Small occurrences of Middle Triassic ore mineralizations in the Western Carpathians

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Abstract: Two small occurrences Ľubietová-Kolba (Veporic Superunit) and Čierna Lehota (Tatric Superunit) are characterized by an earlier assemblage of Ni-Co-Fe arsenides and a later assemblage of chalcopyrite, tennantite, and Bi sulfosalts. The earlier assemblage was previously dated (Re-Os) to Ladinian (Middle Triassic, 238 Ma) and linked to the opening of the Meliata Ocean. Ore textures at Kolba are interpreted in this work as diffusion, not replacement textures. Quantitative diffusion modeling shows that the observed profiles could be produced at ≈ 350 °C over ≈ 6 million years, compatible with the Alpine metamorphic conditions determined for the host rocks. The results thus support the radiometric dating. The stable isotopic composition of sulfur ($\delta^{34}S$) in the Ni-Co minerals is + 12 to + 17 ‰ at Kolba and 0 to – 1 ‰ at Čierna Lehota. The most likely sulfur source is the Permian and Triassic sedimentary cover of the Tatric and Veporic superunits. At Čierna Lehota, there is a distinct contribution of the syngenetic pyrite-pyrrhotite ores to the sulfur budget. There is a cluster of previously published model Pb-Pb Middle Triassic ages for the small ore occurrences Nižné Matejkovo, Čavoj, Častá, and perhaps also Trangoška. They could represent small hydrothermal cells with fluids that leached the local host rocks during a Middle Triassic thermal event. The ore veins have small extent and their content corresponds well to the chemical and mineralogical composition of the leached local rocks.

Key words: ore mineralizations, Western Carpathians, Ľubietová-Kolba, Čierna Lehota, diffusion modeling, sulfur isotopes, Triassic hydrothermal events

1. INTRODUCTION

Hydrothermal mineralizations in the Western Carpathians span a wide range of ages from Variscan to late Alpine (e.g., in the Tatric Superunit; Majzlan et al., 2020), in parallel with the tectonothermal evolution of the Variscan and Alpine orogens (Petrík, 2000; Kohút, 2004; Janák et al., 2001; Kováč et al., 2017; Plašienka, 2018). The voluminous Variscan magmatic activity could have created substantial ore deposits, especially in the apical portions of the intrusions. Even if they indeed existed, they were eroded during the rapid uplift and exhumation at the end of the Variscan orogeny (Kohút, 2002). Such apical bodies with greisen mineralizations were preserved only rarely, for example in Permian granites of the Gemeric Superunit (Kohút & Stein, 2005). The Sb-Au mineralizations in the Tatric Superunit of the Western Carpathians appear to be linked to Variscan metamorphic or magmatic activity (Chovan et al., 2006; Majzlan et al., 2020). Alpine granitoid rocks, either of Cretaceous (Kohút et al., 2013) or Neogene (Lexa et al., 1999) age, generated also substantial ore grades. The Alpine metamorphism was prominent in the Veporic Superunit, to a lesser extent in the Gemeric Superunit, and minor in the Tatric Superunit (see the summary in Plašienka, 2018). A link between Alpine metamorphic events and ore mineralizations was documented by Hurai et al. (2002), Urban et al. (2006), or Kiefer et al. (2020), among others.

This work is a continuation of our recent attempt (Majzlan et al., 2022) to identify and describe Middle Triassic (238 ±13 Ma, Ladinian) ore mineralizations in the Central Western Carpathians. Here we present the detailed results from the Ni-Co mineralizations at two small historical deposits Ľubietová-Kolba (Veporic Superunit) and Čierna Lehota (Tatric Superunit) in the Western Carpathians (Fig. 1). These data are augmented by sulfur isotopic composition of selected minerals, either determined in this study or available in the literature, and previously published model Pb-Pb ages. We discuss the driving force behind the hydrothermal activity in Middle Triassic, the time of relative tectonic quiescence in the Western Carpathians. Diffusion modeling was used to examine the relationship of certain ore textures to the Alpine metamorphic overprint and the compatibility of the data extracted from ores with those from earlier petrological and geochronological work on the country rocks.

2. MATERIALS

Forty-six samples for this study were collected at the dumps of the two small occurrences Ľubietová-Kolba and Čierna Lehota as the old adits and galleries are no longer accessible. Many of these samples were used for previous work on their mineralogy and their age (Mikuš et al., 2013; Pršek & Mikuš, 2006; Majzlan et al., 2022).

3. METHODS

Samples were prepared in the form of standard polished sections and examined in reflected polarized light. Selected sections were carbon-coated and analyzed further by an electron microprobe. The chemical composition of ore minerals was determined by using a wavelength-dispersive spectrometry (WDS) with an electron microprobe (EPM) JEOL JXA 8530FE (at Earth Sciences Institute of Slovak Academy of Sciences in Banská Bystrica) with the following conditions: accelerating voltage 20 kV, probe current 15 nA, beam diameter 2 – 3 μm, ZAF correction, counting time 20 s on peak, 10 s on background. For

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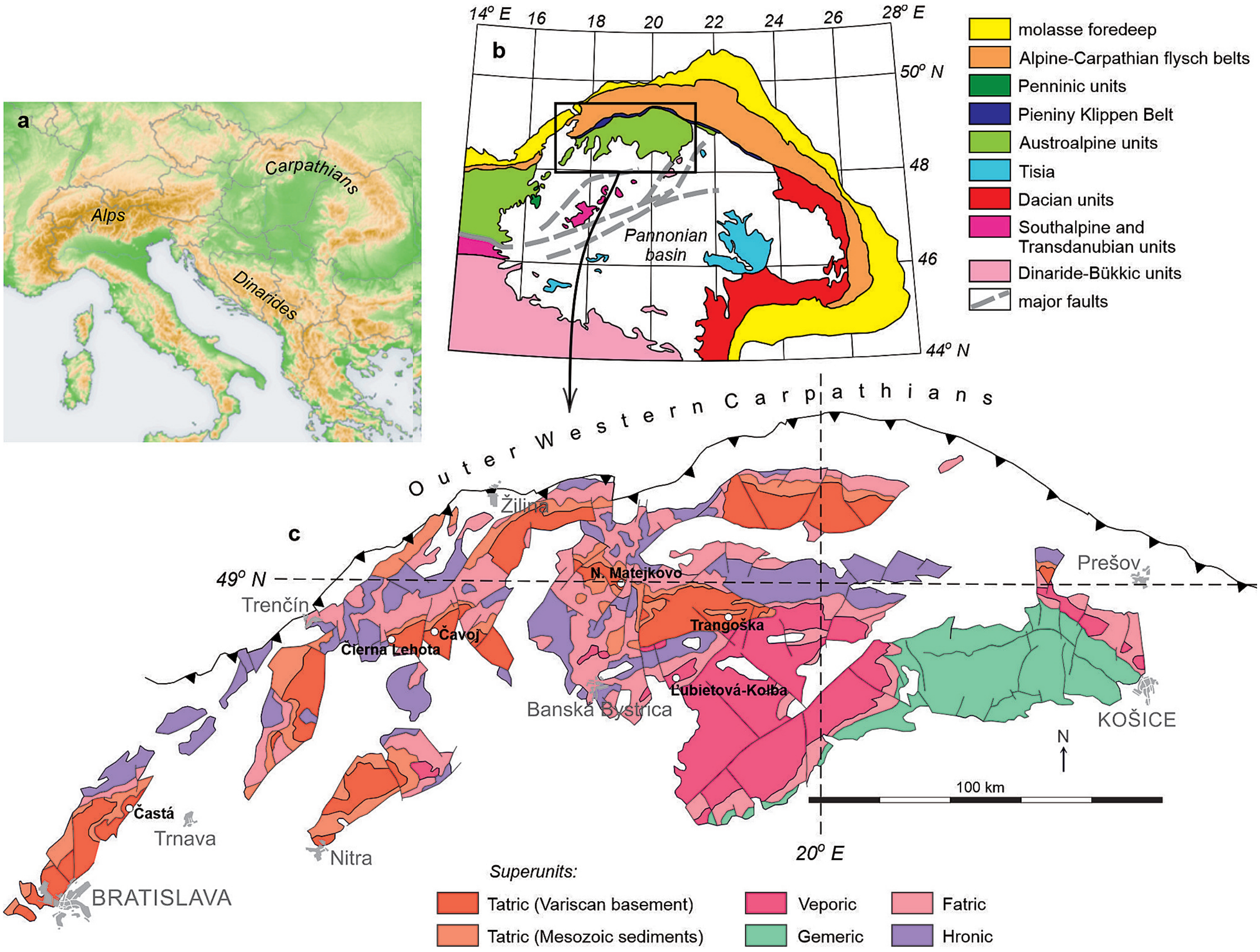

