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= **RUBRICS** =

New Ore Minerals from the Kingash Ultramafic Massif, Northwestern Eastern Sayan

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Abstract—The paper discusses earlier poorly studied mineralized rocks of the Kingash ultramafic complex in the Kan Block of the Eastern Sayan, including the large Cu–Ni–PGE deposit of the same name. Despite many researchers' increased interest in the Kingash massif, a number of questions related to the petrology, formation mechanism, and localization of Cu–Ni–PGE ore remain controversial. Along with already known ore minerals, we have identified and described a number of new mineral species: argentite, Fe-enriched sperrylite, a bismuth variety of merenskyite, gersdorffite, cobaltite, and thorianite. The ore minerals are distinguished by a higher relative amount of Fe, and this makes the Kingash deposits close to other Paleoproterozoic Cu–Ni deposits, e.g., the Jinchuan in China, Pechenga in Russia, Ungava in Canada, Mt. Scholl in Australia, etc.

Keywords: Kingash massif, ultramafic rocks, ore mineral, thorianite, chemical composition **DOI:** 10.1134/S107570151707011X

INTRODUCTION

Ultramafic and mafic–ultramafic intrusions are derivatives of mantle melts; they not only bear both valuable information on deep-seated zones of the Earth, they also make it possible to trace the evolution of ultramafic and mafic rocks. Chromite, copper– nickel sulfide, and PGE deposits are related to these rocks.

Various bodies of ultramafic and mafic rocks, frequently small in size, are widespread in the Kan Block of the Eastern Sayan. They are mapped as numerous massifs, usually not large, and they draw the attention of many geologists owing to their potential mineralization (*Platinonosnost* ..., 1995; Kornev et al., 2004; Chernyshov et al., 2010; Yurichev, 2013; Yurichev et al., 2013). However, typification and metallogenic specialization of these objects are often debatable and require further study.

The object of our study is the mineralization hosted in the Kingash ultramafic massif. This massif is, in turn, a reference object in the dunite—wehrlite—picrite complex of the same name (Chernyshov et al., 2004); it comprises a large Cu—Ni—PGE deposit (Glazunov et al., 2003). Despite keen interest in the Kingash massif, a number of questions related to the depth of its formation, comagmatic relationships between mafic and ultramafic rocks, the formation conditions, and localization of related Cu—Ni—PGE ore remain controversial. The results make it possible to widen the mineralogical ore specialization of the Kingash massif and refine the compositions of the initial ore-controlling magmatic melt.

GEOLOGICAL OVERVIEW

The Mesoarchean–Paleoproterozoic ultramafic massif is localized within the greenstone belt of the Kan Block in the Eastern Sayan (Kornev and Ekhanin, 1997). Many aspects of its internal structure and origin remain a matter of debate. Some authors refer it to layered intrusions (Glazunov et al., 2003); some suggest that the massif is a subvolcanic intrusive body linked to a basalt–komatiite association (Tsypukov, et al., 1993; Nozhkin et al., 1995; Chernyshov et al., 2004). Still others consider it a fragment of the Kingash basalt–komatiite volcanic complex (Kornev and Ekhanin, 1997; Kornev et al., 2004), while there are some who assume that the massif closely fits polygenetic complexes rather than layered intrusions (Gertner et al., 2009).

The Kingash massif is mapped in plan view as a large lens $(3 \times 0.7 \text{ km})$ elongated in the near-meridional direction and lies conformably with the structure 1 of framework rocks. Its contacts with country rocks are tectonic (Nozhkin et al., 1996). The massif is made up of ultramafic and gabbroic rocks with significant prevalence of the former in abundance. Ultramafic



Fig. 1. Schematic geological map of Kingash mafic—ultramafic massif, compiled by N.A. Tret'yakov and V.A. Prokhorov; edited by A.N. Yurichev and A.I. Chernyshov. (1) host rocks: gneiss, amphibolite, marble; (2) granitic rock; (3) serpentinite; (4) ultramafic rock; (5) clinopyroxenite; (6) gabbroic rock; (7) faults: (a) reliable, (b) inferred; (8) geological boundary.

rocks are exposed in its northern part and are overlapped by gabbroic rocks in the south (Fig. 1).

According to our investigations, the ultramafic part of the massif is largely composed of cumulative dunite and its serpentinitized varieties, whereas wehrlite and picrite are less abundant. The aforementioned rocks do not reveal any stratification in the massif, but are disturbed chaotically. It is suggested that the ultramafic body formed in a magma chamber under conditions of an active tectonic setting, when the compressive regime periodically gave way to extension (Chernyshov et al., 2004). At the time of extension, pulsatory intrusions of heterogeneous ultramafic melts apparently penetrated into the chamber along weakened zones. These melts arose as a result of magma fractionation in deep-seated intermediate magma chambers.

Gabbroic rocks overlapping the ultramafics apparently are the subsequent, intrusion phase, which is detached in time. Clinopyroxenite at the contact between ultramafic and gabbroic rocks is apparently their reaction product (Chernyshov et al., 2010).

