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**THE STATE AND COMPOUND OF THE PLATINOIDS AND
RARE EARTH METALS WITHIN THE PICRITES SULFIDES
OF THE KARA-TURGAI ASSEMBLAGE OF THE NORTHERN ULYTAU**

Abstract. Violarite, siegenite, platinum telluride (moncheite), silver telluride, lead telluride (altaite), lead selenide, solid solutions of iridium group metals (Ir, Os, Ru), rare earth metals (Dy, Er, Y, Ce) have been discovered for the first time in picrites of the Kara-Turgai assemblage alongside previously known sulfides of copper, nickel and cobalt (copper pyrite, pentlandite, cobaltite, nickeline, gersdorffite). The sulfides constitute three mineral formations. The first two mineral formations form segregation "droplets", having a round and elongate elliptical shape, while the third one is represented by exudations of irregular acute-angled shapes. The platinoids in sulfides are established to exist only in the segregation droplets of the first formation, which accumulated of pyrrhotite, copper pyrite, pentlandite, violarite, and sphalerite. The sulfides of the second formation do not contain platinoids and are represented by pyrrhotite, copper pyrite, and sphalerite. The sulfides of the third formation are represented by pyrrhotite, copper pyrite, sphalerite, and pyrite. The whole of three mineral formations contain magnetite and are commonly confined to the most graded picrites horizons and apopicrotic olivinites. Single sulfides inclusions were detected within the picritic diabases, represented by pentlandite, siegenite, millerite, pyrite, and galenite. Cu-Ni - ore formation (platinum group minerals [PGM]) – (rare earth elements [REE]) of Kara-Turgai ores was presumed to occur in an open magmatic system, which was favorable for accumulation of commercial bulk of sulfide.

Key words: Ulytau, copper-nickel ores, platinoids, rare earth metals.

Introduction. A diabase-picritic Kara-Turgai assemblage that is dimensionally and genetically linked with the copper and nickel sulfides [1] is long ago well-known in the west of Central Kazakhstan, in the Kara-Turgai River basin (Figure 1). The platinum group metals (PGM) [2, 3] availability in the sulfides arose the keeping interest for their study [3-13].

The copper, nickel and iron sulfide clusters are in the picrites and apopicrotic serpentinites, which constitute the inclusions of three mineral formations. The first two formations constitute a segregation "droplets", of a rounded and ellipsoid-elongated shape, the third formation is irregular acute-angled shapes.

O.B. Bejseyev and his joint authors [6] have studied the mineral compound of mineralization in detail and distinguished pyrrhotite, pentlandite, copper pyrite, magnetite, nickeline, cobaltite, sperrylite, titanomagnetite, titano-ferrite and chromite in descending order. K.Sh. Dyusembayeva [8] has enlarged this ore formation with gersdorffite, covellite, bravoite, arsenic pyrite.

Currently, the platinum group metals are well-known in the sulfides of the Kara-Turgai and Akzhal occurrences, which are concentrated in the intrusive sheet compound underlying among the Proterozoic formations (figure 1). Pursuant to O.B. Bejseyev's data [6] the sulfide copper-nickel-cobalt ores of the Kara-Turgai occurrence contain Pt-5 g/t, Pd-16 g/t, whereas S.S. Chudin [7] states of the total platinoids content reaches only 10 g/t in the copper-nickel concentrate of these ores.

An extremely low Pt + Pd concentrations (up to 0.2-0.4 g/t), as to S.S. Chudin's data [7], are pointed out in apopicrotic serpentinites of the Akzhal massif. The state and compound of the platinoids in sulfides were not previously established.

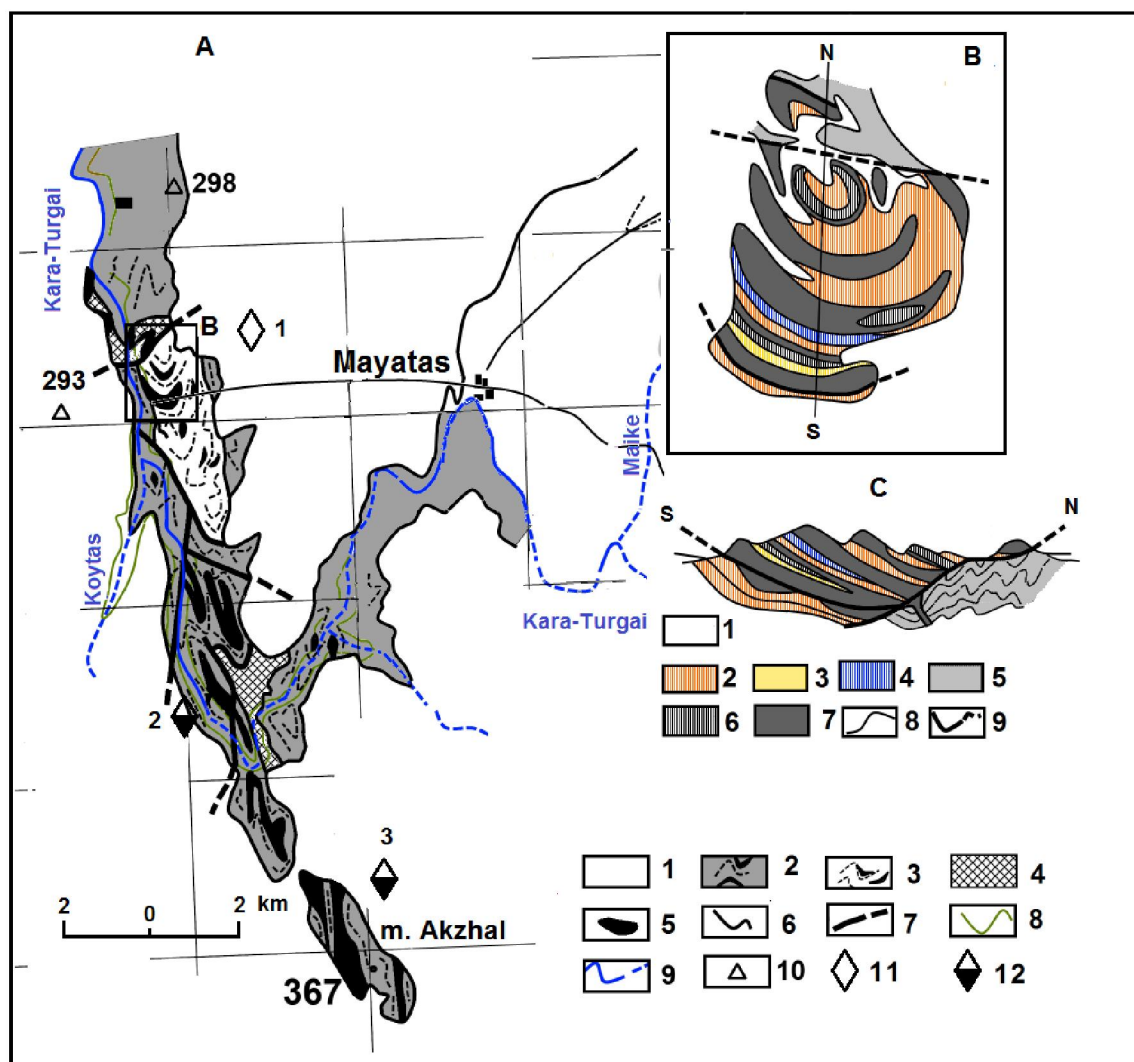


Figure 1 –

A. A geological sketch map of the middle stream area of Kara-Turgai River by I.I. Vishnevskaya and I.F. Trusova [4], S.S. Chudin [7], amended and supplemented by the authors: 1 – Cainozoic sediments; 2-3 – Karsakpai group (Mesozoic-Proterozoic): 2 – metabasalts stratum, less commonly andesites with the tributary levels of muscovite-quartzite and quartzite shales, 3 – variegated tuffs strata of quartz albitophyres and ash banded tuffs of the average compound, 4 – muscovite-albite and graphite shales, albite gneisses and micro-gneisses of the Aralbai group (PR_{1ar}); 5 – the Kara-Turgai diabase-picritic assemblage (PR_{3k}); 6 – geological boundaries; 7 – tectonic faultings; 8 – topographical contour lines; 9 – the Kara-Turgai River and its Koytas and Maikhe inflows; 10 – trigonometric heights. 11, 12 – genetic types of minerals; 11 – magmatic group (segregation type), sulfide copper-nickel ores with platinoids and rare-earth elements (Dy, Er, Y, Ce) in the picrites, 12 – carbonatite group (fluid-magmatic type), carbonatites of quartz-carbonate-albite compound with copper sulfides and platinoids. The ore manifestations: 1 – Kara-Turgai, 2 – North Akzhal, 3 – Eastern Akzhal.

A geological sketch map of the Kara-Turgai massif (B) and the SN section (C) through the central part of the massif. The source of data is by N.P. Mikhailov, Yu.L. Semenov [1], I.I. Vishnevskaya and I.F. Trusova [4], O.B. Bejseyev [6] amended and supplemented by the authors: 1 – Cainozoic sediments; 2-4 – Karsakpai group (PR_{2kr}): 2 – tuffs of quartz albitophyres, 3 – banded tuffs of average compound; 4 – tuffs of main compound; 5 – graphite-albite shales of the Aralbai group (PR_{1ar}); 6-7 – Kara-Turgai diabasepicritic assemblage: 6 – quartz diabases, diabases, 7 – picritic diabases, picrites, apopicritic serpentinites, primary spherical, porphyreous; 8 – geological boundaries; 9 – faultings and thrusts.

Research Methods. Platinoids microinclusions within the copper and nickel sulfides from the picrites of the Kara-Turgai assemblage were studied in the mineralogy department of the IGS LLP named after K.I. Satpayev (Almaty) by means of the energy dispersive spectrometer by INCA ENERGY, OXFORD INSTRUMENTS, England, installed on an electron probe micro-analyzer Superprobe 733 by JEOL, Japan (accelerating voltage is 25 kV, probe current is 25 nA, probe diameter is 1-2 μm). When analyzing minerals as a comparison samples used the following: pure metals for the PGM; the artificial

compounds (A) PO_4 for REE; CuFeS_2 for Fe, Cu, S; PbS for Pb, ZnS for Zn, the pure metals for the rest of metals. The analysis results rate was 100%. All the photos were taken in the back-scattered electron mode, the image contrast of which depends on the effective atomic number of the $\bar{Z}$ phase. The bigger $\bar{Z}$ is, i.e. the more heavy elements are in the phase being studied, and the lighter it is on the image.

Research Results. The sulfides of three mineral formations were thoroughly studied by us as a part of the Kara-Turgai assemblage picrites. The first is represented by the segregational globules containing: pyrrhotite, pentlandite, copper pyrite, sphalerite, magnetite. The second formation forming globules as well consists of: pyrrhotite, copper pyrite, sphalerite, magnetite. The third formation is represented by irregular shape inclusions, containing: pyrrhotite, copper pyrite, sphalerite, pyrite, magnetite.