Fig. 1. a) Topographic map of central and southern Europe, showing the position of the Alps, Carpathians, and Dinarides (published under Creative Commons Attribution-Share Alike 3.0 Unported, from Wikimedia Commons); b) Geological map of the Carpathian arc and the adjacent areas (from Plašienka 2018). The black rectangle marks the area shown in c); c) A geological sketch of the superunits of the Central Western Carpathians (simplified after Lexa et al., 2000) and parts of their pre-Paleogene sedimentary cover, with the position of larger cities in Slovakia. The position of the localities discussed in this work are shown by white circles.

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.

Stable sulfur isotopes were measured on isotope ratio mass spectrometer (IRMS) MAT 253 coupled to an elemental analyzer Flash2000HT Plus via a continuous-flow interface ConFlo IV (all Thermo Scientific) (at Earth Sciences Institute of Slovak Academy of Sciences in Banská Bystrica). Separated samples of chalcopyrite and gersdorffite (150 – 400 μg) and S-poor skutterudite and pararammelsbergite (4500 – 4800 μg) were powdered, mixed with about same amount of V_2O_5, wrapped into tin capsules and combusted with oxygen in quartz tube filled with WO_3 and electrolytic copper at 1000 °C. Yielded SO_2 gas was purified on a packed GC-column (5Å mol sieve at 90 °C) and introduced into the IRMS. Raw measurements were calibrated using two international reference materials IAEA-S2 and IAEA-S3 with + 22.70 and – 32.30 ‰ CDT, respectively. Precision of measurement is 0.21 ‰; all the values are reported as permil *versus* CDT.

4. GEOLOGICAL SETTING

The small historical Ni-Co-Ag deposit Kolba is located 6.5 km E from the village of Ľubietová (48.748513° N and 19.445786° E, altitude 981 m a.s.l.), in the head of the Peklo valley, on the slopes of Kolba hill. The hydrothermal veins at Kolba were targeted by exploration and briefly exploited until the middle of the 19th century (Koděra et al., 1990). They were opened by a number of bell pits on an area of 600 × 200 meters and the adits Pauli and Arnoldi.

The veins are hosted by the crystalline basement of the Veporic Superunit, namely by biotite-quartz gneisses and amphibolites affected by Alpine retrograde metamorphism. The veins are built by a system of lenses with a maximum thickness of several decimeters, general NE–SW or N–S strike and steep dip to E (Koděra et al., 1990). Láznička (1966) investigated mineralogy of the Ni-Co ores and reported cobaltite. The younger Cu-Bi mineralization was investigated by Pršek and Mikuš (2006) who found chalcopyrite, tennantite, and Bi sulfosalts.

The abandoned mines near the village of Čierna Lehota are located about 2 km SSE from the center of the village (Mikuš et al., 2013; 48.854485° N, 18.354002° E, altitude 678 m a.s.l.). The mineralization is located in a narrow (20 m) zone of metamorphosed carbonaceous shales, graphitic biotite gneisses, and biotite quartzites, hosted by quartz-biotite gneisses. The zone with a SSW–NNE strike was targeted by a number of bell pits still traceable on the surface today.

The metamorphosed carbonaceous rocks belong to the Tatric Superunit, to the Variscan basement of the Suchý Mts. They are supposed to be a member of the uppermost part of an ophiolitic sequence (Ivan & Méres, 2015). They contain syngenetic, metamorphosed pyrite-pyrrhotite mineralization, and epigenetic Ni-Co-Cu-Bi mineralizations. The Ni-Co-As ores are the object of this study and their mineralogy was previously addressed by Mikuš et al. (2013). Pršek et al. (2005) investigated the younger Bi mineralization and identified chalcopyrite, tennantite, hodrušite, and kupčíkite.

5. RESULTS

5.1. Ore mineralization at Kolba

The Ni-Co-As mineralization at Kolba is found in veinlets (up to 10 cm thick) in the metamorphic rocks. The veinlets comprise massive albite and carbonates with disseminations of opaque minerals (Fig. 2a). The oldest mineral is albite, followed by carbonates. The dominant carbonate mineral is dolomite with Fe/(Fe + Mg) molar ratio of 0.19. Less common are Mg-Fe carbonates with Fe/(Fe + Mg) molar ratio of 0.39. The Ni-Co-Fe sulfarsenides are located mostly at the outer rims of the veinlets and form euhedral and subhedral crystals up to 100 μm large. The sulfarsenides are brecciated and the fractures are filled by a younger assemblage with chalcopyrite, tetrahedrite, rare sphalerite, and Bi sulfosalts (Pršek & Mikuš, 2006).

The predominant mineral among the Ni-Co-Fe sulfarsenides is gersdorffite, nominally NiAsS. At Kolba, the composition of this mineral is highly variable (Table 1, Fig. 3), with diffuse, oscillatory, and sector zonality (Figs. 4a, 5). The elemental variations are large for all major elements: Ni ranges between 11.82 – 30.20 wt. % (0.34 – 0.90 atoms per formula unit, apfu), Co 0.83 – 14.01 wt. % (0.02 – 0.40 apfu), Fe 2.39 – 15.00 wt. % (0.07 – 0.50 apfu), As 44.11 – 56.97 wt. % (1.00 – 1.40 apfu), and S 10.25 – 19.12 wt. % (0.59 – 1.00 apfu).

