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Satbayev University

ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ
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NAS RK is pleased to announce that News of NAS RK. Series of geology and technical sciences scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of geology and technical sciences in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of geology and engineering sciences to our community.

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**ACCESSORY COPPER ORE MINERALS AS A KEY ISSUE IN
UNDERSTANDING THE GENESIS OF THE MAYATAS META-
CARBONATITE ORES (ULYTAU, CENTRAL KAZAKHSTAN)**

Abstract. The copper-rich ores of the Maike occurrence are a classic magmatic (hydrothermal) association of sulphides located as a vein within carbon-bearing muscovite-clinochlore-quartz schists. These ores are sub-solidus (<600°C) products of decomposition of intermediate solid solution (ISS), which was crystallised (950-800°C) from highly fractionated sulphide liquid enriched with the elements: Pt, Pd, Ir, Ru, Rh, Os, Ag, As, Bi, Cd, Pb, Te, Zn, Y, Ce, La.

Study of accessory minerals from the Maike copper ores occurrence, including sulphoarsenides and tellurides (containing platinoids, Ni, Pd, Sb, Ag, Pb and Co), allowed us to describe the mineral formation sequence of carbonatites genetically connected to intrusive and hydrothermal high-temperature activation of ultrabasic magmatism, possibly associated in early Paleozoic with a suprasubduction zone. Pentlandite of extremely low quantity contains Co, and pyrite is rich in Ni. Lead is held in galena, while Zn and Cd are in sphalerite. Rare earth elements (REE) are associated with phosphates and fluorophosphates.

Platinoids are not concentrated in nonferrous metal sulphides (chalcopyrite, pentlandite, galena and sphalerite) and form the minerals we have identified (testibiopalladite ($Pd(Sb,Bi)Te$), sperrylite ($PtAs_2$)). They also are part of zonal sulphoarsenides and tellurides (melonite ($NiTe_2$) and vavrinite (Ni_2SbTe_2)). The zonal nickel cobaltite is the richest in Pt, Ir, Rh, Ru, Os.

The rhenium sulphides found in chalcopyrite and, extremely rarely, in pyrite, are of mineralogical significance only.

The association of copper ores, carbonates (siderite, apatite), titanite, chrome-spinel, albite, quartz, garnet (pyrope-almandine series), chromium-bearing muscovite and chromium-rich clinochlore and their spatial relationship with graphite-quartz-chlorite schists allow us to consider these rocks as part of the silicate-carbonate-carbonaceous complex, reflecting the composition of mantle growth melt.

Key words: Ulytau, carbonatite, copper ores, platinoid, sulphide, sulfarsenide, arsenide, antimonide, rhenium mineral.

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МАЯТАС КЕҢДІ АУДАНЫ (ҰЛЫТАУ, ОРТАЛЫҚ ҚАЗАҚСТАН) МЕТАКАРБОНАТИТТЕРИНІң РУДАГЕНЕЗ ПРОЦЕСТЕРИН ТҮСІНУ КІЛТІ – МЫС КЕҢДЕРІНІң ҚОСЫМША МИНЕРАЛДАРЫ

Аннотация. Мысқа бай Майке кенбілінімдерінің рудалары құрамында көміртегі бар мусковит-клинохлор-кварцты тақтатастары ішінде желі түрінде орналасқан сульфидтердің классикалық магмалық / гидротермалық ассоциациясы. Бұл рудалар жоғары фракцияланған Pt, Pd, Ir, Ru, Rh, Os, Ag, As, Bi, Cd, Pb, Te, Zn, Ce, La элементтерімен байыған сульфидті сұйықтықтан (950-800°C) кристалданған аралық қатты ерітіндінің (АҚЕ) субсолидустық (<600°C) ыдырау өнімдері болып табылады.

Майке кенбілініміндегі мыс рудаларының аксессорлық минералдарын олардың арасында сульфоарсенидтер мен теллуридтерге (құрамында платиноидтар, Ni, Pd, Sb, Ag, Pb және Co) назар аударып зерттеу, ерте палеозойда субдукция үсті аймақпен біріктірілген ультранегізді магматизмнің интрузивті және гидротермалды жоғары температуralы белсенділігімен генетикалық байланыстаі карбонатиттердің минералдық түзілу тізбегін дәлелді түрде сипаттауға мүмкіндік берді. Мөлшері өте аз пентландиттің құрамында Со бар, ал пирит Ni-мен байытылған. Қорғасын

галенитте, ал Zn және Cd сфалеритте кездеседі, сирек жер элементтер (СЖЭ) фосфаттар мен фторфосфаттармен байланысты.

Платиноидтар түсті металл сульфидтерінде (халькопирит, пентландит, галенит және сфалерит) шоғырланбайды және біз анықтаған мына минералдарды құрайды: тестибиопалладит ($Pd(Sb,Bi)Te$), сперрилит ($PtAs_2$), сонымен қатар белдемді сульфоарсенидтер мен теллуридтердің (мелонит ($NiTe_2$), вавринит (Ni_2SbTe_2)) құрамына кіреді Pt, Ir, Rh, Ru, Os элементтеріне ең бай – белдемді никельді кобальт. Халькопиритте және өте сирек пиритте кездесетін рений сульфидтері тек минералологиялық мәнге ие.

Мыс рудаларының, карбонаттардың (сидерит, апатит), титаниттің, хромшпинельдің, альбиттің, кварцтың, гранаттың (пиро-альмандин қатарының), құрамында хром бар мусковиттің және хроммен байытылған клинохлордың қауымдастыры және олардың графит-кварц-хлоритті тақтатастармен кеңістіктік байланысы бұл жыныстарды мантиядан шыққан өсу балқымасының құрамын көрсететін силицит-карбонат-көміртекті кешенниң құрамдас бөлігі ретінде қарастыруға мүмкіндік береді.

Түйін сөздер: Ұлытау, карбонатиттер, мыс рудалары, платиноидтар, сульфидтер, сульфоарсенидтер, арсенидтер, антимонидтер, рений минералдары.

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АКЦЕССОРНЫЕ МИНЕРАЛЫ МЕДНЫХ РУД КАК КЛЮЧ К ПОНИМАНИЮ ПРОЦЕССОВ РУДОГЕНЕЗА МЕТАКАРБОНАТИТОВ МАЯТАССКОГО РУДНОГО РАЙОНА (УЛЫТАУ, ЦЕНТРАЛЬНЫЙ КАЗАХСТАН)

Аннотация. Богатые медью руды проявления Майке представляют собой классическую магматическо/гидротермальную ассоциацию сульфидов, расположенную в виде жилы в составе углеродсодержащих мусковит-клинохлор-кварцевых сланцев. Эти руды являются субсолидусными (<600°C) продуктами распада промежуточного твердого раствора (ISS), который кристаллизовался (950-800°C) из высокофракционированной сульфидной жидкости, обогащенной Pt, Pd, Ir, Ru, Rh, Os, Ag, As, Bi, Cd, Pb, Te, Zn, Y, Ce, La.

Изучение акцессорных минералов медных руд проявления Майке, среди которых основное внимание уделено сульфоарсенидам и теллуридам (содержащим платиноиды, Ni, Pd, Sb, Ag, Pb и Co), позволило аргументировано описать последовательность минералообразования карбонатитов, генетически связанных с интрузивной и гидротермальной высокотемпературной активизацией ультраосновного магматизма, вероятно, сопряженного в раннем палеозое с надсубдукционной зоной. Пентландит, количество которого крайне мало, содержит Co, а пирит обогащен Ni. Свинец содержится в галените, а Zn и Cd – в сфалерите, редкоземельные элементы (РЗЭ) связаны с фосфатами и фторфосфатами.

