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RARE METAL MINERALIZATION OF TIN MANIFESTATIONS IN THE AREA OF LITHIUM-FLUORIC GRANITES (VERKHNEURMIYSK ORE CLUSTER, THE AMUR RIVER REGION)

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Rare-Metal Mineralization of Sn Occurrences in the Area of Li–F Granites, Verkhneurmiysky Ore Cluster, Amur Region

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Abstract—The by-products of the Far East Sn deposits related to Li–F granites include trace elements. The petrography and mineral composition of the Sn-bearing metasomatites of the Verkhneurmiysky ore cluster (VUOC) of the Amur region (feldspatites, greisens, zwitter, tourmalinites, and chloritites) and the multistage complex rare-metal (RM) mineralization of the Sn occurrences in area of Li–F granites are studied. The minerals of strategic metals (Nb, Ta, W, Y, REE (from La to Lu), Be, Li, Rb, Zr, Hf, In, Sc, Se, Cd, and Te) are found. The RMs occur as minerals (fergusonite, plumbopyrochlore, allanite, monazite, roquesite, saku-raiite, etc.) and isomorphic substitution in the ore (wolframite; cassiterite; Cu, Sn, Fe, Mo, Zn, and Pb sulfides; native bismuth; etc.) and rock-forming (fluorite, siderophyllite, muscovite, and epidote) minerals. Some RMs (Y, REEs, Nb, In, and Sc) most frequently occur in Sn-bearing metasomatites. The RM minerals formed during the VUOC evolution (from the premineral feldspatite to the postmineral chloritite stage) with decreasing intensity of RM mineral formation and compositional evolution from lithophile to chalcophile RMs: (LREE, Zr, Hf) → (W, Nb, Ta, Y, HREEs, Sc) → (Sn, In, Cd, Se, Te). The formation of the VUOC RM mineralization was caused by magmatic, metasomatic, and crystal chemical factors. The possible complex exploration of the Far East Sn deposits is shown for areas of Li–F granites.

Keywords: rare metals, Li–F granites, feldspatites, greisens, zwitter, tourmalinites, Verkhneurmiysky ore cluster, Amur region

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INTRODUCTION

The growing use of rare metals (RMs) in the production of new types of materials and high-tech production, their importance in strengthening national defense capabilities, and the need to reduce the dependence of Russia on imports pose the challenge of finding new sources of RMs. In terms of known RM (including critical REEs such as Nb, Be, Li, Ta, Sc, In, Cd, and Hf) reserves, Russia occupies one of the first places in the world; however, the exploitation of their potential is hindered by the scarce data on by-product RMs in the ores from the deposits. One of the main trends in the development of the RM mineral base is enhanced mineralogical–geochemical re-estimation of complex deposits and searched areas as sources of critical RMs [7, 9, 16].

Sn deposits associated with Li–F granites can be a RM source along with RM deposits [3, 5–7, 9–11, 24, 28, 29]. In this paper, we characterize the Sn-bearing metasomatites of the cassiterite–quartz and cassiterite–silicate occurrences of the Verkhneurmiysky ore cluster (VUOC) in the Amur region. The composition and mode of occurrence of RMs in the hydrothermal

minerals and their evolution are studied. The aim of the paper is to draw attention to the by-product RM mineralization of W–Sn deposits related to Li–F granites.

Sn-BEARING DEPOSITS AS A SOURCE OF RARE METALS

The term “rare metals” has changed through time depending on the advancement of geological exploration and processing technologies and the conditions of the mineral market [24, 32]. The relatively recent involvement of RMs in industry is related to their mineralogical–geochemical features, including low content and heterogeneous distribution in the crust, dispersion in rock-forming and ore minerals, and species diversity and compositional complexity of RM minerals. The geological economic types of RM deposits are diverse and are caused by the types of ore-bearing igneous complexes and the genetic class of ores. Productive complexes include alkaline–granite, subalkaline–granite, normal granite, nepheline–syenite, alkaline–gabbroic, and alkaline–ultramafic intrusives with related ore-bearing plutonites, pegmatites, car-

[†] Deceased.

Table 1. Comparative characteristic of geological economic types of the deposits with RM granites [2, 5–8, 23, 29, 32, 33]

Feature	Alkali-granite type		Subalkali-granite type	
	Alkali granites	Feldspatites	Li-F granites	Zwitter
RM minerals	Pyrochlore, columbite, zircon, gagarinite, cryolite, yttrifluorite, fluorite, xenotime, monazite, polyolithionite	Beryl, phenakite, bertrandite, fluorite, zirconite, pyrochlore, columbite, polycrase, euxenite, fergusonite	Microlite, tantalite–columbite, strüverite, cassiterite, lepidolite, zinnwaldite, amblygonite, fluorite	Cassiterite, wolframite, beryl, fluorite, lepidolite, zinnwaldite, tantalite–columbite
Major metals	Ta Nb Zr	Ta Nb Zr Be	Ta Li	Sn W
By-product rare metals	Y HREE Hf cryolite	Y HREE Li Hf Rb Cs fluorite cryolite	Nb Sn Rb Cs fluorite amazonite	Ta Li Rb Be fluorite
Reserves	Large and unique	Large and unique	Small and medium	Large and unique
Deposits	Zashikha, Ulug-Tanzek, Snezhnoe (Russia); Verkhnee Espe, Losevskoe (Kazakhstan); Khan-Bogdo, Khaldzan-Buregtei (Mongolia); Madeira (Brazil); Jos-Bukuru (Nigeria)	Zashikha, Erma-kovskoe , Katugin, Snezhnoe, Bugunda, Ulkan (Russia); Verkhnee Espe, Kurmenty (Kazakhstan); Tor Lake (Canada); Kaffo (Nigeria)	Orlovskoe, Etykin, Alakhi, Bitu-Dzhida (Russia); Golubye Sopki (Kazakhstan); Urt-Goigor (Mongolia); Suchzhou (China); Montebra (France); Abu-Dabbab (Egypt)	Etykin , Spokoininskoe (Transbaikalia); Pogranichnoe, Voznesenskoe , Tigrinoe, Olonoï, Nevskoe, Pravourmiyskoe, Kester , Odinskoe, Polyarnoe, Pyrkakai (Far East); Maikul, Karasu (Kazakhstan); Baga-Gazryn, Zhanchivilan, Barun-Tsogto (Mongolia); Krupka, Zinovec (Czech Republic); Altenberg (Germany); Echassier , Pui-le-Vin (France); Tin-Amzi (Algeria), Ichun, Syankhualin (China)

Rare metals were extracted in the highlighted deposits.

bonatites, volcanic rocks, metasomatites, RM weathering mantle, and placers [5–7, 9, 16, 24, 32].

