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Tungstates of the Boyovskoye tungsten deposit (Southern Urals)

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Abstract
The relevance of the work is due to the need for a mineralogical study of tungsten deposits in the Ural region, which have been mined since the end of the 19th century.
The purpose of the work is the diagnostics and detailed description of tungstates from the Boyovskoye tungsten deposit located on the border of the Chelyabinsk and Sverdlovsk regions in the Southern Urals.
Analytical studies were carried out in the Laboratory of Physical and Chemical Research Methods of the Institute of Geology and Geochemistry, UB RAS, Ekaterinburg. The chemical composition of minerals was analyzed in polished sections on a CAMECA SX 100 microanalyzer. Measurement conditions: accelerating voltage 15 kV, current 150 nA, electron beam diameter 2 μm. The pressure in the sample chamber is $2 \cdot 10^{-4}$ Pa. The spectra were obtained on tilted wave spectrometers; the intensity was measured from analytical lines. Standard samples: scheelite, wolframite, galena, rutile and chromite. Raman spectra of minerals were obtained using a LabRam HR Evolution spectrometer (Horiba Scientific). A red laser, 532 nm, was used for analysis.
As a result of the work, new data on the chemical composition of hubnerite and scheelite were obtained and their Raman spectra were presented. For the first time for the Boyovskoye tungsten deposit, a reliable diagnosis and description of lead tungstate – stolzite was made. The mineral was found in samples with veined quartz in association with muscovite, fluorite, hubnerite and scheelite. It fills cracks and voids in hubnerite, rarely overgrows scheelite or fills cracks in scheelite. It is a later mineral in relation to hubnerite and scheelite. Its chemical composition contains impurities of manganese, calcium, iron and titanium. The stolzite found by us is a mineral of the oxidation zone and, most likely, was formed due to the weathering of wolframite and galena, which is also present in quartz veins.

***Keywords*:** hubnerite, scheelite, stolzite, Boyovskoye tungsten deposit, Southern Urals.

Introduction
The Boyovskoye tungsten deposit is located 9.4 km northwest of the village of Bagaryak in the Kasli district of the Chelyabinsk region in the Southern Urals. The deposit has been developed since the end of the 19th century. The geology of the Boyovskoye deposit is well studied [1]. In the central block of the deposit, the largest wolframite-quartz veins up to 40 cm thick are located, which have a sublatitudinal strike and dip to the south at angles from 60 to 90° and are confined to the body of gabbro-dolerites. Less powerful quartz veins are found in amphibolites in the western part of the ore field. In addition to quartz, veins along the walls contain muscovite, fluorite, beryl and pyrite. Wolframite is mainly found in selvedges, forming fine-grained aggregates in association with beryl. On the edges along the veins, secondary changes in the host rocks are noted in the form of muscovitization, the development of quartz, fluorite, and pyrite [2]. In 1957, ore-bearing beryl-fluorite-muscovite metasomatites, which are greisens, were discovered at the Boyovskoye deposit during prospecting and exploration for tungsten-beryllium mineralization [3]. More deposits of beryllium ores were later found. Beryl-fluorite-muscovite metasomatites form 5 ore bodies of complex morphology, which contain beryl, phenakite, wolframite, and scheelite [4]. In terms of tungsten reserves, the Boyovskoye deposit is classified as a small artisanal deposit, and in terms of beryllium reserves it is classified as a large deposit, but with a low content of beryllium oxide [2]. At the Boyovskoye deposit, N. A. Grigoriev first discovered two rare minerals: glucine [5] and uralolite [6]. At present, the deposit is not mined and consists of overgrown numerous ditches up to several meters deep (fig. 1).

The mineralogy of the deposit is poorly studied. This paper presents new data on the chemical composition and Raman spectroscopy of hubnerite, scheelite and the first reliable description of stolzite.

Research methodology
Analytical studies were carried out in the Laboratory of Physical and Chemical Research Methods of the Institute of Geology and Geochemistry, UB RAS, Ekaterinburg. The chem-

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Figure 1. A ditch with a depleted quartz vein. Boyovskoye deposit, photo 2020
Рисунок 1. Канава с отработанной кварцевой жилой. Боёвское месторождение, фото 2020 г.

