

Article

Mineralogy and Origin of Vein Wolframite Mineralization from the Pohled Quarry, Havlíčkův Brod Ore District, Czech Republic: Interaction of Magmatic and Basinal Fluids

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Abstract: Mineralogy and formation conditions were studied in a newly found vein wolframite mineralization, cutting migmatitized paragneisses in the exocontact of a small Carboniferous granite body in the Pohled quarry, Moldanubian Zone of the Bohemian Massif, Czech Republic. The early stage of the rich mineral assemblage (36 mineral species) involves wolframite, columbite-group minerals, molybdenite, and scheelite hosted by quartz–muscovite–chlorite gangue, which was followed by base-metal sulfides in a quartz gangue, whereas the last stage included calcite gangue with fluorite and minor sulfides. The mineral assemblage points to the mobility of usually hardly soluble elements, including W, Sn, Zr, Nb, Th, Ti, Sc, Y, and REEs. A fluid inclusion study indicates a significant decrease in homogenization temperatures from 350–370 °C to less than 100 °C during vein formation. Fluids were aqueous, with a low salinity (0–12 wt. % NaCl eq.) and traces of CO₂, N₂, CH₄, H₂, and C₂H₆. The $\delta^{18}\text{O}$ values of the fluids giving rise to quartz and scheelite are positive (min. 4‰–6‰ V-SMOW). The Eh and pH of the fluid also changed during evolution of the vein. Both wolframite and columbite-group minerals are anomalously enriched in Mg. We suggest that the origin of this distinct mineralization was related to the mixing of Mo,W-bearing granite-derived magmatic fluids with external basinal waters derived from contemporaneous freshwater (but episodically evaporated) piedmont basins. The basinal waters infiltrated into the subsurface along fractures formed in the extensional tectonic regime, and their circulation continued even after the ending of the activity of magmatic fluids. The studied wolframite mineralization represents the most complete record of the ‘hydrothermal’ history of a site adjacent to a cooling granite body in the study area. Moreover, there are broad similarities in the mineral assemblages, textures, and chemical compositions of individual minerals from other occurrences of wolframite mineralization around the Central Moldanubian Plutonic Complex, pointing to the genetic similarities of the Variscan wolframite-bearing veins in this area.

Keywords: Havlíčkův Brod Ore District; ore veins; wolframite; scheelite; fluid inclusions; magmatic fluids; basinal fluids; hydrothermal alteration



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1. Introduction

The Bohemian Massif, as the easternmost segment of the European Variscan Belt [1], hosts a number of deposits and occurrences of wolframite mineralization bound to greisens and associated ore veins. The most prominent deposits are situated especially in its northwestern part of the Bohemian Massif in the Krušné Hory/Erzgebirge Mts. and

Slavkovský les Mts., which are formed by crystalline complexes of the Saxothuringian Zone. Here, typical greisens and ore veins with Sn-W mineralization are developed in apical parts of shallow-seated, geochemically specialized late-Variscan Li,F-rich granite bodies, which were important sources of both metals in the past. This area has also become important in present times, because it hosts one of the world's largest (and the largest European) "hard-rock" Li deposits at Cínovec/Zinnwald [2,3], which is recently under intense exploration. The geology, mineralogy, and formation conditions of ore deposits in this area were intensely studied in the past. Origin of these Sn–W–Li deposits is interpreted due to ore element enrichment during the fractional crystallization of geochemically distinct granitic magma followed by the activity of both magma-exsolved and envelope- or surface-infiltrated aqueous fluids [4–9].

In contrast, much less attention was paid to the small occurrences of W mineralization located in other parts of the Bohemian Massif. This is also the case in the Moldanubian Zone of the Bohemian Massif, which hosts several small non-economic occurrences of wolframite mineralization bound to fracture-related greisens and quartz veins around the largest granitic body (Figure 1a). The mineralogy of these occurrences is poorly constrained by modern data, apart from the most recent work on Jihlava occurrence [10], which was focused on the mineralogical and crystal-chemical study of the whole mineral paragenesis and was also supplemented by enough analytical data. In contrast, the earlier papers were either focused only on certain mineral phase(s) (typically wolframite) or based on a very low number of investigated samples and/or collected analytical data, making them questionably conclusive. Direct evidence on the genesis of these mineralizations, based on fluid inclusion and stable isotope studies, is still completely missing in this area.

Nevertheless, even the very limited amount of existing knowledge about the Moldanubian occurrences suggests that they would be interesting from a scientific point of view. First, they often contain Mg-bearing wolframite, which is, in general, a composition that is very rare worldwide, although even the Mg-dominated endmember of the wolframite group, huanzalaite, was described from two sites to date (Ochtiná, Slovakia [11], and Huanzala, Peru [12]). The Moldanubian wolframite contains up to 3–11 mol. % of huanzalaite component [10,13–15] and the reason of such Mg-enrichment is not known here. Second, the scarce available compositional data suggest that micas from these mineralizations belong to low-F low-Li muscovite [10,15], indicating a chemically contrasting genetic environment with respect to typical Saxothuringian greisens, which are usually F- and Li-rich [5,6,8,16]. Third, some Moldanubian occurrences are considered to be overprinted by the regional (Variscan) metamorphism together with their host rocks [17,18], which is, again, a feature usually unrecognized worldwide. However, much future work is necessary to constrain the mineralogical and genetic aspects of these mineralizations adequately.

The aim of this study is to characterize a new occurrence of vein wolframite mineralization, in the Moldanubian Zone of the Bohemian Massif, which was recently discovered in an active quarry at the Pohled village in the Havlíčkův Brod Ore District (Figure 1b). This occurrence yielded few scheelite specimens belonging to the best ones known from the territory of the Czech Republic [19] (Figure 2a). Our mineralogical study addressed the whole mineral association of the vein and is based especially on the electron microprobe study of mineral phases in order to increase the still very limited amount of compositional data on vein W mineralizations in the Moldanubian part of the Bohemian Massif. The compositional data are compared with the available regional data from the Moldanubian W mineralizations as well as from the other vein-type mineralizations in the Havlíčkův Brod Ore District to allow possible parallelization of hydrothermal events. Furthermore, our mineralogical study is supplemented by investigations of fluid inclusions and oxygen isotopes in order to specify the formation conditions of the studied mineralization.

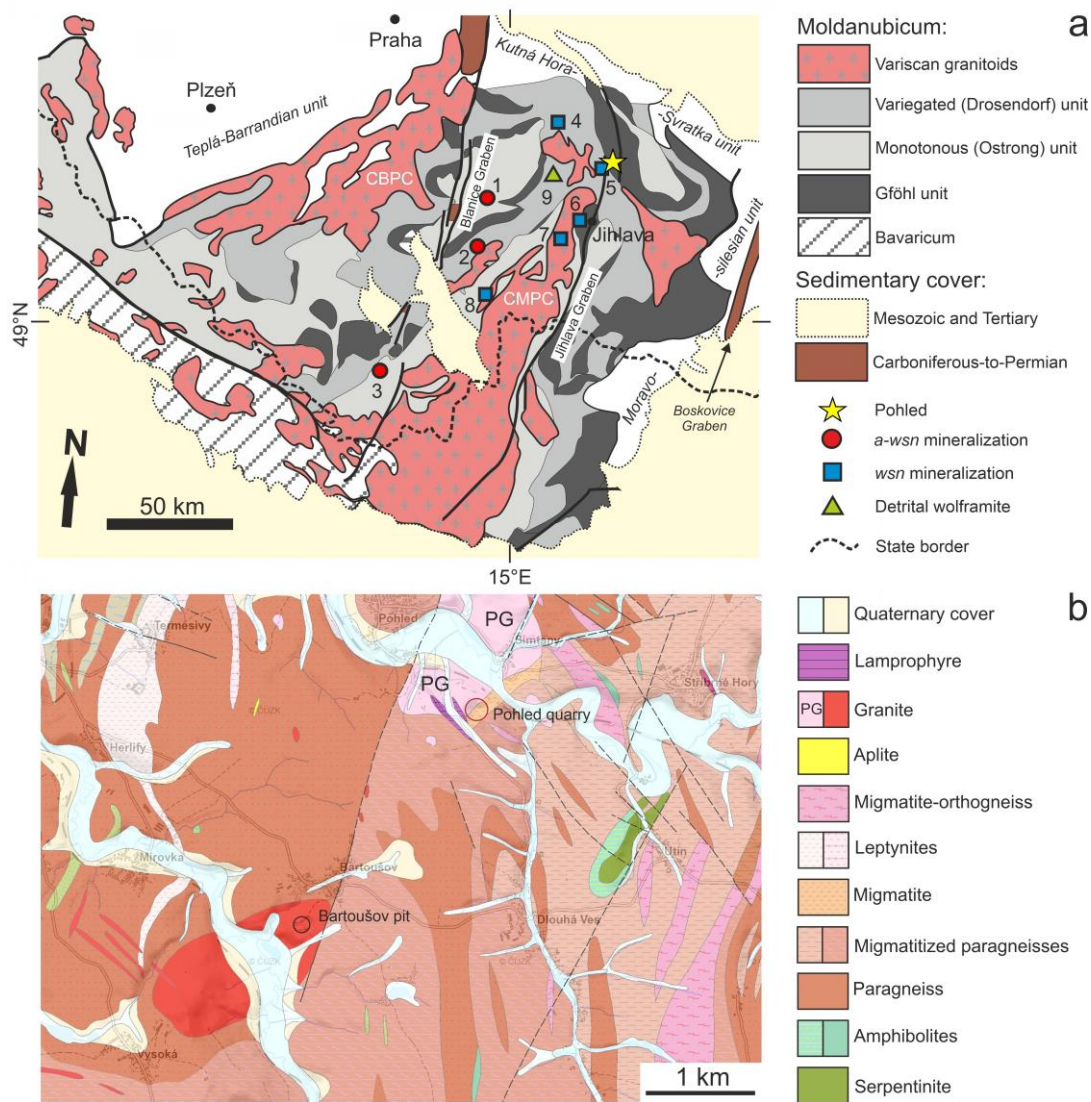


Figure 1. Simplified geology of the studied site. **(a)** Position of the Pohled site and other localities of vein/detrital wolframite in the Moldanubian Zone of the Bohemian Massif. PG—Pohled Granite, CBPC—Central Bohemian Plutonic Complex, CMPC—Central Moldanubian Plutonic Complex. Wolframite localities: 1—Cetoraz, 2—Deštná, 3—Malčice, 4—Ovesná Lhota, 5—Vysoká, 6—Jihlava–Pekelský vrch, 7—Těšenov, 8—Lásenice, 9—Trubáča-Valcha near Humpolec. **(b)** Local geology around the Pohled quarry (modified from [20]).

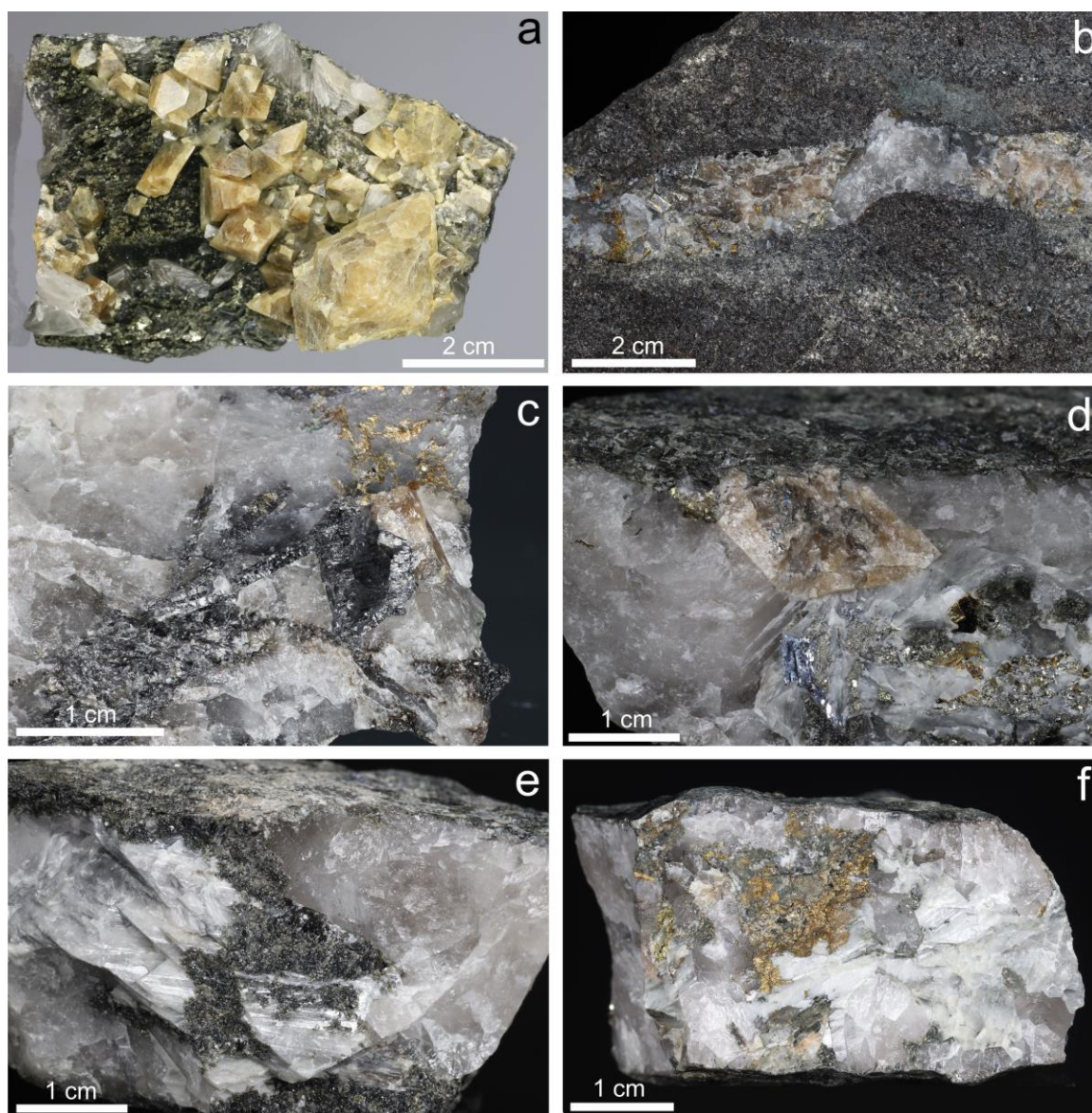


Figure 2. Macroscopic appearance of the studied wolframite-bearing vein mineralization from the Pohled quarry. (a) A group of scheelite crystals associated with quartz and chlorite. The youngest calcite fill was etched out. Photo courtesy T. Kadlec. (b) Quartz vein with scheelite and wolframite mineralization cutting the host gneiss. (c) A rosette of black wolframite tables hosted by quartz gangue. (d) A scheelite crystal enclosing minor black wolframite in quartz gangue. In lower right part there is a young white calcite infill with fine-grained greenish chlorite and sulfides (pyrite, galena). (e) An ancient drusy cavity in quartz filled with white calcite and fine-grained greenish chlorite. (f) Grey quartz crystals overgrown by pyrite and white calcite.

2. Background

2.1. Geological Setting

The wolframite occurrences bound to quartz veins and greisenized zones are concentrated in the central part of the Moldanubian Zone (Figure 1a), which represents the deeply eroded root of the Variscan Orogen. It is formed by high-grade metamorphic rocks intruded by granitic plutons. Metamorphic rocks are dominated by various types of paragneisses with local bodies of granulites, eclogites, orthogneisses, amphibolites, skarns, marbles, serpentinites, quartzites, and graphitic lithologies. The protolith of metamorphites was of the Upper Proterozoic to the Lower Paleozoic age and the main metamorphism was

related to the Variscan orogeny (Devonian to Carboniferous), although some earlier events were recorded locally. Numerous studies have illustrated the polymetamorphic history of many Moldanubian rocks, which were overprinted by a HT-LP event associated with the migmatitization and formation of cordierite due to intrusion of granitic plutons represented by the Central Moldanubian Plutonic Complex (CMPC) in the study area (Figure 1a). It is a composite granitic body, dominated by two-mica peraluminous granites, which intruded between 328 and 315 Ma [21,22]. The end of the Variscan orogenetic events led to the rapid uplift and erosion of the basement in the Uppermost Carboniferous and the Lower Permian. These processes were associated with formation of NNE-SSW trending graben structures giving rise to freshwater piedmont basins, filled with contemporaneous molasse sediments. Although the original thickness of this early post-Variscan sedimentary cover is estimated at 2500 m locally [23–25], most of these sediments were eroded during continuing uplift during the Mesozoic and Tertiary, leaving poorly preserved relics only (i.e., Blanice, Jihlava, and Boskovice Grabens in Figure 1a).

The studied site is situated at the NE exocontact of the CMPC in northern part of a deeply eroded tectonic structure of the Jihlava Graben (Figure 1a), represented (in the present erosional section) by NNE-SSW trending normal faults and a small relic of Lower Carboniferous conglomerates at the Stržbrné Hory village [26] (Figure 1b). The quarry Pohled is situated just at the contact point of the migmatitized biotite and the sillimanite-biotite paragneisses (locally containing small boudins of amphibolites and serpentinites) with a small post-kinematic intrusive body of a Pohled granite (Figure 1b). The Pohled granite is considered to be an apophyse of the CMPC and petrographically corresponds to biotite granodiorite [27,28]. It is composed mainly of quartz, K-feldspar, plagioclase (An_{16–45}), and ca. 12 vol. % of biotite corresponding to annite with $Fe/(Fe + Mg) = 0.60–0.63$, $Al = 1.11–1.12\ apfu$, $Ti = 0.16–0.18\ apfu$, and low F ($0.15–0.23\ apfu$). Accessory minerals include fluorapatite, monazite-(Ce), zircon, and ilmenite. The rock is weakly peraluminous ($A/CNK = 1.05–1.15$) and weakly evolved, as is documented by high CaO (2.0–2.9 wt. %), high Ba (828–951 ppm), high Sr (603–668 ppm), low Rb (147–172 ppm), relatively poorly fractionated REE patterns ($La/Yb_{CN} = 12.3–23.5$), and slightly negative to missing Eu anomaly ($Eu_{CN}/Eu^* = 0.73–1.05$) [27,28]. Both the mineralogical and the geochemical features suggest that the Pohled granite is just between S- and I-type granite. Metamorphites are frequently cut by dykes and irregular bodies of rather primitive granitic pegmatites with signs of intense superimposed hydrothermal alteration associated with the introduction of sulfur and ore metals [29,30]. In addition, both the granite and the metamorphites are cut by several types of hydrothermal veins. As the Pohled quarry is situated in the Havlíčkův Brod Ag–Pb–Zn ore district [31], the most frequent are Zn₂Pb₂(Ag) ore veins rich in pyrrhotite, pyrite, arsenopyrite, black Fe-rich sphalerite, and galena, which are hosted by quartz-(calcite) gangue [32–36]. The Alpine-type veins with quartz, calcite, chlorite, prehnite, allanite, titanite, minor sulfides, and zeolites are less common [36–39]. Other types of hydrothermal veins include quartz–dolomite–calcite–pyrite veins, molybdenite-bearing quartz veins, barren quartz veins, calcite veins, and palygorskite veins [32,33,35,36,40]. In addition, a nest of rich molybdenite mineralization was found directly in the Pohled granite, with molybdenite sheets disseminated directly in the rock matrix [35,41,42].

2.2. Wolframite Mineralization in the Moldanubicum

Neglecting sporadic wolframite occurrence in some pegmatites [43], there were distinguished two types of wolframite mineralization in the Moldanubian Zone of the Bohemian Massif: (1) pre-Variscan (Assyntian) W–Sn mineralization (*a-wsn*) and (2) Variscan W–Sn mineralization (*wsn*) sensu [16].

The pre-Variscan *a-wsn* mineralization was described from the localities Cetoraz, Deštná, and possibly Malčice [16,44] (Figure 1a). Greisenized zones and boudinated quartz veins lined by greisens are hosted by orthogneisses and are interpreted as pre-Variscan mineralizations initially hosted by granites, which were metamorphosed together with W-mineralization during the Variscan Orogeny [17,18]. In addition to the boudinated texture

of quartz vein (with boudins arranged parallel with the overall rock foliation), the metamorphic overprint is inferred from common occurrence of feldspars, gahnite, and garnet in the muscovite greisens [17,18]. The ore mineralization is represented by wolframite and scheelite as well as minor native bismuth, native gold, cassiterite, and sulfides (chalcopyrite, pyrite, molybdenite, galena). At Cetoraz, early wolframite I (Frb_{72–75}Hub_{21–25}Hua_{3–4}) is replaced by scheelite, whereas late wolframite II replaces scheelite [14,44,45].

The Variscan *wsn* mineralization is known from the localities Ovesná Lhota, Lásenice, Jihlava-Pekelský vrch, Vysoká near Havlíčkův Brod, and Těšenov [16,44,46] (Figure 1a). It is represented by quartz veins, locally rimmed with greisenized rocks, which are hosted by granites or paragneisses in the proximity of small apophyses of the CMPC. Mica from the greisenized rocks is reported as low-F low-Li muscovite. Apatite and/or tourmaline are locally abundant. Ore minerals are dominated by tabular wolframite (Frb_{53–88}Hub_{8–45}Hua_{2–4}; the Mg contents were analyzed at two sites only), which is accompanied especially by scheelite and minor sulfides (pyrite, arsenopyrite, molybdenite, chalcopyrite, and galena) and locally by cassiterite, joserite, and native bismuth. The exceptions are columbite-(Fe) to qitianlingite, gustavite, matildite, and/or pyrrhotite [10,15,44]. At the Jihlava-Pekelský vrch site, there also occurs late wolframite II (Frb_{99–100}Hub_{0–1}), replacing scheelite [10].

In addition, panning prospection proved the accessory presence of wolframite at several other sites in the Moldanubian area, but its primary source(s) is not known yet. Detrital wolframite from the locality Trubáča-Valcha near Humpolec (Figure 1a) contains the highest known Mg content (Frb_{77–89}Hub_{4–10}Hua_{8–13}) in the Moldanubian area [13,44].

3. Material and Methods

Only samples collected by the authors in the Pohled quarry in 2020 and 2023 were used in this study. Polished sections mounted in epoxy resin and doubly polished plates cemented by super glue were prepared from representative samples and checked first in the transmitted and/or reflected light of the Nikon Eclipse ME600 (Nikon Co., Tokyo, Japan) polarizing microscope equipped with a digital camera Nikon DXM1200F. Subsequently, a ~30 nm thick carbon layer was deposited on all samples in vacuum, followed by electron microprobe study on a Cameca SX-100 (AMETEK, Inc., Berwyn, PA, USA). The energy-dispersive X-ray microanalysis (EDS) was applied to identify each mineral phase and textural features of minerals were investigated by the back-scattered electron (BSE) imaging. Quantitative chemical compositions of selected phases were measured by means of 950+ spot wavelength dispersive (WDS) analyses, which are contained in an electronic Supplementary File. Beam current of 20 nA, beam size 0.7–2 µm and acceleration voltage of 25 kV were applied for analyses of sulfides. There were used following standards and analytical lines: NaCl (ClKα), Mn (MnKα), FeS₂ (FeKα), Co (CoKα), Ni (NiKα), CuFeS₂ (CuKα, SKα), ZnS (ZnKα), GaAs (GaLα), Ge (GeLα), NiAs (AsLβ), PbSe (SeLβ), Ag (AgLα), CdTe (CdLα), InAs (InLα), Sn (SnLα), Sb₂S₃ (SbLα), PbTe (TeLα), Au (AuMα), HgTe (HgLα), Tl (BrI) (TlLα), PbS (PbMα), and Bi₂S₃ (BiMβ). Oxygen-bearing minerals were studied at 15 kV, using a beam current of 20 nA (oxides, titanite, zircon, xenotime, and U-minerals), 10 nA (phyllosilicates, apatite, K-feldspar, and Ca-Y-REE silicate), or 5 nA (calcite) and a beam diameter 0.7 µm (oxides, titanite, zircon, xenotime, and U-minerals), 2 µm (phyllosilicates, apatite, K-feldspar, and Ca-Y-REE silicate) or 4 µm (calcite). The following elements were determined in *zircon*, *Ca-Y-REE silicate*, and *xenotime*: N, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, V, Mn, Fe, Cu, Zn, As, Sr, Y, Ba, W, Pb, Bi, La, Ce, Pr, Nd, Sm, Eu, Gd, and Dy, in *oxide minerals*: N, Na, Mg, Al, Si, P, S, Ca, Sc, V, Cr, Mn, Fe, As, Y, Zr, Nb, Mo, Sn, Ta, W, Pb, and U, in *apatite*: F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Mn, Fe, Zn, As, Sr, Y, Ba, Pb and Ce, in *phyllosilicates*: N, F, Na, Mg, Al, Si, P, K, Ca, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Sb, Cs, Ba and Pb, in *K-feldspar*: N, Na, Mg, Al, Si, P, K, Ca, Mn, Fe, Rb, Sr, Cs, Ba, and Pb, in *U-minerals*: F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Mn, Fe, Co, Ni, Cu, As, Rb, Sr, Y, Zr, Nb, Ba, Hf, Ta, W, Pb, Bi, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th and U, and in *calcite*: Na, Mg, Al, Si, P, Ca, Mn, Fe, Co, Ni, Cu, Zn, Sr, Ba, and Pb. The following standards and analytical lines were used: BN (Nkα), LiF (Fkα), albite (NaKα), diopside (MgKα), almandine

(AlK α , FeK α), sanidine (KK α , AlK α , SiK α), fluorapatite (CaK α , Pk α), celestite (SK α , SrL β), halite (ClK α), wollastonite (CaK α , SiK α), ScVO $_4$ (ScK α), TiO $_2$ (TiK α), V (VK α), Cr $_2$ O $_3$ (CrK α), rhodonite (MnK α), hematite (FeK α), Co (CoK α), Ni (NiK α), chalcopyrite (CuK α), clinoclase (AsL α), Rb-Ge glass (RbL α), YVO $_4$ (YL α), zircon (SiK α , ZrL α), Nb (NbL α), wulfenite (MoL α), Sn (SnL α), stibnite (SbL α), Cs-glass (CsL α), baryte (BaL α), Hf (HfM α), CrTa $_2$ O $_6$ (TaL α), scheelite (WL α), vanadinite (PbM α), Bi (BiM α), LaPO $_4$ (LaL α), CePO $_4$ (CeL α), PrPO $_4$ (PrL β), NdPO $_4$ (NdL β), SmPO $_4$ (SmL α), EuPO $_4$ (EuL α), GdPO $_4$ (GdL α), TbPO $_4$ (TbL α), DyPO $_4$ (DyL β), HoPO $_4$ (HoL β), ErPO $_4$ (ErL α), TmPO $_4$ (TmL α), YbPO $_4$ (YbL α), LuPO $_4$ (LuL α), Th (ThM α), and UO $_2$ (UM α). The peak counting time (CT) was usually between 10 and 30 s (for N 100 s) and background CT was taken at half of the peak time. The measured intensities were recalculated to wt. % using the standard PAP algorithm [47]. The contents of the above-listed elements, which are not included in the tables of chemical compositions (and included as a electronic Supplementary File), were always below the limits of detection, which usually ranged between 0.05 and 0.1 wt. % for most elements, except for N, F, Hg, W, Ta, Bi, and most of REEs, which were around 0.2–0.3 wt. %. Oxygen was computed from stoichiometry. Corrections were made for overlapping elements: F vs. Ce, Ti vs. V, K vs. U, Ca vs. P, Mn vs. Cr, Ag vs. Cd, Ta vs. Si, Bi vs. Ce, La vs. Dy, Eu vs. Dy, and Th vs. U. The REE contents were normalized to C1 chondrite using values by [48]. The numerical values of Ce, Eu, and Yb anomalies were calculated using equations given by [49] and those of tetrad effect by Equation (1) given by [50].

The in situ Raman analyses of minerals and fluid inclusions were realized using a DXR dispersive Raman Spectrometer (Thermo Fisher Scientific, Inc., Waltham, MA, USA) mounted on a confocal Olympus microscope (Olympus Co., Tokyo, Japan). The unpolarized 532 nm solid-state diode-pumped laser provided the Raman signal and CCD detector was used to detect it. Calibrations of laser frequency, Raman shift, and laser intensity of the spectrometer were preformed using Raman bands of polystyrene, emission lines of neon, and a standardized source of white light, respectively. The measurements were provided with these conditions: 8–15 mW laser power, 100 $\times$ objective, 50 μ m pinhole spectrograph aperture, 5 s exposure time, 200–300 exposure, and 50–4500 cm $^{-1}$ spectral range. In addition, a 780 nm laser working in a spectral range of 40–3410 nm was used for collection of spectra of a Ca-Y-REE silicate. The Omnic 9 software (Thermo Scientific) was used as tool for spectral manipulations. The obtained Raman spectra of minerals were compared to the reference spectra contained in the RRUFF database. The presence of gases (including CH $_4$, C $_2$ H $_6$, C $_3$ H $_8$, CO, CO $_2$, N $_2$, H $_2$ S, H $_2$, and O $_2$) was checked in the vapor phase of fluid inclusions. The quantification of the contents of CH $_4$, CO $_2$, and N $_2$ was based on the measurement of peak areas [51] and the calibration of the measurement using natural fluid inclusions with known compositions. In addition, a 633 nm laser allowing measurement in a spectral range of 50–3200 cm $^{-1}$ was also used to check the composition of vapor bubbles in scheelite-hosted fluid inclusions.

Standard doubly polished plates were made for the fluid inclusions study. The inclusions were classified as primary (P), pseudosecondary (PS), or secondary (S) according to the petrographic criteria given by [52,53]. Microthermometric parameters were obtained using the Linkam THMSG 600 stage (Linkam Scientific Instruments, Surrey, UK) equipped with the Olympus BX-51 microscope. The temperature measurement was calibrated between −56.6 and 374.1 °C with natural fluid inclusions with known temperatures of phase transitions and inorganic standards. The measuring preciseness is within 0.1 °C for temperatures between −56.6 and 0 °C, and within 1 °C for temperature of 374.1 °C. The measured parameters were: freezing temperature (Tf), eutectic temperature (Te), melting temperature of ice (Tm $_{ice}$), and homogenization temperature (Th). In order to minimize decrepitation of high-density inclusions by overheating, initial homogenization measurement up to 200 °C was followed by cryometric measurements and then by homogenization measurement above 200 °C to finish. Calculations of salinity of aqueous solutions were preformed according to [54] and the ISOC program [55] was used for construction of isochores with calibration by [56].

Pure mineral separates weighing approximately 0.1 g were handpicked under a binocular microscope and ground in an agate mortar for oxygen isotope analyses. The samples were then washed with 1:1 HCl at 25 °C to remove possible impurities (especially carbonates). Samples were decomposed using fluorination technique with aid of gaseous fluorine and cleaned on a 5 Å molecular sieve. The $\delta^{18}\text{O}$ value was then determined at the University of Lausanne on a Finnigan MAT 253 mass spectrometer (Finnigan MAT GmbH, Bremen, Germany). The results are conventionally expressed in delta (δ) notation as per mil (‰) deviation from the commonly used V-SMOW standard. The uncertainty is better than ± 0.1 ‰.

4. Results

4.1. Mineralogy

The vein mineralization containing wolframite is very scarce in the Pohled quarry. It was found two times only, in the years 2020 and 2023. In both cases, the tungsten mineralization was found in blasted rock material but never in the quarry walls; thus, the relationship between mineralization and the wall rocks cannot be fully evaluated. Nevertheless, the collected samples clearly indicate that the vein cut the foliation of the host migmatitized biotite paragneisses. Although the course of the vein seems to be undulated, the contact between the vein and the host rock is sharp (Figure 2b) and no color changes of the wall rock are observed on the contact with the vein. The vein thickness is laterally variable and ranges between 0.5 and 4 cm.