The globules of the first formation included platinum telluride (moncheite), silver telluride, lead telluride, lead selenide, polymetallic solid solutions of platinum group metals (Ir, Os, Ru), rare earth metals (Dy, Er, Y, Ce) were discovered for the first time along with the previously known copper and nickel sulfides (pentlandite and copper pyrite). The microinclusions of silver telluride, platinoids and the rare earth elements were not discovered in the sulfides globules of the second formation. The sulfides of the third formation, such as pyrrhotite, copper pyrite and sphalerite do not contain inclusions of platinum group minerals detected in the back scattered electron mode (compound) and the rare earth elements, and just very small inclusions containing Ce and Os were found in the FeOS_2 phase.

Segregation Group Minerals.

The first mineral formation. The ore-forming sulfides of the first picrites formation are represented by pyrrhotite, pentlandite, violarite, copper pyrite, sphalerite.

Pyrrhotite (FeS) has a fine sulfur excess. Chemically it is close to the troilite formula in theory (see table 1). The states of the solid solutions decay are clearly observed in the pyrrhotite (figure 2 (B)). It contains microinclusions of platinum telluride (PtTe_2), silver telluride (Ag_2Te), altaite (PbTe). When arsenic occurs in pyrrhotite (As to 3.44%) at performing an analysis of the small heavy microinclusions in pyrrhotite, then Os (up to 29.77%), Ir (up to 6.89%), Ru (up to 15.27%) is certainly found, and also a high content of Y (11.41%). Once arsenic concentration increases (up to 10.83%), then Ir content grows (up to 16.41%), and Pt (> 4.62%) appears, as well as Te admixture (> 0.62%). It makes consider dealing with the polymetallic solid solutions of platinoids.

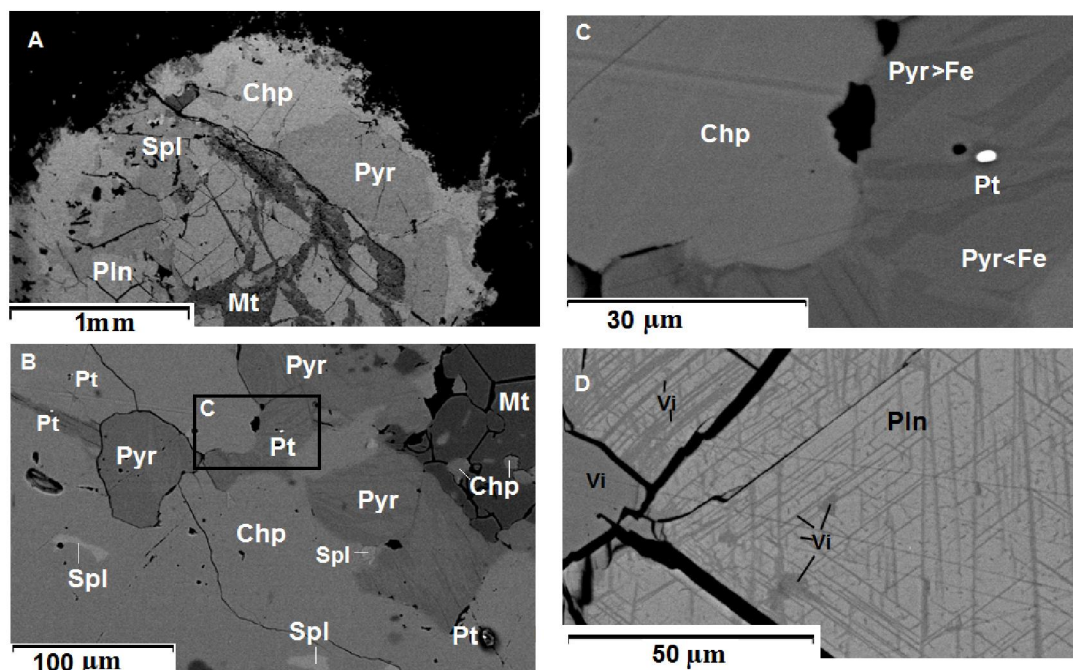


Figure 2 – Back-scattered electron image of the parts of polished sections made from ore samples containing pyrrhotite (Pyr), copper pyrite (Chp), pentlandite (Pln) violarite (Vi), sphalerite (Spl), magnetite (Mt) with the platinum (Pt) microinclusions. Figures A, B show a structure of a sulfide drop and the minerals interaction. Figure C demonstrates the nature of copper pyrite ratio to pyrrhotite (with the solid solution decay structure), and Figure D shows the slaty structure of the pentlandite-violarite decay

The pyrrhotite crystals form a two-phase area (figure 2 (C)), where the lighter areas are represented by a phase of greater Fe_2O_3 (61.85%, see Table 1, 9-12) content than in the dark phase.

Pentlandite ($(\text{Fe,Ni})_9\text{S}_8$) contains cobalt (1.04-1.31%) admixture and is specified by sulfur deficiency, and the lack of cobalt leads to a sulfur excess. The pentlandite is undersaturated by sulfur, as a rule, contains platinum telluride (PtTe_2) microinclusions with Pd, Bi admixtures and contains Rh (1.99%), Ir (1.84%) extremely rarely. There are also sometimes Dy (1.65%), Er (1.6%), and Y (0.08%) admixtures. The slaty structure of the solid solutions decay is established in the pentlandite (Fig. 2 (D)), where the dark decay phase is depleted in Fe (<26.11%). Chemically this phase is similar to violarite (table 1).

Violarite ($(\text{Fe,Ni})_3\text{S}_4$) pseudomorphic in pentlandite is less common. It similar to pentlandite has a lack of sulfur. Violarite contains rare small microinclusions providing Er up to 1.76% and Os up to 15.43% in the analysis, which indicates the availability of an independent mineral state of osmium.

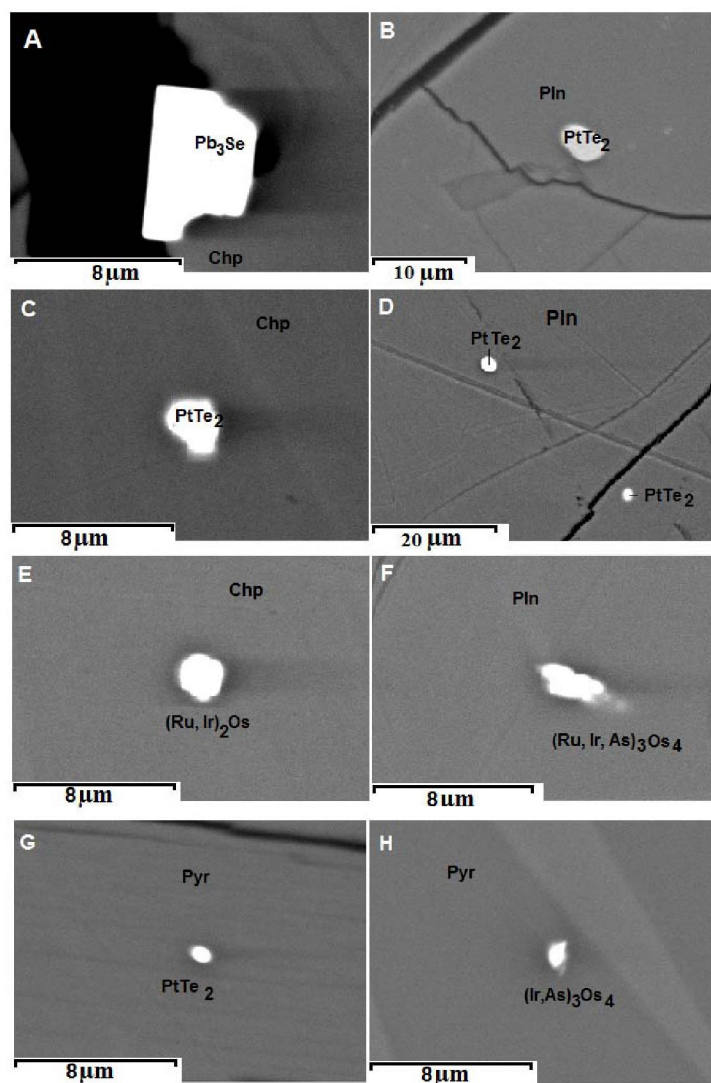


Figure 3 – Back-scattered electron image of the parts of polished sections made from ore samples containing pentlandite, copper pyrite with the platinoids and platinum telluride II (PtTe_2) microinclusions

Copper pyrite (CuFeS_2) displays a constant sulfur excess (see Table 1). Platinum telluride (PtTe_2) with Pd, Bi admixtures; silver telluride (Ag_2Te); altaite (PbTe) microinclusions are rarely contained, but lead selenide (PbSe) is predominant, and Os (11.31%), Ir (1.60%) and Rh 11.17%) form polymetallic solid solutions. Ce (11.27%) and F inclusions which, apparently, jointly form a CeF_3 phase appear in the copper pyrite exceedingly rare.

Table 1 – The sulfides compound of the first mineral formation with the magnetite, together with PGM, REE picrites of the Kara-Turgai assemblage (wt. %, 100% total)

Sr. No	Mineral	S	Fe	Cu	Co	Ni	Zn	Pb	Er	Os	Te
The first ore mineral formation with magnetite, together with PGM, REE.											
1	Cooper pyrite	36.61	30.00	33.39							
2	Cooper pyrite	36.44	30.19	33.37							
3	Cooper pyrite	36.46	29.97	33.57							
4	Cooper pyrite	33.50	30.05	33.45							
5	Cooper pyrite	37.28	29.43	33.19	0.10						
6	Cooper pyrite	34.99	30.52	34.50							
7	Cooper pyrite	35.53	30.04	34.43							
8	Cooper pyrite	35.39	30.44	34.17							
9*	Cooper pyrite	35.23	28.89	32.43							3.44
10	Sphalerite	35.09	9.05	1.02			54.83				
11	Sphalerite	34.98	8.88	0.32			55.82				
12	Sphalerite	35.29	10.31	0.80			53.60				
13	Sphalerite	35.12	9.41	0.71			54.75				
14	Sphalerite	33.65	10.19	0.54		1.17	54.45				
15	Sphalerite	33.83	9.44	1.19		0.16	55.38				
16*	Pyrrhotite	41.20	49.35	0.59		0.50				8.36	
17	Pyrrhotite	38.15	61.85								
18	Pyrrhotite	38.16	61.84								
19	Pyrrhotite	38.15	61.85								
20	Pyrrhotite	38.15	61.85								
21	Pyrrhotite	40.37	59.63								
22	Pyrrhotite	40.29	59.71								
23	Pyrrhotite	40.52	59.48								
24	Pyrrhotite	40.39	59.61								
25	Pyrrhotite	38.93	61.07								
26	Pyrrhotite	38.82	61.18								
27*	Pyrrhotite	39.73	59.03							1.24	
28*	Pyrrhotite	33.50	52.60								4.74
29*	Pyrrhotite	31.54	61.98								6.47
30	Pentlandite	35.04	33.24		1.18	30.54					
31	Pentlandite	35.28	33.56		1.04	30.13					
32	Pentlandite	35.75	32.78		1.31	30.16					
33	Pentlandite	35.28	33.56		1.04	30.13					
34	Pentlandite	35.75	31.78		1.31	30.16					
35	Pentlandite	34.01	32.82			31.60			1.57		
36	Pentlandite	34.00	33.60			31.55			0.85		
37	Pentlandite	34.13	33.54			31.46			0.88		
38	Pentlandite	34.37	33.55			30.55			1.24		
39	Pentlandite	33.91	33.59			30.90			1.60		
40	Violarite	40.66	24.81			32.86			1.68		
41	Violarite	40.27	26.11			31.86			1.76		
42	Violarite	40.70	22.95			35.19			1.16		
43*	Violarite	39.84	25.49			31.36			1.42	15.43	
44	Violarite	41.58	24.20			34.22					
*The analysis point contains a small inclusion.											

