ISSN 2518-170X (Online),
ISSN 2224-5278 (Print)

ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ
Қ. И. Сәтпаев атындағы Қазақ ұлттық техникалық зерттеу университеті

Х А Б А Р Л А Р Ы

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
Казахский национальный исследовательский
технический университет им. К. И. Сатпаева

N E W S

OF THE ACADEMY OF SCIENCES
OF THE REPUBLIC OF KAZAKHSTAN
Kazakh national research technical university
named after K. I. Satpayev

SERIES
OF GEOLOGY AND TECHNICAL SCIENCES

2 (434)

MARCH – APRIL 2019

THE JOURNAL WAS FOUNDED IN 1940

PUBLISHED 6 TIMES A YEAR

ALMATY, NAS RK

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«ҚР ҰҒА Хабарлары. Геология мен техникалық ғылымдар сериясы».
ISSN 2518-170X (Online),
ISSN 2224-5278 (Print)
Меншіктенуші: «Қазақстан Республикасының Ұлттық ғылым академиясы» РҚБ (Алматы қ.).
Қазақстан республикасының Мәдениет пен ақпарат министрлігінің Ақпарат және мұрағат комитетінде 30.04.2010 ж. берілген **№10892-Ж** мерзімдік басылым тіркеуіне қойылу туралы куәлік.

Мерзімділігі: жылына 6 рет.
Тиражы: 300 дана.

Редакцияның мекенжайы: 050010, Алматы қ., Шевченко көш., 28, 219 бөл., 220, тел.: 272-13-19, 272-13-18,
http://www.geolog-technical.kz/index.php/en/

Редакцияның мекенжайы: Қазақстан, 050010, Алматы қ., Қабанбай батыра көш., 69а.
Қ. И. Сәтбаев атындағы геология ғылымдар институты, 334 бөлме. Тел.: 291-59-38.

Типографияның мекенжайы: «Аруна» ЖК, Алматы қ., Муратбаева көш., 75.

«Известия НАН РК. Серия геологии и технических наук».
ISSN 2518-170X (Online),
ISSN 2224-5278 (Print)
Собственник: Республиканское общественное объединение «Национальная академия наук Республики Казахстан (г. Алматы)
Свидетельство о постановке на учет периодического печатного издания в Комитете информации и архивов Министерства культуры и информации Республики Казахстан **№10892-Ж,** выданное 30.04.2010 г.

Периодичность: 6 раз в год
Тираж: 300 экземпляров

Адрес редакции: 050010, г. Алматы, ул. Шевченко, 28, ком. 219, 220, тел.: 272-13-19, 272-13-18, http://nauka-nanrk.kz /geology-technical.kz

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Адрес редакции: Казахстан, 050010, г. Алматы, ул. Кабанбай батыра, 69а.
Институт геологических наук им. К. И. Сатпаева, комната 334. Тел.: 291-59-38.

Адрес типографии: ИП «Аруна», г. Алматы, ул. Муратбаева, 75

News of the National Academy of Sciences of the Republic of Kazakhstan. Series of geology and technology sciences.
ISSN 2518-170X (Online),
ISSN 2224-5278 (Print)
Owner: RPA "National Academy of Sciences of the Republic of Kazakhstan" (Almaty)
The certificate of registration of a periodic printed publication in the Committee of information and archives of the Ministry of culture and information of the Republic of Kazakhstan N 10892-Ж, issued 30.04.2010

Periodicity: 6 times a year
Circulation: 300 copies

Editorial address: 28, Shevchenko str., of. 219, 220, Almaty, 050010, tel. 272-13-19, 272-13-18,
http://nauka-nanrk.kz/geology-technical.kz

Editorial address: Institute of Geological Sciences named after K.I. Satpayev
69a, Kabanbai batyr str., of. 334, Almaty, 050010, Kazakhstan, tel.: 291-59-38.

Address of printing house: ST "Aruna", 75, Muratbayev str, Almaty

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES OF GEOLOGY AND TECHNICAL SCIENCES
ISSN 2224-5278
Volume 2, Number 434 (2019), 21 – 29 **https://doi.org/10.32014/2019.2518-170X.34**

UDC 549:552.323.6, 549:553.491

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MINERALS OF NOBLE AND RARE ELEMENTS IN KARATURGAY AND MAYKE ORE TYPES OF MAYATAS ORE REGION (NORTH ULYTAU, KAZAKHSTAN)

Abstract. Significant outcome of the studies is a discovery of accessory siegenite, platinum telluride - moncheite, silver telluride - hessite, lead telluride - altaite, lead selenide, solid solutions of metals of the iridium group (Ir, Os, Ru), REEs (Dy, Er, Y, Ce), reported for the first time from picrites of the Karaturgay complex, where they occur in association with previously known sulfides. Zigenite and millerite are found in picrite diabases in association with pentlandite, pyrite, and galena. These minerals have not been previously recorded from rocks of the Karaturgay complex. Numerous mineral microinclusions identified in present study show unusual mineral associations not previously documented in the region, including cobaltite-gersdorffite minerals with Pt, Ir, Rh, Ru, Os; ullmannite, silver telluride – hessite, lead telluride - altaite, sperrylite, testibiopalladite, native silver, acanthite, melonite, vavrinite, REE-bearing phosphates and fluorophosphates and rhenium minerals.

From the sequence of formation of mineral phases and the analysis of the isothermal sections of the condensed Fe–Ni–S system it can be concluded that formation of the Karaturgay type sulfide copper-nickel mineralization apparently took place in several temperature regimes. Schematic model of the sequence of formation of PGE, rare minerals and sulfide of copper-sulfide ores from the Mayke ore occurrence with a discussion of the stages of mineral formation is presented.

Keywords: REE, PGM, chemical composition of minerals, picrites, picrite diabases, carbonatites, Mayatas ore region, Northern Ulytau, Kazakhstan.