Diarsenides (Table 1) are less abundant than the sulfarsenides. Their composition and their isotropy in reflected polarized light suggest that this mineral belongs to krutovite (nominally $NiAs_2$). They form irregular aggregates and grains, up to 20 μm large, in gersdorffite (Fig. 5). The transition between krutovite and

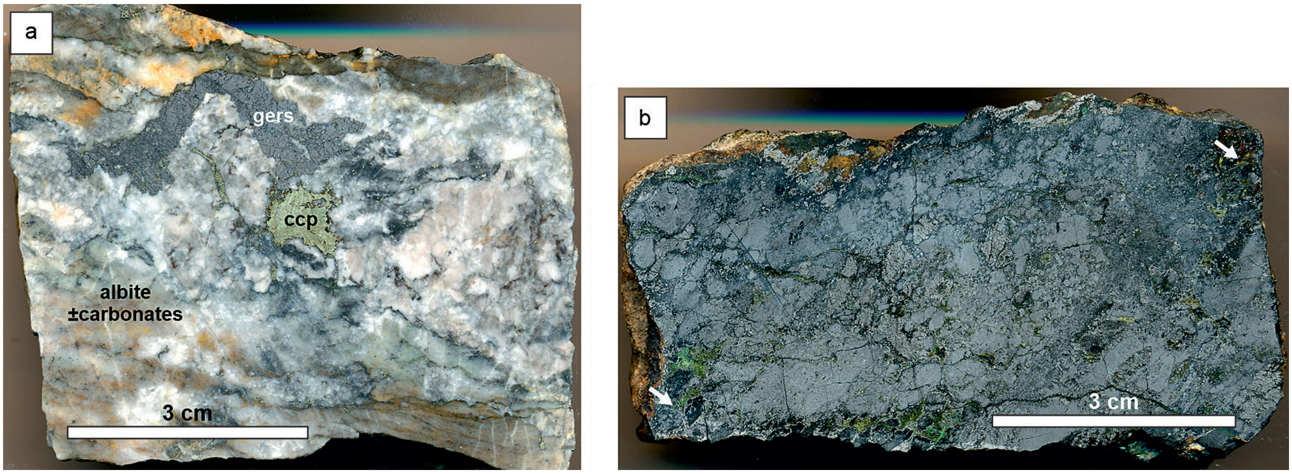

Fig. 2. Typical textures for the ore mineralizations from a) Kolba and b) Čierna Lehota. The sample from Kolba shows albite-carbonate vein with aggregates of gersdorffite (gers) and later chalcopyrite (ccp). The sample from Čierna Lehota is a hand specimen of massive Ni-Co arsenides with small parts made of the metamorphosed black shales (marked by the white arrows).

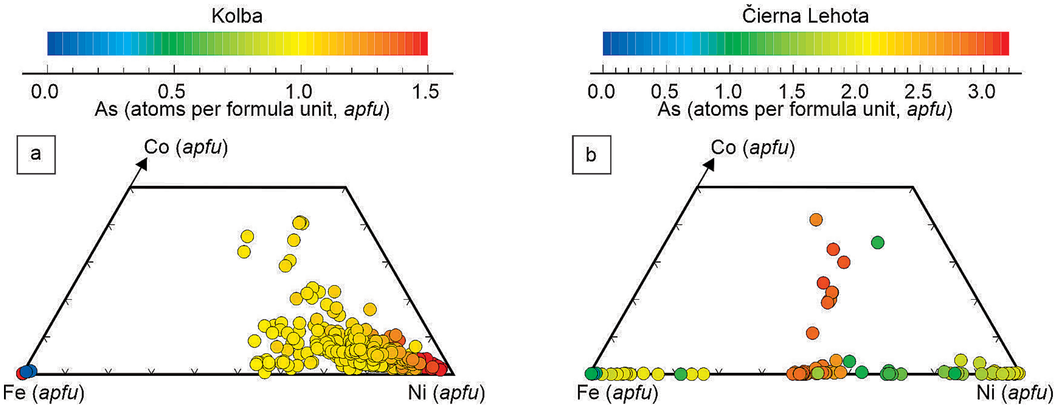

Fig. 3. Chemical composition of the arsenides and sulfarsenides from a) Kolba and b) Čierna Lehota. Colors of the symbols correspond to the number of As atoms per formula unit. All data from spot EMP analyses.

Table 1. Representative EMP analyses of sulfarsenides and diarsenides from Kolba. apfu = atoms per formula unit.

	diarsenides sulfarsenides											
Fe	0.82	0.56	1.63	1.22	0.71	14.05	2.50	15.00	4.87	1.68	12.24	7.22
As	61.59	65.44	62.39	60.92	62.25	44.88	52.01	44.76	46.72	45.81	45.14	46.55
Ni	29.45	29.06	28.32	28.52	29.54	20.05	30.20	19.12	15.50	30.63	18.54	16.77
Co	0.50	0.49	0.57	1.30	0.37	0.98	0.51	0.96	14.01	2.62	3.94	10.92
S	8.39	5.43	6.65	7.91	6.87	19.66	14.31	19.42	17.73	18.63	19.11	18.26
total	**100.75**	**100.99**	**99.59**	**99.88**	**99.77**	**99.64**	**99.59**	**99.27**	**98.85**	**99.37**	**99.61**	**100.22**
apfu	3	3	3	3	3	3	3	3	3	3	3	3
Fe	0.03	0.02	0.06	0.04	0.02	0.41	0.08	0.44	0.15	0.05	0.36	0.23
As	1.53	1.68	1.60	1.53	1.59	0.99	1.22	0.99	1.06	1.03	1.00	1.04
Ni	0.94	0.95	0.93	0.92	0.96	0.56	0.90	0.54	0.45	0.88	0.52	0.48
Co	0.02	0.02	0.02	0.04	0.01	0.03	0.02	0.03	0.40	0.07	0.11	0.31
S	0.49	0.33	0.40	0.47	0.41	1.01	0.78	1.00	0.94	0.97	0.99	0.95

gersdorffite is diffuse (Fig. 4a) and krutovite appears as relics in the gersdorffite aggregates. The Fe and Co concentrations are minor, max. 2.24 wt. % (0.08 apfu) and 1.28 wt. % (0.04 apfu), respectively. There is more variability on the anionic position, with maximal S concentration of 9.55 wt. %, the average S content of 7.71 wt. %.

5.2. Ore mineralization at Čierna Lehota

The epigenetic, strata-bound Ni-As-Bi mineralization at Čierna Lehota is embedded in the metamorphosed carbonaceous shales (Fig. 2b). As mentioned above, these rocks host also syngenetic ores dominated by massive aggregates and impregnations of pyrrhotite and pyrite. The Ni-Co-As ores have spherulitic, concentric, or colloform textures (Figs. 4b, 6) that are in striking contrast to the textures commonly seen in hydrothermal arsenides, for example those at Kolba.

The most abundant minerals are the early skutterudite [(Co,Ni,Fe)As_3] and pararammelsbergite ($NiAs_2$) (cf. also Mikuš et al., 2013). The earliest skutterudite contains up to 8.9 wt. % Co and little S (no more than 1.1 wt. %) (Figs. 3b, 6, Table 2). The early pararammelsbergite is chemically near the composition $NiAs_2$, with very little Fe, S and no Co.

The abundant and early skutterudite and pararammelsbergite are overgrown by later skutterudite that is essentially devoid of Co (Fig. 6). All three of them show the spherulitic or concentric textures and form porous aggregates. They are associated with löllingite with elevated Ni content (up to 7.7 wt. % Ni).

A later assemblage consists of much less abundant, small euhedral crystals of parammelsbergite (with S concentration up to 12 wt. %), skutterudite, löllingite, arsenopyrite, and gersdorffite. Elevated S content in the minerals is typical for the latest phases among the Ni-Co-As mineralization. There is no evidence of intermineralization tectonics between the assemblages or a clear cross-cutting relationship. Therefore, we assume that the Ni-Co-As mineralization formed in a single hydrothermal pulse, with evolution of the fluid chemistry from Co-richer and S-poor at the beginning, to Ni-As minerals and towards S-richer assemblage in the very end of the mineralization event.

