Identification of mineral associations in skarn-rare-metallic deposits in Western Uzbekistan

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Abstract. This article solves the applied scientific problem of identifying mineral carriers and mineral associations of platinum mineralization in the skarn-gold-rare metal Koytash and Lyangar deposits. One of the applied research tasks was to identify the forms of mineral carriers and mineral associations of platinum-metal mineralization for these deposits. We carried out geological fieldwork of the Koytash and Lyangar deposits, which included a sampling of sulphide-rare metal and silver-polymetallic ores, and conducted laboratory studies by using mass spectrometry, atomic absorption, electron microprobe, and other modern methods. This article addresses the complex formation of sulphide-rare-metal and silver-polymetallic ores of the above-mentioned deposits. The formation of mineral associations bearing rare-metal (W-Mo) mineralization that formed in the early alkaline stage, in almost all sites, is completed by sulphide-rare metal and silver-polymetallic mineralization that often carry industrial-grade concentrations of noble and other metals. We have identified a recommended location for the concomitant extraction of useful components, the mineral composition, and the impure elements in them. These data show the prospects of sulphide-rare metals and sulphide-polymetallic ores in the Koytash deposit for precious metals, bismuth, etc.

1 Introduction

This article studies non-traditional manifestations of platinum group elements in the skarn-rare-metal deposits of western Uzbekistan. This research identifies the forms of carrier minerals and mineral associations of platinum mineralization in the Koytash and Lyangar skarn-rare metal deposits in western Uzbekistan with the aim of increasing their economic value and participation in industrial development [1]. The growing need for platinoids has intensified geological searches for platinum-bearing raw materials, which has led to the discovery of a number of unconventional deposits worldwide [2]. Globally, large-scale research has been conducted to assess the platinoid content in gold, silver, polymetallic, porphyry copper ores, and other types of deposits for the purpose of their extraction [3]. Platinoids are extremely rare in skarn deposits, including skarns in the northern part of the

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Bushveld complex in the Republic of South Africa. In recent years, due to the emergence of new methods for the determination of low noble metal contents, platinoids have been discovered in non-traditional geochemical situations, such as impurities in various sulphides, quartz, and other minerals within ores and host rocks, including sulphide ores in skarn deposits [4]. Using the atomic absorption method, high contents of platinum and palladium have been found in sulfides within sulfide-rare metal ores in the Koytash and Lyangar deposits.

2 Materials and methods

2.1 Study area

Uzbekistan, especially it's western part, was recognized as a pronounced rare metal province long before the discovery of its gold content. This is evident from the fact that the first notable person in the mining industry of Uzbekistan was the tungsten mining entrepreneur Lyangar; after his work, the Koytash and other deposits began to be developed.

The Lyangar field consists of a group of skarn ore occurrences at the western and south-western contacts of the Aktau granitoid massif in the South Nuratau Mountains. It includes the following sections: the main (main ore field), watershed, quartz veins, western, northern, and Tuteksai sections [5]. Scheelite-bearing skarns of the Lyangar deposit were established by N. A. Smolyaninov in 1934, and afterward, a mining enterprise for the extraction of scheelite concentrate began.

An exploration of the field and its surroundings has revealed that the stratigraphy and tectonic position of the sedimentary-metamorphic strata are not clear [6]. There are two viewpoints on the position of limestones in the stratigraphy of the area. According to the first viewpoint, the limestones in the Aktau and Bakhiltau Mountains are middle Paleozoic in age and lie on a metamorphosed sand-shale layer [7]. According to previous researchers, the limestone strata of both mountains are Silurian in age and comprise two wings of one extensive syncline. The intrusive magmatism in the area, in particular, the Aktau granitoid massif, has been studied sufficiently. Its upper Carboniferous-lower Permian age, three-phase structure, hybrid (assimilated) nature of the rocks in the first and second phases of the intrusion, and formation in hypo-Meso-abyssal conditions have been unanimously agreed upon [8].

The skarn ore bodies of the Lyangar area are confined to the contact between carbonate rocks and the Aktau granitoid massif. Skarns are mainly located on granodiorite and adamellite contacts [9]. They are not developed around the contact but rather form separate sections with industrial-grade contents of tungsten and molybdenum at the north-western and western contacts of the Aktau intrusion. At these locations, the surface of the intrusion has uneven, wavy outlines with numerous apophyllites floating in enclosing carbonate rocks [5]. The angles of incidence of the contact surface range from 15-30° (in the main ore field) to 60-70° (in the western part of the watershed division) and are usually 40-45°. In the endocontact zones of skarn ore deposits, in addition to quartz feldspathic metasomatosis, the processes of albitization, greisenization, silicification, sulfidation, etc. are present [10].