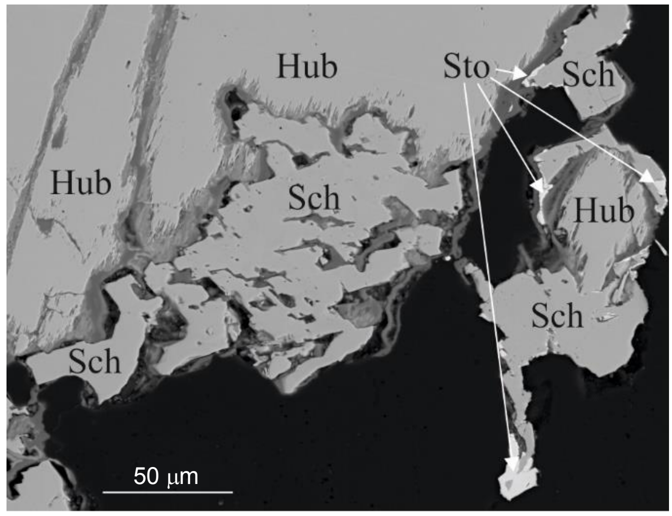

Figure 2. Scheelite (Sch) and stolzite (Sto), growing on hubnerite (Hub). Polished thin section. BSE photo
Рисунок 2. Шеелит (Sch) и штольцит (Sto), нарастающие на гюбнерит (Hub). Полированный шлиф. BSE-фото

ical composition of minerals was analyzed in polished sections on a CAMECA SX 100 microanalyzer, analyst I. A. Gottman. Raman spectra of minerals were obtained using a LabRam HR Evolution spectrometer (Horiba Scientific), analyst E. A. Pankrushin. To excite the minerals, a red laser – 532 nm was used.

Research results

The samples found by us in numerous ditches and dumps at the Boyovskoye deposit are represented by fragments of quartz veins with tungsten mineralization. According to microprobe analysis, we have identified three tungstates: hubnerite, scheelite, and a mineral corresponding to the chemical composition of $PbWO_4$. To date, two dimorphic minerals with such a chemical composition are known, the first is tetragonal stolzite (β-$PbWO_4$) and the second is monoclinic raspit (α-$PbWO_4$).

Hubnerite is the most common tungstate at the deposit. According to the literature, in the Boyovsko-Biktimirovskaya zone of quartz-hubnerite deposits such as Boyovskoe, Karasevskoe, Porokhovskoe, etc., hubnerite occurs in quartz veins up to 25 cm thick in the form of small grains, columnar crystals and nests in association with muscovite, fluorite, pyrite, rarely sphalerite, galena, chalcopyrite and beryl. It is noted that hubnerite is partially replaced by scheelite in patches [7]. The literature [8] gives the chemical composition of the hubnerite of the Boyovskoe deposit, wt. %: FeO 4.50; MnO 19.79; WO_3 75.70; total 99.99. Hubnerite was found by us in the form of clusters of grains and separate fissured individuals (fig. 2, 3) in fragments of veined milky-white quartz. The color of the mineral is dark brown, translucent in thin chips in red. The size of hubnerite individuals encountered by us is up to 2 cm. The mineral is characterized by a stable chemical composition (table 1, an. 1–10). Of the impurities in the mineral, an admixture of FeO from 3.61 to 7.70 wt. % is noted, which corresponds to 0.16–0.34 formula units in the crystal chemical formula of hubnerite. Up to 0.12 wt. % TiO_2 is noted as an insignificant impurity. The Raman spectrum of the mineral (fig. 4) fully corresponds to the hubnerite standard.

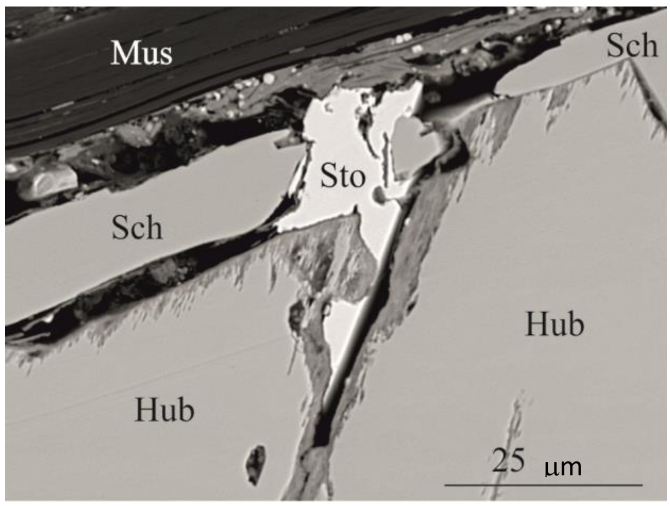

Figure 3. Stolzite (Sto) intergrown with hubnerite (Hub) and scheelite (Sch). Mus – muscovite. Polished thin section. BSE photo
Рисунок 3. Штольцит (Sto) в срастании с гюбнеритом (Hub) и шеелитом (Sch). Mus – мусковит. Полированный шлиф. BSE-фото