The Karaturgay and Mayke types of ores are confined to the diabase-picritic Karaturgay complex widely represented in the Karaturgay river basin and to the carbonatite complex, which is exposed on the right bank of the Mayke river, within the Mayatas ore region [1, 2].

Detailed mineralogical studies using electron probe were conducted, to investigate mineral composition sulfide ores taking in mind that the knowledge of ore composition of ores and general characters of precious metals (platinoids, rare and rare earth elements) occurrences can significantly affect the economic value of the Karaturgay and Mayke ore occurrences.

Significant outcome of this studies is a discovery of accessory siegenite $(Co,Ni)_3S_4$, platinum telluride - moncheite $(Pt,Pd)(Te,Bi)_2$, silver telluride - hessite Ag_2Te, lead telluride - altaite PbTe, lead selenide PbSe, solid solutions of metals of the iridium group (Ir, Os, Ru), REEs (Dy, Er, Y, Ce) (table 1), reported for the first time from picrites of the Karaturgay complex, where they occur in association with previously known sulfides (pyrrhotite, pentlandite and chalcopyrite). These sulfides form three mineral associations: the first two occur in liquation droplets of rounded and elliptical shape; the third association forms droplets of irregular, subangular shape. Platinoids in sulfides of copper and nickel are present only in sulfide droplets of the first association, composed of pyrrhotite, chalcopyrite, pentlandite, and sphalerite. Sulfides from the two other associations do not contain platinoids. The second mineral association includes pyrrhotite, chalcopyrite and sphalerite, while the third - pyrrhotite, chalcopyrite, sphalerite and pyrite. All three mineralogical associations contain magnetite and are usually confined to the most differentiated horizons of picrites and apopicrite olivinites [1, 2].

In general, the set of minerals in the form of sulfide droplets is characteristic for liquation-type ores; however, there are some differences in composition. For example, pyrrhotite from the Karaturgay ore area does not contain nickel and cobalt. Also there is no sperillite in ores associated with Karaturgay type picrites. Palladium and selenium are extremely rare, but rare earth elements are widely represented. Platinum telluride in Karaturgay type ores is found in all main ore minerals (pentlandite, chalcopyrite and pyrrhotite) of the first association, silver telluride - hessite is frequently found, but gold is absent. The presence of lead selenide, iridium-arsenide and a high content of the yttrium group REEs is one of the characteristic features of the Karaturgay type ores.

Zigenite $(Co,Ni)_3S_4$ and millerite NiS are found in picrite diabases in association with pentlandite, pyrite, and galena. These minerals have not been previously recorded from rocks of the Karaturgay complex. Characteristically, pentlandite is supersaturated with S, does not contain Co, and is poorly enriched in Cr in relation to pentlandite of Kararatay type picrites.

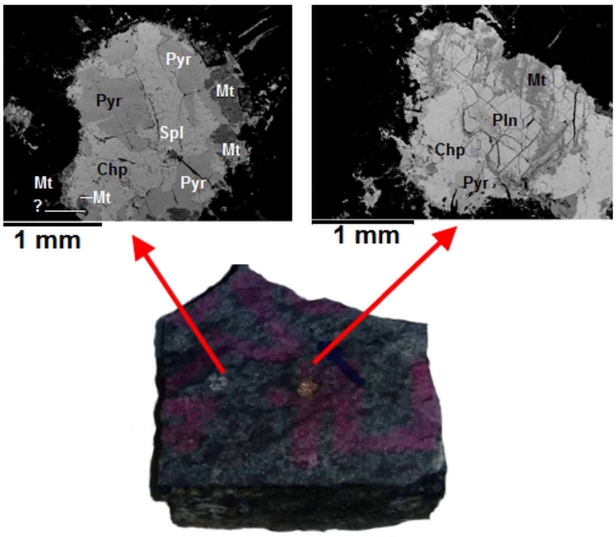
A drill core through the vein up to 35 cm thick taken at the depth 100 m from the Mayke ore deposit contains chalcopyrite (> 95%), violarite, pyrite, sphalerite, pyrrhotite, galena, cassiterite, as well siderite and hematite. The main ore minerals recovered from carbonatites are chalcopyrite, violarite, pentlandite, pyrrhotite, pyrite, and sphalerite.

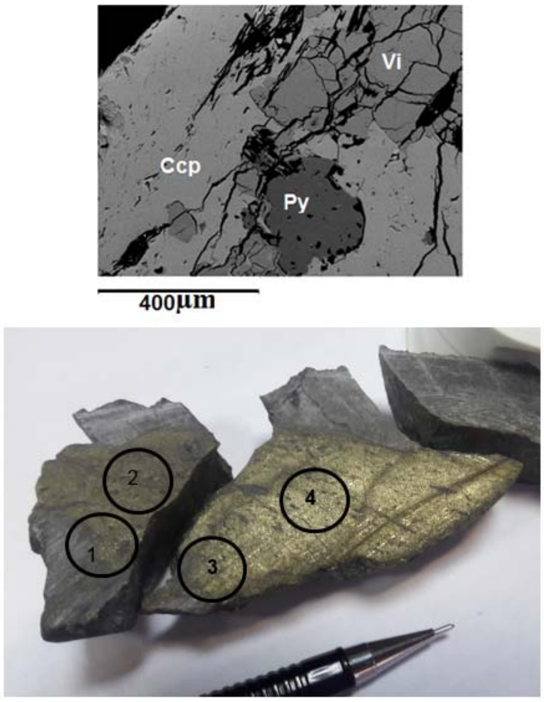
Numerous mineral microinclusions identified in present study show unusual mineral associations not previously documented in the region, including cobaltite-gersdorffite minerals with Pt, Ir, Rh, Ru, Os; ullmannite NiSbS, silver telluride – hessite Ag_2Te, lead telluride - altaite PbTe, sperrylite $PtAs_2$, testibiopalladite Pd(Sb,Bi)Te, native silver, acanthite Ag_2S, melonite $NiTe_2$, vavrinite Ni_2SbTe_2, REE-bearing phosphates and fluorophosphates. A special group of micro-inclusions is formed by the rhenium minerals first found in Kazakhstan (table 1).

