

Rare mineralization from quartz-plagioclase veins of the Mariinsky deposit (Ural emerald mines)

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Abstract

Relevance – the study and description of rare and new minerals for the Ural emerald mines. To do this, within the framework of the work, we made a study of the compositions and relationships of previously known, but poorly studied sulfides, with minerals newly discovered for the Mariinsky deposit.

The purpose of the work is to study the features of the structure and material composition and the conditions for finding rare sulfides and native elements for this type of deposits.

Research methodology. The main diagnostics and study of the compositions of minerals from the discovered association was carried out using a Zeiss AxioScope.A1 optical microscope and a Tescan Vega 3 sbu scanning electron microscope with Oxford Instruments X-act EMF (South University Federal Scientific Center MiG, Ural Branch of the Russian Academy of Sciences, analyst M. A. Rassomakhin). The detection limits for the contents of chemical elements do not exceed 0.2 wt. %. Some of the minerals were studied using a VEGA 4 LMS scanning electron microscope with an Xplore 30 energy-dispersive attachment (FSFEI HE UGGU RTL VSPiR, analyst L. A. Demina).

Results. Data are given on the structural features and chemical composition of rare minerals for the Mariinsky deposit: galena, zinc greenockite, bismuthine, matildite.

Conclusions. A mineralogical study was carried out and the chemical composition of sulfide mineralization rare for the Ural emerald mines was studied. Previously, zinc greenockite and matildite were not described, so this is the first find of these minerals at the Mariinsky deposit.

Keywords: Ural emerald mines, sphalerite, chalcopryrite, galena, zinc greenockite, bismuthine, matildite, electrum.

Introduction

Deposits and occurrences of rare metals and precious stones in the eastern frame of the Murzinsko-Aduisky anticlinorium, known throughout the world as the Ural emerald mines (UEM), are a unique ore and mineralogical object known since 1831. During this time, dozens of deposits and occurrences with various mineralization; tons of mineralogical samples of precious stones, hundreds of tons of semi-precious and collection raw materials, hundreds of thousands of tons of ore concentrates were mined. Currently, about 290 minerals and varieties are known and described on the territory of the UEM. Every year, new minerals are discovered that are not typical for objects of this type.

At present, based on the results of studying newly discovered emerald deposits, two main geological and industrial types of deposits of this gemstone have begun to be distinguished in the world. *The first type* is represented by carbonate-albite-pyrite-quartz veins and tectonic breccias in carbonaceous and carbonate shales [1, 2]. Sometimes they form in terrigenous-carbonate and sulfate-terrigenous-carbonate rocks [3]. Since the main large deposits of this type are located

in Colombia, the type was called “Colombian”. Deposits of *the second type* are located at the contacts of massifs of basic and ultrabasic compositions or in zones of junction of non-metamorphosed ultramafic rocks with felsic rocks. Such contacts can be both intrusive and tectonic. This type of deposits is often referred to as “shale”. In view of the fact that for the first time such objects were found in the Urals in 1831 (Sretenskoye deposit, UEM), many researchers call the second type “Ural”. Host rocks occurring in “suture zones” usually form “tectonic mélange” [4, 5]. In addition, rocks hosting emerald mineralization are often metamorphosed volcanic rocks of basic composition. These can be epidote-chlorite-actinolite rocks, chlorite and talc-chlorite schists (Kafubu deposit, Zambia) [6], mafic gneisses and amphibolites (Tanzania, Madagascar) [7]. Most emerald deposits have described minor sulfide mineralization that accompanied the formation of the gemstone. These are numerous finds and inclusions of pyrite in crystalline raw materials (Columbian type) and molybdenite, pyrite, chalcopryrite in ore bodies with emerald (Ural type). Within the ore region of the UEM, the main geological and genetic types of

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rare-metal mineralization were identified: vein, metasomatic ores, and hydrothermalites [8, 9].