Crystallo-chemical formulas.

1. $\text{Cu}_{0.999}\text{Fe}_{1.011}\text{S}_{2.149}$;
2. $\text{Cu}_{0.996}\text{Fe}_{1.014}\text{S}_{2.133}$;
3. $\text{Cu}_{0.992}\text{Fe}_{1.008}\text{S}_{2.136}$;
4. $\text{Cu}_{0.989}\text{Fe}_{1.011}\text{S}_{2.08}$;
5. $\text{Cu}_{0.99}\text{Fe}_{1.0}\text{S}_{2.21}$;
6. $\text{Cu}_{1.0}\text{Fe}_{1.01}\text{S}_{2.0}$;
7. $\text{Cu}_{1.0}\text{Fe}_{1.01}\text{S}_{2.04}$;
8. $\text{Cu}_{1.0}\text{Fe}_{1.01}\text{S}_{2.04}$;
9. $\text{Cu}_{0.97}\text{Fe}_{0.98}\text{Te}_{0.05}\text{S}_{1.99}$;
10. $\text{Zn}_{0.838}\text{Fe}_{0.161}\text{S}_{1.030}$;
11. $\text{Zn}_{0.843}\text{Fe}_{0.157}\text{S}_{1.080}$;
12. $\text{Zn}_{0.816}\text{Fe}_{0.184}\text{S}_{1.096}$;
13. $\text{Zn}_{0.832}\text{Fe}_{0.167}\text{S}_{1.089}$;
15. $\text{Fe}_{1.00}\text{S}_{1.075}$;
16. $\text{Fe}_{1.00}\text{S}_{1.075}$;
17. $\text{Fe}_{1.00}\text{S}_{1.075}$;
18. $\text{Fe}_{1.00}\text{S}_{1.075}$;
19. $\text{Fe}_{1.00}\text{S}_{1.179}$;
20. $\text{Fe}_{1.00}\text{S}_{1.175}$;
21. $\text{Fe}_{1.00}\text{S}_{1.187}$;
22. $\text{Fe}_{1.0}\text{S}_{1.18}$;
23. $\text{Fe}_{0.91}\text{S}_{1.09}$;
24. $\text{Fe}_{0.92}\text{S}_{1.08}$;
25. $\text{Fe}_{0.95}\text{S}_{1.05}$;
26. $\text{Fe}_{0.95}\text{S}_{1.05}$;
27. $\text{Fe}_{0.99}\text{S}_{1.16}$;
28. $\text{Fe}_{0.96}\text{Te}_{0.04}\text{S}_{1.07}$;
29. $\text{Fe}_{0.95}\text{Te}_{0.05}\text{S}_{0.85}$;
30. $(\text{Fe}_{4.72}\text{Ni}_{4.12}\text{Co}_{0.16})_{\Sigma 9.0}\text{S}_{8.66}$;
31. $(\text{Fe}_{4.78}\text{Ni}_{4.08}\text{Co}_{0.14})_{\Sigma 9.0}\text{S}_{8.75}$;
32. $(\text{Fe}_{4.70}\text{Ni}_{4.12}\text{Co}_{0.18})_{\Sigma 9.0}\text{S}_{8.94}$;
33. $(\text{Fe}_{4.78}\text{Ni}_{4.08}\text{Co}_{0.14})_{\Sigma 9.0}\text{S}_{8.75}$;
34. $(\text{Fe}_{4.63}\text{Ni}_{4.19}\text{Co}_{0.18})_{\Sigma 9.0}\text{S}_{9.08}$;
35. $(\text{Fe}_{4.66}\text{Ni}_{4.27}\text{Er}_{0.07})_{\Sigma 9.0}\text{S}_{8.04}$;
36. $(\text{Fe}_{4.73}\text{Ni}_{4.23}\text{Er}_{0.04})_{\Sigma 9.0}\text{S}_{8.34}$;
37. $(\text{Fe}_{4.73}\text{Ni}_{4.23}\text{Er}_{0.04})_{\Sigma 9.0}\text{S}_{8.39}$;
38. $(\text{Fe}_{4.79}\text{Ni}_{4.15}\text{Er}_{0.06})_{\Sigma 9.0}\text{S}_{8.55}$;
39. $(\text{Fe}_{4.76}\text{Ni}_{4.17}\text{Er}_{0.07})_{\Sigma 9.0}\text{S}_{8.37}$;
40. $(\text{Fe}_{1.33}\text{Ni}_{1.37}\text{Er}_{0.03})_{\Sigma 3.03}\text{S}_{3.79}$;
41. $(\text{Fe}_{1.39}\text{Ni}_{1.61}\text{Er}_{0.03})_{\Sigma 3.03}\text{S}_{3.73}$;
42. $(\text{Fe}_{1.39}\text{Ni}_{1.61}\text{Er}_{0.03})_{\Sigma 3.03}\text{S}_{3.73}$;
43. $\text{Fe}_{1.38}\text{Ni}_{1.62}\text{Er}_{0.03}\text{S}_{3.76}$;
44. $(\text{Fe}_{1.28}\text{Ni}_{1.72})_{\Sigma 3.0}\text{S}_3$

Sphalerite (ZnS) is a relatively uncommon mineral that is oversaturated with sulfur and contains up to 10.31% Fe and Cu up to 1.02% (see table 1). Chemically, it matches marmatite $(\text{Zn}_{0.84}\text{Fe}_{0.16})_{\Sigma 1.00}\text{S}_{1.08}$. A high level of Fe and S excess is presumably determined by a pyrrhotite in formation as a product of solid solution decay. Considering the iron entering into the sphalerite structure greatly increases the total system storage, then the iron amount in the solid solution decreases at a high pressure, and consequently, as the pressure releases, the iron amount in the sphalerite structure increases.

The mineral of oxides group. Magnetite (Fe_3O_4), combined with the first formation sulfides, contains (wt.%): Fe (73.92 -74.66). A fine grain is detected in, which produced Os (6.44), Ru (2.01), and Rh (0.22) in the general review. A Y (2.15) admixture is also detected in this grain. These data indicate a solid solution of platinoids and yttrium is established.

Precious and rare minerals microinclusions in the first formation sulfides are represented both as the intermetallic compounds (intermetallides) that form independent round, ellipsoidal, less irregular shapes of exudations of not more than 3 μm diameter (figure 3), and in the form of tellurides, selenides and arsenides.

The most common is **platinum telluride** with Pd, Bi admixtures, which chemically is close to the stoichiometric formula of **moncheite PtTe_2** (see table 2, No. 1-3). **Silver telluride** generates a perfectly rounded grain (figure 3). Chemical compositions of the inclusions in copper pyrite correspond to **Ag_2Te** (see table 2, No. 4). Occasional **altaite (PbTe)** inclusions in pyrrhotite and copper pyrite (see table 3)

The **(Ru, Ir) Os** entity was found in the pentlandite (see table 3), its empirical formula can be represented as $(\text{Ru}_{0.61}\text{Ir}_{0.17}\text{As}_{0.08})_{\Sigma 0.86}\text{Os}_{1.14}$ with the chemical compound (wt%) (without matrix elements): Os (29.77), Ru (8.60), Ir (4.39), As (0.87).

A grain of no more than 1.0 μm was detected in copper pyrite (see Table 3), which contains (wt. %): Ru (11.17), Os (11.31), Ir (1.60), Bi (0.11) along with iron, copper and sulfur in the analysis. The empirical formula of such a high-temperature solid solution can be represented as $(\text{Ir}_{0.153}\text{Ru}_{0.1841})_{\Sigma 2.004}\text{Os}_{0.996}$, which perfectly corresponds to the osmiridium **(Ru, Ir) $_2$ Os** formula. Also an ellipsoidal grain of up to

Table 2 – Microinclusions analysis in the sulfides of the first picrites formation of the Kara-Turgai assemblage (wt. %) without matrix elements

Sr.No.	Mineral	Pt	Pd	Rh	Ru	Te	Bi	Ag	Pb	Se	Σ
1	$\text{PtTe}_2(\text{pln})$	35.66	2.37	1.27		47.94	7.99				95.23
2	$\text{PtTe}_2(\text{pln})$	32.03	1.65	1.99		42.66	8.83				87.16
3	$\text{PtTe}_2(\text{chp})$	32.73	2.10		0.02	42.48	8.58				85.91
4	$\text{Ag}_2\text{Te}(\text{chp})$					30.89		51.46			82.35
5	$\text{PbSe}(\text{chp})$								62.38	20.41	82.79
6	$\text{Pb}_3\text{Se}(\text{chp})$								83.51	11.01	94.52

Crystallo-chemical formulas.

1. $(\text{Pt}_{0.89}\text{Pd}_{0.11}\text{Rh}_{0.06})_{\Sigma 1.06}(\text{Te}_{1.77}\text{Bi}_{0.18})_{\Sigma 1.95}$;
2. $(\text{Pt}_{0.86}\text{Pd}_{0.08}\text{Rh}_{0.10})_{\Sigma 1.04}(\text{Te}_{1.74}\text{Bi}_{0.22})_{\Sigma 1.96}$;
3. $(\text{Pt}_{0.84}\text{Pd}_{0.10})_{\Sigma 0.94}(\text{Te}_{1.873}\text{Bi}_{0.191})_{\Sigma 2.06}$;
4. $\text{Ag}_{2.02}\text{Te}_{0.98}$;
5. $\text{Pb}_{0.54}\text{Se}_{0.46}$;
6. $\text{Pb}_{2.97}\text{Se}_{1.03}$.