Among the deposits of deficient RMs (Ta, Be, HREE, Y, Li, Rb, and Hf) in Russia, of special interest are the economic objects related to RM granites, which include alkaline agpaite and subalkaline plumasite granites significantly distinct in geological setting, composition, and size of ore mineralization. The alkali granites and associated metasomatites host large and unique complex Ta, Nb, Zr, and Be deposits: Katugin in Transbaikalia, Ulug-Tanzek in Tuva, Ermakovskoe in Buryatia, and their analogs abroad. Subalkali Li–F granites (LFGs) contain small and medium Ta and Li deposits with by-product Nb, Sn, Rb, and Cs. Zwitter and other metasomatites, however, bear the richest W–Sn mineralization; by-product Ta, Li, and Be minerals; and fluorite. Tens of deposits of Sn–RM zwitter are known in Europe, Middle and Southeast Asia, North Africa, and South America [2, 5, 7, 9, 13, 16, 24, 30, 31, 33, 34] (Table 1).

Large deposits of RM–Sn zwitter are abundant in LFG areas of east Russia: Voznesenskoe, Pogranichnoe, Tigrinoe, Stlanikovy, Olonoï, Pravourmiyskoe,

Nevsky, Kester, Odinskoe, Polyarnoe, Pyrkakai, etc. [2–7, 9–13, 18–20, 22, 23, 25, 26, 28, 29] (Table 1). From the viewpoint of traditional classification, these deposits belong to the cassiterite–quartz type. In the Far East, it is suggested to ascribe them to a new RM–Sn (cassiterite–RM) type [13, 26]. The mineralogical–geochemical study of the RM potential of Sn deposits is a topical problem. The deposits of the fluorite–Be–Li–Rb–Cs (Voznesensky and Pogranichnoe in Primorye) and Ta–Nb–Li (Kester in Yakutia, Tigrinoe in Primorye) types with columbite, strüverite, microlite, wadginite, fenakite, amblygonite, zinnwaldite, lepidolite, and other RM minerals are relatively well-studied [19, 20, 25, 26, 29]. However, the presence, distribution, and modes of occurrence of RMs of the Sn deposits of East Russia are studied insufficiently: only a few RM minerals and Sc and In contents of ore minerals are determined [2, 7, 9–11, 13, 20, 22, 23, 28]. The works [3, 4] describe the composition of the RM accessory minerals of LFGs.

In this paper, we chose the VUOC for study of by-product RM mineralization of Sn deposits related to LFGs. This cluster hosts the Pravyi Urmi LFG com-

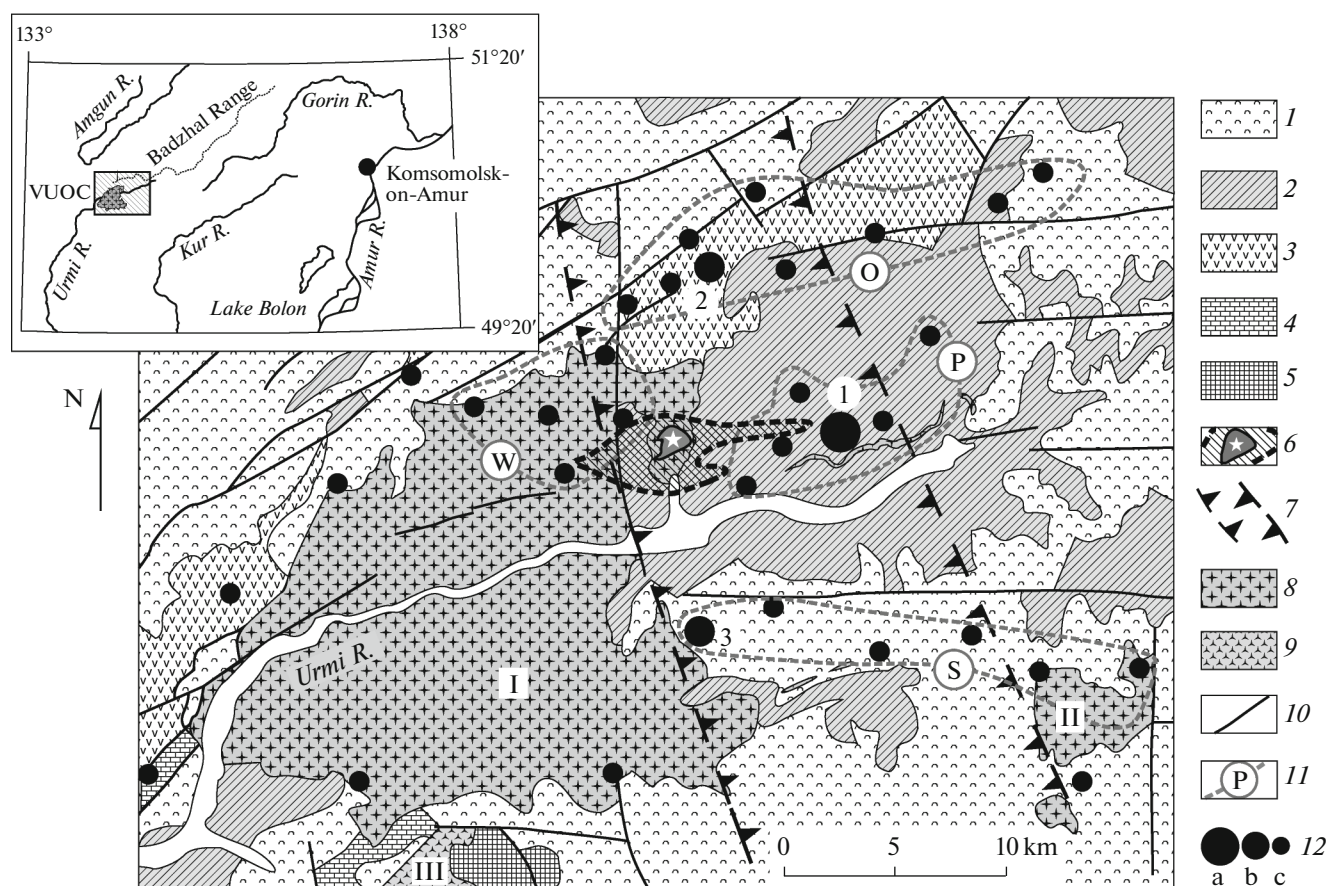


Fig. 1. Geological scheme of the Verkhneurmiskiy ore cluster modified after [15] and data of the Komsomolskaya Geological Prospecting Expedition of PGO Dal'geologiya and original data. 1, Upper Cretaceous ignimbrites and rhyolite and rhyodacite tuffs; 2, subvolcanic rhyolites, rhyodacites, and porphyry granites; 3, Early Cretaceous andesites, andesidacite, and tuffs; 4, Devonian–Permian terrigenous and clayey rocks, limestones of fold basement; 5, Lower Proterozoic gneisses, amphibolites, and quartzites of the Bureya pluton; 6–8, Late Cretaceous intrusives: 6, areal of Li–F granites with Dozhdliv stock (Pravy Urmi complex); 7, Orokot zone of monzonitic dikes (Silin complex); 8, biotite granites and porphyry granites (Badzhala–Dussealin complex); I, Verkhneurmiskiy pluton; II, Syugachan pluton; 9, Early to Late Cretaceous granodiorites, quartz diorites (Lak complex); III, Annik pluton; 10, faults; 11, ore fields: O, Osbadzhal; P, Pravy Urmi; S, Sychuga; W, Wolframovoe; 12, large (a) and small (b) deposits: 1, Pravourniyskoe; 2, Dvoinoe; 3, Vysokoe; occurrences (c). Inset shows the geographic position of the Verkhneurmiskiy ore cluster (VUOC) (rectangle).

plex and the exploited eponymous Sn deposit with by-product Sc [9] and In [7, 10, 11, 22]. The paper describes the RM minerals of the VUOC Sn-bearing metasomatites: feldspatites, greisens, zwitter, tourmalinites, and chloritites.

