Rhenium-osmium geochronology of gersdorffite and skutterudite-pararammelsbergite links nickel–cobalt mineralization to the opening of the incipient Meliata Ocean (Western Carpathians, Slovakia)

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Abstract

The multi-orogenic crustal segment of the Central Western Carpathians comprises a Variscan basement that is host to small nickel–cobalt (Ni–Co) arsenide and sulfarsenide mineralizations at Ľubietová-Kolba and Čierna Lehota (Slovakia). Here, we constrain the timing of Ni–Co mineralization by using rhenium–osmium (Re–Os) isotope geochemistry of (1) gersdorffite (NiAsS) after krutovite (NiAs₂) at Ľubietová-Kolba, and (2) a mixture of skutterudite-pararammelsbergite (CoAs₃–NiAs₂) from the Čierna Lehota deposit, hosted by metamorphosed carbonaceous rocks. Gersdorffite, which is bereft of common Os, returns a Re–Os model age of 238.2 ± 1.0 (2 σ) million years (Ma). Four aliquots of the skutterudite-pararammelsbergite mixture define a robust model 1 isochron at 238.2 ± 12.7 (2 σ) Ma (mean square weighted deviates – MSDW = 0.95). A crustal source of Os, and by inference other metals, is inferred from the initial ¹⁸⁷Os/¹⁸⁸Os ratio of 0.90 ± 0.01 of this isochron. We conclude that studied Ni–Co mineralizations are related to an extensional tectonic regime and hydrothermal fluid flow in connection with the opening of the Meliata ocean in the Middle Triassic (Ladinian).

Keywords Re–Os isotope geochemistry and geochronology · Arsenides · Western Carpathians

Introduction

Untangling the relationships between ore formation and tectono-metamorphic, magmatic-hydrothermal, or basinal-hydrothermal processes in polyphased crustal segments, such as the Western Carpathians, can be achieved by acquisition of accurate and precise geochronological data. Hydrothermal mineral deposits in the Western Carpathians formed in connection with tectonothermal events (Petrík 2000; Kohút 2004; Plašienka 2018) of Variscan (e.g.,

Carboniferous, Majzlan et al. 2020) and Alpine ages (e.g., Cretaceous, Kohút et al. 2013). Yet, there is a long-standing controversy whether siderite-copper mineral deposits actually relate to mineralizing processes of Variscan or Alpine age in the Western Carpathians. For example, copper mineral deposits near Ľubietová, including the Kolba Cu–Ni–Co occurrence, were considered to be syngenetic-stratiform of Variscan age, Variscan with Alpine remobilization, or epigenetic of Alpine age (Ilavský 1976; Varček 1978). Similar siderite-copper mineralization elsewhere in the Western Carpathians were proposed to be of Permian (Radvanec and Grecula 2016) or Cretaceous age (Hurái et al. 2002; Kiefer et al. 2020).

To resolve this ambiguity, absolute geochronology directly targeting minerals of economic interest (i.e., sulfides, sulfarsenides, or arsenides) is ideal. To this end, recent development of the ¹⁸⁷Re–¹⁸⁷Os chronometer has seen its application to sulfarsenides and arsenides (cobaltite—CoAsS, Saintilan et al. 2017; gersdorffite—NiAsS, Kiefer et al. 2020; rammelsbergite—NiAs₂, Chernonozhkin et al. 2020). Herein, we investigate the mineralogy and timing

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of Ni–Co mineralization at two small historical deposits Ľubietová-Kolba (Veporic Superunit) and Čierna Lehota (Tatric Superunit) in the Western Carpathians in central Slovakia. Nickel–cobalt sulfarsenides and arsenides dated by Re–Os geochronology in this work provide direct timing of the ore-forming events. Therefore, we were able to place the mineralizing processes in the greater context of the geodynamic evolution of the Western Carpathians in the Middle Triassic.