The Ni-Co-As minerals are crushed, healed and replaced by

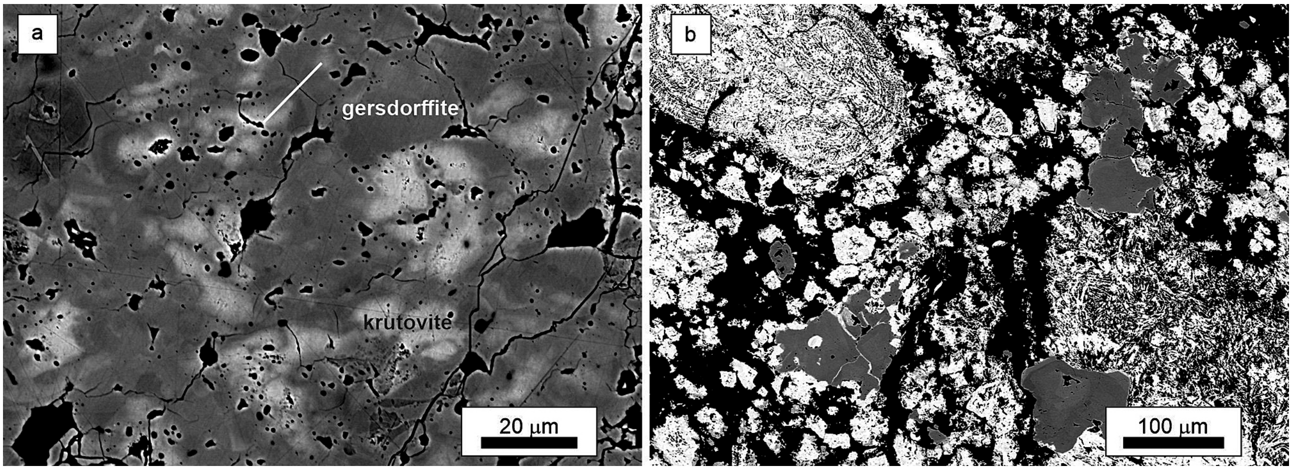

Fig. 4. Back-scattered electron (BSE) images of arsenides and sulfoarsenides. a) Massive gersdorffite with relics of krutovite. Note the smooth, diffuse transitions between the two minerals. Kolba, sample K-2. The short white line is the profile whose results are quantitatively shown in Fig. 8. Electron microprobe analyses were acquired with a regular step of 2 µm along this profile. The analyses are listed in the electronic supplementary Table S1. b) Spherulitic aggregates of skutterudite and acicular pararammelsbergite with younger arsenopyrite and löllingite crystals. Čierna Lehota.

Table 2. Representative EMP analyses of sulfarsenides and arsenides from Čierna Lehota. The analyses are recalculated and normalized to the number of atoms specified in the lowermost row of the table.

	triarsenides				diarsenides			sulfoarsenides	
Fe	5.45	9.35	10.08	6.62	20.33	25.48	0.49	9.93	12.63
As	75.38	78.93	79.17	79.00	72.21	72.59	71.50	49.97	48.66
Ni	6.82	11.55	10.48	9.66	7.68	2.20	28.15	23.88	20.47
Co	8.87	0.10	0.16	4.67	0.01	0.01	0.08	0.33	1.20
S	3.29	0.13	0.10	0.08	0.57	0.58	0.72	15.75	16.24
Total	99.86	100.06	100.00	100.04	100.79	100.87	100.93	99.86	99.20
Fe	0.27	0.47	0.51	0.33	0.74	0.92	0.02	0.31	0.39
As	2.73	2.96	2.97	2.97	1.96	1.96	1.95	1.14	1.11
Ni	0.32	0.55	0.50	0.46	0.27	0.08	0.98	0.70	0.60
Co	0.41	0.00	0.01	0.22	0.00	0.00	0.00	0.01	0.03
S	0.28	0.01	0.01	0.01	0.04	0.04	0.05	0.84	0.87
Total	**4**	**4**	**4**	**4**	**3**	**3**	**3**	**3**	**3**

Table 3. Results of the sulfur isotope analyses of the ores from Kolba (samples K, KL, KO) and ČiernaLehota (CL). All values in ‰ relative to CDT.

Sample	mineral	$\delta^{34}S$	Sample	mineral	$\delta^{34}S$
K-2	gersdorffite	+12.73	CL-1	skutterudite, parammelsbergite	–0.36
KL-24	gersdorffite	+14.88	CL-1	skutterudite, parammelsbergite	–0.74
KO1	gersdorffite	+16.38			
KO2	gersdorffite	+16.94			
KL-43	chalcopyrite	+12.96			

native bismuth, tennantite, and a variety of bismuth sulfosalts (Pršek et al., 2005). The Bi mineralization is distinctly younger than the Ni-Co-As mineralization.

5.3. Sulfur isotopes

Isotopic composition of sulfur is different between the two studied occurrences (Table 3). At Kolba, the $\delta^{34}S$ values correspond to isotopically heavy sulfur, with a range between + 12 to + 17 ‰ ($n = 5$). All values were determined for the abundant gersdorffite. An isotopic analysis of chalcopyrite that is distinctly younger than the gersdorffite gave a value near + 13 ‰.

At Čierna Lehota, the values determined for the early, most abundant skutterudite and pararammelsbergite, lie between 0 and – 1 ‰ ($n = 2$). Because these minerals contain little sulfur, larger amounts had to be separated and digested for the isotopic analysis. Care was taken, as much as possible, not to include the late but sparse gersdorffite in these samples.

6. DISCUSSION

During Triassic, the external (Tatric and Veporic) superunits of the Western Carpathians experienced time of relative tectonic quiescence. This period lied between the main Variscan phase of igneous and tectonometamorphic activity (Late Devonian-Mississippian; Petrík et al., 2020; Kohút & Larionov, 2021) and the main Alpine thrusting and metamorphism (Cretaceous; Plašienka 2018). Large portions of the voluminous Variscan granitic rocks of I- and S-type (Petrík et al., 1994; Broska & Svojtka, 2020; Kohút & Larionov,2021) were already exhumed and covered by Permian and Lower Triassic continental clastic rocks. Some of these rocks were deposited directly onto the granitic rocks. Thermal modeling of some of the Tatric metamorphic complexes showed that they cooled to 200 °C at the latest at 290 Ma (Moussallam et al., 2012).

Permian or even Triassic igneous rocks in the Western Carpathians are less voluminous than their Carboniferous counterparts but are well documented. Triassic volcanic activity can be discerned from volcanogenic detritus in Triassic sediments of the Lunz Formation (Kohút et al. 2008) in the Tatric, Fatric, and Hronic superunits. Such igneous rocks are more abundant in the internal superunits of the Western Carpathians – especially Gemeric, also Silicic Superunit (Uher & Broska, 1996; Uher et al., 2002; Kohút & Stein, 2005; Radvanec et al., 2009; Broska & Kubiš, 2018; Ondrejka et al., 2018, 2022). Some of these rocks are known only as pebbles in Cretaceous-Miocene conglomerates (Uher & Broska, 1996). More abundant equivalents of the Permian granitoids can be found in the Austroalpine basement of the Eastern Alps (Yuan et al., 2020), with their origin linked to the opening of the Meliata ocean.

The Veporic and Tatric superunits, considered in this work, also contain late Variscan igneous rocks, although not in the abundance comparable to the internal superunits. As already mentioned above, Triassic igneous activity is traceable in Carnian sedimentary rocks (Kohút et al. 2008). The Veporic Superunit hosts the Hrončok A-type Permian granite (Uher & Broska, 1996) and Permian granite porphyries (Bezák et al., 2008; Vozárová et al., 2010) found as pebbles in Upper Permian sediments (Vozárová, 1979). Smaller bodies of plutonic and volcanic rocks of Permian age in the Tatric Superunit have been described by Putiš et al. (2016) and Spišiak et al. (2018). A small body of Ľubochňa leucogranite (Tatric Superunit) was dated to 231 ±17 Ma (Poller et al., 2005), even though the authors discuss recent Pb loss as a possible reason for such a young age.

