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Chemical Composition of Wolframite from the Porokhovskoe and Yugo-Konevskoe W Deposits (Central Urals): Implications for Fluid Evolution and Ore Genesis

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Abstract: The composition of wolframite from ores of the Porokhovskoe and Yugo-Konevskoe W greisen deposits in the Central Urals is studied using SEM-EDS and LA-ICP-MS analyses. The Porokhovskoe deposit is localized in a metamorphosed volcanosedimentary sequence of Lower Silurian age, and the Yugo-Konevskoe is enclosed in an eponymous granite pluton of Middle Permian–Lower Triassic age. Most studied wolframite grains belong to hübnerite. The Fe/(Fe + Mn) value of wolframite varies in a range of 0.02–0.50. Wolframite from both deposits is enriched in Zn, Nb, and Mg. The wolframite from the Porokhovskoe deposit is enriched in V, Sc, Zn, and Mg and is depleted in Mo, U, rare earth elements (REEs), Nb, and Ta, compared to wolframite from the Yugo-Konevskoe deposit. It is suggested that this difference is due to the occurrence of ore veins in different rocks at different distance from the source of the ore-forming fluid, which cools down as it moves away from the source, leading to a decrease in the incorporation of trace elements by the lower-temperature wolframite. The predominance of heavy REEs over light REEs in all the studied wolframite is explained by the close ionic radii of heavy REEs to the main mineral-forming elements Fe and Mn.

Keywords: Porokhovskoe; Yugo-Konevskoe; Boevsko-Biktimirovo; Central Urals; wolframite; hübnerite; trace elements



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1. Introduction

In nature, the main W form comprises complex oxides, in which W occurs in a 6+ state. The dominant tungstates (AXO₄) include scheelite and wolframite, which belong to different structural types. The structural type of tungstates is generally controlled by the ionic radius of the A²⁺ cation [1,2]. Cations with a radius of >0.9 Å (Ca, Pb, etc.) can occur in the A position in minerals with a scheelite structural type, crystallizing in the tetragonal system. A cation radius in position A of <0.9 Å results in the formation of minerals with a monoclinic wolframite structural type. In the minerals of the wolframite group, Fe, Mn, Sc, Mg, Co, and Zn occupy position A and W, Ta, Nb, and Ti occupy position X. The minerals of the wolframite group encompass a continuous isomorphic series, the end members of which include ferberite FeWO₄ and hübnerite MnWO₄. A limited isomorphic series exists between ferberite, hübnerite, and huanzalaite MgWO₄ [3]. Wolframite with a predominance of zinc (up to 18.18 wt.% ZnO) in position A is described as sanmartinite (Zn,Fe)WO₄ [4]. A technogenic phase, krasnoselskite CoWO₄, which is not approved by the International Mineralogical Association (IMA), was found in burnt dumps of the Chelyabinsk coal basin [5]. In addition, the wolframite group contains minerals with other

species-forming elements: heftetjernite ScTaO_4 , nioboheftetjernite ScNbO_4 , rossovskyite $(\text{Fe}^{3+}, \text{Ta})(\text{Nb}, \text{Ti})\text{O}_4$, and dmitryvarlamovite $\text{Ti}_2(\text{Fe}^{3+}\text{Nb})\text{O}_8$ [6–10].

Wolframite is spatially and genetically associated with granitic intrusions. It is found in quartz–wolframite veins, stockworks, greisens, and rarely in skarns [11,12] and often occurs in complex W–Mo, Sn–W, and rare-metal deposits. Wolframite can either be a single W host or is associated with scheelite. The wolframite in the deposits is typically associated with quartz, fluorite, topaz, muscovite, tourmaline, cassiterite, molybdenite, pyrite, and arsenopyrite.

The chemical composition of wolframite is rather well studied [11,13–20]. The main attention in these studies was paid to a link between the formation conditions (temperature, pressure, and fluid composition) and the chemical composition of the ferberite–hübnerite isomorphic series, trace element content, morphological features, unit cell parameters, defects in the crystal structure, and density and strength characteristics [18].

The first data on the chemical composition of wolframite, including samples from the Boevskoe deposit located close to the studied Porokhovskoe and Yugo-Konevskoe ones in the Central Urals, had been published already in the 19th century [21]. Geochemical features were considered mostly for the main components—Mn and Fe [14,22–24]. Petrov [15] established the correlation between the composition of wolframite and a number of factors, including fluid temperature, the composition of host rocks, Eh–pH values of the ore deposition conditions, and the activity of the fluid components.

The works that study the composition of wolframite are based on the application of various analytical methods. Early studies relied on chemical and spectral analysis of monomineral fractions, whereas later geochemical studies used microprobe analysis and optical emission spectroscopy [15,18–20,25–27]. The development of laser ablation inductively coupled plasma with (LA–ICP–MS) in recent years made it possible to detect the widest spectrum of trace elements in wolframite [17,28–39]. The distribution of trace elements in wolframite depends on many factors, including the genetic type of mineralization, geochemical features of individual deposits and regions, the composition of host rocks, and distance from the fluid source (plutons, faults).

Structural trace elements in wolframite can enter both position A, replacing Fe and Mn, and position X, where they replace W. Tungsten is most often replaced by Nb and Ta and rarely by Sn and Mo [13,14,17,40]. Magnesium, Zn, Co, and Cd with an ionic radius of $<0.9 \text{ \AA}$ can enter the wolframite lattice, replacing Fe and Mn, up to the formation of Mg–huanzalaite and Zn–sanmartinite.

The aim of this work is to characterize the geochemical features of wolframite from the Yugo-Konevskoe and Porokhovskoe deposits in the Central Urals in order to reveal the correlation between the composition of wolframite and the type of host rocks and the distance from the ore-generating intrusion. The deposits differ in geological setting: The Yugo-Konevskoe deposit is localized within a granitic pluton of Middle Permian–Lower Triassic age and the Porokhovskoe deposit occurs among metamorphosed volcanosedimentary rocks of Lower Silurian age, the relation of which to this granitic pluton is unclear. It is suggested that both deposits are associated with one ore-generating intrusion [41].

2. Geological Structure

Six near-longitudinal zones are distinguished in the southern segment of the Urals fold belt: the Pre-Uralian foredeep and West Uralian, Central Uralian, Magnitogorsk, East Uralian, and Transuralian zones (Figure 1) [42,43]. The first three zones represent the passive margin of the Russian Platform, which formed in the Late Cambrian–Early Ordovician, evolved from the Ordovician to the Devonian, and was deformed in the Carboniferous–Permian, when it became part of the Urals fold belt [43]. The Magnitogorsk and East Uralian

zones comprise Paleozoic rocks of mid-ocean ridges (ophiolites), island arcs, Andean-type belts, flysch troughs, and intra-arc basins. They are separated from the complexes of the Russian Platform by the Main Uralian Fault, which is one of the largest sutures in Eurasia [42,43]. Tungsten mineralization is controlled mainly by Carboniferous–Permian granitoid intrusions associated with the Hercynian collision and is mainly associated with the Mo, Be, and Bi mineralization of vein quartz and stockwork facies of greisens, skarns, and gumbaites (feldspathic metasomatic rocks) [41,43].