GEOLOGICAL CHARACTERISTIC OF THE REGION

The VUOC is part of the Badzhara region located in the interfluvium of the Kur and Amgun rivers on the slopes of the eponymous range. Its structure is dominated by a thick Cretaceous sequence of felsic volcanic rocks, occurring on dislocated Paleozoic–Jurassic volcanosedimentary rocks and penetrated by subvolcanic and hypabissal granitic intrusions. The VUOC occupies the area of the Verkhneurmiskiy granitic

pluton and adjacent Urmi ignimbrite volcanic structure [12–15] (Fig. 1).

The Verkhneurmiskiy pluton contains three phases of Late Cretaceous biotite granites of the Badzhala–Dussealin complex and is rimmed by the Annik Pluton of the Early–Late Cretaceous granodiorites of the Lak complex from the south and by extrusive bodies of monzonite diorites and trachandesites of the Silin complex, including the large Kurkalty pluton, from the north [12–15]. In the northeastern part of the Verkhneurmiskiy pluton and its contacts, the dikes of zinnwaldite LFGs and ongonites (including Dozhdliv stock), which form the Pravyi Urmi RM–granite complex, were mapped by an expedition of the Leningrad Mining Institute under the leadership of Professor Yu.B. Marin [2, 3, 18].

The intrusion of LFGs into biotite granites and country volcanic rocks led to the formation of ore-

bearing zwitterites, tourmalinites, and numerous W–Sn occurrences [1, 2, 12, 13, 18, 21]. The VUOC includes the large Pravourmiyskoe and small Dvoinoe and Vysokoe deposits and tens of Sn and W occurrences. The measured and indicated base-metal reserves of the Pravourmiyskoe deposit are 115.9 Mt Sn, 8.2 Mt WO_3 , 89.4 Mt Cu, and 1.3 Mt Bi; the inferred RM reserves are 37.65 t Nb, 385.8 t In, and 4.927 t Sc. The possible resources of the Verkhneurmiysky cluster are 89 Mt Sn, 11.2 Mt WO_3 , and 414 Mt Cu [14, 15]. Three ore fields are located at the contact of the Verkhneurmiysky pluton and are longitudinally elongated according to the strike of the ore-controlling faults: Osbadzhal, Pravyi Urmi, and Synchuga. We also distinguish the Wolframovoe ore field located in the northeastern part of the granite pluton at the intersection of the longitudinal Wolframitovy and latitudinal faults.

An important element of the geological structure of the VUOC is related to the Orokot tectono–magmatic zone transverse to the ore-bearing structures, which controls the richest Sn occurrence and is saturated by late products of subalkaline magmatism: the monzonitic rocks of the Silin complex and LFGs and ongonites of the Pravyi Urmi complex [2, 17]. Most occurrences of Sn (Pravourmiyskoe, Grustnoe, Alenushkino, Vysokoe, etc.) and W (Wolframitovoe, Syuigachan, etc.) are composed of greisens and zwitterites of the Sn–RM (cassiterite–quartz) and wolframite–quartz types and are related to the LFGs of the Pravyi Urmi complex. The Sn occurrences of the Osbadzhal field (Dvoinoe, Orokot, Omot-Makit, Ulun, etc.) consist of tourmaline and chlorite metasomatites of the cassiterite–silicate type and are related to the monzonitic rocks of the Silin complex [2, 13, 17] (Fig. 1).

ANALYTICAL METHODS

In our work we employ a systematic approach to the study of hydrothermal–metasomatic rocks encompassing their composition, zoning, stages, and ore potential. Its basic principle is the use of a rational complex of structural–geological, petrographic, mineralogical, geochemical, and mineragenic study of metasomatites of different stages on the basis of mapping of ore fields on a scale of 1 : 5000–1 : 10000 [8, 18].

Mineralogical study of the metasomatites included determination of their mineral composition, identification of RM minerals and mechanisms of accumulation of RMs, and study of their role in ore genesis and evolution at various stages of mineral formation [1–4, 8]. In the mineralization areas distinguished according to geochemical mapping, we sampled typical metasomatites of various stages and facies, which underwent minor later metasomatic and supergene alteration. Genetically similar metasomatites were sampled from

different occurrences of the cluster. The samples were first verified using Leica DM2500 M and Olympus BX51 optical microscopes. The chemical composition of the samples was analyzed with emission spectral and X-ray spectral fluorescent analyses (ED-2000, XRF-1800), inductively coupled plasma mass spectrometry (ICPE-9000), and atomic absorption (AA6300, AAS5EA) at the Center for Collective Use of St. Petersburg Mining University.

The RM minerals with higher RM contents were investigated using electron microscopes (JSM-6460LV, JSM-7001F, JIB-4500, Cameca MS-46; Mining University, Russian Geological Research Institute (VSEGEI), St. Petersburg). The analytical interpretation was carried out using the INCA Energy (Oxford) software. The chemical composition of the micas, fluorite, wolframite, cassiterite, and sulfides was analyzed in monomineral fractions using classical chemical methods, ICP MS, and AAS. The composition of the microminerals was studied on microprobes with wave spectrometers (CamScan MV2300, VSEGEI; JXA-8230, Mining University) and natural minerals, pure oxides, and metals as standards.

SN-BEARING METASOMATITES OF THE VERKHNEURMIYSKY ORE CLUSTER

The region is characterized by propylite-type premineral metasomatites and Sn-bearing metasomatite of zwitter-tourmalinite formations of five stages: feldspatites → greisens → zwitterites → tourmalinites → chloritites [1, 10, 12, 18]. The feldspatites of the first premineral stage, including biotite–feldspar and feldspar–biotite–muscovite metasomatites, are the earliest Sn-bearing rocks. The biotite feldspatites compose steeply dipping longitudinal zones 0.1–2.0 m thick and 2–200 m long grouped into biotitization bands a few tens of meters wide in the Wolfram–Makit, Dvoinoe (Osbadzhal ore field), Pravourmiyskoe, Dozhdlivoe, Alenushkino, Sulfidnoe, Pravyi Omot (Pravyi Urmi field), Lesnoe, Wolframitovoe (Wolframovoe field), Vysokoe, and Dlinnoe (Synchuga field) occurrences.

The premineral feldspatites are composed of albite, K-feldspar, biotite, and muscovite with subordinate quartz, garnet, and tourmaline and are characterized by microlepidoblastic or glomeroblastic textures and spotty and striated structures. K-feldspar, quartz, sulfides, and garnet form veinlets saturated with accessory minerals. The accessory and ore minerals of the biotite–feldspar metasomatites include pyrrhotite, chalcopyrite, fluorite, apatite, allanite, monazite, xenotime, zircon, rutile, ilmenite, thorite, and scheelite.