The textural features of the vein are usually rather simple, with no or little indication of a more significant tectonic deformation of the vein fill. The vein is dominated by massive grey quartz, which, in places, hosts up to 1 cm long and 2 mm wide black laths (sometimes rosette-arranged) of wolframite (Figure 2c), which are often overgrown by well-developed isometric dipyratidal crystals or isolated irregular grains of honey-yellow scheelite up to 3 cm in size (Figure 2a,b,d). Both these minerals crystallized directly on the wall rock and the free space among them was usually cemented by quartz. Ancient drusy cavities are present locally in quartz vein, being lined by coarse crystal faces of quartz. The residual free space was later completely cemented especially by coarse-grained white calcite, and to a lesser extent, by fine-grained chlorite (Figure 2e) and minor sulfides (Figure 2d,f). In addition, macroscopic elongated branchy aggregates of chlorite reaching up to several mm in length are sometimes enclosed in quartz or calcite. Sulfides form small (several mm big) nests or isolated grains in the late portion of the vein, except for molybdenite, which represents an early phase concentrating along the contact between the vein and the host rocks. Calcite forms also thin (up to 2 mm thick) veinlets cutting the vein or following the re-juvenated contact between the host rock and the early vein fill.

A detailed mineralogical study of the polished sections revealed a rich mineral assemblage involving a total of 36 mineral species, including quartz, molybdenite, pyrrhotite, sphalerite, chalcopyrite, galena, pyrite, violarite, gersdorffite, arsenopyrite, cobaltite, anite, phlogopite, clinocllore, chamosite, hisingerite, muscovite, titanite, scheelite, ferberite, hübnerite, columbite-(Mn), columbite-(Fe), qitianlingite, rutile, brookite, anatase, adularia, calcite, fluorite, xenotime-(Y), an unknown Ca-Y-REE silicate, zircon, uraninite, coffinite, and fluorapatite. The individual minerals are characterized in the following paragraphs.

4.1.1. Ore Minerals

Wolframite is a characteristic constituent of the vein, forming up to 1 cm long and 2 mm wide laths that are sometimes rosette-arranged. It is typically strongly replaced by scheelite (Figure 3a) and to a lesser extent, by pyrite (Figure 3b), chlorite, hisingerite, and calcite. Wolframite occasionally encloses isolated crystals or grains of columbite-group minerals, biotite, and chlorite. In the BSE image, wolframite usually does not display a chemical zonation; in two crystals only, somewhat darker small cores significantly enriched in Mn were found (Figure 3c). The spot WDS analyses (Table S1) confirm the overall chemical homogeneity of most wolframite crystals, composed of **ferberite** with a minimal

variability of hübnerite and huanzalaite components (Frb_{72–79}Hub_{18–24}Hua_{2–3}). The Mn-enriched cores were composed of ferberite in one case (Frb_{55–60}Hub_{37–41}Hua₃) and of **hübnerite** in another case (Frb_{16–30}Hub_{61–74}Hua_{0–2}; Figure 4a). A negative correlation is observed between the Mg and Mn contents (Figure 4b), stressing a more significant Mg enrichment in the younger Fe-rich parts of crystals. In addition to Fe, Mn, Mg, and W, other elements were scarcely above detection limits, including Si (<0.019 *apfu*; base of recalculation is 4 atoms of oxygen), S (<0.005 *apfu*), Nb (<0.047 *apfu*), and/or Sc (<0.008 *apfu*). Detectable contents of both Nb and Sc were largely recorded in hübnerite. Ferberite from Pohled yielded the following mean empirical formula based on 91 spot WDS analyses: (Fe_{0.76}Mn_{0.21}Mg_{0.03}) Σ 1.00(W_{1.00}Si_{0.01}) Σ 1.01O_{4.00}. Meanwhile, the mean empirical formula of hübnerite (based on 11 spot WDS analyses) is (Fe_{0.26}Mn_{0.69}Mg_{0.01}Nb_{0.02}) Σ 0.98W_{0.99}O_{4.00}.

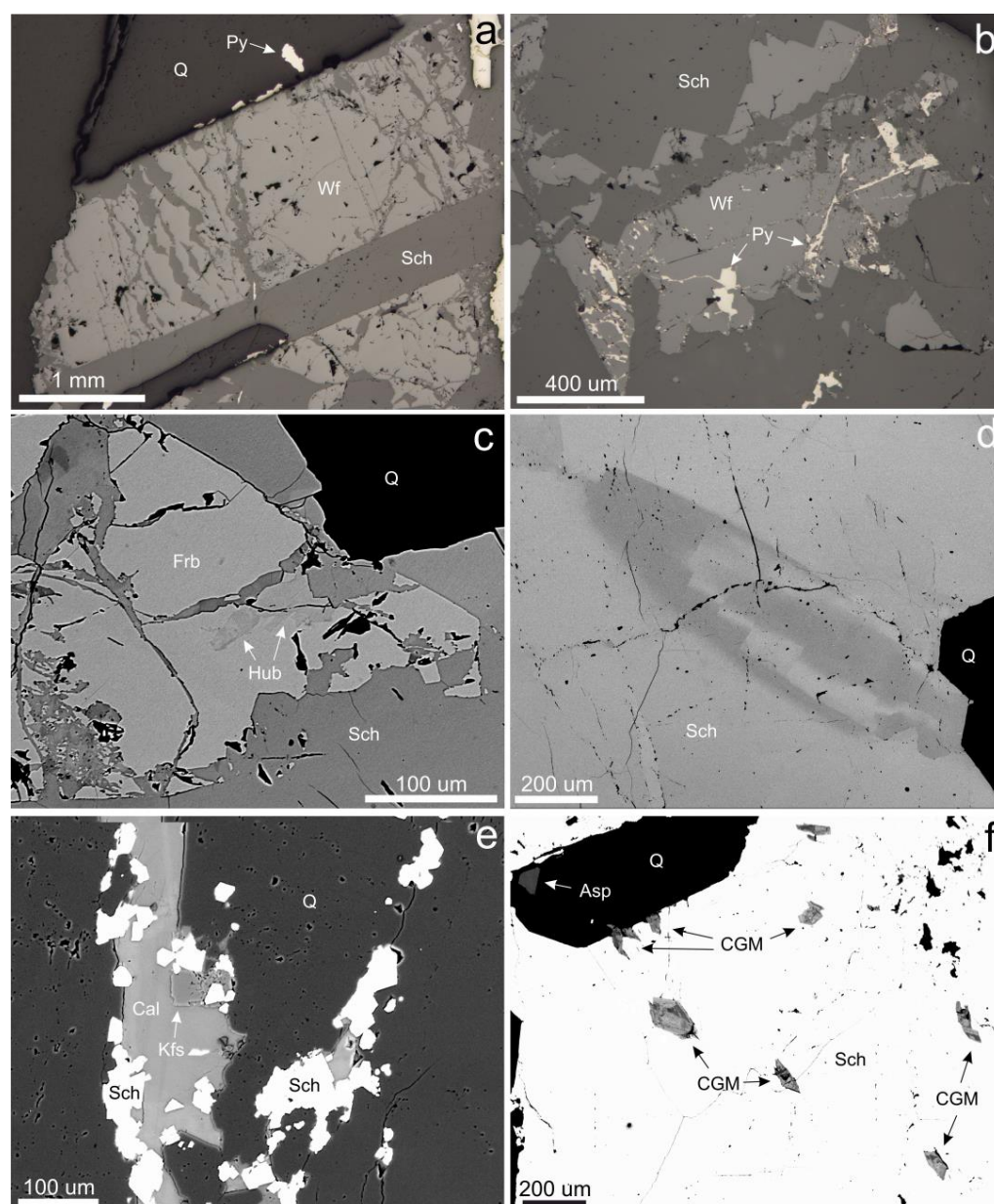


Figure 3. Mineral assemblage and development of individual minerals from the studied mineralization. (a) A table of wolframite (Wf) corroded by scheelite (Sch) and hosted by quartz (Q). Py—pyrite. Sample Po-75, reflected light. (b) Wolframite replaced by scheelite and pyrite. Sample Po-76, reflected light. (c) Zoned wolframite with small hübnerite (Hub) core and large ferberite (Frb) rim, strongly

replaced by scheelite. Sample Po-30, BSE image. (d) Apparently zoned scheelite with no differences in compositions indicated by WDS analyses. Sample Po-75, BSE image. (e) A veinlet composed of scheelite II (Sch), adularia (Kfs), and calcite (Cal), cutting the quartz gangue. Sample Po-73, BSE image. (f) A group of zoned crystals of columbite-group minerals (CGM) enclosed in scheelite after wolframite. Quartz contains a crystal of arsenopyrite (Asp). Sample Po-76, BSE image.

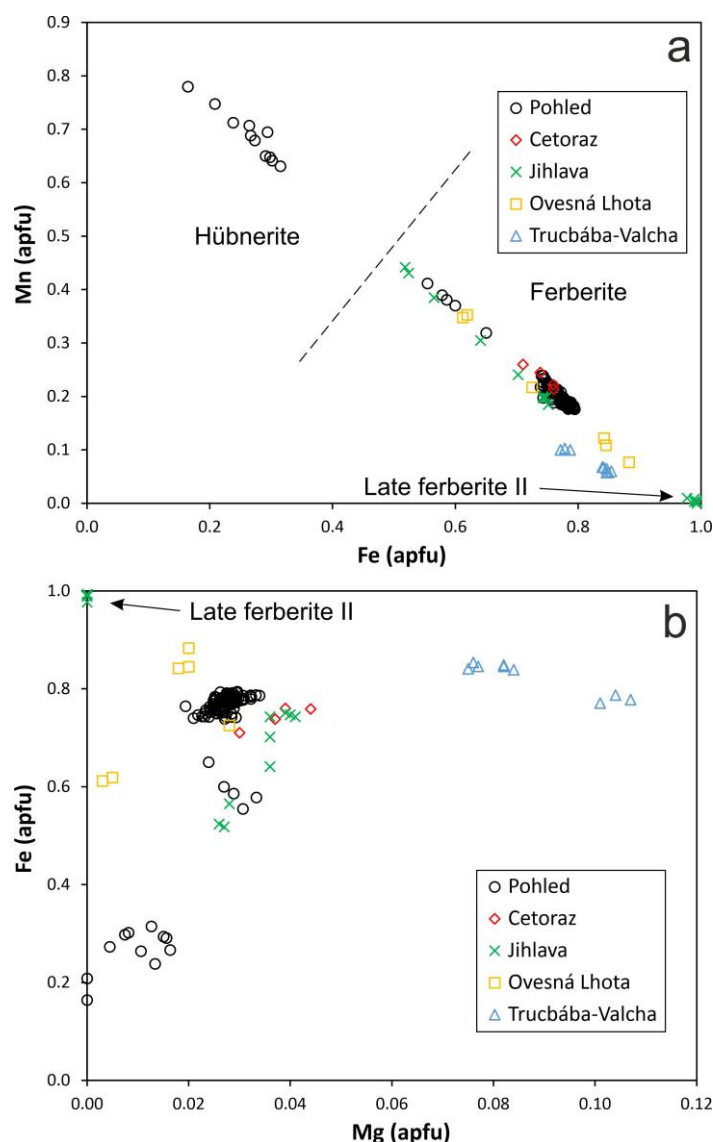


Figure 4. Variations in chemical composition of wolframite from Pohled (this work) and its comparison with published data from the Moldanubian area. (a) Fe vs. Mn plot. (b) Fe vs. Mg plot. The comparative data are from [10,13–15,45].

Scheelite occurs in two generations. Scheelite I is a widespread mineral phase in the studied mineralization. It forms individual dipyratidal honey-yellow translucent crystals or irregular grains up to 4 cm in size, which are enclosed in quartz or (rarely) calcite gangue. Macroscopically, a weak color zonality is sometimes observed, with darker cores and lighter margins of the crystals. Scheelite I is found in places finely fractured with tiny cracks filled up by calcite, pyrite, or chlorite II. It often grows over wolframite and strongly replaces it from its outer margins and along cracks (Figure 3a–c). Although a distinct zoning of some crystals of scheelite I is observed in BSE images (Figure 3d), the spot WDS analyses (Table S2) collected from contrasting domains did not prove any systematic compositional differences. Where wolframite is completely consumed, scheelite

I encloses inherited crystals of columbite-group minerals that remained untouched by this replacement process. The composition of scheelite I is very simple. In addition to Ca and W, small admixtures of P were also recorded in most analyses (<0.007 apfu; base of recalculation is four atoms of oxygen), while Si (<0.014 apfu) and S (<0.004 apfu) were found in a minor part of analyses. The mean empirical formula of scheelite I (based on 45 spot WDS analyses) is $\text{Ca}_{1.00}\text{W}_{1.00}\text{O}_{4.00}$. Scheelite II was observed only in a single polished section. It is a minor component of a veinlet cutting the quartz-wolframite-scheelite I vein, composed of scheelite II, adularia, quartz, and calcite. Scheelite II forms isometric crystals and irregular grains up to $150\text{ }\mu\text{m}$ in size, growing over quartz, and is postdated by adularia and calcite (Figure 3e). No zonality is observed in the BSE images. Chemical homogeneity is also confirmed by WDS analyses, which show a nearly pure composition with low P recorded in most analyses (<0.007 apfu). The mean empirical formula of scheelite II (based on 8 spot WDS analyses) is $\text{Ca}_{1.00}\text{W}_{1.00}\text{O}_{4.00}$.

Columbite-group minerals are accessories hosted by wolframite or by minerals replacing wolframite, namely, scheelite I (Figure 3f) or pyrite (Figure 5a). Columbite-group minerals form isolated isometric or elongated faceted crystals or lenticular grains reaching typically around $50\text{ }\mu\text{m}$ and at maximum up to $200\text{ }\mu\text{m}$ in size. No marks of dissolution of crystal margins of columbite-group minerals are usually observed in the scheelite host, whereas signs of corrosion by pyrite observed in a single polished section (Figure 5a). Although non-zonal examples are also observed, columbite-group minerals typically display complex zonation in BSE images (Figures 3f and 5a,b), including oscillatory zoning, sectorial zoning, and/or replacement features. At least three compositional types can usually be distinguished within single grain; however, the sequence of them is not unified, although the brightest component in BSE image mostly appear to be the latest one, which overgrowths and often also replaces the darker ones (Figure 5a,b). The detailed microprobe study identified three members of the columbite group: columbite-(Mn), columbite-(Fe), and qitianlingite. **Columbite-(Mn)** is the rarest one, being recorded in two columbite grains only. In both cases, it forms single thin lamellae through the whole columbite grain, which seems to be rimmed and partly replaced by columbite-(Fe) (inset in Figure 5a). Lamellae of columbite-(Mn) appear the darkest in the BSE images and reach up to $8\text{ }\mu\text{m}$ in thick. The Fe/(Fe + Mn) ratio ranges 0.21–0.36 and Nb/(Nb + Ta) varies from 0.99 to 1.00. Subordinated to minor constituents of columbite-(Mn) include W (0.032–0.047 apfu; base of apfu calculation is six atoms of oxygen; Table S3), Ti (0.180–0.240 apfu), Sc (0.162–0.205 apfu), Mg (0.004–0.010 apfu), Ca (0.003–0.011 apfu), and F (0.119–0.135 apfu). Both the major volume of all grains/crystals and a majority of collected WDS analyses belong to **columbite-(Fe)**. Distinct zones observed in the BSE images differ especially in variously elevated W (0.021–0.300 apfu; recalculation to six atoms of oxygen; Table S3), and to a lesser extent, in the Fe/(Fe + Mn) ratio (0.70–0.88) and contents of Ti (0.046–0.239 apfu) and Sc (0.006–0.248 apfu). The contents of other substituents are less variable (0.030–0.050 apfu Mg, 0.085–0.114 apfu F, and in part of collected analyses, also <0.033 apfu Ca, and <0.008 apfu V were recorded). The Nb/(Nb + Ta) ratios vary from 0.97 to 1.00. **Qitianlingite** is the most W-enriched columbite-group mineral, in terms of chemical composition continuously evolving from W-enriched columbite-(Fe). Therefore, the 50% IMA compositional rule was applied to distinguish both phases. In the BSE images, qitianlingite forms the brightest outer rims around some columbite grains/crystals or irregularly shaped domains/sectors inside them (Figure 5a,b). The W contents range between 0.502 and 1.269 apfu (apfu values are based on 10 atoms of oxygen; Table S3). Both the Nb/(Nb + Ta) and Fe/(Fe + Mn) ratios are very close to those of columbite-(Fe), ranging from 0.99 to 1.00 and from 0.75 to 0.88, respectively. Like other recorded members of the columbite-group, qitianlingite from Pohled shows elevated contents of Ti (0.059–0.259 apfu), Sc (0.043–0.355 apfu), Mg (0.056–0.088 apfu), F (0.110–0.176 apfu), and, in part of collected WDS analyses, also low S (<0.012 apfu). Comparing the chemical compositions of all found columbite-group minerals (Figures 6 and 7), there are mostly observed broad overlaps between columbite-(Fe) and qitianlingite, while columbite-(Mn) usually occupies distinctly different com-

positional spaces characterized by lowest contents of Mg and W and the highest contents of F and, mostly, also Ti and Sc. Columbite-(Mn) from the Pohled quarry yielded the following mean empirical formula (based on six spot WDS analyses and six atoms O): $(\text{Fe}_{0.21}\text{Mn}_{0.54}\text{Sc}_{0.18}\text{Mg}_{0.01}\text{Ca}_{0.01})_{\Sigma 0.95}(\text{Nb}_{1.77}\text{Ta}_{0.01}\text{Ti}_{0.21}\text{W}_{0.04})_{\Sigma 2.03}\text{O}_{5.94}\text{F}_{0.13}$. That of columbite-(Fe) (based on 80 spot WDS analyses and six atoms O) is $(\text{Fe}_{0.67}\text{Mn}_{0.14}\text{Sc}_{0.12}\text{Mg}_{0.04})_{\Sigma 0.97}(\text{Nb}_{1.69}\text{Ta}_{0.01}\text{Ti}_{0.15}\text{W}_{0.14})_{\Sigma 1.99}\text{O}_{5.95}\text{F}_{0.10}$, and that of qitianlingite (based on 28 spot WDS analyses and 10 atoms O) is $(\text{Fe}_{1.37}\text{Mn}_{0.26}\text{Sc}_{0.19}\text{Mg}_{0.07})_{\Sigma 1.89}(\text{Nb}_{2.11}\text{Ta}_{0.01}\text{Ti}_{0.16})_{\Sigma 2.28}\text{W}_{0.79}\text{O}_{9.93}\text{F}_{0.14}$.

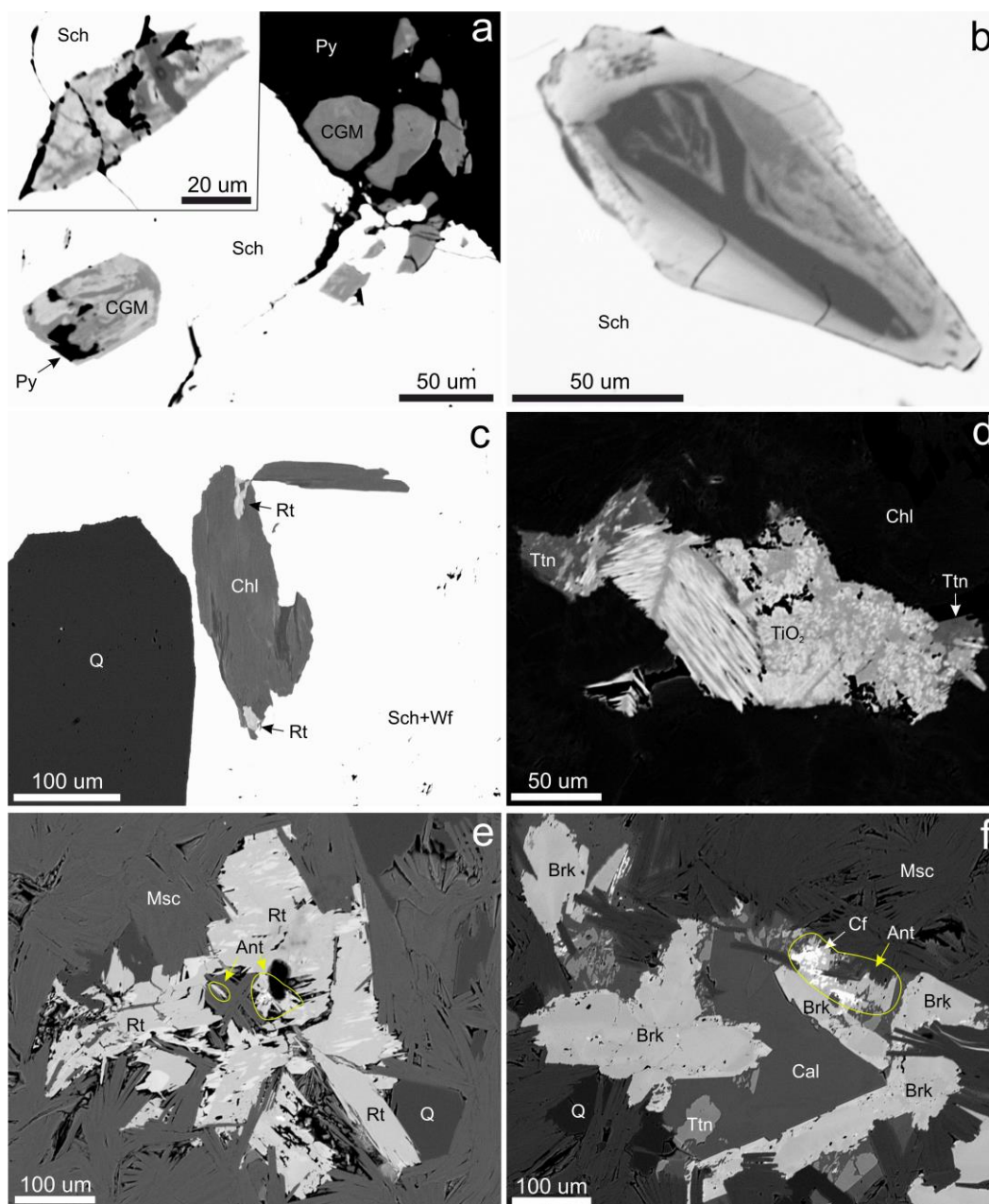


Figure 5. Mineral assemblage and development of individual minerals from the studied mineralization on BSE images. (a) Zoned crystals of columbite-group minerals enclosed in scheelite and pyrite. Note some corrosion of columbite by pyrite. Inset—The darkest lamella of columbite-(Mn) in a composite crystal of columbite-group mineral. Sample Po-76. (b) Zoned crystal composed of dark columbite-(Fe) core and bright W-rich qitianlingite rim, enclosed in scheelite. Sample Po-78. (c) W-enriched inclusions of rutile (Rt) hosted by chlorite (Chl) pseudomorphs after biotite enclosed by scheelite with relics of wolframite. Sample Po-75. (d) A Nb,W-zoned TiO_2 mineral (TiO_2) enclosed

in chlorite, partly replaced by titanite (Ttn). Sample Po-30. (e) An aggregate of W-zoned TiO_2 minerals, hosted by muscovite (Msc), and composed of minor anatase (Ant) in the centre (outlined) and predominating rutile in the rim. Sample Po-81. (f) A group of zoned crystals of predominating brookite (Brk) and minor anatase (outlined) in assemblage with titanite, coffinite (Cf), muscovite, calcite, and quartz. Sample Po-74.

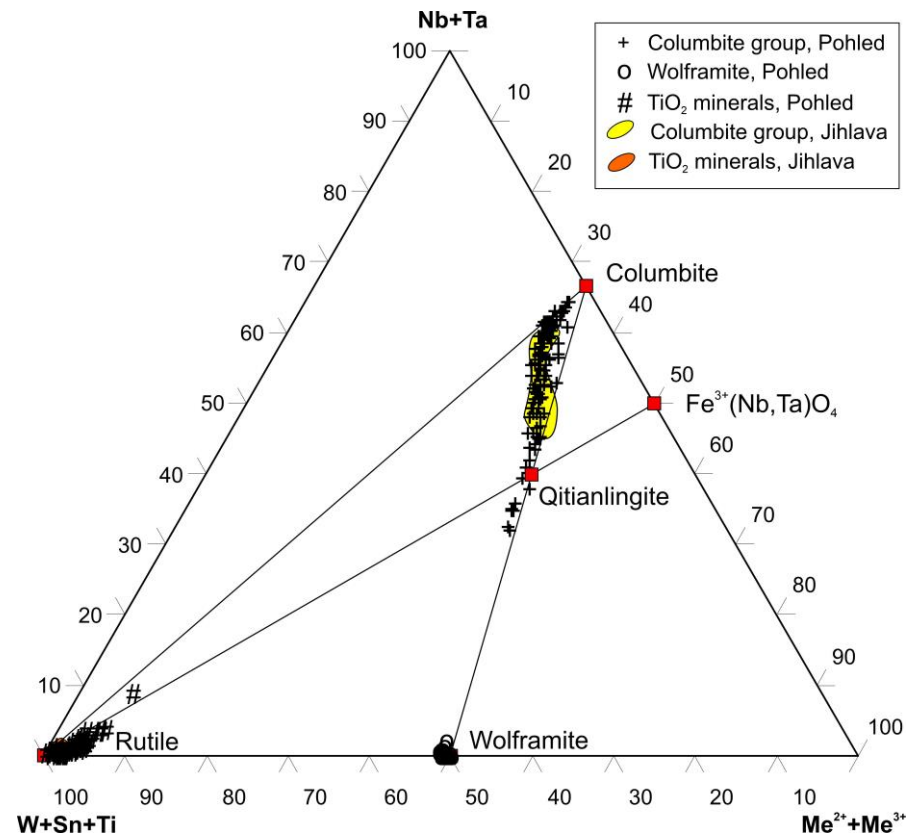


Figure 6. Variations in chemical composition of wolframite, TiO_2 minerals, and columbite-group minerals from Pohled (this work) in a $\text{W} + \text{Sn} + \text{Ti}$ vs. $\text{Me}^{2+} + \text{Me}^{3+}$ vs. $\text{Nb} + \text{Ta}$ plot (modified from [57]) and comparison with published data from wolframite mineralizations in the Moldanubian area. Data in at. %. The comparative data are from [10].

TiO_2 minerals occur predominantly in marginal parts of the vein close to the contact with wall rock, where they are associated with apatite, chlorite, and muscovite. They form anhedral to subhedral isometric to slightly elongated grains, reaching up to 200 μm . Specifically, TiO_2 minerals are often enclosed in chloritized biotite (Figure 5c). Although homogeneous grains are also observed, the TiO_2 minerals usually show chemical zonation in the BSE images. The single grain usually contains a bright core or several mutually isolated bright domains (Figure 5d). Oscillatory zoning is sometimes observed in the darker rim of a crystal, although non-zoned rims are also frequent. Exceptionally, minor replacement by titanite is observed from the margins of TiO_2 grains (Figure 5d). The observed zonation is caused by variations in contents of Nb (up to 0.086 apfu; Table S4), Fe (up to 0.042 apfu), W (up to 0.023 apfu), and, to a lesser extent, in many analyses, also V (up to 0.018 apfu), Ca (up to 0.009 apfu), and Cr and Sc (both up to 0.004 apfu). A few analyses also show traces of Sn (up to 0.002 apfu) and slightly elevated Si (up to 0.013 apfu) and/or Al (up to 0.007 apfu), the latter two elements possibly representing minor contamination from host silicates of quartz. Neglecting one Nb-enriched outlier, the Nb and W contents correlate positively, although not very tightly ($R^2 = 0.47$; Figure 8). Other pairs of minor elements do not show any correlations. The mean empirical formula of

TiO₂ phases from the studied mineralization (based on 52 WDS analyses and two atoms of oxygen) is (Ti_{0.95}Fe_{0.02}W_{0.01}Nb_{0.01}V_{0.01})_{Σ1.00}O_{2.00}. The Raman spectroscopy confirmed the presence of **rutile**, **brookite**, and **anatase**. Rutile forms small xenomorphic grains hosted by chloritized biotite (Figure 5c), whereas all three TiO₂ polymorphs build up the larger neomorphic grains and aggregates hosted by polymineral aggregates of phyllosilicates (Figure 5d–f). In the latter case, various assemblages of TiO₂ minerals were observed, with predominance of rutile and/or brookite, with anatase being the least frequent component (Figure 5e,f). Based on their appearance in the BSE images, it is impossible to distinguish the TiO₂ polymorphs mutually.

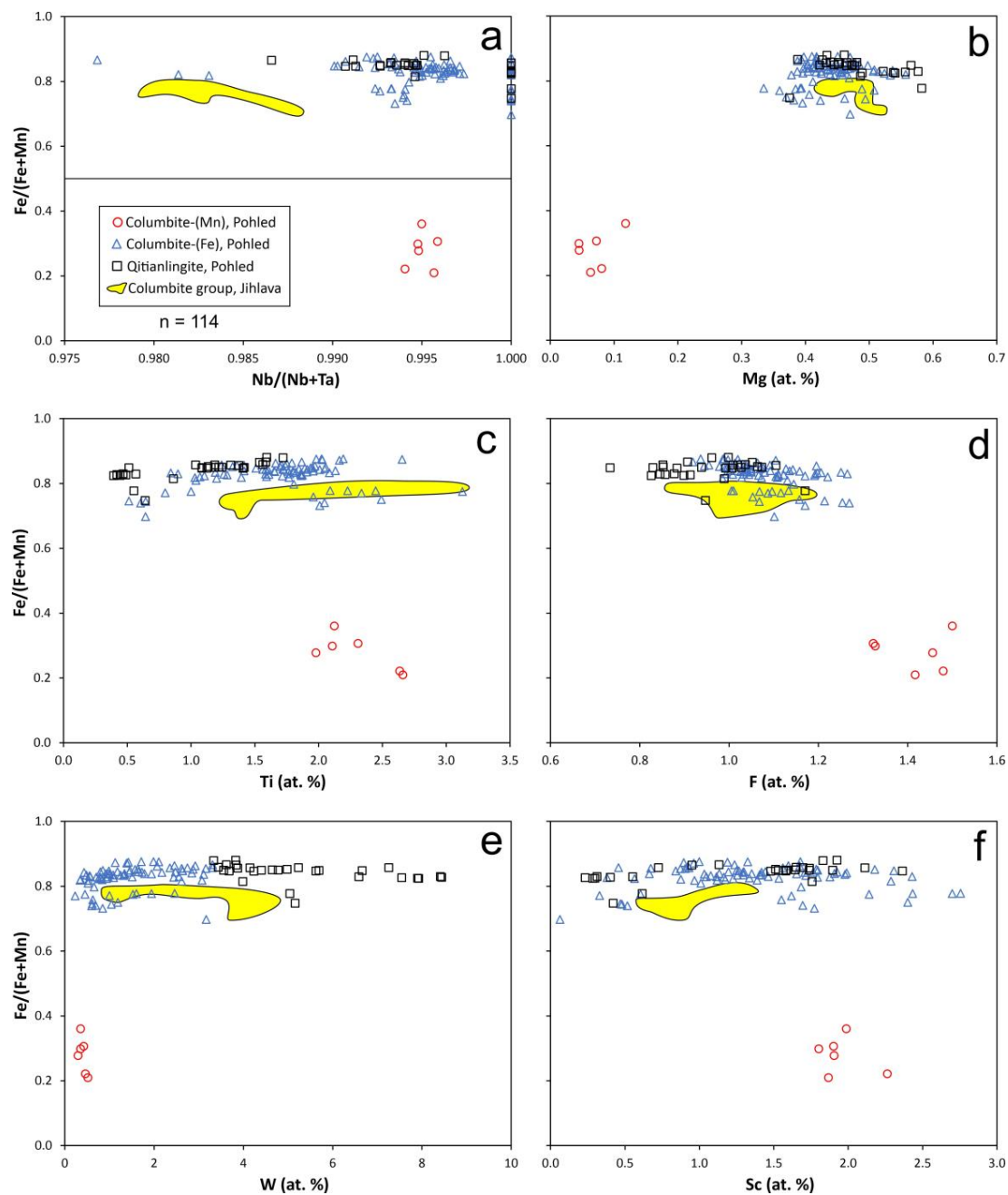


Figure 7. Variations in chemical composition of columbite-group minerals from Pohled (this work) and comparison with published data from wolframite mineralizations in the Moldanubian area, manifested in plots Fe/(Fe + Mn) vs.: Nb/(Nb + Ta) (a), Mg (b), Ti (c), F (d), W (e), and Sc (f). Data in at. %. The comparative data are from [10].