Table 3 – The chemical compound of the mineral phases in the sulfides of the picrites first formation of the Kara-Turgai assemblage (wt. %, amount 100%)

Mineral	pyr	pyr	pyr	pyr	pyr	pyr	pyr	pyr	pyr	pyr
Sr.No. of element	1	2	3	4	5	6	7	8	9	10
S	34.32	39.35	33.66	32.12	36.62	37.89	36.54	33.50	31.54	39.10
Fe	19.70	49.34	39.95	35.39	37.71	43.59	51.55	52.60	61.98	50.20
Cu						0.54				
Ni	1.71									
Co										
As	2.15	3.44	7.49	10.83	1.29	0.99				3.06
Os	15.43	0.99			14.03	12.20				1.09
Ir		6.89	14.21	16.41	2.15					6.55
Ru	15.27		0.21		6.25	4.51				
Pt			4.24	4.62	1.94					
Ag							7.89	9.16		
Te			0.24	0.62			4.01	4.74	6.47	
Bi										
Y	11.41									
Pb						0.28				

Table 3. Extension 1

Mineral	pyr	pyr	chp	chp	chp	chp	chp	chp	chp	chp
Sr.No. of element	11	12	13	14	15	16	17	18	19	20
S	27.79	23.42	26.24	22.55	19.63	14.38	15.55	31.22	30.00	31.22
Fe	40.97	31.06	27.85	18.59	15.24	12.10	8.87	25.89	24.65	25.89
Cu			14.91	12.90	13.96	11.39	2.78	28.16	25.99	28.16
Pt		18.05							9.08	
Pd		0.95							1.05	
Ag			1.43			39.32		9.73		9.73
Te	10.14	21.12	11.30			22.81		5.01	9.23	5.01
Bi		5.41								
Pb	21.09		18.27	45.96	44.96		72.16			6.08
Se					2.03		0.64			
O					4.17					

Table 3. Extension 2

Mineral	chp	chp	chp	pln	pln	pln	gm
Sr.No. of element	22	23	24	25	26	27	28
S	37.16	22.62	17.66	31.65	33.33	30.18	
Fe	19.59	19.41	13.13	13.78	30.31	27.14	19.45
Cu	18.83	7.01	7.03				
Ni			4.15	10.93	28.53	24.01	
Co					0.61	0.72	
As				0.87			
Os	11.31			29.77			
Ir	1.60			4.39	1.84		
Ru	11.17			8.60			
Pt					2.23	7.17	25.50
Te						7.48	25.71
Bi	0.11					3.30	10.93
Dy					1.62		
Pb		47.84	45.30		1.52		
Ce							
Se		1.87	3.44				
Zn		1.25					
Si			0.95				
Mg			0.57				1.21

Table 3. Extension 3

Mineral	chp	chp	mg	chp	mg	mg	
Sr.No. of element	29	30	31	32	33	34	35
S	22.55	19.63	4.38	23.52	9.62	3.27	13.71
Fe	18.59	15.24	53.35	18.99	33.72	53.74	16.18
Cu	12.90	13.96		20.26			
As			1.59				
Os			6.44				
Ir			1.74				
Ru			2.01				
Rh			0.22				
Y			2.15				
Pb	45.96	44.96			22.43	11.53	53.61
Ce				11.27			
Se		2.03			3.14	1.25	6.82
Si				2.05	4.13	2.81	
Mg				3.72	2.33	2.27	
Al				0.68			
F				0.55			
O			28.11	18.96	24.64	25.13	9.68

3 μm is found in copper pyrite, which has a complex chemical compound (wt. %): Pt (11.87), Pd (1.11), Te (13.69), Mo (10.42), Bi (3.42), Ag (0.71). Supposing molybdenum is not associated with copper pyrite, then, in terms of 8 units, the crystallo-chemical formula $(\text{Pt}_{1.624}\text{Bi}_{0.437})_{2.061}(\text{Te}_{2.864}\text{Ag}_{0.176})_{\Sigma 3.04}\text{Mo}_{2.9}$ is obtained, the formula of this solid solution is perfectly represented as - $(\text{Pt,Bi})_2 (\text{Te,Ag})_3 \text{Mo}_3$

Arsenides. High-temperature metals of the IPGM (Ir, Os, Ru) platinum group and As generate platinoid arsenides, which are found in pyrrhotite and less often in iron sulfide (see Table 3). They all are represented by extremely fine grains of irregular shape (figure 3), which makes it difficult to obtain an authentic grains consistence, since when analyzing characteristic X-ray radiation is recorded not only from the elements composing inclusion but also from the matrix elements.

If the iron and sulfur amount is subtracted out of these analyses, the two types of entities may be conditionally distinguished. The first entity with the chemical compound (wt. %): As (3.44), Ir (6.89), Os (1.09) in terms of 100% recalculation has the following empirical formula: $(\text{Ir}_{0.85}\text{Os}_{0.13})_{\Sigma 0.98}\text{As}_{1.02}$, then its formula perfectly corresponds to arsenide of iridium (**Os, Ir**) **As**. The second entity (wt. %): As (10.83), Ir (16.41), Pt (4.62), Te (0.62) in terms of 100% recalculation has the following empirical formula $(\text{Ir}_{0.68}\text{Pt}_{0.18})_{\Sigma 0.86}(\text{Te}_{0.04}\text{As}_{1.1})_{\Sigma 1.14}$, which corresponds to the ultimate formula (**Ir, Pt**) **As**.

Lead selenide (II) (PbSe) is enclosed in copper pyrite (see table 2, No. 5). Also, the Pb_3Se phase was detected (see table 2, No. 6), which forms rectangular crystal of a regular shape, $8 \times 4 \mu\text{m}$ (figure 3). It has straight-line boundaries with iron sulfide, while copper pyrite absorbs it, which indicates the lead selenide phase appeared earlier than copper pyrite.

Altaite (PbTe) is extremely rare. It forms isometric microinclusions in pyrrhotite and copper pyrite grains (see table 3).

The second mineral formation. Chemically, the sulfides of the second formation (pyrrhotite, copper pyrite, sphalerite) has no difference from those of the first formation (see table 4), but pentlandite is absent nevertheless. **A moncheite** is found in none of the sulfides (pyrrhotite, copper pyrite and sphalerite) of this formation, which is widely present in the sulfides of the first formation.

Copper pyrite is compositionally close to the stoichiometric formula (**CuFeS₂**). In **pyrrhotite** (figure 4 (B)), the structure of the solid solutions decay is clearly observed, where the pyrrhotite's light part corresponds to the theoretical formula of troilite (**FeS**) by composition, and the pyrrhotite's dark part is oversaturated with sulfur ($\text{FeS}_{1.13}$). **Sphalerite** by chemical compound is close to the theoretical formula of marmatite $((\text{Zn}_{0.8}\text{Fe}_{0.2})_{\Sigma 1.0}\text{S}_{1.0})$. When Fe (17.97%) significance grows, the Cu (9.03%) concentration increases and its crystallo-chemical formula modifies $((\text{Zn}_{0.6}\text{Fe}_{0.3}\text{Cu}_{0.1})_{\Sigma 1.00}\text{S}_{1.00})$.

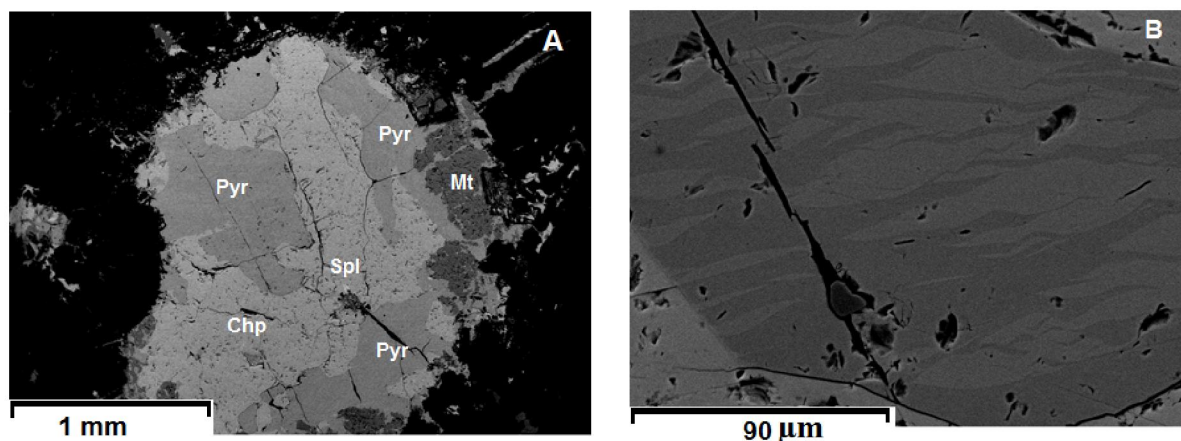


Figure 4 – Back-scattered electron image of the parts of polished sections made from sulfides of the picrites second formation of the Kara-Turgai assemblage. A. The figure shows the nature of sulfides interrelations with the silicate minerals.

Figure B demonstrates the structure of the pyrrhotite solid solutions decay

Group of oxides mineral. Magnetite (Fe_3O_4), combined with the second sulfides formation, contains Fe (72.06 -72.36%), which is lower than in those of the first formation.

Table 4 – The minerals compound of the second picrites formation of the Kara-Turgai assemblage (wt. %)

Sr. No	Mineral	S	Fe	Cu	Zn	O
1	Copper pyrite	35.64	30.47	33.88		
2	Copper pyrite	35.35	30.45	34.21		
3	Copper pyrite	35.33	29.98	34.69		
4	Sphalerite	33.59	11.69	1.55	53.17	
5	Sphalerite	33.64	17.94	9.03	39.40	
6	Pyrrhotite	37.62	62.38			
7	Pyrrhotite	37.02	62.98			
8	Pyrrhotite	36.87	63.13			
9	Pyrrhotite	39.42	60.58			
10	Pyrrhotite	39.34	60.66			
11	Pyrrhotite	39.24	60.76			
12	Magnetite		72.06			27.94
13	Magnetite		72.36			27.64
14	Magnetite		72.18			27.82

Crystallo-chemical formulas.

1. $\text{Cu}_{0.99}\text{Fe}_{1.01}\text{S}_{2.06}$;

2. $\text{Cu}_{0.99}\text{Fe}_{1.01}\text{S}_{2.04}$;

3. $\text{Cu}_{1.01}\text{Fe}_{0.99}\text{S}_{2.04}$;

4. $(\text{Zn}_{0.78}\text{Fe}_{0.20}\text{Cu}_{0.02})_{\Sigma 1.0}\text{S}_{1.00}$;

5. $(\text{Zn}_{0.57}\text{Fe}_{0.31}\text{Cu}_{0.15})_{\Sigma 1.03}\text{S}_{1.00}$;

6. $\text{Fe}_{0.98}\text{S}_{1.02}$;

7. $\text{Fe}_{0.99}\text{S}_{1.01}$;

8. $\text{Fe}_{0.99}\text{S}_{1.01}$;

9. $\text{Fe}_{0.94}\text{S}_{1.06}$;

10. $\text{Fe}_{0.94}\text{S}_{1.06}$;

11. $\text{Fe}_{0.94}\text{S}_{1.06}$

The third mineral formation. The sulfides of the third formation are represented by pyrrhotite, copper pyrite, pyrite, sphalerite, which differ from those of the first and second formations by chemical compound (see table 5) and have a number of structural and texture features. The pentlandite is not peculiar to this formation, however, pyrite and the FeOS_2 phase occurs. The availability of lead selenide and magnetite, as well as Os solid solution and the Ce admixture are the conspicuity factor that aggregates them with the minerals of the segregation category.