Structurally, it is located in the eastern North Nuratau anticlinorium and is located in the northern part of a small brachysyncline (the Koytashskoy trough), which is a folded bundle of carbonate rocks of medium carboniferous age C2; they form an angular and stratigraphic unconformity with Ordovician-Silurian and Cambrian strata and with sediments of an Ordovician – Cambrian (Cambrian) layer (I). On the eroded surface of C2 sediments, there lies a small bundle of C3 conglomerates. The carbonate strata consist mainly of limestone, and partly of shale and conglomerates [10].

Due to the contact of the intrusion, limestone was turned into marble, and shale was converted into hornfels. The lower Paleozoic sediments (Ordovician-Silurian and Cambrian) consist mainly of flyschoid sand-shale formations with interlayers of quartzite and carbonate rocks. The latter are mainly represented by limestones, and their thickness ranges from 2-3 m to 20 m (for example, in the north-western contact zone of the Jailau area) [11]. These rocks also underwent both regional and contact metamorphism: in the Jaylau and Kokbulak sections and in the northern contact zone, the schists were transformed into various hornfelses and knotty biotite-cordierite, andalusite, amphibole, and other shales, and the limestones were transformed into marble. Note that two-thirds of the intrusive contact lies on these deposits, but only separate ore areas (Khauzbulak, Shait, and Djailau) with small ore potentials occur within them [12].

The intrusive contact with the carbonate-terrigenous sediments of the upper Carboniferous-lower Permian age is approximately one-third of the total intrusive contact, but all areas that are part of ore operations (Central, Eastern, Northern, Dunyotepa and Koytash-Ugat Strip) are associated with it [13]. In these deposits, the decisive role of the lithological composition of the host rocks in the localization of the mineralization of the Koytash ore field is clear [14].

2.2 Research methodology

In previous geological studies focusing on major minerals, sulphide-rare-metal and sulphide-polymetallic ores of the Koytash and Lyangar deposits were studied using mass spectrometry, atomic absorption, electron microprobe, and other modern methods [15]. With the electron microprobe method, high contents of platinum, palladium, gold, and, less often, rare-earth elements were identified in sulphides [16]. Additionally, in sulphides, the electron-microprobe analysis revealed elevated levels of gold impurities: gold was detected in 36 of 63 grains of pyrrhotite in sulfide-rare-metal ores of the Koytash-Ugat Strip; in chalcopyrite (in 17 tests), gold was found in 7 samples; and in pyrite (in 5 tests), gold was recorded in three samples. Bismuth minerals are also widely developed in silver-polymetallic ores and are represented by Ag-bursaite, pilsenite, wittite, galeno-bismuthite, and cannizzarite. Bursaite, platinite, heyrovskite, and weibulite are less common and have been found in the Koytash deposit [17]. Mass spectrometric analysis of monomineralic sulphide fractions in skarn-rare-metal ores has shown that they are elevated in chalcopyrite, but their pyrrhotite content is twice as low. In 11 samples in this research, 5 samples contained native bismuth and tellurium bismuth, 2 samples contained bismuth and one sample contained Ag bismuthite.

3 Results and discussion

In recent decades, complex sulphides, rare metal, and silver polymetallic ores, which were previously unknown in this area, have been identified in the skarn-rare metal Koytash deposit, which includes new typomorphic mineral associations. To assess the presence and extent of the manifestations of similar associations in other fields, we analyzed literary materials and conducted additional studies to reveal their manifestation in almost all large deposits that have been studied; however, the extent of their manifestation is different. Taking into account these data and information from previous researchers, the following tables of the formation sequence of mineral associations in the skarn-rare metal deposits of western Uzbekistan have been compiled. Table 1 includes all mineral associations in the deposits, including representatives of the magmatic stage; however, given that they are usually barren, in the text, we give a brief description of only postmagmatic mineral associations that comprise the ore bodies in the deposits. The Koytash deposit was developed as a typical skarn-tungsten-molybdenum body and was considered a low-sulphide deposit, but 40 years after its development, large reserves of skarn-sulphide-rare-metal ores with complexes, including noble metal mineralization, were discovered. The wide development of such ores occurred in skarns and wollastonite-garnet skarnoids, which contributed to an even greater variety of mineral associations at the site [18].