Geological setting

Regional geology

The Western Carpathians represent a segment of the Alpine-Carpathian fold belt that formed as a result of subduction-collision in the Late Jurassic to Paleogene-Neogene within the mobile belt between the stable North European Platform and drifting continental fragments of Apulia/Adria (Plašienka 2018). The Western Carpathians are composed of (1) fragments of Early Paleozoic basement intruded by Variscan granitoids, (2) late Paleozoic to Mesozoic autochthonous sedimentary cover, and (3) Mesozoic, Paleogene, and Neogene sediments and volcanic rocks. The Central Western Carpathians (CWC) consist of the pre-Paleogene components grouped from north to south in three tectonic superunits: the Tatric sheet thrust over the Veporic wedge, which is overlain by the Gemeric Superunit (Plašienka 2018). The Tatric and Veporic Superunits comprise large Devonian to Late Carboniferous syn- to post-collisional I- and S-type granitoids, Variscan felsic orthogneisses, paragneisses, migmatites, calc-silicate rocks, scarce metamorphosed black shales, and remnants of retrogressed meta-ultramafic rocks (Broska and Kubiš 2018; Kohút and Larionov 2021; Janák et al. 2020). Some Tatric complexes contain larger bodies of metamorphosed basalts, dolerites, gabbros, and sediments with variable amount of meta-organic matter and pyrite (Ivan and Méres 2015). These rocks are considered to represent metamorphosed and tectonically dismembered ophiolite sequences. Alpine metamorphic overprint was weak to negligible in the Tatric Superunit (Plašienka 2018) but significant in the Veporic Superunit (Jeřábek et al. 2012) where it reached the upper amphibolite facies.

Ore geology

The studied sites Ľubietová-Kolba and Čierna Lehota were small historical deposits and the former adits and galleries are no longer accessible. The veins at the Ľubietová-Kolba deposit are hosted by Variscan basement of the Veporic Superunit—biotite-quartz gneisses and amphibolites

affected by retrograde Alpine metamorphism (Fig. 1). The veins are built by a system of lenses that strike NE-SW or N-S, dip steeply to the E, and reach a maximum thickness of several decimeters (Koděra et al. 1990). Pršek and Mikuš (2006) identified gersdorffite as the main mineral of the nickel–cobalt (Ni–Co) mineralization. A younger copper–bismuth (Cu–Bi) mineralization contains chalcopyrite, tennantite, and rare sulfosalts of the bismuthinite–aikininite series and kobellite.

Cobalt–nickel mineralization near Čierna Lehota is located in a SSW–NNE-striking lenses of metamorphosed carbonaceous pelitic and silicic rocks and amphibolites hosted by quartz–biotite paragneisses of the Tatric Superunit (Fig. 1). The graphitic rocks are interpreted to belong to the uppermost part of a dismembered ophiolitic sequence (Ivan and Méres 2015). The metamorphosed carbonaceous rocks contain pyrite–pyrrhotite horizons and crosscutting epigenetic Ni–Co–Cu–Bi arsenide–sulfarsenide mineralization. In this study, we focus on this epigenetic Ni–Co arsenide–sulfarsenide mineralization (Mikuš et al. 2013) and the younger Cu–Bi mineralization with chalcopyrite, tennantite, hodrušite ($\text{Cu}_8\text{Bi}_{12}\text{S}_{22}$), and kupčíkite ($\text{Cu}_{3.4}\text{Fe}_{0.6}\text{Bi}_5\text{S}_{10}$) (Pršek et al. 2005).

Materials and methods

Materials

Forty-six samples for this study were collected on dumps of the two small-scale mineral occurrences at Ľubietová-Kolba and Čierna Lehota. These samples were used for previous work on their mineralogy (Mikuš et al. 2013; Pršek and Mikuš 2006).

