rocks. On the other hand, the base metal mineralization at Padrť postdates the age of the associated Padrť granite. Most Re–Os ages for disseminated Mo mineralizations in the granitic bodies and pegmatites of Cadomian and Variscan age overlap with the previously published U–Pb and Ar–Ar geochronological data for the host rocks, which indicates a contemporaneous evolution. However, molybdenite related to the Sázava suite granites of the Central Bohemian Plutonic Complex (CBPC) returns resolvable younger ages than the host granites, but similar to previously obtained Re–Os ages for molybdenite from spatially related Au mineralizations. This may imply a close relationship to the latest evolution stages of the CBPC.

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