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Research Article

ANALYSIS OF THE MINERAL-GEOCHEMICAL FEATURES OF NONSKARN TUNGSTEN MINERALIZATION AT THE SARYKUL DEPOSITS (KARATYUBINSKY ORE FIELD)

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ABSTRACT
The article considers the main geochemical features of apometaterrigenous tungsten mineralization confined to a fragment of a trog structure made by rocks of the olistostromic complex. The mineralization was formed from rocks of coarse flysch transformed in the contact zone of a granitoid intrusive geochemically specialized for tungsten into shale rocks, which formed ore-bearing metasomatites. The ore process has a carbon dioxide specificity and is characterized by a significant addition of phosphorus. The geochemical field is formed by elements of a typomorphic complex (W – Bi – Cd – Te – Be – Au – Zn – Cu – Sn).

Keywords: *Apometaterrigene, Tungsten Mineralization, Trog Structure, Oleostromic Complex, Ore-Bearing Metasomatites, Typomorphic Geochemical Complex, Scheelite, Iron Disulfides, Skarnoids, Ganitoids*

The Karatyubinsky ore field is located in the western part of the Karatyubinsky Mountains and is confined to a fragment of the central Gissar trough. The ore field unites two objects with different ore-formation nature (the Karatyube deposit of the skarn–sheelite formation and the Sarykul deposit with a new apometaterrigenous tungsten mineralization for the region) (Fig.1).
Apometaterrigenous tungsten mineralization at the Sarykul deposit was revealed largely by chance during prospecting for gold on the area. The objects of gold prospecting were the zones of calcification in the metaterrigenous rocks of the matrix of the olistostromic stratum, which subsequently turned out to be tungsten-bearing (Juraev *et al.*, 2017)
Apometaterrigenous tungsten mineralization is developed in an area that, with its southern part, covers the endocontact zone of the Sarykul intrusive, which is an oval-shaped body elongated in the latitudinal direction. Its area is about 15 km2. The plane of the northern contact of the intrusive falls steeply (65-80 °) to the south, and the southern one – in the same direction, but more gently – up to 40 °. This array belongs to hypabyssal intrusions. The intrusive was formed in difficult tectonic conditions, breaking through the nuclear part of the anticline, composed of rocks of the olistostromic strata.
The peculiarity of the geological structure of the area lies in the fact that the mineralization zones are confined to a fragment of the trog structure made by rocks of the olistostromic complex (Burtman VS (2006) Leonov M (1984)).
The skarn ore bodies at the Karatube deposit are traced by a curving strip of the north-westerly direction in the southwestern exocontact zone of the Sarykul intrusive, developed along the carbonate olistolites of the olistostromic complex and confined mainly to their interplastic and interformational stratifications (Dautov A (1974)). The morphology of skarn-ore bodies is diverse, but interplastic bodies of a plast-like and lenticular shape significantly predominate. By composition, the most common are garnet, garnet-vesuvianite, vesuvianite and garnet-pyroxene associations of skarns. The most rich in Vesuvianite tungsten

are garnet skarns. Scheelite in skarn ore bodies occurs in the form of uneven inclusions ranging in size from fractions of a millimeter to the first centimeters.