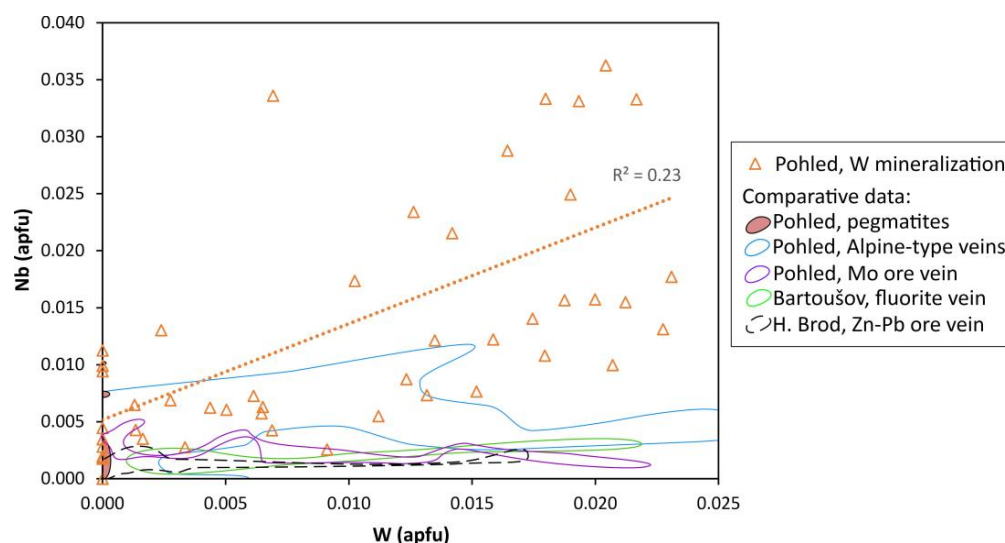


Figure 8. Variations in chemical composition of TiO_2 minerals from W mineralization from Pohled (this work) in the W vs. Nb plot and comparison with data from various parageneses in the Pohled quarry and from other vein mineralizations in the Havlíčkův Brod ore district. The comparative data are from [29,40,58,59].

Uraninite was found sporadically in the oldest marginal parts of the vein. It is represented by isometric anhedral grains up to 70 μm in diameter (Figure 9a,b). Uraninite is associated with chlorite, coffinite, pyrite, and TiO_2 minerals in quartz gangue. From the mentioned minerals, only pyrite and coffinite are clearly younger, both rimming uraninite grains. Uraninite appears partly homogeneous in BSE images, but some grains are patchy due to irregular hydration and coffinitization. Most WDS analyses (Table S5) exhibit lowered analytical totals (91.4–99.7 wt. %) and an elevated sum of cations (1.029–1.065 apfu), suggesting the metamictization of uraninite and associated hydration and partial oxidation of U^{4+} to U^{6+} . In addition, WDS analyses reveal the presence of a number of admixtures, including Th (0.005–0.102 apfu), Y (0.016–0.057 apfu), Pb (0.023–0.051 apfu), and F (0.059–0.099 apfu), which were found in all WDS analyses. Most of them contained in addition elevated Fe (up to 0.041 apfu) and REE (up to 0.036 apfu), while the detectable contents of S, W, As, P, Si, Al, Ti, Zr, and Mg are rarely recorded and may largely represent local contamination due to alteration, as is suggested from composition of the associated coffinite. The chondrite normalized REE spectra, although very fragmentary, illustrate the overall increasing abundance of REEs with increasing atomic number (Figure 10a), which is in line with crystal-chemical behavior of uraninite [60]. The mean empirical formula of uraninite from the studied mineralization (based on 22 WDS analyses, two atoms O + F, and all U considered to be tetravalent) is $(\text{U}_{0.84}\text{Th}_{0.05}\text{Si}_{0.04}\text{Pb}_{0.04}\text{Y}_{0.03}\text{Fe}_{0.01}\text{Ca}_{0.01}\text{REE}_{0.01})_{\Sigma 1.04}\text{O}_{1.96}\text{F}_{0.08}$.

Coffinite is an accessory phase, which replaces uraninite grains from their margins and along cracks and infiltrates also into neighboring chlorite (Figure 9a). Coffinite rims and veinlets do not exceed 7 μm in thick. In addition, small inclusions of coffinite were, exceptionally, found in central part of two anatase/brookite crystals (Figure 5f). In the BSE images, coffinite often has a patchy appearance, which corresponds well with variations in chemistry indicated by WDS spot analyses (Table S6). The mostly lowered analytical totals (93.6–99.2 wt. %) suggest the hydration and/or metamictization of coffinite. These changes are also manifested by a poor stoichiometry of the empirical formula showing an excess of metallic cations in the position of U (1.015–1.228 apfu) and a deficit of elements in the position of Si (0.907–1.115 apfu). Such variations, however, can be commonly observed in coffinite [60]. Uranium and Si are substituted by the same elements as in the case of uraninite, but mostly in several-times higher concentrations. The most significant are the contents of Y (0.066–0.219 apfu), Ca (0.052–0.192 apfu), REE (0.019–0.090 apfu), Fe (0.026–0.068 apfu), P (0.014–0.267 apfu), W (0.007–0.017 apfu), F

(0.067–0.121 *apfu*), and, in part of the collected analyses, also Th (up to 0.11 *apfu*), Nb, Ti, Zr, Mg, Pb, Mn, S, and As (up to 0.04 *apfu* each). The chondrite normalized REE patterns have a similar shape to those of uraninite, with maxima in the area Dy–Er (Figure 10b). The Eu anomaly seems to be highly variable, from negative to positive ($\text{Eu}/\text{Eu}^* = <0.95$ to >2.18). The mean empirical formula of coffinite (based on nine WDS analyses, four atoms O + F, and all U considered to be tetravalent) is $(\text{U}_{0.57}\text{Y}_{0.14}\text{Al}_{0.11}\text{Ca}_{0.11}\text{REE}_{0.05}\text{Fe}_{0.05}\text{Th}_{0.04}\text{Mg}_{0.02}\text{K}_{0.02}\text{Ti}_{0.01}\text{Pb}_{0.01})_{\Sigma 1.13}(\text{Si}_{0.93}\text{P}_{0.08}\text{W}_{0.01})_{\Sigma 1.02}\text{O}_{3.96}\text{F}_{0.09}$.

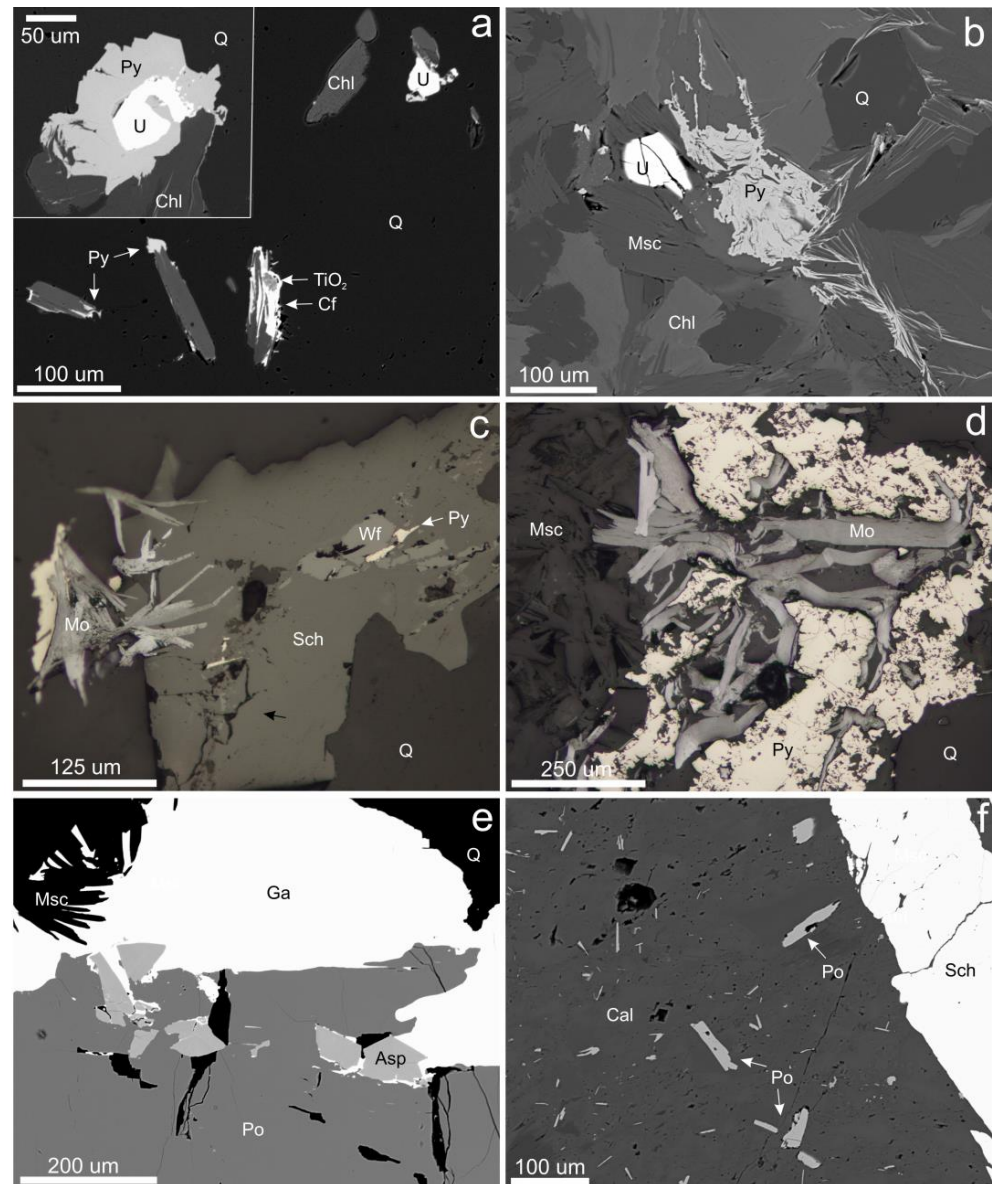


Figure 9. Mineral assemblage and development of individual minerals from the studied mineralization. (a) Uraninite (U) grain hosted by quartz with inclusions of chlorite and a TiO_2 mineral. Uraninite is rimmed by coffinite, which, together with pyrite, also replaces chlorite. Inset—a grain of uraninite rimmed by pyrite. Sample Po-77, BSE images. (b) Uraninite in a phyllosilicate-rich marginal portion of the vein cut by pyrite veinlets. Sample Po-30, BSE image. (c) Molybdenite (Mo) tables overgrown by wolframite strongly replaced by scheelite and pyrite. Sample Po-81, reflected light. (d) Terminations of molybdenite tables ripped by crystallization of late pyrite. Sample Po-77, reflected light. (e) A sulfide aggregate composed of pyrrhotite I (Po), galena (Ga), and minor arsenopyrite hosted by muscovite-quartz gangue. Sample Po-81, BSE image. (f) Abundant tabular pyrrhotite II crystals hosted by late calcite in the neighborhood of scheelite. Sample Po-30, BSE image.

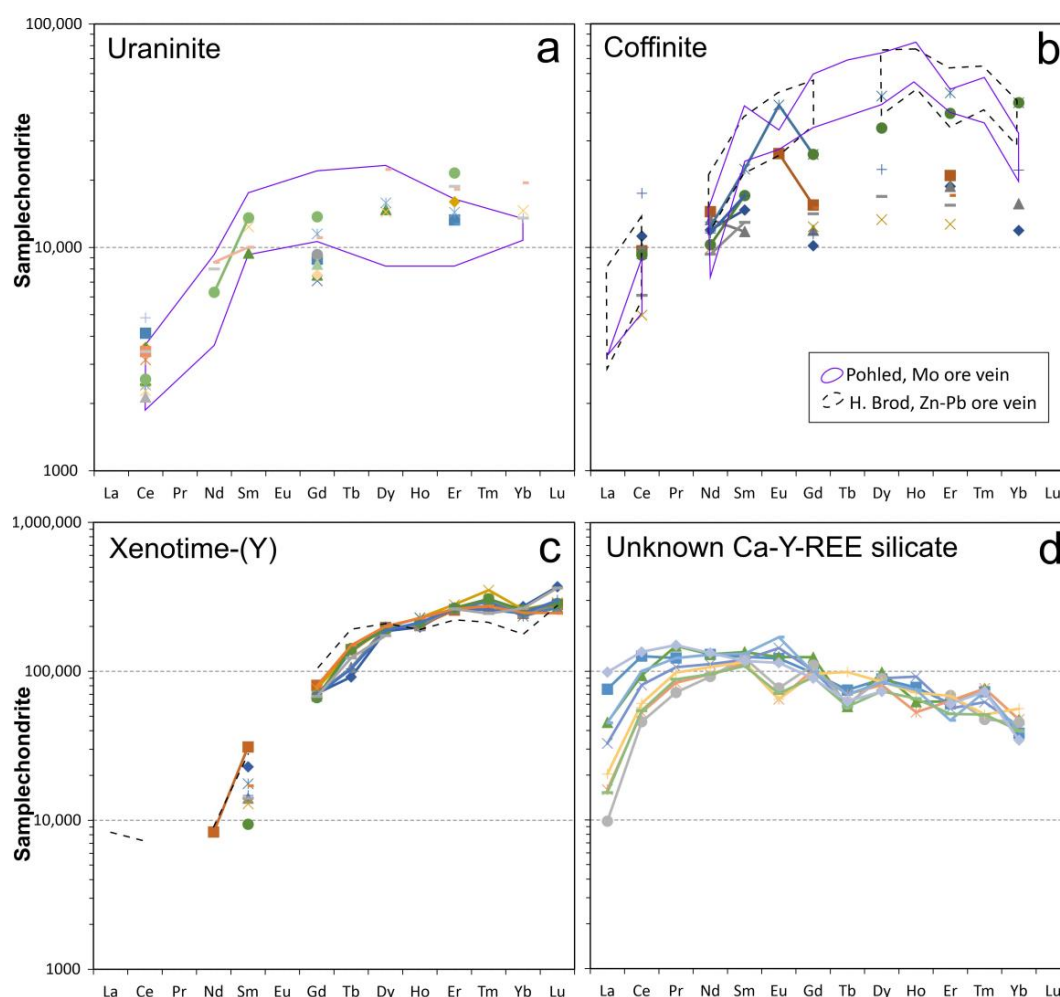


Figure 10. Chondrite-normalized REE patterns of uraninite (a), coffinite (b), xenotime-(Y) (c), and unknown Ca-Y-REE silicate (d). The comparative data are taken from [40] and [59].

Molybdenite is a characteristic minor component of the vein, which forms fine blue-grey streaks with a metallic lustre on the contact of the early quartz vein and wall rock. It is typically developed in tabular aggregates, sometimes with fan arrangement of individual subhedral tables, which reach sizes up to first tenths of a mm. Molybdenite is overgrown by wolframite, scheelite (Figure 9c), and, exceptionally, also by other sulfides including arsenopyrite, pyrrhotite I, and pyrite (Figure 9d). In reflected polarized light, the undulatory extinction of molybdenite is frequently observed.

Pyrrhotite occurs in two generations. Early pyrrhotite I is in association with other sulfides in quartz gangue (Figure 9e). It forms irregular isometric to slightly elongated xenomorphic grains and massive aggregates up to several mm in size. In contrast, pyrrhotite II occurs as individual euhedral tabular crystals with sizes up to 60 μm disseminated in the early part of late calcite (Figure 9f). No twinning or deformation is observed in polarizing microscope and the BSE imaging suggests the compositional homogeneity of both generations of pyrrhotite. The WDS analyses (Table S7) showed mostly simple compositions with undetectable or very low amounts of admixtures including Co, Ni, Pb, and Au, whose concentrations usually do not exceed 0.001 *apfu*. More elevated Ni contents were observed in pyrrhotite in two polished sections, ranging from 0.003 to 0.017 *apfu*. Pyrrhotite exhibits the usual deficit of metals against sulfur; the contents of 0.851–0.902 *apfu* of metals (=46.0–47.4 at. %) correspond largely to those of monoclinic pyrrhotite and only exceptionally to those of hexagonal pyrrhotite [61,62]. The higher metal/sulfur ratios mostly characterize later pyrrhotite II (Figure 11a). The mean empirical

formula of pyrrhotite I (based on 38 WDS analyses) is $\text{Fe}_{0.87}\text{S}_{1.00}$ and that of pyrrhotite II (based on eight WDS analyses) is $\text{Fe}_{0.89}\text{S}_{1.00}$.

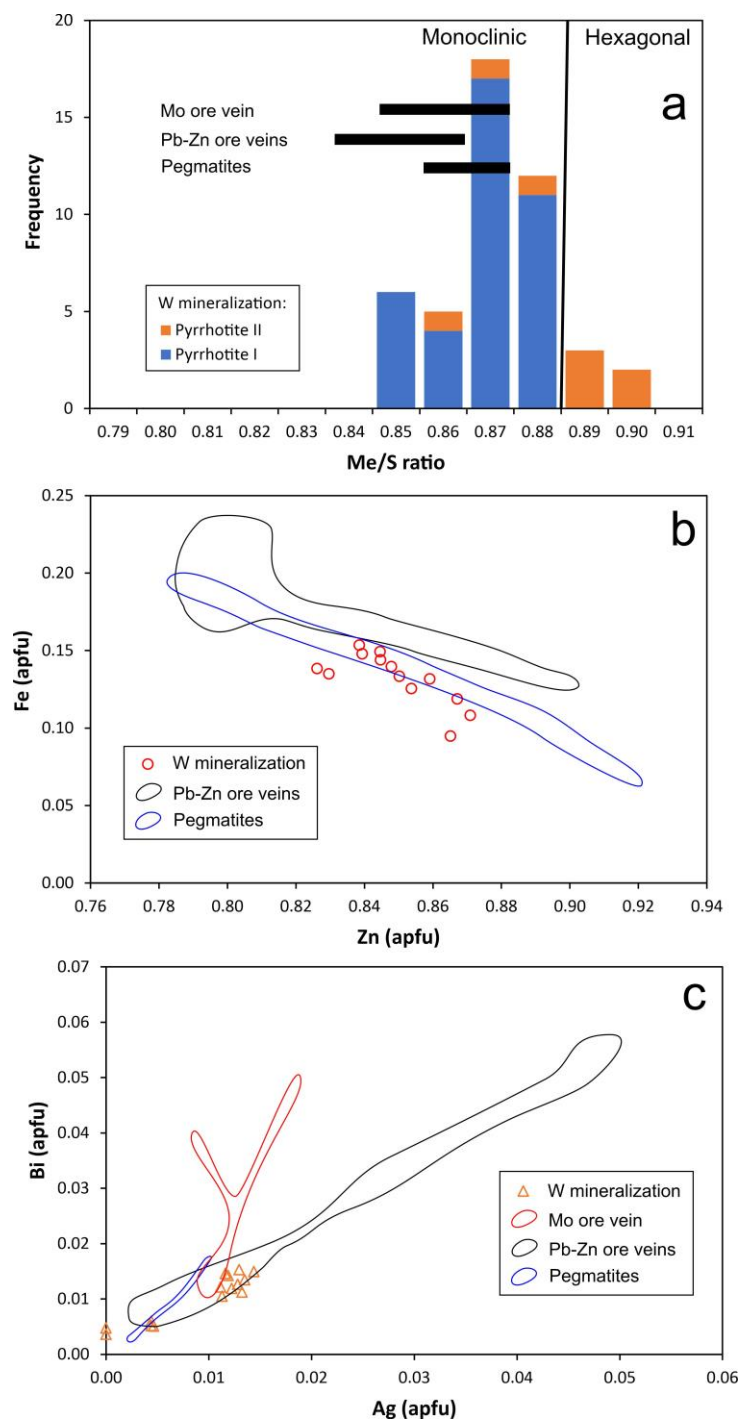


Figure 11. Variations in chemical composition of pyrrhotite (a), galena (b), and sphalerite (c) from the studied W mineralization (this work) and comparison with other mineralizations in the Pohled quarry. The boundary between monoclinic and hexagonal pyrrhotite is adopted from [62]. The comparative data are from [30,35,36,40].

Pyrite frequently occurs within sulfidic aggregates as well as in form of small monomineral accumulations, isolated grains, and veinlets across almost all associations (Figures 3a,b, 5a and 9a–d). Idiomorphic to xenomorphic pyrite grains reach up to 1 mm in size. Multiple generations of pyrite are suggested in some cases, although their exact

distinguishing is not possible in every case due to their textural similarity and chemical purity. Pyrite sometimes encloses irregular grains of arsenopyrite or pyrrhotite (Figure 12a,b). Pyrite containing pyrrhotite inclusions sometimes shows increased porosity (Figure 12a), suggesting its origin due to pyrrhotite sulfurization. In addition, minor replacement of wolframite and chlorite I by pyrite is also rather common. Pyrite is largely homogeneous in BSE, but in some grains or crystals growing together with arsenopyrite, there occur irregular lighter zones or domains enriched in As (Figure 12b). Pyrite is mostly characterized by a nearly pure composition with traces of Pb (0.001 *apfu*; Table S8); approximately one third of collected analyses showed, in addition, minor contents of Ni and Co (up to 0.003 *apfu* each), without correlation between both elements ($R^2 = 0.25$). The content of As reaches up to 0.078 *apfu* and does not correlate with either Ni or Co. The mean empirical formula of pyrite based on 31 WDS analyses and three *apfu* is $(\text{Fe}_{1.00}\text{Ni}_{0.01})_{\Sigma 1.01}(\text{As}_{0.01}\text{S}_{1.99})_{\Sigma 2.00}$.

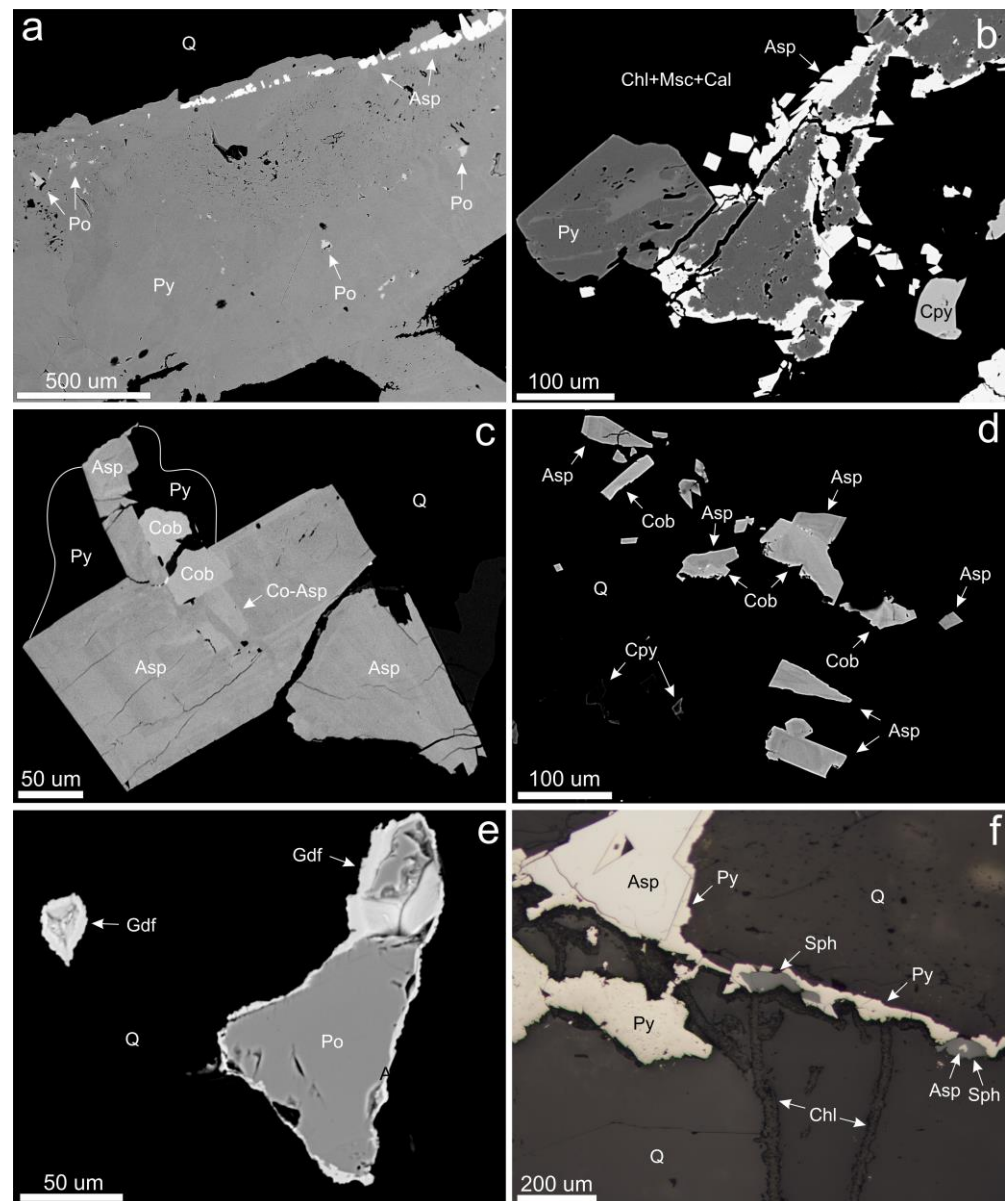


Figure 12. Mineral assemblage and development of individual minerals from the studied mineralization. (a) Finely porous pyrite containing small relics of pyrrhotite and an interposition of arsenopyrite crystals. Sample Po-78, BSE image. (b) Irregularly zoned (As contents) pyrite overgrown by arsenopyrite, in assemblage with minor chalcopyrite and gangue composed of chlorite, muscovite,

and calcite. Sample Po-75, BSE image. (c) Euhedral arsenopyrite crystal enclosing a cobaltite (Cob) core overgrown by Co-enriched arsenopyrite. The weak zonation in the outer part of arsenopyrite is caused by As/S variations only. Sulfoarsenides are overgrown by pyrite and hosted by quartz. Sample Po-78, BSE image. (d) A group of arsenopyrite and cobaltite crystals, with sporadic overgrowth of arsenopyrite on cobaltite, hosted by quartz. Sample Po-77, BSE image. (e) Gersdorffite (Gdf) rimming pyrrhotite I hosted by quartz gangue. Sample Po-75, BSE image. (f) Sulfides developed along a fracture in quartz with veinlets of chlorite II. Grains of arsenopyrite are rimmed by sphalerite (Sp) and then by pyrite. Sample Po-78, reflected light.

Arsenopyrite is a frequent but subordinate constituent of sulfidic assemblage of the studied vein mineralization. Its euhedral crystals (partly metacrysts with respect to enclosed inclusions of the host mineral phase) are usually enclosed in chlorite I, quartz, pyrite, or pyrrhotite, and are overgrown by calcite, late pyrite, galena, and/or chlorite II (Figures 3f, 9e and 12a–d). The crystals reach up to 0.5 mm in size. Less frequent are anhedral grains enclosed in pyrite. In both cases, a linear arrangement of arsenopyrite crystals/grains is frequent, reflecting their positions in ancient fractures or overgrowths on the fossil surfaces of pre-existing mineral phases (Figure 12a). The electron-microprobe study shows a chemical purity of most arsenopyrite grains based on EDS spectra, although the BSE imaging shows, even in these cases, some oscillatory or sectorial zoning due to a variable As/S ratio (Figure 12c). The spot WDS analyses (Table S9) were preferentially (but not exclusively) collected from crystals showing some admixtures on EDS spectra. These substituted grains of arsenopyrite do not exhibit systematically a different paragenetic position, size, or morphology in comparison with pure grains. Both compositional varieties often occur together as individual chemically contrast grains (Figure 12c), but separate clusters composed only of substituted grains are also observed. Exceptional are the overgrowths of pure arsenopyrite on cobaltite and/or substituted arsenopyrite (Figure 12c,d). Iron is substituted by various amounts of Co (below detection to 0.349 *apfu*), and, to much lesser extent, by Ni (up to 0.052 *apfu*; Figure 13a), and, exceptionally, in traces, by Cu, Pb, Au, and/or Zn (all below 0.010 *apfu*). Arsenic is replaced by traces of Sb (up to 0.007 *apfu*) in part of the collected analyses. The amount of S (1.012–1.153 *apfu*) always exceeds those of As (0.831–0.992 *apfu*), resulting in low (As + Sb)/(As + Sb + S) ratios ranging from 0.419 to 0.495. The correlation of the (As + Sb)/(As + Sb + S) ratio to the content of Co did not occur ($R^2 = 0.01$; Figure 13b). The average empirical formula of arsenopyrite (based on 65 WDS analyses and three *apfu*) is $(\text{Fe}_{0.96}\text{Co}_{0.04})_{\Sigma 1.00}\text{As}_{0.92}\text{S}_{1.07}$.

Cobaltite is very rare, forming small isometric to elongated euhedral to subhedral grains up to 200 μm in length, which are, in a few cases, overgrown by Co-substituted arsenopyrite and/or pure arsenopyrite (Figure 12c,d). Some grains of cobaltite are associated with sphalerite, and show, similar to arsenopyrite, linear spatial distribution. Anisotropy is not observed under a polarizing microscope. The identification is confirmed by in situ Raman analyses, showing only spectra of cobaltite and never those of glaucodot. No zoning is observed in the BSE images. A limited chemical variability is observed from the collected WDS analyses (Table S10). Cobalt is substituted by some Fe (0.130–0.235 *apfu*), and, to a lesser extent, by Ni (0.019–0.198 *apfu*; Figure 13a), whereas other admixtures, recorded in a small part of analyses, are very low (mostly <0.002 *apfu* In, Zn, Cu, and Mn). The contents of S and As oscillated strongly around stoichiometric value (0.968–1.106 and 0.891–1.017 *apfu*, respectively). The As/(As + S) ratios ranged between 0.446 and 0.511 without any correlation with the Co/(Co + Ni + Fe) ratio ($R^2 = 0.14$; Figure 13b). The average empirical formula of cobaltite (based on 26 WDS analyses and three *apfu*) is $(\text{Co}_{0.76}\text{Fe}_{0.17}\text{Ni}_{0.08})_{\Sigma 1.01}\text{As}_{0.97}\text{S}_{1.02}$.

Gersdorffite was exceptionally recorded in one polished section. It replaces quartz-hosted pyrrhotite I from its margin, forming continuous rims reaching up to 12 μm in thick (Figure 12e). Gersdorffite seems to be compositionally homogeneous in the BSE image. The WDS analyses (Table S11) revealed some substitution of Ni by Fe (0.270–0.360 *apfu*) and traces of Co (up to 0.004 *apfu*; Figure 13a), whereas As is marginally replaced by Sb (0.001–0.004 *apfu*). All collected analyses but one exhibit an excess of As (1.079–1.291 *apfu*)

and a deficit of S (0.670–0.929 *apfu*) in comparison with ideal formula. A single analysis showed opposite As–S behaviour (0.954 *apfu* As, 1.058 *apfu* S). The (As + Sb)/(As + Sb + S+Te) ratios range between 0.475 and 0.659, making gersdorffite the most As-enriched sulfoarsenide in the studied assemblage (Figure 13b). The mean empirical formula of gersdorffite (based on eight WDS analyses and 3 *apfu*) is $(\text{Ni}_{0.69}\text{Fe}_{0.31})_{\Sigma 1.00}\text{As}_{1.16}\text{S}_{0.83}$.