Scheelite at the Boyovskoye deposit was discovered by P. V. Eremeev in 1867 [9]. It is often observed in the wall-vein muscovite-fluorite greisens [1]. It forms pseudomorphs along hubnerite and associates with fluorite, muscovite, pyrite, sometimes galena, sphalerite, and chalcopyrite [7]. We found scheelite in samples with veined quartz, hubnerite, muscovite, fluorite, pyrite, and galena. Thin sections show traces of hubnerite dissolution and its replacement by scheelite (fig. 2). The mineral is painted in beige color. It forms grains of irregular and isometric shape up to 1 cm. The chemical composition of scheelite (table 1, an. 11–20) sometimes contains impurities of chromium (up to 1.21 wt. % Cr_2O_3) and titanium (up to 0.15 wt. % TiO_2). In general, the composition of the mineral studied by us from the Boyovskoye deposit is close to that of scheelites from other Ural objects. The Raman spectrum of the mineral (fig. 5) fully corresponds to the scheelite standard.

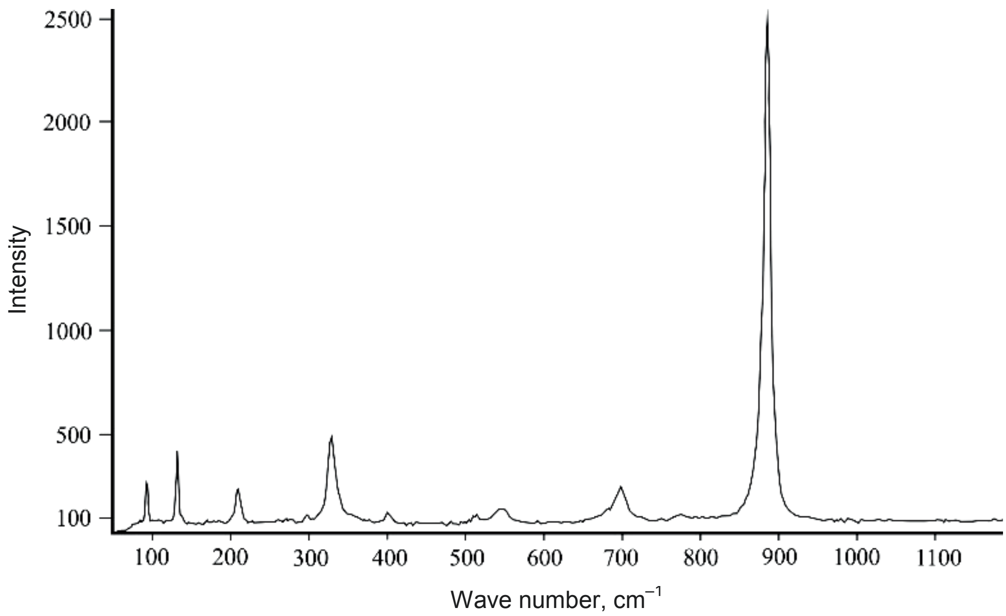

Figure 4. Raman spectrum of hubnerite
Рисунок 4. Рамановский спектр гюбнерита

Table 1. Chemical composition of tungstates from the Boyovskoye deposit, wt. %
Таблица 1. Химический состав вольфраматов из Боёвского месторождения, мас. %