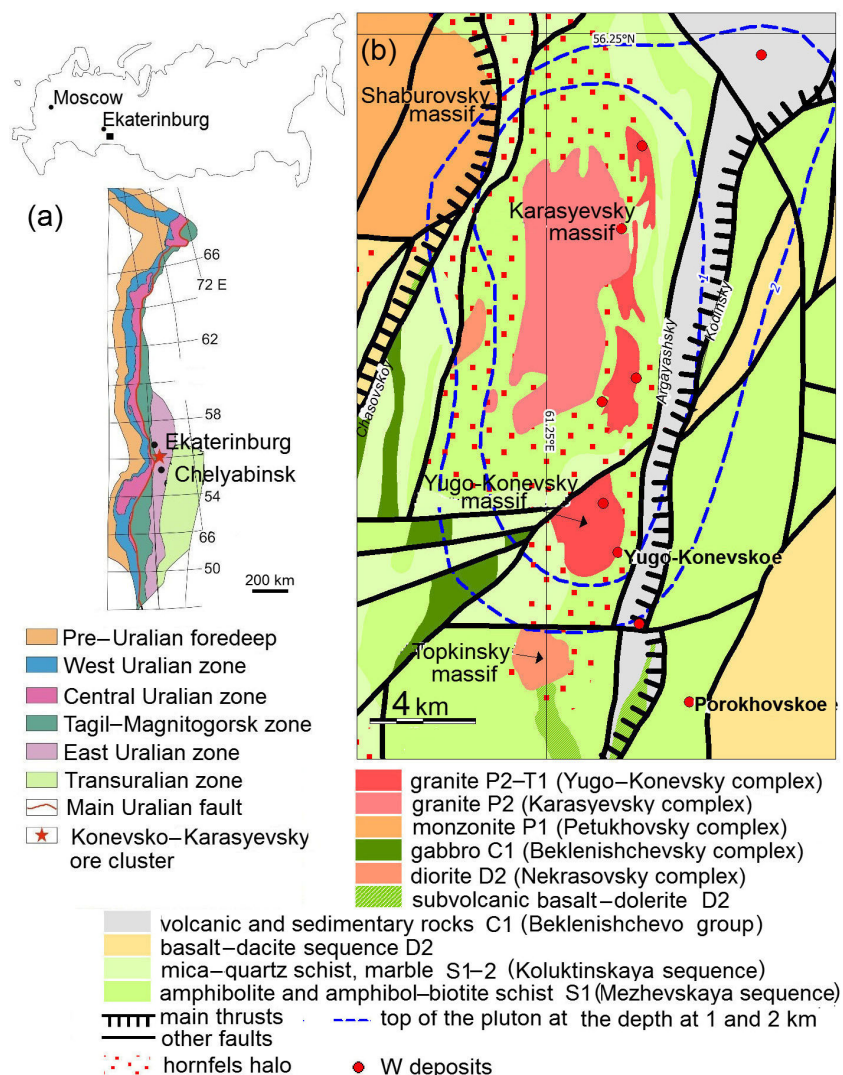


Figure 1. Scheme of tectonic-magmatic zoning of the Urals [43] (a) and geological structure of the region [44] (b).

The Yugo-Konevskoe and Porokhovskoe deposits belong to the Konevsko-Karasyevsky ore cluster, which is part of the Boevsko-Biktimirovo rare metal zone with Mo–W (Yugo-Konevskoe and Porokhovskoe), W–Be (Novo-Boevskoe, Pyankovskoe, Karasyevskoe), and Be–W (Boevskoe, Igish) deposits and a number of ore occurrences [41]. The ore cluster, approximately 40 km long, has a near-longitudinal strike (Figure 1) and is located in the East Uralian Zone [41]. The distribution of mineralization is controlled by reverse-thrust dislocations of the Kodinsky, Argayashsky, and Shaburovo fault zones among volcanic and sedimentary formations of the Lower Silurian Mezhevskaya Sequence and Lower Carboniferous Beklenishchevo Group [44]. The Mezhevskaya Sequence includes amphibolites and amphibole–biotite schists, which are interpreted as products of metamorphism of intermediate–mafic volcanic rocks. The age of metamorphism is unclear. The rocks

of the Beklenishchevo Group are characterized by strong tectonic dislocations and facies variability along the section. They include volcanic (basalts, andesites, dacites, and their tuffs) and sedimentary (sandstones, siltstones (often carbonaceous), and marbles) varieties. The volcanic rocks of the Beklenishchevo Group and the eponymous comagmatic complex form an Early Carboniferous volcanic association.

The W mineralization of the ore cluster is mainly associated with granitoid plutons of the post-collision Middle Permian–Lower Triassic Yugo-Konevsky granite–leucogranite complex [44]. This complex includes the Yugo-Konevsky, Igish, and Pyankovsky plutons exposed on the surface, as well as buried Mylnikovsky (the depth of 100–150 m) and Boevsky (the depth of 400 m) plutons. According to geophysical data, all these plutons merge into a single batholith at depth.

The Yugo-Konevsky complex is composed of rocks of two intrusion phases. The biotite and muscovite–biotite granites and granodiorites of the first phase are porphyritic, with a fine- to medium-grained matrix and accessory titanite, apatite, magnetite, ilmenite, and allanite [44,45]. The leucocratic and alaskitic granites of the second phase are biotite–muscovite, medium- or coarse-grained, weakly porphyritic, often cataclased, greisenized. Fluorite, apatite, titanite, magnetite are accessory minerals. The rocks of the complex have a slightly higher content of alkalis, Be, Mo, and W [44,45]. Leucogranites are characterized by a low rare earth element (REE) content (11–13 ppm), a moderate predominance of light REEs over heavy REEs ($La_n/Yb_n = 7–9$), and a small negative Eu anomaly [46].

The W deposits and ore occurrences of the region are localized both directly in granite plutons and their apophyses and in supra-intrusive host rocks. Mostly vein-type mineralization is accompanied by greisenization zones.

The Yugo-Konevskoe deposit was discovered in 1930, and the W ores were being mined from 1934 to 1957. The deposit is confined to the eastern periphery of the eponymous granitic pluton [41]. The W-bearing quartz veins occur in medium-grained leucogranites and fine-grained porphyritic adamellites in the northern and southern parts, respectively. Three vein systems of different ages developed in the deposit (Figure 2). The earliest system (type 1) include longitudinal veins with an azimuth of 170–195° and a western dip at an angle of 55–90°. The thickness of the veins is low, and the length does not exceed 100 m. These veins are composed of quartz, muscovite, fluorite, pyrite, sphalerite, chalcopyrite, bismuthinite, and minor molybdenite. The longitudinal veins are intersected by veins with a near-latitudinal strike (type 2), thickness of 3–10 cm, and a length of a few tens of meters. Their composition is similar to the NW-trending ore veins, but they are enriched in beryl. The latest NW-trending veins (type 3) are up to 1.5 m thick (15–20 cm, on average). They are traced to a depth of 200 m and up to 400 m along the strike. They are composed of quartz, fluorite, wolframite, scheelite, beryl, pyrite, sphalerite, chalcopyrite, galena, and rare cassiterite, arsenopyrite, fahlore, Bi sulfides and sulfosalts, and cubanite [41,47,48]. The ore veins are surrounded by alteration rims 5–8 to 20–60 cm thick. Molybdenite, scheelite, wolframite, and beryl are observed in altered granites. According to spectral analysis, the Be content of the greisenized granites is 0.001–0.004%, and the Mo content is 0.002%. The WO_3 content reaches 0.06%. The higher content of Be (0.005%–0.01%), W (up to 0.02%), and Mo (0.003%–0.03%) is determined in sericitized, carbonated, and locally fluoritized crystalline schists at the contacts with veins [41].