Платиноиды не концентрируются в сульфидах цветных металлов (халькопирит, пентландит, галенит и сфалерит) и образуют выявленные нами минералы: тестибиопалладит ($Pd(Sb, Bi)Te$), сперрилит ($PtAs_2$), а также входят в состав зональных сульфоарсенидов и теллуридов: мелонит ($NiTe_2$), вавринит (Ni_2SbTe_2). Наиболее богатым Pt, Ir, Rh, Ru, Os является зональный никелистый кобальтин.

Сульфиды рения, обнаруженные в халькопирите и, крайне редко, в пирите, имеют только минералогическое значение.

Ассоциация медных руд, карбонатов (сидерит, апатит), титанита, хромшпинели, альбита, кварца, граната (пироп-альмандинового ряда), хромсодержащего мусковита и обогащенного хромом клинохлора и их пространственная связь с графит-кварц-хлоритовыми сланцами позволяют рассматривать данные породы составной частью силицит-карбонат-углеродистого комплекса, отражающего состав ростового расплава мантийного происхождения.

Ключевые слова: Улытау, карбонатиты, медные руды, платиноиды, сульфиды, сульфоарсениды, арсениды, антимониды, минералы рения.

Introduction. Previously, we reported the results of mineralogical studies of rhenium sulphides of copper ores of fracture-type carbonatites of the Mayatas ore district of Northern Ulytau (Stepanets, 2019 a: 8), which briefly considered ore formation stages for copper ores of the Maike occurrence (Levin, 2020: 16). In the present paper, we will elaborate on the composition of accessory minerals, focusing on sulfarsenides that contain light and heavy platinoids, Ni and Co, and tellurides of Ni, Pd, Sb, Ag, and Pb. It can allow us to describe a possible sequence of mineral formation of carbonatites, genetically connected with ultrabasic magmatic probably linked to the early Palaeozoic supra-subduction zone, and to later high-temperature magmatic-hydrothermal. A formation of carbonatites during Late Proterozoic mantle plume, the product of melting the subducted oceanic crust (Hofmann, 1997: 10), cannot be excluded.

Research materials and methods. The core sample for our study was taken from the π-10 borehole, provided by the “Mayatas” company, which has been prospecting and exploring the area within the Mayatas ore district for the last ten years.

Minerals of copper ores have been identified in polished sections made from the borehole core in the Laboratory of Mineralogy at the Satpayev IGS (Almaty) using the energy dispersive spectrometer (INCA Energy - the Oxford Instruments, UK) with the following characteristics: accelerating voltage 25 kV, probe current 25 nA, probe diameter 1-2 μm), mounted on electron-probe microanalyser Superprobe 733, JEOL (Japan). Comparison samples and analytical lines for respective elements: Cu, Fe, S (CuFeS_2 , Cu K, Fe K, S K); Pb (PbS, Pb L); Mo (MoS_2 , Mo L), Re (Re M), Ni (Ni K), Zn (Zn K), Rh (Rh L), Sb (Sb L), Bi (Bi L), Sn (Sn L).

Geological structure. The Mayatas ore district includes a group of occurrences and small deposits of gold, REE, copper, and lead exposed in the Kara-Turgai, Boshke, and Maike interfluves. There, they are localised along the fault system trending to north and north-east and extending over 8 km. Its southwestern edge begins at the Mayatas wintering site and terminates at the headwaters of the Boshke River, which flows into the Kara-Turgai River. The Mayatas ore district is part of the Bozai-Sulutas mineralisation zone associated with the outcrops of fracture-type ultrabasic intrusions extending more than 80 km in the meridional direction.

The Maike ore occurrence is located north-east of the village of Mayatas in the basin of the river of the same name flowing into the Kara-Turgai River. A large part of the Mayatas ore district is overlain by a thick Mesozoic weathering crust, where yttrium-rare earth mineralisation is known practically within the Maike occurrence contour (Nsanov, 1993: 17). To the south, weathering crusts of carbonaceous-dolomitic shales with lead ores of the Zarechnoye deposit are exposed 3.5 km away from the Maike manifestation. Similar ores are also known in the source area of the Boshke River. Gold-quartz ore occurrences are encountered throughout the fault zone but not in-depth. According to Muratbekov (2017), all the occurrences mentioned above were studied by the “Mayatas” LLP in recent years.

The litho-geochemical anomaly within the Maike ore occurrence contour has a sub-meridional strike up to 4.0 km, 20 to 400 m wide. The mineralised zone at a depth of 120 m wedges out and is carrot-shaped in cross-section, with a thickness of more than 30 m at the surface, dipping steeply (70-80°) to the east along its sub-meridional strike. The mineralisation zone with copper ores no thicker than 35 cm is confined to outcrops of the graphite-quartz-rutile-siderite-muscovite-chlorite schists, part of the graphite-quartz-chlorite sequence (Stepanets, 2019 a:

8), historically identified in the Early Proterozoic Aralbay Series (Vishnevskaya, 1967: 11).

According to Vishnevskaya (1967), the accessory minerals in graphite-quartz-rutile-siderite-muscovite-chlorite schists are represented by apatite, titanite, zircon, tourmaline, garnet (3%), graphite (up to 12%). The chemical composition of garnet: almandine ($\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$) 50 mol%, grossular ($\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$) 32 mol%, pyrope ($\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$) 18 mol%. Zircon, apatite, and titanite often form rounded grains, 0.02 mm in size, which appears to result from their movement in the magmatic melt (Litvin, 2012 a: 33). The range of accessories and the normative mineral composition of the quartz-rutile-siderite-chlorite and siderite-muscovite-chlorite schists do not exclude the possibility (Stepanets, 2019 a: 8) of these rocks to be the outcome of metamorphism of ultra-mafic rocks. According to Litvin (2009 b: 12, 2012 a: 33), a highly effective diamond-forming medium is a silicate-coal-bearing carbonatite melt. This is confirmed by the finds of diamonds in the graphite-muscovite-feldspar-quartz schists of Northern Ulytau (Chudin, 2012: 4). The role of carbon in the formation of copper ores is traced by the presence of accessory minerals such as apatite and tellurides of Pd and Bi (Blanks, 2020: 9), Ag, and Pb (Shaibekov, 2013: 108). In carbonate-sulphide associations, palladium tellurides and bismuthides are spatially related to copper ores, where carbon is of mantle origin (Graham, 2017: 23).

In existing volumetric models of vertical mineralisation zoning of the plutonic-type carbonatite massifs (Frolov, 2005: 540), the thorium-rare-earth occurrences with copper, lead, and zinc sulphides are usually located above hematite and barite-strontianite deposits, which are confined to ankerite-dolomite veins, such as the Zarechnoye and Kurgasyn deposits (Bespaev, 1997: 152). The type we describe is characterised by the presence of graphite-muscovite-clinochlore and graphite-muscovite-clinochlore-carbonate-quartz veins containing the platinum- and REE-rich copper ores.