Chemical analyses of ore minerals

The major and minor element mineral chemistry of Ni–Co arsenides and sulfarsenides was determined by wavelength-dispersive spectrometry (WDS) with an electron microprobe JEOL JXA 8530FE using the following analytical conditions: accelerating voltage 20 kV, probe current 15 nA, beam diameter 2–3 μm , ZAF correction (Donovan et al. 1993), counting time 20 s on peak, 10 s on background (Earth Science Institute of the Slovak Academy of Sciences, Banská Bystrica). For WDS analyses, the following standards and X-ray lines were used: Ag($L\alpha$)–Ag metal, S($K\alpha$)–pyrite, Cu($K\alpha$) and Fe($K\alpha$)–chalcopyrite, As($L\alpha$)–GaAs, Sb($L\alpha$)–stibnite, Bi($L\alpha$)– Bi_2S_3 , Ni($K\alpha$)–gersdorffite, Co($K\alpha$)–Co metal.

Fig. 1 Geological maps of the small deposits a) Čierna Lehota (with GPS coordinates 48.854485° N, 18.354002° E) and Ľubietová-Kolba (48.748513° N, 19.445786° E), simplified after Hraško (2021) and

Polák (2003), respectively. The inset shows the position of the two deposits in central Europe

Production and characterization of mineral separates

A subset of four samples from Ľubietová-Kolba and ten samples from Čierna Lehota, which were extensively studied by means of reflected-light microscopy and electron microprobe analyses, were selected for the separation of arsenide/sulfarsenide minerals. The samples were crushed to fragment size of ≈ 0.5 cm and examined under binocular microscope. Fragments of massive mineralization were taken for further size reduction in an agate mortar and pestle to particle sizes between 1 and 2 mm. Fragments that were deemed to only contain Ni–Co arsenides and sulfarsenides and no younger chalcopyrite or Bi-sulfosalts were hand-picked under binocular microscope. For each sample, a total of 1 g of material was collected, i.e., either gersdorffite-only mineral separate or mixture of skutterudite-pararammelsbergite.

Before undertaking full Re–Os isotope geochemistry procedures, each mineral separate was characterized by powder X-ray diffraction to document the purity of this separate. Then, ca. 20-mg aliquots of each mineral separate were analyzed for their Re contents to determine the ideal sample weight to be digested with an adequate volume of “Re + Os” in the full protocols.

For each Re–Os analysis, between 90 and 125 mg of gersdorffite (Kolba) and a mixture of pararammelsbergite

and skutterudite (Čierna Lehota) were weighed into thick-walled borosilicate Carius tubes (Shirey and Walker 1995) then dissolved in inverse Aqua Regia (2 mL of 10 N HCl and 6 mL 16 N HNO₃) at 220 °C for 48 h at the Crustal Re–Os Geochronology Laboratory, University of Alberta, Edmonton, Canada. An initial Re–Os analysis using a ¹⁸⁵Re + ¹⁹⁰Os spike showed little common Os in sample KO-4, with ¹⁸⁷Os* comprising > 99.6% of the Os measured. As such, for this sample, a mixed double-Os spike (¹⁸⁵Re + ¹⁹⁰Os + ¹⁸⁸Os) was then used (Markey et al. 2007). For the CL samples, initial analyses revealed high levels of common Os and low Re/Os ratios. The laboratory protocol used here is described in full by Morelli et al. (2010) and Hnatyshin et al. (2020). In brief, Os was isolated and purified from the inverse aqua regia solution by chloroform (CHCl₃) solvent extraction, hydrobromic acid reduction, and microdistillation. The Re was isolated using HCl–HNO₃-based anion exchange chromatography. The Re and Os isotopic compositions were determined by negative thermal ionization mass spectrometry using a Thermo Scientific Triton mass spectrometer at the University of Alberta. Rhenium and Os were loaded onto Ni and Pt filaments, respectively. Rhenium was measured as ReO₄[−] in static mode on Faraday collectors, whereas Os was measured as OsO₃[−] in peak-hopping mode on a single electron multiplier (Creaser et al. 1991; Völkening et al. 1991). Measurement quality was monitored by measurements of