The formation of biotite feldspatites is followed by the formation of greisens of the second premineral stage composing longitudinal, northwestern, and latitudinal zones 0.1–4.0 m thick (up to 20 m) and 200–

1800 m wide in the Grustnoe and Granitnoe (Osbadzhal ore field); Alenushkino and Yuzhnoe (Pravyy Urmi field); Lesnoe, Kresty (Wolframovoe field); and Vysokoe and Daikovo (Synchuga field) occurrences. The massive or stringer greisens are composed of muscovite and quartz: the quartz forms veins and veinlets with muscovite, fluorite, topaz, and sulfides. The ore mineralization includes rare grains of cassiterite, wolframite, molybdenite, bismuthinite, and arsenopyrite.

The third synmineral stage is characterized by the formation of the W–Sn zwitter of the Pravourmiyskoe deposit; the Alenushkino and Sulfidnoe occurrences (Pravyy Urmi field); the Dvoynoe deposit and Wolfram–Makit and Grustnoe occurrences (Osbadzhal ore field); the Lesnoe and Wolframitovoe (Wolframovoe field); and the Vysokoe, Syuigachan, and Rogatnoe occurrences (Synchuga field), which are described in detail in [4, 10, 12, 18, 21]. The zwitter compose numerous thin (n cm) halos around large stockworks of topaz and quartz veinlets and thick (up to 40 m) bodies, which cross-cut premineral feldspatites and greisens. The zwitter are dominated by quartz, siderophyllite, and topaz; fluorite and muscovite are also typical. The zonal position of the zwitter facies (quartz–topaz, siderophyllite–topaz–quartz, muscovite–siderophyllite–quartz, quartz–topaz–muscovite, mica–feldspar, quartz–albite) is controlled by LFGs [1, 2, 21].

The zwitter exhibit fine- to small-grained (after volcanic rocks) or small- to medium-grained (after granites) lepidogranoblastic, automorphic, blastoporphyratic, or blastogranitic textures and massive, fine-banded, or stringer structures. The dark brown zwitter are crossed by white fluorite–quartz–topaz, quartz, and feldspar–quartz veins and veinlets 0.5–10.0 cm thick. Their accessory and ore minerals include fluorite, cassiterite, wolframite, arsenopyrite, löllingite, scheelite, native bismuth, bismuthinite, sphalerite, rutile, fergusonite, euxinite, pyrochlore, beryl, zircon, hedleyite, etc.

The products of the fourth synmineral stage are dominated by metasomatic tourmalinite veins of quartz–tourmaline and albite–tourmaline facies. In the greisen occurrences (Pravourmiyskoe, Wolfram–Makit, Syuigachan, Vysokoe, etc.), small tourmaline veinlets and thick (up to 20–40 cm) veins with brecciated structures are often confined to the quartz–topaz and muscovite–quartz Sn-bearing greisens. In these heterogeneous rocks, the small-grained quartz–tourmaline aggregate hosts greisen clasts and partly replaces topaz, biotite, cassiterite, arsenopyrite, and other clastic minerals. Close to the veins, the host rocks underwent moderate quartz and tourmaline alteration.

The Sn-bearing tourmalinites of the Dvoynoe, Proskurnikova, Orokot, and Omot–Makit (Osbadzhal field); Dozhdilovoe (Pravyy Urmi field);

and Dlinnoe, Vostochnoe, and Goluboe (Synchuga field) occurrences are characterized by a significant role of quartz–sericite and quartz–albite metasomatites. These occurrences exhibit steeply dipping metasomatic zones 0.3–2.0 m thick (up to 9 m) and 500–600 m long of latitudinal, longitudinal, and northwestern strike. Their external parts are composed of lepidonematogranoblastic aggregates of quartz, sericite, and albite with minor tourmaline, chlorite, and fluorite; numerous tourmaline veinlets with quartz, sericite, and albite halos are locally dominant. Metasomatic quartz–tourmaline veins 5–15 cm thick are observed in the axial parts of the zones. The tourmalinites contain dissemination, pockets, and veinlets of cassiterite, chalcopyrite, and bornite, as well as rare stannite, stannoidite, mawsonite, wittichenite, roquesite, sakuraiite, sphalerite, pyrrhotite, pyrite, monazite, tetrahedrite, native bismuth, REE–epidote, and zircon.

Chlorite metasomatites of the fifth postmineral stage are abundant along the steeply dipping longitudinal and northeastern faults, rarely along the flat latitudinal reverse faults forming the zones 0.1–26 m thick and 500–1600 m long in the Chloritovoe and Irungda–Makit (Osbadzhal field); Yuzhnoe, Pravyy Omot, and Sulfidnoe (Pravyy Urmi field); and Vostochnoe (Synchuga field) occurrences. The major minerals of the chloritites are chlorite, albite, sericite, and quartz; abundant minerals are epidote, calcite, tourmaline, prehnite, and zeolites. The chloritites are characterized by micrograined and rare small- to medium-grained (0.1–1.0 mm) textures and spotty and stringer structures caused by quartz–chlorite, epidote–chlorite, and calcite stringer-pocket aggregates enriched in sulfides. There are brecciated chloritites with clasts of earlier metasomatites. Accessory and ore minerals of the postmineral metasomatites are fluorite, pyrite, sphalerite, galena, marcasite, stibnite, and cassiterite.

RM MINERALIZATION OF METASOMATITES OF THE VERKHNEURMIYSKY ORE CLUSTER

The biotite feldspatites of the first premineral stage contain allanite–(Ce), monazite–(Ce), xenotime–(Y), zircon, apatite–(CaF), ilmenite, thorite, and biotite (Table 2). The euhedral prismatic crystals of allanite–(Ce) 3–30 μm across may be of economic interest. The mineral forms intergrowths and lens pockets 30–500 μm in size in K-feldspar–biotite aggregate and occurs in K-feldspar veinlets 10–100 μm thick (Fig. 2a).

It contains 4.76–17.52 wt % Ce_2O_3 , 6.78–26.52 wt % ΣLREEs (La, Ce, Nd), up to 3.93 wt % ThO_2 , and up to 0.93 wt % SnO_2 . The allanite of the Sulfidnoe occurrence (VUOC eastern flank) contains up to 8.56 wt % Y_2O_3 (Table 3). The allanite aggregates host monazite and xenotime microinclusions (1–

Table 2. Minerals of most important rare metals, Sn, and W in Sn-bearing metasomatites of the Verkhneurmisky ore cluster (Amur region)