Table 1 – Comparative characteristics of the mineral composition of picrites, picritic diabases and carbonatites from Ulytau

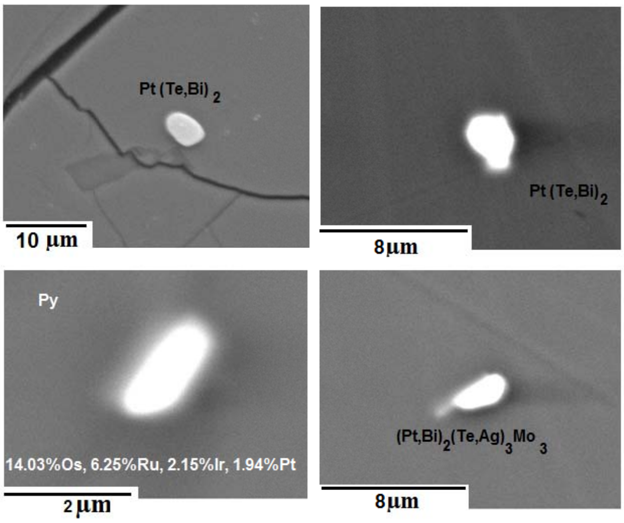
Magmatic group	Carbonatite group
Liquation class	Hydrothermal fluid magmatic carbonatite class
Picrites	Alkaline picrites
Main ore minerals	
Pyr- Pyrrhotite (FeS) Pln- Pentlandite $(Fe,Ni)_9S_8$ Vi- Violarite $(Fe,Ni)_3S_4$ Ccp- Chalcopyrite $(CuFeS_2)$ Cpl- Sphalerite (ZnS) Mt- Magnetite $(Fe^{3+},Fe^{2+})Fe^{3+}{}_2O_4$	Ccp- Chalcopyrite $(CuFeS_2)$ Vi- Violarite $(Fe,Ni)_3S_4$ +Er, Co Py- Pyrite (FeS_2) Cp- Sphalerite (ZnS) Pyr- Pyrrhotite (FeS) Gn- Galena (PbS)
Microinclusions	
Moncheite $(Pt,Pd)(Te,Bi)_2$ Hessite (Ag_2Te) Lead selenide (PbSe) Altaite (PbTe) (Ru,Ir)Os $(Ru,Ir)_2Os$ $(Pt,Bi)_2(Te,Ag)_3Mo_3$ Arsenides: (Os,Ir)As (Ir,Pt)As Oxides: titanohematite and manganoilmenite	Minerals of cobaltite-gersdorffite series with Pt, Ir, Rh, Ru, Os Cob- Cobaltite (CoAsS) Ni- cobaltite NiCoAsS(Ru, Rh, Pt, Ir, Os) Fe- cobaltite (FeCoAsS) Gersdorffite (NiAsS) Ull- ullmannite (NiSbS) Silver telluride β-Ag_2Te, γ-Ag_2Te Lead telluride (PbTe) Sperrylite **($PtAs_2$)** Tes-Testibiopalladite Pd(Sb,Bi)Te Native Silver Ac- Acanthite (**Ag_2S**) Mel- Melonite $(NiTe_2)$ Vav-Vavrinite (Ni_2SbTe_2) REE-bearing phosphates and fluorophosphates Previously undescribed rhenium minerals

Pt free drop	Drop containing Pt

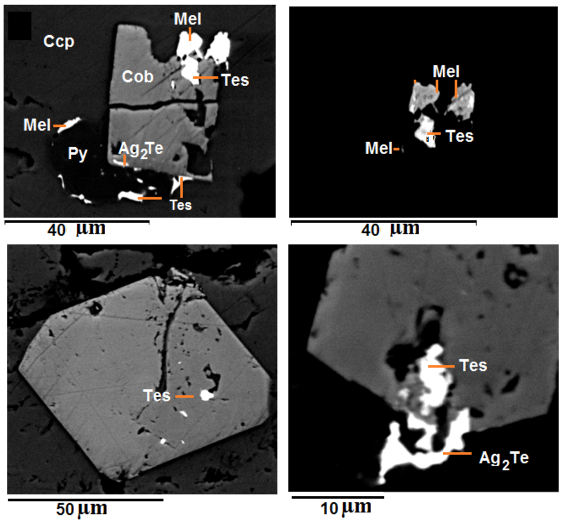




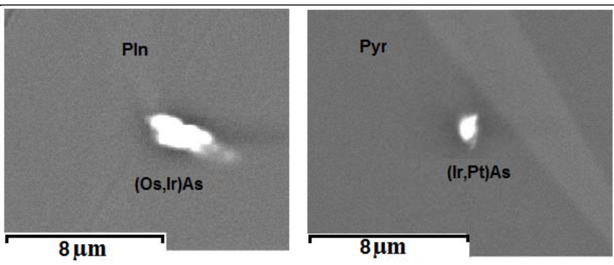
Images of polished sections from p-10 drill core. Symbols indicate position of analysed samples.