Brief geological structure of the Mariinsky deposit. The Mariinsky (Malyshevskoye) deposit is the largest in Russia and one of the most famous emerald deposits in the world, which was discovered in 1833. Quartz-plagioclase veins are quite common at the deposit and are confined to northeast-ern cracks. They mainly occur in diorite porphyrites, as well as talc schists and serpentinites, and are represented by lenticular bodies, 1–3 m thick and 5–15 m long along strike [10]. The morphology and size of quartz-plagioclase veins depend on the conditions of their occurrence (shearing zones, intersections of tectonic faults). Quartz-plagioclase veins are in close genetic connection with emerald-bearing mica, but they are located in different geological and structural settings, as if they cross mica veins. Therefore, significant series of quartz-plagioclase veins with industrial rare-metal (Ta–Nb–Be) mineralization are found in large emerald-beryl deposits (Mariinskoye, Krasnoarmeiskoye). On small manifestations, the veins are represented by single bodies. In composition, they are close to rare-metal pegmatites of the region, but differ from them in structural and textural characteristics and mineral associations of secondary minerals [11].

Beryl in quartz-plagioclase veins forms nest-like accumulations, which are filled with medium-large crystalline crystals. The shapes and sizes of beryl are different – from short-prismatic, reaching several tens of centimeters in diameter, to parallel-columnar aggregates oriented perpendicular to the

contacts. Large-flake muscovite often contains prismatic translucent crystals of colorless and slightly bluish beryl of later generation. Sulfide minerals (sphalerite, pyrite, chalcopyrite) are often found in quartz-plagioclase veins, which are formed together with prehnite, late chlorite, beryl, fluorite, bavenite.

A detailed study of granular sphalerite aggregates growing on late-generation beryl crystals from voids in a quartz-plagioclase vein from the Mariinsky deposit revealed the following rare minerals for the deposit: galena, zinc greenockite, bismuthine, matildite. When studying a fragment of a quartz-plagioclase vein from the Mariinsky deposit, dust-like segregations of *electrum* and *native bismuth* were found, which form several elongated sections located in the oligoclase matrix. Together with the described minerals, plagioclase contains laths of phlogopite and separate isolated segregations of *bismuth sulfosalt*.

Methodology for studying the features of the composition of rare mineralization. To study the relationships between minerals, polished sections were made. The diagnostics and study of the compositions of minerals from the discovered association was carried out using a Zeiss AxioScope.A1 optical microscope and scanning electron microscopes: Tescan Vega 3 sbu with EMF Oxford Instruments X-act (Southern University Federal Scientific Center MiG, Ural Branch of the Russian Academy of Sciences, analyst M. A. Rassomakhin, chemical elements do not exceed 0.2 wt. %) and VEGA LMS with Xplore 30 energy dispersive attachment (FSFEI HE UGGU RTL VSPiR, analyst L. A. Demina).