Pyroxene-wollastonite and pyroxene-feldspar-garnet -vesuvian associations are products of the early alkaline (skarn) stage of post-magmatic mineral formation. The composition of the mineral associations is determined by the lithological composition of the original rocks subjected to skarn-forming processes: at the contact between carbonate rocks and granitoid rocks, diffusive-metasomatic pyroxene-wollastonite skarns are developed. The composition of pyroxene in exocontacts is ferrosalite and hedenbergite, and in endocontacts, it is salite and diopside-salite. At the contact between the carbonate rocks a pyroxene-feldspar mineral association of infiltration-metasomatic character is developed, which forms layer-like bodies. Here, pyroxene is represented by salite and ferrosalite. The garnet-vesuvianite association also forms at the contact between carbonate rocks and granitoid rocks at this stage of mineral formation. Still, it occurs later than the above-described mineral associations and indicates an increase in the chemical potential of aluminium in the solution.

Quartz-sericite association is characteristic of the greisen stage and is formed in feldspathoid rocks. Instances of quartz-sericite formations of quartz-scheelite and quartz-sulphide veinlets have also been established, which suggests that they are simultaneous or that the veinlets were formed slightly earlier than quartz-sericite metasomatites.

Albite-amphibole (actinolite)-scheelite and quartz-amphibole (actinolite and tremolite)-scheelite associations are superimposed on skarns, near skarn rocks, and hornfelses and indicate a slight increase in the acidity of the solutions. The main industrial-grade concentration of tungsten is associated with this mineral association. Simultaneously, in granitoid rocks, quartz-scheelite associations with sericite, chlorite, and albite occur and are selected as "apogranite" tungsten ores. Feldspar-quartz-molybdenite with scheelite is widely developed in the Koytash field.

Table 1. Formation sequence of paragenetic mineral associations of the Koytash ore field.

Mineralization stage	Nature of the solution	Mineral formation stage	Paragenetic association	Observed localities
Magmatic	Thermal metamorphic	Contact hornfels	Biotite hornfelses, biotite-cordierite, andalusite, etc., shales	Central, Eastern, Northern, Dunyotepa, Koytash-Ugat, Shait, Khauzbulak, etc.
		Marble limestone	Calcite-graphite-silicates	
		Lime-silicate hornfelses	Wollastonite-feldspar-calcite-quartz	
			Wollastonite-pyroxene-calcite	
			Wollastonite-pyroxene-garnet (± vesuvian)	
Postmagmatic	Early alkaline	Quartz-feldspar-muscovite (pegmatite)	Quartz-feldspar-muscovite	Band Koytash-Ugat, Shait, Dunyotepa
			Quartz-feldspar	
		Pyroxene garnet-	Pyroxene-feldspar	

Mineralization stage	Nature of the solution	Mineral formation stage	Paragenetic association	Observed localities
		feldspar (skarn)	with scheelite	
			Garnet (± vesuvian) with scheelite	
	Acid	Quartz-sericite (muscovite)	Quartz-sericite (muscovite)	In all areas
		Quartz-albite-amphibole-scheelitic	Albite-amphibole (actinolite and hornfels)-scheelite	Koytash-Ugat Strip, Gailau, Shait, Ugat, Koytash-Ugat Strip
			Quartz-scheelite	
			Feldspar-quartz-molybdenite with scheelite	
			Wollastonite-quartz-calcite-scheelite	Koytash-Ugat Strip, East section
			Quartz-pyrrhotite-stilpnomelane with scheelite	
	Late alkaline	Quartz-feldspar-sericite (± chlorite)-sulfide	Quartz-sericite-chlorite-pyrite-chalcopyrite	Koytash-Ugat Strip
			Pyrrhotite-pyrite	
			Quartz-pyrite-arsenopyrite-gold containing	
			Quartz-chalcopyrite with pyrite and marcasite	Koytash-Ugat, Shurkunda, Ugat Strip
			Quartz-joseite-tellurium bismuth	
			Quartz-carbonate-sphalerite - galena-freibergite with native bismuth	
		Quartz-calcite-apophyllite-zeolite-sulphide	Apophyllite-zeolite-calcite with pyrite	Koytash-Ugat Strip
			Calcite-quartz	Koytash Ugat Strip East section

There have been cases where veins and veinlets of the above-mentioned associations cut skarn ore bodies and enter the host rocks. In a cross-section of the 3 exploration mines, the veins of this mineral association, the second pyroxene skarn with scheelite, are cut by a pyrrhotite-chalcopyrite vein. The presence of molybdenite indicates a weakly acidic environment. This mineral association is most widely manifested in the central and eastern sections, where higher levels of mineralization are developed; however, in the Koytash-Ugat Strip, which represents deep levels of mineralization, it is rare. This mineral association is a reliable criterion for determining the level of erosion of a deposit [14].

Pyroxene-wollastonite-quartz-calcite-scheelite association is located in the infiltration-metasomatic pyroxene veins in the hornfelses of the Koytash-Ugat Strip. Pyroxene is represented by hedenbergite and ferrosalite. It is replaced by wollastonite. Given that this wollastonite develops alongside hedenbergite and is associated with scheelite, it was likely formed at the end of the early alkaline stage.