in-house Re and Os standards over the analysis period ($^{85}\text{Re}/^{187}\text{Re} = 0.59775 \pm 0.00042$, $n = 8$; AB-2 Os Standard, $^{187}\text{Os}/^{188}\text{Os} = 0.10689 \pm 0.00061$ 1SD, $n = 14$). A total procedural blank of 1.62 pg Re and 59 fg Os with a blank $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.26 was measured at the time of analysis. The Reference Material 8599 Henderson molybdenite (Markey et al. 2007) is routinely analyzed as an age standard with the mixed double-Os spike, and during the past 6 years returned an average Re–Os date of 27.78 ± 0.07 Ma ($n = 26$), indistinguishable from the reference age value of 27.7 ± 0.1 Ma (Wise and Watters 2011). The ^{187}Re decay constant used is $1.666 \times 10^{-11} \pm 5.165 \times 10^{-14} \text{ a}^{-1}$ (Smoliar et al. 1996). The analytical uncertainties quoted result from full error propagation of mass spectrometer analyses, blanks, and long-term uncertainties in standard Re and Os.

Results

Ore mineralization at Kolba

The Ni–Co mineralization at Kolba is confined to veinlets (up to 10 cm thick) in the host metamorphic rocks. The paragenetic sequence, as determined from observation of hand specimens, polished sections in polarized-light microscopy, and electron microprobe, is shown in Fig. 2. The oldest minerals are massive albite and carbonates. Carbonates are sparse, dispersed in the albite mass, dominated by dolomite with average Fe/(Fe + Mg) molar ratio of 0.19 (analyses 1–8, ESM Table 1). Magnesium-Fe carbonates with Fe/(Fe + Mg) molar ratio of 0.39 are less common (analyses 9–12, ESM Table 1). The predominant mineral among the Ni–Co–Fe

sulfarsenides is gersdorffite, but its composition is variable (analyses 24–149, ESM Table 2), with diffuse, oscillatory, and sector zoning observed (Fig. 3a, b, ESM Fig. 1). Gersdorffite commonly shows cores enriched in As and rims bearing more S (Fig. 3a). Locally, cores may attain the composition of diarsenides (Fig. 3b, analyses 13–23 ESM Table 2), e.g., $(\text{Ni}_{0.95}\text{Co}_{0.02}\text{Fe}_{0.02})(\text{As}_{1.68}\text{S}_{0.33})$ in the parts the richest in As (analysis 16, ESM Table 2). Based on optical (isotropy, reflectance higher than that of gersdorffite) and chemical composition, these diarsenides are identified as krutovite. The contacts between krutovite and gersdorffite show diffuse, gradual change in the chemical composition (Fig. 3b). Gersdorffite is replaced along fractures and rims of the crystals by Cu–Bi minerals, chalcopyrite, tennantite, or Bi sulfosalts (Fig. 3c).

In light of its standard paragenetic association, a mineral composition matching the main mineralization type described here, and its high Re content (264 ng g^{-1}), sample KO-4, was selected for Re–Os dating. The mineral separate used for the Re–Os geochronology consists of single-phase gersdorffite as confirmed by powder X-ray diffraction.

Ore mineralization at Čierna Lehota

The ore mineralization at Čierna Lehota is hosted by metamorphosed carbonaceous rocks and the paragenetic sequence there is shown in Fig. 2. It consists of syngenetic mineralization, dominated by massive aggregates and impregnations of pyrrhotite and pyrite and epigenetic Ni–Co–As–Cu–Bi mineralization.