Rare metal	Metasomatites of different stages of ore-magmatic process				
	Feldspatites (1)	Greisens (2)	Zwitter (3)	Tourmalinites (4)	Chloritites (5)
Y, HREE	Xenotime, thorite, <u>allanite</u> , biotite	Wolframite	Xenotime, fergusonite, euxenite, pyrochlore, fluorite, <u>wolframite</u>	Fluorite, wolframite	Fluorite
LREE	<u>Monazite</u> , <u>allanite</u> , apatite	Wolframite	Monazite, xenotime, fergusonite, fluorite, <u>wolframite</u>	Epidote, fluorite	Fluorite
Nb	—	Wolframite, <u>molybdenite</u> , cassiterite	Fergusonite, euxenite, pyrochlore, <u>wolframite</u> , <u>cassiterite</u>	Wolframite, <u>cassiterite</u>	—
In	—	Cassiterite	Cassiterite	Roquesite, <u>chalcopyrite</u> , <u>stannoidite</u> , <u>bornite</u> , wittichenite, sakuraiite, <u>cassiterite</u>	<u>Sphalerite</u> , <u>galena</u>
Sc	Ilmenite	Wolframite, cassiterite	<u>Wolframite</u> , <u>cassiterite</u> , fluorite	Wolframite, <u>cassiterite</u> , fluorite	—
W	Ilmenite, biotite	Cassiterite, muscovite	<u>Wolframite</u> , scheelite, pyrochlore, euxenite, <u>cassiterite</u> , muscovite, siderophyllite	Cassiterite	—
Sn	<u>Allanite</u> , biotite	Cassiterite, muscovite	<u>Cassiterite</u> , siderophyllite, muscovite, fluorite	<u>Cassiterite</u> , <u>stannoidite</u> , stannine, mawsonite, roquesite, <u>chalcopyrite</u> , bornite, kesterite, fluorite	<u>Sphalerite</u> , <u>galena</u> , fluorite

Major accessory and ore minerals are underlined. Number of stage is given in brackets.

10 μm). The REE phosphates mostly include single euhedral platy grains up to 50 μm in size with round apices and rare intergrowths in biotite–feldspar aggregate (Fig. 2b). The monazite contains 52.05–69.54 wt % LREE_2O_3 and 0.00–10.45 wt % ThO_2 and the xenotime contains 41.62–48.94 wt % Y_2O_3 , 6.56–17.28 HREE_2O_3 , 0.00–0.75 wt % ThO_2 , and 0.00–0.90 wt % UO_2 .

The biotite–feldspar metasomatites contain pervasive single short-columnar zircon (54.81–68.42 wt % ZrO_2) crystals in assemblage with monazite, allanite, and xenotime and rarely prismatic REE fluorapatite (Fig. 2c). The crystal rims are rich in HfO_2 up to 2.15 wt %, ThO_2 up to 1.58 wt %, and UO_2 up to 1.88 wt %. The Zr-bearing feldspatites rarely contain inclusions of apatite-(CaF) with 0.22–32.99 wt % LREE_2O_3 (La, Ce, Nd) and 1.21–2.96 wt % ThO_2 , ilmenite (Fig. 2a) with 3.62–5.56 wt % WO_3 and up to 1.24 wt % Sc_2O_3 , and thorite with up to 6.65 wt % Y_2O_3 . The biotite contains numerous trace elements

(wt %): 0.04–0.43 Li_2O , 0.06–0.32 Rb_2O , 0.01–0.06 Cs_2O , 0.02–0.20 ZrO_2 , 0.00–0.05 Y_2O_3 , 0.00–0.09 WO_3 , and 0.00–0.01 SnO_2 (Table 3).

Cassiterite (0.02–0.18 wt % Nb_2O_5 , 0.001–0.004 wt % Sc_2O_3 , 0.02–0.56 wt % WO_3) and wolframite (0.05–1.25 wt % Nb_2O_5 , 0.00–0.91 wt % Ta_2O_5 , 0.01–0.27 wt % Sc_2O_3 , 0.00–0.007 wt % La_2O_3) are rare RM minerals of the muscovite–quartz greisens of the second premineral stage (Tables 2, 3). Molybdenite with up to 0.05 wt % Nb_2O_3 occurs only in the muscovite–quartz greisens of the Verkhneurmisky pluton and its nearest contact zone (the Wolframovoe field and the western part of the Osbadzhal field) (Fig. 2d). Molybdenite is observed in quartz veinlets as chains of small (n mm) euhedral scales. The muscovite of the greisens contains (wt %) 0.01–0.56 Li_2O , 0.00–0.02 WO_3 , 0.00–0.01 SnO_2 (Table 3).

The RM-bearing minerals are especially diverse in the zwitter of the third synmineral stage (Table 2). These include (wt %) monazite–(Ce) (49.28–66.86

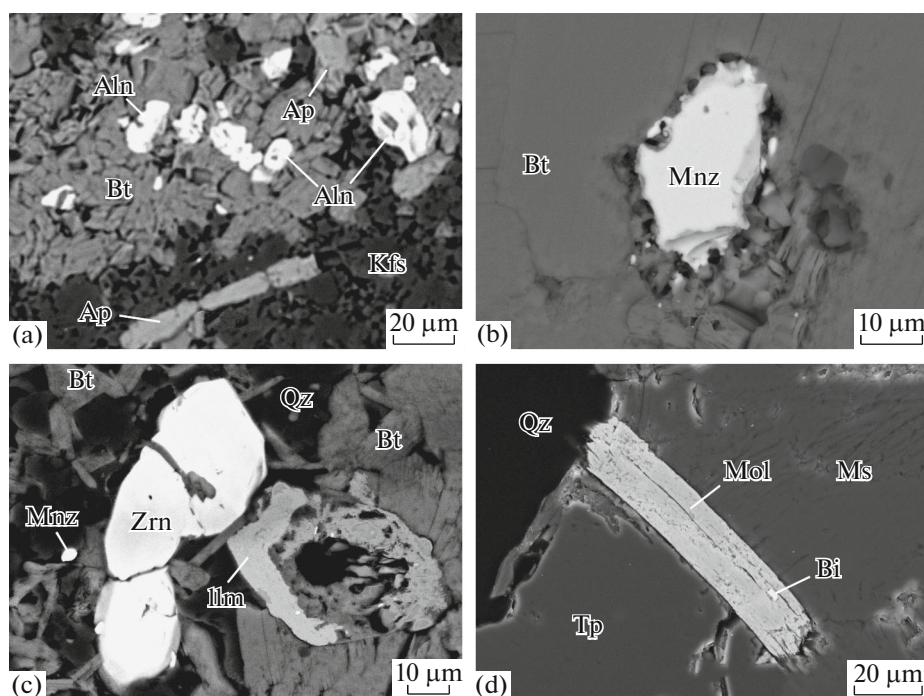


Fig. 2. RM minerals of premineral feldspatites and greisens of the Verkhneurmisky ore cluster (here and hereafter in Fig. 3: BSE images; JSM-6460LV and JSM-7001F SEMs, Mining University, St. Petersburg): a, b, c, K-feldspar–biotite metasomatites with allanite–(Ce), Ce apatite, monazite–(Ce), Hf zircon, and Sc–ilmenite; d, topaz–quartz–muscovite greisen with Nb–molybdenite. Minerals: Aln, allanite–(Ce); Ap, apatite–(CaF); Bi, native bismuth; Bt, biotite; Ilm, ilmenite; Kfs, K-feldspar; Mnz, monazite–(Ce); Mol, molybdenite; Ms, muscovite; Qz, quartz; Tp, topaz; Zrn, zircon.