The Porokhovskoe deposit was discovered in 1942, was exploited in 1943–1957 by the mine, and was re-evaluated in 2021–2023. The deposit is composed of metaandesites and intermediate volcanoclastic rocks with marble interbeds (Figure 3). The volcanic rocks are often epidotized up to the formation of epidotes and epidote–amphibole schists. The W mineralization is associated with quartz veins and skarn bodies (Figure 4). The orientation of the vein zone coincides with the SE direction of the ridge of the buried part

of the Yugo-Konevsky granitic pluton. A series of closely located NW-trending veins with a western dip at an angle of $70\text{--}85^\circ$ forms a narrow linear zone 1 km long. A group of shorter veins with a strike of $135\text{--}150^\circ$ is observed to the northwest of the main zone. In total, there are more than 40 quartz–wolframite veins 200–250 m (locally, up to 300 m) long and 15–35 cm thick. In addition to quartz and muscovite, they always contain wolframite, scheelite, pyrite, sphalerite, molybdenite, galena, bismuthinite, various sulfosalts, calcite, fluorite, and rare beryl [41,47,48]. Most veins are accompanied by sharp linear zones of lightened sericitized metaandesites with an abundant pyrite dissemination. The thickness of the alteration zone does not exceed 35 cm [41].

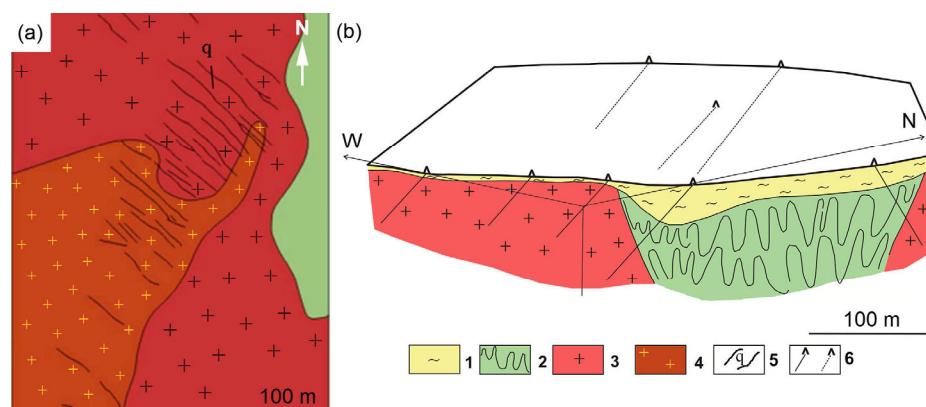


Figure 2. (a) Geological map, with overburden removed, of the Yugo-Konevskoe deposit [41] and block diagram of the Yugo-Konevskoe deposit (created by K. Novoselov on base prospection works) (b): 1—loam; 2—amphibole schists of the Lower Silurian Mezhevskaya Sequence, 3–4—Middle Permian–Lower Triassic Yugo-Konevsky pluton, 3—biotite granite of the first phase and unspecified granite (on block diagram), 4—leucocratic granite of the second phase, 5—ore quartz veins, 6—boreholes.

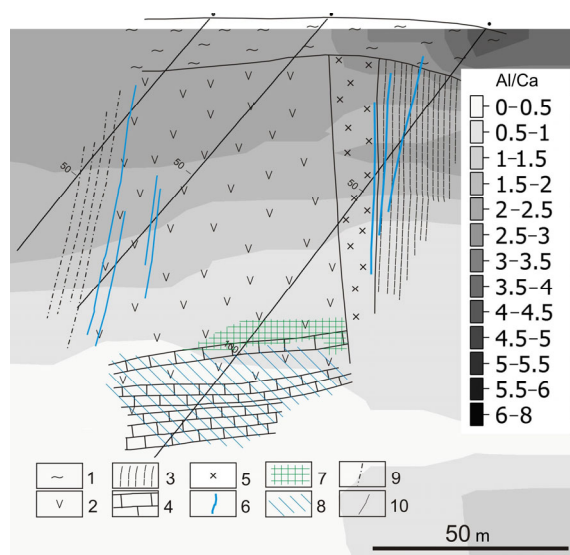


Figure 3. Geological section through the central part of the Porokhovskoe deposit: 1—loam; the Lower Silurian rocks of Mezhevskaya Sequence: 2—alternation of metamorphosed intermediate volcanic rocks and volcanoclastic rocks, 3—epidote–actinolite schist, 4—marble; 5—diorite porphyrite; 6—W-bearing quartz veins; 7—garnet–epidote–pyroxene skarn; 8—greisen stockwork; 9—disintegrated rocks of the fault zone; 10—borehole. The Al/Ca ratio shows the relationship between aluminosilicate and calcareous rocks.

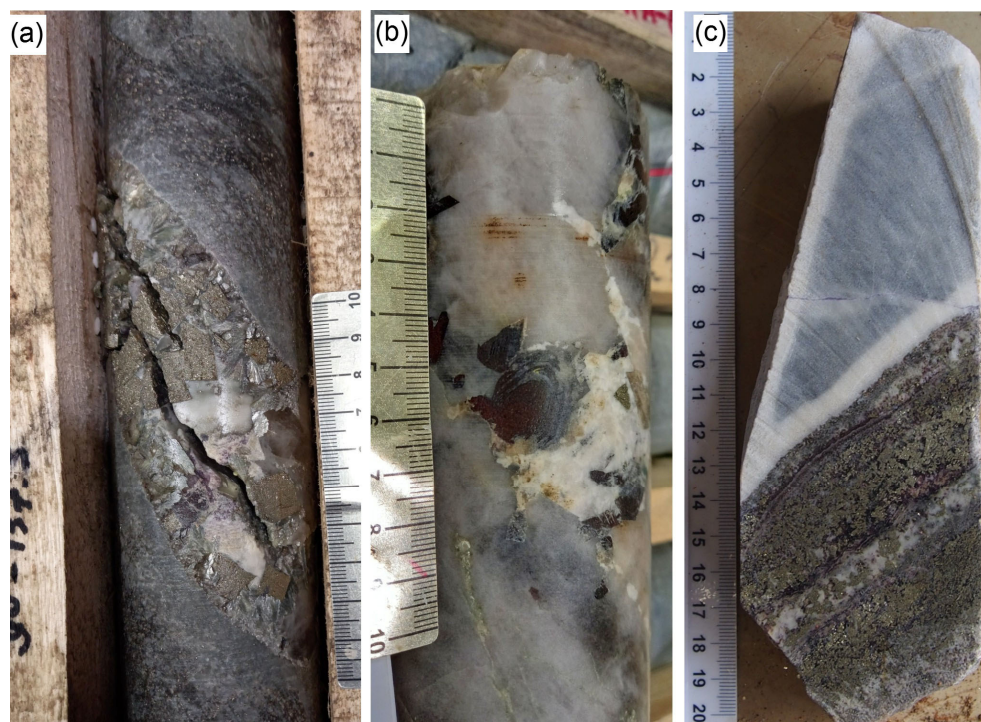


Figure 4. Ore veins at Porokhovskoe deposit: (a) Pyrite–muscovite–quartz vein with light rims in meta-andesites; (b) quartz vein with zonal distribution of wolframite and scheelite; (c) pyrite–fluorite vein in marbles.