The epigenetic Ni–Co–As ores considered here have spheroid, concentric, or collomorph textures (Fig. 3d–f,

Fig. 2 Paragenetic sequences for the mineralizations from Čierna Lehota (right) and Ľubietová-Kolba (left)

	Ni-Co-As mineral.	Cu-Bi mineral.		syngenetic mineral.	Ni-Co-As mineral.	Cu-Bi mineral.
Ľubietová-Kolba			Čierna Lehota			
albite	—		pyrite	—		
dolomite/siderite	—		pyrrhotite	—		
krutovite	—		sphalerite			—
gersdorffite	—		galena			—
arsenopyrite	—		chalcopyrite			—
pyrite	—		quartz		—	
quartz		—	siderite		—	
sphalerite		—	Co skutterudite		—	
chalcopyrite		—	Ni-Fe skutterudite		—	
tennantite		—	parammelsbergite		—	
Bi sulfosalts		—	Ni-löllingite		—	
			bismuth		—	
			löllingite		—	
			arsenopyrite		—	
			gersdorffite		—	
			tennantite			—
			Bi sulfosalts			—

Fig. 3 Back-scattered electron (BSE) images of arsenides and sulfarsenides from Kolba (a–c) and Čierna Lehota (d–f). **a** Zoned aggregates of gersdorffite. The light gray cores are enriched in Ni, As; the darker gray rims are richer in Fe (EMP analyses 103–124 in Table S2). Sample KL-10. **b** Anhedral, early krutovite enclosed in gersdorffite (an. 13–17 and 66–82 in ESM Table 2). Sample K-1. **c** Gersdorffite with cores enriched in Ni and As and rims enriched in Fe (an. 83–99 in ESM Table 2) replaced by younger tennantite. Sample K-4. **d** Earlier Co skutterudite with numerous minute bismuth inclusions is overgrown by Ni-Fe skutterudite (an. 150–188 in ESM Table 3). The contact between the two skutterudite types is highlighted in one of the aggregates by the dashed red line. Skutterudite

associates with parammelsbergite. Sample CL-1. **e** Spheroid, concentric aggregates of early parammelsbergite, overgrown by Ni-Fe skutterudite, with tiny bismuth inclusions in the center of the aggregate. Sample CL-1. **f** Spheroid aggregate of parammelsbergite and Ni-Fe-bearing skutterudite is replaced by gersdorffite. The subhedral löllingite crystal belongs also the latest minerals of the Ni-Co-As mineralization. The minute bismuth inclusions and Bi sulfosalts fill fractures in the aggregates of the Ni-Co-As minerals. Mineral abbreviations: Skt, skutterudite; prm, parammelsbergite; gdf, gersdorffite; ab, albite; Bi-sulf, Bi sulfosalts; lö, löllingite; tnt, tennantite; kru, krutovite

ESM Figs. 2, 3) and consist of fine-grained intergrowths of early skutterudite [(Co,Ni,Fe)As₃] and parammelsbergite (NiAs₂), occasionally with inclusions of native bismuth (Fig. 3d, ESM Fig. 2). Skutterudite is Co-rich (analyses 150, ESM Table 3), whereas parammelsbergite is chemically near the composition NiAs₂, with little Fe (average 1.9 wt%), S (3.7 wt%), and no Co (analyses 197–225, ESM Table 3).

The abundant aggregates of Co-rich skutterudite and parammelsbergite are overgrown by later skutterudite that is essentially devoid of Co (Fig. 3d, e, analyses 151–188, ESM Table 3) and by later parammelsbergite. Texturally, the two skutterudite types are difficult to distinguish because both are part of spheroid, concentric, and porous aggregates. Those discrete skutterudite

types can only be distinguished from one another by their Co content. The later skutterudite contains fewer or no bismuth inclusions (Fig. 3d) but may contain inclusions of löllingite with distinctly elevated Ni content (up to 7.7 wt% Ni, analyses 189–191, ESM Table 3). The later, darker gray pararammelsbergite in back-scattered electron images contains less As and more S than the early pararammelsbergite (analyses 197–225, ESM Table 3, Fig. 3d). The Ni–Co–As mineralization terminated with the crystallization of much less abundant, small (up to 20 μm) euhedral crystals of pararammelsbergite (with S concentration up to 12 wt%), skutterudite, löllingite, arsenopyrite, and gersdorffite (Fig. 3f, analyses 192–196 and 226–235, ESM Table 3). The Ni–Co–As minerals are crushed, healed, and replaced by native bismuth, tennantite, and a variety of bismuth sulfosalts (Fig. 3f).