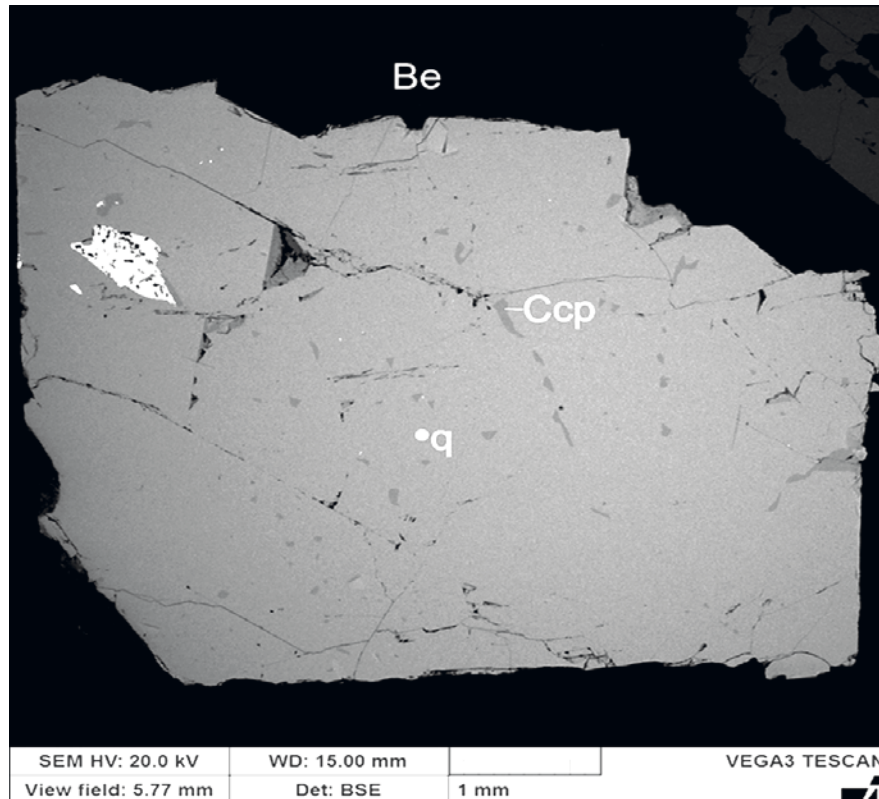


Figure 1. A granular aggregate of sphalerite (light grey) and beryl (Be) with inclusions of chalcopyrite (Ccp) and a complex intergrowth of bismuthine, matildite, native bismuth (large white spot in the upper left part of the aggregate). Photo in BSE
Рисунок 1. Зернистый агрегат сфалерита (светло-серое) и берилла (Be) с включениями в нем халькопирита (Ccp) и сложное срастание висмутина, матильдита, самородного висмута (большое белое пятно в верхней левой части агрегата). Фото в BSE

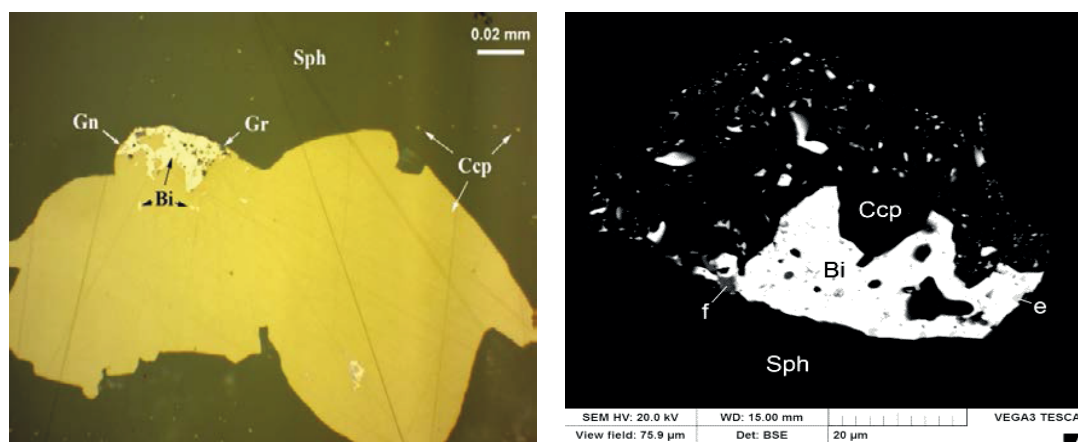


Figure 2. Complex intergrowth of galena (Gn, point e), native bismuth (Bi), greenockite (Gr, point f), and chalcopyrite (Ccp) in sphalerite (Sph). Left – reflected light, right – BSE
Рисунок 2. Сложное срастание галенита (Gn, точка e), самородного висмута (Bi), гринокита (Gr, точка f) и халькопирита (Ccp) в сфалерите (Sph). Слева – отраженный свет, справа – BSE

Table 1. Chemical composition of sphalerite, chalcopyrite, galena and greenockite, wt. %
Таблица 1. Химический состав сфалерита, халькопирита, галенита и гринокита, мас. %

Analysis	S	Fe	Zn	Cu	Cd	Pb	Bi	Total	Formula
bdl 1 (point q)	32.81	1.56	65.2	bdl	0.43	bdl	bdl	100.00	$Zn_{0.97}Fe_{0.03}Cd_{0.004}S_1$
2 (point a)	33.83	30.93	0.46	34.19	bdl	bdl	bdl	99.42	$Cu_{1.00}Fe_{1.03}Zn_{0.01}S_{1.96}$
3 (point e)	13.13	2.10	7.10	2.28	bdl	69.92	6.29	100.18	$Pb_{0.70}Zn_{0.23}Fe_{0.06}Cu_{0.07}Bi_{0.07}S_{1.15}$
4 (point f)	24.23	6.05	10.63	4.98	54.11	bdl	bdl	100.00	$Cd_{0.61}Zn_{0.20}Fe_{0.14}Cu_{0.10}S_{0.95}$

Note: The formula is calculated on the number of f.u., bdl – below the detection limit. EMF, operator M. A. Rassomakhin.