3. Materials and Methods

Hand specimens from the drill cores and trenches for the studies was provided by the Urals Geological Expedition and collected by the authors as well. We also used group samples, which include various ore types. The group samples were crushed and washed in water to yield a heavy concentrate, which was finally washed in bromoform. The analytical methods included optical microscopy in reflected light using an Axioscope A1 (Zeiss) polarizing microscope, scanning electron microscopy (SEM) with energy-dispersive analysis (EDA), and LA-ICP-MS.

The composition of wolframite was analyzed on a VEGA3 TESCAN SBU SEM (TESCAN, Czech Republic, Brno) equipped with an Oxford Instruments X-act ED spectrometer (Oxford Instruments, Abingdon, UK) at an accelerating voltage of 20 kV, a beam current of 0.3 nA for quantitative analysis, and MINM-25-53 standards from ASTIMEX Scientific Limited (standard No. 01-044) (Oxford, UK) and Microanalysis Consultants Ltd. (standard No. 1362) (Cambridgeshire, UK). Standards used include metallic W ($WM\alpha$) and Mn ($MnK\alpha$), magnetite ($FeK\alpha$). The detection limit was ~ 0.2 wt.%.

The content of trace elements in wolframite was determined in polished sections using an Agilent 7700x mass spectrometer (Agilent Technologies, Santa Clara, CA, USA) equipped with the MassHunter software package (G7201A, A.01.02) and a New Wave Research UP-213 laser device (Fremont, CA, USA) with a UV Nd:YAG laser at a wavelength of 213 nm and flux density settings of 12.0 – 15.0 J/cm² and a repetition rate of 10 Hz. The carrier gas in the cell is He; the flow rate is 0.65 L/min. The mass spectrometer settings included a high-frequency signal power of 1500 W; Ar as a carrier gas; a flow rate of 0.95 L/min; a plasma-forming gas flow rate (Ar) of 15 L/min; and an auxiliary gas flow rate (Ar) of 0.9 L/min.

The analysis was carried out in the point ablation mode; the beam diameter was 55–80 μ m. To remove surface contaminants, a 2 s pre-ablation was performed before each analysis. During the first 30 s, a blank signal was recorded without ablation of the

substance, and then the signal from the ablated material was processed during the next 60 s. The mass spectrometer was calibrated using the NIST SRM-612 international standard reference sample (Gaithersburg, MD, USA). In this case, the amount of molecular oxide ions ($^{232}\text{Th}^{16}\text{O}/^{232}\text{Th}$) did not exceed 0.2%. The $^{238}\text{U}/^{232}\text{Th}$ ratio was close to 1. The USGS GSD-1g international reference material was used for the calculation. To account for the instrumental drift of the laser and mass spectrometer, the standard sample was analyzed every 10–12 points. The calculation of the element content was carried out on the Iolite software package (v. 2.5) [49] using the approaches described in [50] and using ^{57}Fe as an internal standard or normalization of the total signal, taking into account the ^{55}Mn content.

4. Results

Pyrite, wolframite, and scheelite are major ore minerals of the studied ores both of the Yugo-Konevskoe and Porokhovskoe deposits. Chalcopyrite and sphalerite are subordinate, and molybdenite and various Bi chalcogenides are rare. Wolframite mostly occurs close to the selvages of quartz–muscovite veins and is often observed among the muscovite in their rim. The size of wolframite crystals varies from tenths of a millimeter to 5 cm (Figures 4 and 5). Wolframite typically forms columnar and elongated–flattened crystals [48]. Scheelite is often confined to fractures and the periphery of wolframite crystals. Thin molybdenite flakes are rarely observed on the surface of the wolframite grains. Locally, wolframite contains inclusions of pyrite, which occasionally tends to cleavage fractures, as well as fluorite and dolomite. In contrast to the Porokhovskoe deposit, the ores of the Yugo-Konevskoe deposit are characterized by the presence of stolzite, which is intergrown with wolframite. In the oxidation zone, wolframite is replaced by Fe and Mn oxides. The studied wolframite grains exhibit no zonation both under an optical microscope and in characteristic Fe, Mn, and W radiation (Figure S1). Some grains are characterized by a lower Fe/(Fe + Mn) ratio in the marginal part. This was noted for wolframite in close association with pyrite. It is possible that during the nearly simultaneous crystallization of pyrite and wolframite, iron is preferentially incorporated in the sulfide. Accordingly, the content of the ferberite end member in wolframite decreases.

According to the SEM-EDS analysis (Table S1), most grains from both deposits belong to hübnerite (Table 1, Figure 6). The median MnO content is 22.1 wt.%. The FeO content varies from 0.4 to 11.6 wt.% with a median value of 0.9 wt.%. The Fe/(Fe + Mn) ratio varies in a range of 0.02–0.50 (Figure 6 and Figure S1). Most Fe-bearing wolframite grains are identified in the northern part of the Porokhovskoe deposit; however, no evident compositional patterns are revealed. There is no distinct zoning in the distribution of major elements in wolframite grains. Some grains show a decrease in the Fe/(Fe + Mn) index value in the marginal part (Figure S1). However, we cannot talk about the patterns of compositional changes. The LA-ICP-MS-based trace element composition of wolframite is shown in Table S2 and Figure 7. The representative time-resolved spectra of wolframite showing an homogeneous trace element composition are presented in Figure S2.

Table 1. Chemical composition * of wolframite according to SEM-EDS analysis (wt.%).

Occurrence	MnO	FeO	WO ₃	Fe/(Fe + Mn)
Yugo-Konevskoe (N = 3)	(20.79–22.34)	(1.05–2.73)	(76.48–76.94)	(0.04–0.12)
Porokhovskoe (N = 61)	22.15 (11.54–22.98)	0.9 (0.36–11.61)	76.78 (76.14–77.49)	0.04 (0.02–0.50)

* Median (minimum–maximum); no median was calculated for the Yugo-Konevskoe deposit due to an insufficient amount of analyses.

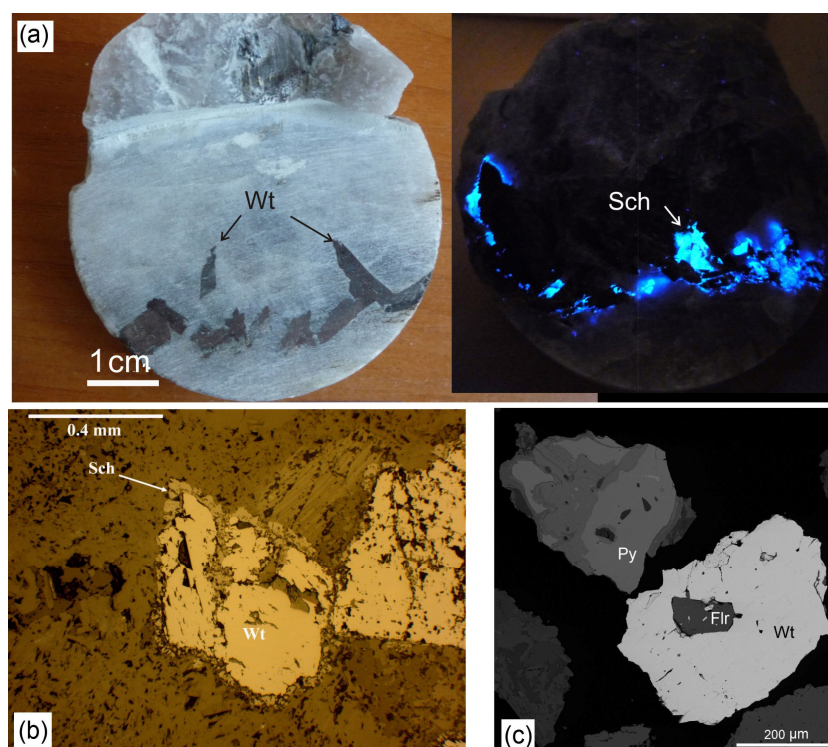


Figure 5. Wolframite (Wt) from ores of Porokhovskoe deposit: (a) wolframite and scheelite (Sch) in quartz vein (sample in normal and ultraviolet light); (b) wolframite crystals with scheelite rims (reflected light); (c) fluorite (Flr) inclusion in wolframite (BSE image). Pyrite—Py.