LREE₂O₃, 0.48–10.71 ThO₂, 0.37–2.14 UO₂), xenotime–(Y) (35.75–51.45 Y₂O₃, 14.34–25.67 HREE₂O₃, 0.00–2.38 LREE₂O₃, 0.00–1.63 ThO₂, 0.58–3.73 UO₂), and zircon (55.38–70.11 ZrO₂, 0.29–1.98 HfO₂, 0.00–0.41 ThO₂, 0.00–1.48 UO₂%) (Table 4, Fig. 3a). The W–Sn zwitter of the Wolframovoe ore field also contain tantaloniobates (wt %): fergusonite–(Y) (49.18–54.16 Nb₂O₅, 22.15–32.50 Y₂O₃, 9.27–34.41 HREE₂O₃, 0.00–2.71 LREE₂O₃), euxenite–(Y) (52.99–62.81 Nb₂O₅, 9.88–22.12 Y₂O₃, 9.52–13.72 WO₃), and plumbopyrochlore (44.56–56.22 Nb₂O₅, 0.00–13.98 Y₂O₃, 10.34–18.54 WO₃) [3, 4] (Fig. 3b). Hedleyite (22.30 wt % TeO₂, 2.74 wt % SeO₂) and poorly studied beryl are observed in the muscovite–biotite–feldspar and muscovite–biotite–topaz metasomatites of the Verkhneurmisky pluton and Pravourmiyskoe deposit.

The major ore minerals of the zwitter contain minor RM amounts (wt %): 0.01–0.13 Nb₂O₅, 0.001–0.012 Sc₂O₃, 0.000–0.001 In₂O₃, and 0.00–0.94 WO₃ in the cassiterite and 0.00–2.15 Nb₂O₅, 0.00–1.41 Sc₂O₃, and 0.00–0.07 Y₂O₃ in the wolframite (Figs. 3b, 3c). Cassiterite as subhedral crystals and irregular intergrowths 0.01–3.00 cm in size is unevenly distributed in the zwitter and quartz–topaz veins and is characterized by light and dark brown zonal color. The dark zones are enriched in Nb and W by an order

of magnitude, whereas the light zones contain In. Wolframite is observed as euhedral prismatic and platy crystals 0.5–2.0 to 10–100 mm in size in close assemblage with Fe and Cu sulfides in the quartz–topaz veins. Ferroan wolframite (0.08–0.48 wt % MnWO₄) is dominant. The higher Nb, Sc, and other RM contents are in particular typical of the cassiterite and wolframite of the occurrences of the Verkhneurmisky pluton [4, 10]. The minerals of the upper parts of the ore bodies of the Pravourmiyskoe deposit are enriched in Nb, In, and Sc. No microinclusions of RM minerals were found in the cassiterite and wolframite under an electron microscope.

The secondary ore minerals are also rich in RMs (wt %): 0.36–10.46 wt % MoO₃ in the scheelite and 0.00–1.04 wt % CdO in the sphalerite. Locally, native bismuth (up to 11.43 wt % TeO₂, up to 1.50 wt % SeO₂), rutile (up to 1.30 wt % Nb₂O₅, up to 4.17 wt % WO₃), and ilmenite (up to 2.84 wt % WO₃) are enriched in RMs. A significant RM amount is capsulated in the vein fluorite, siderophyllite, and muscovite of the zwitter: [10, 23]. The fluorite is enriched in Y₂O₃ (up to 0.47 wt %) and contains a broad spectrum of heavy (up to 0.14 wt %) and light (up to 0.07 wt %) REEs. The siderophyllite contains (wt %) 0.05–1.53 Li₂O, 0.12–0.60 Rb₂O, 0.01–0.15 Cs₂O, 0.01–0.62 SnO₂, and 0.001–0.015 WO₃ and the muscovite con-

Table 3. Average contents of rare metals, Sn, and W (wt %) of minerals of feldspatites and greisens of the Verkhneurmisky Sn cluster

Rare metal металл	Feldspatites								Greisens			
	Aln	Mnz	Xtm	Zrn	Ap	Ilm	Thr	Bt	Wlf	Cst	Mol	Ms
Li ₂ O								0.17				0.10
Sc ₂ O ₃						1.24			0.13	0.002		
Y ₂ O ₃	0.21		45.09				5.56	0.01	0.07			
ZrO ₂				65.95				0.09				
Nb ₂ O ₅									0.57	0.08	0.01	
In ₂ O ₃										0.002		
LREE ₂ O ₃	17.50	52.57			17.20				0.001			
HREE ₂ O ₃	0.01		12.92									
HfO ₂				0.57								
Ta ₂ O ₅									0.14			
SnO ₂	0.004							0.005		99.65		0.003
WO ₃						4.65		0.03		0.27		0.01
<i>n</i>	229	10	5	80	4	6	3	15	8	4	7	9

Here and hereafter: *n*, number of samples. For symbols of minerals, see Fig. 2. Cst, cassiterite; Thr, thorite; Wlf, wolframite; Xtm, xenotime-(Y).

Table 4. Average contents of rare metals, Sn, and W (wt %) of minerals of zwitter and greisens of the Verkhneurmisky Sn cluster

Rare metal	Frg	Eux	Pcl	Mnz	Xtm	Zrn	Wlf	Cst	Sch	Sdp	Ms	Sp	Fl
Li ₂ O										0.40	0.10		
Sc ₂ O ₃							0.15	0.005					0.001
Y ₂ O ₃	29.73	11.98	3.15		41.74		0.001						0.17
ZrO ₂						66.79							
Nb ₂ O ₅	52.24	68.47	50.24				0.86	0.05					
CdO												0.60	
In ₂ O ₃								0.001					
LREE ₂ O ₃	0.75			59.38	1.54		0.001						0.01
HREE ₂ O ₃	16.37				20.12								0.05
HfO ₂						0.69							
Ta ₂ O ₅							0.06						
SnO ₂								99.74		0.34	0.005		0.003
WO ₃		11.61	15.27				74.27	0.20	82.92	0.005	0.03		
<i>n</i>	18	7	12	61	24	31	84	100	24	21	16	17	33

Eux, euxenite; Fl, fluorite; Frg, fergusonite-(Y); Pcl, plumbopyrochlore; Sch, scheelite; Sdp, siderophyllite; Sp, sphalerite.

tains 0.01–0.65 Li₂O, 0.03–0.11 Rb₂O, 0.00–0.01 Cs₂O, 0.00–0.03 SnO₂, and 0.01–0.18 WO₃ (Table 4).