Results

Sphalerite is represented by a medium-grained aggregate 5 x 7 mm in size, which grows on the verge of bluish beryl of late generation. The color of the mineral is yellow-brown. At the boundary between beryl and sphalerite, there is a joint growth boundary. Inside, zinc sulfide contains emulsion dissemination of chalcopyrite and inclusions of bismuthine, native bismuth, and matildite (fig. 1). Intergrowths are observed between minerals. Sphalerite contains an insignificant admixture of iron and cadmium (table 1, analysis 1).

Chalcopyrite occurs as an emulsion dissemination in sphalerite (fig. 1), which can grow together with matildite and in complex inclusions with bismuthine, native bismuth, and matildite (fig. 3), as well as with greenockite and galena (fig. 2). Quite rarely, the mineral contains inclusions of native bismuth, bismuthine. The size of chalcopyrite varies from emulsion to 0.25 mm. The chemical composition is shown in table 1 (analysis 2).

Galena and greenockite occur as single inclusions in sphalerite (fig. 2), where they are in a complex intergrowth with chalcopyrite and native bismuth. The size of sulfides is 4–7 microns. The chemical composition of minerals is displayed in table 1 (analyses 3 and 4). The elevated contents of Zn, Cu, and Fe in galena are most likely associated with the partial capture of elements from nearby sphalerite and chalcopyrite. The found greenockite, according to the Zn–Cd–S ternary system, can be attributed to zinc greenockite [12].

Bismuthine is found in sphalerite as the basis of a complex

inclusion (fig. 3), which grows together with native bismuth, chalcopyrite, and matildite. The size of the accretion is 0.8 mm. No impurities were found in the composition of bismuthine (table 2, analyzes 1 and 2).

Matildite is noted as dissemination in sphalerite, which can grow together with chalcopyrite and with bismuthine + native bismuth. May contain submicron inclusions of native bismuth. The size of matildite is 10–15 µm, single 30 µm. The composition of matildite is displayed in table 2 (analyses 3 and 4).

Electrum is represented by small lamellar segregations with uneven edges, the size of which reaches from 3 to 15 microns. The mineral was found together with grains of native bismuth (fig. 4). Native metals are well diagnosed by the element distribution map and EMF spectra (figs. 2, 3). Electrum has a fairly stable composition, in which the silver content varies from 39 to 42 wt. % (table 1). A small amount of silicon most likely comes from the substrate of the sample.

Results discussion

The formation of minerals of the described association occurred at the late stages of hydrothermal processes superimposed on quartz-plagioclase veins of the Mariinsky deposit. Rare sulfide mineralization – galena, zinc greenockite, matildite, is found in association with beryl, which is a rather rare case. Bismuth and silver sulfides in the Urals were previously described in gold deposits [13], polymetallic [14], and porphyry deposits in the Southern Urals [15, 16]. The association of matildite and beryl is described only in the cassiterite-silicate-sulfide type of tin deposits (field