In light of their predominance, Re–Os dating was carried out on mixtures dominated by skutterudite and pararammelsbergite. Powder X-ray diffraction measurement showed that the separates contain mostly these two minerals, but also minor gersdorffite and arsenopyrite. Owing to the fine-grained nature of the arsenides and sulfarsenides, it is impossible to separate the individual minerals from each other.

Re–Os geochronology of the Ni–Co sulfarsenides

The result of the Re–Os age determination for Kolba gersdorffite sample KO-4 is a model age of 238.2 ± 1.0 Ma using the mixed double-Os spike (Table 1). Samples of skutterudite-pararammelsbergite from Čierna Lehota show low Re/Os ratios (4.2–7.7) and high Os contents (320–390 ppt). The $^{187}\text{Re}/^{188}\text{Os}$ ratios (22.5–41.9) are positively correlated with highly radiogenic $^{187}\text{Os}/^{188}\text{Os}$ ratios (0.99–1.07), yielding a 4-point model 1 isochron regression (mean square weighted deviates, MSWD = 0.95) with a date of 238.2 ± 12.7 Ma (2σ) and an initial $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.90 ± 0.01 (Table 2, Fig. 4).

Discussion

Timing and source of metals in Ni–Co–As mineralization

At Čierna Lehota, there is no evidence of intramineralization tectonics or cross-cutting relationships among the various arsenides and sulfarsenides. We interpret that the Ni–Co–As mineralization formed in a single hydrothermal pulse, and the mineralizing fluids evolved from an early Co-rich and S-poor one yielding Co–Ni–As minerals to fluids poorer in metals but enriched in S late in the mineralizing sequence. Such evolution is characteristic for the so-called five-element association (Scharer et al. 2019) in which the triarsenides are commonly Co-dominated. At Čierna Lehota, the presence of skutterudite is a testament of highly reducing conditions, logically ensured by the host metamorphosed carbonaceous rocks. The spheroid, concentric, and collo-morph textures attest to rapid precipitation of the arsenides during influx of the fluids into these rocks. Therefore, the Re–Os isochron from mineral separates consisting of skutterudite-pararammelsbergite from Čierna Lehota most likely correctly dates mineralization at ca. 238 Ma. This interpretation is further supported by the Re–Os model age of gersdorffite at Kolba.

The age of the metamorphosed carbonaceous rocks in Čierna Lehota is known only as Early Paleozoic (Ivan and Méres 2015), but it is reasonable to expect that such rocks will have elevated $^{187}\text{Os}/^{188}\text{Os}$ ratios at the time of mineralization, given up to 300 Myr of growth in radiogenic ^{187}Os after deposition of the black shale precursors. The initial $^{187}\text{Os}/^{188}\text{Os}$ of 0.90 ± 0.01 points to interaction of the fluids with crustal lithologies, such as the metabasic and metamorphosed carbonaceous rocks as a source of Os, and possible leaching of the elements in the Ni–Co mineralizations from these rocks. The metabasic rocks contain on average 152 ppm Ni and 46 ppm Co (Ivan and Méres 2015). The metamorphosed carbonaceous rocks have much lesser Ni (5 ppm) and Co (0.8 ppm) contents. Hence, the assumed source of Ni and Co are the metabasic rocks.