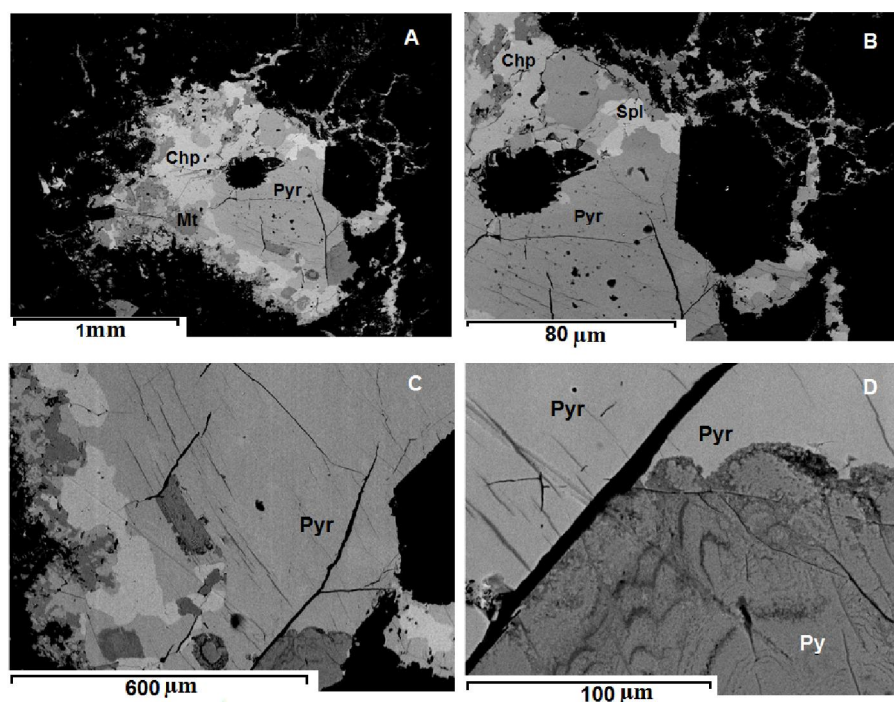


Figure 5 – Back-scattered electron image of the parts of polished sections made from sulfides of the third picrites formation of the Kara-Turgai assemblage. The figure demonstrates the nature of interrelations between sulfides and silicate minerals. The substitution feature of pyrrhotite by a mineral with the typical undulated colloidal gel texture is displayed in figures C, D.

Table 5 – The minerals compound of the third picrites formation of the Kara-Turgai assemblage (wt. %)

Sr.No	Mineral	S	Fe	Cu	Zn	Ni	Ce	Os	Si	O
1	Pyrrhotite	39.59	60.41							
2	Pyrrhotite	39.49	60.51							
3	Pyrrhotite	39.56	60.44							
4	Pyrrhotite	39.19	60.81							
5	FeOS ₂	41.79	47.08						0.69	10.44
6	FeOS ₂	41.87	47.64						0.76	9.73
7	FeOS ₂	42.36	47.96						0.67	9.01
8	FeOS ₂ spectrum	42.73	47.36			0.12			0.11	9.68
9	FeOS ₂	37.96	46.67				1.08		0.43	13.86
10*	FeOS ₂	36.99	46.44					0.92	0.40	15.25
11	FeOS ₂	40.18	48.26						0.72	10.85
12	Fe ₂ O ₃ S ₁	17.38	54.97						0.48	27.17
13	Пирит	51.95	48.05							
14	Copper pyrite	35.25	30.18	34.57						
15	Copper pyrite	35.48	30.50	34.02						
16	Copper pyrite	35.38	30.55	34.06						
17	Copper pyrite	35.33	30.68	33.99						
18	Sphalerite	34.16	9.61		56.23					
19	Sphalerite	34.10	9.72		56.19					
20	Sphalerite	34.42	9.47		56.11					
21	Sphalerite	34.36	9.53		56.11					
22	Magnetite		72.62							27.38
23	Magnetite		71.47							28.11
24	Magnetite		72.56							27.44
25	Magnetite		72.45							27.55
26	Magnetite		72.23							27.77
27	Magnetite		72.61							27.39

*The analysis point contains a small inclusion.

Crystallo-chemical formulas.

- | | | |
|---|---|---|
| 1. $\text{Fe}_{0.94}\text{S}_{1.06}$; | 10. $(\text{Fe}_{1.25}\text{O}_{1.43})_{\Sigma 2.68}\text{S}_{1.73}$; | 19. $(\text{Zn}_{0.81}\text{Fe}_{0.16})_{\Sigma 0.97}\text{S}_{1.00}$; |
| 2. $\text{Fe}_{0.94}\text{S}_{1.06}$; | 11. $(\text{Fe}_{1.21}\text{O}_{0.95})_{\Sigma 2.16}\text{S}_{1.75}$; | 20. $(\text{Zn}_{0.80}\text{Fe}_{0.16})_{\Sigma 0.96}\text{S}_{1.00}$; |
| 3. $\text{Fe}_{0.94}\text{S}_{1.06}$; | 12. $\text{Fe}_{1.91}\text{O}_{3.30}\text{S}_{1.05}$; | 21. $(\text{Zn}_{0.80}\text{Fe}_{0.16})_{\Sigma 0.96}\text{S}_{1.00}$; |
| 4. $\text{Fe}_{0.94}\text{S}_{1.06}$; | 13. $\text{Fe}_{1.04}\text{S}_{1.96}$; | 22. $\text{Fe}_{2.99}\text{O}_{4.01}$; |
| 5. $\text{Fe}_{1.17}\text{O}_{0.90}\text{S}_{1.80}$; | 14. $\text{CuFeS}_{2.02}$; | 23. $\text{Fe}_{2.92}\text{O}_{4.08}$; |
| 6. $(\text{Fe}_{1.16}\text{O}_{0.84})_{\Sigma 2.0}\text{S}_{1.80}$; | 15. $\text{Cu}_{0.99}\text{Fe}_{1.01}\text{S}_{2.05}$; | 24. $\text{Fe}_{2.99}\text{O}_{4.01}$; |
| 7. $(\text{Fe}_{1.17}\text{O}_{0.77})_{\Sigma 1.94}\text{S}_{1.80}$; | 16. $\text{Cu}_{0.99}\text{Fe}_{1.01}\text{S}_{2.04}$; | 25. $\text{Fe}_{2.98}\text{O}_{4.02}$; |
| 8. $(\text{Fe}_{1.16}\text{O}_{0.83})_{\Sigma 1.99}\text{S}_{1.83}$; | 17. $\text{Cu}_{0.99}\text{Fe}_{1.01}\text{S}_{2.03}$; | 26. $\text{Fe}_{2.96}\text{O}_{4.04}$; |
| 9. $(\text{Fe}_{1.23}\text{O}_{1.28})_{\Sigma 2.52}\text{S}_{1.75}$; | 18. $(\text{Zn}_{0.81}\text{Fe}_{0.16})_{\Sigma 0.97}\text{S}_{1.00}$; | 27. $\text{Fe}_{2.99}\text{O}_{4.01}$. |

The deficiency of solid-solution decay structures, which is typical for the first-formation platinum-containing pyrrhotite (figures 2 and 3) is a peculiarity of, for example, **pyrrhotite** ($\text{FeS}_{1.1}$) (figure 5 (C)). **Copper pyrite** is close to the stoichiometric formula by consistency and does not have a sulfur excess (CuFeS_2) with respect to platinum-containing copper pyrite. **Sphalerite** ($(\text{Zn}_{0.81}\text{Fe}_{0.16})_{\Sigma 0.97}\text{S}$) does not contain Cu, which is typical for the sphalerite of the first formation too (see table 5). One of the peculiarities of this formation is the **pyrite** (FeS_2) and formations with a colloidal-gel texture. The presence of Ce (1.08%) as part of this formation does not except its accomplishment due to pyrrhotite, in the process of oxidation of the latter, the FeOS_2 phase originates. Its ultimate formula in the Hille system, per total number of atoms equal to 4, can be introduced as FeOS_2 with 11.77% O, 41.07% Fe and 47.16% S. Magnetite and copper pyrite contain lead selenide inclusions (PbSe) (see table 2).

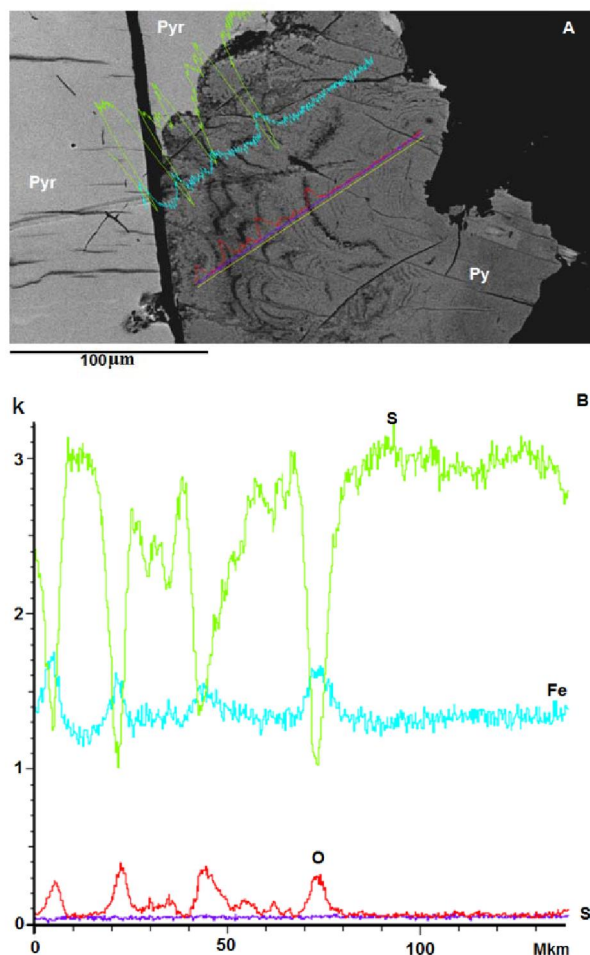


Figure 6 – A – An image of the colloidal-gel texture of pyrite (white iron pyrite) with overlaid log of concentration curves of the separate elements along the white line. B – Independent logging of the concentration curves

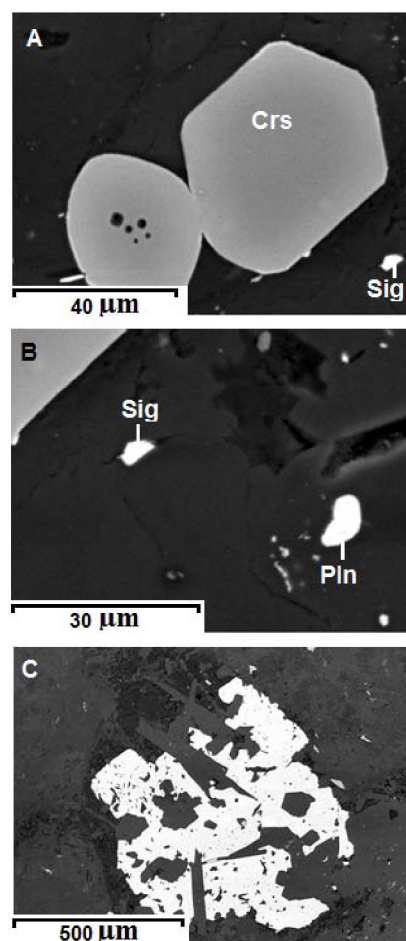


Figure 7 – Back-scattered electron image of the parts of polished sections made of picrite diabase containing chromium spinel (CrS), siegenite (Sig), pentlandite (Pln), pyrite (Py)

Oxides Category Mineral. Magnetite (Fe_3O_4), connected with the third sulfides formation, contains Fe (<72.62%), which is lower than in the first magnetite formation.