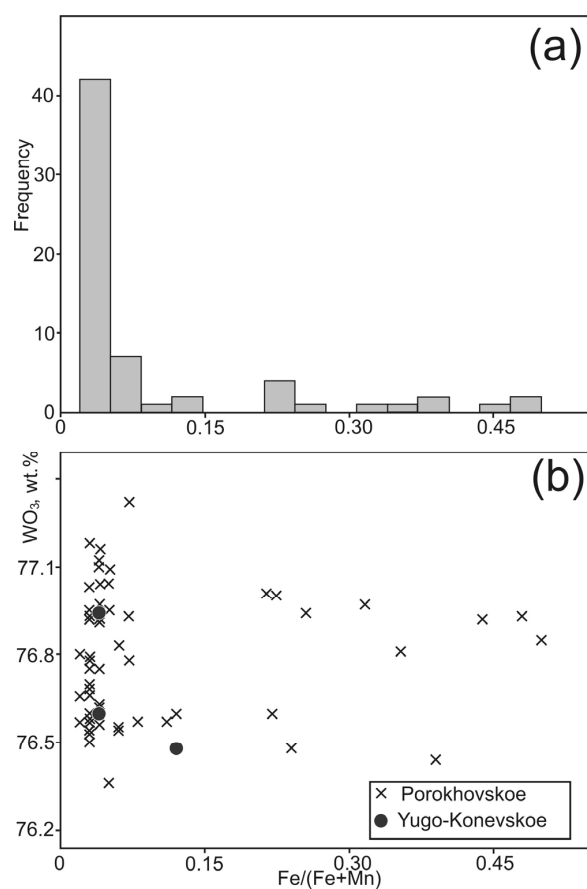


Figure 6. Variations in composition of wolframite on histogram of Fe/(Fe + Mn) ratio for all analyses (n = 64) (a) and on binary diagram for Yugo-Konevskoe and Porokhovskoe deposits (b).

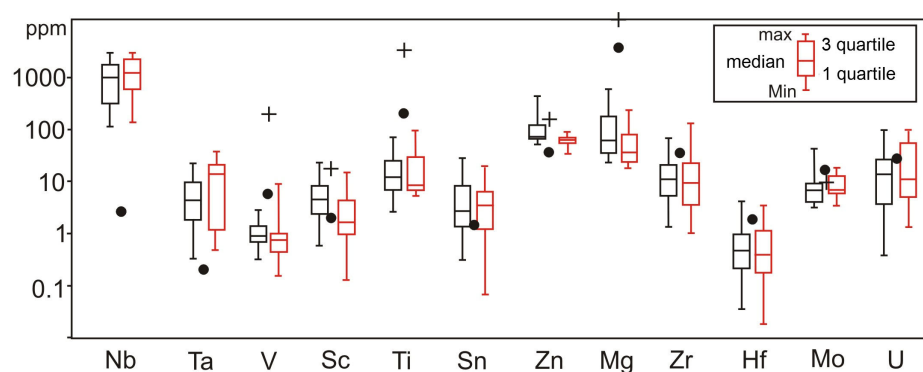


Figure 7. Box-and-whisker plot for main trace elements of hübnerite of the Porokhovskoe (black) and Yugo-Konevskoe (red) deposits. The dots show the content of the corresponding elements in granites of the Yugo-Konevsky pluton (123/31.9–32.3); the crosses show the median content for host volcaniclastic rocks of the Porokhovskoe deposit [51].

Iron and Mn in wolframite are isovalently replaced by Mg^{2+} , Zn^{2+} , Ni^{2+} , Cd^{2+} , and Co^{2+} . The wolframite of both deposits is characterized by a high Zn content, reaching 424 ppm at the Porokhovskoe deposit; however, the median Zn content of wolframite is similar for both deposits. Wolframite of the Porokhovskoe deposit is enriched in Mg: 60 ppm vs. 36 ppm (median values) in the wolframite of the Yugo-Konevskoe deposit. The Ni, Cd, and Co content of the studied wolframite is extremely low.

A wide spectrum of cations can enter the lattice of wolframite following heterovalent isomorphism: Nb^{5+} , Ta^{5+} , V^{5+} , V^{4+} , Ti^{4+} , Sn^{4+} , Zr^{4+} , Hf^{4+} , U^{4+} , Sc^{3+} , REEs. Niobium is the most significant trace element. At the Yugo-Konevskoe deposit, the Nb content of wolframite is 135–4283 ppm, with a median value content of 1224 ppm. The Nb content of wolframite from the Porokhovskoe deposit varies from 115 to 3121 ppm with a median value of 989.8 ppm (Table 2). Skewness is positive in both cases; kurtosis is positive for the Yugo-Konevskoe deposit and close to 0 for the Porokhovskoe deposit.

The Ta content of wolframite is significantly lower than the Nb content. The median Ta content of wolframite is 14.1 ppm (a range of 0.5–37.4 ppm) for the Yugo-Konevskoe and 4.3 ppm (a range of 0.3–22.7 ppm) for the Porokhovskoe deposit. Both the central position and the spread statistics differ significantly. Wolframite from both deposits is similar in Ti content: 8.6 and 12.4 ppm (median values) of Ti content for the Yugo-Konevskoe and Porokhovskoe ore, respectively. A similar range of content is characteristic of U and Zr.

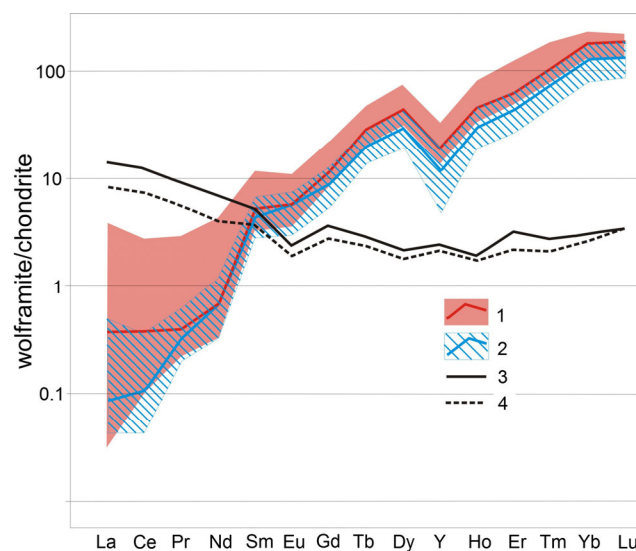
The Sc content of wolframite of the Yugo-Konevskoe deposit is several times lower than that of the Porokhovskoe deposit (Figure 7, Table 2). The median Sc content of wolframite is similar for both deposits: 1.7 and 4.6 ppm, respectively.

The median Mo content of wolframite is 6.9 and 6.5 ppm for the Yugo-Konevskoe and Porokhovskoe deposits, respectively. The Sn, V, and Hf content are also low.