6.1. Diffusion modeling of the textures of gersdorffite-krutovite at Kolba

The rocks of the Veporic Superunit, including those at the locality Kolba, underwent Cretaceous Alpine greenschist-facies metamorphism (Jeřábek et al., 2008). Thus, one may ask if the ore textures at Kolba (Fig. 4a) conform to the metamorphic overprint. With certain limitations, the textures in the ore minerals can be roughly modeled and understood. Such textures could be seen as the result of replacement of the earlier krutovite by later gersdorffite. In our opinion, the transition between these two minerals is too smooth for a replacement texture. In such textures, the replacement front can be identified in back-scattered electron images (Kiefer et al., 2017) and replacement itself can be tracked by the ubiquitous porosity. Therefore, we will model these textures as the result of solid-state diffusion.

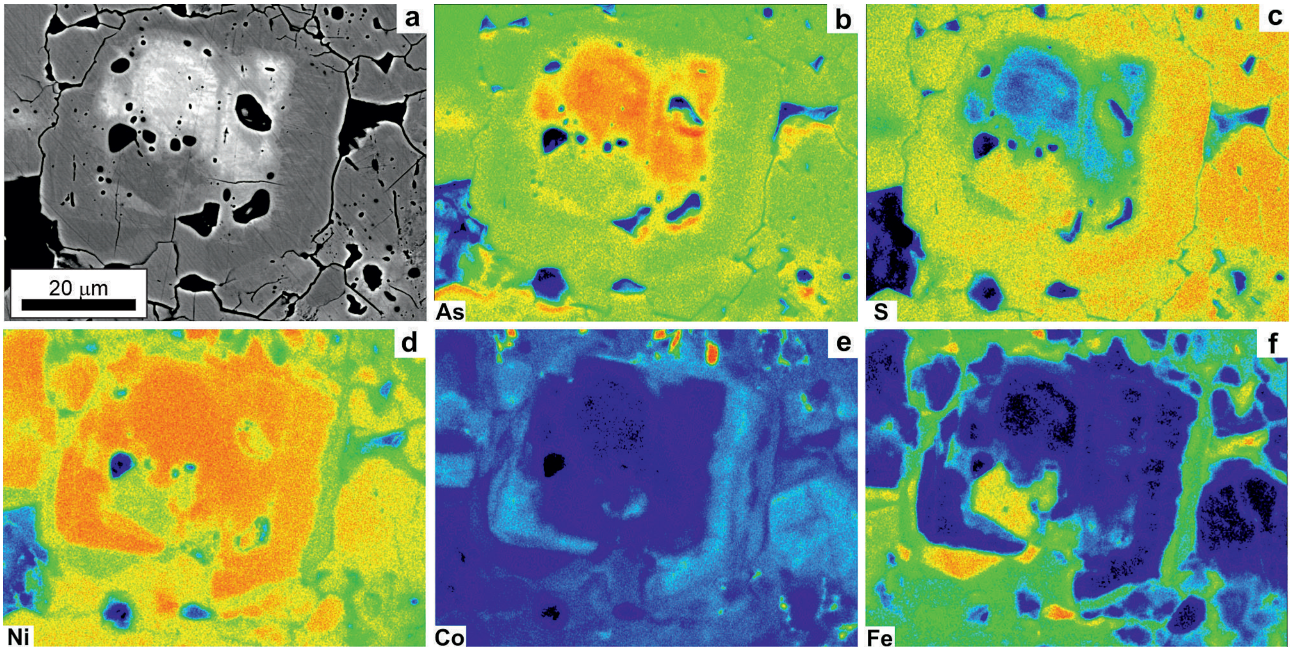

Fig. 5. BSE image and element distribution maps of a krutovite relic embedded in gersdorffite from Kolba, sample KL-15.

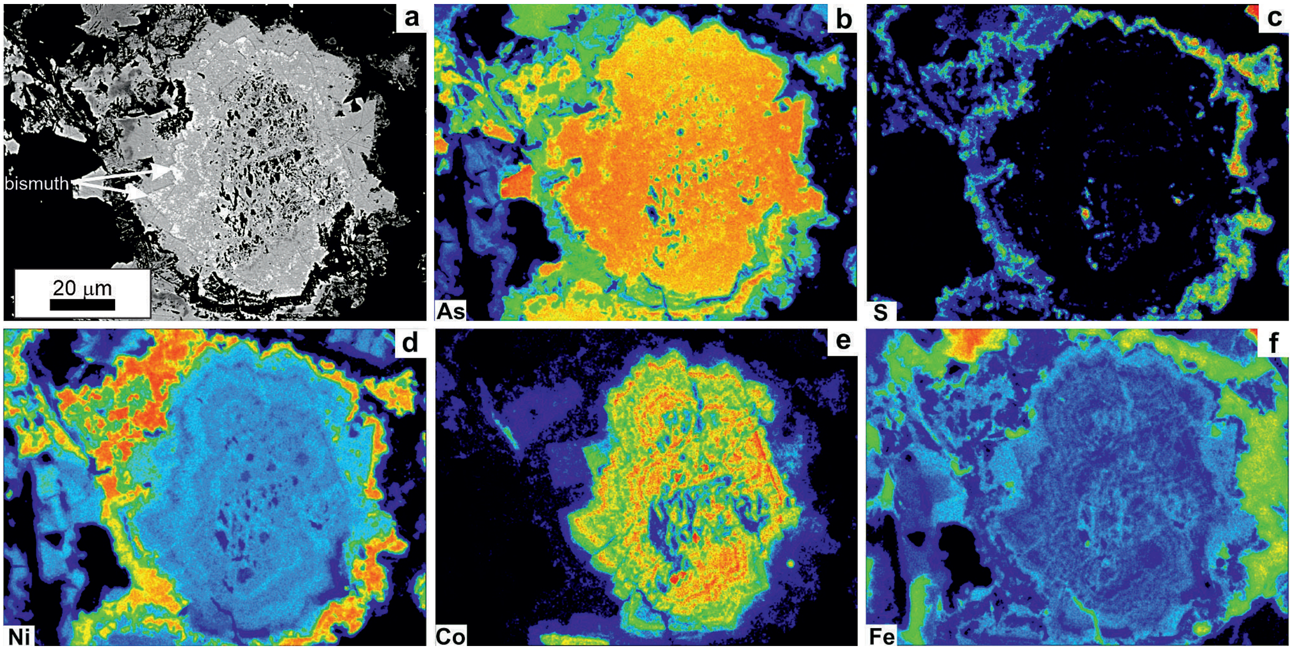

Fig. 6. BSE image and element distribution maps of a skutterudite aggregate (gray) with bismuth inclusions (white, indicated by white arrows) from Čierna Lehota, sample CL-1.