Analysis number	Oxides							Total	Formulas
	TiO_2	Cr_2O_3	WO_3	FeO	MnO	PbO	CaO		
				Hubnerite					
1	–	0,03	77,37	3,61	18,78	–	0,02	99,81	$(Mn_{0.85}Fe_{0.16})_{1.01}W_{1.00}O_4$
2	0,02	–	77,80	3,85	18,73	–	0,01	100,41	$(Mn_{0.84}Fe_{0.17})_{1.01}W_{1.00}O_4$
3	–	0,02	77,87	4,39	18,05	–	0,01	100,34	$(Mn_{0.81}Fe_{0.19})_{1.00}W_{1.00}O_4$
4	0,12	–	77,13	3,87	18,84	–	0,02	99,98	$(Mn_{0.85}Fe_{0.17})_{1.02}W_{0.99}O_4$
5	0,08	–	77,06	3,69	18,88	0,07	0,02	99,80	$(Mn_{0.85}Fe_{0.16})_{1.01}W_{0.99}O_4$
6	0,04	0,05	77,56	3,90	18,60	–	0,05	100,20	$(Mn_{0.83}Fe_{0.17})_{1.00}W_{0.99}O_4$
7	–	0,04	76,91	4,11	18,65	–	0,04	99,75	$(Mn_{0.84}Fe_{0.18})_{1.02}W_{0.99}O_4$
8	–	–	76,87	7,70	15,43	–	–	100,00	$(Mn_{0.69}Fe_{0.34})_{1.03}W_{0.99}O_4$
9	–	–	76,73	6,97	16,29	–	–	99,99	$(Mn_{0.73}Fe_{0.0,31})_{1.04}W_{0.99}O_4$
10	–	–	76,91	6,87	16,22	–	–	100,00	$(Mn_{0.73}Fe_{0.30})_{1.03}W_{0.99}O_4$
				Scheelite					
11	–	0,03	81,25	0,01	0,01	0,03	19,43	100,76	$Ca_{1.04}W_{0.99}O_4$
12	–	–	80,98	–	0,01	–	19,21	100,20	$Ca_{1.04}W_{0.99}O_4$
13	0,15	1,21	79,99	0,00	–	0,02	19,29	100,66	$Ca_{1.03}(W_{0.96}Cr_{0.05})_{1.01}O_4$
14	–	–	80,88	0,03	0,01	–	19,52	100,44	$Ca_{1.05}W_{0.98}O_4$
15	–	–	80,62	–	–	–	19,38	100,00	$Ca_{1.05}W_{0.98}O_4$
16	0,07	0,27	81,06	0,02	0,01	–	19,49	100,92	$Ca_{1.04}(W_{0.98}Cr_{0.01})_{0.99}O_4$
17	–	–	81,08	0,06	0,01	0,01	19,30	100,46	$Ca_{1.04}W_{0.99}O_4$
18	–	–	80,31	0,20	–	–	19,50	100,01	$(Ca_{1.05}Fe_{0.01})_{1.06}W_{0.98}O_4$
19	–	–	80,20	0,25	0,37	–	19,18	100,00	$(Ca_{1.04}Mn_{0.02}Fe_{0.01})_{1.07}W_{0.98}O_4$
20	–	–	79,64	0,35	–	–	20,02	100,01	$(Ca_{1.08}Fe_{0.01})_{1.09}W_{0.97}O_4$
				Stolzite					
21	0,02	–	51,77	0,04	–	48,76	0,15	100,74	$(Pb_{1.03}Ca_{0.01})_{1.04}W_{0.99}O_4$
22	0,07	0,02	51,16	–	0,02	48,51	0,04	99,82	$Pb_{1.04}W_{0.98}O_4$
23	–	0,04	52,33	0,06	–	48,56	0,04	101,03	$Pb_{1.02}W_{0.99}O_4$
24	0,08	0,01	51,77	0,10	0,03	48,38	0,04	100,41	$(Pb_{1.02}Fe_{0.01})_{1.03}W_{0.99}O_4$
25	0,09	0,03	50,56	–	0,03	49,97	–	100,68	$Pb_{1.07}W_{0.97}O_4$
26	–	0,04	51,72	0,03	0,03	48,78	0,27	100,87	$(Pb_{1.03}Ca_{0.02})_{1.05}W_{0.98}O_4$
27	–	0,02	52,25	–	0,02	48,31	0,15	100,75	$(Pb_{1.02}Ca_{0.01})_{1.03}W_{0.99}O_4$
28	–	–	50,20	0,32	–	49,48	–	100,00	$(Pb_{1.06}Fe_{0.02})_{1.08}W_{0.97}O_4$
29	–	–	50,26	0,54	0,74	48,13	0,33	100,00	$Pb_{1.11}W_{0.96}O_4$
30	–	–	50,39	–	–	49,61	–	100,00	$Pb_{1.07}W_{0.98}O_4$

Note: Empirical formulas of minerals are based on 4 oxygen atoms.
Примечание: эмпирические формулы минералов рассчитаны на 4 атома кислорода.