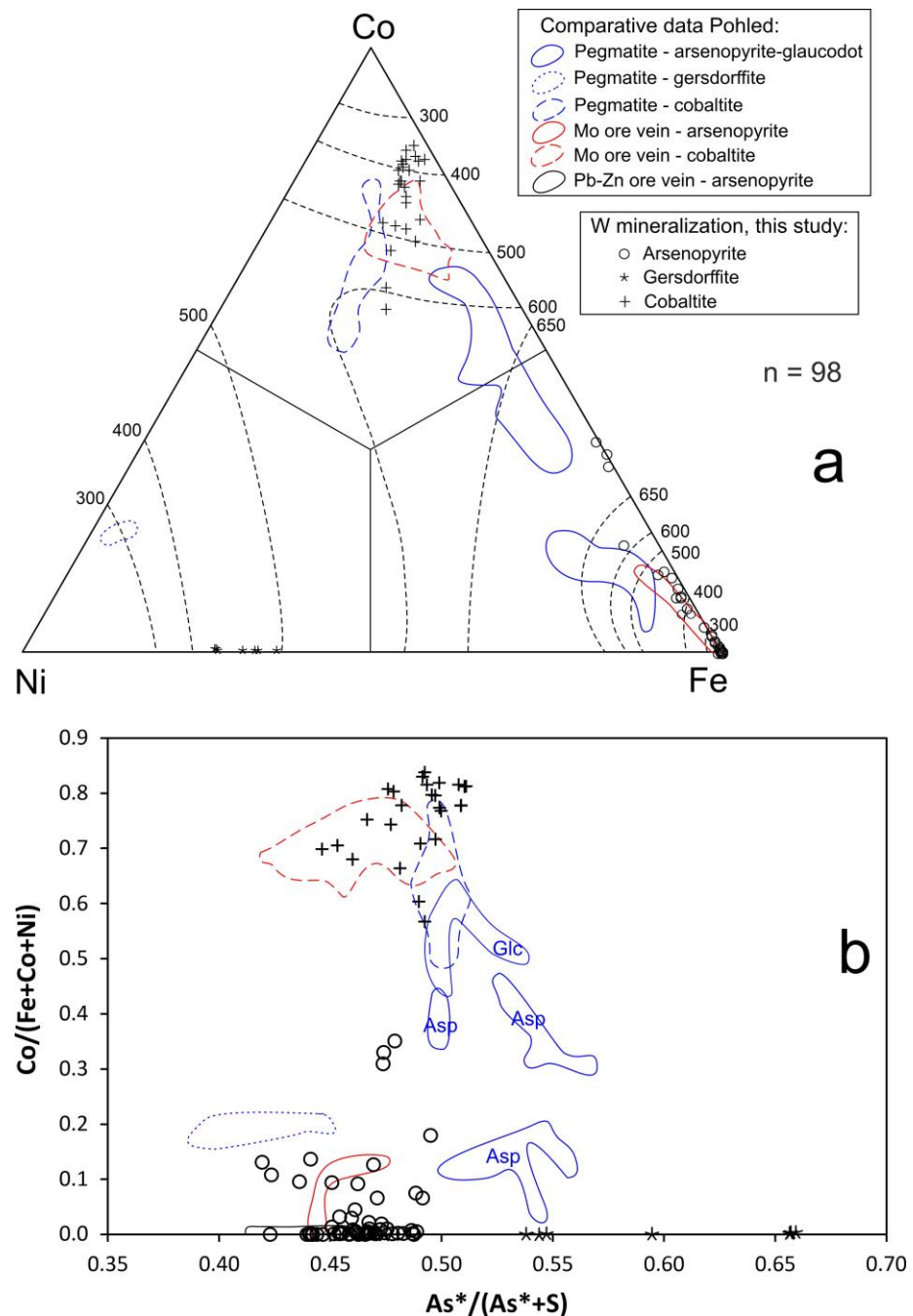


Figure 13. Variations in chemical composition of sulfoarsenides from the studied mineralization and comparison with published data from the Pohled quarry. (a) Ternary plot Fe–Co–Ni. The classification 50% boundaries and isotherms for system FeAsS–NiAsS–CoAsS according to [63] are also visualized. Note that arsenopyrite from Zn–Pb ore veins contains Fe only. (b) Plot $\text{As}^*/(\text{As}^* + \text{S})$ vs. $\text{Co}/(\text{Co} + \text{Fe} + \text{Ni})$. The comparative data for arsenopyrites from the ore veins are taken from [35,36] and those for sulfoarsenides from pegmatites from [30].

Sphalerite is a common but minor component of sulfidic assemblage. Macroscopically, it forms isometric black grains up to 5 mm associated with pyrite, arsenopyrite, pyrrhotite, and galena in quartz gangue (Figure 12f). In reflected light, xenomorphic sphalerite is isotropic and exceptionally displays dark brown internal reflections. It contains common microscopic rounded or elongated chalcopyrite inclusions (i.e., “chalcopyrite disease”). Zonality of sphalerite is not observed on the BSE images. The WDS analyses (Table S12) show rather homogeneous compositions within single grains as well as in various polished sections. Zinc is substituted especially by Fe (0.095–0.153 *apfu*; Figure 11b), and, to a lesser extent, by Cd (0.004–0.007 *apfu*), Mn (0.001–0.009 *apfu*), and Cu (mostly 0.001–0.004 *apfu*; exceptional significantly higher values up to 0.031 *apfu* are likely related to contamination of the analyzed volume by inclusions of chalcopyrite). Part of the analyses also show traces of Pb and In (below 0.0005 *apfu*). The mean empirical formula of sphalerite, based on a base of two *apfu* and 13 WDS analyses, is $(\text{Zn}_{0.85}\text{Fe}_{0.13}\text{Cu}_{0.01}\text{Cd}_{0.01})_{\Sigma 1.00}\text{S}_{1.00}$.

Galena is a late ore component in sulfidic aggregates filling the remaining open space (Figure 9e). The anhedral grains of galena attaining up to 0.5 mm form aggregates up to 3 mm across. The cleavage planes are often highlighted by triangular pits and straight course of both phenomena indicates a negligible superimposed deformation of this mineral phase. The homogeneity in the BSE images is confirmed by WDS analyses (Table S13) showing a limited chemical variability. The main minor admixtures, recorded in almost all analyses, are Ag (0.000–0.014 *apfu*) and Bi (0.004–0.015 *apfu*), whose contents correlate well mutually ($R^2 = 0.88$), suggesting a common $2\text{Pb} = \text{Ag} + \text{Bi}$ substitution (Figure 11c). A prevailing part of the analyses contain, in addition, elevated contents of Fe (up to 0.011 *apfu*) and/or Cl (up to 0.005 *apfu*). Galena, in one polished section, also contain slightly elevated Se (0.005–0.009 *apfu*). The detectable contents of Te and In (both up to 0.002 *apfu*) are rarely recorded. The average empirical formula of galena, based on two *apfu* and 15 spot WDS analyses, is $(\text{Pb}_{0.97}\text{Ag}_{0.01}\text{Bi}_{0.01})_{\Sigma 0.99}\text{S}_{1.00}$.

Chalcopyrite is a minor phase of sulfidic aggregates. It occurs either as minute round, oval or elongated, inclusions in sphalerite or larger irregular xenomorphic grains up to 30 μm in size intergrown with other sulfides (Figure 12b,d). There are found no manifestations of anisotropy including polysynthetic twinning in larger grains of chalcopyrite. The overall homogeneity observed in the BSE images is confirmed by WDS analyses (Table S14), which proved a pure composition close to the ideal formula. The mean empirical formula of chalcopyrite (based on five WDS analyses and four *apfu*) is $\text{Cu}_{1.02}\text{Fe}_{0.99}\text{S}_{2.00}$.

Violarite is a rare phase. It occurs in two forms and positions. First, its irregular, skeletal crystals, or corroded grains, up to 50 μm in size, are enclosed in calcite adjacent to pyrite (inset in Figure 14a). Second, elongated, subparallel-arranged grains of violarite up to 20 $\mu\text{m} \times 5 \mu\text{m}$ in size line elongated chlorite aggregates in calcite gangue (Figure 14a). The BSE images show the homogeneity of this mineral phase. The Me/S ratios of collected WDS analyses (Table S15) equal to 3:4 fit well to the stoichiometry of thiospinels. The compositions show only little variability (Figure 15). The major cationic constituents are Ni (1.77–1.84 *apfu*) and Fe (1.05–1.21 *apfu*), which are accompanied by minor Co (0.02–0.14 *apfu*) and, in part of the analyses, also by traces of Mn and/or Pb (both in the range of 0.001–0.004 *apfu*). The mean empirical formula of violarite (based on 21 WDS analyses and seven *apfu*) is $(\text{Ni}_{1.81}\text{Fe}_{1.11}\text{Co}_{0.08})_{\Sigma 3.00}\text{S}_{4.00}$.

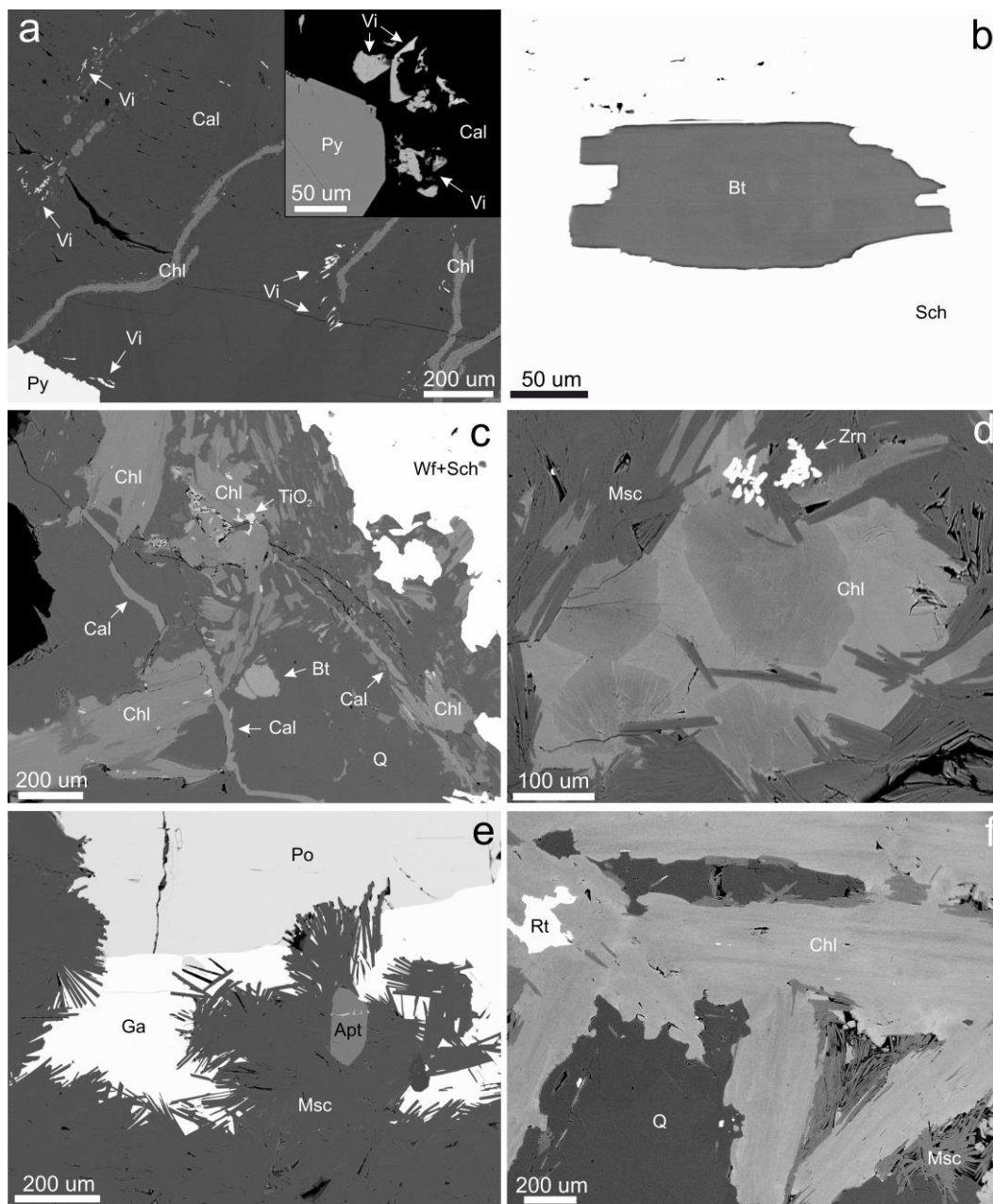


Figure 14. Mineral assemblage and development of individual minerals from the studied mineralization in BSE images. (a) Calcite containing strongly elongated aggregates of chlorite II and clusters of grains of violarite (Vi). Inset—irregular grains and a skeletal crystal of violarite adjacent to pyrite in calcite gangue. Sample Po-78. (b) An isolated table of compositionally homogeneous biotite (Bt) enclosed in scheelite I. Sample Po-73. (c) A fresh biotite grain enclosed in quartz in association with completely chloritized aggregates with inclusions of TiO_2 phases in the proximity of scheelitized wolframite. The vein is cut by late calcite veinlets. Sample Po-78. (d) Muscovite laths in an ancient drusy cavity cemented by zoned chlorite I. Muscovite encloses a group of crystals of zircon (Zrn). Sample Po-74. (e) A fossil drusy cavity lined by muscovite crystals and cemented by pyrrhotite I and galena. Muscovite encloses an apatite (Apt) crystal. Sample Po-81. (f) Elongated weakly zoned aggregates of chlorite I (likely pseudomorphs after biotite) with inclusions of rutile. Chlorite is overgrown by muscovite and quartz. Sample Po-74.

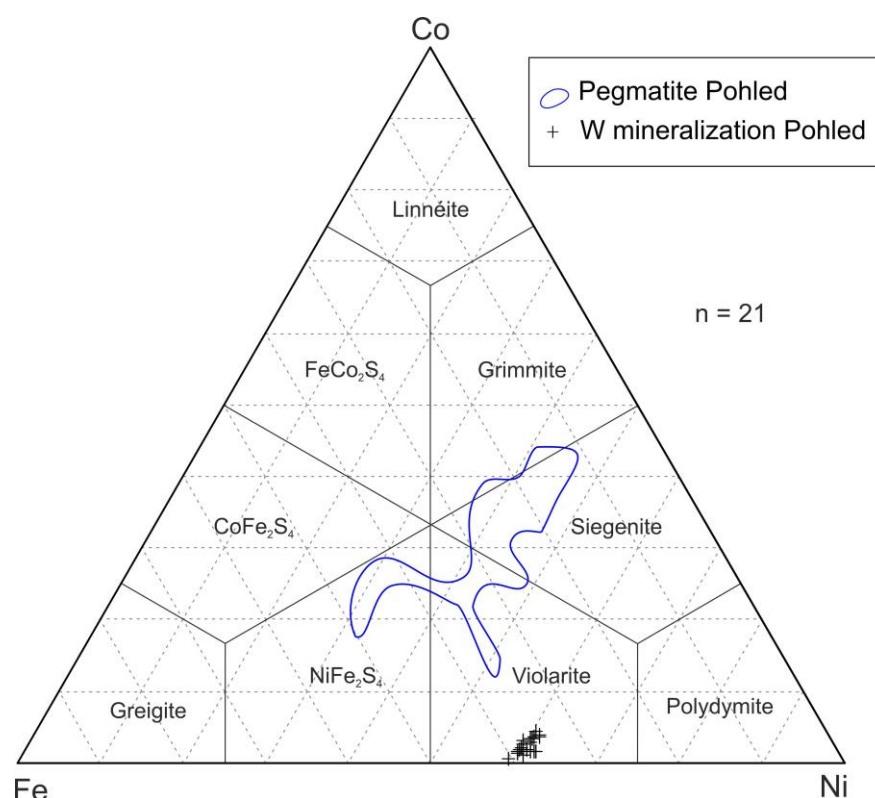


Figure 15. Variations in chemical composition of thiospinels from the studied mineralization and comparison with published data from the Pohled quarry. The classification boundaries and nomenclature are according to [64,65], the unnamed phases are marked by appropriate formulae. Comparative data are from [30].

4.1.2. Gangue and Other Accessory Minerals

Biotite is a rare mineral. It was found in few fresh isolated laths to isometric grains up to 150 μm in size, which are completely enclosed in quartz, wolframite, or scheelite I (Figure 14b). Subhedral to anhedral biotite crystals are often associated with chlorite aggregates (often containing small inclusions of titanite or TiO_2 phases) that exhibit similar shape and size as neighboring biotite (Figure 14c). Exceptionally, a polycrystalline aggregate formed by partly chloritized biotite laths was found to be enclosed in quartz. Zonality is not observed in the BSE images of biotite (Figure 14b). The WDS analyses (Table S16), recalculated to 11 atoms of oxygen, show Si contents between 2.706 and 2.913 *apfu*, Ti 0.025–0.102 *apfu*, Al 1.451–1.721 *apfu*, Mg 0.862–1.459 *apfu*, Mn 0.015–0.031 *apfu*, and Fe 1.062–1.418 *apfu*. The Fe/(Fe + Mg) ratio ranges from 0.42 to 0.62. The contents of inter-layer cations vary between 0.879 and 1.012 *apfu*, and they are dominated by K, while the contents of others are very low (<0.062 *apfu* Na, <0.009 *apfu* Ca, <0.015 *apfu* Rb). The content of F ranges 0.157–0.480 *apfu* and that of Cl 0.008–0.016 *apfu*. The obtained compositions fall just around the classification boundary of **annite** and **phlogopite** in the classification scheme by [66] (Figure 16a). The correlation between the contents of F and the Fe/(Fe + Mg) ratio was not observed (Figure 16b). The mean empirical formula of biotite (based on 36 WDS analyses) is $(\text{K}_{0.93}\text{Na}_{0.02}\text{Rb}_{0.01})_{\Sigma 0.96}(\text{Ti}_{0.06}\text{Al}_{0.42}\text{Mg}_{1.11}\text{Mn}_{0.02}\text{Fe}_{1.22})_{\Sigma 2.82}(\text{Al}_{1.20}\text{Si}_{2.80})_{\Sigma 4.00}\text{O}_{10.00}(\text{OH}_{1.73}\text{F}_{0.27})_{\Sigma 2.00}$.

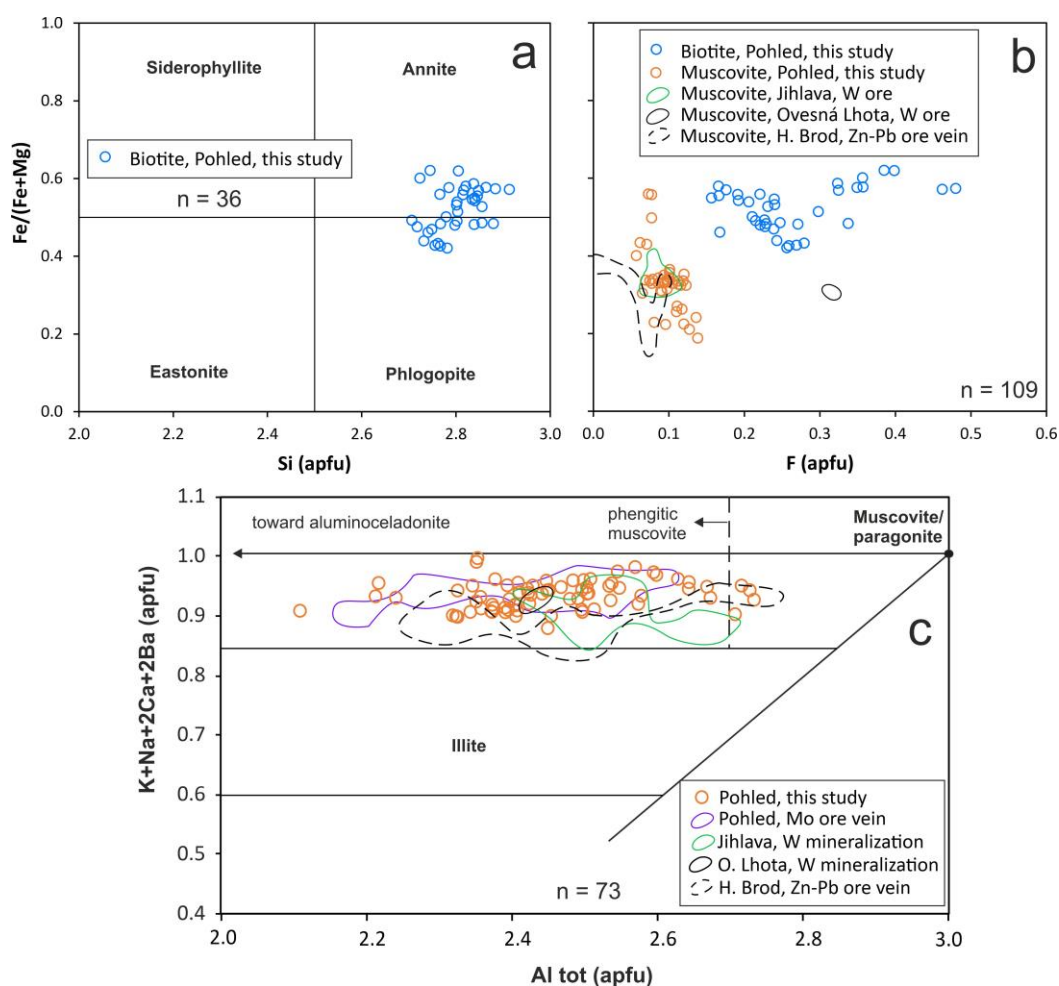


Figure 16. Variations in chemical composition of micas from the studied mineralization and comparison with published data. (a) Biotite in a Fe/(Fe + Mg) vs. Si plot sensu [66]. (b) Micas in a Fe/(Fe + Mg) vs. F plot. (c) Muscovite in the plot Al vs. sum of interlayer cations. The diagram is according to [67] with boundaries for illite modified after [66]. The comparative data are taken from [10,15,40,59].

Muscovite is a common mineral of the vein in areas close to the wall rock (Figures 5e,f and 9b,d). The anhedral to euhedral muscovite is associated especially with chlorite, molybdenite, apatite, and TiO₂ phases. Thin tables of muscovite reaching up to 0.3 mm show often radial arrangement in the youngest parts of its aggregates and are overgrown by calcite, chlorite, pyrrhotite, or galena (Figure 14d,e). No zonation is observed in the BSE images. The re-calculation of WDS analyses (Table S17) to anhydrous basis of 11 atoms of oxygen showed the Si content was always higher than the theoretical value of 3 apfu (3.073–3.341 apfu), which is compensated by lower contents of Al (2.109–2.732 apfu) and elevated contents of Mg (0.081–0.485 apfu) and Fe (0.080–0.224 apfu). The contents of interlayer cations range between 0.880 and 0.997 apfu; they are dominated by K, whereas contents of other elements are very low (<0.068 apfu Na, and in a small part of the analyses, <0.052 apfu Ca, <0.005 apfu Rb, and <0.007 apfu Ba). The content of F is low (0.051–0.172 apfu; Figure 16b). The given composition corresponds to *phengitic* muscovite (Figure 16c). The mean empirical formula of muscovite (based on 73 WDS analyses) is (K_{0.91}Na_{0.03})Σ0.94(Ti_{0.02}Al_{1.67}Mg_{0.25}Fe_{0.12})Σ2.06(Al_{0.79}Si_{3.21})Σ4.00O_{10.00}(OH_{1.91}F_{0.09})Σ2.00.

Chlorite is a relatively frequent mineral, which occurs in two generations. Early chlorite I is developed in two morphological forms. Most frequent are complete pseudomorphs after biotite, which are present in the marginal parts of the vein. They are

enclosed in quartz, and, rarely, in wolframite, scheelite, or massive sulfides. An elongated shape of these objects is typical in polished sections, with lengths reaching up to 0.5 cm (Figures 5c, 9a and 14f). This morphological variety often contains inclusions of TiO₂ phases or titanite. The identity of mineral precursor is confirmed by rarely preserved partially chloritized biotite laths and associated scarce fresh biotite inclusions completely enclosed in the host mineral (Figure 14c). No or indistinct zonality is observed in these chlorite pseudomorphs (Figure 14f). The second variety of chlorite I is represented by neomorphic chlorite, grown into open space. Massive, spherical, or hemispherical aggregates of this morphological variety overgrows early quartz and muscovite, and forms the filling of tiny veinlets in wolframite. No inclusions of Ti minerals are enclosed in this type of chlorite I. In the BSE images, a compositional zonation is frequently observed, in general, evolving from a voluminous darker core to a rather narrow brighter rim and the possible occurrence of a tiny dark interposition (Figures 14d and 17a). In general, chlorite I is stable in vacuum. Based on anhydrous basis of 14 atoms of oxygen, chlorite I contains 2.66–3.15 *apfu* Si, 2.00–2.73 *apfu* Al, 1.38–3.31 *apfu* Mg, 0.03–0.41 *apfu* Mn, and 1.21–2.99 *apfu* Fe (Table S18). In a small part of the WDS analyses, low amounts of Zn (<0.022 *apfu*), Ti (<0.019 *apfu*), V, Cr (both <0.010 *apfu*), Na (<0.081 *apfu*), K (<0.046 *apfu*), and F (<0.046 *apfu*) were encountered. The Fe/(Fe + Mg) ratios range between 0.27 and 0.69. Therefore, chlorite I belongs to trioctahedral Fe–Mg–Al chlorites of the clinochlore-chamosite series [68], which are largely classified as **clinochlore** and less frequently as **chamosite** in a classification scheme by [69]. According to the more detailed classification by [70], most analyses belong to clinochlore, fewer to chamosite and *ripidolite*, and, exceptionally, to *pennine* (Figure 18a). The mean empirical formula of chlorite I (based on 120 WDS analyses) is (Mg_{2.48}Mn_{0.09}Fe_{2.02}Al_{1.32}Ca_{0.01}Na_{0.01})_{Σ5.93}(Al_{1.15}Si_{2.85})_{Σ4.00}O_{10.00}(OH_{7.99}F_{0.03})_{Σ8.00}.

Late chlorite II is less frequent and grows into residual open space over quartz, sulfides, chlorite I, and early calcite and is overgrown by late calcite (Figures 14a and 17a,b). Chlorite II lacks inclusions of TiO₂ phases and/or titanite and is less stable in vacuum, as is indicated by frequently observed desiccation cracks (Figure 17a,b). The zonality sporadically observed in BSE images is usually attributed to various porosity of individual growth zones than compositional variations. The WDS analyses (Table S18) reveal that chlorite II contains higher Si, Fe, and Ca and lower Al and Mg than chlorite I. The Si contents range from 3.06 to 3.58 *apfu*; Al contents range from 0.94 to 2.13 *apfu*, Mg from 0.64 to 2.68 *apfu*, Mn from 0.01 to 0.23 *apfu*, Fe from 1.69 to 4.93 *apfu*, and Ca from 0.04 to 0.15 *apfu*. In a small part of the collected analyses, low amounts of Zn, Co, Ni (all <0.014 *apfu*), Na (<0.081 *apfu*), and K (<0.010 *apfu*) were recorded. The Fe/(Fe + Mg) ratios range between 0.39 and 0.88. Chlorite II thus also belongs to the clinochlore-chamosite series; it is mostly classified as **chamosite** and exceptionally as **clinochlore** sensu [69]. According to the classification by [70], there occurs mostly *delessite* and only exceptionally *pennine* and chamosite (Figure 18a). The mean empirical formula of chlorite II (based on 35 WDS analyses) is (Mg_{1.04}Mn_{0.09}Fe_{3.60}Al_{1.01}Ca_{0.08}Na_{0.02})_{Σ5.84}(Al_{0.70}Si_{3.30})_{Σ4.00}O_{10.00}(OH)_{8.00}. A positive correlation (although not tight) between Si and the sum of alkalis and Ca points to the presence of smectite/mica component in the studied chlorites, which is significant especially in late chlorite II (Figure 18b). Easy dehydration in a vacuum prefers the smectite possibility.

K-feldspar was recorded only once in a veinlet cutting the quartz–wolframite–scheelite I vein fill. It is associated with quartz, pyrite, scheelite II, and late calcite. Euhedral crystals of K-feldspar with typical adularia morphology grow directly on the walls of the veinlet and reach up to 90 µm in size (Figures 3e and 17c). No zoning is observed in the BSE images. The chemical composition (Table S19) suggests the predominance of orthoclase with low admixtures of albite (1.3–4.3 mol. %), anorthite (0.0–1.0 mol. %), celsian (0.0–0.7 mol. %), and rubicline (0.0–0.7 mol. %) components. The mean empirical formula of adularia from Pohled, based on 15 WDS analyses, is (K_{0.97}Na_{0.02})_{Σ0.99}(Al_{1.00}Si_{3.00})_{Σ4.00}O_{8.00}.