Table 1 Re–Os isotopic data and model age for gersdorffite from sample KO-4 (Lubietová-Kolba) using a mixed double-Os $^{185}\text{Re} + ^{188}\text{Os} + ^{190}\text{Os}$ spike

Sample	Weight	Re	$\pm 2\sigma$	^{187}Re	$\pm 2\sigma$	^{187}Os	$\pm 2\sigma$	Total common Os ^a	Model age	$\pm 2\sigma^b$
	mg	ppb		ppb		ppb		pg	Ma	
KO-4	112	264.0	0.7	165.9	0.4	0.6597	0.0010	4.6	238.2	1.0

^aTotal common Os includes analytical blank of 0.059 pg Os

^bAge uncertainty includes uncertainty in ^{187}Re decay constant

mg milligrams, ppb parts per billion, Ma millions of years before present, pg picograms

Table 2 Re–Os isotopic data for skutterudite-paramamelsbergite samples (Čierna Lehota) using a conventional $^{185}\text{Re} + ^{190}\text{Os}$ spike

Sample	Weight mg	Re ppb	$\pm 2\sigma$	Total Os ppt	$\pm 2\sigma$	$^{187}\text{Re}/^{188}\text{Os}$	$\pm 2SE$	$^{187}\text{Os}/^{188}\text{Os}$	$\pm 2SE$	% Re blank	% ^{187}Os blank	% ^{188}Os blank	rho
CL-1	95	2.251	0.012	322.9	0.5	37.62	0.25	1.0478	0.0048	0.47	0.10	0.36	0.495
CL-1 rpt ^a	107	2.822	0.012	364.6	0.4	41.87	0.22	1.0675	0.0034	0.33	0.08	0.28	0.515
CL-2	104	1.936	0.011	324.6	0.5	32.12	0.21	1.0261	0.0039	0.49	0.09	0.32	0.449
CL-8	110	1.622	0.010	387.0	0.4	22.47	0.15	0.9897	0.0032	0.56	0.08	0.26	0.337

^aReplicate analysis of the mineral separatemg milligrams, ppb parts per billion, ppt parts per trillion, pg picograms, SE standard error, rho error correlation factor

Link of the investigated mineralizations to the tectonic evolution of Western Carpathians

During the Triassic, the Tatric and Veporic superunits of the Western Carpathians experienced a period of relative tectonic and magmatic quiescence between the main Variscan phase of igneous and tectonometamorphic activity (Late Devonian–Mississippian; Petřík et al. 2020; Kohút and Larionov 2021) and the main Alpine phase of thrusting and metamorphism (Cretaceous; Plašienka 2018). An extensional setting in Middle-Late Triassic (Plašienka 2018) related to the incipient stage of the opening of the Meliata ocean is documented in the magmatic (Putiš et al. 2019) and sedimentary record in the study area (Gawlick and Missoni 2015; Plašienka et al. 2019). Such an extensional regime could have opened pathways for fluid circulation and perhaps also fueled short-lasting and small, localized heat pulses of igneous activity. Metals were extracted by the circulating fluids locally, from crustal sources (see discussion above), as indicated by the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio for the samples from Čierna Lehota. Triassic model Pb–Pb ages from several small barite-galena occurrences in the Western Carpathians (Chernyshev et al. 1984) suggest that the conditions of extensional tectonics related to the opening of the Meliata ocean may have created a number of small hydrothermal deposits, not only those investigated in this work. Therefore, additional work combining geology applied to mineral deposits and high-precision Re–Os geochronology of sulfides and sulfarsenides is warranted to decipher further the long-lived history of hydrothermal events in the Western Carpathians.

Fig. 4 Re–Os isochron diagram for skutterudite-paramamelsbergite analyses from Čierna Lehota using IsoplotR (Vermeesch 2018). Age uncertainty includes uncertainty in the ^{187}Re decay constant (Smoliar et al. 1996)

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Data availability The supporting electronic information contains: Electron-microprobe analyses of carbonates, arsenides/sulfarsenides from Ľubietová-Kolba and Čierna Lehota (XLSX).

Declarations

Conflict of interest The authors declare no competing interests.

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