METHODS

The chemical composition of ore minerals was analyzed by X-ray spectral microanalysis (Reed, 2005) on a Tescan VEGA II LMU SEM equipped with EDS (with the Si(Li) standard) INCA Energy 350 and wave dispersion INCA Wave 700. Parallel-sided polished platelets 3–4 mm thick were produced for the study using the technique recommended by Taylor and Radtke (1965) and Reed (2005). A carbon layer 25–30 nm in thickness was preliminarily sputtered before analysis. The chemical compositions were subsequently calculated in the INCA-Issue 18b program.

For reliable quantitative analysis of the revealed ore mineral compositions, they were studied on a Camebax microprobe under the following conditions: accelerating voltage 20 kV, probe current 20-30 nA, time of counting at each analytical line 10 s. Pure metals were used for determination of Pd, Pt, Ag, Fe, Ni, and Co; NiAs for As; Bi₂S₃ for Bi; and PbTe for Te.

NOBLE METAL MINERALIZATION

Our studies allowed us to identify for the first time in ultramafic rocks of the Kingash massif a new silver sulfide—*argentite*—in addition to other Au—Ag minerals (hessite, native gold, copper and palladium gold, electrum, küstelite, auricupride, tetra-auricupride, and gold and silver amalgams). A new mineral is observed as single inclusions in pyrrhotite grains. They have a tabular shape and a size up to 0.01 mm (Fig. 2a). The chemical composition of argentite is close to its stoichiometric formula. Separate grains contain an insignificant iron admixture (Table 1).

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Fig. 2. Newly identified ore minerals in ultramafic rocks of Kingash deposit.

Among platinum group minerals (PGM), we identified Fe-enriched sperrylite and Bi-enriched merenskyite. As follows from Shvedov et al. (1997, 2001), sperrylite is the most abundant PGM in all types of Cu–Ni ores (disseminated, breccia-like, massive) hosted in ultramafic rocks of the Kingash massif. Two generations of sperrylite are suggested: early primary magmatic and late redeposited. *Ferriferous* sperrylite identified by us is represented by single large, almost isometric grains up to 0.05 mm in size (Fig. 2b). They do not reveal any link to other PGM and constantly

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contain up to 2.8 wt % Fe. The typomorphic and chemical features of this sperrylite variety correspond to the first magmatic generation. Earlier-identified late (redeposited) sperrylite commonly occurs in close association with other PGM (michenerite, merenskyite) or makes up intimate intergrowths with sulfides represented by chalcopyrite and pentlandite (Kornev et al., 2001).

After michenerite, merenskyite is the Pd mineral next in abundance at the Kingash deposit. It occurs in high-grade breccia-like Cu–Ni ore, as well as epigen-

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Mineral	Fe	Ni	As	Co	Pt	Te	Pd	Bi	Ag	s	Total	Formula
Argentite	_	_	_	_	_	_	_	_	87.27	12.72	99.99	Ag _{2.04} S _{0.96}
	0.06	_	_	_	_	_	_	_	86.99	12.69	99.14	$Ag_{2.04}S_{0.96}$
Fe-enriched	1.84	0.74	42.66	_	52.76	_	_	_	_	_	99.00	$(Pt_{0.95}Fe_{0.11}Ni_{0.04})_{1.10}As_{1.90}$
sperrylite	1.26	—	42.40	—	55.06	—	—	—	—	_	98.72	$(Pt_{0.99}Fe_{0.08})_{1.07}As_{1.90}$
	1.43	0.50	42.74	—	54.96	_	_	—	_	_	99.63	$(Pt_{0.98}Fe_{0.09}Ni_{0.03})_{1.10}As_{1.90}$
Bi-enriched merenskyite	—	_	_	_	9.70	46.49	16.01	27.80	—	—	100.00	$(Pd_{0.66}Pt_{0.2l})_{0.87}(Te_{l.57}Bi_{0.57})_{2.13}$
	_	0.11	_	_	9.52	45.43	16.78	28.12	—	_	99.96	$(Pd_{0.68}Pt_{0.21}Ni_{0.01})_{0.90}(Te_{1.53}Bi_{0.57})_{2.10}$
Maucherite	1.50	49.89	48.45	0.41							100.25	$(Ni_{10.51}Co_{0.09}Fe_{0.33})_{10.93}As_{8.07}$
Gersdorffite	7.32	30.20	46.14							16.24	99.90	$(Ni_{0.83}Fe_{0.21})_{1.04}As_{1.14}S_{0.82}$
Cobaltite	3.50	3.46	45.49	28.69						18.85	99.99	$(Co_{0.80}Ni_{0.10}Fe_{0.10})_{1.00}As_{1.03}S_{0.97}$
	3.48	4.09	45.75	28.02						18.66	100.00	$(Co_{0.78}Ni_{0.11}Fe_{0.10})_{0.99}As_{1.06}S_{0.95}$

Table 1. Chemical composition of ore minerals newly found in Kingash massif, wt %

Here and below, the chemical composition was determined by X-ray spectral microanalysis using a Tescan Vega II LMU SEM equipped with EDS and WDS at the Shared Analytical Facilities of the Analytical Center for Natural System Geochemistry, Tomsk State University, Tomsk, and a Camebax-micro microprobe at the Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences, Novosibirsk.