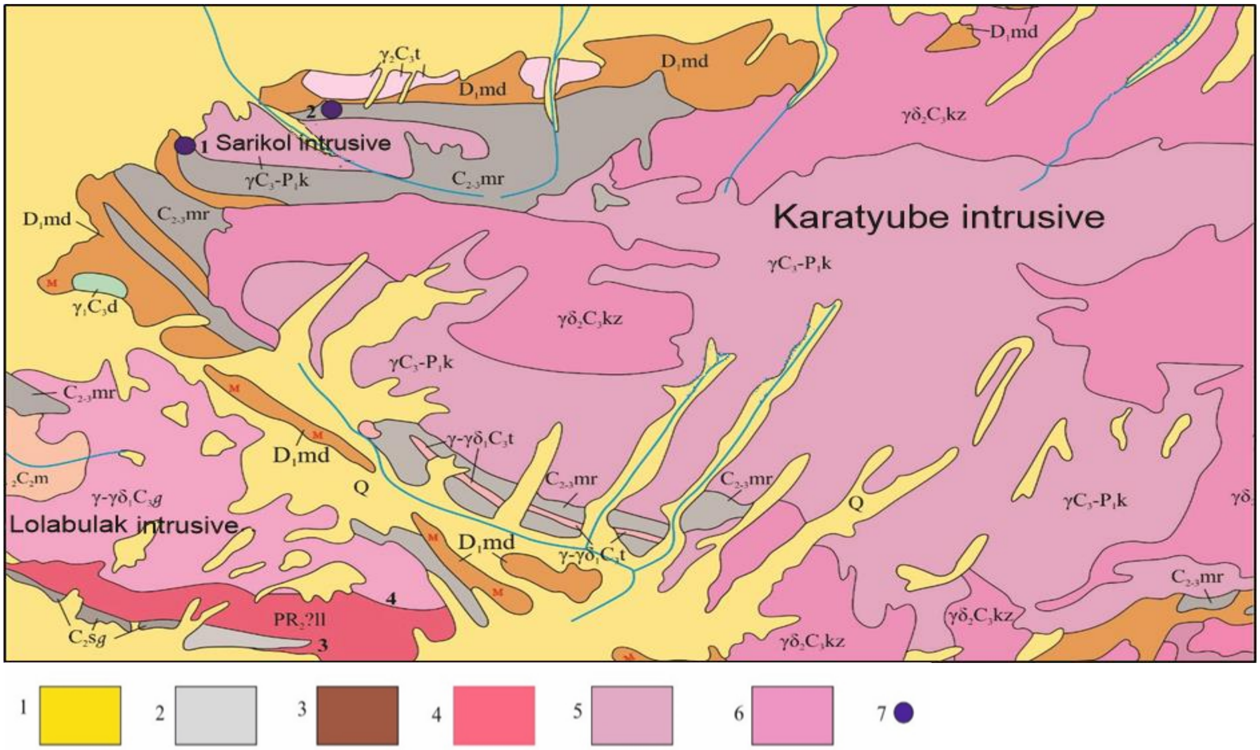


Fig. 1. The scheme of the geological structure of the Karatyubinsk mountains (based on the materials of B. Gapparov).
1 – Quaternary deposits, undifferentiated Q; 2 – C2-3 Olistostromic complex: shales, hornstones, sandstones, siltstones, mudstones with olistolites and olistolites of various age carbonate and siliceous rocks; 3 – Limestones and dolomites D1; 4 – Crystalline shales, gneiss, migmatites, amphibolites PR2; 5 – Muscovite and muscovite granitesbiotite C3-P1; 6 – Granodiorites of hornblende-biotite, porphyritic C3; 7 – Deposits of tungsten: 1) Karatube; 2) Sarykul.

The ore bodies of the Sarykul deposit are localized in the northern exocontact zone of the Sarykul intrusive (Fig.1), composed of rocks of diorite, granodiorite, granite and Alaskan formations.
The genetic relationship of the Sarykul deposit with biotite and leucocrate granites is indicated by the same composition of impurity elements; high tungsten contents in biotite granites (up to 100 g/t) and leucocrate granites (up to 250 g/t), as well as the presence of accessory scheelite in tungsten-based granitoids (Otroshchenko VD, Krikunova LM (1974) Khamrabaev I. (2000)).
The structural position of the ore field is characterized by its proximity to the northern exocontact of the Sarykul intrusive biotite and leucocratic granites (C3 – P1) and is stretched along it in the form of a strip of intensively metamorphosed rocks up to 500-800 m wide and up to 2.5 km long.
Discontinuous tectonics plays a crucial role in the formation of the deposit structure (Jumagulov A, Juraev M, Rakhmatov U, Gaibnazarov S, Khoshzhanova K (2024)). The main ore-controlling structure is a longitudinal tectonically weakened zone, represented by numerous linearly elongated weakly branched ruptures consistent with the direction of the main folding and the strike of the rocks of the area (Ushakov VN (1991)). The internal structure of the structures of this plan is characterized by varying degrees of fragmentation, sometimes accompanied by quartz vein-veining, more often fixed by subparallel dissociation of the host rocks. The total drop is steep to the north-northwest (65-85^0), the total power reaches

the first hundreds of meters. The power of the components of the rupture zone is from the first meters to the first tens of meters.

Transverse discontinuous faults of the SV and VSV directions largely complement the structural plan, forming the frame-block structure of the Sarykul deposit. The most common is a group of violations of the VSV direction. The fall of faults in the CVD direction at angles of 50-70 °. The internal structure of the zones is characterized by linear fracturing, less often by oriented crushing (Burtman VS (2006)). These violations are the most recent and, in relation to others, are of a secant nature.

According to the time of formation, the tectonic disturbances of the northeastern strike are clearly post-intrusive, as clearly evidenced by the displacement of the contacts of the Sarykul intrusive along them.

The chemical composition of granitoids of the Sarykul intrusive and petrochemical coefficients are given in Table 1.