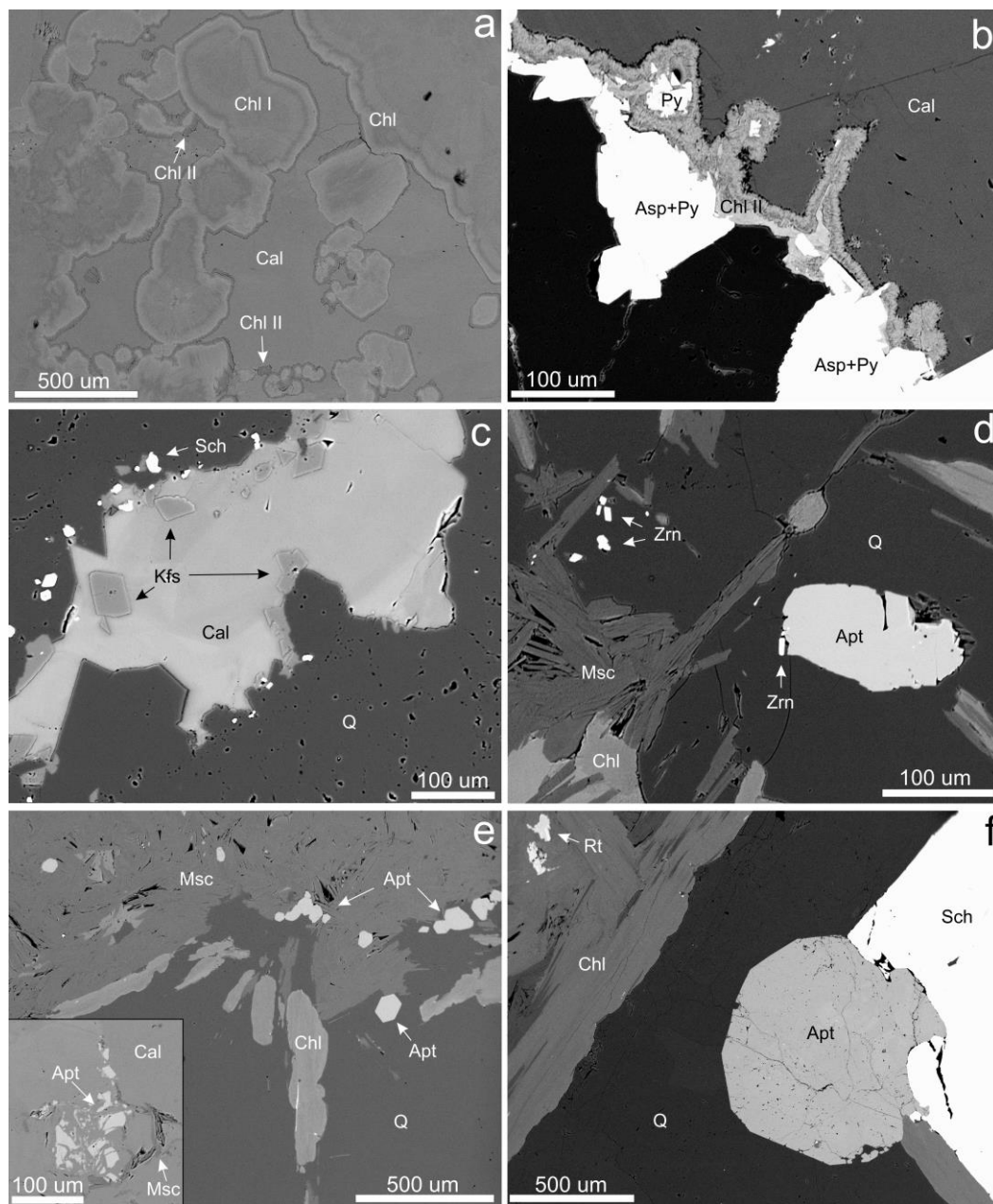


Figure 17. Mineral assemblage and development of individual minerals from the studied mineralization in BSE images. (a) Strongly zoned aggregate of chlorite I with thin outermost darkest zone of chlorite II. Residual porosity is cemented by calcite. Sample Po-79. (b) Zoned layer of chlorite II coating quartz-pyrite-arsenopyrite vein and followed by calcite. Sample Po-78. (c) Euhedral crystals of adularia with scheelite and quartz growing in a fracture of quartz gangue cemented by calcite. Sample Po-73. (d) A grain of apatite enclosed together with minute crystals of zircon hosted by quartz-muscovite-chlorite gangue. Sample Po-74. (e) Euhedral crystals of apatite together with muscovite and chlorite I overgrown by quartz. Inset—apatite strongly corroded by calcite. Sample Po-81. (f) Euhedral crystal of apatite growing over a crystal of scheelite, in assemblage with aggregates of chlorite I (likely pseudomorphs after biotite) with inclusions of rutile and late quartz. Sample Po-74.

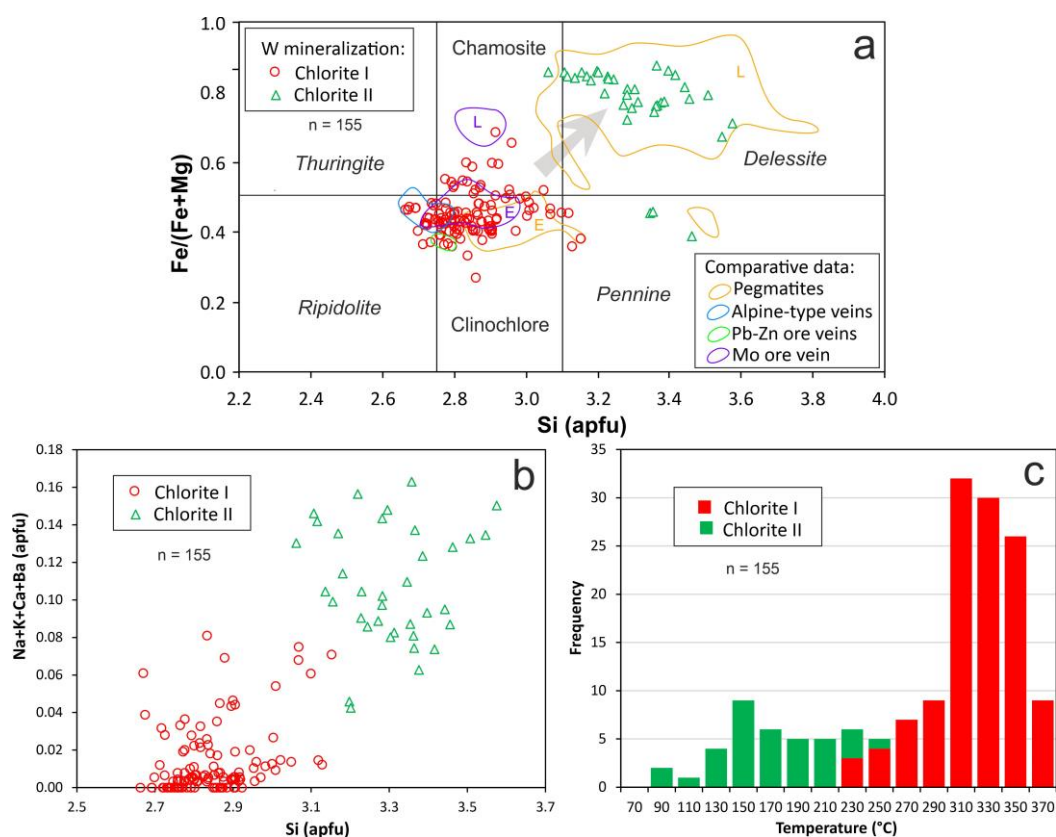


Figure 18. Variations in chemical composition of chlorite from the studied mineralization and comparison with published data from the Pohled quarry. (a) Chlorite I and II in classification scheme Si vs. $\text{Fe}/(\text{Fe} + \text{Mg})$ after [70]. The IMA-non-valid mineral names are italicized. The comparative data are taken from [29,35,36,40]. Letters E and L refer to early and late chlorite, respectively. Arrow refers to evolutionary trend. (b) Plot Si vs. $\text{Na} + \text{K} + \text{Ca} + \text{Ba}$. (c) Histogram of formation temperatures calculated by chlorite compositional thermometry according to [71].

Titanite is a rare mineral, which occurs almost exclusively in association with chlorite I formed at the expense of biotite. It substitutes the occurrence of TiO_2 mineral in the same position. In a few cases, titanite consumes TiO_2 minerals from the margins (Figure 5d). Titanite occurs as anhedral, irregularly shaped, and mostly elongated aggregates, which reach up to 20 μm in length (Figure 5f). No significant zonation is observed in the BSE images, but different grains differ in composition. Silica is slightly substituted by P (0.002–0.010 apfu; recalculated to basis of three cations per formula unit, Table S20). Calcium is in some cases slightly replaced by Sc (<0.041 apfu), Y (<0.004 apfu) and LREE (<0.006 apfu La + Ce + Nd). Titanium is substituted especially by Al (0.114–0.345 apfu), and, in part of the collected analyses, also by Nb (<0.070 apfu), Fe (<0.046 apfu), V (<0.017 apfu), and Sn and Zr (both <0.001 apfu). Elevated contents of F (0.082–0.269 apfu) were recorded in all analyses and its contents correlate well with Al ($R^2 = 0.87$). The mean empirical formula of titanite (based on 18 WDS analyses) is $(\text{Ca}_{0.98}\text{Sc}_{0.01})_{\Sigma 0.99}(\text{Ti}_{0.72}\text{Al}_{0.24}\text{Nb}_{0.02}\text{Fe}_{0.01})_{\Sigma 0.99}\text{Si}_{1.00}\text{O}_{4.91}\text{F}_{0.19}$.

Apatite is a minor constituent of the vein. A relatively frequent accessory mineral is the apatite in marginal parts of the vein, where it associates with chlorite, muscovite, and TiO_2 minerals. Isolated subhedral to euhedral hexagonal sections up to 100 μm in size are typically found here (Figures 14e and 17d,e). Exceptional was a find of a corroded apatite grain strongly consumed by calcite (inset in Figure 17e). In addition, anhedral to euhedral grains of apatite are sporadically found also in inner parts of the quartz vein. An isometric euhedral crystal, 0.6 mm across, was found to grow on a scheelite crystal (Figure 17f). All observed varieties of apatite appear homogeneous in BSE images. The WDS analyses (Table S21) reveal that they are all chemically similar

stoichiometric fluorapatites (2.972–3.025 *apfu* P and 0.936–1.346 *apfu* F; based on five cations in the position of Ca) with low admixtures of Y (0.011–0.022 *apfu*), Mn (0.007–0.026 *apfu*), and, exceptionally, also Fe (<0.030 *apfu*) and/or Cl (<0.015 *apfu*). The observed high F, in all but three analyses exceeding the theoretical stoichiometric maximum, is likely related to the easy diffusion of F in apatite crystals unsuitably oriented with respect to incident electron beam [72]. The average empirical formula of apatite (based on 16 WDS analyses) is $(\text{Ca}_{4.97}\text{Y}_{0.01}\text{Mn}_{0.01}\text{Fe}_{0.01})_{\Sigma 5.00}\text{P}_{2.99}\text{O}_{11.92}(\text{F}_{1.15}\text{Cl}_{0.01})_{\Sigma 1.16}$.

Zircon was rarely recorded in marginal part of the vein in assemblage with quartz, phyllosilicates, apatite, and uraninite. The most frequent were tiny euhedral zircon inclusions up to 7 μm in size, usually forming clusters in quartz or phyllosilicates (Figures 14d and 17d). They appear homogeneous in the BSE image and yielded WDS analyses (Table S22) with satisfactory analytical totals and stoichiometry. In contrast, one larger (30 μm) euhedral zircon crystal was found in assemblage with uraninite, chalcopyrite, and pyrite in calcite-muscovite matrix (Figure 19a). This zircon showed patchy appearance in BSE image, partial replacement by pyrite from margins, instability under focused electron beam, low analytical totals of WDS analyses, and poor stoichiometry. We suggest a pronounced metamictization of the latter crystal, which is enriched in REE (up to 0.202 *apfu*; *apfu* values are based on four atoms of oxygen), Y (up to 0.160 *apfu*), Ca (up to 0.093 *apfu*), Al (up to 0.038 *apfu*), Mn, Th, and As (all up to 0.004 *apfu*) in comparison with fresh zircon. Minor admixtures of P (0.015–0.064 *apfu*), Hf (0.011–0.021 *apfu*), Sc (0.003–0.016 *apfu*), U (0.002–0.012 *apfu*), Fe (0.002–0.026 *apfu*), Sr (<0.006 *apfu*), and K (<0.004 *apfu*) are similar in both zircon types. Fresh zircon yielded the following mean empirical formula based on six spot WDS analyses: $(\text{Zr}_{0.94}\text{Y}_{0.02}\text{REE}_{0.02}\text{Hf}_{0.02}\text{U}_{0.01}\text{Sc}_{0.01}\text{Ca}_{0.01}\text{Fe}_{0.01})_{\Sigma 1.04}(\text{Si}_{0.95}\text{P}_{0.03})_{\Sigma 0.98}\text{O}_{4.00}$, whereas the empirical formula of metamictised zircon (mean of three WDS analyses) is $(\text{Zr}_{0.83}\text{Y}_{0.14}\text{REE}_{0.18}\text{Ca}_{0.08}\text{Al}_{0.03}\text{Hf}_{0.01}\text{Fe}_{0.01})_{\Sigma 1.28}(\text{Si}_{0.90}\text{P}_{0.02})_{\Sigma 0.92}\text{O}_{4.00}$.

Xenotime-(Y) was found as a single subhedral grain reaching 100 μm in size, which was enclosed at the boundary between a brookite crystal and phyllosilicate matrix in marginal part of the vein (Figure 19b). Its chemical composition is very homogeneous, which is manifested by both the BSE image and the spot WDS analyses (Table S23). The 19%–22% of Y atoms are substituted by REE; in traces, there occur also Zr (0.002–0.008 *apfu*; base of *apfu* calculation are four atoms of oxygen), Ca (0.002–0.007 *apfu*), and, in a smaller part of collected analyses, also Fe (<0.013 *apfu*). The chondrite normalized REE patterns show a minimum variability with a continuous increase of abundances with increasing atomic number (Figure 10c). The smooth shape of the patterns is interrupted by negative Eu ($\text{Eu}/\text{Eu}^* = <0.36$ –<0.72) and weak negative Yb ($\text{Yb}/\text{Yb}^* = 0.82$ –0.95) anomalies. The chondrite normalized Gd/Yb_{CN} ratio has almost constant values between 0.26 and 0.33. Xenotime-(Y) yielded the following mean empirical formula based on nine spot WDS analyses: $(\text{Y}_{0.78}\text{Gd}_{0.02}\text{Tb}_{0.01}\text{Dy}_{0.06}\text{Ho}_{0.01}\text{Er}_{0.05}\text{Tm}_{0.01}\text{Yb}_{0.05}\text{Lu}_{0.01})_{\Sigma 1.00}\text{P}_{1.00}\text{O}_{4.00}$.

An unknown **Ca-Y-REE silicate** with analytical totals of WDS analyses (Table S24) around 84 wt.% is an extremely rare phase. It was found as a single isometric xenomorphic grain reaching 20 μm in size, which is enclosed in late calcite overgrowing early calcite with numerous inclusions of pyrrhotite II. Calcite gangue fills a small drusy cavity in quartz. In the BSE image, the mineral displays an apparent zonation (Figure 19c) with a darker margin (richer in Ca) and a brighter core (richer in REE + Y). The overall silica-to-metals ratio of the collected WDS analyses is close to 1, suggesting stoichiometry of either caysichite-(Y) or kainosite-(Y). However, significant deviations from the ideal formulae of both minerals exist in a cationic part of formula, manifested by low Y contents, high REE and Fe contents, and a predominance of LREE over HREE. The contents of Si range from 3.97 to 4.03 *apfu* (*apfu* values are calculated to sum of Si and metallic cations equal to eight atoms); those of Ca range from 1.23 to 1.89 *apfu*, REE from 0.83 to 1.40 *apfu*, Y from 0.87 to 1.00 *apfu*, and Fe from 0.31 to 0.40 *apfu*. Minor components are Al and Mg (both ranging from 0.01 to 0.04 *apfu*), and, in a few analyses, Sc (up to 0.02 *apfu*). The average partial (probably present volatiles are not included) empirical formula based on the sum of eight cations and nine WDS analyses is $(\text{Ca}_{1.58}\text{Mg}_{0.02}\text{Fe}_{0.35}\text{Al}_{0.02})_{\Sigma 1.97}\text{Y}_{0.95}(\text{Sc}_{0.01}\text{La}_{0.05}\text{Ce}_{0.28}\text{Pr}_{0.05}\text{Nd}_{0.28}\text{Sm}_{0.09}\text{Eu}_{0.03}\text{Gd}_{0.10}\text{Tb}_{0.01})_{\Sigma 1.00}\text{P}_{1.00}\text{O}_{4.00}$.

$\text{Dy}_{0.10}\text{Ho}_{0.01}\text{Er}_{0.04}\text{Tm}_{0.01}\text{Yb}_{0.05}\text{Lu}_{0.01}\text{Si}_{3.99}$. The identity of the mineral was also checked with the aid of Raman spectroscopy; however, the obtained spectrum (Figure 20) does not fit to the available spectra of any known mineral including caysichite-(Y) and kainosite-(Y). The Raman spectrum suggests the presence of water in the crystal structure. Bands in the region between 3300 and 3400 cm^{-1} are assigned to the ν OH stretching vibrations of hydrogen-bonded hydroxyls and hydrogen-bonded water molecules [73]. The chondrite-normalized REE patterns (Figure 10d) show first increase from La to Sm and then decrease towards Yb with a more pronounced zig-zag shape of patterns at heavy REE. The shape of the patterns is broken by an Eu anomaly, which tends to be more negative ($\text{Eu}/\text{Eu}^* = 0.60\text{--}0.71$) in Ca-rich parts and more positive ($\text{Eu}/\text{Eu}^* = 0.96\text{--}1.46$) in REE + Y-rich parts of the crystal. The first tetrad (La–Nd) is in both cases characterized by an instructively developed M-type tetrad effect ($\text{TE}_1 = 1.24\text{--}1.91$; Figure 10d). The rather flat shape of the patterns is illustrated by low $\text{Nd}/\text{Yb}_{\text{CN}}$ ratios between 1.91 and 3.85.

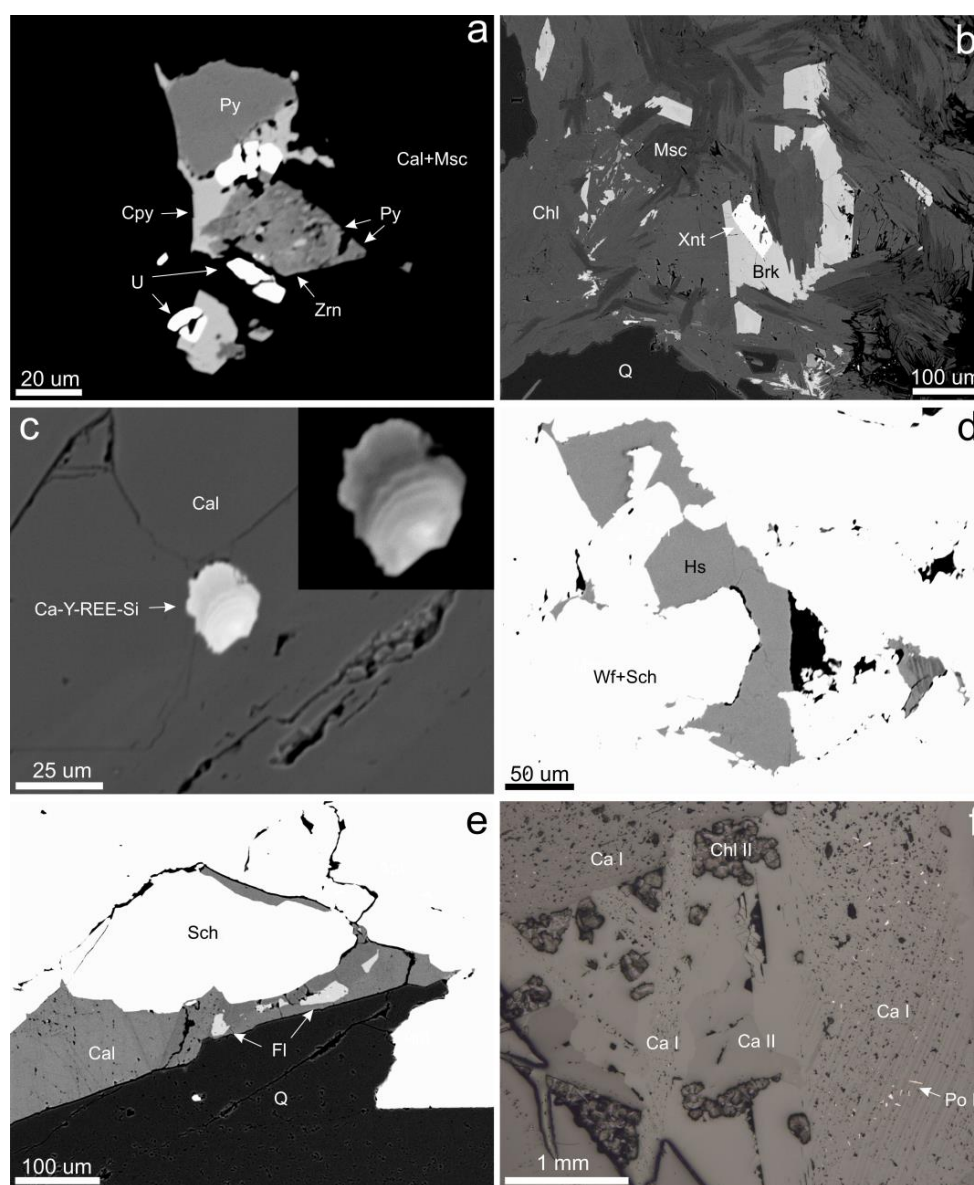


Figure 19. Mineral assemblage and development of individual minerals from the studied mineralization. (a) A euhedral crystal of zircon partly replaced by pyrite, rimmed by grains of uraninite, chalcopryrite, and pyrite in a calcite-muscovite gangue. Sample Po-81, BSE image. (b) Euhedral xenotime-(Y) (Xnt) overgrown by brookite in a matrix composed of chlorite and muscovite. Sample Po-77,

BSE image. (c) A xenomorphic zoned grain of an unknown Ca-Y-REE silicate (Ca-Y-REE-Si) hosted by calcite. Inset—highlighted zonation of the same grain. Sample Po-79, BSE images. (d) Homogeneous hisingerite (Hs) fills vugs in altered wolframite. Sample Po-76, BSE image. (e) Scheelite corroded by calcite along the boundary with quartz gangue. Calcite contains inclusions of fluorite. Sample Po-30, BSE image. (f) Two generations of calcite separated by chlorite II. Calcite I is more porous and contains inclusions of pyrrhotite II, whereas calcite II is homogeneous and without mineral inclusions. Sample Po-79, reflected light.

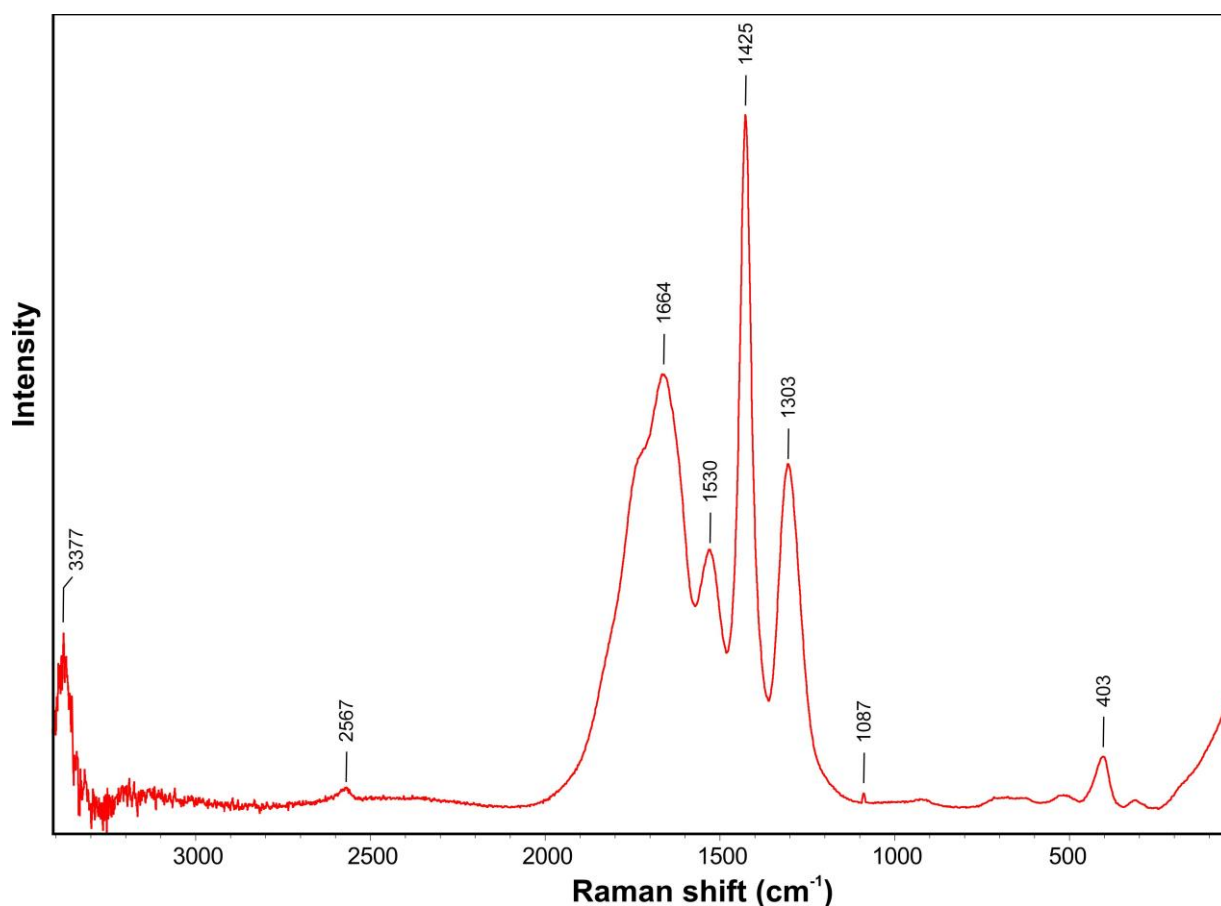


Figure 20. Raman spectrum (laser 780 nm) of the unknown Ca-Y-REE silicate from Pohled.

Hisingerite was found in two polished sections only. It fills irregularly shaped residual cavities reaching up to 100 μm in size hosted by wolframite altered to scheelite. In reflected light, the mineral shows good transparency indicated by strong whitish internal reflections. In BSE image, hisingerite aggregates are homogeneous and massive, with desiccation cracks likely produced by loss of water in vacuum of microprobe chamber (Figure 19d). Recalculation of the collected WDS analyses (Table S25) to an anhydrous base of 7 O atoms shows rather poor stoichiometry, probably reflecting the amorphous or poorly crystalline nature. The contents of Si are always deficient (1.788–1.825 *apfu*). Trivalent iron (1.686–1.882 *apfu*) is substituted especially by Mg (0.137–0.172 *apfu*) and Mn (0.176–0.337 *apfu*), and, to a lesser extent, by Al (0.014–0.051 *apfu*), Ca (0.003–0.011 *apfu*), and, exceptionally, by traces of monovalent cations (<0.011 *apfu* Na and <0.003 *apfu* K). Hydroxyl is sometimes replaced by traces of Cl (<0.003 *apfu*). The mean empirical formula of hisingerite from Pohled based on 13 spot WDS analyses is $(\text{Fe}_{1.82}\text{Mn}_{0.22}\text{Mg}_{0.16}\text{Al}_{0.03}\text{Ca}_{0.01})_{\Sigma 2.24}\text{Si}_{1.81}\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$.

Fluorite is a rare mineral. It was encountered in various paragenetic positions in a late calcite veinlet corroding scheelite (Figure 19e) as well as in a quartz–molybdenite–chlorite I

assemblage in the marginal part of the vein. It forms anhedral isometric grains reaching up to 200 μm in size. Its EDS spectra showed only Ca and F.

Calcite is a late mineral phase filling tiny fractures or residual drusy cavities in the earlier vein. It occurs in at least two generations, which are mutually separated by chlorite II. Early calcite I is coarse-grained to tabular and macroscopically grey as it hosts numerous minute crystals of pyrrhotite II (Figure 19f). Late calcite II is white and exceptionally encloses violarite inclusions (Figure 14a). The parallelization of other occurrences of calcite with these two distinct generations is not possible due to both differences in chemistry and lack of characteristic mineral inclusions or texture. Calcite also overgrows crystals of scheelite II, adularia, and quartz in a veinlet cutting the early vein (Figures 3e and 17c). In marginal parts of the vein, calcite replaces early phyllosilicates (muscovite and chlorite I), and, exceptionally, also apatite (inset in Figure 17e). Although lacking Mg in all collected WDS analyses, the composition of calcite (Table S26) varies significantly in terms of Fe and Mn contents ($\text{Ca}_{98.1-99.9}\text{Rdc}_{0.0-1.7}\text{Sid}_{0.0-0.8}$). The mean empirical formula of calcite based on 11 spot WDS analyses and one metallic cation is $(\text{Ca}_{0.99}\text{Mn}_{0.01})_{\Sigma 1.00}\text{CO}_3$.

4.2. Fluid Inclusions

The fluid inclusion study was conducted on four samples, which came from the two finds in the years 2020 (sample Po-30) and 2023 (samples Po-79, Po-81, Po-83). Samples Po-30 and Po-79 included quartz gangue with enclosed scheelite and wolframite. Sample Po-81 is a portion of the quartz vein rich in sulfides, chlorite, and muscovite, which is found along the contact with wall rocks cut by late calcite veinlet. Sample Po-83 is formed by quartz gangue in the vicinity of an ancient drusy cavity filled up by chlorite and calcite. Exclusively aqueous fluid inclusions were found in all samples.

Scheelite hosts abundant primary, pseudosecondary and secondary two-phase (L + V) fluid inclusions. Primary and pseudosecondary inclusions have a low degree of fill ($F = 0.6-0.8$), a size usually between 8 and 50 μm , and an often regular morphology close to the shape of a negative crystal. The primary inclusions occur either in three-dimensional clusters or as solitary inclusions (Figure 21a). Pseudosecondary inclusions are situated along variably long trails that do not cut the whole scheelite grain (Figure 21b,c). Secondary fluid inclusions are arranged along continuous trails and show an irregular morphology and a higher degree of fill ($F = 0.90-0.95$; Figure 21d). The relative chronology was confirmed by refilling phenomena in a group of primary inclusions cut by a trail of secondary fluid inclusions. Most of the present inclusions have a dark appearance, making the microthermometric measurements complicated. Primary and pseudosecondary fluid inclusions yielded much higher homogenization temperatures (311–375 $^{\circ}\text{C}$; Table 1) than secondary inclusions (109–290 $^{\circ}\text{C}$). Few differences between the various genetic groups of inclusions are observed in the cryometric parameters. Inclusions froze at temperatures from -52 to -34 $^{\circ}\text{C}$, whereas they became slightly darker. The first melting was observed at temperatures between -37 and -34 $^{\circ}\text{C}$. The last ice melted at temperatures ranging between -2.0 to -5.2 $^{\circ}\text{C}$ and -0.6 to -5.3 $^{\circ}\text{C}$ for P + PS and S inclusions, respectively.

Table 1. Summary of results of microthermometry of fluid inclusions. Temperature parameters are in $^{\circ}\text{C}$, salinity in wt. % NaCl eq. Numbers in parentheses refer to number of measurements. Explanations: Gen—genetic classification of inclusions, P—primary inclusions, PS—pseudosecondary inclusions, S—secondary inclusions, L—liquid, V—vapor, Th—homogenization temperature (to liquid in all cases), Tf—freezing temperature, Te—eutectic temperature, Tm_{ice} —temperature of melting of ice, n.d.—not determined.

Sample	Mineral	Gen.	Phase Comp.	Th (L)	Tf	Te	Tm_{ice}	Salinity
Po-30	Scheelite	P, PS	L + V	311–366 (47)	$-42/-40$	$-37/-35$	$-2.0/-5.2$ (31)	3.4–8.1
Po-30	Scheelite	S	L + V	114–290 (30)	$-50/-42$	$-38/-35$	$-1.0/-5.3$ (19)	1.7–8.3
Po-30	Quartz	P, PS	L + V	160–313 (64)	$-49/-37$	$-38/-35$	$-2.0/-6.3$ (70)	3.4–9.6

Table 1. Cont.