The diffusion took place between the small earlier krutovite crystals and the later gersdorffite mass that replaces them (Fig. 5) after the deposition of gersdorffite. The concentration profiles are smooth, with no abrupt changes (Fig. 7). The steady-state flux condition is not fulfilled in this case because the krutovite crystals are small and their composition is continuously changing. In such a case, the second Fick's law must be used:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

The solution to this equation for an inclusion confined between *h* and –*h* is (modified equation 2.15 from Crank, 1975):

$$C(x,t) = C_s + \frac{1}{2}(C_0 - C_s)\left[\operatorname{erf}\left(\frac{x+h}{2\sqrt{DT}}\right) - \operatorname{erf}\left(\frac{x-h}{2\sqrt{DT}}\right)\right]$$

where $C(x,t)$ is the concentration at the position x and time t, C_0 is the initial concentration between h and $-h$ and C_s is the initial concentration outside of this interval. D is the diffusion coefficient, with temperature dependence defined as:

$$D = D_0\exp\left(-\frac{Q}{RT}\right)$$

where R is the universal gas constant and T the thermodynamic temperature. The parameters D_0 and Q are not available for minerals as krutovite, rammelsbergite, or gersdorffite. All these minerals, however, are structurally and to a certain extent chemically related to pyrite. Hence, the measured parameters D_0 and Q for self-diffusion of sulfur in pyrite (Watson et al., 2009; Cherniak, 2010) were taken for the diffusion models presented in Fig. 8. The parameters for the diffusion of As in pyrite-type

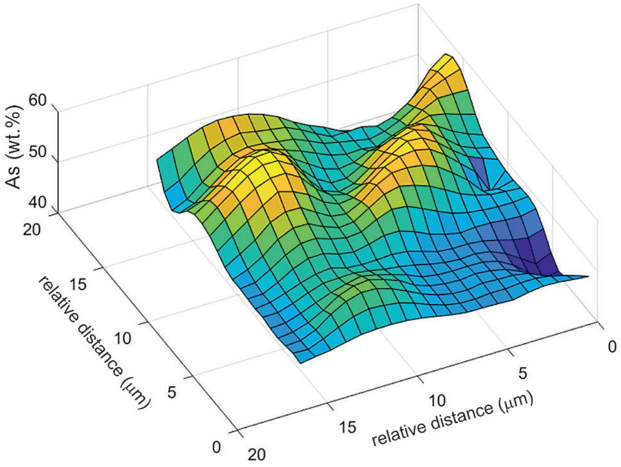

Fig. 7. Distribution of measured As concentrations (WDX analyses) from the deposit Kolba, sample K-2 (BSE image of that sample is in Fig. 4a). Note the smooth, gradual transitions between the As-richer and As-poorer parts of the analyzed area.

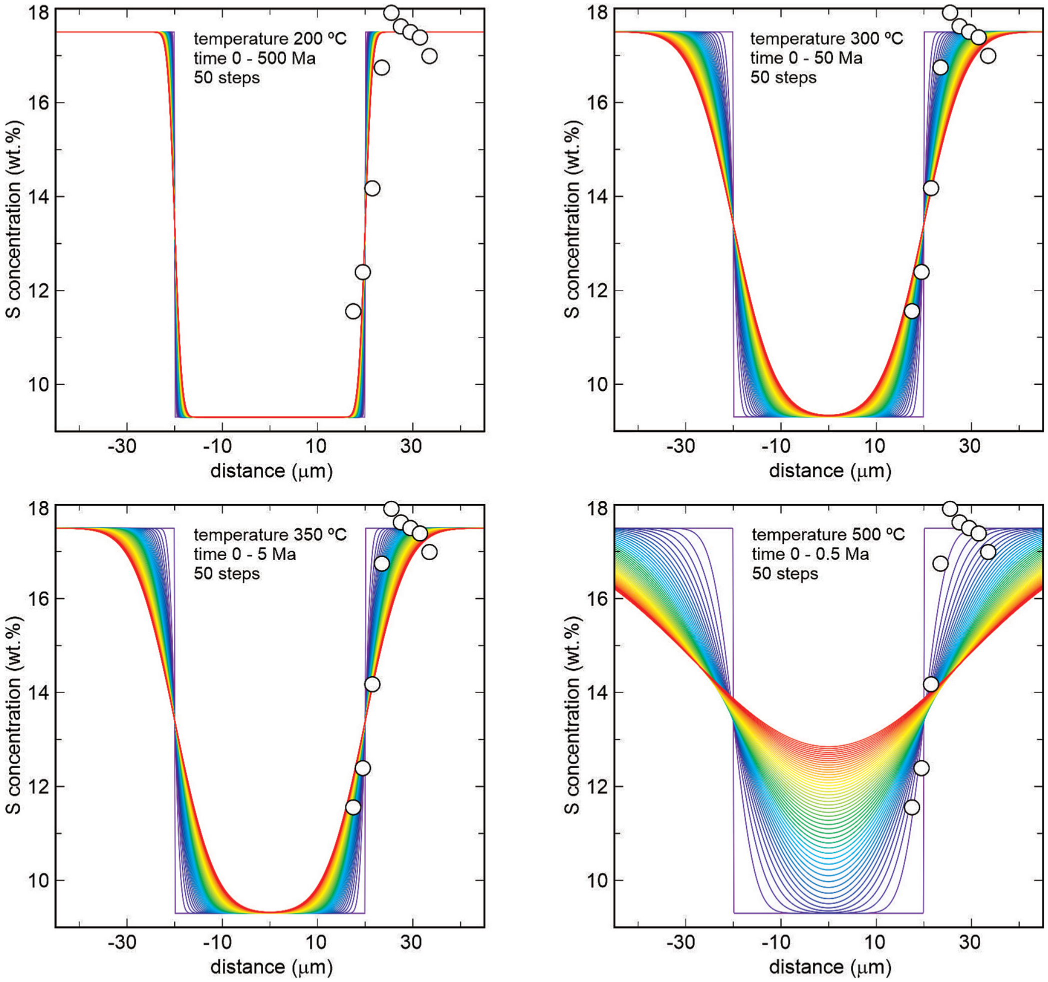

Fig. 8. Diffusion models calculated from the temperature and time specified in each panel. The initial concentration profile is shown by the violet curve and changes progressively with time toward the red curves. Circles show the measured concentration profile in the sample K-2 (see Fig. 4a, S1, and Table S1). For details and assumptions, see text. Note that only the steep portions of the analytical and calculated profiles were compared, without the outermost points that are influenced by the heterogeneity of the sample.

structures are not known. Diffusion of As^- is likely slower than diffusion of S^- because of the size difference between the two ions (cf. Chen & Harvey, 1975) but this effect cannot be included in the models because of the missing diffusion coefficients.

Diffusion modeling between krutovite and gersdorffite does not include the effect of gradients in the chemical potential. The sulfarsenides and diarsenides form an extensive and continuous solid solution, especially in the Ni-rich parts of the system (Kiefer et al., 2017). The existence of this solid solution hints that the mixing is nearly ideal (in thermodynamic sense) or at least not strongly unfavorable for the intermediate compositions. Under such conditions, as a rough approximation, the diffusion models can be constructed without considering chemical potential differences. The models do not start with the nominal compositions ($NiAs_2$ and NiAsS) for the values of C_0 and C_s, but with the chemical composition measured in our samples (Table 1).

The diffusion models are overlain with a typical concentration profile determined in the sample K-2 (Fig. 4a). The model at 200 °C (Fig. 8) shows that the measured profile would be matched after time of more than 500 Ma, a grossly unrealistic duration for a metamorphic event. On the other hand, at 500 °C, the duration of the thermal event would have to be 10,000 years. This time is very short for an ore body metamorphosed together with the country rocks in upper-crustal conditions but not near the surface. There is no evidence whatsoever for a short-lived contact-metamorphic event of Alpine age in the Veporic Superunit.

The quality of the matches between the calculated profiles and the data was evaluated as the sum of the squares of the deviations between the steep portions of the two data sets (i.e., measured and calculated). One of the best matches can be achieved for 300 °C (Fig. 8) and duration of ≈ 6 Ma. There is a range of sets of temperatures and times that perform in a similar way. At 350 °C, the duration time would be ≈ 1 Ma to reproduce the measured data.