Table 1: Chemical composition and petrochemical coefficients of granitoids

Component	1	2	3	Cp.	Coefficients (К)	Meaning К
SiO_2	71.50	71.86	71.54	71.63	al^1	14.0
TiO_2	0.30	0.08	0.15	0.18	f	1.32
Al_2O_3	14.28	16.43	15.60	15.44	Кф	96.3
Fe_2O_3	0.41	0.01	0.27	0.23	$Na_2O + K_2O$	8.62
FeO	2.15	1.39	0.43	1.32	Na_2O / K_2O	1.23
MnO	0.05	0.01	0.06	0.04	K_2O / TiO_2	21.5
MgO	0.70	0.60	0.40	0.06	Кa	0.55
CaO	1.19	1.54	1.96	1.56	Fe_2O_3 / FeO	0.17
Na_2O	3.70	4.71	5.83	4.75		
K_2O	4.52	4.08	3.02	3.87		

Petrochemical coefficients: - al^1 – alumina content - Al_2O_3/ (Fe_2O_3 + FeO + MgO); - f – femicity - Fe_2O_3 + FeO + MnO + MgO + TiO2; - Cf – ferruginousness – (Fe_2O_3 + FeO) / (Fe_2O_3 + FeO + MgO) x 100; - Na_2O + K_2O – alkalinity range; - Na_2O / K_2O – type of alkalinity. series; - Fe_2O_3/ FeO – degree oxidation of iron; - Ka - agpaicity - Na_2O + K_2O/ Al_2O_3.

The granitoids of the Sarykul intrusive belong to the moderately alkaline series. the potassium - sodium series. mainly high alumina. with a very low degree of femicity. medium and high degree of ferruginousness (Divaev FK. Yudalevich ZA (1984). The rocks of the complex are characterized by a very low degree of iron oxidation.

Geochemical profile: lithium. tin. tungsten. bismuth. beryllium. The content of rubidium is 248 g/t. strontium is 136 g/t. The type of accessory mineralization is scheelite-apatite-sphene.

The accessory minerals occupying about 1% of the rock contain sphene (0.1-0.5%). apatite (0.1-0.3%). ilmenite (0.03-0.05%). orthite and rutile (0.04-0.05%). magnetite (0.05-0.1%).

The characteristics of the initial rocks (dometamorphic substrate) at the Sarykul deposit are their characteristics associated with the conditions of formation of coarse fleece. This facies of the olistostromic complex are formed in an environment of intensively manifested landslide processes in the sedimentation basin. leading to intensive mixing of non-lithified sediment and the formation of rocks with a combination of pelitic. siltstone and psammite particles and an uneven distribution of carbonate matter (Kukhtikov and Cherenkov, 1984).

Formed under geodynamically stressed conditions. they are characterized by high granulometric dispersion. which provides significant initial porosity of the ore-containing medium (Jumagulov *et al.*, 2024)).

Recrystallization of a primary heterogeneous sedimentary rock under conditions of regional. contact and dynamometamorphism leads to the formation of shale rocks. the basis of which are quartz- feldspar micas (biotite. muscovite. sericite. chlorite) and amphibole.

Distribution of the main petrogenic elements in the rocks of the conditional background sample (unchanged metamorphic shales. average for 61 samples. g/t): Na – 18379 (1.9); Mg – 21822 (1.45); Al – 64917 (0.75);

P – 935.8 (1.34); K – 20281 (0.75); Ca – 21675 (1.08); Fe – 44822 (0.93). Clarke concentrations of petrogenic elements are indicated in parentheses.

The doric substrate is characterized by increased concentrations (relative to Clark) of Na. Mg. P. Ca and reduced values of Al. K and Fe.

The distribution of the main ore elements in the rocks of the conditionally background sample: W – 1.99; Au - 0.047; Pb - 20.56; Bi - 0.77; Mo - 8.74; Ag - 0.43; Sn - 12.44; Sb - 1.68; As - 19.6; Cu - 54.12; Zn - 122.4; Li - 109.6; Be - 5.05 ; Se - 5.63; Te - 0.15; Ba – 807; Zr - 94.3; Nb - 10.22; Cd - 0.33; V - 164.6; Cr - 75.58; Mn – 716; Co - 17.22; Ni - 47.78; U - 5.63; B - 36.7; Ti – 3854.

Thus. the chemical elements in metamorphic shales behind the contour of ore bodies are quite clearly divided into 3 groups: with subclark values – W. Pb. Sb. Nb. Cd. Mn. Co. Ti; As. Ba. V. Zn. Cu; with lower–clark values - Zr. Cr. Ni. B and superclark values (in parentheses. Clark concentration values) - Te (150). Bi (77). Au (47). Se (11.3) – Ag (6.1). Mo (3.4) – Sn. Li. Be (2.1 – 1.7).