Results. Copper ore mineralogy. Main ore minerals. The Maike occurrence ores are 95% stoichiometric chalcopyrite (Stepanets, 2019 a: 8; Levin, 2020: 16), where platinum group elements (PGE) and REEs impurities are not detected. Significantly less frequent in copper ores are:

- violarite (FeNi_2S_4), weakly enriched in Co (<1.25%), generally characterised by an excess of sulphur and iron;
- pentlandite ($\text{Fe}_4\text{Ni}_4(\text{Fe},\text{Co},\text{Ni})\text{S}_8$) is extremely rare and enriched with sulphur;
- pyrite (FeS_2), with Ni (0.41-3.71%) constantly present as an impurity; high concentrations of Ni and, much less frequently, Cu (0.63-0.75%) are typical of crystals associated with violarite;
- pyrrhotite (FeS) is rare and characterised by excess sulphur;

- sphalerite (Zn, Fe)S is extremely rare and often occurs together with micro-inclusions of cobaltite. As a rule, sphalerite contains Cd (0.66-0.76%), Cu (0.80-1.30%) and Fe (6.77-7.03%);

- sphalerite, found in association with acanthite, does not contain Cd but is enriched in Fe (8.45%) and Cu (2.46%).

Accessory ore minerals. Chalcopyrite contains micro-inclusions of the following minerals: sperrylite ($PtAs_2$); testibiopalladite ($Pd(Sb, Bi)Te$); hessite (Ag_2Te) and idiomorphic inclusions of minerals of the cobaltite-gersdorffite series with platinoid admixtures (Pt, Ir, Rh, Ru, Os); vavrinite (Ni_2SbTe_2) and melonite ($NiTe_2$) containing only Pd; violarite ($FeNi_2S_4$) with inclusions of hessite (Ag_2Te). Several acanthite (Ag_2S) and galena (PbS) grains were found. Altaite ($PbTe$) was encountered. Phosphates and fluorophosphate containing Y and elements of the cerium subgroup (light La, Ce, Pr, Nd, Sm) are also identified. Molybdenite and rhenium sulphides are extremely rare. Considering the importance of PGE presence in zonal sulfarsenides and PGM proper, which, as well as REE, serve as reliable thermobarometers for understanding the ore-forming processes (Dare et al., 2010), we consider their compositions and relations with main ore minerals in detail.

Rhenium sulphides. A special group of rare sulphides are rhenium's minerals, and mineral phases described previously (Levin, 2020: 16). Here we mention only those minerals helpful in determining the sequence of the copper ore formation: $Re(Mo, Cu)S_3$, $(Re, Mo)S_2$, ReS_2 , $(Re, Fe)(Pb, Bi)S_3$, $(Re, Pb, Fe)S_2$, $(Pb, Re)S_2$. Figure 1 shows forms of rhenium sulphides.

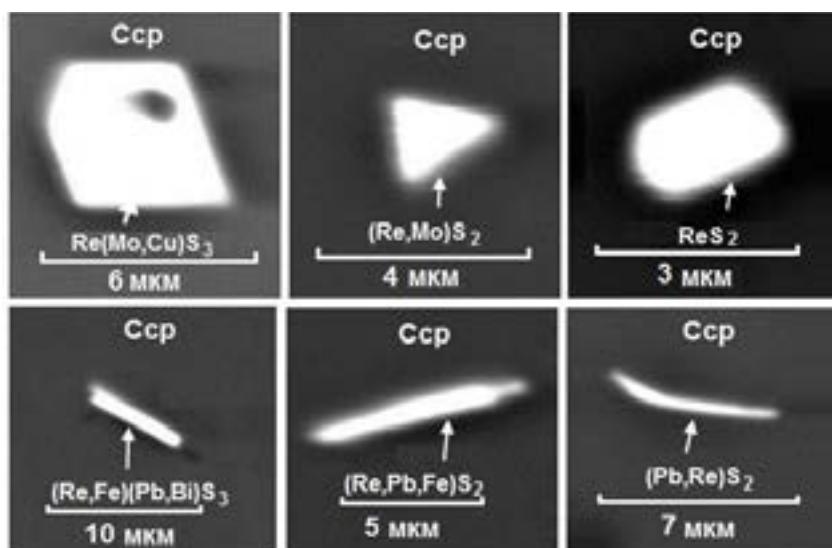


Figure 1. Microcrystals of rhenium sulphides (Levin, 2020: 16).
The back-scattered electron image (BEI)

Sulfarsenides. Intermediate members of the cobaltite-gersdorffite series mainly represent sulfarsenides of Ni and Co: nickel-containing cobaltite and less frequently cobaltite, ferro-cobaltite and gersdorffite. They form minerals of two types: zonal and non-zonal crystals, forming, in the plane of polished sections, chains of crystals and single well-cut rectangular, rhombic, pentagonal, and hexagonal plates (figure 2). The maximum size of single plates does not exceed 30 μm ; as a rule, they are 5 to 15 μm . The association of cobaltite with sphalerite is quite common. The crystals are often framed by melonite, testibiopalladite, silver telluride and magnetite (figure 2). In the composition, arsenic significantly predominates over sulphur irrespective of the level of Co and Ni.

Gersdorffite (NiAsS) has stoichiometric composition $(\text{Ni}_{1.02}\text{As}_{0.99}\text{S}_{0.99})$ with insignificant amount of impurities Sb (1.60%), Fe (0.2%) and Co (0.1%) (table 1).

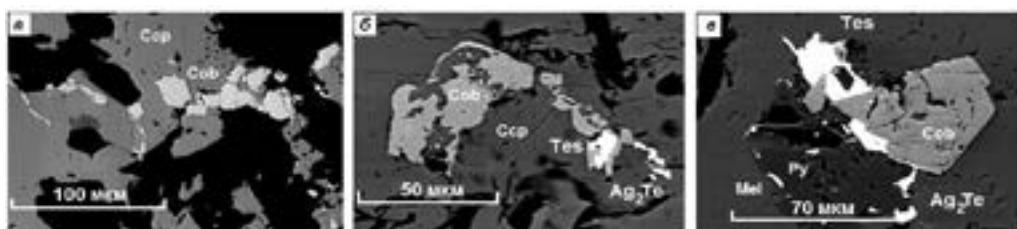


Figure 2. Polished section of ore minerals from core no. π-10: a-б – the nature of the relationship between chalcopyrite (Ccp) and the cobaltite-gersdorffite series mineral (Cob), which forms solid masses and sometimes crystals, в – the cobaltite-gersdorffite series mineral ingrown with testibiopalladite (Tes) and silver telluride. Pyrite (Py) and melonite (Mel) in chalcopyrite. BEI

Minerals of cobaltite-gersdorffite series $(\text{Co}, \text{Fe})\text{AsS} - (\text{Ni}, \text{Fe})\text{AsS}$ are among the most frequent micro-inclusions in chalcopyrite. The varieties are represented by single crystals and aggregates (tables 1 and 2). Aggregate crystals do not contain platinoids (except for Pd), while single crystals may contain them and appear as zonal. Cut such crystals in polished sections often show a central nucleus-germ with high platinoid content. In the case of PGE present in the analysis and the cut of the polished section does not pass through the centre of the grain, the core cannot be observed. In some single crystals, the platinoids are not fixed, probably, because of the low concentration of the latter.

Table 1. Results of microprobe analyses (wt. %) of gersdorffite and nonzonal crystals of minerals of the cobaltite-gersdorffite series.