Sample	Mineral	Gen.	Phase Comp.	Th (L)	Tf	Te	Tm _{ice}	Salinity
Po-30	Quartz	S	L + V, L	72–128 (4)	−42/−37	−37	−1.6 (2)	2.7
Po-30	Calcite	P, PS	L + V	150–221 (29)	−50/−43	−39/−35	−3.8/−4.9 (21)	6.2–7.7
Po-30	Calcite	S	L + V	140–156 (12)	−41/−38	n.d.	−0.2/−0.5 (9)	0.4–0.9
Po-79	Scheelite	P, PS	L + V	348–375 (24)	−52/−34	−37/−34	−2.6/−3.6 (19)	4.3–5.9
Po-79	Scheelite	S	L + V	109–212 (16)	−45/−38	−35/−34	−0.6/−3.1 (12)	1.1–5.1
Po-79	Quartz	P, PS	L + V	138–200 (27)	−50/−47	−39/−36	−3.9/−5.5 (23)	6.3–8.5
Po-79	Quartz	S	L + V, L	129–159 (10)	−42/−32	−35	−1.1/−2.4 (7)	1.9–4.0
Po-81	Quartz	P, PS	L + V	119–324 (52)	−51/−48	−38/−35	−2.7/−5.4 (49)	4.5–8.4
Po-81	Quartz	S	L + V, L	77–151 (11)	−50/−35	−36	−3.7/−5.4 (5)	6.0–8.4
Po-81	Calcite	P, PS	L + V, L	105–142 (23)	−48/−41	−35	−0.3/−3.8 (6)	0.5–6.2
Po-81	Calcite	S	L, L + V	86–115 (9)	−42/−40	n.d.	−0.2/−0.3 (3)	0.4–0.5
Po-83	Quartz	P, PS	L + V	122–249 (48)	−55/−48	−41/−34	−2.6/−8.8 (51)	4.3–12.6
Po-83	Calcite	P, PS	L + V	186–245 (11)	−50/−39	−35	−1.7/−5.5 (11)	2.9–8.5
Po-83	Calcite	S	L + V	126–182 (9)	−42/−40	n.d.	−0.1/−1.2 (5)	0.2–2.1

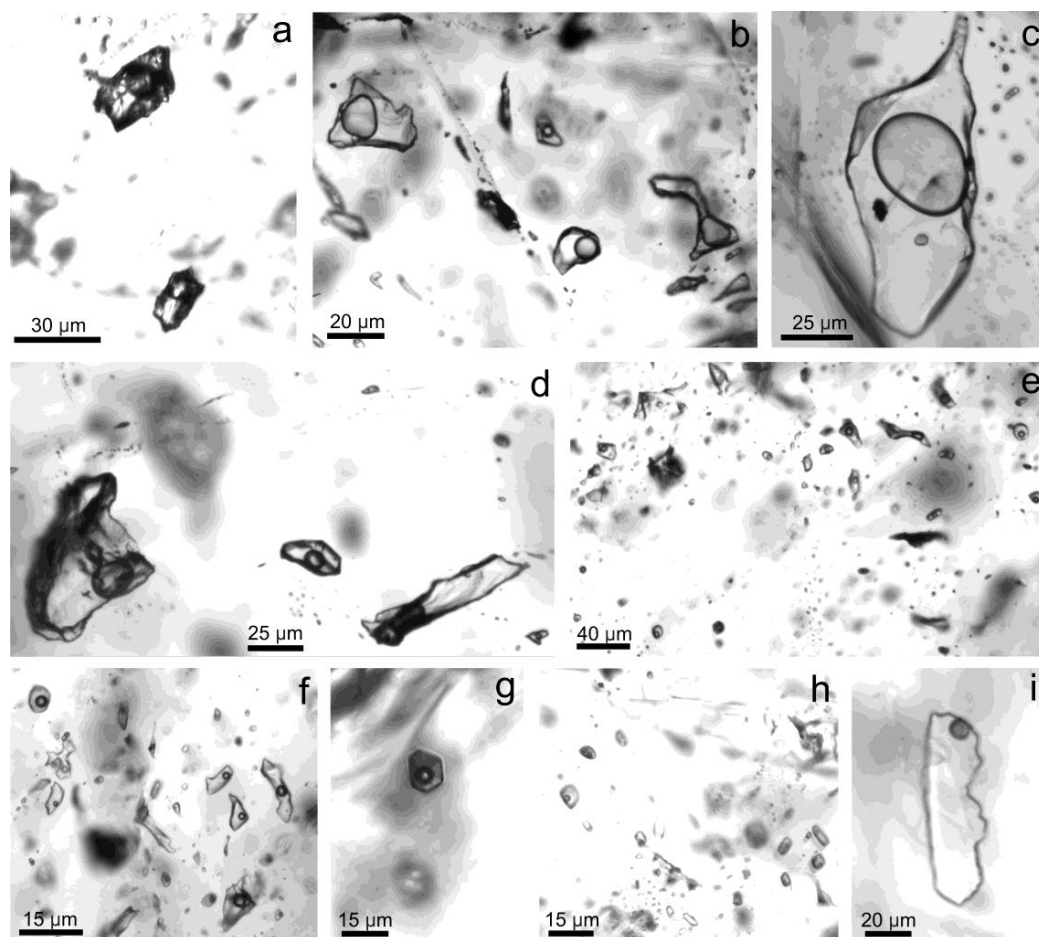


Figure 21. Appearance of fluid inclusions from the studied mineralization. (a) Primary fluid inclusions hosted by scheelite, sample Po-79. (b,c) Flat pseudosecondary fluid inclusions with consistent degree of fill hosted by scheelite, sample Po-30. (d) Secondary fluid inclusions hosted by scheelite, sample Po-30. (e) Typical occurrence of primary and pseudosecondary inclusions in quartz, sample Po-83. (f) A cluster of primary inclusions with consistent degree of fill hosted by quartz, sample Po-81. (g) A solitary negative-crystal shaped primary fluid inclusion in quartz, sample Po-81. (h) A group of primary inclusions in calcite, sample Po-83. (i) A flat pseudosecondary or secondary fluid inclusion in calcite, sample Po-81.

Quartz is usually rich in fluid inclusions (Figure 21e,f). Primary inclusions are negative-crystal shaped and are arranged in three-dimensional clusters or occur as solitary (Figure 21g). Abundant oval, flat, and/or irregularly shaped pseudosecondary fluid inclusions are hosted by short non-continuous trails. Both P and PS inclusions have a higher degree of fill ($F = 0.8\text{--}0.9$) and sizes usually between 5 and 28 μm (Figure 21e–g). Secondary inclusions have highly irregular shapes and belong to the L and L + V types, the latter having a high degree of fill ($F = 0.85\text{--}0.95$). The P and PS inclusions usually show higher homogenization temperatures than secondary ones (119–324 $^{\circ}\text{C}$ and 72–159 $^{\circ}\text{C}$, respectively; Table 1). Although significant overlaps exist, differences also occur in the $T_{m_{ice}}$ values of both groups (−2.0 to −8.8 $^{\circ}\text{C}$ and −1.1 to −5.4 $^{\circ}\text{C}$, respectively), whereas their T_e values are mutually comparable (−41 to −34 $^{\circ}\text{C}$). The rather large spread of T_h and $T_{m_{ice}}$ data was recorded in all quartz samples (Table 1). It is largely related to occurrence of spatially isolated domains (not well-defined growth zones but isolated three-dimensional clusters or trails) with different parameters of fluid inclusions, although there are also observed groups (including trails) showing wider variability of microthermometric parameters. Within the latter, there were observed trails with T_h variations up to 48 $^{\circ}\text{C}$, in which neighboring inclusions had both almost identical (within 0.1 $^{\circ}\text{C}$) or variable (within 4.1 $^{\circ}\text{C}$) $T_{m_{ice}}$ values, in the latter case, without any indication of refilling. The low amount of collected microthermometric data of secondary inclusions is due to frequently observed metastable behavior, caused by elimination of vapor bubble during freezing. Where this was not the case, it was found that the all-liquid (L) FI show similar cryometric parameters to the co-existing L + V inclusions.

Calcite contained relatively scarce fluid inclusions. Solitary three-dimensional examples are considered as primary inclusions (Figure 21h) and trail-hosted flat irregular inclusions are either pseudosecondary or secondary (Figure 21i). Both studied calcite samples yielded rather different fluid inclusion parameters. Whereas the L + V type prevails over L-only inclusions in the P and PS FI in samples Po-30 and Po-83, an opposite situation was observed in sample Po-81. They also differ in homogenization temperatures of L + V FI, ranging from 150 to 245 and from 105 to 142 $^{\circ}\text{C}$, respectively (Table 1). Similarly shifted are the T_h values of secondary L + V inclusions (126–182 $^{\circ}\text{C}$ and 86–115 $^{\circ}\text{C}$, respectively; Table 1). The P + PS inclusions mostly have lower $T_{m_{ice}}$ values than S ones in all samples (−0.3 to −5.5 $^{\circ}\text{C}$ and −0.1 to −1.2 $^{\circ}\text{C}$, respectively; Table 1). The rarely observed T_e values are close to −35 $^{\circ}\text{C}$ in the P and PS inclusions in both calcite samples. Although attempts to stretch FI by overheating were realized, many of them behave metastably during cryometric runs, showing the melting of overheated ice in the absence of a vapor bubble.

Although the formation or melting of clathrate was never observed in the studied fluid inclusions during cryometry, we have checked the vapor bubbles of some L + V fluid inclusions hosted by scheelite and quartz by microRaman analysis. Approximately one third of the tested fluid inclusions with a larger vapor bubble yielded spectra showing the presence of volatile gases. In the case of inclusions with a small vapor bubble, the measurement is obscured due to the bubble movement. In the P and PS FI hosted by quartz samples, the presence of CH_4 , CO_2 , and N_2 was usually recorded, at 16.3–96.2, 0.0–83.3, and 0.5–78.1 mol. %, respectively. Interestingly, there are different compositions and/or compositional trends observed in different quartz samples (Figure 22). In addition, some CH_4 -rich compositions contained small amounts of ethane and molecular hydrogen (Figure 23). In the case of scheelite-hosted fluid inclusions, the measurement with the aid of a 532-nm laser is partly hampered due to the occurrence of a group of scheelite bands overlapping N_2 peak (at $\sim 2331\text{ cm}^{-1}$). Nevertheless, bubbles in scheelite hosted fluid inclusions that again contained variable CH_4 and CO_2 and traces of C_2H_6 . The use of a 633-nm laser helped to restrain the mineral excitation around N_2 peak, which allowed a safe confirmation of the presence of this gas in a few scheelite-hosted fluid inclusions. The occurrence of H_2 was not checked in scheelite-hosted inclusions because the 633-nm-laser-allowed measuring range terminating at ca. 3200 cm^{-1} does not include the hydrogen peak at $\sim 4156\text{ cm}^{-1}$.

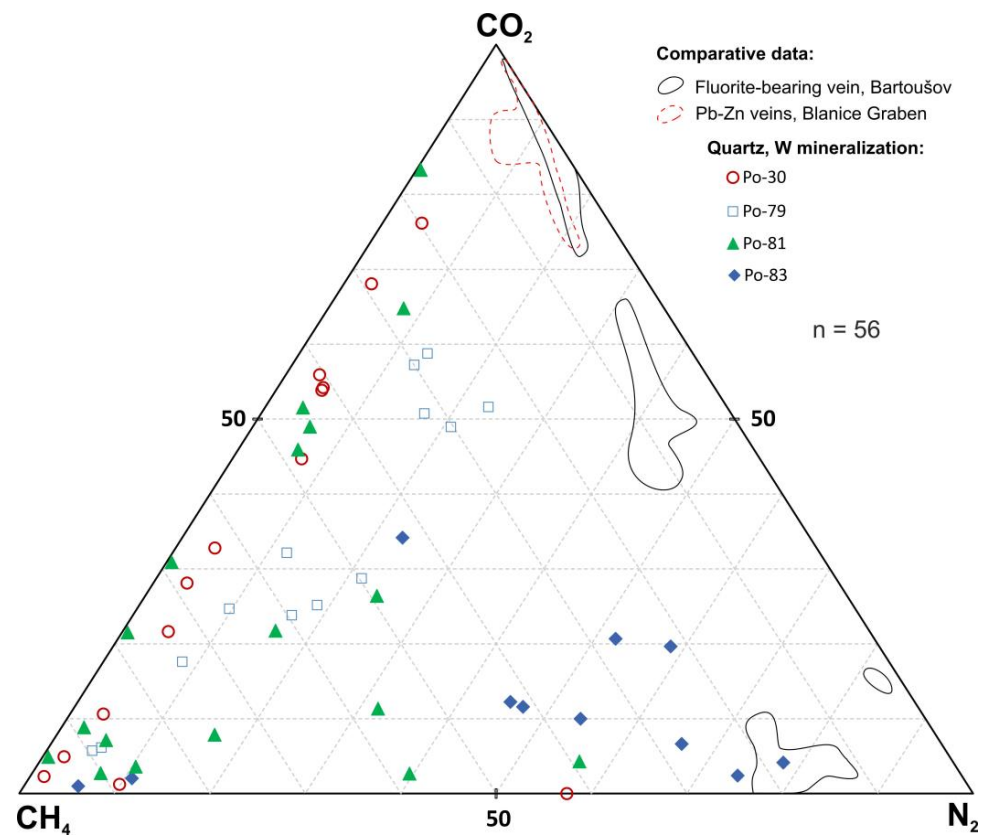


Figure 22. Raman-based composition of gases in vapor bubbles of primary and pseudosecondary quartz-hosted fluid inclusions in the CH_4 – N_2 – CO_2 plot. The comparative data are taken from [74] and [58].

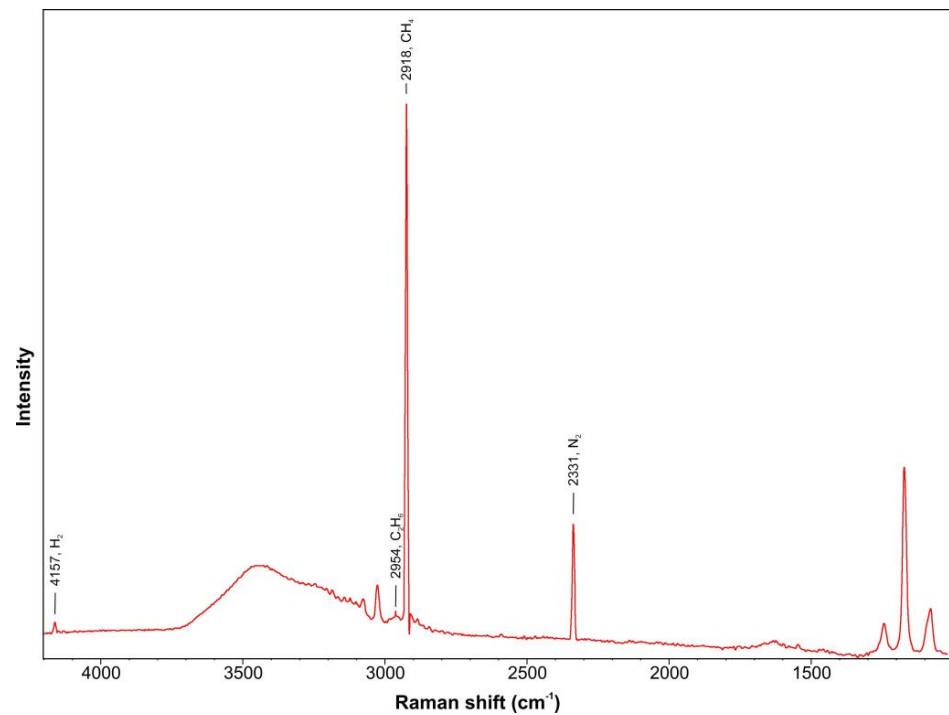


Figure 23. Raman spectrum (laser 532 nm) of vapor bubble in a quartz-hosted fluid inclusion (sample Po-30) containing methane, ethane, nitrogen, and hydrogen. The unlabeled peaks belong to host quartz or inclusion water.

4.3. Stable Isotopes

The $\delta^{18}\text{O}$ values were determined in two mineral separates from a single sample, which was used for fluid inclusion study (Po-30). The quartz and scheelite samples yielded the $\delta^{18}\text{O}$ values 12.8 and 3.8‰ V-SMOW, respectively.

5. Discussion

5.1. Paragenetic Evolution of the Mineral Assemblage

The rich mineral assemblage (a total of 36 mineral species, some of them in addition present in multiple generations) in combination with only sporadic occurrence of many minerals forming only isolated grains creates serious problems for the construction of the paragenetic scheme of the studied mineralization. Moreover, the used research methods do not allow to distinguish individual generations safely even in case of some major/frequent minerals, such as quartz, calcite, and pyrite. Therefore, we present only a simplified paragenetic scheme (Figure 24).

Stage	1	2	3
Biotite, molybdenite	■		
Wolframite, columbite-group minerals	■		
Scheelite I	■		
Muscovite	■		
Apatite	■		
Quartz	■	■	
Zircon	■		
Chlorite I, TiO_2 minerals, titanite, uraninite, xenotime	■		
Coffinite	■		
Pyrrhotite I		■	
Pyrite		■	■
Cobaltite, arsenopyrite		■	
Sphalerite		■	
Chalcopyrite, galena		■	
Calcite			■
Pyrrhotite II			■
Chlorite II			■
Violarite, Ca-Y-REE silicate, fluorite			■

Figure 24. Simplified paragenetic scheme of the studied mineralization. Note that some minerals are missing because of lacking sufficient paragenetic information.

The earliest portion of the studied vein is represented by molybdenite and wolframite with inclusions of columbite-group minerals. Later on, scheelite strongly corroding wolframite took place. These ore minerals are accompanied by gangue dominated by biotite, muscovite, chlorite I, and, especially, quartz. Zircon, xenotime, uraninite, apatite, TiO_2 minerals, and titanite are accessories at this stage. We cannot exclude that some of these minerals occurring just along the contact of the vein and wall rocks are in fact inherited from wall rocks, but textural as well as compositional evidence clearly suggests that if so, they must have been completely recrystallized during fluid–rock interactions. For example, muscovite from the contact area has a composition indistinguishable from muscovite evidently formed in open space. Similarly, biotite from the studied mineralization usually contains a small admixture of Rb, which was never recorded in the granite/gneiss rock-forming biotite from the Pohled quarry. Zircon forms clusters of small crystals, which

is a textural arrangement never observed in fresh wall rocks. Chlorite I, titanite, and TiO_2 minerals often form either pseudomorphs after biotite or newly formed grains/aggregates grown into open space. Our observations suggesting for a deep recrystallization and re-equilibration of possibly present material originating from wall rocks fit well with earlier observations on molybdenite bearing quartz vein mineralization from the same locality [40]. The usually observed antipathetic relationship of inclusions of TiO_2 minerals and titanite, hosted by part of chlorite I which was formed at the expense of biotite, is likely related to local availability or absence of Ca.

The second mineralizing stage is represented by most sulfides (pyrrhotite I, pyrite, sphalerite, galena, cobaltite, and arsenopyrite). All these minerals are hosted by quartz gangue. A part of the pyrite originated due to the sulfurization of pyrrhotite I, as suggests the porous fine-grained texture of pyrite [75,76] containing small relics of pyrrhotite.

The latest portion of the studied vein is represented by late pyrite, pyrrhotite II, chlorite II, violarite, a Ca-Y-REE silicate, and probably also fluorite, hosted by calcite gangue.

The exact paragenetic position of a mineralogically interesting veinlet containing quartz, scheelite II, adularia, and calcite remains unresolved, because this veinlet cut a portion of vein containing the earliest portion of paragenesis only, and its relationship to later mineral assemblages thus remains unknown.

5.2. Fluid Composition and Trapping Mode

Based on measured eutectic temperatures clustering around ca. -35 and -37 °C (Table 1), the systems $\text{NaCl-MgCl}_2\text{-H}_2\text{O}$ and/or $\text{NaCl-FeCl}_2\text{-H}_2\text{O}$ can be inferred in the studied fluid inclusions [77]. Because no melting of salt hydrates was observed in the studied fluid inclusions, the ratios of the individual chlorides cannot be specified. The salinities of the aqueous solutions, based on the melting temperature of ice, range between 0.2 and 12.6 wt. % NaCl eq. (Table 1).

No simple correlation is observed between the homogenization temperatures and the melting temperatures of ice (Figure 25). This may be associated with either a complicated fluid evolution involving multiple pulses of fluids with variable temperatures and salinities, or some post-entrapment alteration of the studied fluid inclusions. The petrographic evidence, at least in some cases, does not support the possibility of necking-down, because there are tightly neighboring, irregularly shaped fluid inclusions showing not only distinctly different homogenization temperatures but also salinities within a single trail (without any evidence of refilling). Nevertheless, the density of the enclosed fluids could be potentially altered by stretching during the significant non-isochoric changes of P–T conditions; however, no occurrence of the exploded inclusions rimmed by coronas of tiny inclusions containing ejected fluid [78] was observed in our samples, making such an explanation rather improbable. Therefore, we suggest that the studied inclusions largely reflect a complicated long-lasting fluid evolution involving multiple pulses of aqueous fluids with different salinities and temperatures. This opinion is also supported by the distinct mutual proportions of individual volatile gases in the vapor bubbles of fluid inclusions hosted by various quartz samples (Figure 22).

The amount of volatile gases, whose presence was confirmed by Raman spectroscopy in part of the fluid inclusions (Figure 22), cannot be quantified for bulk fluid, because no necessary phase changes (i.e., melting of clathrate or partial homogenization of non-aqueous phase) occurred during microthermometry. Therefore, the amount of these gases is very low in all inclusions.

Only liquid homogenization was observed in the studied inclusions, suggesting that they were trapped from a homogeneous fluid phase [52,53].

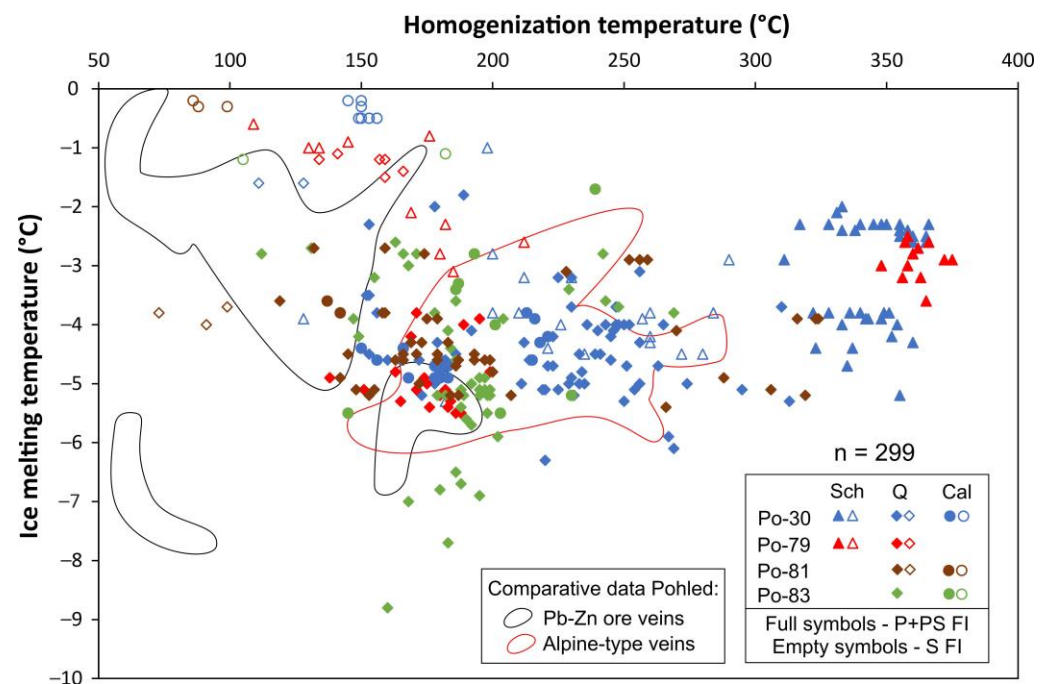


Figure 25. The T_h vs. $T_{m_{ice}}$ plot for fluid inclusions from the studied mineralization and comparison with published data. The comparative data are from [36].

5.3. Formation Conditions

The collected data offer several lines of evidence constraining the temperature conditions of the studied mineralization. However, the value of these temperature estimates is sometimes questionable, as exemplified below.

1. Primary and pseudosecondary aqueous fluid inclusions hosted by the studied vein minerals yielded highly variable homogenization temperatures across the vein paragenesis, ranging from ca. 370 °C (scheelite) to less than 100 °C (late L-only fluid inclusions hosted by quartz and calcite). Because fluid inclusions appear to be trapped from a homogeneous fluid in all cases, they represent the minimum possible trapping temperatures. The true formation of P–T conditions can be located somewhere on appropriate isochores using independent temperature and/or pressure estimates [52]. However, it is impossible to prove the contemporaneous timing of certain observed fluid episodes and independent temperature estimates derived from another mineral phases (see below). Therefore, the determination of pressure conditions remains uncertain (Figure 26).
2. The application of a quartz–scheelite oxygen isotope thermometer by [79] to the measured $\delta^{18}O$ values yielded a temperature estimate of 132 °C, which is clearly strongly underestimated, when compared with the homogenization temperatures of primary and pseudosecondary fluid inclusions showing T_h values mostly above 200 °C in both minerals. This indicates that quartz and scheelite have crystallized out of isotope equilibrium, presumably during different periods and from different fluids. This interpretation is consistent with the different T_h values and, partly, also the salinities of the fluid inclusions in both minerals.

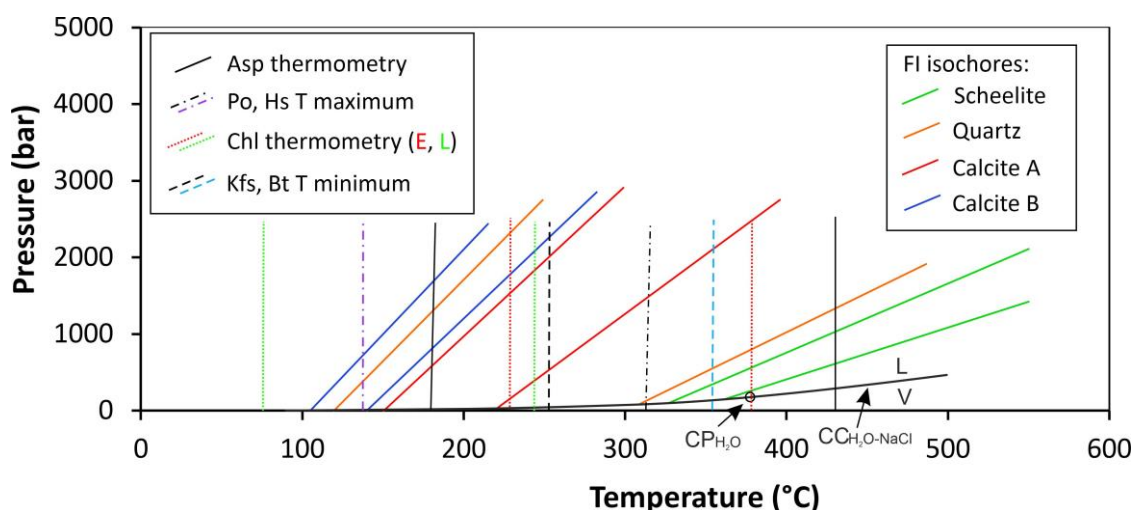


Figure 26. The course of representative isochores of P + PS fluid inclusions hosted by individual minerals in P–T space, combined with other available temperature estimates. Calcite A includes data from samples Po-30 and Po-83, whereas calcite B is sample Po-81. The letters E and L refer to early chlorite I and late chlorite II, respectively. CC—critical curve, CP—critical point, L—liquid, V—vapour.

3. The cationic (Fe–Co–Ni) composition of sulfoarsenides yields, for many obtained WDS analyses, high temperature estimates exceeding 550 °C (Figure 13a). These temperatures are significantly higher than those suggested from other thermometers and mineral phases. In addition, the missing positive correlation between As and Co (Figure 13b), which is commonly reported for natural sulfoarsenides [63,80,81], is unusual, and probably indicates a chemical disequilibrium. The latter is also clearly suggested from the sector zoning of some grains (cf. [82]). In this case, we suggest that the entrance of cations into the structure of crystallizing sulfoarsenides was likely not primarily driven by the temperature, but by the actual availability of individual elements. Another approach involves thermometry based on the contents of As in arsenopyrite [80,83]. For these thermometric purposes, [81] does not recommend the use of arsenopyrite containing as little as 0.2 wt. % Co. Excluding these Co-enriched compositions, the measured As contents between 28.1 and 32.5 at. % suggest (though there is a high uncertainty in estimation of sulfur fugacity from mineral assemblage) a more reasonable range of crystallization temperatures between ca. 430 and <200 °C (Figure 26).
4. The elevated contents of Th in uraninite are consistent with a high-temperature origin of this mineral phase [84].
5. Crystallization of a K-feldspar and biotite suggests temperatures above ca. 250 and 350 °C, respectively [85,86].
6. Empirical chlorite thermometry based on contents of ^{iv}Al [71] suggests crystallization temperatures of chlorite I between 228 and 366 °C, whereas those of chlorite II range from 75 to 240 °C (Figures 18c and 26).
7. The absence of polysynthetic twinning of chalcopyrite suggests that its formation temperature did not exceed 550 °C [87,88].
8. The upper limit of the temperature stability of monoclinic pyrrhotite lies between 225 and 315 °C, according to both experimental data and natural evidence [89].
9. A stable negative Eu anomaly in xenotime (Figure 10c) indicates that the temperature was above ca. 200 °C, because divalent Eu is stable at high temperatures [90] and Eu²⁺ has a larger ion size with respect to neighboring trivalent REEs, preventing its incorporation into crystallizing REE minerals. In contrast, a variability of temperature around the critical value of ca. 200 °C, associated with the thermochemical oxida-

tion/reduction of Eu^{2+} to Eu^{3+} and vice versa [90], can be the reason for the highly variable Eu/Eu^* values in late unknown Ca-Y-REE silicate (Figure 10d).

10. Hisingerite is an alteration mineral, originating in near-surface to late-hydrothermal conditions at temperatures up to 140 °C [91,92].

From the available evidence, it is suggested that temperature was likely subject to substantial changes during the crystallization of the studied mineralization. In general, a temperature decrease during the paragenetic evolution of the vein took place. We have little direct evidence about the temperature conditions of the earliest portion of the vein involving biotite, columbite-group minerals, and wolframite. Here, the temperature was likely not lower than the homogenization temperatures of fluid inclusions hosted by later scheelite reaching up to 370 °C. The superimposed formation of chlorite, muscovite, xenotime, zircon, titanite, TiO_2 minerals, part of quartz, and most sulfides took place during ca. 350 and 200 °C. The latest portion of the studied vein, involving late quartz, late calcite, chlorite II, unknown Ca-Y-REE silicate, pyrrhotite II, and violarite, likely formed around and below ca. 200 °C. Hence, the studied vein mineralization covers a significant portion of the cooling history of the envelope around the Pohled granite body.

Temperature was not the only variable factor influencing the development of the studied mineralization. The available data suggest significant changes in Eh and pH. The changes in Eh are usually accompanied by the crystallization of uraninite. Uranium is easily mobile in oxidized (U^{6+}) form in hydrothermal fluids and its immobilization, manifested by the precipitation of uraninite, requires at least a local decrease of Eh (e.g., [93]). A very low oxygen fugacity in the ore-forming environment is also necessary to allow the precipitation of pyrrhotite. In contrast, the sulfurization of pyrrhotite is usually associated with an increase in Eh allowing partial oxidation of H_2S to H_2S_2 ; the second possibility is the formation of H_2S_2 by the mutual reaction of H_2S and thiosulfate anions present in the late low-temperature fluids [94]. The variability in Eh of the parent fluid can also be mirrored in the variable Eu/Eu^* values of the REE-bearing minerals. The stable negative Eu/Eu^* values observed in xenotime (Figure 10c) can be related to a stable reducing environment, whereas the highly variable nature of Eu/Eu^* in the unknown Ca-Y-REE silicate (Figure 10d) can be associated with a changing Eh [95–97]. The pH of the fluids was likely acidic in the early portion of the hydrothermal activity, where muscovite formed in addition to common quartz. A low pH would also favor the precipitation of anatase and brookite instead of rutile [98]. An acidic pH is also suggested by the occurrence of CO_2 in most of the quartz-hosted fluid inclusions. In contrast, the late stage of the vein evolution associated with the crystallization of calcite was characterized by neutral or slightly alkaline fluids.

The frequently observed replacement textures (including chloritization of biotite and wolframite, scheelitization of wolframite, pyritization of wolframite, chlorite I and pyrrhotite I, coffinitization of uraninite, leucoxenization of TiO_2 minerals, and carbonatization of apatite) illustrate the re-equilibration(s) of early minerals under a change in the temperature and/or the compositional parameters of fluids during the later evolution of the studied vein.