The multicomponent composition of metamorphic rocks inherited from the heterogeneous matrix of the olistostromic stratum and structures emphasizing its heterogeneity are conditions for the formation of fractured porous rocks when stress deformations are applied to them. which ultimately determines favorable opportunities for the course of metasomatic processes in the ore-bearing zone of the Sarykul deposit.

Postmagmatic processes of hydrothermal action on the formed metamorphic shales in the tectonically weakened zone of the northwestern strike led to the rearrangement of mineral components and the appearance of new mineral associations forming various rocks of the skarnoids series – biotite-feldspar-quartz metasomatites – sericite-chlorite-quartz-feldspar metasomatites (Divaev and Yudalevich, 1984).

These products of metasomatosis probably form a single row with indistinct boundaries between them and a large group of through minerals (quartz – plagioclase – sericite – calcite and possibly amphibole). The appearance of various formations in this series may be related to the ratio of carbonate. pelitic and psammite components in the pre-metamorphic substrate and the inheritance of the process from early metamorphic stages to late metasomatosis.

Skarnoids with significant variations in mineral composition from differences where the quartz-plagioclase-sericite mineral association is the leading one to feldspar-carbonate-amphibole rocks. Pyroxene (hedenbergite) is present everywhere in various quantities. which occurs in the form of nests and aggregative clusters together with quartz. chlorite. amphibole and pyrite.

The mineral composition includes approximately 40 minerals (Table 2). The main minerals of the host rocks. metasomatites of vein formations are quartz. feldspar (plagioclase-Na predominates). sericite. biotite. carbonate (calcite. Fe-carbonate). pyroxene (Fe-Ca series). amphibole (Ca-Mg-Fe series).

The generalized mineral composition of scarnoids with a significant proportion of dark-colored minerals (%): pyroxene + amphibole 25-28. quartz 22-24. plagioclase 10-20. sericite 3-22. calcite 1-5. The chemical composition of skarnoids also reflects their unstable mineral composition (%): SiO2 – 49-65. Aℓ2o3 -11-14. CaO - 3-10. MgO – 3-5.5.

Biotite-feldspar-quartz metasomatites have an obscurely manifested banding. along which the release of carbonaceous matter is characteristic. Biotite (the main mineral of this group of metasomatites) forms large-leaved clusters along the shale. associated with plagioclase. quartz and carbonaceous matter. According to biotite. chlorite often develops. preserving its relics.

The above type of metasomatites is characterized by a relatively stable composition (%): biotite 18-44; quartz 13-40%. plagioclase 21-29 (in a single case 5.5). chlorite 3-7. clay minerals 6-10; calcite 0.5-3 and sericite 0-8 are slightly developed. The chemical composition indicates the relative stability of the mineral composition (%): SiO2 – 64-69%. Aℓ2o3 -11-14; CaO – 2-3. MgO – 2.6-4.

Sericite-chlorite-quartz-feldspar metasomatites are massive. often cataclysmic. Their structure is heterogeneous – from fine to medium-grained. mainly lepidogranoblastic.

The mineral composition is significantly variable (%): chlorite – 13-29. sericite 3-21. plagioclase 8-20. quartz 4-20; calcite 2.5-15. clay minerals 1.5-20.

Table 2: Mineral composition of metasomatites. skarnoids and root formations

Prevalence	Non - metallic	Metallic	Hypergenic
Main (prevalence)	Pyroxene Garnet (grossular) Amphiboles Ca-plagioclase Orthoclase Carbonate (calcium) Chlorite Sericite Biotite Quartz	Scheelite Pyrite Marcasite Melnikovite Pyrrhotite Chalcopyrite Bismuth Bismuthin	Clay Covellin Chalcosine Goethe Limonite
Frequently encountered	Rutile Sphen Zircon	Cassiterite Apatite Sphalerite Galena Bi. Pb – sulfosols with silver	Gypsum Leucoxene
Rare accessory	Monazite Barite	Arsenopyrite Sulfotellurides Magnetite	Native copper

The main mineral of the isolated metasomatites. chlorite associates with sericite. quartz. plagioclase and replaces pyroxene. garnet. amphibole and feldspar. The chemical composition is relatively stable (%): SiO2 – 30-42. Aℓ2o3 -12-14; CaO – 10-13. MgO – 2.2-5.