Stolzite at the Boyovskoye deposit, as mentioned by P. V. Pokrovsky [9] was first described in 1954 by M. N. Albov [10]. When studying that article, it turned out that the description of the mineral is given without mentioning the place of the find. Perhaps this is due to the fact that the description of ore objects of strategically important metals was classified in those years. This implies the fact that stolzite from the Boyovskoye deposit was not described in the open press. We found the mineral

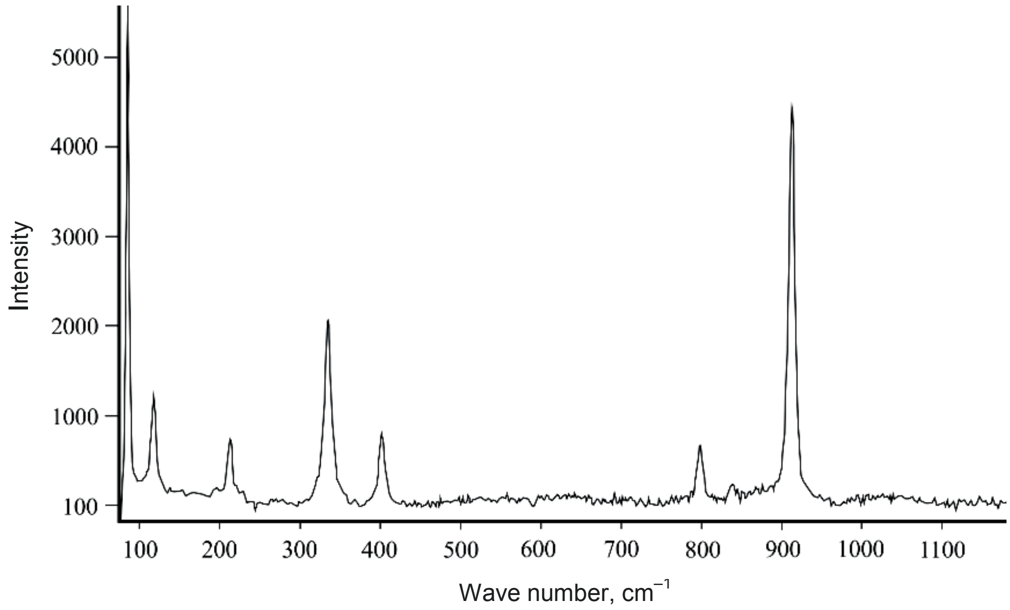

Figure 5. Raman spectrum of scheelite
Рисунок 5. Рамановский спектр шеелита

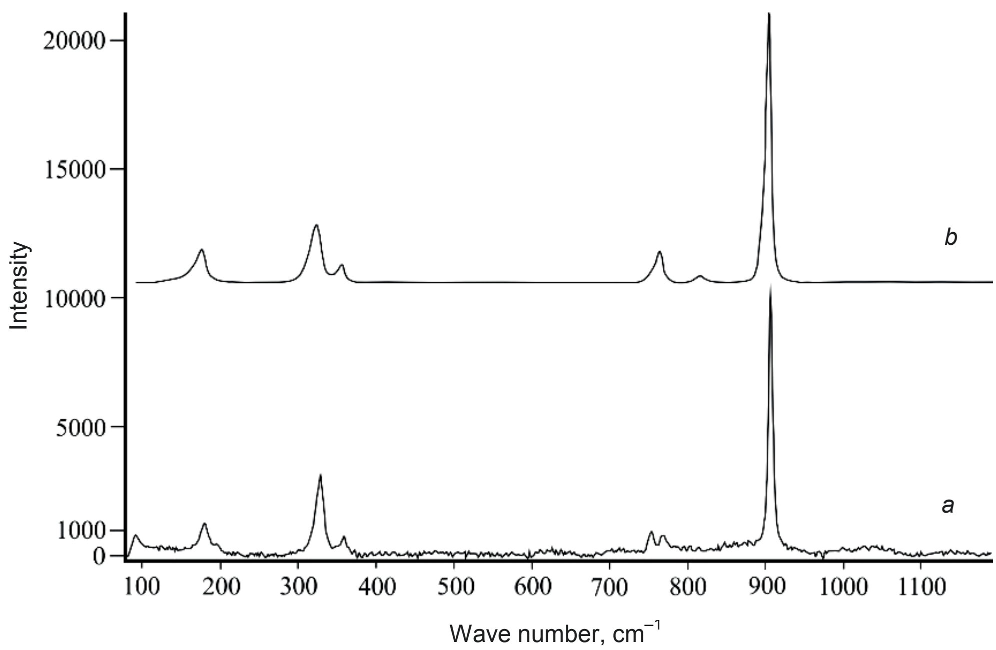

Figure 6. Raman spectrum of stolzite from the Boyovskoye deposit (*a*) and reference (*b*)
Рисунок 6. Рамановский спектр штольцита из Боёвского месторождения (*а*) и эталона (*б*)