Quartz-pyrrhotite-stilpnomelane association with scheelite is superimposed on the feldspar-quartz-molybdenite association with scheelite. It is widely developed in the skarn ore bodies of the Koytash-Ugat Strip and is represented by banded, massive sulphide-rare metal ores with relics of skarns, skarnoids, and hornfelses. This association consists of pyrrhotite, pyrite, chalcopyrite, pyroxene, actinolite-tremolite, granite, quartz, stilpnomelane, sphene titanite, tungsten trioxide, gold, and silver. In addition, native bismuth, bismuthite, tellurium bismuthite, tetradymite, joseite, hedleyite, sphalerite, galena, and other minerals are found.

In the central and eastern sections of the ore field, this association is only weakly developed and forms small lenses and veins in skarn ore bodies. The uneven distribution of this mineral association in different parts of the ore field is considered to be a result of zonation within the mineralized system [19].

Quartz-sericite-chlorite-pyrite-chalcopyrite association is a modified granitoid rock in the endocontact part of the intrusion; this also includes pyroxene-feldspathic rocks, which are similar in composition. This type, named by Khambrabaev as "apogranite ores", consists of feldspar, quartz, muscovite, and chlorite. According to atomic absorption spectroscopic analysis, bismuth, tellurium, selenium, zinc, lead, copper, gold, and silver have been established in these ores. The content of tungsten trioxide (WO3) was determined according to chemical analysis.

Pyrrhotite is associated with pyrite. Depending on the composition of the host rocks and ores, two types of this association are distinguished: pyrite and pyrrhotite. The pyrite type is mostly manifested in the Koytash-Ugat area.

The pyrite-pyrrhotite variety is confined to silicified pyroxene-feldspar hornstones and wollastonite-calcite to vesuvian skarnoids. The pyrite-pyrrhotite mineral association is located in the crushed zone of massive pyrrhotite ores in the form of independent veinlets (Figure 1). In the pyrite association, high contents of bismuth, zinc, copper, and silver are established. The high contents of these elements are associated with the inclusions of their minerals.

Fig. 1. Massive pyrrhotite ore with band-disseminated polymetallic mineralization from the Koytash-Ugat Strip.

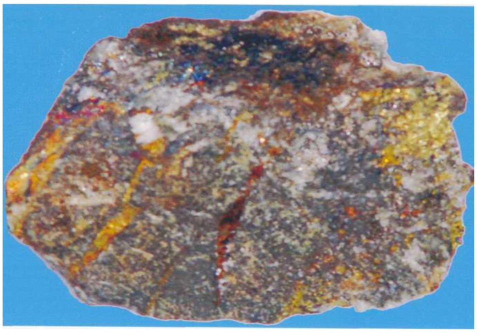

Fig. 2. Vein-discharged chalcopyrite, bornite, and covellite in silicified biotite hornfels with pyrrhotite in the Koytash deposit

Quartz-pyrite-arsenopyrite-gold-bearing association, which is in the form of impregnation, is found in quartz, quartz-carbonate veins, brecciated rock with cemented carbonate material, chloridized pyrrhotite ores, apogranites, and other metasomatized. This paragenesis is often associated with superimposed polymetallic mineralization (sphalerite, galena, native bismuth, galena-bismuthite, lillianite, etc.). The content of gold and silver increases with depth (as part of this association) in the “main” mine shaft. The joint finding of arsenopyrite with native gold, pyrite, and quartz in this association is considered an indicator of gold mineralization since industrial gold facilities in western Uzbekistan are associated with this association.

For quartz-chalcopyrite with pyrite and marcasite association, cases of the intersection of massive pyrrhotite ores and apogranites with veins of this mineral association have been established. They meet in the Koytash-Ugat Strip in the form of veins reaching 5-6 cm thick. In this location, chalcopyrite is associated with bornite, covellite (Figure 2), arsenopy, rite, and superimposed polymetallic mineralization. Atomic absorption and chemical analyses in this association have established pyrite, zinc, tin, bismuth, wolfram trioxide, gold, and silver. This association is widely manifested in the Koytash-Ugat Strip and decreases in an eastward direction.

The quartz-Josette-hedleyite-tellurium bismuth association is confined to massive sulfide ores, quartz veins, and veinlets in greisenized granitoid rocks. It is characterized by high gold and tellurium contents. The telluride complex contains bismuth tellurides (joseite, hedleyite, tellurium bismuth, and tetradymite) and rarely silver tellurides (e.g., hessite). This association is also widely represented in the Koytash-Ugat Strip. A slight increase in the depth of arsenic, gold, and tellurium is noted along the trunk of the “home” mine of the Koytash-Ugat Strip.