A special group of tungsten-containing rocks at the Sarykul deposit is formed by metasomatically altered limestones. which. with a relatively low degree of marbling. contain carbonaceous graphite substance and aluminosilicate admixture scattered in the rock mass. The non-carbonate admixture of limestones undergoes intense metasomatic changes (before the formation of albite-quartz segregation) and is the main medium for the deposition of scheelite in them. With a decrease in the albite component. newly formed areas in limestones have a quartz-carbonate composition. with different ratios of quartz and metasomatic calcite (before the formation of almost monomineral nests). The intensity of metasomatic transformation of limestones leads to a significant decrease in their composition of carbonates (the content of CaO can decrease to 15%). the appearance of MgO in an amount of up to 1.2% and an increase in the volume of quartz rock (up to 12%).

Distribution of the main petrogenic elements in aluminosilicate metasomatites (49 samples): Na – 13039 (0.7); Mg – 16559 (0.76); P – 3482 (3.7); Ca – 74689 (3.4); Al – 58409 (0.9); K – 11393 (0.56); Fe – 54373 (1.2). Accumulation coefficients are indicated in parentheses.

The ore process has a carbon dioxide specificity (more than three times the addition of calcium). accompanied by a significant accumulation of phosphorus and a slight addition of iron (Borodin LS. Lashin AV. Pyatenko IK (1976)). At the pre-ore stage of metasomatite formation. the removal of sodium. magnesium and aluminum from the near-ore space is observed.

Distribution of the main ore elements in metasomatites (49 samples): W – 3921.7; Au - 0.14; Pb – 12.4; Bi - 92.8; Mo -9.0; Ag - 1.1; Sn - 57.1; Sb -1.2; As - 18.6; Cu - 298.2; Zn -761.6; Li - 65.6; Be - 54.1; Se - 5.9; Te - 1.85; Ba – 563.4; Zr - 55.9; Nb – 13.0; Cd - 12.5; V - 180.3; Cr - 56.9; Mn – 2145.4; Co - 12.3; Ni - 47.7; U – 6.0; B - 32.0; Ti – 2514.1.

Metasomatites are characterized by: significant input into the near–ore space (accumulation coefficients in parentheses) W (1970.7); Bi (120.5) and Cd (37.8); noticeable input - Te (12.3); Be (10.7); Zn (6.2); Cu

(5.5); Sn (4.6); moderate input - Au (3.0); Mn (3.0); Ag (2.5); removal from the near–ore space - Pb. Li. Zr (0.6); Ti (0.65); Sb. Ba. Co (0.7); Cr (0.75) and neutral behavior of Mo. As. Se. Nb. V. Ni. In.
A feature of the ore mineralization of the Sarykul deposit is the abundance of iron sulfides in mineralized zones. which. as a result of intra-ore processes. form a chain from the initial pyrrhotite to the final pyrite. with intermediate products in the form of melnikovite and marcasite.
Pyrite is the most widespread mineral in mineralized zones. forming massive clusters. veins. and scattered inclusions in the peripheral parts of mineralized zones (pyrite content is 10-15% in areas of pyrite mineralization accumulation). According to the results of chemical analysis of pyrite concentrate. pyrite is enriched with W (8%). Zn (0.5%). Sn (0.1%). Bi (500 g/t). Cu (300 g/t). Mo (100 g/t). Ag (5.1 g/t) and Au (1.4 g/t). The impurities of ore elements are explained by the imposition of later mineral associations on pyrite (magnetite. chalcopyrite. sphalerite. scheelite. cassiterite). The metamorphogenic nature of pyrite is confirmed by the frequent contents of pyrrhotite relics transformed in hypogenic conditions.
Pyrrhotite is closely associated with chalcopyrite. sphalerite. Bi minerals. and is enriched with tungsten (up to 1.3%).
A group of minerals found in ores in small quantities: chalcopyrite (forms small xenomorphic clusters in a non-metallic mass. or in accretions with pyrrhotite. sphalerite. pyrite. scheelite and bismuth). cassiterite (associates with chalcopyrite. sphalerite. scheelite. pyrite and quartz). silver-containing sulfosols of Bi-Pb composition (contain as impurities of Cu. Se. Te) (Raskin VE. Juraev MN (2017)).
A group of minerals found in ores in the form of microinclusions: sphalerite (found among cassiterite; also noted in fusion with bismuthin. chalcopyrite and pyrite). bismuthin (found as an ultrathin impregnation in pyrite. chalcopyrite. sphalerite. scheelite and garnet). native bismuth (found among scheelite and pyrite). galena.
Scheelite is the main and only tungsten-containing mineral that determines the practical significance of ores. In the form of uneven inclusions. it is present in the I natural type of ores (Fig.2.) – metasomatites of sericite-chlorite-feldspar-quartz-carbonate composition with iron disulfides. Grain size from < 0.0 n to 1-2 mm. Microscopic studies have shown that scheelite is confined to iron disulfides (Fig.2). feldspar-sericite-chlorite aggregate (Fig.3.). amphibole. sulfides. Often. scheelite grains contain inclusions of feldspar. chlorite. and iron hydroxides. Luminescent glow in blue tones (fig.4.).