in samples with veined quartz in association with muscovite, fluorite, hubnerite, and scheelite. It fills cracks and voids in hubnerite, rarely overgrows scheelite or fills cracks in scheelite (fig. 2, 3). Stolzite is painted light beige. The size of isometric grains of the mineral does not exceed 25 μm, and in cracks in hubnerite it can reach 180 μm. It is a later mineral in relation to hubnerite and scheelite. The chemical composition of the mineral (table 1, an. 21–30) contains impurities: manganese (up to 0.74 wt. % MnO), calcium (up to 0.33 wt. % CaO), iron (up to 0.54 wt. % FeO) and titanium (up to 0.09 wt. % TiO_2). The obtained Raman spectrum of the mineral (fig. 6) completely coincides with the reference spectrum of stolzite from the Reef mine in Arizona (USA) [11].

In the Urals, stolzite is known from the Balkanskoye deposit, where it occurs in the hypergenesis zone in calcite and quartz-calcite scheelite-bearing nests in skarns. Stolzite with an admixture of CaO 0.78 wt. % is described at the Buranovskoye tungsten deposit in the Southern Urals, where it develops along scheelite, forming rims around it [12]. At the Trebiatskoye deposit, stolzite was found in a quartz vein among serpentinites. At the Pervomaiskoye gold deposit, stolzite is found in clayey mass in the voids of a quartz vein and at the Bersuatskoye deposit in the Southern Urals, in voids in quartz with wolframite [9, 13]. It has been noted among quartz crystals at the Pelingichi crystal-bearing deposit in the Subpolar Urals [14], as well as at the Torgovskoye deposit in cracks in quartz and on scheelite and limonite crystals [15] and at the Astafievskoye crystal-bearing deposit [7]. The stolzite found by us is a mineral of the oxidation zone and, most likely, was formed due to the weathering of wolframite and galena, which are present in quartz veins.

Conclusions

Thus, we have obtained new data on the mineralogy of tungstates from the Boyovskoye tungsten deposit. The chemical composition of hubnerite and scheelite has been studied, and their Raman spectra have also been obtained. For the first time, a reliable diagnosis and description of lead tungstate – stolzite was made for the Boyovskoye deposit.

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Вольфраматы Боёвского вольфрамового месторождения (Южный Урал)

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Аннотация
Актуальность работы обусловлена необходимостью минералогического изучения вольфрамовых месторождений Уральского региона, отработка которых осуществлялась с конца XIX в.
Целью работы является диагностика и детальное описание вольфраматов из Боёвского вольфрамового месторождения, расположенного на границе Челябинской и Свердловской областей на Южном Урале.
Аналитические исследования выполнены в лаборатории физико-химических методов исследования Института геологии и геохимии УрО РАН, г. Екатеринбург. Химический состав минералов проанализирован в полированных шлифах на микроанализаторе CAMECA SX 100. Условия измерения: ускоряющее напряжение 15 кВ, сила тока 150 нА, диаметр пучка электронов 2 мкм. Давление в камере образцов $2 \cdot 10^{-4}$ Па. Спектры получены на наклонных волновых спектрометрах, измерение интенсивности проводилось по аналитическим линиям. Стандартные образцы: шеелит, вольфрамит, галенит, рутил и хромит. Рамановские спектры минералов получены с помощью спектрометра LabRam HR Evolution (Horiba Scientific). Для анализа использовался красный лазер – 532 нм.
В результате работы получены новые данные о химическом составе гюбнерита и шеелита и приведены их рамановские спектры. Впервые для Боёвского вольфрамового месторождения сделана достоверная диагностика и описание вольфрамата свинца – штольцита. Минерал был найден в образцах с жильным кварцем в ассоциации с мусковитом, флюоритом, гюбнеритом и шеелитом. Выполняет трещины и пустоты в гюбнерите, реже обрастает шеелит или заполняет трещины в шеелите. Он является более поздним минералом по отношению к гюбнериту и шеелиту. В его химическом составе отмечаются примеси марганца, кальция, железа и титана. Штольцит, найденный нами, является минералом зоны окисления и скорее всего образовался за счет выветривания вольфрамита и галенита, которые также присутствуют в кварцевых жилах.

***Ключевые слова*:** гюбнерит, шеелит, штольцит, Боёвское вольфрамовое месторождение, Южный Урал.

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