The quartz-carbonate-sphalerite-galena-freibergite association with native bismuth is widely developed in the areas of Ugat, Koytash-Ugat, Shurkunda, and Dunyotepa. On the surface, it is manifested in the form of quartz-carbonate sulfide veins and streaks with submeridional strikes (10–20°) and steep dips. They are found both in the endocontact and in the exocontact of the intrusion.

Their strike length is greater than 1 km with a capacity reaching 3-5 m. Numerous veins and veinlets of this mineral association are found in the cores of more than 40 wells of the Koytash-Ugat Strip, where they are located in quartz veins and quartzification zones and form vein stockwork (Figures 3 and 4).

Fig. 3. Coarse polymetallic ore with a massively banded texture, with pyrrhotite ore relics and lenses of biotite hornfels from the Koytash-Ugat Strip.

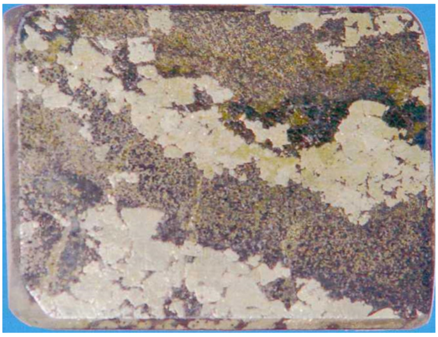

Fig. 4. Coarse polymetallic ore with banded texture in fine-grained pyrrhotite ore from the Koytash-Ugat group

The veins of the described mineral association are cut by dykes of diorite porphyrites, which in turn intersect skarns, massive pyrrhotite, and other ores. These dykes carry xenoliths from the lower layers of the Earth's crust and are considered to have originated from levels deeper than the Koytash intrusion and the associated skarn-rare metal mineralization [20]. Based on this, the latter mineral association is considered a new ore formation for the deposit and bears noble metal mineralization. Based on the mineral composition of associations, their formation temperature, and other features of these ores, we tend to consider skarn - rare metal and silver - polymetallic mineralization as evolutionary products of a single postmagmatic mineral formation process, and some increase in temperature and fluid concentration by the end of the process is most likely due to manifestation of "intrametallic " magmatism.

Two mineral associations are distinguished within this ore formation: 1) gold and silver-bearing quartz-carbonate-pyrite-arsenopyrite and 2) tin-bearing quartz-carbonate-silver-polymetallic ore with gold. They are similar in mineral composition, time, and formation conditions, which leads to their frequent joint association [21].

Matildite, freibergite, galeno-bismuthite, and unnamed minerals containing tin, bismuth, iron, sulfur, acanthite, hessite, and cassiterite are identified and described in silver-polymetallic ores of these sites, which include stannite, tillite, antimonite bournonite, and boulangerite.

In recent years, in these mineral associations, we have identified 15 more previously unknown minerals in the deposit, including 5 silver minerals; thus, the total amount of silver minerals found in polymetallic ores of the Koytash deposit has amounted to 12 varieties.

All these minerals are found in macro-paragneisses with galena, sphalerite, pyrite, and, less commonly arsenopyrite, chalcopyrite, and pyrrhotite. A wide variety of silver-bearing minerals characterizes the duration and intensity of the manifestation of this stage in the Koytash-Ugat Strip and makes by-product extraction of silver and gold from its ores promising.

Additionally, in the process of studying the main minerals, sulphide-rare-metal and sulphide-polymetallic ores from the Koytash and Lyangar deposits with mass spectrometry, atomic absorption, electron microprobe, and other modern methods, we discovered high contents of platinum, palladium, gold and, less often, rare earth elements in the sulfides.

Platinoids. In connection with the non-typicality of the platinum group elements for skarn deposits, as well as the lack of reliable methods for determining their low content in minerals, there is not much information in the literature about the content of platinoids in ores within the skarn-rare metal deposits of Uzbekistan. Platinoids are mainly present as impurities in the sulfide minerals from the Koytash deposit. Pyrrhotite and chalcopyrite are rich in platinum and palladium.

Considering the significant reserves of sulphide-rare metal ores from the Koytash deposit, which are mainly composed of pyrrhotite, the high prospects of this deposit for the associated extraction of components, including platinoids, should be noted.