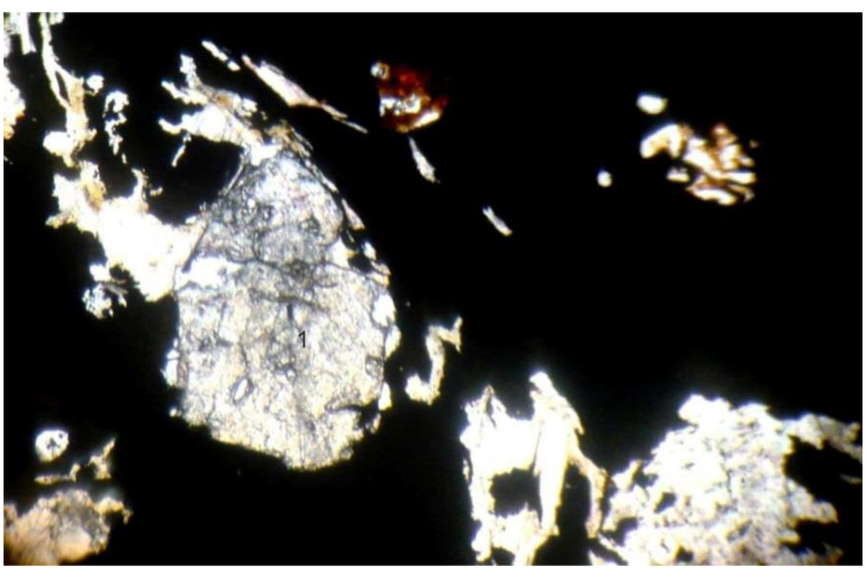


Fig. 2. Scheelite in iron disulfides:
1 – Scheelite; black-pyrite mixed with marcasite. melnikovite.