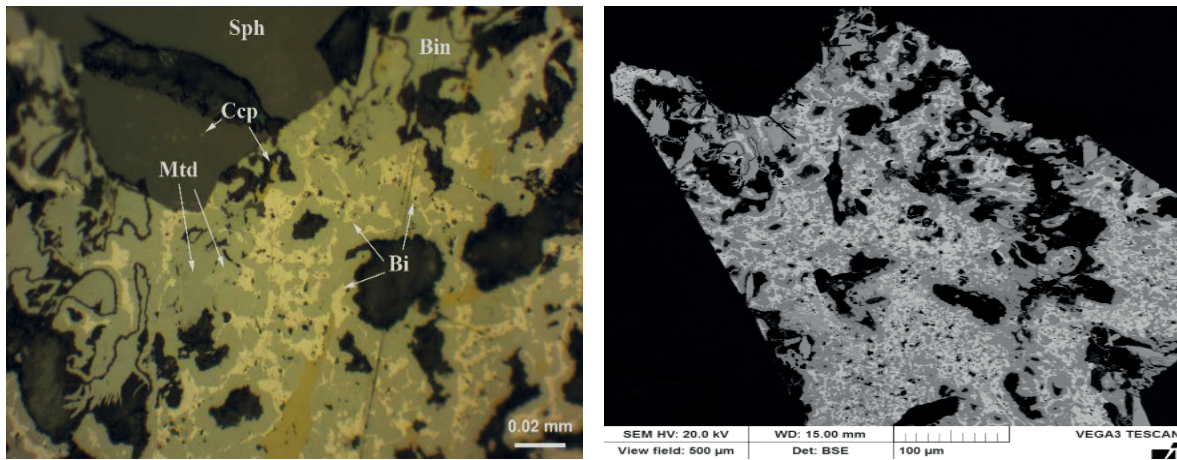


Figure 3. Complex intergrowth of bismuthine (Bin, point r), matildite (mtd, point s), native bismuth (Bi, point t), and chalcopyrite (Ccp) in sphalerite (Sph). Left – reflected light, right – BSE
Рисунок 3. Сложное срастание висмутина (Bin, точка r), матильдита (mtd, точка s), самородного висмута (Bi, точка t) и халькопирита (Ccp) в сфалерите (Sph). Слева – отраженный свет, справа – BSE

Table 2. Chemical composition of bismuth and silver minerals, wt. %
Таблица 2. Химический состав минералов висмута и серебра, мас. %

Analysis	S	Fe	Cu	Zn	Te	Ag	Pb	Bi	Total	Formula
1 (point r)	18.72	bdl	bdl	bdl	bdl	bdl	bdl	81.28	100	Bi_2S_3
2 (point r')	18.44	bdl	bdl	bdl	bdl	bdl	bdl	81.56	100	$Bi_{2.02}S_{2.98}$
3 (point s)	16.21	bdl	bdl	bdl	bdl	28.79	bdl	55.00	100	$Ag_{1.03}Bi_{1.02}S_{1.95}$
4 (point c)	16.49	0.68	1.47	3.31	bdl	12.45	8.82	56.63	99.85	$Ag_{0.65}Zn_{0.19}Cu_{0.13}Pb_{0.05}Bi_{1.03}S_{1.95}$
5 (point t)	bdl	bdl	bdl	bdl	bdl	bdl	bdl	100	100	$Bi_{1.00}$

Note: The formula is calculated on the number of f.u., bdl – below the detection limit. SEM, operator M. A. Rassomakhin.

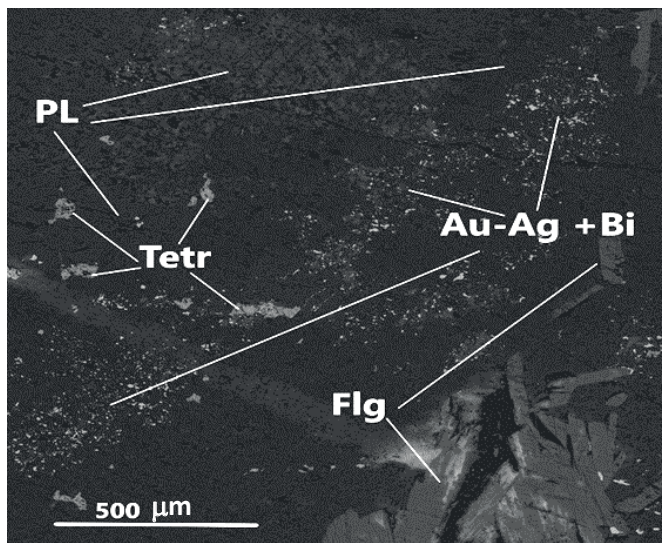


Figure 4. Segregations of electrum (Au–Ag) and bismuth (Bi) in plagioclase (Pl) together with phlogopite (Flg) and bismuth sulfosalts (Tetr)
Рисунок 4. Выделения электрума (Au–Ag) и висмута (Bi) в плагиоклазе (Pl) совместно с флогопитом (Flg) и сульфосолями висмута (Tetr)