In the process of studying sulphide-rare-metal and sulphide-polymetallic ores of the Lyangar deposit, we established high contents of platinum, palladium, and, less often, rare earth elements. The electron-microprobe method reveals that platinum and gold are contained in pyrrhotite pyrite-pyrrhotite ore, and over 4 analyses, the contents average 0.52 and 0.48 wt.%, respectively. In addition, the presence of the following elements (in wt.%) are established: Co-0.04, Ni-0.13, Se-0.06, Pd-0.13, and Ag-0.08. Pyrite from these ores has a high content of platinum and gold, as well as nickel, palladium, and silver.

Chalcopyrite, which forms abundant disseminations in apogranite, contains thorium. Notably, all samples of the Lyangar deposit contain palladium and have high silver contents. Samples from the Koytash deposit show lower contents of these elements (except gold).

The results of the study of sulphide-rare metal ores from the Koytash and Lyangar deposits by mass spectrometry give lower platinum contents. It is well known that this method is not very reliable for determining small impurity contents in ores; they usually give an underestimate.

Studying the mineral composition of sulfide-rare-metal and silver-polymetallic ores from the Koytash and Lyangar deposits using the electron-microprobe method reveals that most of the impure elements in the ores occur as their own minerals. At the same time, a significant part of these elements is in a dispersed state in sulfide minerals, including pyrrhotite, chalcopyrite, and pyrite. The microprobe analysis did not detect minerals containing platinum group elements in the Koytash and Lyangar ores. However, high platinum and palladium contents are found in pyrrhotite and chalcopyrite from the Koytash and Lyangar deposits.

Platinum is absent in pyrrhotites of the Lyangar deposit (in 46 analyses), and the palladium content reaches to 0.69 wt.%, but it is found only in 17% of the analyses. In the chalcopyrite of the Koytash deposit, the platinum content reaches up to 0.5 wt.% and the palladium content reaches to 0.21 wt.%; their frequencies of occurrence are 47% and 59%, respectively. Chalcopyrites of the Lyangar deposit in addition to the pyrrhotites of this deposit do not contain platinum, and palladium reaches to 0.26 wt.%.

Gold mineralization is widely manifested in the ores of the Koytash deposit. Prospects for gold mineralization fields have increased dramatically due to the discovery of large deposits of skarn-sulphide-rare-metal and gold-silver-polymetallic ores in the Koytash-Ugat Strip, in which the gold content in certain locations reaches mineable grades. Gold occurs as native gold, electrum, and gold tellurides. Additionally, electron microprobe analysis of sulphides indicated elevated concentrations of gold: in a total of 63 grains of pyrrhotite sulphide-rare-metal ores of the Koytash-Ugat Strip, gold is detected in 36 grains; in chalcopyrite (17 analyses), gold is detected in 7 samples; and in pyrite (5 analyses), gold is detected in three samples.

The primary amount of gold was released after the skarn-rare metal stage of ore formation, in association with pyrrhotite, arsenopyrite, and chalcopyrite in the quartz-sulfide stage, i.e., rare metal and gold mineralization are consistent.

In these and other ores, sites also have elevated, often mineable grades of bismuth, selenium, and tellurium contents, which may be objects associated with extraction (Table 2).

The compositional study of this mineralization showed the ubiquitous presence of gold, silver, bismuth, selenium, tellurium, etc. (Table 2). In the gold-silver-polymetallic and sulphide-rare-metal ores of the Koytash-Ugat Strip, the previously unknown minerals of silver, bismuth, tellurium, tin, and rare earth were found.

Table 2. Composition of silver and silver-bearing minerals in silver-polymetallic ores from the Koytash deposit.

Sample number	MINERAL	Au	Ag	Cu	Fe	Zn	Sb	Bi	Pb	Se	Te	S	Sum
К-34	Acanthite (8)*		86,32									12,95	99,53
К-35	Bi-Acanthite	0,46	80,74	1,98	0,75			2,97		0,72		12,77	100,38
К-36	Acanthite (8)		83,12	0,60	0,62	0,01	1,18	0,06	0,5	0,06		13,80	99,95
К-35	Cervelleite		70,14		0,06				3,08		20,89	5,51	99,68
К-34	Stutzite		51,26	0,09		0,01		8,26			39,24		98,87
К-34	Acanthite+galena		43,42	0,12	1,95	0,03		0,94	38,79	1,29		13,11	99,64
К-35	Acanthite+galena (5)		27,45	0,38	3,03		0,10	0,43	52,49	0,09	0,32	15,57	99,89
К-36	Acanthite+galena		22,89	0,37	2,14				58,19			16,15	99,72
К-35	Ag-bursaite (2)		8,91	0,18	0,05		0,05	31,86	40,87		0,68	16,63	99,22
К-35	Ag-galena (2)		10,86	0,57	2,73		0,09		70,91		0,12	14,37	99,74
К-39	Ag-galena (2)		10,95	0,21					70,96	0,56		17,29	99,97
К-40	Ag-galena (2)		5,66	0,03			0,30		78,80	0,12	0,74	14,16	99,81
К-34	Weibullite (3)		7,22	0,10	0,45		0,15	40,59	31,84	0,28		19,30	99,93