The detailed study of the chemical composition of the individual minerals also indicates that the early phase of the studied vein assemblage originated from aqueous fluids, which were able to transport even the hardly remobilizable elements such as W, Sn, Zr, Nb, Th, Ti, Sc, Y, and REE. In addition to the high temperature of the parent fluids, the presence of suitable complexing agents in the fluids likely had the positive influence, allowing the dissolution and stabilization of hardly soluble elements in the solution. For example, the REE are effectively complexed especially by fluoride or (only in an alkaline environment) hydroxide or carbonate (CO_3^{2-}) anions [95,99,100]. The mobilization of Ti and Zr is favored by the increased contents of sulfate or fluoride anions, mainly in acidic solutions [101,102]. Trace amounts of sulfate detected in many WDS analyses of columbite-group minerals and wolframite can underline the role of sulfate anions in the origin of the earliest W-rich portion of the studied vein assemblage.

5.4. Origin of Fluids and Mineral-Forming Components

The source of parent hydrothermal fluids can be interpreted if the fluid $\delta^{18}\text{O}$ value is calculated from mineral $\delta^{18}\text{O}$ values and known formation temperatures. Because no reliable additional P–T estimates are available for the isotopically analyzed minerals, the use of homogenization temperatures of homogeneously trapped fluid inclusions yields only the minimum possible fluid $\delta^{18}\text{O}$ values. Based on fractionation factor scheelite–water by [79] and temperatures of 370 and 450 °C (i.e., the maximum Th temperature and an average Th value shifted by a value corresponding to a pressure of ca. 1 kbar; cf. Figure 26), the calculated $\delta^{18}\text{O}$ values of water are 5.1 and 5.8‰ V-SMOW, respectively. Based on fractionation factor quartz–water by [103] and temperatures of 260 and 300 °C (the meaning of both temperatures is the same as above), the calculated $\delta^{18}\text{O}$ values of water are 4.3 and 5.8‰ V-SMOW, respectively. The calculated fluid $\delta^{18}\text{O}$ values are, in both cases, consistent with either magmatic waters (5 to 10‰ V-SMOW) [104,105], metamorphic waters (3 to 20‰ V-SMOW) [104,105], or waters of any other origin, which have equilibrated with crustal rocks at high temperatures [106,107]. If the true pressure conditions will be higher than 1 kbar, the calculated fluid $\delta^{18}\text{O}$ values will also increase; however, this does not disturb the above interpretation of the water source.

Whereas the admixture of low amounts of CO_2 , N_2 , or CH_4 can be in accordance with a magmatic or a metamorphic origin of the fluids, the identification of traces of H_2 and C_2H_6 in high-temperature quartz-hosted fluid inclusions is surprising. Higher hydrocarbons can be produced in a purely inorganic way in magmatic systems via CO_2 reduction by H_2 and subsequent polymerization of the produced CH_4 [108–110], but the lack of CO as a common intermediate of this process does not favor this explanation. Alternatively, methane and ethane could have been produced by the thermal degradation of unmetamorphosed organic matter. In the given geological setting, the source of immature organic matter can only be found in contemporaneous sedimentary basins developed above the high-grade basement rocks, which, in places, contain bitumenic horizons and/or coal seams in their basal parts [24]. These sediments were subject to intense compaction and thermal alteration soon after their deposition [25]. The thermal maturation of sediments rich in organic matter would release huge amounts of various volatile components including CO_2 , N_2 , CH_4 , H_2 , and higher hydrocarbons that are expelled into pore fluids, which can, subsequently, effectively act as mineralizing hydrothermal fluids [111–114].

Apart from fluids, the possible origin of some ore elements can be suggested from the available data. Because a nest of rich molybdenite mineralization occurred directly in the Pohled granite [35,41,42], the source of Mo can be suggested in the granite body. Similarly, the origin of Rb hosted by early biotite was likely in magmatic fluids leaving after crystallization of granite body. Zirconium, Th, U, Nb, and REE could be sourced from both gneisses and granites because accessory minerals containing these elements (i.e., zircon, monazite) are contained in both lithotypes [28,29]. In contrast, the source of Mg, Cr, Co, Ni, and, likely, at least a part of V was probably in boudins of (ultra)basic rocks (amphibolites and serpentized peridotites) hosted by the paragneisses; a contamination by these elements was documented in both magmatic and hydrothermal stages of pegmatites [29,30] and in ore veins [40] occurring in the Pohled quarry. The ultimate source of some other metals (W, Sn, Sc, and Y) remains unclear since their carriers were not identified in any rock type in the area. Taken together, the available, rather puzzling data are compatible with the participation of fluids derived from different source rocks and/or wide fluid circulation involving alteration of various lithologies.

5.5. Genetic Model

The available data allow to formulate the following scenario of origin of the studied mineralization, which is illustrated in Figure 27. The initiation of the fracture, in which the studied mineral vein formed, followed the intrusion of the Pohled granite body and the associated migmatitization of the host metamorphic series. Presumably, the opening of the vein was associated with volume contractions of rocks, associated with cooling of the granite

body. The first mineral phases, which crystallized in the vein, were biotite, wolframite, columbite-group minerals, and molybdenite. We suggest that these minerals formed from fluids that contained both magmatogenic and an external (non-magmatic) components (Figure 27a). Magmatogenic fluids, left after the crystallization of the Pohled granite, transported Mo, Rb, and likely W [115–118]. Because the fully crystallized granite body cannot exsolve additional portions of aqueous fluids during cooling, we suggest that the activity of the magmatogenic fluid was a relatively short episode. This logical argument is further supported by available geochemical evidence. The increasing activity of an external non-magmatic fluid component even during this early stage is suggested by the increasing amounts of Mg incorporated during crystallization of both wolframite and columbite-group minerals, which is an unusual feature that cannot be explained in terms of granite source only. Similarly, the compositional evolution of columbite-group minerals, conventionally expressed in terms of Fe/Mn and Nb/Ta, does not follow trends observed in rare-metal granites (Figure 28). Because high-grade metamorphic rocks cannot produce low-salinity low- $\delta^{18}\text{O}$ aqueous fluids during retrograde cooling, we presuppose that major portion of external water infiltrated along fractures and faults from the surface. We suggest that this external source of fluids was active during the formation of the whole rest of the studied mineral paragenesis. In the given setting of the tectonically-ground extensional Jihlava Graben, we presuppose the formation of a long-lived hydrothermal cell driven by residual heat from cooled granitic body and involving circulation of basinal waters (Figure 27). The basin becomes filled out by Upper Carboniferous-to-Lower Permian freshwater clastic sediments, in places with coal seams. High thermal flow characterizing basement rocks during this period allowed for the rapid maturation of these sediments (reaching up to anthracite stage) [25,119], releasing volatile components (CO_2 , CH_4 and other hydrocarbons, H_2 , N_2) into fluid phase. The subsequent infiltration of pore fluids from sediments into the basement was allowed due to the extensional tectonic regime characterized by the activity of normal faults and possibly further reinforced by the mechanism of a suction-pump [120]. The heating of sedimentary fluids in the hot basement rocks resulted in almost complete cracking of higher hydrocarbons to methane [121] and increase of fluid $\delta^{18}\text{O}$ values. The observed variations in the salinity of hydrothermal fluids can reflect either variable consumption of water during interactions of fluids with hot basement rocks or primary variations in the salinity of basinal fluids. The latter was allowed due to the seasonal hot semi-arid climate in the Lower Permian, resulting in variable levels of the evaporation of basinal waters manifested by the occasional occurrence of carbonate and gypsum evaporites in the basinal sedimentary sequences [122,123]. The long-lasting circulation of basinal fluids, characterized by episodic infiltration of fluids with variable composition, is consistent with the observed complexity of fluid salinities, temperatures, Eh, pH, and volatile gas contents, which are, in turn, mirrored in the complexity of the mineral assemblage of the studied vein.

The infiltration of sedimentary fluids into the crystalline basement was frequently reported to explain the origin of numerous types of hydrothermal mineralizations [124–128] including the tungsten ones [9,129,130]. In the Bohemian massif, the participation of fluids derived from contemporaneous freshwater Permo-Carboniferous piedmont basins was interpreted during the formation of vein/shear zone uranium [106,131,132], vein Ag-Pb-Zn [106,107,133], and vein barite deposits [123]. In the Jihlava Graben, a genetic model involving fluids derived from piedmont basin was formulated to explain the origin of a fluorite-rich vein from the neighboring Bartoušov site [58].

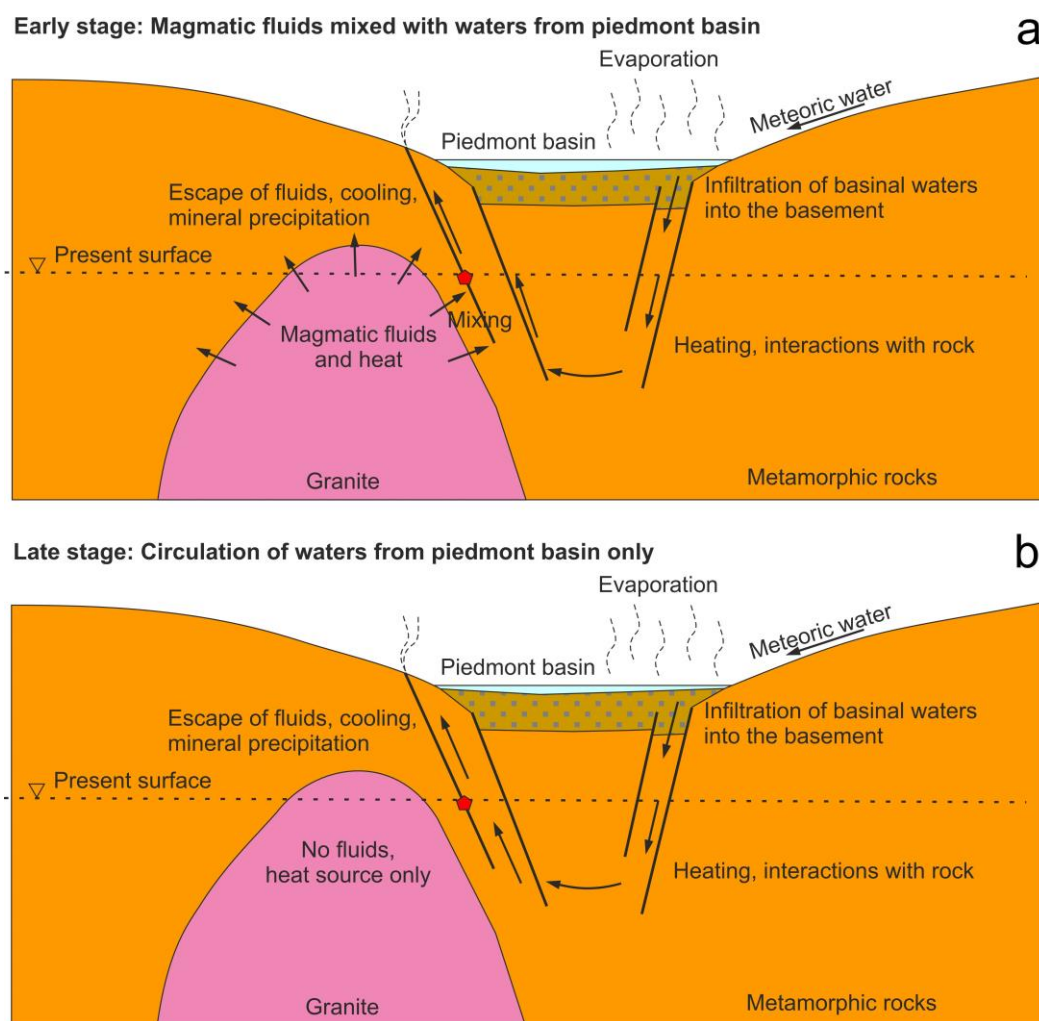


Figure 27. The interpreted scenario of the origin of the studied W mineralization from Pohled. (a) Early stage involving the mixing of both magmatic and basinal fluids. (b) Late stage involving the circulation of basinal fluids only.

5.6. Regional Metallogenic Implications

The vein wolframite mineralization, newly discovered in the Pohled quarry, cut the migmatitized paragneisses in the close exocontact of a small Variscan granite body. Its geological position clearly indicates the Variscan age of this mineralization. Hence, the studied occurrence belongs to *wsn* mineralization sensu [16]. The mineral paragenesis and chemical compositions of the main minerals (low-Li, low-F muscovite, Figure 16b,c; Mg-enriched wolframite, Figure 4; Sc,Mg-enriched columbite-group minerals, Figures 6 and 7) as well as a lack of garnet and gahnite in mineral assemblage also agree with this classification. These similarities also suggest that the mechanism of formation should be comparable. The tight spatial association of mineralization with granitic rocks (Figure 1a) suggests that the primary source of W (giving rise to wolframite) would be in granite, as already suggested by [40]. In contrast, one cannot exclude that a major portion of scheelite-hosted W was re-cycled from previously crystallized wolframite. This is indicated by (1) common intense replacement of wolframite by scheelite at many localities, and (2) accessory occurrence of scheelite within Alpine-type veins [39,134] and Zn–Pb ore veins [36] in the Pohled quarry, potentially suggesting some dissemination of W from the earliest (wolframite-bearing) veins by superimposed hydrothermal events.

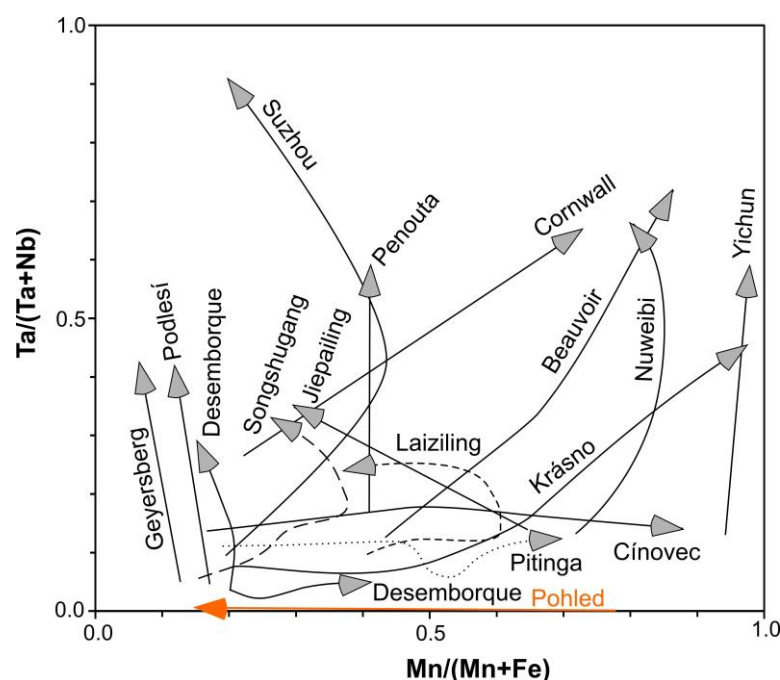


Figure 28. Compositional trend of columbite-group minerals from Pohled and its comparison with those from F- and Li-rich rare-metal granitic systems and associated greisens worldwide. Comparative data are taken from [135–149].

The mineral assemblage and textural features of sulfidic mineralization associated with the studied wolframite-bearing vein are, in general, well comparable with those from Alpine-type veins and ore veins occurring in the Pohled quarry. Moreover, broad similarities are also usually observed in the chemical composition of the mineral phases and microthermometric parameters of fluid inclusions from different vein types (Figures 8, 10a,b, 11, 13, 16c, 18a and 25). These observations strongly support an idea about the unified origin of minerals occurring within distinct types of veins, suggested by [40]. In other words, these data would be consistent with repeated episodic (but not contemporaneous) opening of individual veins, which, in turn, resulted in different volumetric proportions of minerals crystallizing during the individual sub-stages of long-lasting hydrothermal activity in individual veins.

Sulfide minerals are usual subordinate to minor components of other wolframite-bearing occurrences in the Moldanubian area [44]. Specifically, the Bi-bearing assemblages (containing Ag–Bi substituted galena, native bismuth, and, locally, (Ag)–Pb–Bi sulfosalts) are common ([150,151], this work). Surprisingly, this is also the case in the area of the Havlíčkův Brod ore district, where Bi mineralization is commonly completely lacking and Sb is present instead ([33,59] and references therein). This feature can be associated with the same local source of Bi and W presumably in the granite intrusions.

The occurrence of magmatic breccias in apical parts of greisenized granitic bodies is a common feature at some sites containing rich Sn–W mineralization in the Saxothuringian Zone of the Bohemian Massif [7,143]. The origin of magmatic breccias was linked with increasing fluid pressure during the late stages of crystallization of the shallow-seated host granite body and was associated with the secondary boiling of exsolved fluids, giving rise to a low-salinity steam and a high-salinity brine, in which ore elements were concentrated [4,7,9]. The hydraulic fracturing of rocks above the apical part of granite body further contributed to the focused flow of ore fluids and the origin of rich ores. Because of the deeper setting of the Moldanubian granite bodies, the overpressure generated by the exsolved fluids did not exceed the strength of the overburden envelope rocks (Figure 27) and the above processes did not participate during further evolution. Consequently, the exsolved magmatic fluids remained in a homogeneous state and have been dispersed into

numerous small fractures around the cooling granite body, which was the reason that only small sub-economic occurrences of wolframite mineralization originated in this area.

6. Conclusions

The vein wolframite mineralization at the Pohled quarry is hosted by migmatitized paragneisses in close exocontact of a small Variscan post-kinematic geochemically primitive granite body. A rich mineral assemblage involving 36 mineral species was identified during a detailed mineralogical study. Early wolframite is strongly replaced by scheelite and followed by abundant phyllosilicates (Fe–Mg chlorite and low-F and low-Li muscovite) and base-metal sulfides. The gangue is dominated by quartz in the early stage and by calcite in the latest stage. The occurrence of numerous accessory minerals indicates that U, Th, Ti, Nb, W, Sc, Y, and REE were remobilized by hydrothermal fluids, especially in the early stage of vein evolution. In addition, an unusual compositional evolution characterized by increasing Mg contents was documented during the crystallization of wolframite and columbite-group minerals, which was likely caused by a specific fluid regime allowing the participation of Mg leached from the host rocks.

The fluid inclusion study of scheelite, quartz, and calcite identified the homogeneously trapped aqueous solutions with salinities between 0.2 and 12.6 wt. % NaCl eq. The homogenization temperatures decrease significantly from early scheelite (up to 370 °C) to late calcite (below 100 °C). The Raman analyses of vapor bubbles in part of fluid inclusions indicate the trace amounts of CO₂, N₂, CH₄, and, sometimes, also H₂ and C₂H₆, which are present in highly variable mutual proportions. The calculated $\delta^{18}\text{O}$ values of fluids giving rise to quartz and scheelite are positive (min. 4.3 to 5.8‰ V-SMOW) and are compatible with the activity of magmatic, metamorphic, or any other waters that interacted with crustal rocks at high temperatures.

We formulated a genetic model in accordance with geological evolution of the area. The earliest portion of W,Mo-bearing fluids had likely magmatic origin, leaving after the crystallization of the Pohled granite body. However, even within this early stage and also during the formation of the whole rest of the studied mineral paragenesis, the participation of externally derived fluids is suggested. The source of this second fluid was likely in contemporaneous freshwater piedmont basins, whose waters (with episodically increased salinity due to evaporation in a semi-arid climate) were infiltrated into the basement along extensional faults. Residual heat from the cooling granite body drove the fluid circulation and allowed a long-lasting hydrothermal activity. The maturation of sediment-hosted organic-rich horizons exposed to high thermal flow from the underlying basement could be the source of all gaseous components (CO₂, N₂, CH₄, H₂, and C₂H₆) identified in the fluids.

Except for the earliest portion of the vein assemblage involving biotite, wolframite, and columbite-group minerals, great similarities between the mineral assemblages and the chemical compositions of individual minerals are observed when the rest of the studied vein paragenesis is compared with other mineralogically distinct vein types occurring in the area (Mo ore vein, Zn–Pb ore veins, Alpine-type veins). This implies for unified origin of these veins, which, in fact, differ only in the volumetric proportions of individual paragenetic sub-stages. This can be easily explained by the episodic non-contemporaneous opening of different veins during the long-lasting hydrothermal activity.

The geochemically unevolved parent granite is likely the reason for the absence of higher amounts of Li, F, and Ta in the studied mineralization. Furthermore, a greater depth of the granite intrusion likely prevented hydraulic fracturing of metamorphic envelope above granite intrusion in the end of granite crystallization. The absence of local fracturing of the granite cap also prevented a focused fluid flow of metal-bearing magmatic fluids. All these features were likely the main reasons why no larger accumulation of W mineralization originated in the Moldanubian area.

Supplementary Materials: The full dataset of electron-microprobe analyses of minerals can be downloaded at: <https://www.mdpi.com/article/10.3390/min14060610/s1>, file Pohled-W-ESF.xlsx, containing the following tables: Table S1: Analyses of wolframite, Table S2: Analyses of scheelite, Table S3: Analyses of columbite-group minerals, Table S4: Analyses of TiO₂ minerals, Table S5: Analyses of uraninite, Table S6: Analyses of coffinite, Table S7: Analyses of pyrrhotite, Table S8: Analyses of pyrite, Table S9: Analyses of arsenopyrite, Table S10: Analyses of cobaltite, Table S11: Analyses of gersdorffite, Table S12: Analyses of sphalerite, Table S13: Analyses of galena, Table S14: Analyses of chalcopyrite, Table S15: Analyses of violarite, Table S16: Analyses of biotite, Table S17: Analyses of muscovite, Table S18: Analyses of chlorite, Table S19: Analyses of K-feldspar, Table S20: Analyses of titanite, Table S21: Analyses of apatite, Table S22: Analyses of zircon, Table S23: Analyses of xenotime-(Y), Table S24: Analyses of an unknown Ca-Y-REE silicate, Table S25: Analyses of hisingerite, Table S26: Analyses of calcite.

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References

1. Franke, W. The mid-European segment of the Variscides: Tectonostratigraphic units, terrane boundaries and plate tectonic evolution. In *Orogenic Processes: Quantification and Modelling in the Variscan Belt*; Franke, W., Haack, V., Oncken, O., Tanner, D., Eds.; Geological Society, Special Publications: London, UK, 2000; Volume 179, pp. 35–61.
2. Neßler, J.; Seifert, T.; Gutzmer, J.; Müller, A. Contribution to the exploration and metallogenic characteristic of the Li-Sn-W-greisen deposit Zinnwald, eastern Erzgebirge, Germany. *Freiberg. Forschungsheft. C* **2017**, *552*, 1–390. (In German)
3. Hreus, S.; Výravský, J.; Cempírek, J.; Breiter, K.; Galiová, M.; Krátký, O.; Šešulka, V.; Škoda, R. Scandium distribution in the world-class Li-Sn-W Čínovec greisen-type deposit: Result of a complex magmatic to hydrothermal evolution, implications for scandium valorization. *Ore Geol. Rev.* **2021**, *139*, 104433. [\[CrossRef\]](#)
4. Thomas, R. Fluid evolution in relation to the emplacement of the Variscan granites in the Erzgebirge region: A review of the melt and fluid inclusion evidence. In *Metallogeny of Collisional Orogens*; Seltnmann, R., Kämpf, H., Möller, P., Eds.; Czech Geological Survey: Prague, Czech Republic, 1994; pp. 150–158.
5. Dolejš, D.; Štemprok, M. Magmatic and hydrothermal evolution of Li-F granites: Čínovec and Krásno intrusions, Krušné hory batholith, Czech Republic. *Bull. Czech Geol. Surv.* **2001**, *76*, 77–99.
6. Štemprok, M.; Pivec, E.; Langrová, A. The petrogenesis of a wolframite-bearing greisen in the Vykmánov granite stock, Western Krušné hory pluton (Czech Republic). *Bull. Geosci.* **2005**, *80*, 163–184.
7. Dolníček, Z.; René, M.; Prochaska, W.; Kovář, M. Fluid evolution of the Hub Stock, Horní Slavkov-Krásno Sn-W ore district, Bohemian Massif, Czech Republic. *Miner. Depos.* **2012**, *47*, 821–833. [\[CrossRef\]](#)
8. Breiter, K.; Ďurišová, J.; Hrstka, T.; Korbelová, Z.; Hložková Vaňková, M.; Vašinová Galiová, M.; Kanický, V.; Rambousek, P.; Knésl, I.; Dobeš, P.; et al. Assessment of magmatic vs. metasomatic processes in rare-metal granites: A case study of the Čínovec-Zinnwald Sn-W-Li deposit, central Europe. *Lithos* **2017**, *292*, 198–217. [\[CrossRef\]](#)
9. Krejčí Kotlánová, M.; Dolníček, Z.; René, M.; Prochaska, W.; Umanová, J.; Kapusta, J.; Mašek, V.; Kropáč, K. Fluid evolution of greisens from Krupka Sn-W ore district, Bohemian Massif (Czech Republic). *Minerals* **2024**, *14*, 86. [\[CrossRef\]](#)
10. Pauliš, P.; Kopecký, S.; Dolníček, Z.; Sejkora, J.; Pour, O.; Umanová, J.; Kopecký, S., Jr. Wolframová a sulfidická hydrotermální mineralizace z Pekelského vrchu u Jihlavy (Česká republika). *Bull. Mineral. Petrol.* **2022**, *30*, 73–94. (In Czech) [\[CrossRef\]](#)
11. Ferenc, Š.; Uher, P. Magnesian wolframite from hydrothermal quartz veins in the Rochovce granite exocontact, Ochtná, Western Carpathians, Slovakia. *Neues Jahrb. Mineral. Abh.* **2007**, *183*, 165–172. [\[CrossRef\]](#)

12. Miyawaki, R.; Yokoyama, K.; Matsubar, S. Huanzalaite, MgWO_4 , a new mineral species from the Huanzala Mine, Peru. *Can. Mineral.* **2010**, *48*, 105–112. [CrossRef]
13. Losertová, L.; Houzar, S.; Buřival, Z.; Losos, Z. Wolframit ve šlichových vzorcích lokality Tručbába—Valcha, moldanubikum. *Acta Mus. Morav. Sci. Geol.* **2012**, *97*, 77–84. (In Czech)
14. Losertová, L.; Buřival, Z.; Losos, Z.; Houzar, S. Minerální asociace a chemické složení Mg-wolframitu a scheelitu z Cetoraze u Pacova, Česká republika. *Acta Mus. Morav. Sci. Geol.* **2013**, *98*, 41–48. (In Czech)
15. Losertová, L.; Buřival, Z.; Losos, Z. Minerální asociace Sn-W zrudnění z Ovesné Lhoty u Světlé nad Sázavou, Česká republika. *Acta Mus. Morav. Sci. Geol.* **2014**, *99*, 69–76. (In Czech)
16. Bernard, J.H. Minerals of ore-bearing hydrothermal processes—The Bohemian Massif. In *Mineralogy of Czechoslovakia*; Bernard, J.H., Čech, F., Dávidová, Š., Dudek, A., Fediuk, F., Hovorka, D., Kettner, R., Koděra, M., Kopecký, L., Němec, D., et al., Eds.; Academia: Prague, Czech Republic, 1981; pp. 186–343. (In Czech)
17. Němec, D.; Tenčík, I. Regionally metamorphosed greisens at Cetoraz, The Bohemian-Moravian heights (Českomoravská vrchovina), Czechoslovakia. *Mineral. Depos.* **1976**, *11*, 210–217. [CrossRef]
18. Němec, D.; Páša, J. Regionally metamorphosed greisens of the Moldanubicum. *Mineral. Depos.* **1986**, *21*, 12–21. [CrossRef]
19. Kadlec, T. Nové mineralogické nálezy z kamenolomu Pohled u Havlíčkova Brodu I. *Minerál submitted*. (In Czech)
20. Geological Map of the Czech Republic 1:50000. Available online: <https://mapy.geology.cz/geocr50/> (accessed on 3 February 2023).
21. Breiter, K.; Gnojek, I.; Chlupáčová, M. Radioactivity patterns—Constraints for the magmatic evolution of the two-mica granites in the Central Moldanubian pluton. *Věst. Čes. Geol. Úst.* **1998**, *73*, 301–311.
22. Žák, J.; Verner, K.; Finger, F.; Faryad, S.W.; Chlupáčová, M.; Veselovský, F. The generation of voluminous S-granite in the Moldanubian unit, Bohemian Massif, by rapid isothermal exhumation of the metapelitic middle crust. *Lithos* **2011**, *121*, 25–40. [CrossRef]
23. McCann, T. *The Geology of Central Europe: Precambrian and Palaeozoic*; Geological Society: London, UK, 2008.
24. Pešek, J.; Holub, V.; Jaroš, J.; Malý, L.; Martínek, K.; Prouza, V.; Spudil, J.; Tásler, R. *Geology and Deposits of the Upper Paleozoic Limnic Basins of the Czech Republic*; Czech Geological Survey: Prague, Czech Republic, 2001; 243p. (In Czech)
25. Suchý, V.; Zachariáš, J.; Sýkorová, I.; Kořínková, D.; Pešek, J.; Pachnerová Brabcová, K.; Luo, Q.; Filip, J.; Světlík, I. Palaeo-thermal history of the Blanice Graben (the Bohemian Massif, Czech Republic): The origin of anthracite in a late-Variscan strike-slip basin. *Int. J. Coal Geol.* **2022**, *263*, 104129. [CrossRef]
26. Koutek, J. Occurrence of unmetamorphosed conglomerates in gneissic area near Německý Brod. *Věst. Stát. Geol. Úst.* **1940**, 53–56. (In Czech)
27. Doleželová, T. Hydrotermální Alterace Vybraných Typů Hornin v Havlíčkobrodském Rudním Revíru (Moldanubikum). Master's Thesis, Palacký University, Olomouc, Czech Republic, 2015. (In Czech).
28. René, M.; Dolníček, Z. Granitoids of the Mauthausen type in the Czech part of the Moldanubian Batholith. In *Recent Advances in Mineralogy*; René, M., Ed.; InTech Open: London, UK, 2023; pp. 11–29.
29. Dolníček, Z.; Malý, K.; Ulmanová, J.; Havlíček, J.; Vrtiška, L. Minerály kontaminovaných granitových pegmatitů z lomu Pohled u Havlíčkova Brodu (moldanubikum), část I: Oxidy, karbonáty, silikáty a fosfáty. *Bull. Mineral. Petrol.* **2020**, *28*, 132–151. (In Czech) [CrossRef]
30. Dolníček, Z.; Ulmanová, J.; Malý, K.; Havlíček, J.; Sejkora, J. Minerály kontaminovaných granitových pegmatitů z lomu Pohled u Havlíčkova Brodu (moldanubikum), část II: Prvky a sulfidy. *Bull. Mineral. Petrol.* **2021**, *29*, 90–107. (In Czech) [CrossRef]
31. Houzar, S.; Hrazdil, V.; Hršelová, P.; Toman, J.; Buřivalová, L.; Grossmannová, D.; Hladišová, T.; Litochleb, J.; Malý, K.; Škrdla, P.; et al. *Historické Dolování Drahých Kovů na Českomoravské Vrchovině*; Moravské Zemské Muzeum Brno: Brno, Czech Republic, 2021; 476p. (In Czech)
32. Hak, J.; Johan, Z. Mineralogicko-geochemický výzkum indiové anomálie Pohled u Havlíčkova Brodu. *Sborn. Geol. Věd Technol. Geochem.* **1961**, *2*, 77–101. (In Czech)
33. Dobeš, P.; Malý, K. Mineralogie polymetalických rudních výskytů ve střední části havlíčkobrodského revíru. *Vlast. Sborn. Vysoč. Odd. Přír. Věd.* **2001**, *15*, 51–85. (In Czech)
34. Malý, K.; Dolníček, Z. Pb–Zn–Ag vein mineralization of the central part of the Českomoravská vrchovina Upland (Czech Republic): S, C, and O stable isotope study. *Bull. Geosci.* **2005**, *80*, 307–319.
35. Mastíková, E. Geologická Dokumentace Lomu Pohled (Moldanubikum). Bachelor's Thesis, Palacký University, Olomouc, Czech Republic, 2009. (In Czech).
36. Mastíková, E. Mineralogie a Podmínky Vzniku Vybraných Mineralizací v Lomu Pohled (Moldanubikum). Master's Thesis, Palacký University, Olomouc, Czech Republic, 2011. (In Czech).
37. Pauliš, P.; Kopecký, S.; Jebavá, I.; Havlíček, J. Nové mineralogické nálezy z kamenolomu Pohled u Havlíčkova Brodu. *Minerál* **2013**, *21*, 317–322. (In Czech)
38. Havlíček, J.; Výravský, J.; Malý, K. Nálezy zeolitů v lomu Pohled u Havlíčkova Brodu. *Acta Rer. Nat.* **2018**, *22*, 1–3. (In Czech)
39. Kadlec, T. Nález scheelitového zrudnění v kamenolomu Pohled u Havlíčkova Brodu. *Minerál* **2018**, *24*, 502–508. (In Czech)
40. Dolníček, Z.; Ulmanová, J.; Malý, K.; Havlíček, J.; Krejčí Kotlánová, M.; Koutňák, R. Mineralogická charakteristika žilné křemenné mineralizace s molybdenitem z lomu Pohled, havlíčkobrodský rudní revír, Česká republika. *Acta Mus. Morav. Sci. Geol.* **2023**, *108*, 145–170. (In Czech)

