
MINERALS
AND MINERAL ASSEMBLAGES

Niobium Minerals As Indicators of a Genetic Link Between Tin-Bearing Zwitter and Lithium–Fluorine Granite of the Verkhneurmisky Massif in the Amur River Region

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Abstract—Niobium minerals in zwitter and lithium–fluorine granite of the Verkhneurmisky granitic massif in the Amur River region—fergusonite-(Y), euxenite-(Y), samarskite-(Yb), aeschynite, Nb-bearing wolframite—have been described and the similarity of their species composition established. The same-named and crystal-chemically allied minerals from zwitter and granite are characterized by similar complexes of such trace elements as W, REE, Mn, Fe, Pb, U, and Sc. A genetic link between Sn-bearing zwitter and Li–F granite is stated. Compositional varieties of niobium minerals in granite and zwitter reflect a change in the physicochemical conditions of mineral formation, when the magmatic stage is followed by a pneumatolytic–hydrothermal process. The postmagmatic evolution of niobium minerals is characterized by increased concentrations of Y, Pb, U, Fe and decreased concentrations of W, Ta, REE, Ti, Sc, and Th. The mineral occurrences in the western sector of the Verkhneurmisky Cu–W–Sn cluster are appraised as promising for Nb, Y, and REE. Fergusonite, samarskite, euxenite, and Nb-bearing wolframite are indicators of rare metal mineralization.

Keywords: fergusonite, euxenite, samarskite, aeschynite, wolframite, zwitter, lithium–fluorine granite, rare metal mineralization, tungsten–tin deposit, Verkhneurmisky granitic massif, Amur River region, Russian Far East

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INTRODUCTION

Russia possesses a significant resource potential of highly technological rare metals (Nb, Ta, Zr, Re, Li, Y, REE), i.e., strategic raw materials used in Russia's national security. One of the ways to advance the raw-material basis of rare metals is to refine the geological and mineralogical reappraisal of earlier explored deposits and prospected areas in mining territories in Russia. In particular, tin deposits in the Far East may be a source of accessory rare chemical elements, including REE (Alekseev and Marin, 2015; Beskin and Marin, 2015).

Forecasting, prospecting, and geological exploration carried out in 1980–1990 in the Badzhal district of the Khabarovsk region resulted in the discovery of many ore occurrences in the form of tin- and tungsten-bearing bodies of quartz–topaz–siderophyllite greisen and zwitter (Bogdanov et al., 1979; *Geology ...*, 1986; Semenyak et al., 1988; Alekseev, 1989; *Geodynamics ...*, 2006). Rare metal mineralization has been recorded in the Verkhneurmisky granitic massif (Alekseev and Marin, 2015) and quartz–topaz–muscovite greisen (Gavrilenko et al., 1995).

Zwitter in worldwide tin provinces (Erzgebirge, Cornwall, Eastern Mongolia, Transbaikalia Region, Primorye (Maritime Zone) in the Far East, Yakutia, etc.) are genetically related to rare metal Li–F granite (Beskin et al., 1999). In the Badzhal District, the formation of zwitter was for a long time explained by intrusions of biotite granite making up the Verkhneurmisky granitic pluton (Bolotnikov et al., 1975; Bogdanov et al., 1979; Burde and Kravchenko, 1981; Semenyak et al., 1983; *Geology ...*, 1986; Gavrilenko et al., 1992; Grigor'ev, 1997). Later on, in the Verkhneurmisky massif and in the outskirts of the Pravormyskoe large deposit, Li–F zinnwaldite granite was revealed. This granite intruded immediately before ore formation, and it is now commonly regarded as a cause of the latter (Marin et al., 1990; Brusnitsyn et al., 1993; Gonenchuk, 2002; Alekseev, 2014). According to a hypothetical paragenetic link of endomorphic zwitter and Li–F granite of the Verkhneurmisky massif, both formed under the effect of a general deep-seated source of material (Gavrilenko and Panova, 2001).

Thus, the problem of the tin–tungsten mineralization source in the Badzhal district is closely related to the mineral base of strategic metals in the Russian Far

East (Gonevchuk, 2002; *Geodynamics* ..., 2006; Alekseev, 2014; Alekseev and Marin, 2015). An important question remains about the possibility of mining rare metals simultaneously with tin–tungsten greisen deposits accompanying Li–F granite, because economic rare metal mineralization (Nb, Zr, REE, Y) is characterized mainly by feldspathic metasomatic rocks related to alkali granite (Kuz'menko and Es'kova, 1968; Beskin et al., 1999; Beskin and Marin, 2015). In our paper we perform a comparative study of niobium minerals (fergusonite, samarskite, aeschynite, euxenite, and Nb-bearing wolframite) in zwitter and Li–F granite of the Verkhneurmisky massif; we also consider the genesis and rare metal mineralization of zwitter.