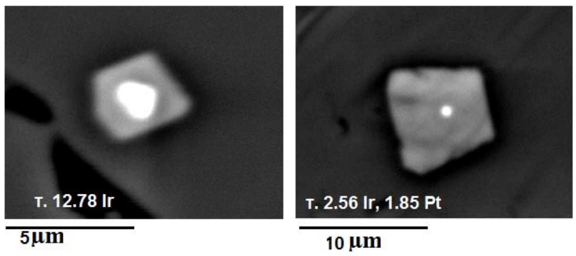


Platinoid forms

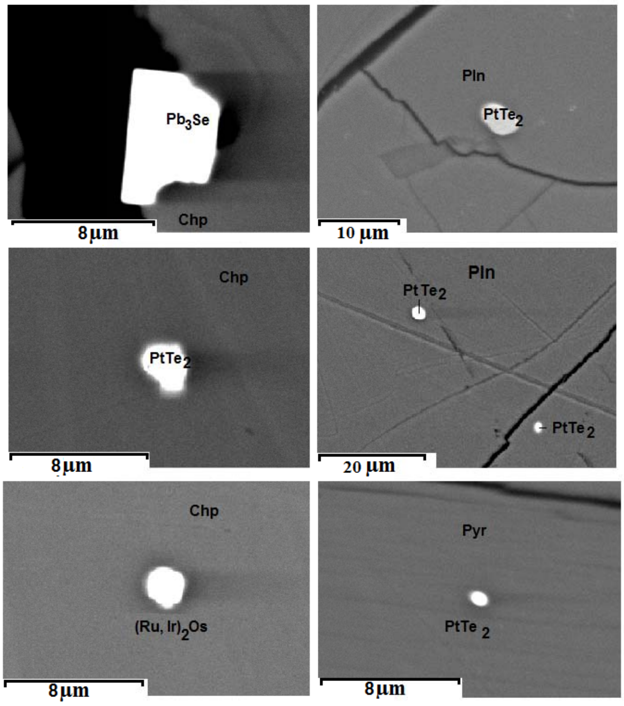


Cobaltite and Ni-Cobaltite

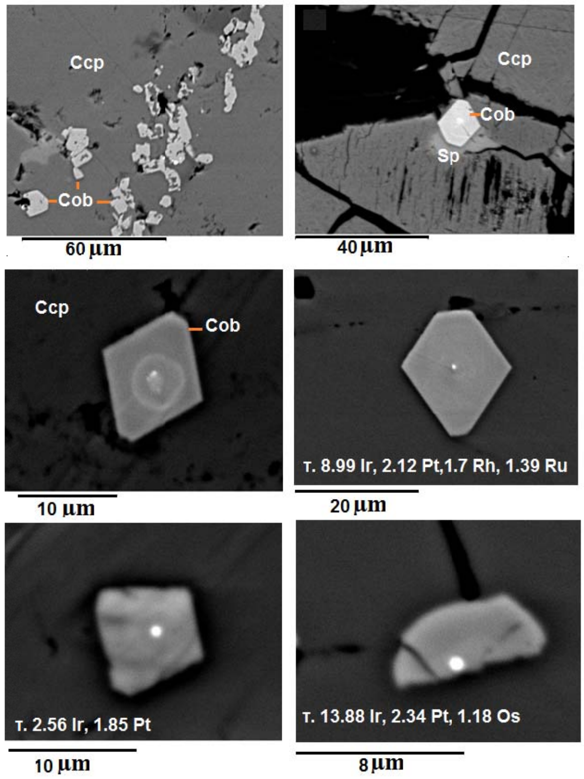




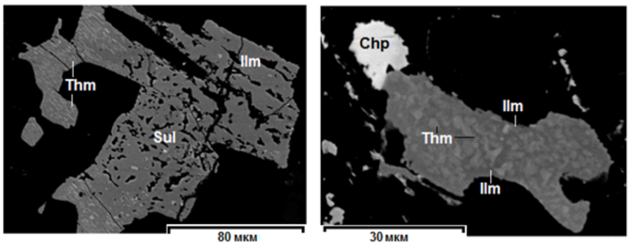
Ni-cobaltite with platinoid cores



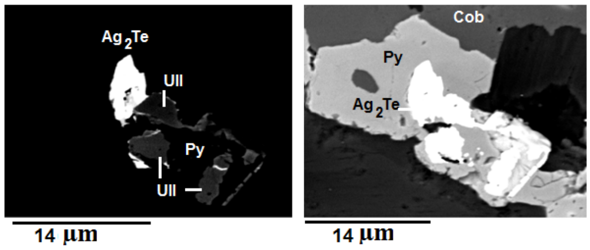
Mineral grains of rare elements



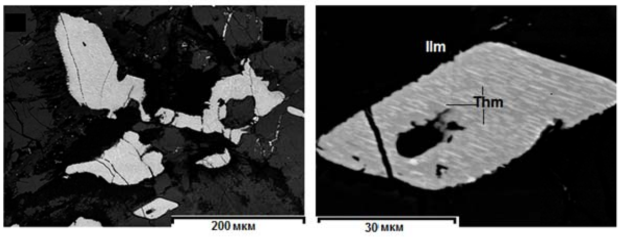
Ni-cobaltite with platinoid cores



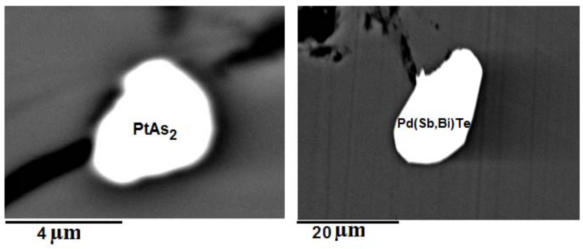
Decomposition structures of ilmenite solid solutions