Table 2. Chemical composition of thorianite from cumulative dunite at Kingash ore deposit, wt %

Sample	ThO ₂	UO ₂	FeO	Total	Formula
1	71.87	26.58	0.84	99.29	$(Th_{0.72}Fe_{0.03}U_{0.26})_{1.01}O_{1.99}$
2	74.36	24.47	1.18	100.01	$(Th_{0.74}Fe_{0.04}U_{0.24})_{1.02}O_{1.98}$
3	72.94	25.53	0.97	99.44	$(Th_{0.73}Fe_{0.03}U_{0.25})_{1.01}O_{1.99}$
Average	73.06	25.52	1.00	99.58	

etic disseminated and stringer disseminated varieties of ore in the form of tiny (up to 0.01 mm) oval grains. The mineral frequently occurs in close association with michenerite in pyrrhotite—pentlandite or pentlandite aggregates (Fig. 2c). *Bi-merenskyite* with up to 28.1 wt % Bi (Table 1) was not mentioned earlier at this deposit and is apparently an intermediate variety in the michenerite—merenskyite solid solution series, as corroborated by the close association of these minerals. Replacement of tellurium with bismuth, as well as the constant presence of Pt (up to 9.7 wt %) and Ni (up to 0.11 wt %) admixtures are typical of this mineral from other platinum deposits (Isokh et al., 1992; Barkov et al., 1994).

ARSENIDES AND SULFOARSENIDES

Arsenides and sulfoarsenides limited in occurrence—maucherite, gersdorffite, and cobaltite—have been identified and studied in this work. Maucherite and gersdorffite have been noted in close association with chalcopyrite aggregates (Fig. 2d). *Maucherite* is represented by hypidiomorphic-granular and small round grains (up to 0.04 mm) with corona rims of *gersdorffite*. The chemical composition of maucherite (Table 1) coincides in chemistry with an earlier found single maucherite grain: 49.63 wt % Ni, 0.91 wt % Co, 1.67 wt % Fe, and 47.77 wt % As (Kornev et al., 2001). Gersdorffite does not reveal a Co admixture in its composition. Meanwhile, a mixture of Co in the range

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of 13,5 to 15.5 wt % was constantly noted earlier at the Kingash deposit. This mineral apparently is an intermediate variety in the gersdorffite–cobaltite solidsolution series.

We have identified *cobaltite* in ultramafic rocks at the Kingash deposit for the first time as tiny octahedral inclusions within pyrrhotite grains (Fig. 2e). An insignificant Ni admixture in the chemical composition of cobaltite is caused by isomorphic substitution of Co with Ni, whereas an insignificant amount of isomorphic substitution by Fe is caused by contamination of grains with fine mechanical pyrrhotite admixture (Table 1).

THORIANITE

Thorianite grains found for the first time are characterized by a euhedral appearance, small size (0.005-0.015 mm), and semimetallic to metallic luster (Fig. 2f). In chemical composition (Table 2), the thorianite is close to its stoichiometric formula and always reveals an Fe admixture (up to 1.2 wt % Fe).

DISCUSSION AND CONCLUSIONS

(1) Along with known ore minerals, the first established argentite, ferriferous sperrylite, Bi-enriched merenskyite, gersdorffite, cobaltite, and thorianite are characterized.

(2) The compositions of noble metal minerals at the deposit are characterized by a small deviation from stoichiometry. This feature, which was also noted by Kornev et al. (2001) and Shvedov et al. (2001), is apparently caused by geochemical specialization of the ore-magmatic system and multiple superposition of high-temperature metamorphism.

(3) The Fe admixture in primary magmatic Feenriched sperrylite, along with the special composition of the sulfide mineral assemblage with the participation of troilite, mackinawite, and constantly Feenriched pentlandite, point to the high-Fe Kingash ore-magmatic system, and bring it into the group of other Paleoproterozoic Cu-Ni deposits: Jinchuan in China, Pechenga in Russia, Ungava in Canada, Mt. Scholl in Australia, etc.

(4) The occurrence of Fe-sperrylite corroborates the earlier suggestion (Kornev et. al., 2001) about two generations of these minerals at the Kingash deposit. We refer the sperrylite identified by us for the first time to the primary magmatic generation.

(5) Chemical composition of the identified maucherite is rigourously compared with that of a single maucherite grain described by Kornev et al. (2001). This is evidence for the higher abundance of this mineral at the deposit than had been assumed until now.

(6) Thorianite from the Kingash deposit is apparently contaminated with magmatic melt derived from host amphibolite-gneiss sequences, where Th-TR anomalies have been recorded (oral communication by A.N. Smagin, 2008).

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Translated by V. Popov

SPELL: 1. conformably