The tourmalinites of the fourth synmineral stage contain diverse RM-bearing minerals: cassiterite, wolframite, roquesite, sakuraiite, stannoidite, chalcopyrite, bornite, native bismuth, pyrite, monazite-(Ce), REE-epidote, zircon, scheelite, and fluorite

(Table 2). The tourmaline hosts inclusions of (wt %) monazite (49.20–51.04 LREE₂O₃, 3.17–3.95 ThO₂), zircon (61.68–70.73 ZrO₂, 0.13–3.04 HfO₂, 0.09–1.00 ThO₂, 0.20–1.25 UO₂), roquesite (51.26–56.91 In₂O₃, 0.55–0.99 CdO, 0.75–1.16 SnO₂), and rare sakuraiite (38.28–39.44 In₂O₃) (Table 5). The roquesite occurs as very small (0.01–0.05 mm) grains

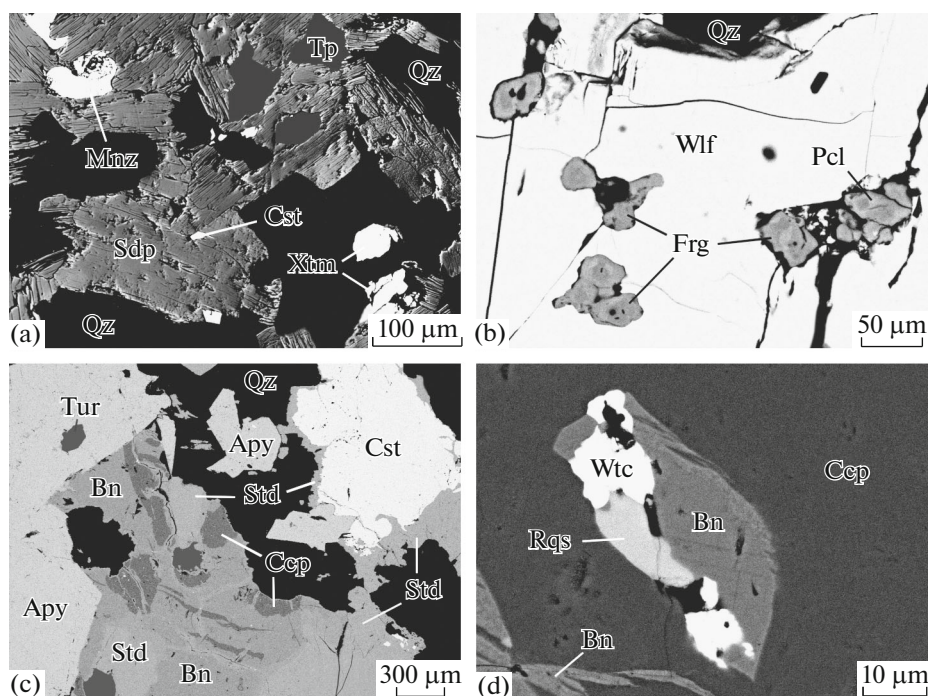


Fig. 3. RM minerals of ore zwitter and tourmalinites of the Verkhneurmiskiy ore cluster: a, quartz–topaz–siderophyllite zwitter with monazite–(Ce), xenotime–(Y), and In–Nb cassiterite; b, Sc–Nb wolframite in zwitter with inclusions of fergusonite–(Y) and plumbopyrochlore; c, topaz–siderophyllite zwitter with In–Nb cassiterite and arsenopyrite replaced by tourmaline–quartz metasomatites with In–stannoidite and chalcopyrite; d, quartz–tourmaline metasomatite with roquesite, In–wittichenite, and bornite. For symbols of minerals, see Fig. 2 and Tables 2 and 4. Bn, bornite; Ccp, chalcopyrite; Rqs, roquesite; Std, stannoidite; Tur, tourmaline; Wtc, wittichenite.

intergrown with chalcopyrite, bornite, wittichenite, sphalerite, and stannoidite in the intermediate horizons of the Pravourmiyskoe deposit and Sulfidnoe occurrence (Fig. 3d).

In the tourmaline metasomatites, numerous minerals contains trace RM amounts including major ore minerals (wt %): cassiterite (0.00–0.07 Nb₂O₅, 0.00–0.01 Sc₂O₃, 0.00–0.002 In₂O₃, 0.07–0.18 WO₃), wolframite (0.05–0.53 Nb₂O₅, 0.01–0.03 Sc₂O₃, 0.001–0.002 Y₂O₃), chalcopyrite (0.01–0.94 In₂O₃, 0.12–3.17 SnO₂),

stannoidite (0.00–0.67 In₂O₃, 0.00–0.37 CdO, 24.42–26.89 SnO₂), bornite (0.00–0.54 In₂O₃, 0.00–3.75 SnO₂), bismuth (0.00–1.50 SeO₂, 0.00–0.63 CdO, 0.00–0.83 SnO₂), and pyrite (1.69–4.35 WO₃, 0.00–0.17 SnO₂) (Figs. 3c, 3d). The abundant Cu sulfides (chalcopyrite, bornite, chalcocite; Pravourmiyskoe, Orokot, Omot-Makit, Sul'fidnoe, etc.) and Cu sulfostannates (stannoidite, stannite, mawsonite; Pravourmiyskoe, Dvoinoe, Vysokoe) contain In. The tourmalinites also contain gangue minerals with Y, LREEs (La, Ce, Nd), and other RMs: epidote (15.84–21.21 LREE₂O₃, 0.00–0.99 ThO₂, 0.00–0.69 SnO₂) and fluorite (0.01–0.07 Y₂O₃, 0.00–0.02 HREE₂O₃, 0.00–0.06 LREE₂O₃, 0.000–0.001 Sc₂O₃, 0.002–0.007 SnO₂) (Table 5).

No RM minerals are hosted by the chlorite metasomatites of the fifth postmineral stage. However, their typical sulfides contain In, Cd, Se, and other RMs (wt %): 0.09–2.12 CdO, 0.003–1.085 In₂O₃, and 0.00–0.79 SnO₂ in the sphalerite and 1.57–10.83 SeO₂, 0.00–0.07 SnO₂, and 0.000–0.001 In₂O₃ in the galena (Table 2). The epidote of the chloritites in the east of the Pravyi Urmi field contains 1.53–6.87 wt % LREE₂O₃ and 0.44–6.40 wt % SnO₂ (Table 5). The fluorite of the chloritites is locally enriched in Y and REEs (wt %: 0.00–0.64 Y₂O₃, 0.00–0.02 HREE₂O₃, 0.00–0.03 LREE₂O₃, 0.00–0.01 SnO₂).

DISCUSSION

The presence of RM mineralization in the VUOC has been known since the beginning of exploration of the Pravourmiyskoe deposit with calculated Nb, In, and Sc reserves [14]. Viable resources of the VUOC, however, are available only for Sn, W, and Cu. The prospects of the region with respect to RMs, in particular In and Sc, are unclear, because they are based only on their contents in the cassiterite without consideration of other minerals (wolframite, sulfides, etc.) [7–11, 22, 28]. At the same time, as follows from the above description, the VUOC metasomatites host many unaccounted RM minerals. In this paper, we

Table 5. Average contents of rare metals, Sn, and W (wt %) of minerals of synore tourmalinites and postmineral chloritites of the Verkhneurmitsky Sn cluster

Rare metal	Tourmalinites											Chloritites		
	Cst	Wlf	Rqs	Std	Ccp	Bn	Wtc	Bi	Mnz	Zrn	Fl	Ep	Sp	Gn
Sc ₂ O ₃	0.003	0.02									0.001			
SeO ₂								1.50						2.29
Y ₂ O ₃		0.001									0.04			
ZrO ₂										66.99				
Nb ₂ O ₅	0.04	0.21												
CdO			0.66	0.07				0.15					0.55	
In ₂ O ₃	0.001		55.36	0.11	0.20	0.03	0.92						0.11	0.001
LREE ₂ O ₃									50.12		0.01	5.60		
HREE ₂ O ₃											0.01			
HfO ₂										0.90				
SnO ₂	99.81		0.99	25.33	1.27	0.51		0.22			0.003	2.82	0.08	0.03
WO ₃	0.15													
<i>n</i>	7	6	27	9	54	24	30	6	2	12	18	22	62	24