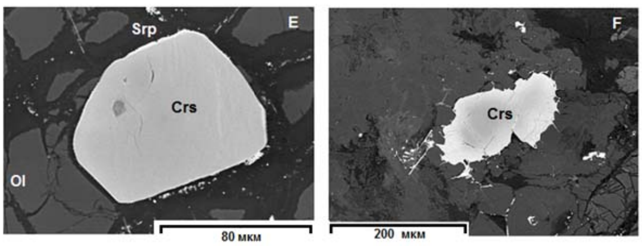
The shape and size of ullmannite grains

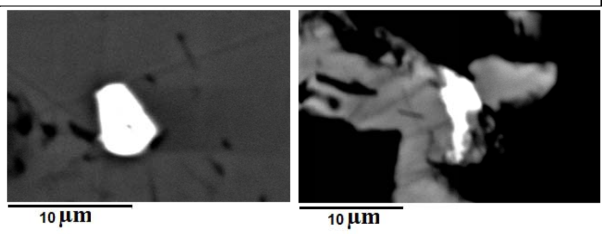


Decomposition structures of ilmenite solid solutions

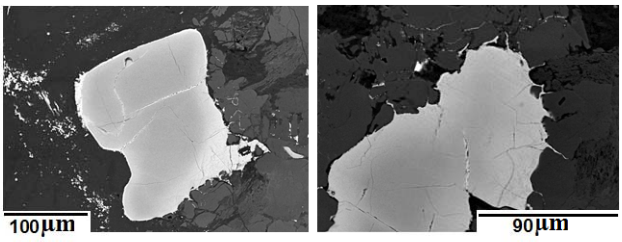


Sperrylite Testibiopalladite

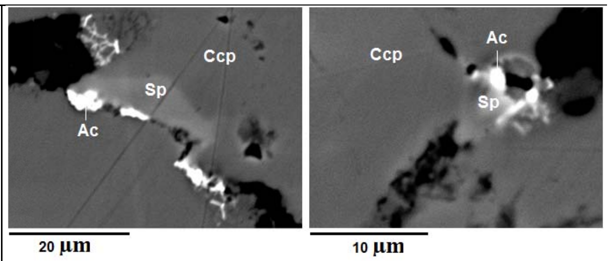




Sperrylite Native Silver



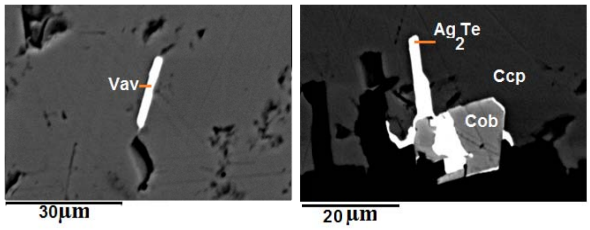
The shape and size of the chrome spinel grains



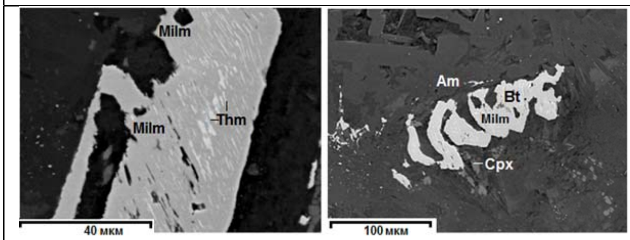
The shape and size of acanthite grains

Picrite diabases

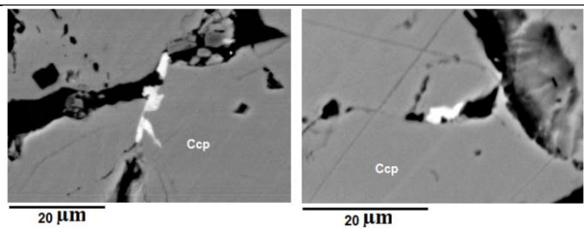
Pin- Pentlandite $(Fe,Ni)_9S_8$
Sig- Siegenite $(Co,Ni)_3S_4$
Mil- Millerite (NiS)
Gn- Galena (PbS)
Py- Pyrite (FeS_2)



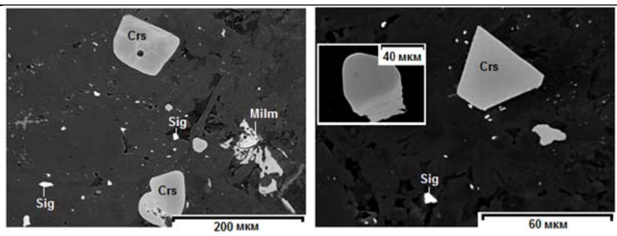
Vavrinite plate Silver telluride

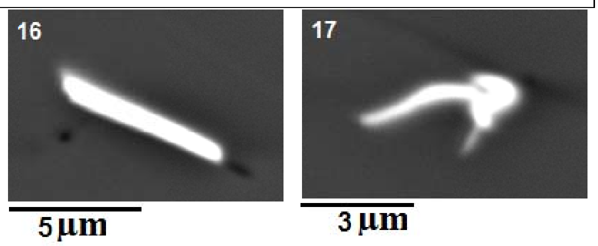


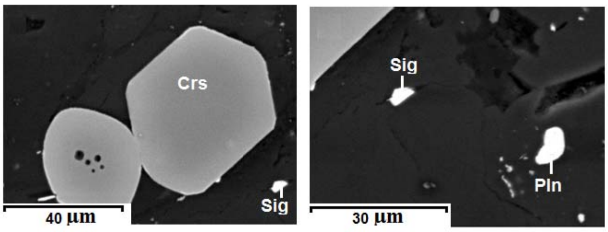
Decomposition structures of ilmenite solid solutions



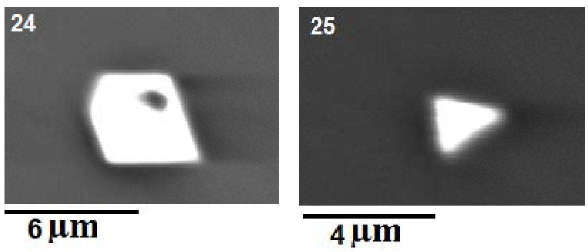
The shape and size of REE-bearing phosphate grains







The shape and size of Crs, Sig, Pln



The shape and size of Re-bearing minerals and phases

The revealed crystals of cobaltine, apparently, belong to two generations. The first is single crystals with heavy visible cores that fall into the plane of polished section or without visible cores, but with good zoning due to variations of PGE (osmium, iridium and platinum) in the mineral composition. These crystals were formed first and “sucked in” the platinoids from the ore magma. The ratio of platinoids between them varies from analysis to analysis. The second generation is the crystal aggregates, which by electron microprobe do not contain impurities. Analyzes of the chalcopyrite matrix in both cases also show the absence of impurities.