These results can be reconciled with the P-T-t data for the northern part of the Veporic Superunit that hosts the Kolba occurrence. Here, the Cretaceous Alpine overprint appears to be weaker than in the central part of the Veporic Superunit (Hók & Hraško, 1990; Putiš, 1991; Madarás et al., 1994; Jeřábek et al., 2012; Plašienka, 2018). The peak temperatures of Alpine metamorphism in the vicinity of Kolba were estimated as 350 °C or slightly lower. The P-T-t path (Plašienka, 2018) shows that the peak temperatures were reached between 80 and 70 Ma. Hence, modeling of the diffusion profile in the minerals at Kolba is in an excellent agreement with the earlier petrological and geochronological data (Jeřábek et al., 2008, 2012), supporting the Ladinian age determined from the Re-Os geochronometer (Majzlan et al., 2022).

We note that the model assumes that the diffusion took place in solid state. Fluid-assisted diffusion would have been presumably faster. No fluid pathways were discerned in the samples with diffusive textures, though.

6.2. Known and supposed ore mineralizations of Triassic age in the Tatric and Veporic superunits

The ore mineralizations in the Tatric and Veporic superunits were mostly considered to be linked to the late phases of the Variscan orogen or the peak and post-peak times of the Alpine orogen (mostly Cretaceous). Such views were proposed and confirmed for the economically important mineralizations in the Nízke Tatry Mts. (e.g., Chovan et al., 2006; Majzlan et al., 2020). In the Veporic Superunit, the regionally present but economically insignificant quartz-tourmaline stage (so-called „Alpine veins“) was dated to Late Cretaceous (Hurai et al., 1991),broadly coinciding with the peak of Alpine metamorphism and with the time of collision of the Veporic and Tatric superunits (Vojtko et al., 2017). The regional Fe-Cu mineralization is texturally clearly younger than the „Alpine-veins“, bound to Alpine structures (Slavkay & Petro, 1993).

So far, there were no clear indications for hydrothermal ore mineralizations of Triassic age in the Western Carpathians. The recently determined Re-Os ages of the Ni-Co minerals from Kolba and Čierna Lehota confirm that these ore mineralizations formed during Ladinian (Majzlan et al., 2022). It is therefore of interest to investigate the previously published data for similarities and hints of mineralizations of such age.

Isotopic analyses of lead (Kantor et al., 1967; Chernyshev et al., 1984; Poller & Kohút in Kohút, 2002; Andrášet al., 2010) (Fig. 9) gave model ages which agree roughly with the geological and tectonic position of the deposits studied by these authors. The ratios of lead isotopes differentiated the pre-Variscan deposits in low-grade Variscan metamorphic rocks (e.g., massive volcanogenic sulfides, Smolník), late Variscan deposits, and deposits confined to Neogene volcanic rocks. The latest Pb-Pb data collection (Andráš et al., 2010) was focused on a few specific deposits instead of the earlier regional screening. It showed that one deposit may yield a set of significantly different ages which is in a good agreement with the later radiometric dating of these deposits (Majzlan et al., 2020), with multiple stages that differ in their ages by more than 300 Ma.

There is a distinct cluster of Triassic model Pb-Pb ages of ore occurrences (Table 4), even though with a μ parameter near 10.0 (Fig. 9), higher than μ = 9.74 proposed originally by Stacey and Kramers (1975). They include small accumulations of ores at Nižné Matejkovo (Veľká Fatra Mts), Čavoj (Suchý Mts), Častá (Malé Karpaty Mts) in the Tatric Superunit (Fig. 1, Table 4). The

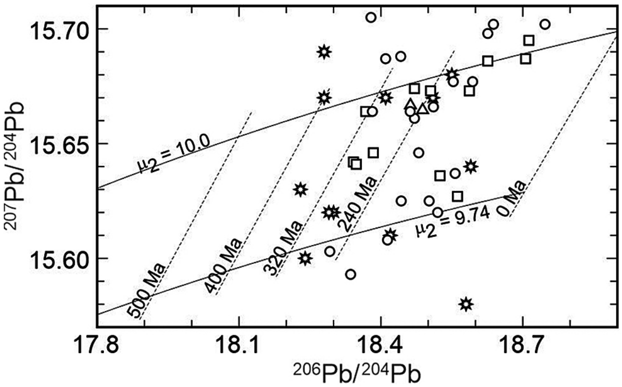

Fig. 9. Evolution diagram of lead isotopic composition, according to the model of Stacey and Kramers (1975). Symbols shown represent lead isotopic analyses from ore deposits in the Tatric and Veporic superunits in the Western Carpathians. Squares: Chernyshev et al. (1984), stars: Kantor et al. (1967), triangles: Kohút (2002), circles: Andráš et al. (2010).

Table 4. Summary and selected data for the Middle Triassic ore occurrences in the Tatric and Veporic superunits in the Western Carpathians.

Deposit (tectonic superunit)	Main hydrothermal minerals; country rocks	Age (Ma)	$\delta^{34}S$ ‰ (mineral)
Ľubietová-Kolba **(Veporic)**	albite, ankerite-dolomite, gersdorffite, younger chalcopyrite; gneisses and amphibolites	239±1 Ma (Re-Os on gersdorffite, Majzlan et al., 2022)	+12 to +17 (gersdorffite)
Čierna Lehota **(Tatric)**	skutterudite, pararammelsbergite; black shales	239±13 (Re-Os on pararammelsbergite, skutterudite, Majzlan et al., 2022)	−1 to 0 (skutterudite, pararammelsbergite)
Čavoj **(Tatric)**	siderite, galena, sphalerite, baryte; gneisses and granodiorites	240–250 (Pb-Pb, Kantor & Rybár, 1964), 240–270 (Pb-Pb, Chernyshev et al., 1984)	+23.7 (baryte) (Kantor & Ďurkovičová, 1977)
Častá **(Tatric)**	albite, ankerite, pyrite, chalcopyrite, galena, gersdorffite; graphitic phyllites	238 (Pb-Pb, Chernyshev et al., 1984)	
Nižné Matejkovo **(Tatric)**	baryte, accessory galena; granites and Lower Triassic sandstones	235 (Pb-Pb, Kohút, 2002)	+17.7 to +19.7 (baryte); −1.6 (sphalerite) (Kantor & Ďurkovičová, 1977)
Trangoška **(Tatric)**	baryte, galena, tetrahedrite; gneisses and Lower Triassic sandstones	320 (Pb-Pb, Chernyshev et al., 1984)	+18.0 to +18.3; +23.5 (all values for baryte) (Kantor & Ďurkovičová, 1977)

occurrence in Čavoj is geographically close to that in Čierna Lehota, the two being only about 11 km apart. The mineralization in Čavoj commenced with the first Ni-Co stage with arsenopyrite, gersdorffite, and a $NiAs_2$ phase (Mikuš et al., 2003). This stage was followed by a later assemblage with quartz, carbonates, and Ag mineralization. The deposit Častá in the Malé Karpaty Mts. also contains Ni-Co ore minerals but they were assigned to the latest stage, together with galena, sphalerite, and chalcopyrite (Cambel, 1952).

The veins at Nižné Matejkovo contain no Ni-Co mineralization, they are made up of massive baryte and accessory amounts of sulfides, especially galena (Turan, 1959). Another small occurrence at Trangoška contains also massive baryte, galena, and tetrahedrite (Turan, 1961; Hak & Losert, 1962). The puzzling and obviously incorrect model Pb-Pb age for Trangoška is Variscan (Chernyshev et al.,1984; Table 4), even though the vein follows the contact between the Variscan crystalline rocks and Lower Triassic sediments.