No.	Mineral	S	Fe	Cu	Co	Ni	As	Sb	Σ
1	2	3	4	5	6	7	8	9	10
Nonzonal crystals									
1	Gersdorffite	19.00	0.20	0.00	0.10	35.70	44.30	1.60	99.30

2	Cobaltite	20.23	4.83	1.39	25.00	6.05	42.50	0.00	100.01
3	Mineral of the cobaltite-gersdorffite series	20.67	5.69	2.14	23.90	6.19	41.41	0.00	99.99
4		20.72	5.97	2.93	20.46	7.68	42.25	0.00	100.10
5		19.80	5.43	1.48	21.08	8.69	42.51	0.00	98.99
6		20.11	5.37	1.08	20.46	9.20	42.98	0.00	99.20
7		20.23	6.70	0.80	13.54	15.33	44.43	0.00	101.03
8		20.52	7.22	1.28	13.37	14.86	43.87	0.00	101.12
9		19.77	8.09	2.00	12.28	14.88	42.98	0.00	100.01
10		20.04	8.20	0.00	10.03	18.21	43.52	0.00	99.99
11		18.96	7.36	1.22	9.37	17.75	43.84	0.00	98.50
12		18.68	6.29	0.33	7.75	21.17	46.37	0.00	100.59
Structural formula based on three atom									
1	Gersdorffite	0.99	0.00	0.00	0.00	1.02	0.99	0.00	
2	Cobaltite	1.03	0.14	0.04	0.69	0.17	0.93	0.00	
3	Mineral of the cobaltite-gersdorffite series	1.05	0.17	0.05	0.66	0.17	0.90	0.00	
4		1.05	0.17	0.08	0.57	0.21	0.92	0.00	
5		1.02	0.16	0.04	0.59	0.257	0.94	0.00	
6		1.04	0.16	0.03	0.57	0.26	0.94	0.00	
7		1.00	0.20	0.02	0.38	0.43	0.97	0.00	
8		1.04	0.21	0.03	0.37	0.41	0.95	0.00	
9		1.01	0.24	0.05	0.34	0.42	0.94	0.00	
10		1.00	0.20	0.02	0.38	0.43	0.97	0.00	
11		0.99	0.22	0.03	0.27	0.51	0.98	0.00	
12		0.96	0.19	0.00	0.22	0.60	1.02	0.00	

The crystal aggregates reach 90 μm in cross-section. They are well-cut, with hexagonal and rectangular plates (figures 2-3) and contain micro-inclusions of testibiopalladite, melonite and silver telluride, sometimes skeletal crystals (figure 3, c).

The cobaltite-gersdorffite series minerals vary in the cationic part (nickel, cobalt, iron, and copper), sulphur, and arsenic (tables 1 and 2).

Table 2. Microprobe analyses (wt. %) of zonal crystals of the cobaltite-gersdorffite series minerals.

No.	Mineral	S	Fe	Cu	Co	Ni	As	Pt	Ir	Rh	Ru	Os	Σ
Zonal crystals													
1	the cobaltite-gersdorffite series mineral	19.39	8.42	1.26	14.56	12.73	42.40	0.00	0.00	0.00	0.00	0.00	98.76
2		18.60	8.32	1.14	10.25	14.11	40.46	2.50	4.93	0.00	0.00	0.00	100.31
3		18.94	7.76	1.17	10.10	15.74	42.37	2.39	2.99	0.00	0.00	0.00	101.46
4		18.42	7.67	2.76	9.06	13.86	39.87	3.93	3.48	0.80	0.00	0.00	99.85
5		19.31	7.36	1.25	9.45	17.11	43.46	1.60	0.00	0.00	0.00	0.00	99.54
6		19.42	7.40	1.97	9.91	15.24	41.72	1.84	1.50	0.00	0.00	0.00	99.00
7		19.73	7.78	1.59	10.13	15.68	42.67	1.45	0.12	0.00	0.00	0.00	99.15
8		19.36	7.81	2.03	10.26	15.51	42.96	1.50	0.56	0.00	0.00	0.00	99.99
9		19.96	8.01	2.41	10.76	14.35	40.11	1.82	1.91	0.00	0.00	0.00	99.33

10		19.88	8.40	2.08	9.54	16.38	42.22	1.60	0.00	0.00	0.00	0.00	100.10
11		21.41	10.61	0.00	10.91	14.73	39.88	0.98	0.00	0.00	0.00	0.00	98.52
12		19.10	7.46	1.83	9.10	17.18	43.61	0.89	0.00	0.00	0.00	0.00	99.17
13		20.78	8.50	2.89	9.49	15.53	41.20	0.98	0.50	0.00	0.00	0.00	99.87
14		19.01	7.39	1.68	8.57	17.44	43.58	1.48	0.00	0.00	0.00	0.00	99.15

Table 2 continue

15		19.74	7.57	0.59	12.45	15.84	43.28	0.76	0.00	0.00	0.00	0.00	100.23
16		18.46	6.95	2.14	7.65	17.07	41.96	1.98	0.78	0.35	1.94	0.91	100.19
17		20.57	9.49	6.39	6.42	8.09	30.68	2.34	13.88	0.00	0.00	1.18	99.04
18		19.04	7.67	1.74	9.15	16.22	41.80	0.98	2.98	0.41	0.00	0.00	99.99
19		19.25	7.77	1.70	9.79	16.88	42.30	0.65	1.66	0.00	0.00	0.00	100.00
20		21.87	11.54	6.74	8.83	13.17	37.00	0.63	0.00	0.00	0.00	0.63	100.41
21		19.77	7.18	2.50	9.52	14.65	41.99	0.00	0.00	0.00	2.70	1.69	100.01
22		18.33	5.47	1.39	8.12	13.22	39.49	2.08	8.83	1.68	1.37	0.00	99.88
23		22.03	9.77	6.11	8.10	10.38	35.60	1.13	6.87	0.00	0.00	0.00	99.98
24		19.69	6.81	2.81	8.30	12.34	38.24	2.48	6.37	1.09	1.87	0.00	100.01
25		18.72	7.18	2.85	8.69	13.21	39.17	1.50	8.23	0.44	0.00	0.00	99.99