Stages of ore formation. From the sequence of formation of mineral phases and the analysis of the isothermal sections of the condensed Fe–Ni–S system (figure 1) it can be concluded that formation of the Karaturgay type sulfide copper-nickel mineralization apparently took place in several temperature regimes.

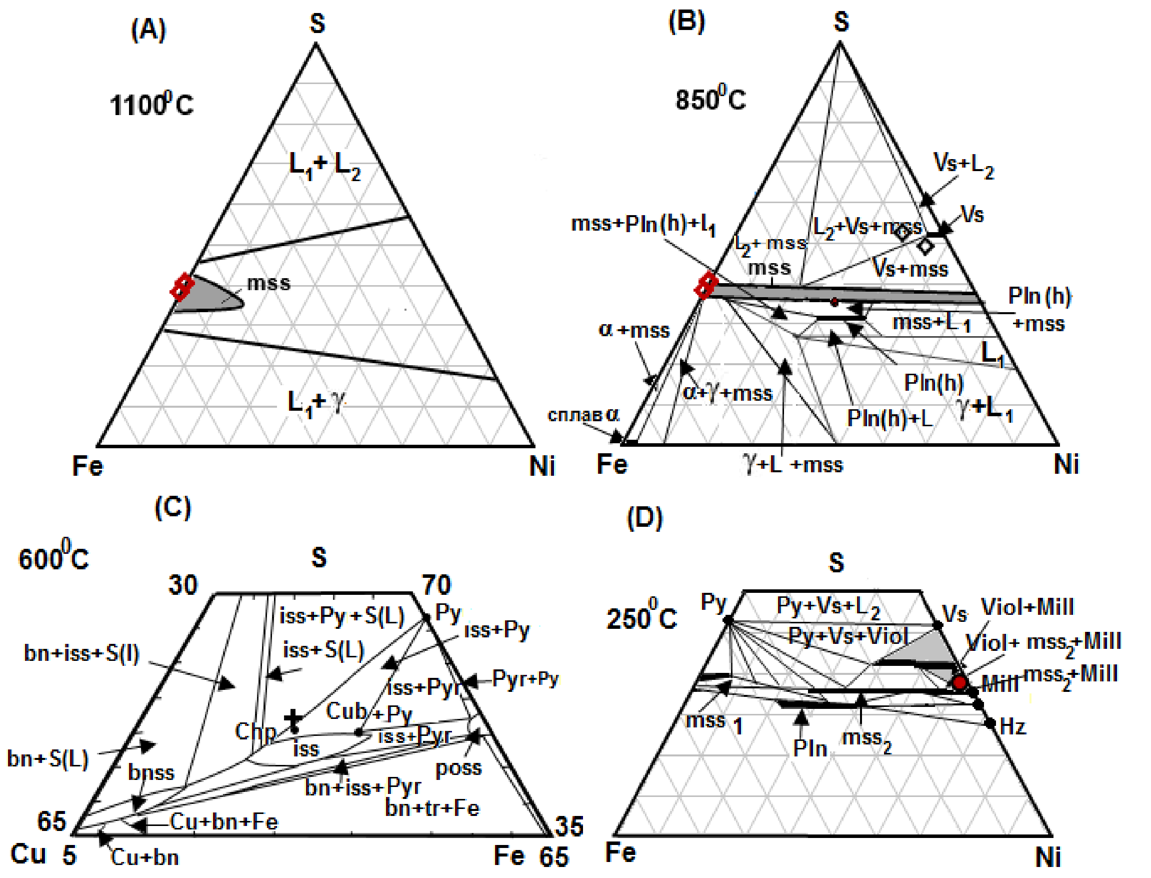


Figure 1 – Isothermal sections of condensed Fe-Ni-S systems [3] at temperatures of 1000° C (A), 850° C (B), 250° C (D) and Cu-Fe-S [4] at 600° C (C) for pyrrhotite (red rhombus), pentlandite (black mugs), chalcopyrite (black cross), siegenite (black rhombus), and millerite (red dot) from picrites and picritic diabases of the Karaturgay complex. mss - monosulfide solid solution; iss - intermediate solid solution; chalcopyrite (Chp); pentlandite (Pln); vaesite (Vs); pyrrhotite (Pyr); pyrite (Py); violarite (Viol); millerite (Mill); melt (L)

It is well established that troilite crystallized at 1190°C (Figure 1 (A). When cooled, the sulfide liquid, according to D. Ebel and A. Naldrett [5], becomes more saturated with Ni, which contributes to crystallization high-temperature polymorphic pentlandite [6] (figure 1 (B)).

The presence of siegenite, as suggested by A. Frolov, A. Lapin, *et al.* [7], indicates a decrease in temperature of the magma chamber below 806ºC. Following acquired data on composition of the studied sulfides and in agreement with conclusions of J. Craig and G. Kullerud [8], it can be inferred that the liquid in equilibrium with mss at 850ºC was enriched in Cu, but depleted in Ni relative to mss.

Taking into account the isothermal sections of the Cu–Fe–S system [4], it can be stated that the intermediate solid solution (iss) is separated from the Cu-containing mss. With a decrease in temperature (up to 400°C and less), iss supposedly decomposed into chalcopyrite-pyrrhotite mineral phases. The presence of millerite in the Fe-Ni-S system (figure 1 (D)), in accordance with findings of Craig [9], indicates that at 250°C mss divided into phases mss1 and mss2 + millerite. It is not contradict the conclusions made by K. Misra and M. Fleet [10] that at low temperature millerite and heazlewoodite (which was not indicated in our samples) stably coexist.