41. Moupic, Z.; Tošer, Z. Nález molybdenitového zrudnění na lokalitě Pohled u Havlíčkova Brodu. *Čas. Mineral. Geol.* **1985**, *30*, 331–332. (In Czech)
42. Seidlová, V. Mineralogická charakteristika molybdenitového výskytu z lomu Pohled u Havlíčkova Brodu. Bachelor's Thesis, Masaryk University, Brno, Czech Republic, 2011. (In Czech).
43. Novák, M. Granitické pegmatity Českého masívu (Česká republika); mineralogická, geochemická a regionální klasifikace a geologický význam. *Acta Mus. Morav. Sci. Geol.* **2005**, *90*, 3–75. (In Czech)
44. Losertová, L. Přehled wolframitové mineralizace vázané na centrální moldanubický pluton a na ortorulová tělesa v moldanubiku. *Acta Mus. Morav. Sci. Geol.* **2015**, *100*, 45–67. (In Czech)
45. Prchlík, I.; Jeřábek, M. Wolframové zrudnění u Cetoraze, západně od Pacova. *Věst. Ústř. Úst. Geol.* **1965**, *40*, 47–49. (In Czech)
46. Pauliš, P.; Kopecký, S. Occurrence of tungsten mineralization at Vysoká near Havlíčkův Brod (Czech Republic). *Acta Rer. Nat.* **2007**, *3*, 47–50. (In Czech)
47. Pouchou, J.L.; Pichoir, F. "PAP" ($\rho\rho Z$) procedure for improved quantitative microanalysis. In *Microbeam Analysis*; Armstrong, J.T., Ed.; San Francisco Press: San Francisco, CA, USA, 1985; pp. 104–106.
48. Anders, E.; Grevesse, N. Abundances of the elements: Meteoritic and solar. *Geochim. Cosmochim. Acta* **1989**, *53*, 197–214. [\[CrossRef\]](#)
49. McLennan, S.M. Rare earth elements in sedimentary rocks: Influence of provenance and sedimentary processes. *Rev. Mineral.* **1989**, *21*, 169–200.
50. Monecke, T.; Kempe, U.; Monecke, J.; Sala, M.; Wolf, D. Tetrad effect in rare earth element distribution patterns: A method of quantification with application to rock and mineral samples from granite-related rare metal deposits. *Geochim. Cosmochim. Acta* **2002**, *66*, 1185–1196. [\[CrossRef\]](#)
51. Burke, E.A.J. Raman microspectrometry of fluid inclusions. *Lithos* **2001**, *55*, 139–158. [\[CrossRef\]](#)
52. Roedder, E. Fluid inclusions. *Rev. Mineral.* **1984**, *12*, 1–644.
53. Shepherd, T.J.; Rankin, A.H.; Alderton, D.H.M. *A Practical Guide to Fluid Inclusion Studies*; Blackie and Glasgow: London, UK, 1985.
54. Bodnar, R.J. Revised equation and table for determining the freezing point depression of H₂O–NaCl solutions. *Geochim. Cosmochim. Acta* **1993**, *57*, 683–684. [\[CrossRef\]](#)
55. Bakker, R.J. Package FLUIDS 1. Computer programs for analysis of fluid inclusion data and for modelling bulk fluid properties. *Chem. Geol.* **2003**, *194*, 3–23. [\[CrossRef\]](#)
56. Zhang, Y.G.; Frantz, J.D. Determination of the homogenisation temperatures and densities of superficial fluids in the system NaCl–KCl–CaCl₂–H₂O using synthetic fluids inclusions. *Chem. Geol.* **1987**, *64*, 335–345. [\[CrossRef\]](#)
57. Dixon, A.; Cempírek, J.; Groat, L.A. Mineralogy and geochemistry of pegmatites on Mount Begbie, British Columbia. *Can. Mineral.* **2014**, *52*, 129–164. [\[CrossRef\]](#)
58. Dolníček, Z.; Ulmanová, J.; Havlíček, J.; Malý, K.; Jačková, I. Fluorite-bearing vein mineralization from Bartoušov near Havlíčkův Brod: A complex fluid history related to post-Variscan uplift of the Moldanubian basement (Bohemian Massif, Czech Republic). *J. Geosci.* **2023**, *68*, 261–279. [\[CrossRef\]](#)
59. Pauliš, P.; Kopecký, S.; Dolníček, Z.; Sejkora, J. Hydrotermální sulfidická mineralizace ze Skalky v havlíčkobrodském rudním revíru (Česká republika). *Acta Mus. Morav. Sci. Geol.* **2024**, *109*, 3–35. (In Czech)
60. Fojt, B.; Dolníček, Z.; Kopa, D.; Sulovský, P.; Škoda, R. Paragenetická charakteristika hypogenních minerálních asociací uranového ložiska Zálesí u Javorníku ve Slezsku. *Acta Mus. Silesiae A* **2005**, *54*, 223–280. (In Czech)
61. Kaneda, H.; Takenouchi, S.; Shoji, T. Stability of pentlandite in the Fe–Ni–Co–S system. *Miner. Depos.* **1986**, *21*, 169–180. [\[CrossRef\]](#)
62. Becker, M.; De Villiers, J.; Bradshaw, D. The mineralogy and crystallography of pyrrhotite from selected nickel and PGE ore deposits. *Econ. Geol.* **2010**, *105*, 1025–1037. [\[CrossRef\]](#)
63. Klemm, D. Synthesen und Analysen in den Dreiecksdiagrammen FeAsS–CoAsS–NiAsS und FeS₂–CoS₂–NiS₂. *Neues Jahrbuch Mineral. Abh.* **1965**, *103*, 205–255. (In German)
64. Bossi, F.; Biagioni, C.; Pasero, M. Nomenclature and classification of the spinel supergroup. *Eur. J. Mineral.* **2018**, *31*, 183–192. [\[CrossRef\]](#)
65. Škácha, P.; Sejkora, J.; Plášil, J.; Dolníček, Z.; Ulmanová, J. Grimmerite, NiCo₂S₄, a new mineral of spinel supergroup from Příbram, Czech Republic. *Eur. J. Mineral.* **2021**, *33*, 175–187. [\[CrossRef\]](#)
66. Rieder, M.; Cavazzini, G.; D'yakonov, Y.S.; Kamenetskii, V.A.F.; Gottardi, G.; Guggenheim, S.; Koval', P.V.; Mueller, G.; Neiva, A.M.R.; Radoslovich, E.W.; et al. Nomenclature of the micas. *Can. Mineral.* **1998**, *36*, 905–912. [\[CrossRef\]](#)
67. Maydagán, L.; Franchini, M.; Impiccini, A.; Lentz, D. Phyllosilicates geochemistry and distribution in the Altar porphyry Cu–(Au) deposit, Andes Cordillera of San Juan, Argentina: Applications in exploration, geothermometry, and geometallurgy. *J. Geochem. Explor.* **2016**, *167*, 83–109. [\[CrossRef\]](#)
68. Wiewióra, A.; Weiss, Z. Crystallochemical classifications of phyllosilicates based on the unified system of projection of chemical composition: II. The chlorite group. *Clay Miner.* **1990**, *25*, 83–92. [\[CrossRef\]](#)
69. Bayliss, P. Nomenclature of the trioctahedral chlorites. *Can. Mineral.* **1975**, *13*, 178–180.
70. Melka, K. Návrh na klasifikaci chloritových minerálů. *Věst. Ústř. Úst. Geol.* **1965**, *40*, 23–27. (In Czech)
71. Cathelineau, M. Cation site occupancy in chlorites and illites as a function of temperature. *Clay Miner.* **1988**, *23*, 471–485. [\[CrossRef\]](#)
72. Stormer, J.C., Jr.; Pierson, M.J.; Tacker, R.C. Variation of F and Cl X-ray intensity due to anisotropic diffusion of apatite during electron microprobe analysis. *Am. Mineral.* **1993**, *78*, 641–648.

73. Loun, J.; Čejka, J.; Sejkora, J.; Plášil, J.; Novák, M.; Frost, R.L.; Palmer, S.J.; Keeffe, E.C. A Raman spectroscopic study of bukovskýite $\text{Fe}_2(\text{AsO}_4)(\text{SO}_4)(\text{OH}) \cdot 7\text{H}_2\text{O}$, a mineral phase with a significant role in arsenic migration. *J. Raman Spectrosc.* **2011**, *42*, 1596–1600. [\[CrossRef\]](#)
74. Ulmanová, J. Conditions of Formation of Selected Hydrothermal Vein Deposits in Central Part of the Bohemian Massif. Master's Thesis, Charles University, Prague, Czech Republic, 2018. (In Czech).
75. Murowchick, J.B. Marcasite inversion and the petrographic determination of pyrite ancestry. *Econ. Geol.* **1992**, *87*, 1141–1152. [\[CrossRef\]](#)
76. Qian, G.; Xia, F.; Brugger, J.; Jiafang, B.; Chen, G.; Pring, A. Replacement of pyrrhotite by pyrite and marcasite under hydrothermal conditions up to 220 °C: An experimental study of reaction textures and mechanisms. *Am. Mineral.* **2011**, *96*, 1878–1893. [\[CrossRef\]](#)
77. Borisenko, A.S. Izučeniye solevovo sostava rastvorov gazovo-židkikh vključenij v mineralach metodom kriometrii. *Akad. Nauk SSSR Sibir. Odd.* **1977**, *8*, 16–27. (In Russian)
78. Vityk, M.O.; Bodnar, R.J. Textural evolution of synthetic fluid inclusions in quartz during reequilibration, with applications to tectonic reconstruction. *Contrib. Mineral. Petrol.* **1995**, *121*, 309–323. [\[CrossRef\]](#)
79. Zheng, Y.-F. Oxygen isotope fractionation in wolframite. *Eur. J. Mineral.* **1992**, *4*, 1331–1335. [\[CrossRef\]](#)
80. Kretschmar, U.; Scott, S.D. Phase relations involving arsenopyrite in the system Fe-As-S and their application. *Can. Mineral.* **1976**, *14*, 364–386.
81. Sundblad, K.; Zachrisson, E.; Smeds, S.-A.; Berglund, S.; Ålinder, C. Sphalerite geobarometry and arsenopyrite geothermometry applied to metamorphosed sulfide ores in the Swedish Caledonides. *Econ. Geol.* **1984**, *79*, 1660–1668. [\[CrossRef\]](#)
82. Kerestedjian, T. Chemical and morphological features of arsenopyrite, concerning its use as a geothermometer. *Mineral. Petrol.* **1997**, *60*, 231–243. [\[CrossRef\]](#)
83. Sharp, Z.D.; Essene, E.J.; Kelly, W.C. A re-examination of the arsenopyrite geothermometer: Pressure considerations and applications to natural assemblages. *Can. Mineral.* **1985**, *23*, 517–534.
84. Alexandre, P.; Layton-Matthews, D.; Joy, B.; Uvarova, Y. Chemical compositions of natural uraninite. *Can. Mineral.* **2015**, *53*, 595–622. [\[CrossRef\]](#)
85. Deer, W.A.; Howie, R.A.; Zussman, J. *Rock-Forming Minerals, Vol. 4A: Feldspars*; Geological Society: London, UK, 2001.
86. Fleet, M.A. *Rock-Forming Minerals, Vol. 3A, Micas*; The Geological Society: London, UK, 2003.
87. Kostov, I.; Stefanova, J.M. Sulphide minerals. In *Crystal Chemistry, Parageneses and Systematics*; Bulgarian Academy of Science: Sofia, Bulgaria, 1981; 212p.
88. Čvileva, T.N.; Bezsmertnaja, M.S.; Spiridonov, E.M.; Agroskin, A.S.; Papayan, G.V.; Vinogradova, R.A.; Lebedeva, S.I.; Zavjalov, E.N.; Filimonova, A.A.; Petrov, V.K.; et al. *Handbook for Determination of Ore Minerals in Reflected Light*; Nedra: Moscow, Russia, 1988; 504p. (In Russian)
89. Kontny, A.; De Wall, H.; Sharp, T.G.; Pósfai, M. Mineralogy and magnetic behavior of pyrrhotite from a 260 °C section at the KTB drilling site, Germany. *Am. Mineral.* **2000**, *85*, 1416–1427. [\[CrossRef\]](#)
90. Sverjensky, D.A. Europium redox equilibria in aqueous solution. *Earth Planet. Sci. Lett.* **1984**, *67*, 70–78. [\[CrossRef\]](#)
91. Aplomov, V.S.; Sereda, E.V. Formation temperatures of quartz and hisingerite from massive copper-nickel ores of the Talnakh deposit. *Geol. Geofiz.* **1983**, *3*, 62–67. (In Russian)
92. Mustoe, G. Hisingerite—A rare iron mineral from Walker Valley, Skagit County, Washington. *Wash. Geol.* **1997**, *24*, 14–20.
93. Kojima, S.; Takeda, S.; Kogita, S. Chemical factors controlling the solubility of uraninite and their significance in the genesis of unconformity-related uranium deposits. *Mineral. Depos.* **1994**, *29*, 353–360. [\[CrossRef\]](#)
94. Murowchick, J.B.; Barnes, H.L. Marcasite precipitation from hydrothermal solutions. *Geochim. Cosmochim. Acta* **1986**, *50*, 2615–2629. [\[CrossRef\]](#)
95. Bau, M.; Möller, P. Rare earth element fractionation in metamorphogenic hydrothermal calcite, magnesite and siderite. *Mineral. Petrol.* **1992**, *45*, 231–246. [\[CrossRef\]](#)
96. Lee, S.G.; Lee, D.H.; Kim, Y.; Chae, B.G.; Kim, W.Y.; Woo, N.C. Rare earth elements as indicators of groundwater environment changes in a fractured rock system: Evidence from fracture-filling calcite. *Appl. Geochem.* **2003**, *18*, 135–143. [\[CrossRef\]](#)
97. Kučera, J.; Cempírek, J.; Dolníček, Z.; Muchez, P.; Prochaska, W. Rare earth elements and yttrium geochemistry of dolomite from post-Variscan vein-type mineralization of the Nížký Jeseník and Upper Silesian Basins, Czech Republic. *J. Geochem. Explor.* **2009**, *103*, 69–79. [\[CrossRef\]](#)
98. Cassaignon, S.; Koelsch, M.; Jolivet, J.P. Selective synthesis of brookite, anatase and rutile nanoparticles: Thermolysis of TiCl_4 in aqueous nitric acid. *J. Mater. Sci.* **2007**, *42*, 6689–6695. [\[CrossRef\]](#)
99. Bau, M. Rare-earth element mobility during hydrothermal and metamorphic fluid-rock interaction and the significance on the oxidation state of europium. *Chem. Geol.* **1991**, *93*, 219–230. [\[CrossRef\]](#)
100. Migdisov, A.A.; Williams-Jones, A.E. Hydrothermal transport and deposition of the rare earth elements by fluorine-bearing aqueous liquids. *Mineral. Depos.* **2014**, *49*, 987–997. [\[CrossRef\]](#)
101. Rubin, J.N.; Henry, C.D.; Price, J.G. The mobility of zirconium and other immobile elements during hydrothermal alteration. *Chem. Geol.* **1993**, *110*, 29–47. [\[CrossRef\]](#)
102. Jiang, S.-Y.; Wang, R.-C.; Xu, X.-S.; Zhao, K.-D. Mobility of high field strength elements (HFSE) in magmatic-, metamorphic-, and submarine-hydrothermal systems. *Phys. Chem. Earth Parts A/B/C* **2005**, *30*, 1020–1029. [\[CrossRef\]](#)

103. Zheng, Y.F. Calculation of oxygen isotope fractionation in anhydrous silicate minerals. *Geochim. Cosmochim. Acta* **1993**, *57*, 1079–1091. [[CrossRef](#)]
104. Sheppard, S.M.F. Characterization and isotopic variations in natural waters. *Rev. Mineral.* **1986**, *16*, 165–183.
105. Hoefs, J. *Stable Isotope Geochemistry*, 4th ed.; Springer: Berlin, Germany; New York, NY, USA, 1997.
106. Žák, K.; Dobeš, P. *Stable Isotopes and Fluid Inclusions in Hydrothermal Deposits: The Příbram Ore Region*; Nakladatelství Academia: Prague, Czech Republic, 1991; pp. 1–109.
107. Dolníček, Z.; Ulmanová, J.; Sejkora, J.; Knížek, F.; Škácha, P. Mineralogy and genesis of the Pb–Zn–Sb–Ag vein H32A in the Příbram uranium and base-metal district, Bohemian Massif, Czech Republic. *Ore Geol. Rev.* **2023**, *162*, 105695. [[CrossRef](#)]
108. Potter, J.; Rankin, A.H.; Treloar, P.J. Abiogenic Fischer–Tropsch synthesis of hydrocarbons in alkaline igneous rocks; fluid inclusion, textural and isotopic evidence from the Lovozero complex, N.W. Russia. *Lithos* **2004**, *75*, 311–330. [[CrossRef](#)]
109. Graser, G.; Potter, J.; Köhler, J.; Markl, G. Isotope, major, minor and trace element geochemistry of late-magmatic fluids in the peralkaline Ilímaussaq intrusion, South Greenland. *Lithos* **2008**, *106*, 207–221. [[CrossRef](#)]
110. Nivin, V.A. Molecular–mass distribution of saturated hydrocarbons in gas of the Lovozerskii nepheline–syenite massif. *Dokl. Earth Sci. A* **2009**, *429*, 1580–1582. [[CrossRef](#)]
111. Krooss, B.M.; Littke, R.; Müller, B.; Frielingsdorf, J.; Schwochau, K.; Idiz, E.F. Generation of nitrogen and methane from sedimentary organic matter: Implications on the dynamics of natural gas accumulations. *Chem. Geol.* **1995**, *126*, 291–318. [[CrossRef](#)]
112. Littke, R.; Krooss, B.M.; Idiz, E.F.; Frielingsdorf, J. Molecular nitrogen in natural gas accumulations: Generation from sedimentary organic matter at high temperatures. *Am. Assoc. Petrol. Geol. Bull.* **1995**, *79*, 410–430.
113. Lüders, V.; Reutel, C.; Hoth, P.; Banks, D.A.; Mingram, B.; Pettke, T. Fluid and gas migration in the North German Basin: Fluid inclusion and stable isotope constraints. *Int. J. Earth Sci.* **2005**, *94*, 990–1009. [[CrossRef](#)]
114. Mingram, B.; Hoth, P.; Lüders, V.; Harlov, D. The significance of fixed ammonium in Paleozoic sediments for the generation of nitrogen rich natural gases in the North German Basin (NGB). *Int. J. Earth Sci.* **2005**, *94*, 1010–1022. [[CrossRef](#)]
115. Heinrich, C.A. The chemistry of hydrothermal tin(–tungsten) ore deposition. *Econ. Geol.* **1990**, *85*, 457–481. [[CrossRef](#)]
116. Kelly, W.C.; Turneaure, F.S. Mineralogy, paragenesis and geothermometry of the tin and tungsten deposits of the eastern Andes, Bolivia. *Econ. Geol.* **1970**, *65*, 609–680. [[CrossRef](#)]
117. Lowering, T.S. The origin of tungsten ores of Boulder County, Colorado. *Econ. Geol.* **1941**, *36*, 229–279. [[CrossRef](#)]
118. Lecumberri-Sanchez, P.; Vieira, R.; Heinrich, C.A.; Pinto, F.; Wälle, M. Fluid–rock interaction is decisive for the formation of tungsten deposits. *Geology* **2017**, *45*, 579–582. [[CrossRef](#)]
119. Franců, J.; Sýkorová, I.; Franců, E.; Šafanda, J.; Malý, L. Vitrinite reflectance of coals in the Boskovice Furrow as related to thermal and burial history. In *VIII. Coal Geology Conference, Abstracts*; Pešek, J., Opluštil, O., Eds.; Charles University: Prague, Czech Republic, 1998; p. 28.
120. Sibson, R.H. Earthquake rupturing as a mineralizing agent in hydrothermal systems. *Geology* **1987**, *15*, 701–704. [[CrossRef](#)]
121. Allen, P.A.; Allen, J.R. *Basin Analysis: Principles and Applications*; Wiley and Blackwell: Hoboken, NJ, USA, 1990.
122. Martínek, K.; Blecha, M.; Daněk, V.; Franců, J.; Hladíková, J.; Johnová, R.; Uličný, D. Record of palaeoenvironmental changes in a Lower Permian organic-rich lacustrine succession: Integrated sedimentological and geochemical study of the Rudník member, Krkonoše Piedmont Basin, Czech Republic. *Palaeogeogr. Palaeoclimat. Palaeoecol.* **2006**, *230*, 85–128. [[CrossRef](#)]
123. Žák, K.; Čadek, J.; Dobeš, P.; Šmejkal, V.; Reichmann, F.; Vokurka, K.; Sandstat, J.S. Vein barite mineralization of the Bohemian Massif: Sulfur, oxygen and strontium isotopes and fluid inclusion characteristics and their genetic implications. In *Proceedings of the Symposium on Barite and Barite Deposits*; Poole, F.G., Dobeš, P., Eds.; Geological Survey: Prague, Czech Republic, 1990; pp. 35–49.
124. Gleeson, S.A.; Wilkinson, J.J.; Stuart, F.M.; Banks, D.A. The origin and evolution of base metal mineralising brines and hydrothermal fluids, South Cornwall, UK. *Geochim. Cosmochim. Acta* **2001**, *65*, 2067–2079. [[CrossRef](#)]
125. Boiron, M.C.; Cathelineau, M.; Banks, D.A.; Buschaert, S.; Fourcade, S.; Coulibaly, Y.; Michelot, J.L.; Boyce, A. Fluid transfers at a basement/cover interface. Part II. Large-scale introduction of chlorine into basement by Mesozoic basinal brines. *Chem. Geol.* **2002**, *192*, 121–140. [[CrossRef](#)]
126. Dutkiewicz, A.; Volk, H.; Ridley, J.; George, S.C. Geochemistry of oil in fluid inclusions in a middle Proterozoic igneous intrusion: Implications for the source of hydrocarbons in crystalline rocks. *Org. Geochem.* **2004**, *35*, 937–957. [[CrossRef](#)]
127. Schubert, F.; Diamond, L.W.; Tóth, T.M. Fluid-inclusion evidence of petroleum migration through a buried metamorphic dome in the Pannonian Basin, Hungary. *Chem. Geol.* **2007**, *244*, 357–381. [[CrossRef](#)]
128. Dolníček, Z.; Fojt, B.; Prochaska, W.; Kučera, J.; Sulovský, P. Origin of the Zálesí U–Ni–Co–As–Ag/Bi deposit, Bohemian Massif, Czech Republic: Fluid inclusion and stable isotope constraints. *Miner. Depos.* **2009**, *44*, 81–97. [[CrossRef](#)]
129. Hoffmann, C.F.; Henley, R.W.; Higgins, N.C.; Solomon, N.; Summons, R.E. Biogenic hydrocarbons in fluid inclusions from the Aberfoyle tin–tungsten deposit, Tasmania, Australia. *Chem. Geol.* **1988**, *70*, 287–299. [[CrossRef](#)]
130. Polyá, D.A.; Foxford, K.A.; Stuart, F.; Boyce, A.; Fallick, A.E. Evolution and paragenetic context of low δD hydrothermal fluids from the Panasqueira W–Sn deposit, Portugal: New evidence from microthermometric, stable isotope, noble gas and halogen analyses of primary fluid inclusions. *Geochim. Cosmochim. Acta* **2000**, *64*, 3357–3371. [[CrossRef](#)]

131. Kříbek, B.; Žák, K.; Dobeš, P.; Leichmann, J.; Pudilová, M.; René, M.; Scharm, B.; Scharmová, M.; Hájek, A.; Holeczy, D.; et al. The Rožná uranium deposit (Bohemian Massif, Czech Republic): Shear zone-hosted, late Variscan and post-Variscan hydrothermal mineralization. *Miner. Depos.* **2009**, *44*, 99–128. [\[CrossRef\]](#)
132. Dolníček, Z.; René, M.; Hermannová, S.; Prochaska, W. Origin of the Okrouhlá Radouň episyenite-hosted uranium deposit, Bohemian Massif, Czech Republic: Fluid inclusion and stable isotope constraints. *Miner. Depos.* **2014**, *49*, 409–425. [\[CrossRef\]](#)
133. Ulmanová, J.; Dolníček, Z.; Škacha, P.; Sejkora, J. Origin of Zn-Pb mineralization of the vein Bt23C, Bytíz deposit, Příbram uranium and base-metal ore district, Czech Republic: Constraints from occurrence of immiscible aqueous-carbonic fluids. *Minerals* **2024**, *14*, 87. [\[CrossRef\]](#)
134. Kopecký, S.; Pauliš, P. Nález krystalovaných scheelitů v kamenolomu Pohled u Havlíčkova Brodu. *Minerál* **2019**, *27*, 511–513. (In Czech)
135. Wang, R.C.; Fontan, F.; Xu, S.J.; Chen, X.M.; Monchoux, P. The association of columbite, tantalite and tapiolite in the Suzhou Granite, China. *Can. Mineral.* **1997**, *35*, 699–706.
136. Abdalla, H.M.; Helba, H.; Mohamed, F. Chemistry of columbite-tantalite minerals in rare metal granitoids, Easterns Desert, Egypt. *Mineral. Mag.* **1998**, *62*, 821–836. [\[CrossRef\]](#)
137. Rub, A.K.; Štemprok, M.; Rub, M.G. Tantalum mineralization in the apical part of the Cínovec (Zinnwald) granite stock. *Mineral. Petrol.* **1998**, *63*, 199–222. [\[CrossRef\]](#)
138. Scott, P.W.; Pascoe, R.D.; Hart, F.W. Columbite-tantalite, rutile and other accessory minerals from the St. Austell topaz granite, Cornwall. *Proc. Usher Soc.* **1998**, *9*, 165–170.
139. Wang, R. *Étude Minéralogique et Cristallographique de Cassitérite, Niobo-Tantalates et Minéraux Disséminés du Granite de Beauvoir (Allier); Implications Métallogéniques*; Paul Sabatier: Toulouse, France, 1998.
140. Belkasmí, M.; Cuney, M.; Pollard, P.J.; Bastoul, A. Chemistry of the Ta-Nb-Sn-W oxide minerals from the Yichun rare metal granite (SE China): Genetic implications and comparison with Moroccan and French Hercynian examples. *Mineral. Mag.* **2000**, *64*, 507–523. [\[CrossRef\]](#)
141. Breiter, K.; Škoda, R.; Uher, P. Nb-Ta-Ti-W-Sn-oxide minerals as indicators of a peraluminous P- and F-rich granitic system evolution: Podlesí, Czech Republic. *Mineral. Petrol.* **2007**, *91*, 225–248. [\[CrossRef\]](#)
142. Bastos Neto, A.C.; Pereira, V.P.; Ronchi, L.H.; De Lima, E.F.; Frantz, J.C. The world-class Sn, Nb, Ta, F (Y, REE, Li) deposit and the massive cryolite associated with the albite-enriched facies of the madeira A-type granite, Pitinga Mining District, Amazonas State, Brazil. *Can. Mineral.* **2009**, *47*, 1329–1357. [\[CrossRef\]](#)
143. René, M.; Škoda, R. Nb-Ta-Ti oxides fractionation in rare-metal granites: Krásno-Horní Slavkov ore district, Czech Republic. *Mineral. Petrol.* **2011**, *103*, 37–48. [\[CrossRef\]](#)
144. Zhu, Z.Y.; Wang, R.C.; Che, X.D.; Zhu, J.C.; Wei, X.L.; Huang, X. Magmatic-hydrothermal rare-element mineralization in the Songshugang granite (northeastern Jiangxi, China): Insights from an electron-microprobe study of Nb-Ta-Zr minerals. *Ore Geol. Rev.* **2015**, *65*, 749–760. [\[CrossRef\]](#)
145. González, T.L.; Polonio, F.G.; Moro, F.J.L.; Fernández, A.F.; Contreras, J.L.S.; Benito, M.C.M. Tin-tantalum-niobium mineralization in the Penouta deposit (NW Spain): Textural features and mineral chemistry to unravel the genesis and evolution of cassiterite and columbite group minerals in a peraluminous system. *Ore Geol. Rev.* **2016**, *81*, 79–95. [\[CrossRef\]](#)
146. Xie, L.; Wang, R.-C.; Che, X.-D.; Huang, F.-F.; Erdmann, S.; Zhang, W.-L. Tracking magmatic and hydrothermal Nb-Ta-W-Sn fractionation using mineral textures and composition: A case study from the late Cretaceous Jiepailing ore district in the Nanling Range in South China. *Ore Geol. Rev.* **2016**, *78*, 300–321. [\[CrossRef\]](#)
147. Xie, L.; Wang, Z.; Wang, R.-C.; Zhu, J.C.; Che, X.; Gao, J.; Zhao, X. Mineralogical constraints on the genesis of W-Nb-Ta mineralization in the Laiziling granite (Xianghualing district, south China). *Ore Geol. Rev.* **2018**, *95*, 695–712. [\[CrossRef\]](#)
148. René, M. Nb-Ta-Ti oxides in topaz granites of the Geyer granite stock (Erzgebirge Mts., Germany). *Minerals* **2019**, *9*, 155. [\[CrossRef\]](#)
149. Siachoque, A.; Garcia, R.; Vlach, S.R.F. Occurrence and composition of columbite-(Fe) in the reduced A-type Desemboque Pluton, Graciosa province (S-SE Brazil). *Minerals* **2020**, *10*, 411. [\[CrossRef\]](#)
150. Pauliš, P.; Kopecký, S.; Pour, O.; Sejkora, J.; Malíková, R.; Civiš, S. Bi-Te mineralizace z Vysoké u Havlíčkova Brodu (Česká republika). *Bull. Mineral.-Petro. Odd. Nár. Muz.* **2014**, *22*, 275–280. (In Czech)
151. Pauliš, P.; Kopecký, S.; Dolníček, Z.; Sejkora, J. Sulfidická mineralizace s Au-bohatým stříbrem z Utína v havlíkobrodském rudním revíru (Česká republika). *Bull. Mineral. Petro.* **2023**, *31*, 25–34. (In Czech) [\[CrossRef\]](#)

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