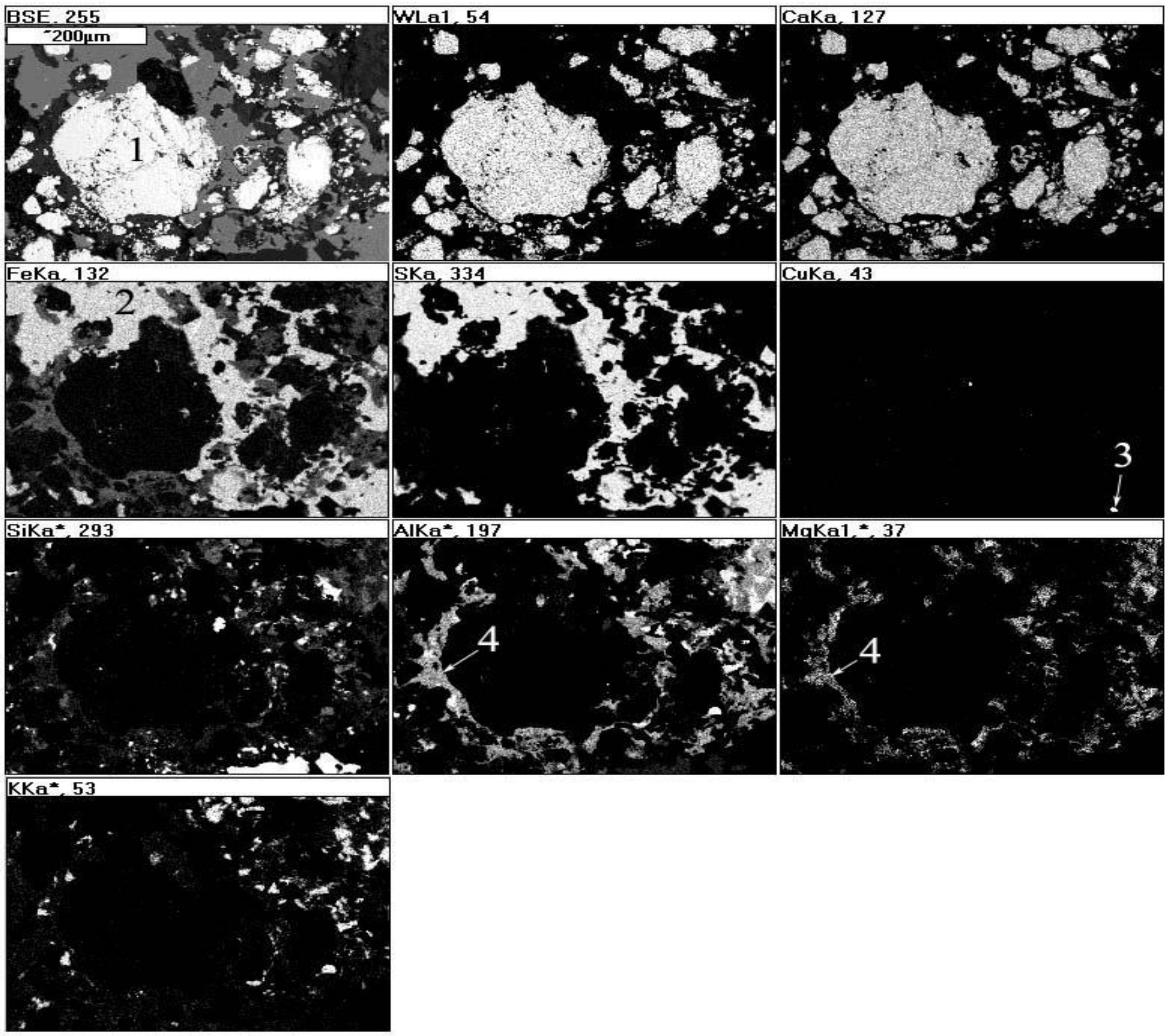
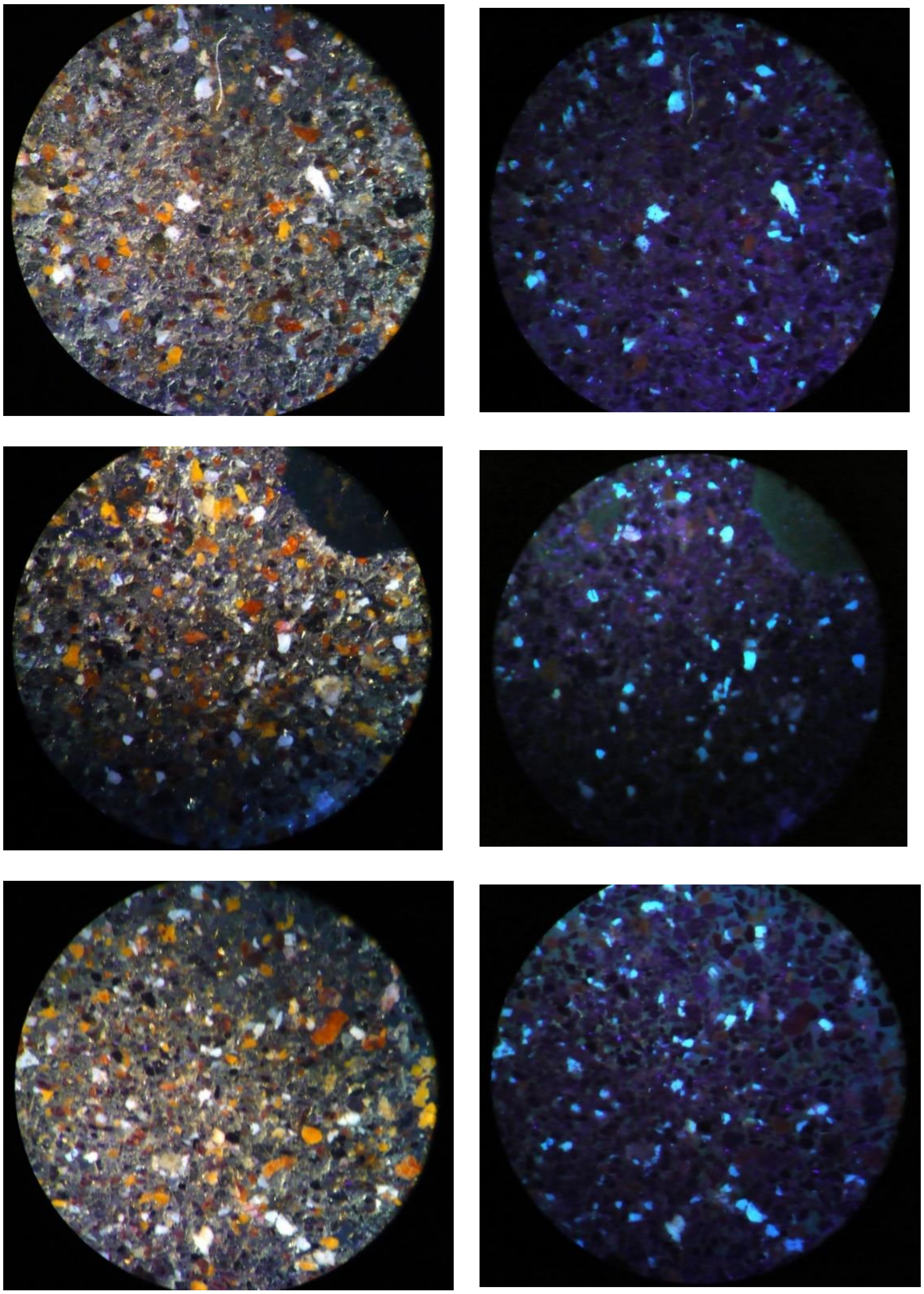