The REEs+Y sum of wolframite of the Yugo-Konevskoe deposit varies from 121 to 395 ppm, with a median value of 164 ppm. At the Porokhovskoe deposit, the REEs+Y content is 23–308 ppm (the median is 101 ppm). Wolframite of the Yugo-Konevskoe deposit is characterized by a higher REE content. The chondrite-normalized REE patterns of wolframite from both deposits have a positive slope and are almost parallel (Figure 8). The light REE (LREE) content is close to the chondrite standard or even lower and exhibits a large dispersion, while the heavy REE (HREE) content is two orders of magnitude higher than that of chondrite. The REE patterns of wolframite typically contain negative Y anomalies.

Table 2. LA-ICP-MS-based content of main trace elements (ppm).

	Mg	Zn	Co	Sc	Nb	Ta	Mo	Sn	Ti	Zr	Hf
Yugo-Konevskoe deposit (N = 12)											
Min	18.2	34.6	0.0	0.1	135	0.5	3.5	0.1	5.5	1.1	0.02
Max	232.7	89.6	0.4	15.2	4283	37.4	18.7	19.9	94.4	132.2	3.4
Average	70.5	61.9	0.1	3.3	1514.5	13.2	8.8	5.2	25.5	24.5	0.8
St. Dev.	78.0	15.3	0.1	4.2	1174.4	11.9	4.6	5.7	31.3	38.7	1.1
Median	36	62.2	0.03	1.7	1224	14.1	6.9	3.6	8.6	9.5	0.4
1 quartile	24.3	55.1	0.01	1	586	1.2	6	1.3	7	3.7	0.2
3 quartile	80.2	68.7	0.1	4.5	2305	21.6	12.8	6.4	30	23.1	1.2
Skewness	1.8	0.1	3.1	2.4	1.1	0.7	1.2	1.8	1.8	2.4	1.7
Kurtosis	1.9	0.4	10.3	6.6	1.7	−0.3	1.4	3.5	1.9	5.8	2.3
Porokhovskoe deposit (N = 20)											
Min	22.1	50	0.001	0.6	115	0.3	3.0	0.3	2.7	1.3	0.03
Max	566	424	3.4	23.6	3121	22.7	40.8	28.6	72.5	66.3	4.0
Average	138.5	98.7	0.3	5.8	1078.5	7	8.6	4.9	21.0	16.7	0.8
St. Dev.	157.9	72.1	0.7	5.2	798.4	6.8	8.1	5.9	19.3	17.8	0.9
Median	60.1	71.9	0.05	4.6	989.8	4.3	6.5	2.8	12.4	10.9	0.5
1 quartile	34.6	63.7	0.02	2.4	314.3	1.9	3.8	1.4	7.0	5.2	0.2
3 quartile	172.7	117.5	0.3	8.4	1780	9.8	8.6	8.2	25.3	20.0	0.9
Skewness	1.8	3.7	4.3	2.1	0.6	1.2	2.9	2.7	1.4	1.9	2.2
Kurtosis	2.5	16	20.6	5.1	−0.3	0.4	9.1	9.1	0.9	3.1	5.0

**Figure 8.** Chondrite-normalized REE patterns: 1—interquartile range and median for wolframite of the Yugo-Konevskoe deposit; 2—the same, for the Porokhovskoe deposit; 3—granite of the Yugo-Konevsky pluton (123/31.9–32.3); 4—greisenized granite of the Yugo-Konevsky pluton (123/30).

5. Discussion

The Porokhovskoe and Yugo-Konevskoe deposits can be considered the different facies of a single hydrothermal system, because both deposits belong to the same geological

structure and are spatially associated with one igneous complex. With distance from the ore-generating intrusion, the hydrothermal fluid was modified due to cooling and interaction with the wall rocks. The mineral zonation is reflected in the compositional features of ore minerals. Although wolframite of the Yugo-Konevskoe (proximal facies of mineralization) and Porokhovskoe (distal facies of mineralization) deposits is similar in the content of main elements corresponding to h  bnerite, they differ in the content of trace elements. Based on the interquartile range (Figure 7) of trace element content, the following groups of trace elements are conditionally distinguished:

1. V, Sc, Zn, and Mg: Wolframite from the Yugo-Konevskoe deposit is slightly depleted in these elements compared to wolframite from the Porokhovskoe deposit;
2. Mo, U, REEs, and maybe Nb and Ta: Wolframite from the Yugo-Konevskoe deposit is slightly enriched in these elements compared to wolframite from the Porokhovskoe deposit;
3. Ti, Zr, Hf, and maybe Sn: Elements without a pronounced enrichment/depletion. The interquartile range of content for Zr and Hf in wolframite from the Porokhovskoe deposit is narrower than in wolframite from the Yugo-Konevskoe deposit.

The composition of wolframite can be affected by the composition of hydrothermal fluid, the crystallization of other phases in assemblage with wolframite, and the composition of host rocks. The study of fluid inclusions [52] in quartz of the ore veins of the studied deposits showed similar PT parameters and salt composition of the fluid for both deposits: pressure of 350 bar, temperature of 245–540  C, and salinity of 0.54–16.13 wt.% NaCl_{eq}. Both deposits are characterized by a similar mineral composition of the W-bearing vein assemblage. The variations in the composition of wolframite are thus probably associated with the different geochemical features of host rocks. Compared to granites and greisenized granites, wolframite of the Yugo-Konevskoe deposit is significantly enriched only in Ta and Nb. The Sc, Sn, and U content of wolframites and granites are similar (Figure 7), whereas the Mg, V, Ti, Zr, Hf, and Mo content of wolframite is lower than of the host granites. The V, Ti, Mg, Sc, and Zn content of the host volcanoclastic rocks of the Porokhovskoe deposit [52] is significantly higher than that of wolframites. Only the Mo content of rocks and wolframites is similar (Figure 7).

During greisenization, Ta and Nb are thus focused in the fluid and further enter the structure of wolframite. On the contrary, V, Ti, Zr, and Hf preferentially remain in magmatic melt without separating into the hydrothermal fluid. These elements are also inert during the greisenization of the sedimentary strata.

Behavior of trace elements

As mentioned above, trace elements in wolframite can enter both position A, replacing Fe (hereinafter, ionic radius of 0.78  ) and Mn (0.83  ), and position X, where they replace W (0.66  ).

Trace elements with isovalent substitution

Position A includes divalent cations Mg²⁺ (0.72  ), Zn²⁺ (0.74  ), Ni²⁺ (0.72  ), and Co²⁺ (0.75  ), which directly replace Fe²⁺ and/or Mn [20]. Magnesium is a typical lithophile element entering the femic minerals of rocks. The Mg content of wolframite is typically low because of the specific chemistry of the ore process and crystal chemical limitations. However, ferberite with a MgO content of up to 7.75 wt.% (magnesioferberite) was found in quartz veins of Permian metasandstones and chlorite–sericite phyllites [53]. Mineralization in this case is associated with a Cretaceous granitic intrusion. The enrichment of wolframite in Mg is mosaic. The high Mg content of wolframite is explained by the assimilation of elements from Paleozoic metabasalts [53]. The anomalous MgO content (average 0.34 wt.%) in wolframite from some W occurrences of the Bohemian Massif [54] is associated with the interaction of magmatic fluid and groundwater in the foothill region.