The single inclusions of sulfides in picritic diabases are represented by sulfide category minerals: pentlandite, pyrite, siegenite (newly discovered mineral), millerite, galenite.

Pentlandite ($\text{Fe, Ni}_9\text{S}_8$) generates fine, rare grains in the bulk (figure 7 (B)). Chemically, it is close to the stoichiometric formula of pentlandite (see Table 6). It is supersaturated with S (38.23%), does not contain Co, and is poorly enriched by Cr (0.16%) with respect to the picrites pentlandite.

Siegenite ($(\text{Co, Ni})_3\text{S}_4$) generates fine grains totally in the rock (figure 6 (A)). It is composed of iron admixture (5.01-7.91%, see table 6), and a constant excess of sulfur is in the siegenite formula and nickel prevails over cobalt.

Millerite (NiS) occurs in the clinopyroxene interstices, where the small crystals form. Iron in its compound was found as an admixture (see table 6).

Galenite (PbS) is available in the form of fine grains in formation with millerite. Fe and Ni admixtures in its compound, the Pb content reaches 83.18%, and S is up to 12.37%.

Pyrite (FeS_2) contains S = 56.31% and Fe = 43.69%.

Oxides Category Minerals. Titanium-hematite and manganotitanoferrite form the solid solutions decay, and **chromium spinel** – grains of isometric shape.

Table 6 – The sulfides compound of picritic diabases of the Kara-Turgai assemblage (wt. %)

Sr. No	Mineral	S	Fe	Co	Ni	Cr	Pb	Total
1	Pentlandite	36.36	33.05		30.59			100.0
2	Pentlandite	38.23	33.87		27.75	0.15		100.0
3	Siegenite	44.29	5.01	9.72	40.47	0.51		100.0
4	Pyrite	56.31	43.69					100.0
5	Siegenite	44.51	7.91	15.25	32.33			100.0
6	Siegenite	44.32	7.97	15.60	32.11			100.0
7	Siegenite	45.30	10.79	12.53	31.38			100.0
8	Millerite	37.58	1.83		60.58			100.0
9	Millerite	37.89	1.70		60.41			100.0
10	Millerite	37.89	1.70		60.41			100.0
11	Galenite	12.37	1.68		2.77		83.18	100.0

Crystallo-chemical formulas.

1. $(\text{Fe}_{4.786}\text{Ni}_{4.214})_{\Sigma 9.0}\text{S}_{9.171}$;
2. $(\text{Fe}_{5.045}\text{Ni}_{3.933}\text{Cr}_{0.022})_{\Sigma 9.0}\text{S}_{9.920}$;
3. $(\text{Ni}_{1.168}\text{Co}_{0.519}\text{Fe}_{0.281}\text{Cr}_{0.093})_{\Sigma 3.062}\text{S}_{4.345}$;
4. $\text{Fe}_{0.924}\text{S}_{2.076}$;
5. $(\text{Ni}_{1.737}\text{Co}_{0.816}\text{Fe}_{0.447})_{\Sigma 3.0}\text{S}_{4.378}$;
6. $(\text{Ni}_{1.719}\text{Co}_{0.832}\text{Fe}_{0.449})_{\Sigma 3.0}\text{S}_{4.345}$;
7. $(\text{Ni}_{1.705}\text{Co}_{0.679}\text{Fe}_{0.616})_{\Sigma 3.0}\text{S}_{4.507}$;
8. $(\text{Ni}_{0.97}\text{Fe}_{0.03})_{\Sigma 1.0}\text{S}_{1.11}$;
9. $(\text{Ni}_{0.97}\text{Fe}_{0.03})_{\Sigma 1.0}\text{S}_{1.11}$;
10. $(\text{Ni}_{0.97}\text{Fe}_{0.03})_{\Sigma 1.0}\text{S}_{1.11}$.

Results and discussion. The siegenite, platinum telluride (moncheite), silver telluride, lead telluride (altaite), lead selenide, solid solutions of metals of the iridium group (Ir, Os, Ru), rare-earth elements (Dy, Er, Y, Ce) are established to be discovered for the first time in the picrites of Kara-Turgai assemblage alongside with the previously known sulfides (pyrrhotite, pentlandite, and copper pyrite) consequently of our investigations. The sulfides constitute three mineral formations. The first two constitute segregation "droplets", of a rounded and elliptical-elongated shape, and the third mineral formation is irregularly sharply angular (figure 8). The platinoids in copper and nickel sulfides are established to appear only in the first-formation segregation droplets, which are composed of pyrrhotite, copper pyrite, pentlandite, sphalerite. The sulfides of the second formation do not contain platinoids and are represented by pyrrhotite, copper pyrite, sphalerite. The sulfides of the third formation are represented by pyrrhotite, copper pyrite, sphalerite, pyrite. Each formation of minerals contains magnetite and as a rule is confined to the most differentiated picrites horizons and apopycrite olivinites. The consistency in the platinoids distribution as a part of the segregation sulfides revealed by us provides explanation to the fact of ore impoverishment has occurred [7].

The picrite sulfides globules of the Kara-Turgai assemblage do not have perfectly even boundaries, as well as the metasomatic halo (figure 8), which is typical for the most sulfide globules of copper-nickel ores of ultrabasic-basitic intrusive assemblages [14]. The flexuous boundary, as the frequent penetration of sulfides into the silicate groundmass, indicates that the process of globules formation was accompanied by simultaneous compression. The traditional globules design which is typical for intrusive assemblages, where the lower part is formed of pyrrhotite, the upper one – copper pyrite, and pentlandite is in the mid is not established either.

The sulfide globules of the Kara-Turgai type are the most similar with the sulfide globules in the picrites of the Norilsk-Talnakh type, where copper pyrite is above, pyrrhotite and pentlandite are in the bottom, and magnetite is located along the edge of the sulfide droplets in the picritic horizon ores. [15]. Although, globules of the first formation have a significant difference regarding magnetite distribution, as a rule, it is located in the central parts of the ore platinum-containing globules (figure 8.1A), whereas the magnetite of the second formation of the Kara-Turgai type is located at the edges of sulfide droplets (figure 8.2A).

The rare grains of the FeOS_2 phase with a colloidal-gel structure is one of the peculiarities of the third mineral formation, which formed as a result of pyrrhotite and oxygen interaction, which was accompanied by a decrease in sulfur rate, an increase in oxygen and iron oxide generation that forms a dark fines in the front of moving waves (figure 8.3C). This can serve as an evidence of such a mineralogical formation generation under hypabyssal factors, where an essential role is assigned to oxidative processes.

The set of minerals of sulphide droplets is generally identical to the segregation ores; except, some differences in their compound. Say, the ores pyrrhotite of the Kara-Turgai type do not contain nickel and cobalt, which is typical for the ores pyrrhotite of Norilsk-Talnakh type. If the latter ore have palladium,

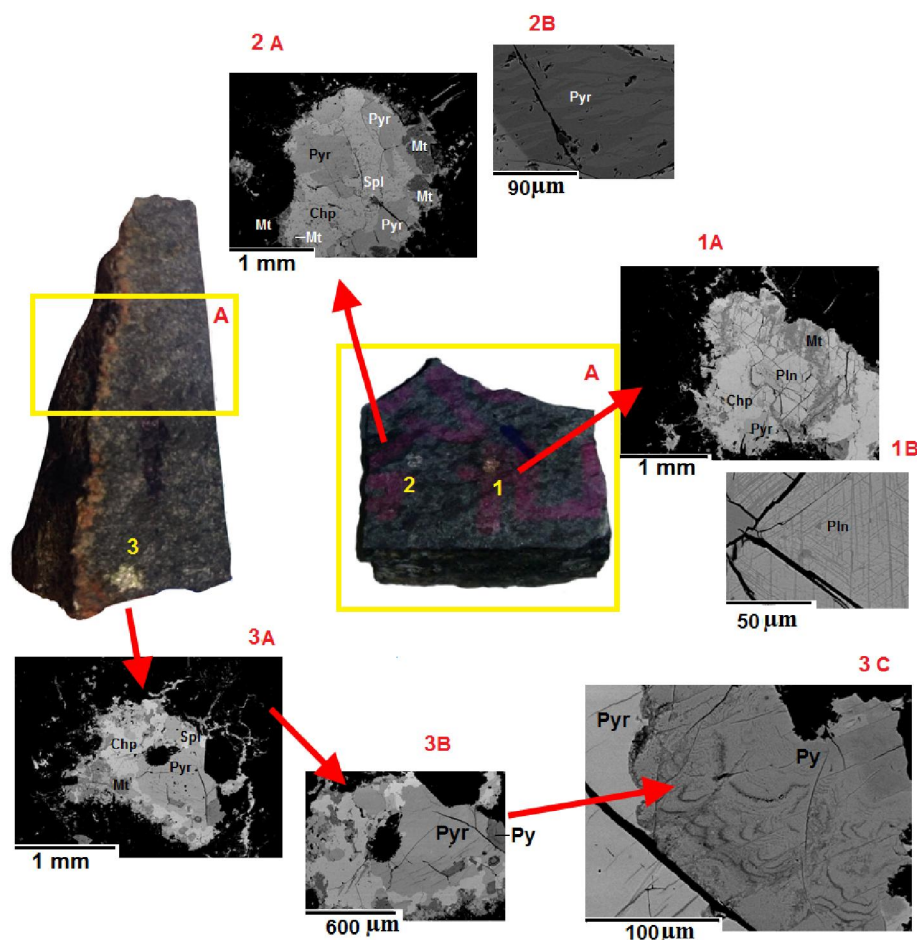


Figure 8 – Background about sulfides compound and aging of the Kara-Turgai assemblage. See "Results and Discussion" for clarification

sperrylite, gold, silver and selenium, then the picrite ores of the Kara-Turai type have no sperrylite, palladium and selenium are extremely rare, yet rare-earth elements are widely represented. Platinum telluride in the Kara-Turgai type ores is found in all main ore minerals (pentlandite, copper pyrite and pyrrhotite) of the first formation, however gold has not been detected, but a lot of silver telluride. One of the specifics of the Kara-Turgai type ores are lead selenide, arsenides of the iridium group and a high rate of rare-earth elements of the yttrium subclass (Y, Dy).