Structural formula based on three atom

1	Mineral of the cobaltite-gersdorffite series	1.01	0.25	0.04	0.41	0.36	0.94	0.00	0.00	0.00	0.00	0.00	3.01
2		1.00	0.26	0.03	0.30	0.41	0.93	0.02	0.05	0.00	0.00	0.00	3.00
3		1.00	0.23	0.03	0.29	0.45	0.95	0.02	0.03	0.00	0.00	0.00	3.00
4		1.00	0.26	0.03	0.30	0.41	0.93	0.02	0.04	0.00	0.00	0.00	2.99
5		1.01	0.22	0.03	0.27	0.49	0.97	0.01	0.00	0.00	0.00	0.00	3.00
6		1.04	0.22	0.05	0.28	0.44	0.94	0.02	0.01	0.00	0.00	0.00	2.99
7		1.03	0.23	0.04	0.29	0.45	0.95	0.01	0.00	0.00	0.00	0.00	3.00
8		1.01	0.23	0.05	0.29	0.44	0.94	0.02	0.00	0.00	0.00	0.00	2.98
9		1.05	0.24	0.06	0.31	0.41	0.90	0.01	0.02	0.00	0.00	0.00	3.00
10		1.03	0.26	0.05	0.27	0.46	0.93	0.01	0.00	0.00	0.00	0.00	3.01
11		1.09	0.31	0.00	0.30	0.41	0.87	0.01	0.00	0.00	0.00	0.00	2.99
12		1.00	0.23	0.05	0.26	0.49	0.96	0.01	0.00	0.00	0.00	0.00	3.00
13		1.06	0.25	0.07	0.26	0.43	0.90	0.01	0.00	0.00	0.00	0.00	2.98
14		1.00	0.22	0.04	0.25	0.50	0.98	0.01	0.00	0.00	0.00	0.00	3.00
15		1.01	0.22	0.02	0.35	0.44	0.95	0.01	0.00	0.00	0.00	0.00	3.00
16		0.98	0.21	0.06	0.22	0.50	0.96	0.02	0.00	0.00	0.03	0.01	2.99
17		1.16	0.31	0.18	0.20	0.25	0.74	0.02	0.00	0.00	0.00	0.01	2.86
18		1.01	0.23	0.05	0.26	0.47	0.94	0.01	0.03	0.01	0.00	0.00	3.01
19		1.00	0.23	0.05	0.28	0.48	0.94	0.01	0.01	0.00	0.00	0.00	2.99
20		1.09	0.33	0.17	0.24	0.36	0.79	0.01	0.00	0.00	0.00	0.01	3.00
21		1.03	0.22	0.06	0.27	0.42	0.94	0.02	0.00	0.03	0.02	0.00	2.99
22		1.03	0.18	0.04	0.25	0.40	0.95	0.02	0.08	0.03	0.02	0.00	3.00
23		1.15	0.29	0.16	0.23	0.30	0.80	0.01	0.06	0.00	0.00	0.00	3.00
24		1.07	0.21	0.08	0.24	0.37	0.89	0.02	0.06	0.02	0.03	0.00	2.99
25		1.03	0.22	0.08	0.26	0.39	0.89	0.01	0.07	0.01	0.00	0.00	2.96

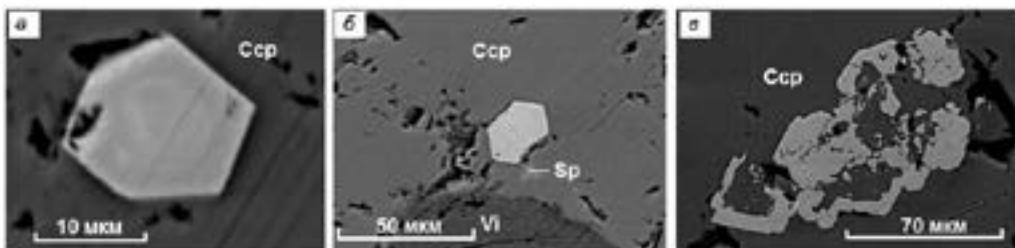


Figure 3. The zonal (a) and nonzonal (b) crystals and the aggregate of skeletal crystals of minerals of the cobaltite-gersdorffite series (c). Sp –fluorophosphate.

Some photos of zonal crystals are shown in figure 4. A core, white in general (seen in the BEI), enriched with platinoids is a characteristic feature of the crystals' structure.

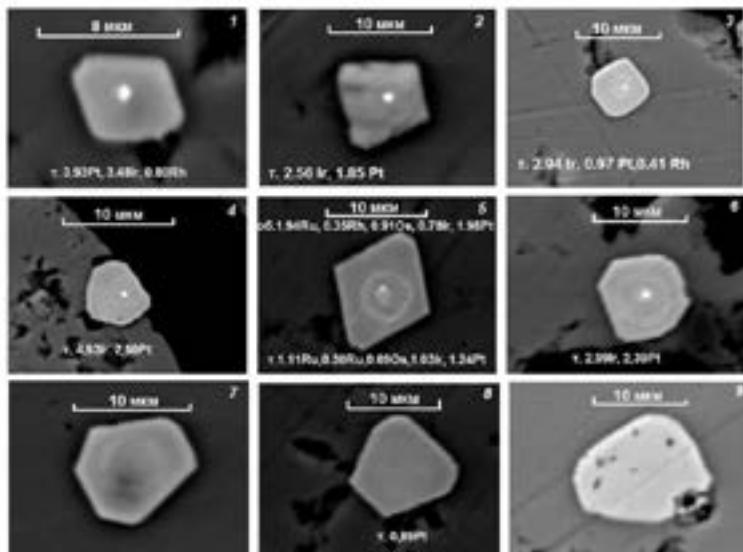


Figure 4. Zonal crystals of minerals of the cobaltite-gersdorffite series. BEI

The maximum platinoid content obtained in one of the zonal crystal analyses was 17.40%, with Ir 13.88, Pt 2.34, Os 1.18. The light (Ru, Rh) and heavy (Pt, Ir, Os) in platinum metals are found together (table 2). Rhenium's minerals and mineral phases of PGE are registered in single crystals of the cobaltite-gersdorffite series minerals: (Pt, Ir), (Pt, Ir, Ru, Os, Rh), (Ir, Pt, Os), (Ir, Pt, Rh), (Ru, Os), (Ir, Pt, Rh, Ru), (Pt, Os) all of them are present. Still, some of the concentration is below the detection limit.

Arsenide. Sperrylite (PtAs_2) occurs much less frequently than crystals of the cobaltite-gersdorffite series and contains Rh (<1.57%), Sb (<2.22%), Pb (1.33%)

and Ag (0.58%) impurities. Micro-inclusions in chalcopyrite shaped from rounded to well-cut forms. The crystals are up to 10 μm (figure 5). The average chemical composition (wt.%) of sperrylite upon five analyses is as follows: As - 40.35; Pt - 58.73; Rh - 0.69; Σ - 99.77. Calculated formula: $\text{Pt}_{1.07}\text{Rh}_{0.02}\text{As}_{1.91}$.

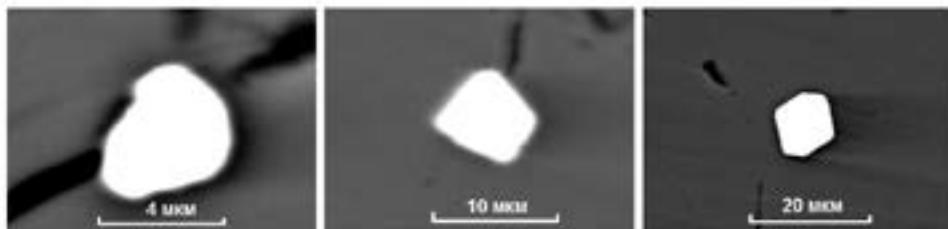


Figure 5. Sperrylite in chalcopyrite. BEI

Antimonide. Ullmannite (NiSbS). One corroded mineral crystal is in a concretion with pyrite and silver telluride (figure 6). The normalized chemical composition (wt%) is S - 10.88; Fe - 1.77; Sb - 41.28; Co - 0.25; Ni - 18.79; As - 1.23; Bi - 8.07; Ag - 7.51; Te - 7.26; Pd - 2.96.

Tellurides. This group of minerals is represented by tellurides of silver, lead, testibiopalladite and extremely rare vavrinite and melonite.

Silver telluride forms frequent micro-inclusions spatially associated with minerals of the cobaltite-gersdorffite series, sphalerite, pyrite (figure 6) and chalcopyrite (figure 7). The habitus of silver telluride crystals is plate-like, but they often form irregular and rounded grains no larger than 10 μm .