From the above discussion it can be concluded that formation of copper-nickel ores containing platinum metal mineralization proceeded with a decrease in temperature from 1200 to 100-135ºC. Apparently, such a rapid decrease in temperature of the igneous melt could occur in hypabyssal conditions. This assumption is supported by the presence of titanohematite in picrites. Although the presence of iron in sphalerite, as well as the presence of altaite, does not contradict this.

The platinoids and REEs, which are identified in sulfides, substantially increase the industrial interest in potential ores of the picrite-diabase Karaturgay complex. All these data indicate that the ore formation of Cu-Ni-(PGE)-(REE) ores of the Karaturgay type occurred within the open magmatic system. Recent studies [11] have shown that open igneous systems are favorable for the concentration of large amounts of sulfides. It also gives hope that large masses of Cu-Ni-(PGM)-(REE) ores can be localized at the bottom and in the root zones of the picrit-diabase Karaturgay complex.

It should be noted that the formation of rocks of the Karaturgay complex is apparently associated with repeated pulses in the magma chamber, which can be linked to the compression processes during the formation of the Rodinia supercontinent [12].

The formation of copper-sulfide ores and associated precious REEs and rare metals of the Mayke ore area took place under conditions of igneous and post-magmatic processes of mineral formation in several stages (figure 2).

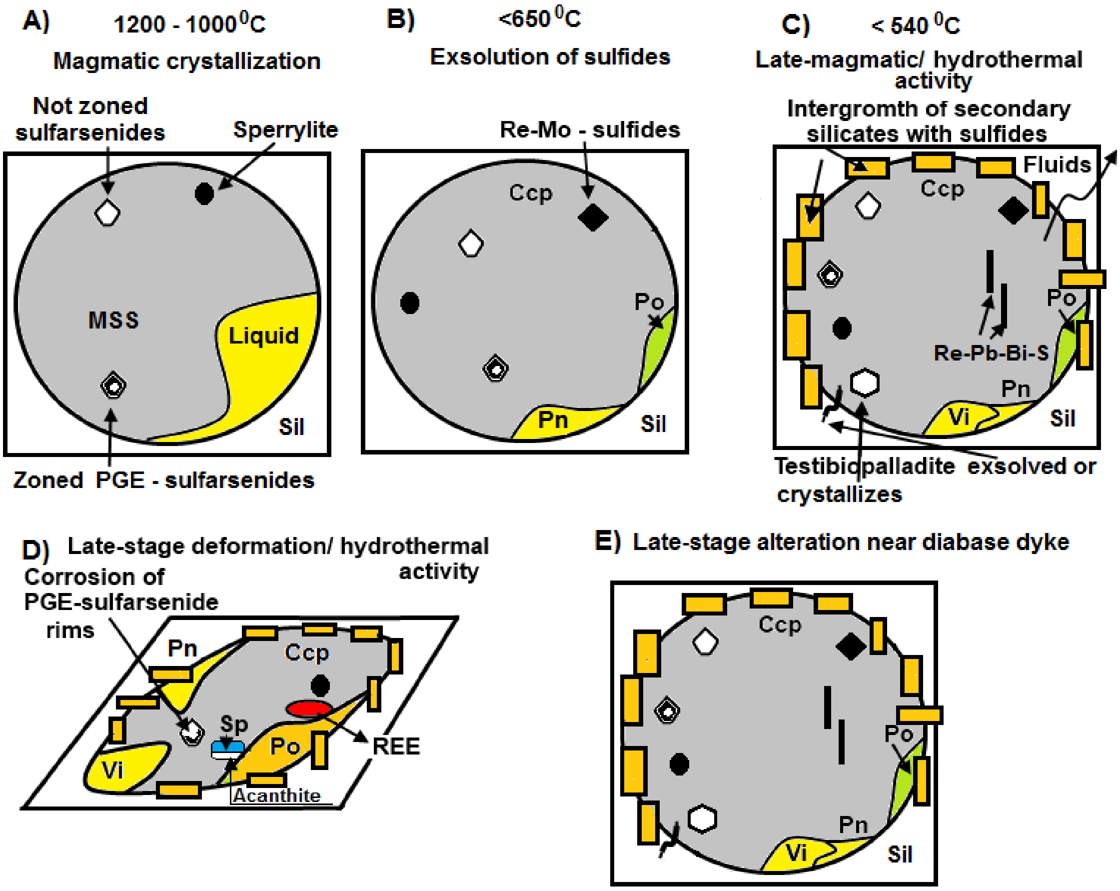


Figure 2 – Schematic model of the sequence of formation of PGE, rare minerals and sulfide of copper-sulfide ores from the Mayke deposit, built on the basis of the materials of the article [13].
A. Early crystallization of small idiomorphic zonal PGE-sulfoarsenides and sperrylite from sulfide liquid and their fusion in MSS.
B. Evolution of sulfide minerals (pentlandite, pyrrhotite, chalcopyrite), including rhenium sulfide and molybdenite, when cooled to a temperature below 650°C.
C. Late magmatic and/or hydrothermal activity and the subsequent recrystallization of sulfides of base metals with secondary silicates simultaneously with the formation of testibiopalladite and Pb-Te-phases either as dissolution of sulfides of base metals, or during crystallization from small volumes of trapped melt.
D. Demobilization of sulfides at a later stage in fracture zones and corrosion of existing PGE sulfoarsenides, formation of acanthite on sphalerite and formation of REEs fluorophosphates and phosphates

Copper-sulphide ores formed during the magmatic stage. They contain nickel and cobalt sulfoarsenides, including Pt, Ir, Rh, Ru and Os-containing minerals. Likewise, platinum arsenide (sperrylite) is found in chalcopyrite.

Tellurium antimonite (testibiopalladite), forming individual crystals, is found in both chalcopyrite and Ni, Co-bearing sulfoarsenides. This mineral is the main source of palladium (up to 25% Pd).

Apparently, rhenium mineral formation also occurred at that stage. Their microinclusions are associated mostly with chalcopyrite and extremely rarely with pyrite.