K-35	Cosalite (5)		2,74	0,42	0,15		1,07	41,92	36,57	0,09	0,05	17,32	99,73
K-35	Bursaite	0,46	2,09	0,29	0,12		1,06	36,33	42,53			16,36	100,07
K-40	Pilsenite		4,16	0,35	0,07	0,02		59,19	6,15		28,88	0,98	99,81

A wide variety of silver- and gold-bearing minerals and their associations characterize the duration and intensity of the gold-silver-polymetallic ore formation stage in the Koytash-Ugat Strip, which signifies the prospect area for precious metal mineralization.

Bismuth mineralization is found in all skarn-rare-metal deposits in western Uzbekistan, but it is most intense in the Koytash field.

A relatively high concentration of bismuth mineralization in comparison with other deposits of the same type has been noted at the Ugat skarn-scheelite deposit, which is actually one of the Koytash deposits. Additionally, in the Koytash-Ugat Strip, new ore deposits have been discovered in recent years that differ from the ores of other areas of the Koytash deposit due to the wide development of sulphides in rare-metal ores. According to their mineral composition, these ores are classified as skarn-sulphide-gold-rare-metal formations. The compositional study showed their enrichment with a number of associated useful components, including bismuth, which is represented by a number of mineral forms – native, telluride, sulphide bismuth – and in the form of unknown compounds consisting of a mixture of gold, silver, and bismuth. At the same time, 55% of the detected bismuth minerals are native bismuth and 30% are tellurium bismuth.

Bismuth minerals are widely developed in silver-polymetallic ores and are represented by Ag-bursaite, pilsenite, wittite, galeno-bismuthite, and cannizzarite. Bursaite, platinite, heyrovskite, and weibulite are less common and have been found for the first time in the Koytash field (Table 3).

The study of monomineralic sulfide fractions, according to the mass spectrometric analysis of skarn-rare metal ores, showed that it is more elevated in chalcopyrite and pyrrhotite.

In 11 samples studied in this research, 5 samples contained native bismuth and tellurium bismuth, 2 samples contained bismuth and one sample contained Ag bismuthite.

The following conclusions can be drawn from the bismuth mineralization of the Koytash deposit:

1. On the Koytash-Ugat Strip, bismuth mineralization was proposed by I. Kh. Khambrabaev. Associated extraction is noted in practically all types of tungsten ores. Its highest concentration is observed in massive pyrite-chalcopyrite-pyrrhotite ores with scheelite, especially in areas where polymetallic mineralization is superimposed.
2. Almost all bismuth found in ores, as well as at the Ugat site, is in the form of minerals containing primarily bismuth. Of the bismuth minerals, native bismuth is the most common, 70% of the discharge of which has a size of 0.03-0.008 mm, which must be taken into account when developing the technology for its extraction.

Selenium is found in all types of ores. Its amount in pyrrhotite-chalcopyrite massive sulphide ores is industrial-grade. High contents of selenium occur in pyrrhotite, chalcopyrite, molybdenite and pyrite. Note that in sulfide-rare metal ores, the maximum content of selenium is noted in pyrrhotite and in skarn-rare metal ores in molybdenite.

For tellurium, the maximum concentration of tellurium is observed in massive sulphide ores of pyrrhotite-chalcopyrite and pyrrhotite-galenic ores. In the apogranite types of tungsten ores with sulphides, the tellurium content varies abundantly, and in pyroxene skarns, the pyroxene-garnet composition varies with sulphides. In sulphide-rare-metal ores, the maximum content of tellurium is concentrated in pyrrhotite. High tellurium contents are noted in molybdenite and pyrite.

Published data and our long-term studies show that these mineral associations, often containing mineable concentrations of noble and other metals (gold, silver, bismuth, selenium, tellurium, etc.), are products of the acidic post-magmatic stage and are shown in large skarn-free enclosed deposits in western Uzbekistan [12].

Table 3. Bismuth minerals in sulphide-rare-metal and silver-polymetallic ores from the Koytash and Lyangar deposits according to the electron microprobe analysis.