Hence, there is a group of small ore deposits, especially in the Tatric Superunit, with convergent mineralogy and similar Pb-Pb model ages to the two deposits studied here.

Some of the Pb isotopic ratios reported by Andráš et al. (2010) fall also in the group with the model ages of around 240 Ma (Fig. 9). The samples in that study came from the larger Sb deposits Pezinok and Dúbrava. The latest radiometric dating (Majzlan et al. 2020) showed that the bulk of the mineralization at Dúbrava is either late Variscan (≈ 320 Ma) or Alpine (Cretaceous). It remains to be examined if some of the ores at Dúbrava or Pezinok were formed or remobilized in the Triassic.

6.3. Sulfur isotopes

Isotopic composition of sulfur in the two studied deposits is different (Table 3). Further $\delta^{34}S$ values from hydrothermal bodies that are considered to be of the same age and origin (Table 4) can help in the search after the source of sulfur.

If the assumed Middle Triassic age is accepted and considering the fact that some of the hydrothermal bodies in Table 4 penetrate into Lower Triassic sediments, the mineralization events must have occurred in relatively shallow depths of the crust. The local tectonic or igneous activity generated short-lasting heat input but the isotopic composition is not compatible with a magmatic source.

The $\delta^{34}S$ values of the considered ore mineralizations (Table 4) are rather scattered. Nevertheless, they can be related to the same source and reconciled with the local geology. The most likely sulfur source is the Permian and Triassic sedimentary cover of the Tatric and Veporic superunits. The Permian sedimentary record in the Western Carpathians was eroded, segmented, and largely obliterated during the Alpine orogenic cycle (Vozárová, 1996). Yet, it is known that these rocks comprise mostly siliciclastic sediments, with less abundant volcanic and volcanoclastic rocks, evaporites, and shales (for details, cf. Vozárová, 1996). In general, Permian evaporites have $\delta^{34}S$ values of + 10 to + 13 ‰ (e.g., Peryt et al., 2010) but the sulfur becomes isotopically heavier shortly after the Permian/Triassic boundary, up to 32 ‰ (Bernasconi et al., 2017). Similar values and trends were observed in the Western Carpathians (Vozárová, 1996). Hence, a mixture of Permian evaporites and Triassic connate water would match the isotopic composition of the considered Middle Triassic ore mineralizations.

Such fluids could circulate in the Variscan granites or gneisses, near the contact to the Lower Triassic sediments. There, they extracted Ba and Pb from the feldspars and deposited baryte veins (Nižné Matejkovo, Trangoška, perhaps also Čavoj) with sparse sulfides. Small parts of the sulfur inventory of the fluids was reduced, with much lower $\delta^{34}S$ values (Table 4, Nižné Matejkovo).

Similar fluids, when in contact with metabasic rocks, extracted Ni, Co, Fe, and As from these rocks and deposited arsenides and sulfarsenides (Kolba, ČiernaLehota, Čavoj). The heavy $\delta^{34}S$ values at Kolba require near-complete reduction of sulfur in the fluids. Precipitation of gersdorffite itself is the evidence of significant reduction of the redox-sensitive species in the fluids. Arsenic is most commonly transported by the hydrothermal fluids as (Pokrovski et al., 2002) and the deposition of arsenides and sulfarsenides requires its reduction. The mechanism of reduction at Kolba is not clear; potentially could the Fe^{2+}-bearing rock-forming minerals in the metabasic rocks act as the reducing agents.

At Čierna Lehota, the fluids that invaded the metamorphosed black shales were reduced by their graphitic material. The δ^{34}S values determined for the early abundant skutterudite and parammelsbergite are near 0 ‰. They can be explained as a mixture of sulfur derived from the Permian/Triassic sediments and sulfur leached from the syngenetic pyrite-pyrrhotite mineralization in the metamorphosed carbonaceous shales. Syngenetic, Paleozoic pyrrhotite-pyrite ores occur also elsewhere in the Tatric or Veporic parts of the Western Carpathians. Their isotopic composition (δ^{34}S) was determined at Pezinok as –8 to – 27 ‰ (Kantor, 1974; Cambel et al., 1980), at Heľpa as – 20 ‰ (Kantor et al., 1971), and at Ratkovské Bystré as – 10 to – 16 ‰ (Kantor & Petro, 1976). Metamorphosed carbonaceous shales near Čierna Lehota and their ores were geologically correlated to these occurrences, especially to those near Pezinok (Ivan & Méres, 2015).

The isotopic composition of baryte in the Tatric deposits and occurrences was investigated by Kantor and Ďurkovičová (1977). They noted that the baryte from Nižné Matejkovo and Trangoška is isotopically distinct from the other occurrences, namely below + 20 ‰. These values can be also explained by a contribution of the Permian evaporites (with lighter sulfur) to the fluids, in addition to the Triassic connate waters. Later baryte-siderite-sulfide mineralizations, associated with the Alpine metamorphism, are isotopically much heavier, up to + 35 ‰ (locality Kumštová, Kantor & Ďurkovičová, 1977). Such differences can be detected even within one small locality, such as Trangoška. There, Kantor and Ďurkovičová (1977) reported δ^{34}S of + 18.0 to + 18.3 ‰ for older baryte associated with galena, but + 23.5 ‰ for the younger baryte, associated with siderite and tetrahedrite.

7. CONCLUSIONS

There is a number of small occurrences in the Tatric and Veporic superunits that have or can be assumed to have Middle Triassic age. They include the Ni-Co ores at Ľubietová-Kolba and ČiernaLehota whose age was determined by Re-Os dating (Majzlan et al., 2022). Similar ages (Pb-Pb model ages) were reported for other occurrences in the Western Carpathians, such as Čavoj, Častá, Nižné Matejkovo, or Trangoška. Small hydrothermal cells, pathway for fluid circulation, and small-scale magmatic activity, could have been formed and fueled in the extension regime propagating from the internal units of the Western Carpathians. This extension was the incipient stage of the opening of the Meliata ocean, as documented in the sedimentary record (Gawlick & Missoni, 2015; Plašienka et al., 2019), and a Middle Triassic thermal event, discernible in the volcanogenic detritus in sedimentary rocks (Kohút et al. 2008). Diffuse textures observed in the ores at Kolba can be related to and quantitatively modeled by the Cretaceous Alpine metamorphic overprint. Such textures are missing at Čierna Lehota because the country rocks there belong to the Tatric Superunit which experienced weak or negligible Alpine metamorphism.

Precipitation of the Ni-Co arsenides and sulfarsenides was triggered by reduction of the fluids in the environment of metamorphosed black shales (Čierna Lehota) or metabasic rocks (Kolba). Especially the massive reduction in the black shales led to rapid and strong supersaturation of the fluids, texturally observed as spherulitic, concentric, or colloform aggregates of Ni-Co arsenides. Fluids circulating through Variscan gneisses, granites, and Lower Triassic sandstones were only weakly reduced. They deposited mostly baryte, with minor amounts of sulfides (Nižné Matejkovo, Trangoška).

The fluids and their sulfur content can be related to the Permian and Triassic sedimentary rocks. At Čierna Lehota, an additional source of sulfur, namely the syngenetic pyrite-pyrrhotite mineralization, can be clearly discerned. Metals were leached locally from the country rocks, as witnessed by the initial ^{187}Os-^{188}Os isotopic composition (Majzlan et al., 2022).

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