Ullmannite is extremely rare. It occurs in association with nickel and cobalt sulfoarsenides. This mineral is characterized by a wide range of impurity elements, including Ag, Pd, Te, Bi, which is characteristic for mineral associations of hydrothermal deposits.

At this stage polymetallic mineralization was superimposed on copper-sulphide ores. Sphalerite is commonly accompanied by the formation of acanthite and native silver. Late minerals are REEs phosphates and fluorophosphates.

The inferred sequence of formation of copper sulfides ores spatially and genetically associated with linear-fissure carbonatites is indirectly supported by data on the isotopic composition of lead in pyrite-polymetallic deposits of the Northern Ulytau, previously studied by Koshevoy [14].

The isotopic composition of lead from the deposits in this region indicates a complex multi-stage formation history of sulphide ore deposits in the Kurgasy region, which involved mixing ancient anomalous lead of the Proterozoic age with ordinary lead, which brought at the time of tectono-magmatic activation in the Early Paleozoic.

It is likely that described formation pathways of carbonatite associated sulfide ore deposits are characteristic for the mantle chambers are initially developed above the subduction zones. Their spatial connection with the subduction zones is confirmed by the presence of NaCl in the initially plutonic ultrabasic rocks.

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МАЯТАС КЕНДІ АУДАНЫНЫҢ ҚАРАТОРҒАЙ ЖӘНЕ МАЙКЕ КЕНДІ ТҮРЛЕРІНДЕГІ АСЫЛ ЖӘНЕ СИРЕК ЭЛЕМЕНТ МИНЕРАЛДАРЫ (СОЛТҮСТІК ҰЛЫТАУ, ҚАЗАҚСТАН)

Аннотация. Қараторғай кешенінің пикриттерінде бұрыннан белгілі сульфидтермен бірге алғаш рет зигенит, платина теллуриді – мончеит, күміс теллуриді – гессит, қорғасын теллуриді – алтаит, қорғасын селениді, ирид тобының металдарының қатты ерітінділері (Ir, Os, Ru), сирекжерэлементтері (Dy, Er, Y, Ce) анықталды. Пикритті диабаздардың құрамында пентландит және пиритпен бірге алғаш рет бұрындары караторғай кешенінің таужыныстарының құрамында сипатталмаған зигенит пен миллерит анықталды. Майке кенбілінімінде карбонат кенді минералдарынан бөлек кобальтин- герсдорфит қатарындағы Pt, Ir, Rh, Ru, Os; ульманит, күміс теллуриді – гессит; қорғасын теллуриді – алтаит, сперрилит; тестибиопалладит; өзіндік күміс; акантит; мелонит; ваврinит; фосфаттар және СЖР фторфосфаттарының микроқоспа минералдары анықталды. Микроқоспаның ерекше тобын Қазақстанда алғаш рет табылған рений минералдары құрайды.

Минералды фазалардың бөліну реттілігі және Fe-Ni-S конденсацияланған жүйенің изотермиялық қималарын талдауды ескере отырып қараторғай түрдегі сульфидті мыс-никель минералдарының түзілу жағдайлары мен температуралық режимдері қарастырылды. Минерал түзілу кезеңдерін талқылай отырып, Майке кенбілінімінің сирек минералдар мен мыстотыққан кендердің сульфидтерін, ПТМ қалыптастыру кезектілігінің схемалық моделі келтірілген.

Түйін сөздер: СЖЭ, ПТМ, минералдардың химиялық құрамы, пикриттер, пикритті диабаздар, карбонатиттер, Маятас кенді ауданы, Солтүстік Ұлытау, Қазақстан.

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МИНЕРАЛЫ БЛАГОРОДНЫХ И РЕДКИХ ЭЛЕМЕНТОВ В РУДАХ КАРАТУРГАЙСКОГО И МАЙКЕЙСКОГО ТИПОВ МАЯТАССКОГО РУДНОГО РАЙОНА (СЕВЕРНЫЙ УЛЫТАУ, КАЗАХСТАН)

Аннотация. В пикритах каратургайского комплекса наряду с ранее известными сульфидами впервые обнаружены зигенит, теллурид платины - мончеит, теллурид серебра - гессит, теллурид свинца - алтаит, селенид свинца, твердые растворы металлов иридиевой группы (Ir, Os, Ru), редкоземельные элементы (Dy, Er, Y, Ce). В составе пикритовых диабазов наряду с пентландитом, пиритом и галенитом впервые обнаружены зигенит и миллерит, ранее не описанные в составе пород каратургайского комплекса. В карбонатитах рудопроявления Майке впервые установлен медный колчедан, а также микровключения минералов кобальтин-герсдорфитового ряда с Pt, Ir, Rh, Ru, Os; ульманит; теллурид серебра – гессит; теллурид свинца - алтаит; сперрилит; тестибиопалладит; самородное серебро; акантит; мелонит; вавринит; фосфаты и фторфосфаты РЗЭ. Особую группу микровключений образуют впервые найденные в Казахстане минералы рения.

С учетом последовательности выделения минеральных фаз и анализа изотермических сечений конденсированной системы Fe-Ni-S рассмотрены температурные режимы и условия образования сульфидной медно-никелевой минерализации каратургайского типа. Приведена схематическая модель последовательности формирования МПГ, редких минералов и сульфидов медноколчеданных руд рудопроявления Майке с обсуждением этапов минералообразования.

Ключевые слова: РЗЭ, МПГ, химический состав минералов, пикриты, пикритовые диабазы, карбонатиты, Маятасский рудный район, Северный Улытау, Казахстан

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Верстка *Д. Н. Калкабековой*

Подписано в печать 12.04.2019.
Формат 70x881/8. Бумага офсетная. Печать – ризограф.
15,2 п.л. Тираж 300. Заказ 2.

Национальная академия наук РК
050010, Алматы, ул. Шевченко 28, т. 272-13-19, 272-13-18