According to our data [51], the MgO content of muscovite from quartz–muscovite veins and greisenized skarnoids reaches 3.93 and 5.94 wt.%, respectively. Chlorite from skarnoids with the ore mineralization of the Porokhovskoe deposit contains up to 8.31 wt.% MgO. This high content indicates the high activity of Mg in the fluid. An almost twofold increase in the median Mg content of wolframite of the Porokhovskoe deposit compared to the Yugo-Konevskoe deposit is possibly due to the interaction of the fluid with intermediate to mafic volcanoclastic rocks, the MgO content of which is significantly higher than that of granites. The Mg content of the wolframite of both deposits is negatively correlated with Mn content, -0.87 for the Porokhovskoe deposit and -0.68 for the Yugo-Konevskoe deposit (Figure 9), which indicates the isomorphous state of Mg in position A of the wolframite.

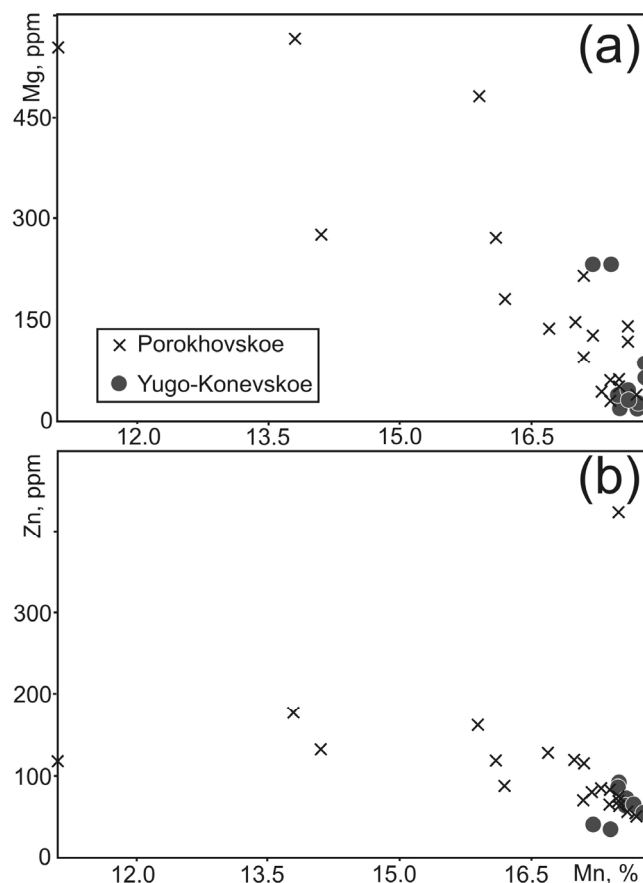
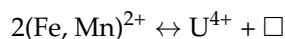


Figure 9. Mg–Mn (a) and Mn–Zn (b) correlation in wolframite of the Yugo-Konevskoe and Porokhovskoe deposits.

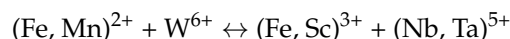
The Zn distribution in the wolframite of the studied deposits somewhat differs. In general, the Zn content exhibits a narrow range. Wolframite from the Yugo-Konevskoe deposit is enriched in Zn relative to host granites. On the contrary, wolframite at the Porokhovskoe deposit is depleted in Zn compared to the host rocks. As shown by Chernyshev and Pastushkova [55] and Buhl and Willgallis [56], zinc is preferentially bound by sulfides in the presence of sulfur in the hydrothermal fluid. Both studied deposits contain sphalerite, which limits the possibility of the incorporation of Zn into wolframite. The absence of a significant correlation between Zn and Mn is noteworthy (Figure 9).

Trace elements with heterovalent substitution

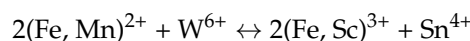
The entry of tetravalent cations (U^{4+} , Zr^{4+} , and Hf^{4+}) to position A is possible with the formation of a vacancy [17]:



The heterovalent scheme with charge compensation by trivalent cations (Fe^{3+} , Sc^{3+} , In^{3+} , Y^{3+} , and REE^{3+}) is most likely for Nb^{5+} (0.64 Å), Ta^{5+} (0.64 Å), and, possibly, V^{5+} (0.54 Å):



A similar scheme can also be applied for the replacement of W^{6+} with Sn^{4+} (0.69 Å), Ti^{4+} (0.61 Å), and V^{4+} (0.58 Å):



Due to the similar structure of wolframite and minerals of the columbite–tantanite series, Ta and Nb are the most frequent trace elements of wolframite. Wolframite from the Tigrinoe Sn–W deposit (Far East, Russia) contains (average of 31 analyses, wt.%) 0.04 Ta_2O_5 and 0.35 Nb_2O_5 [16]. The high Nb content in wolframite from some vein deposits of Portugal [19] does not depend on the metal specialization of ores ($\text{Sn} > \text{W}$ or $\text{W} > \text{Sn}$) or on the Fe content of the mineral. The Nb_2O_5 content of wolframite from the Panasqueira deposit reaches 1.88 wt.%. The Ta_2O_5 content of wolframite from the Argoselo deposit reaches 0.21 wt.%, but it is often below the detection limits of the microprobe analysis. The Nb content of wolframite at the Akshatau deposit (Kazakhstan) is correlated with Fe content [57]. Here, the mineral with 52% of the ferberite end-member from biotite–K-feldspar–quartz veins contains 3860 ppm Nb. The Nb content in wolframite with 32%–45% FeWO_4 from quartz veins is 1060–1430 ppm. The range of Nb and Ta content in ferberite from the Kyzyl-Tau greisen deposit (Western Mongolia) is 3850–8100 and 100–210 ppm, respectively [58].

The Ta/Nb ratio of wolframite is considered to be an indicator of the distance from the hydrothermal source [17]. Wolframite precipitated from hydrothermal fluids of magmatic origin has an elevated Ta and Nb content at a high Ta/Nb ratio. An increase in the Ta/Nb ratio of wolframite from greisens compared to the wolframite from hydrothermal veins has been documented in some tin deposits in China [18]. At the Barocca Grande mine (Portugal), wolframite from the central parts of the ore system was found to be enriched in Nb compared to wolframite from the peripheral part [20]. In our case, no clear patterns of Ta and Nb distribution in wolframite are identified (Figure 10). The interquartile range of Ta content in wolframite from the Yugo-Konevskoe deposit is wider than that at Porokhovskoe, while the median content differs significantly. Tantalum and Nb in wolframites from both deposits are characterized by a strong positive correlation.

Tin is a typical trace element of wolframite from Sn–W deposits. In our case, the ores are almost free of Sn, and its content of wolframite is low (max 30 ppm). The Sc content of the studied wolframite is negligible (Figure 10). The Sc content of wolframites from the Akshatau deposit, e.g., varies in a range of 210–3174 ppm and is correlated with Fe content [57]. Wolframite from the Erzgebirge region contains up to 8800 ppm Sc [27]. At the Tigrinoe Sn deposit, the average Sc content of wolframite is 0.45 wt.% [16]. Thus, the trace element composition and isomorphism patterns in wolframites are largely individual for each ore system.

REEs are considered geochemical indicators of ore formation conditions [58]. The REE patterns of various fluids differ from each other. When fluid flows through the ore deposition zones, the REEs are not involved in exchange reactions, because they are hosted in barely soluble accessory minerals. Variations in the REE content of hydrothermal minerals reflect the geochemical specifics of the fluid itself and changes in physicochemical conditions in terms of Eh–pH [59], as well as the crystal–chemical features of minerals. REE-bearing fluorite, scheelite, calcite, and epidote are of great importance in the studied ore’s mineralization, and they play a key role in the REE distribution in the hydrothermal system.