The siegenite and millerite were first discovered being a part of picritic diabase, along with pentlandite, pyrite and galenite which were not previously described in the rocks of the Kara-Turgai assemblage. The pentlandite is peculiar to be oversaturated with S, does not contain Co, and is poorly enriched by Cr with respect to the pentlandite of Kara-Turai picrits.

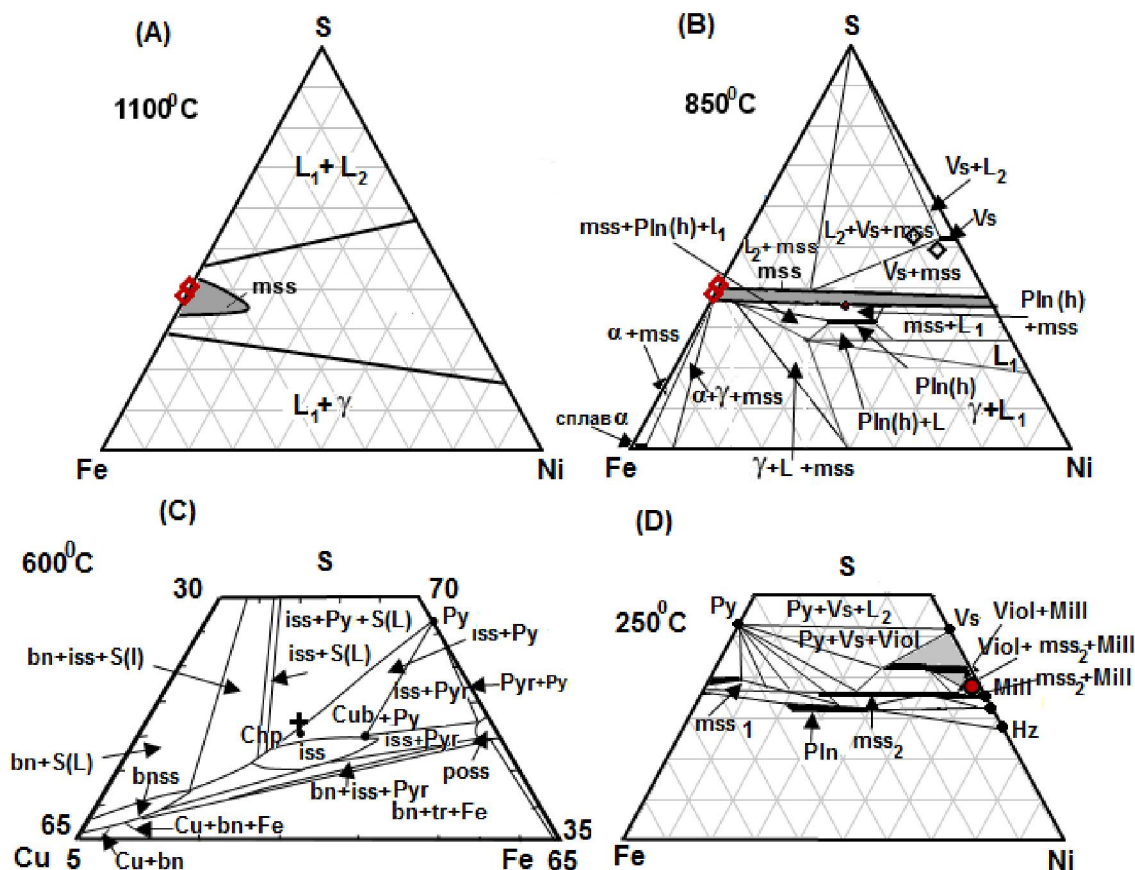


Figure 9 – Isothermal sections of Fe-Ni-S condensed systems [16] at 1000°C (A), 850°C (B), 250°C (D) and Cu-Fe-S [17] at 600°C (C) for pyrrhotite (red colored rhomb), pentlandite (black circle), copper pyrite (black cross), siegenite (black colored rhomb) and millerite (red spot) from picrites and picrite-diabases of the Kara-Turgai assemblage; mss – monosulfide solid solution; iss – intermediate solid solution; copper pyrite (Chp); pentlandite (Pln); vseat (Vs); pyrrhotite (Pyr); pyrite (Py); violarite (Viol); millerite (Mill); the liquid (L)

The representative points of pentlandite in the Fe-Ni-S system (figure 9 (A, B)), proposed by A. Naldrett [16] are located below the barrier S-enriched isolating phase, from the phases plentiful with metals, and attracted to the monosulfide solid solution (mss) field. The pyrrhotite in this system is located on the Fe-S side, apart from that its representative points lie within mss barrier, IPGM, PtTe_2 and Ag_2Te minerals availability in pyrrhotite, and in pentlandite may be probably explained by. In the Cu-Fe-S system (figure 9 (C)), copper pyrite is located in the $\text{iss} + \text{Py} + \text{S (L)}$ field, taking into account the sulfur excess, which, apparently, conforms to the freezing temperature decrease in copper pyrite.

Considering the sequence of mineral phases separation and isothermal sections analysis of the Fe-Ni-S condensed system [16], the genesis of the sulfide copper-nickel mineralization of the Kara-Turgai type seems to subordinate to the following scheme.

In view of the present temperature version and the mss formation, $\text{Fe}_{(1-x)}\text{S}$ (troilite) may be assumed to appear at 1190°C , on the Fe-S line, which spreads to the inner part of the system at the 1100°C , forming the mss field (figure 9 (A)). At this stage mss is enriched in Fe and depleted of Ni in relation to the liquid it is in balance with as suggested by A. Naldrett [16]. Afterwards, mss, formed from a fractionated liquid in the proceeding process of fractional freezing, according to D. Ibel and A. Naldrett [18], becomes enriched by Ni. By A. Sugaki and A. Kitakatse view [19] as a result of the reaction between mss and the liquid, a high-temperature polymorphic pentlandite is formed at 865°C (Figure 9 (B)). Following the A.A. Fedorov and A.V. Sinyakov materials [20], siegenite was instead of vaseat ($\text{Ni}_3 \pm x\text{S}_2$) in our system it can be assumed, then the temperature descended below 806°C in the magmatic chamber. The liquid equals to mss at 850°C may be inferred to be enriched with Cu, but depleted by Ni with regard to mss taking into account the compound of the studied sulfides and accept the conclusions of J. Craig and G. Kullerud [21]. Considering the isothermal sections of the Cu-Fe-S system (Fig. 9 (C)), then the intermediate solid solution (iss) is submitted to be separated from the Cu-containing mss. Iss is presumably dissolved into copper pyrite-pyrrhotite mineral phases with the temperature decrease (up to 400°C or less). The millerite in the Fe-Ni-S system (figure 9 (D)) allows us to assume, in accordance with J. Craig [22], that mss was divided into mss_1 and mss_2 + millerite phases at 250°C . This also corresponds with the K. Misra and M. Fleet conclusions [23] that millerite and, unidentified Heazlewoodite mineral, are sustained at low temperatures.

Conclusions. The abovementioned states that the mineral inclusions formation of copper-nickel ores containing platinum-mineral mineralization was proceeded with a temperature decrease, which varied from 1200°C to $100\text{--}135^{\circ}\text{C}$. Apparently, such a rapid temperature decrease of the magmatic liquid has contributed to the minerals retention of the platinum group and rare earth elements during its fractionation and could proceed under hypabyssal conditions. Titano-haematite in picrites fairly corresponds with this assumption. Titano-haematite is known to be formed at a high oxidation potential of oxygen, which is a direct evidence of the rocks formation containing it under hypabyssal conditions. This is justified by iron in the sphalerite, since an increase in the amount of iron in the sphalerite structure occurs when the pressure decreases; as well as the altaite formed in the conditions of the hydrothermal mid-temperature mineral formation process as a late mineral. The lead selenide and altaite availability, as well as a high content of lead in other sulfides, indicates that igneous, including ore processes occurred in the continental crust. The rare-earth elements Ce, Dy, Er, Y discovered by us, in the sulfides compound, against the platinoids, substantially increase the industrial interest in the potential ores of the picrite-diorite of Kara-Turgai assemblage. The platinoids and rare earth elements within the segregation droplets only, represented by pyrrhotite, copper pyrite, pentlandite and sphalerite, allows conducting technological testing of Kara-Turgai type ores more properly.

The above facts totally indicate the ore formation of Cu-Ni- (PGM) - (REE) ores of the Kara-Turgai type occurred within the open magmatic system. Recent studies [24] have demonstrated that open magmatic systems are favorable for the concentration of a large number of sulfides. Additionally was specified [24] sulfur input from enclosing rocks is not required for the Cu-Ni- (PGM) - (REE) ores formation in open magmatic systems. This also inspires that large masses of Cu-Ni- (PGE) - (REE) ores can be placed in the benthic and root zones of the picrite-diorite of the Kara-Turgai assemblage.

The rocks formation of the Kara-Turgai assemblage is apparently associated with repeated impulses of the magma chamber against compression processes during the formation of the Rodinia supercontinent should be specially emphasized [25].