For symbols of minerals, see Figs. 2 and 3. Ep, epidote; Gn, galena.

significantly expand the list of strategic RM of the region (Nb, Ta, W, Y, REE (from La to Lu), Be, Li, Rb, Zr, Hf, In, Sc, Se, Cd, and Te) and potentially economic RM minerals (Table 2). These conclusions are supported by search data: the pan halos of fergusonite, allanite, monazite, and thorite are known in the Urmi River basin since the 1960s [15]. Along with Nb, In, and Sc, Y and REEs of allanite, monazite, xenotime, fergusonite, pyrochlore, apatite, and fluorite are important components of the VUOC Sn occurrences (Tables 2–5). The extent of the accumulation and distribution of Li, Rb, Ta, and Cd require additional studies.

The RM deposits are characterized as a rule by multistage mineral formation and evolution of RM assemblages. Thus, we paid special attention to RM mineralogy in rocks of various formation stages of the zwitter–tourmalinite type. Our data show that RM minerals formed during the entire evolution of the VUOC: from the premineral stage of feldspatites to the postmineral stage of chloritites including the synmineral stages of zwitter and tourmalinites. The first alkaline stage accumulated Zr–RM metals; the greisens and zwitter of the second and third acid stages concentrate elements of the Y–Nb–W association; and the tourmalinites and chloritites of the subalkaline stages are characterized by the presence of Cd–In–Sn associations: (LREEs, Zr, Hf) → (W, Nb, Ta, Y, HREEs, Sc) → (Sn, In, Cd, Se, Te). One can observe a decrease in intensity of RM mineral formation and compositional evolution from lithophile to chalcophile RMs: the RM minerals are mostly formed at the early stages of the ore-magmatic processes (Table 2).

The magmatic, metasomatic, and crystal chemical factors are responsible for the formation of RM mineralization [5, 7, 8, 10, 13, 24, 32]. The magmatic and metasomatic factors are studied in a series of works. An important factor in the development of the complex Sn deposits of the Far East is the alternation of the suprasubduction and transform geodynamic regimes of the Pacific continental margin, which is crucial for the evolution of magmatism and the related formation of large Sn and W deposits [12, 27–29]. In the Early Cretaceous, the transform regime led to separation and subduction of the oceanic lithosphere to the mantle beneath the eastern margin of Asia. Sliding plates at the boundary of the Early and Late Cretaceous (Cenomanian) formed a slab window and asthenosphere diapirs. Halos of bimodal magmatism of higher alkalinity, including plutons of ore-bearing monzonites and Li–F granites, were formed in the extension zones [27]. The presence of a giant belt of these halos (Far East LFG belt) was suggested for the Pacific Ocean mobile belt [2]. In the territory studied, this belt is extended eastward of the Bureya pluton in the area of the Sychuga inlier. The ore magmatism is controlled by the Orokot structure, which is part of the Kukan regional fault system. A LFG complex with W–Sn occurrences and by-product RM mineralization was formed at the intersection of this structure with the transverse Pravyi Urmi Fault (Fig. 1). The RM granitic magmatism is responsible for RM accumulation in the residual fluids and multistage pneumatolytic–hydrothermal transformation of the host sequences [1–3, 10, 12–15, 18, 21, 22].

The crystal chemical factor affects the diversity and modes of RM concentrations in the minerals of the VUOC Sn occurrences. It is manifested as two mineral-forming processes: (a) formation of RM (along with related Ti, Al, Mn, Fe, and Sn) minerals (fergusonite, euxenite, plumbopyrochlore, allanite, zircon, monazite, xenotime, roquesite, and sakuraiite) and (b) incorporation of RMs (Nb, Sc, Y, REE, In, Se, Te) in the composition of the ore (wolframite; cassiterite; Cu, Sn, Fe, Mo, Zn, and Pb sulfides; native bismuth) and rock-forming (fluorite, siderophyllite, muscovite, epidote) minerals (Table 2). The application of local analytical methods allowed identification of the isomorphic mode of occurrence of RMs and the absence of RM inclusions in the minerals.

The presence of groups of geochemically and crystal chemically related minerals (accessory assemblages) is a striking feature of the RM granites [5]. The following mineralogical–geochemical associations are identified in the Far East LFGs: W–Nb–Sc–Ti, Sn–Ta–Nb–Li, Y–HREE, LREE–Th, and Zr–Hf–U–Y [2]. The geochemical evolution of the VUOC ore–magmatic system is responsible for the accumulation of rare elements in the postmagmatic fluids and the inherited ore–geochemical type of igneous minerals by Sn-bearing metasomatites: W–Nb–Sc–Ti (wolframite, euxenite, fergusonite, pyrochlore), Y–HREE (xenotime, fergusonite, pyrochlore, fluorite), and LREE–Th (allanite, monazite, apatite, epidote). The hydrothermal mineralogical–geochemical associations were formed at the postmagmatic stage: Sn–Nb–In–Sc (cassiterite, roquesite, sakuraiite, stannoidite, chalcopyrite) and Se–Cd–In (bismuth, sphalerite, galena).

CONCLUSIONS

(1) The multistage complex RM mineralization of the Sn occurrences of the Verkhniy Urmi ore cluster have been studied in the area of the Li–F granites. The minerals of strategic RMs have been identified: Nb, Ta, W, Y, REEs (from La to Lu), Be, Li, Rb, Zr, Hf, In, Sc, Se, Cd, and Te.

(2) Two modes of occurrences of RMs have been determined: RM minerals (fergusonite, euxenite, plumbopyrochlore, allanite, zircon, monazite, xenotime, roquesite, sakuraiite, etc.) and RM-bearing ore (wolframite, cassiterite, Cu, Sn, Fe, Mo, Zn, and Pb sulfides, native bismuth, etc.) and rock-forming (fluorite, siderophyllite, muscovite, epidote) minerals. Frequently observed RMs have been identified in the composition of the Sn metasomatites: Y, REE, Nb, In, Sc.

(3) The RM minerals formed during the entire evolution of the Verkhneurmiysky ore cluster: from the premineral stage of feldspates to the postmineral stage of chloritites including the synmineral stage of zwitter and tourmalinites. The intensity of RM min-

eral formation decreases from the early to late stages, as well as the compositional evolution from lithophile to chalcophile RMs: (LREE, Zr, Hf) → (W, Nb, Ta, Y, HREE, Sc) → (Sn, In, Cd, Se, Te).

(4) The formation of RM mineralization of the Verkhneurmiysky ore cluster was affected by magmatic, metasomatic, and crystal chemical factors. The mineralogical–geochemical study of the occurrences of the Verkhneurmiysky ore cluster show possible complex exploration of the Far East Sn deposits in the areas of Li–F granites.

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