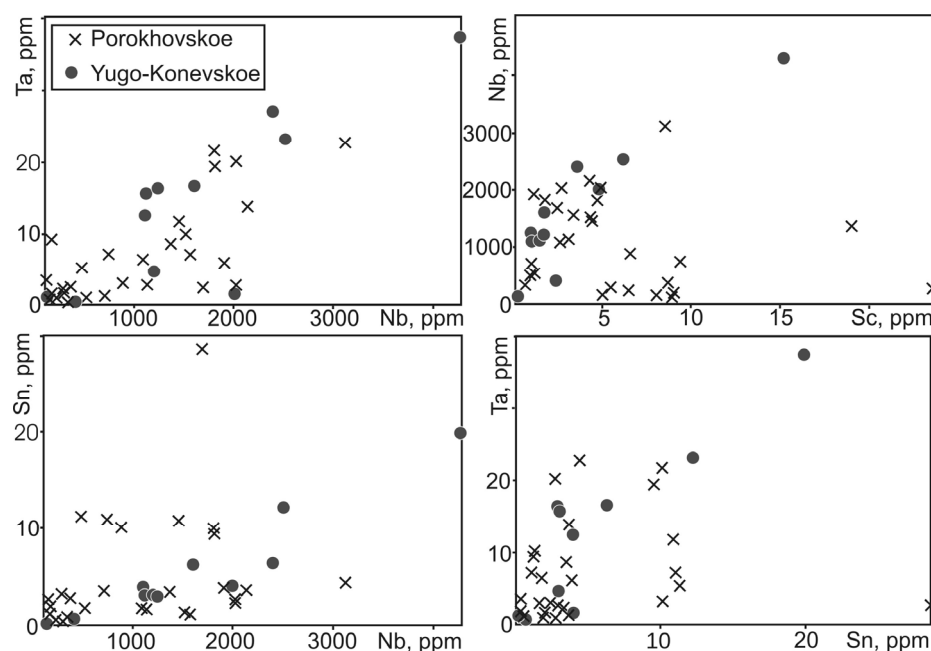


Figure 10. Binary diagrams of Nb-Ta, Nb-Sc, Nb-Sn, Ta-Sn for wolframite from the Porokhovskoe and Yugo-Konevskoe deposits.

Granites of the Yugo-Konevsky pluton and their greisenized varieties have a similar configuration of REE patterns (Figure 8); the sum of REEs+Y in them is only 22 and 15 ppm, respectively. The enrichment of wolframite in HREEs is explained by their similar ionic radii to Fe^{2+} and Mn^{2+} [17]. As a result, HREEs are characterized by higher distribution coefficients between wolframite and the hydrothermal fluid. A positive slope of the chondrite-normalized REE pattern is typical of wolframite from different deposits [17,28,33,34,39,60]. A negative Eu anomaly characteristic of the patterns is inherited from host granites [33]. This anomaly is absent in REE patterns of granites of the Yugo-Konevskoe deposit, as well as in wolframite. The negative Y anomaly in wolframite may be associated with the crystallization of fluorite in altered granites and ore veins and, thus, with the depletion of post-magmatic fluid in Y. The early crystallization of fluorite is evidenced by its rare inclusions in wolframite (Figure 5). Yttrium and REEs are common impurities in fluorite and occupy the Ca^{2+} position. The term “yttrifluorite” is used for REE-containing fluorites, emphasizing their geochemical specificity. In fluorine-rich hydrothermal solutions, the fractionation of geochemically similar Y and Ho occurs [61]. During the subsequent crystallization of wolframite, REEs and yttrium behave coherently, as indicated by the correlation of yttrium and holmium (+0.93).

Considering the studied deposits the parts of one hydrothermal system, it is evident that the REE content of wolframite decreases from proximal to distal facies, whereas the REE pattern remains almost the same. Using the REE partition coefficients between wolframite and the hydrothermal fluid [62], we can calculate the likely REE content of the ore-forming fluids (Figure 11). The hydrothermal fluids of both deposits were characterized by almost parallel REE patterns with a slightly positive slope, a lower LREE content in the case of the Porokhovskoe deposit, and a Eu minimum, indicating that the fluid evolved with LREEs’ depletion. This is obviously related to (i) the crystallization of LREE- and Eu-bearing hydrothermal minerals (e.g., fluorite) and (ii) mixing with “background” waters and changes in pH-Eh conditions.

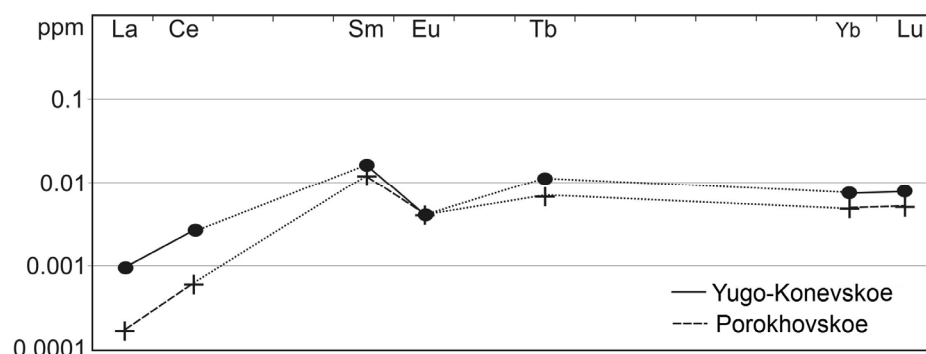


Figure 11. Calculated REE content of the hydrothermal fluid in equilibrium with wolframite at the Yugo-Konevskoe and Porokhovskoe deposits. The median content was used for the calculation. The partition coefficients were taken from [62].

6. Conclusions

The Yugo-Konevskoe and Porokhovskoe W deposits (Central Urals) represent the proximal and distal facies of one magmatic-hydrothermal system. The ores of the Yugo-Konevskoe deposit are confined to the contacts with a granitic pluton, while the ores of the Porokhovskoe deposit are hosted by volcanoclastic rocks of the Lower Silurian age and exhibit no spatial connection with Permian–Triassic granites of the Yugo-Konevsky pluton. Wolframite (hübnerite) from both deposits is the major ore mineral and is characterized by minor variations in Fe content.

The LA-ICP-MS-based trace element composition of wolframite is studied for the first time for the Urals orogenic belt. Wolframite has the highest content of Zn, Nb, and Mg. The specific trace element composition of wolframite reflects the features of ore formation at different distances from the fluid source and within distinct host rocks. The compositional peculiarities of wolframite include the enrichment of wolframite of distal ore facies in V, Sc, Zn, and Mg and a depletion in Mo, U, and REEs (Nb, Ta). The REE content of wolframites decreases from proximal to distal ore facies.

Based on our new data on the composition of wolframite and published information, it is concluded that the composition of wolframite and its specific isomorphic patterns are largely individual for each ore system and/or deposit. They depend both on the crystal-chemical features of wolframite and the fluid composition, which is determined by the specific composition of ore-generating intrusions and host rocks.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min15060661/s1>, Figure S1: BSE images and images in characteristic radiation of Fe, Mn, and W for wolframite grains; Figure S2: Representative time-resolved spectra of wolframite showing homogeneous trace element content; Table S1: Chemical composition of wolframite; Table S2: ICP-MS-LA analyses of wolframite.

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