Fig. 3. Inclusions of scheelite in a pyrite-marcasite aggregate from sericite-chlorite-feldspar-quartz metasomatite. Raster images:
1 – scheelite; 2 – pyrite. marcasite; 3 – chalcopyrite; 4 – chlorite.

Tungsten is characterized by a significant dispersion of contents (from 0.001 to 17%). with an increase in concentrations from metapsammite quartzite differences (0.001-0.01%). quartz-feldspar breccias (0.005-0.2%) and vein quartz (0.005-0.2%) to ore-bearing metasomatites (in metasomatically altered limestones 0.02-0.85%. in in skarnoids 0.015-2.2%. in biotite-feldspar-quartz metasomatites 0.001-2.5%).
According to the results of geochemical studies for the apometaterrigenous tungsten mineralization of the Sarykul deposit. a generalized series of relative intensity has been established. which has the form W – Bi – Cd – Te – Be – Au – Zn – Cu – Sn – Ag – Mn – Mo – U – Se – V – Nb – Ni. Attention is drawn to the high position in the Cd and Te series. as well as the low position in Se and V.
The analysis of correlations between the elements revealed the following patterns:
- W forms significant but weakly expressed correlations with Pb. Ag. Au. Be and Mn. which is probably determined by the autonomy of the formation of scheelite mineralization. followed by the combination of products of different stages in mineralized zones;



А **Б**

Fig. 4. Scheelite from concentrate:
A) Scheelite (white) in concentrate; **B)** Scheelite under a luminoscope.

- the highly significant direct correlation of Au with Bi and Te defines the classical triad for gold accompanying the tungsten mineralization of the region of various ore-formation types;
- the absence of clear connections of As with typomorphic elements of apometaterrigenous tungsten mineralization. with its subclark contents in ore-bearing metasomatites. indicates the arsenic-free specificity of ore-bearing solutions;
- stable bonds of Ag. Bi. Cu. Se and Te on the one hand and Pb with Sb. on the other. indicate a wide involvement in the ore process of sulfosolic mineralization. its diversity and enrichment with rare elements;
- the stable association of Li – Cr – Ni – Co – Ti currently has no confirmation at the mineral level and requires additional research to decipher it.

CONCLUSION

The previously planned predictive prospecting complex of a new apometaterrigenous tungsten mineralization for the region may include the following main elements:
- the proximity of mineralized zones to the near exocontact zone of a geochemically specialized tungsten granitoid intrusive;
- the presence of a powerful and extended longitudinal ore-localizing tectonically weakened zone. complicating the structure of the trog structure;
- widespread in the area of deeply transformed by metamorphic processes sediments of the matrix of the sand-mudstone complex of the olistostromic stratum. characterized by high granulometric dispersion. providing significant initial porosity of the ore-containing medium and being a substrate for the formation of ore-bearing metasomatites;
- a complexly constructed geochemical field defined by a typomorphic complex of elements (W – Bi – Cd – Te – Be – Au – Zn – Cu - Sn);
- features of ore mineralization. expressed by significant volumes in mineralized zones of iron sulfides (pyrrhotite. melnikovite. marcasite. pyrite); widespread groups of minerals found in ores in small quantities (chalcopyrite. cassiterite. sulfosols) and minerals forming microinclusions (sphalerite. bismuthin. native bismuth. galena).
- studies of special forms of internal structures of spatial correlation group matrices of element distribution. as well as spatial separation of halos of individual oreogenic elements. may indicate two groups of geochemical associations (W-Cu-V-Mo and Mo-V-Cu-Cr-Ni). and the presence of reliable correlations in W-Cu pairs. Mo-Cu. W-Mo on the possibility of their telescoping.

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