Lead telluride (PbTe) was identified minor inclusions in chalcopyrite.

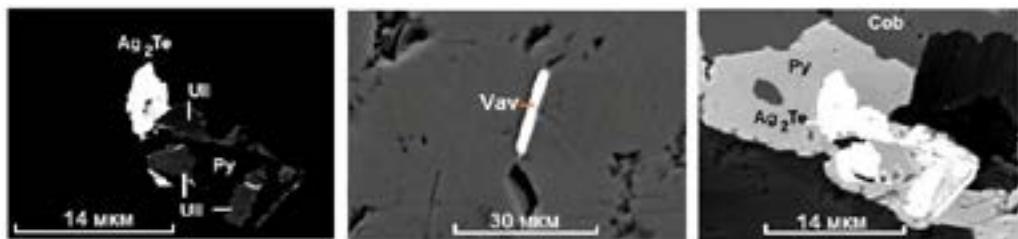


Figure 6. Micro-inclusions of ullmannite (Ull), vavrinite (Vav) and silver telluride. BEI

Testibiopalladite $\text{Pd}(\text{Sb},\text{Bi})\text{Te}$ is observed slightly more often than sperrylite and occurs together with minerals of cobaltite-gersdorffite series (figure 2) and chalcopyrite. In aggregates of cobaltite-gersdorffite crystals, the mineral forms grains up to 2-5 μm , and in chalcopyrite, it reaches 22 microns. It contains impurities: Fe (<1.36%), Cu (<2.10%), Ni (2.49%) and significantly rare Sb, Ag, Co (table 3).

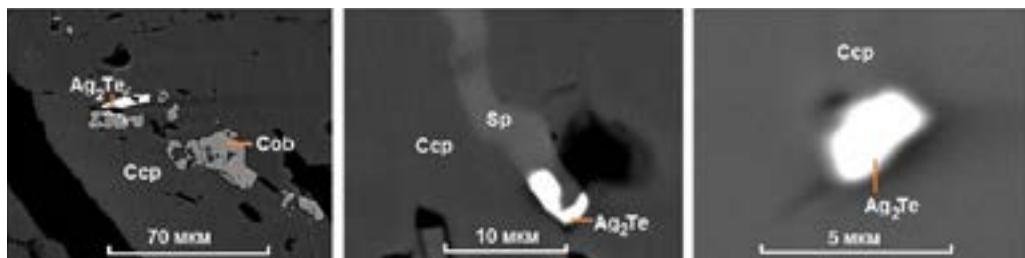


Figure 7. Micro inclusions of ore minerals of copper pyrite. BEI

Quite rare minerals include melonite NiTe_2 and vavrinite Ni_2SbTe_2 , each detected in two tiny crystals. Table 3 (No 9-10) shows two normalised analyses of vavrinite containing elements of the chalcopyrite matrix.

Table 3. Results of microprobe analyses (wt%) of micro-inclusions of testibiopalladite and vavrinite.

No.	Mineral	S	Fe	Cu	Co	Ni	Sb	As	Ag	Te	Pd	Bi	Σ
1	Testibiopalladite $\text{Pd}(\text{Sb},\text{Bi})\text{Te}$	0.00	0.96	1.47	0.00	2.49	23.81	0.00	0.00	39.51	23.48	8.06	99.78
2		0.00	0.87	1.33	0.00	2.47	23.98	0.00	0.00	40.57	23.74	8.20	101.16
3		0.00	1.36	1.31	0.00	2.37	24.17	0.00	0.00	40.13	23.37	7.71	100.42
4		0.00	0.40	0.00	0.00	2.60	22.84	0.00	0.00	39.98	25.94	8.23	99.99
5		0.00	0.29	0.55	0.00	2.78	24.49	0.00	0.48	41.03	23.18	8.52	101.32
6		0.00	0.96	1.47	0.00	2.49	23.81	0.00	0.00	39.51	23.48	8.06	99.78
7		0.00	0.87	1.33	0.00	2.47	23.98	0.00	0.00	40.57	23.74	8.20	101.16
8		0.00	1.36	1.31	0.00	2.37	24.17	0.00	0.00	40.13	23.37	7.71	100.42
9	Vavrinite	5.84	6.34	5.95	0.00	17.31	18.78	0.00	0.19	42.40	3.18	0.00	100.00
10		7.48	8.28	7.93	0.00	14.06	13.72	0.00	4.91	41.17	2.55	0.00	100.00

Table 3 continue

Structural formula based on three atom													
1	Testibiopalladite $\text{Pd}(\text{Sb},\text{Bi})\text{Te}$	0.00	0.06	0.08	0.00	0.15	0.69	0.00	0.00	1.10	0.78	0.14	3.00
2		0.00	0.05	0.07	0.00	0.15	0.69	0.00	0.00	1.11	0.78	0.14	2.99
3		0.00	0.08	0.08	0.00	0.14	0.70	0.00	0.00	1.10	0.77	0.13	3.00
4		0.00	0.02	0.00	0.00	0.16	0.67	0.00	0.00	1.13	0.88	0.14	
5		0.00	0.02	0.03	0.00	0.17	0.71	0.00	0.02	1.14	0.77	0.14	3.00
6		0.00	0.06	0.08	0.00	0.15	0.69	0.00	0.00	1.11	0.78	0.14	3.01
7		0.00	0.05	0.07	0.00	0.15	0.69	0.00	0.00	1.10	0.78	0.14	2.98
8		0.00	0.08	0.07	0.00	0.14	0.69	0.00	0.00	1.10	0.78	0.14	3.00
Structural formula based on five atoms													
9	Vavrinite	0.76	0.46	0.39	0.00	1.23	0.64	0.00	0.01	1.38	0.12	0.00	4.99
10		0.94	0.58	0.50	0.00	0.96	0.45	0.00	0.18	1.29	0.06	0.00	4.96

Phosphates and fluorophosphate. A total of four small ($<5 \mu\text{m}$) inclusions were detected: two phosphates and two fluorophosphate with light REEs, and only

one fluorophosphate inclusion had yttrium (table 4, figure 8). Matrix elements are present in all analyses.

Table 4. Results of microprobe analyses (wt%) of the REE fluorophosphate and phosphate.

No	S	Cu	Fe	Ni	O	Ca	F	P	Y	La	Ce	Pr	Nd	Sm	Σ
1	13.81	12.58	13.00	0.00	23.48	1.94	1.12	7.79	0.31	4.95	11.89	1.69	6.65	1.16	100.37
2	14.81	12.74	14.39	0.72	22.88	2.64	2.06	6.85	0.00	5.13	11.87	1.57	5.86	1.16	102.68
3	13.08	12.72	12.83	0.00	26.08	2.07	0.00	7.82	0.00	6.33	12.18	0.00	5.76	0.37	99.24
4	14.58	12.13	12.46	0.45	25.35	2.06	0.00	7.66	0.00	6.04	13.74	0.00	6.80	0.00	101.27

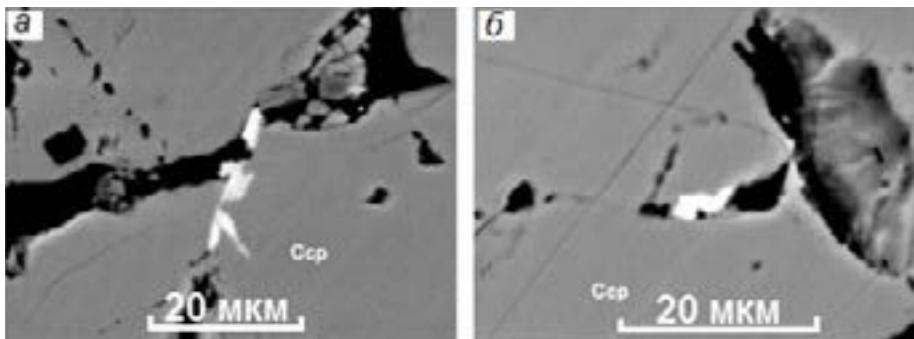


Figure 8. Micro inclusions: a) fluorophosphate, б) phosphate of REE in chalcopyrite. BEI

Rare minerals of the ore-bearing sequence. Sulphides in this group form two mineral subgroups (Figure 9). The first one consists of well-cut single crystals of pyrrhotite, chalcopyrite and pyrite. The second group consists of veins of pyrite-chalcopyrite association, which, like the first, are mainly found in carbon-bearing muscovite-clinochlore-quartz schists.