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REFERENCES

- [1] Mihajlov N.P., Semenov Ju.L. Karaturgajskij diabaz-pikritovyy kompleks v Kazakhstane i nekotorye voprosy petrologii pikritov. (Kara-Turgai diabase-picritic assemblage in Kazakhstan and some issues of petrology picrites. Soviet geology) // Sovetskaja geologija. 1965. N 3. P. 43-58.
- [2] Bejseyev O.B. Sul'fidnoe medno-nikel'-kobal'tovoe orudnenie v massivah ul'traosnovnyh i osnovnyh porod bassejna reki Karaturgaj (Severnyj Ulytau) (Sulfide copper-nickel-cobalt mineralization in massifs of ultrabasic and basic rocks of the Kara-Turgai River basin (Northern Ulytau)). Alma-Ata: ONTI KazIMS, 1968. P. 55.
- [3] Bejseyev O.B. O geologicheskikh osnovah poiskov sul'fidnyh medno-nikelevykh rud v Severnom Ulytau // Geologija, razvedka i metody izuchenija mestorozhdenij poleznykh iskopaemykh. (Geological foundations of the sulfide copper-nickel ores investigation in the Northern Ulytau // Geology, exploration and study methods of mineral deposits). Alma-Ata: KazIMS, 1969. P. 55-57.
- [4] Vishnevskaja I.I., Trusova I.F. Zapadno-Ulytauskij pojas ul'traosnovnyh i osnovnyh porod. (Western Ulytau belt of ultrabasic and basic rocks. Geology and exploration) // Geologija i razvedka. 1967. N 11. P. 32-43.
- [5] Mihajlov N.P., Injahn M.V., Ljapichev G.F. Petrografija Central'nogo Kazakhstana. Vol. 2. Intruzivnye formacii osnovnyh i ul'traosnovnyh porod. (Petrography of the Central Kazakhstan. Vol. 2. Intrusive formations of basic and ultrabasic rocks). M.: Nedra, 1971. 360 p.
- [6] Bejseyev O.B., Bejseyev A.O., Al'piev E.A., Kashkimbaev K.K. Geologicheskie i geotekhnologicheskie kriterii ocenki promyshlennykh perspektiv novykh rudopojavlenij cvetnykh, blagorodnykh metallov i nerudnogo syr'ja Zheskazgan-Ultauskogo rajona kak materialov dlja vysokikh tehnologij. Almazy, zoloto i blagorodnye metally. Geomaterialy. (Geological and geotechnological criteria for assessing the industrial prospects of new ore occurrences of non-ferrous, precious metals and nonmetallic raw materials of the Zheskazgan-Ultausk region as materials for high technologies. Diamonds, gold and precious metals. Geomaterials). 2010. P. 137-141.
- [7] Chudin S.S. K probleme platinosnosti neдр Kazakhstana. Gorno-Geologicheskij Zhurnal. (The problem of platinum bearing capacity of Kazakhstan. Mining-Geological Periodical). 2012. N 3-4. P. 31-32.
- [8] Bajbatsha A. B., Djusembaeva K. Sh., Mamanov E. Zh. Mineralogija rud medno-nikelevogo rudopojavlenija «Karatorgaj» // Izvestija NAN RK. Serija geologii i tehniceskikh nauk. (Mineralogy of ores of copper-nickel ore occurrence "Karatorgai") // NAS RK. Series of geology and engineering sciences). 2015. N 5. P. 90-95.
- [9] Mihajlov N.P. Intruzivnye ofiolitovye komplekсы Vostochnogo Kazakhstana // V kn.: Osnovnye i ul'traosnovnye magmaticheskie formacii i podvizhnyh pojasov. (Intrusive ophiolite complexes of the East Kazakhstan. In: Basic and ultrabasic magmatic formations and moving belts) "Trudy SETEJ", nov. ser. Vol. 80. L.: Nedra, 1962. P. 109-223.
- [10] Polovinkina Ju.I. Osnovnye i ul'traosnovnye porody Karsakpaja v svjazi s problemoj genezisa zhelezistykh kvarcitov. Gosgeolizdat. (Basic and ultrabasic rocks of Karsakpai in connection with the problem of ferruginous quartzites genesis). 1952. 87 p.
- [11] Antonjuk R.M., Evseenko R.D., Ismailov H.K., Maslova I.G. Problemy stratigrafii i metamorfizma dokembrija i nizhnego paleozoja Ulytau. Chast' I. Stratigrafija. (Stratigraphy and metamorphism issues of Precambrian and Lower Paleozoic of Ulytau. Part I. Stratigraphy) // Izvestija NAN RK. Serija geologicheskaja. 2009. N 3. P. 4-18.
- [12] Geologicheskaja karty Kazahskoj SSR, masshtaba 1:500 000, serija Central'no-Kazahstanskaja. Objasnitel'naja zapiska. (Geological maps of the Kazakh SSR, scale 1:500 000, series Central Kazakhstan. Explanatory letter). Alma-Ata, 1981. 322 p.
- [13] Stepanec V.G., Levin V.L., Savel'eva N.A., Hakimzhanov M., Makat D.K. Jevoljucija pikritovogo magmatizma i rudoobrazovanie v Ulytauskom rajone central'nogo Kazakhstana // Izvestija NAN RK. Serija geologii i tehniceskikh nauk. (Evolution of picrite magmatism and ore formation in the Ulytau district of the Central Kazakhstan // NAS RK. Series of geology and engineering sciences). 2017. N 1. P. 19-36.
- [14] Vishnevskij A.V., Cherdanceva M.V. Raskristallizovannye kapli sul'fidnogo rasplava iz massiva Rudnyj v S-Z Mongolii: model'nyj ob'ekt dlja izuchenija raspredelenija i form nahozhdenija jelementov-primesej pri kristallizacii prirodnykh sul'fidnykh zhidkostej. Materialy konferencii // Novosib. gos. un-t. Novosibirsk RIC NGU, (Crystallized drops of sulfide liquid from the Rudny massif in the NW of Mongolia: a model object for studying the distribution and forms of finding impurity elements during the crystallization of natural sulfide liquids. Conference materials). 2014. P. 10-11.
- [15] Marakushev A.A., Panejah N.A., Marakushev S.A. Sul'fidnoe rudoobrazovanie i ego uglevodorodnaja specializacija. (Sulphide ore formation and its hydrocarbon specialization). M.: GEOS, 2014. 184 p.
- [17] Cabri L.J. New Data on Phase relations in the Cu-Fe-S system // Economic Geology. 1973. Vol. 68. P. 443-454.
- [16] Naldrett A.Dzh. Magmaticheskie sul'fidnye mestorozhdenija medno-nikelevykh i platinometal'nykh rud. SPb.: SPbGU, 2003. 487p.
- [18] Ebel D., Naldrett A.J. Experimental fractional crystallization of Cu- and Ni-bearing Fe-sulfide liquids // Economic Geology. 1996. Vol. 91. P. 607-621.
- [19] Sugaki A., Kitakaze A. High form Pentlandite and its thermal stability // American Mineralogist. 1998. Vol. 83. P. 133-140.
- [20] Frolov A.A., Lapin A.V., Tolstov A.V. i dr. Karbonatity i kimberlity. M.: NIA-Priroda, 2005. 540 p.
- [21] Craig J.R., Kullerud G. The Cu-Zn-S system // Carnegie Inst. Wash. Year Book 67. 1969. P. 177-179.
- [22] Craig J.R. Pentlandite-pyrrhotite and other low-temperature relations in Fe-Ni-S systems // American Journal of Science. 1973. Vol. 273-A. P. 496-510.
- [23] Misra K.C., Fleet M.E. The chemical compositions of synthetic and natural pentlandite assemblages // Econ. Geol. 1973. Vol. 68. P. 518-539.
- [24] Ripley E.M., Li C. Sulfide Saturation in Mafic Magmas: Is External Sulfur Required for Magmatic Ni-Cu-(PGM) Ore Genesis? // Society of Economic Geologists, Inc. Economic Geology. 2013. Vol. 108. P. 45-58.

[25] Li Z.X., Bogdanova S.V., Collins A.S., Davidson A., De Waele B., Ernst R., Evans D., Fitzsimons I., Fuck R.A., Gladkochub D.P., Jacobs J., Karlstrom K.E., Lu S., Natapov L., Pease V., Pisarevsky S.A., Thrane K., Vernikovsky V. How not to build a supercontinent: A reply to J.D.A. Piper. Precambrian Research. 2009. 174 (1-2): P. 208-214.

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СОТУСТІК ҰЛЫТАУДЫҢ ҚАРАТОРҒАЙ КЕШЕНІНІҢ ПИКРИТ СУЛЬФИДЫНДАҒЫ СІРЕК КЕЗДЕСЕТІН ЭЛЕМЕНТТЕРДІҢ ЖӘНЕ ПЛАТИНОИДТАРДЫҢ ҚҰРАМЫ ЖӘНЕ ФОРМАСЫ

Аннотация. Біздің зерттеулер нәтижесінде қараторғай кешенінің пикритында ертеден белгілі мыс сульфиді, никель, кобальт (халькопирит, пентландит, кобальтитникелин, герсдорфит) басқа алғаш рет виоларит, сфалерит, зигенит, платина теллурид (мочент), күміс теллурид, қорғасын теллурид (алтаит), қорғасын селенид, ирид тобының металлдарының қатты ерітінділері (Ir, Os, Ru), сирек кездесетін элементтер (Dy, Er, Y, Ce). Сульфидтер үш минералды ассоциация құрайды. Бірінші екі ассоциация домалақ және эллипсті созылған формасы бар ликвациялық «тамшы» құрайды, үшіншісі минералды ассоциация – дұрыс емес өткір-бұрышты формалы шығыстар. Нақытланған, егер пирротин, халькопирит, пентландит, виоларит және сфалиттер құралған бірінші ассоциацияның ликвациялық тамшыларында ғана сульфидтің құрамында платиноидтар болады. Екінші ассоциация сульфидтары құрамында платиноидтар жоқ, олар пирротин, халькопирит, сфалеритпен ұсынылған. Үшінші ассоциация сульфидтері пирротин, халькопирит, сфалерит және пиритпен ұсынылған. Барлық минералогиялық ассоциациялар құрамында магнетит бар, олар еределі түрде пикриттер және апопикритті оливиниттер горизонттарына түстәлған. Пикритті диабаз құрамында сульфидтердің кірістері анықталған: пентландит, зигенит, миллерит, пирит, галенит. Cu- Ni- (платина топтарының минералдары (ПТМ)) – (сирек кездесетін элементтері СКЭ) қараторғай кен түрінің, сульфидтардың өндірістік массаларының шоғырлануына қолайлы, ашық магматикалық жүйе шегінде пайда болуы нақтыланған.

Түйін сөздері: Ұлытау, мыс-никельді кеніштер, платиноидтар, сирек кездесетін элементтер.

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СОСТАВЫ И ФОРМЫ НАХОЖДЕНИЯ ПЛАТИНОИДОВ И РЕДКОЗЕМЕЛЬНЫХ ЭЛЕМЕНТОВ В СУЛЬФИДАХ ПИКРИТОВ КАРАТУРГАЙСКОГО КОМПЛЕКСА СЕВЕРНОГО УЛЫТАУ

Аннотация. В результате наших исследований, наряду с ранее известными сульфидами меди, никеля и кобальта (халькопиритом, пентландитом, кобальтином, никелином, герсдорфитом), в пикритах каратургайского комплекса были впервые обнаружены виоларит, зигенит, теллурид платины (мочент), теллурид серебра, теллурид свинца (алтаит), селенид свинца, твердые растворы металлов иридиевой группы (Ir, Os, Ru), редкоземельные элементы (Dy, Er, Y, Ce). Сульфиды формируют три минеральных ассоциации. Первые две образуют ликвационные «капли», имеющие округлую и эллипсоидно-удлиненную форму, а третья минеральная ассоциация – выделения неправильных остроугольных форм. Установлено, что платиноиды в сульфидах присутствуют только в ликвационных каплях первой ассоциации, которые сложены пирротинном, халькопиритом, пентландитом, виоларитом и сфалеритом. Сульфиды второй ассоциации не содержат платиноидов и представлены пирротинном, халькопиритом, сфалеритом. Сульфиды третьей ассоциации представлены пирротинном, халькопиритом, сфалеритом, пиритом. Все три минералогические ассоциации содержат магнетит и, как правило, приурочены к наиболее дифференцированным горизонтам пикритов и апопикритовых оливинитов. В составе пикритовых диабазов обнаружены единичные включения сульфидов: пентландит, зигенит, миллерит, пирит, галенит. Постулируется, что рудообразование Cu-Ni-(минералов платиновой группы [МПГ]) – (редкоземельных элементов [РЗЭ]) руд каратургайского типа происходило в пределах открытой магматической системы, благоприятной для накопления промышленных масс сульфидов.

Ключевые слова: Улытау, медно-никелевые руды, платиноиды, редкоземельные элементы.