Table 3. Chemical composition of electrum from a quartz-plagioclase vein of the Mariinsky deposit, wt. %
Таблица 3. Химический состав электрума из кварц-плагиоклазовой жилы Мариинского месторождения, мас. %

Analysis number	Au	Ag	Si	Total
1	59.13	40.14	0.71	99.98
2	40.69	57.15	0.61	98.45
3	41.24	58.01	bdl	99.25

Note: The analyzes were performed on a TESCAN VEGA-4 LMS SEM at the VSPiR laboratory of the Ural State Mining University (analyst L. A. Demina). Bdl – below the detection limit.

minerals. The formation of unusual Bi, Bi–Te mineralizations in quartz-plagioclase veins at the deposit is directly related to the formation of rare-metal pegmatites of the nearby Adui granite massif, which is part of the Murzinsko-Adui anticlinorium [18]. Electrum is a fairly rare mineral that occurs in the Urals at gold deposits: Blagodatnoe (Middle Urals) [19]; Kochkarskoe (Southern Urals) [20], and at the Yubileynoe (Cu–Zn) deposit (Southern Urals). Previously, native gold was found at the Mariinsky deposit [21].

Conclusions

1. A rare mineralization for emerald deposits was studied, which reflects the late stage of the formation of the Mariinsky deposit.
2. Rare minerals for the Mariinsky deposit and for the

Alyaskitovoye, Eastern Yakutia) [17]. Bismuth mineralization in mica and quartz-plagioclase veins of emerald-beryl deposits is developed quite intensively and is represented by native bismuth, bismuthine, tetradymite, tellurobismuthite and other

Ural emerald mines are described for the first time: galena, zinc greenockite, bismuthine, matildite, electrum.

3. On the territory of the ore region of the Ural emerald mines there are deposits of native gold Rudnichnoye (native) and Shamei placers. At the Mariinsky emerald deposit, there are minerals of native

metals (gold, electrum) and various forms of Ag–Bi–Te mineralization.

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Редкая минерализация из кварц-плагиоклазовых жил Мариинского месторождения (Уральские изумрудные копи)

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Аннотация

Актуальность – изучение и описание редких и новых для Уральских изумрудных копей минералов. Для этого в рамках работы было проведено изучение составов и взаимоотношений ранее известных, но слабоизученных сульфидов с вновь открытыми редкими для Мариинского месторождения минералами.

Целью работы является изучение особенностей строения и вещественного состава и условий нахождения редких для подобного типа месторождений сульфидов. Полученные данные позволят расширить минеральный кадастр территории Уральских изумрудных копей.

Методология исследования. Основная диагностика и изучение составов минералов из обнаруженной ассоциации проведены с помощью оптического микроскопа Zeiss AxioScore.A1 и сканирующего электронного микроскопа Tescan Vega 3 sbu с ЭДС Oxford Instruments X-act (ЮУ ФНЦ МиГ УрО РАН, аналитик М. А. Рассомахин). Пределы обнаружения содержаний химических элементов не превышают 0.2 мас. %. Часть минералов была изучена на сканирующем электронном микроскопе TESCAN VEGA 4 LMS с энергодисперсионной приставкой Xplore 30 AZtecLite (ФГБОУ ВО УГГУ НИИЛ ВСПиР, аналитик Л. А. Демина).

Результаты. Приведены данные по особенностям строения, химическому составу редких для Мариинского месторождения минералов: галенита, цинкистого гринокита, висмутитина, матильдита.

Выводы. Проведено минералогическое исследование и изучен химический состав редкой для Уральских изумрудных копей сульфидной минерализации. Описанная минерализация позволяет охарактеризовать завершающую стадию минералообразования в позднегидротермальном процессе, проявленном на месторождении. Ранее цинкистый гринокит, матильдит не описывались, поэтому это первая находка данных минералов на Мариинском месторождении.

Ключевые слова: Уральские изумрудные копи, сфалерит, халькопирит, галенит, цинкистый гринокит, висмутин, матильдит, электрум.

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