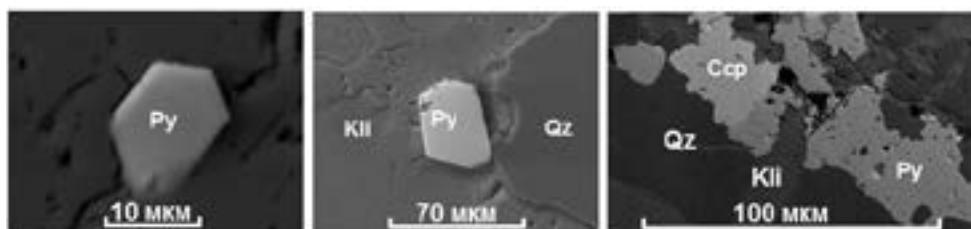


Figure 9. The polished section of unmineralized mass. BEI

The carbon-bearing muscovite-clinochlore-quartz schists were noted to contain veinlets of aluminosilicates (figure 10) with elements of the yttrium and cerium subgroups (table 5).

Table 5. Results of microprobe analyses (wt%) of REE aluminosilicates.

Component	1	2	3	4	5	6	7	8
SiO_2	35.83	32.37	34.63	33.12	33.46	32.84	33.05	35.34
Al_2O_3	23.59	21.03	22.15	20.83	21.06	21.82	21.41	24.16
FeO	8.37	12.28	8.40	8.76	8.69	9.11	9.09	8.38
CaO	16.31	10.96	15.33	13.69	13.56	13.41	14.51	16.96
K_2O	0.03	0.22	0.31	0.19	0.34	0.00	0.00	0.00
Cl	0.00	0.00	0.00	0.00	0.00	0.12	0.15	0.07
Y_2O_3	1.70	1.40	1.14	1.34	0.86	0.83	1.46	1.66
La_2O_3	1.56	3.06	2.02	3.31	2.49	3.18	2.51	1.49
Gd_2O_3	0.85	0.37	0.83	0.77	0.11	0.57	0.48	0.19
Ce_2O_3	3.87	6.13	4.46	7.69	5.94	7.44	5.51	2.99
Pr_2O_3	0.11	0.06	0.59	0.81	0.85	0.75	0.04	0.20
Nd_2O_3	1.45	3.33	2.52	3.25	3.29	3.33	2.54	1.41
Sm_2O_3	0.71	0.87	1.14	0.55	0.44	0.87	0.87	0.63
Eu_2O_3	1.55	1.03	1.84	0.88	0.44	0.98	0.83	0.89
Σ	95.94	93.11	95.36	95.18	91.33	95.24	92.44	94.37

Note. The general formula of the mineral are $(\text{Fe}, \text{Ca}, \text{LREE})\text{SiAlO}_5$

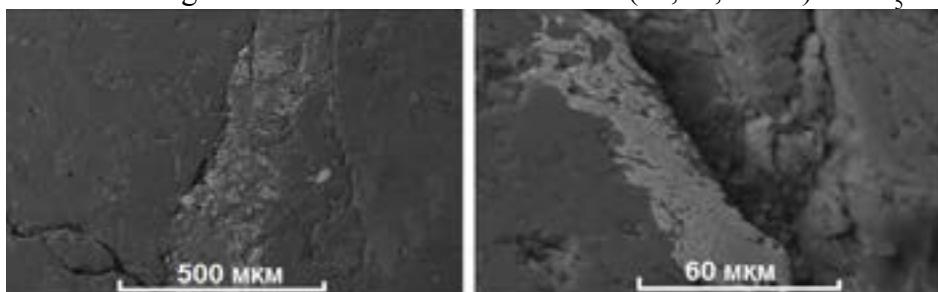


Figure 10. The polished section of carbon-bearing muscovite-clinochlore-quartz schists with the LREE aluminosilicate vein (light grey). BEI

Discussion. Mineralogical investigations of copper ores of the Maike manifestation have shown that elements of the platinum group (Ir, Pt, Rh=Ru, Os) are present only in zonal sulfarsenides, and PGM are presented by platinum arsenide (PtAs_2), testibiopalladite $\text{Pd}(\text{Sb}, \text{Bi})\text{Te}$ and palladium-bearing minerals: melonite (NiTe_2), vavrinite (Ni_2SbTe_2) and ulmannite (NiSbS). The platinum-bearing minerals of the cobaltite-gersdorffite series sharply prevail over all other micro-inclusions containing Pt and Pd and appear to be the primary sources of Pt, along with sperrylite (PtAs_2). These micro-inclusions are reliable thermobarometers, as shown by studies of copper-rich Cu-Ni-PGE Sudbury ores (Dare, 2010 a: 25, 2014 b: 23) and Cu-Ni-PGE Bushveld and Stillwater ores (Mansur, 2020: 23).

Given the ore composition of the Maike occurrence and the sequence model for the formation of PGM, rare earth minerals and the Cu-Ni-PGM ore sulphides developed earlier (Naldrett, 2004: 728, Dare, 2010 a: 25, 2014 b: 23), it can be assumed that the formation of copper ore carbonatites took place under magmatic (figure 11) and post-magmatic mineralisation processes (figure 12).

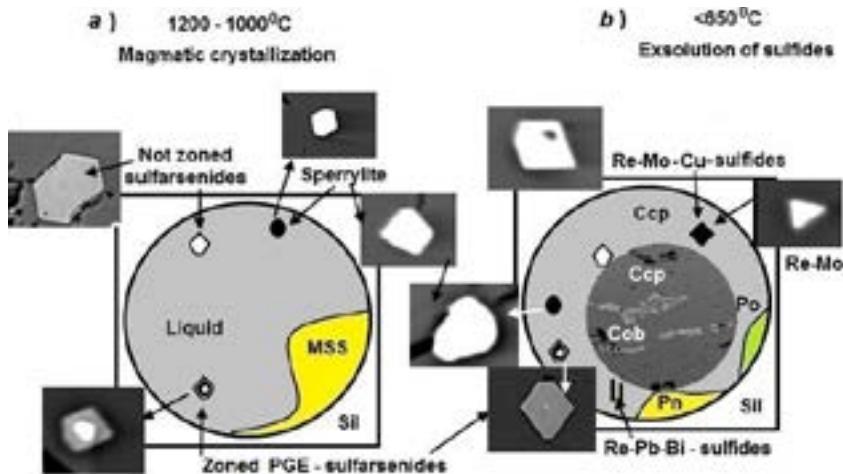


Figure 11. The formation sequence model for PGE, PGM, rare minerals and copper ore sulphides of the Maike deposit is based on materials of the article (Dare, 2010 a: 25).