Minerals	Sample numbers														
Koytash	1	2	3	4	5	7	8	9	32	39	35	36	40		
Lyangar	2919	2938	2975	2976	2380	2115	2477	2871	1976	2063	2065	100	2376	2377	4281
Native bismuth -Bi *	□	□	□	□	□	□	□ □	□	▲ □	▲ □	▲ □		▲	▲	▲
Bismuth telluride - Bi_2Te_3	□	□ □		□	□ □	□	□ □			□	□				
Bismuth sulfide -Bi_2S_3								□□							
Gold-bearing bismuth						□									
Unknown Mineral (Au, Ag, Bi)			□			□									
Ag-bismuth								□							
Bismuth -Bi_2O_3		□					□								
Ag-bursaite –$AgPb_5Bi_4S_{11}$											▲				
Pilsenite -BiTe												▲			
Wittite-$Bi_6Pb_5(Se,S)_{14}$									▲						
Galeno-bismuthite - $PbBi_2S_4$									▲						
Cannizzarite $Pb_2Bi_3S_{11}$									▲	▲					
Bursaite-$Pb_5Bi_4S_{11}$									▲						
Platinite-$Pb_4Bi_7Se_7S_4$										▲					
Heyrovskite (Pb,Bi,Se)												▲	▲		
Weibulite-$PbBi_2(S,Se)_4$												▲			

After its long exploitation, the discovery of a site with unconventional ore types in the Koytash deposit shows that in deposits with complex mineralization, the mineralization that is secondary at one deposit site may be a major component at another site; in addition, a metal that is associated with one zone (area) may become a main component in another zone [13]. This should be taken into account in assessing the potential of deposits with complex mineralization, in particular, in areas of tungsten deposits with complex mineralization. It is necessary to properly assess the possibility of the presence of zones (areas) with gold, silver, and bismuth mineralization.

4 Conclusions

The studied skarn-rare metal fields in western Uzbekistan are characterized by a variety and intense manifestation of mineral associations; this reflects the long, consistent, intensive, and full-bodied manifestation of the post-magmatic acid-base cycle and indicates multiple tectonic activations in the post-magmatic stage with inside manifestation of ore magmatism. Deposits differ little from each other in terms of the set of mineral associations and types of ores, and the differences are mainly related to differences in their formation environment.

Mass spectrometry studies show that the sulphide-rare metal ores of these deposits carry complex mineralization – they contain elevated concentrations of gold, copper, silver, platinum, palladium, selenium, tellurium, and other elements. Moreover, some of the elements are associated with pyrrhotite-pyrite-chalcopyrite, pyrrhotite-arsenopyrite-pyrite, pyrrhotite-pyrite, and other associations of the initial stage of the later alkaline stage; most of them, especially silver, bismuth, selenium, and tellurium, are in the sulphide-silver-polymetallic mineral association, which is in the final stages of the late alkaline stage.

Mineral associations bearing rare-metal (W-Mo) mineralization that formed in the early alkaline stage, in almost all samples, are completed with sulphide-rare-metal and silver-polymetallic mineralization often bearing industrial concentrations of noble and other metals.

Sulphide-rare metal ores of the Koytash deposit are characterized by a different set of typomorphic minerals; minerals containing silver, bismuth, tellurium, selenium, and gold are more widely distributed in ores in the deposit.

Sulphide-rare-metal and silver-polymetallic ores of the Koytash deposit differ in the complexity of typomorphic minerals. Sulphide-rare-metal ores contain accessory and gold-bearing minerals (gold-bearing bismuth, electrum, an unknown mineral (Au, Ag, Bi), ilmenite, uraninite, uranothorite, zircon, and apatite). Silver-polymetallic ores contain a wider, diversity of typomorphic rare minerals – silver, tellurium, and bismuth. Associated useful components of sulphide-rare-metal ores often form their own minerals, but a significant amount of them is in a dispersed state in sulphide minerals.

In the studied fields, the main carriers of associated useful components are sulphides (pyrrhotite, chalcopyrite, and pyrite), and their number at their locations of formation is much higher. Therefore, we can conclude that the prospects of the Koytash deposit for gold, silver, bismuth, and other associated elements, with the current state of their exploration, are much higher.

The studied deposits should be attributed to the skarn-gold-tungsten type, and the gold mining industry of the Republic of South Africa is invited to show interest in these deposits as a new, unconventional gold ore resource; worldwide, there are many examples of large tungsten deposits, where there is associated mining of precious and other metals from similar ores.

It is quite obvious that the complex mining of tungsten, gold, silver, bismuth, and other associated components from ores of the skarn-gold-rare-metal Koytash deposit will increase their economic value and will allow them to be involved in profitable industrial development.

Despite a rather detailed study of the mineral composition of ores, it is not enough for a final assessment of the potential of Koytash deposit mineralization; it is necessary to conduct detailed geological exploration, which will open new areas of the complex ore field, promising tungsten, gold, silver, bismuth and other elements.

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