Legend: Liquid - sulphide melt, Sil – silicates, Ccp – chalcopyrite, MSS – mono-sulphide solid solution, Pn – pentlandite, Po – pyrrhotite.

- a) early crystallisation of small idiomorphic zonal PGE-sulfarsenides and sperrylite from sulphide liquid and their fusion in MSS;
- b) evolution of sulphide minerals (pentlandite, pyrrhotite, chalcopyrite), including sulphides of rhenium and molybdenum, when cooled to a temperature below 650°C.

Following the authors (Dare, 2014 b: 23, Mansur, 2020: 23), we can assume that, at the early stage, the main mass of crystals of platinum-bearing sulfarsenides and sperrylite crystallised from the sulphide melt, which is typical of the magmatic mineral formation stage. This melt also contained a small amount of MSS cumulates void of noble metals (figure 11 a).

Experimental data support this model according to which the PGE sulfarsenides and sperrylite crystallised at high temperature: sperrylite crystallises at $\sim 1400^{\circ}\text{C}$ (Bennett, 1966: 5) and nickel-containing-cobaltite is stable up to at least 800°C (Maurel, 1974: 13).

The bulk of the PGE (Ir, Pt, Rh \pm Ru, Os) as impurities was present in the sulfarsenide phases, less in the arsenide phases; this contributed to the depletion of the sulphide melt PGEs before or during the crystallisation of MSS (figure 11 b).

High-temperature crystallisation of PGE sulfarsenides directly from the sulphide melt has also been reported previously (Power, 2004: 16, McDonald, 2008: 10).

Subsequent decrease of temperature below 650°C stimulates the release of minor amounts of pyrrhotite and pentlandite from MSS and significant masses of chalcopyrite

from intermediate solid solution (ISS). At the same time, the accessory minerals of sulphides of Re-Mo-Cu, Re-Mo, which form idiomorphic thin plates, and sulphides of Re-Fe-Pb-Bi, Re-Pb-Fe, Pb-Re, which form needles, are separated from ISS. Molybdenite plates are formed extremely scarcely.

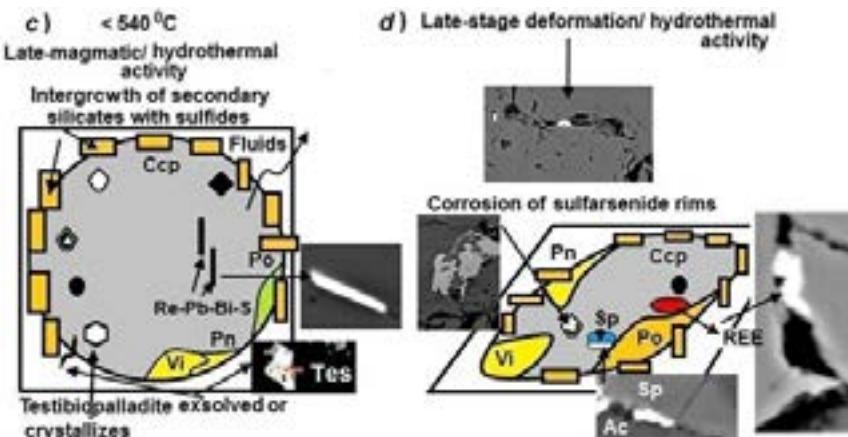


Figure 12. The formation sequence model for PGE, rare minerals, and copper ore sulphides from the Maike deposit, based on materials of the article (Dare, 2010 a: 25):

- c) late magmatic and/or hydrothermal activity and the subsequent recrystallisation of sulphides of base metals with secondary silicates simultaneously with the formation of testibiopalladite and Pb-Te phases either as dissolution of sulphides of base metals or during crystallisation from small volumes of trapped melt;
- d) demobilisation of sulphides at a later stage in fracture zones, corrosion of existing PGE-sulfarsenides, formation of acanthite on sphalerite, and formation of fluorophosphate and REE-phosphates in cracks.

In the late magmatic or hydrothermal stage (figure 12c), non-ferrous metal sulphides which do not form regular crystallographic shapes are superimposed on sulphides from previous steps. These minerals, testibiopalladite, melonite, and vavrinite are significant palladium sources. Ullmannite is exceptionally rarely encountered in association with corroded Ni, Co sulfarsenides. A wide range of impurity elements characterises it: Ag, Pd, Te, Bi, typical of hydrothermal stage mineral associations (Dare, 2014 b: 23). Under the influence of hydrothermal fluids, violarite replaces pentlandite, sometimes up to complete pseudomorphosis (Stepanets, 2019 a: 8).

In the final stage of the magmatic-hydrothermal process (figure 12d), the copper ores were deformed and embedded in the graphite-quartz-muscovite-chlorite Proterozoic schists subsequently subjected to hydrothermal-metasomatic

processing. At this stage, the copper ores are overlain by polymetallic mineralisation. Sphalerite is generally accompanied by the formation of acanthite and native silver. The most recent formations are phosphates and fluorophosphate of REEs.

The assumed sequence of formation of copper ores, spatially and genetically connected with carbonatites of the fracture-type, is indirectly confirmed by the isotopic composition of the lead of the Northern Ulytau pyrite-polymetallic deposits, studied earlier by (Koshevov, 1984: 19). He thought that lead isotopic compositions of deposits in this area indicate a complex multistage history of the formation of several deposits in the Northern Ulytau by mixing ancient anomalous lead of Proterozoic age with common lead, associated with subsequent periods of tectonic-magmatic activations in the Early Palaeozoic (Stepanets, 2020 b: 15).

Probably, most of the deposits of carbonatites associated with mantle chambers, originally formed above subduction zones or in the process of melting of the oceanic crust, were developed according to such a scenario. Their spatial association with subduction zones is confirmed by the presence of halite, rutile, apatite, and monazite in initially plutonic ultrabasic rocks (Manning, 2018: 30, Ayers, 1991: 10, Naumov, 2017: 168).

The ore genesis of the Mayatas ore district is completed by forming Nd-bearing weathering crusts (Nsanov, 1993).

Conclusion. Petrographic and mineralogical studies of copper ores of the Maike occurrence can hardly be compared with the liquation Cu-Ni-PGE ores genetically and spatially associated with ultramafic dikes (Chudin, 2012).

The copper-rich ores are sub-solidus (<600°C) products of the decay of ISS, which has crystallised (950-800°C) from a highly fractionated sulphide liquid, rich in Pd, Ir, Ru, Rh, Os, Ag, As, Bi, Cd, Pb, Te, Zn и Y, Ce, La.

Platinoids are not concentrated in non-ferrous metal sulphides (chalcopyrite, pentlandite, galena and sphalerite). They constitute minerals of the platinum group, which includes testibiopalladite ($Pd(Sb,Bi)Te$), sperrylite ($PtAs_2$), as well as zonal sulfarsenides and tellurides, where platinoids are present as impurities.

The richest in Pt, Ir, Rh, Ru, Os are zonal sulfarsenides Ni, Co, and the palladium impurity is usually present in tellurides.

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