GEOLOGICAL POSITION OF THE DISTRICT

The Verkhneurmisky massif is incorporated into the ore cluster of the Badzhal ore district, which is situated in the Khingan–Okhotsk volcanic belt (*Geology* ..., 1986; Semenyak et al., 1988; Gonevchuk, 2002; *Geodynamics* ..., 2006). The Verkhneurmisky ore cluster is localized in the zone of the Khingan–Okhotsk gravitational step and transregional Tanlu Fault Zone, at the epicenter of the Badzhal asthenospheric dome, which has been recorded as a negative gravity anomaly and intense lithospheric heat flow (Alekseev, 2014). In the ore cluster, two lithotectonic levels are distinguished. Deformed Paleozoic–Jurassic volcano-sedimentary rocks of the lower level are covered by a thick Cretaceous volcanic sequence penetrated by subvolcanic and hypabyssal granitic intrusions. The cluster occupies an area of the Verkhneurmisky pluton and adjacent Urmi River ignimbrite volcanic field. Three phases of biotite granite in the Badzhal–Dussealin Complex have been described. The most abundant at the surface are coarse-grained biotite granite of the main phase. Li–F granite of the Pravourmiskoe Complex has also been identified. Under its influence, zwitter of the largest Pravourmiskoe W–Sn deposit was formed in the eastern exomorphic contact of the Verkhneurmisky massif (Semenyak, 1983; Marin et al., 1990; Brusnitsyn et al., 1993; Gonevchuk, 2002; Alekseev, 2014). Li–F granite controls the ore and metasomatic zoning of the Pravourmiskoe ore field, including the arrangement of aporhyolite and apogranite ore-bearing zwitter of various facies: siderophyllite–topaz–quartz, muscovite–siderophyllite–quartz, and micaceous–feldspathic (Alekseev, 1989, 2014).

Zwitter from the Wolfram-Makit, Lesnoe, Wolframitovoe, and other ore occurrences is encountered in the endomorphic zone of the Verkhneurmisky massif. The dark micaceous greisen is composed of siderophyllite, topaz, muscovite, and quartz. They are characterized by a blastogranitic structure, contain relics of magmatic quartz, biotite, zircon, ilmenite, and impregnations of syngenetic wolframite and arse-

nopyrite. Zwitter occurs as submeridional, steeply dipping bodies of variable thickness (1–20 m), which are controlled by faults in immediate proximity to the Li–F granite of the Dozhdlyv stock (Alekseev, 1989, 2014; Marin et al., 1990). An expedition of the St. Petersburg Mining University supervised by Yu.B. Marin established for the first time rare metal mineralization in zwitter of the Verkhneurmisky granitic massif. This mineralization is close in composition to that in Li–F granite: ilmenorutile, monazite, beryl, Nb-bearing wolframite, fergusonite, and euxenite (Marin et al., 1990; Alekseev and Marin, 2015). Minerals from Li–F granite (fergusonite, samarskite, aeschynite, Nb-bearing wolframite) and their analogs from zwitter (fergusonite, euxenite, Nb-bearing wolframite) are characterized below.

METHOD FOR STUDYING NIOBIUM MINERALIZATION IN GRANITE AND ZWITTER

The method for the mineralogical study of zwitter and Li–F granite of the Verkhneurmisky ore cluster is an integral part of a comprehensive technique related to mineralogical, petrological, and geochemical research used in forecasting, minerogenic and prospecting works by the St. Petersburg Mining University. The basic principle is rational integration of studies assigned for structural–geological, metasomatic, mineralogical, geochemical, and ore zoning based on large-scale geological mapping and compilation of cross-correlated metasomatic, mineralogical, and geochemical maps. The mineralogical study of granites, metasomatic rocks, and their protoliths involves the appraisal of quantitative phase compositions, selection of mineral indicators, and the sequence and conditions of rock formation; research of the mineral composition and its role in petrogenesis; and typomorphic features of minerals and their spatiotemporal variability (Alekseev, 1989, 2014; Brodskaya and Marin, 2016). The forecasting trend in studying the Verkhneurmisky ore cluster determines the preferential study of zwitter in gently dipping fault zones of like the Pravourmiskoe and in submeridional zones of intense fracturing.

Special attention is devoted to accessory and ore minerals of rare chemical elements (Nb, Ta, W, Y, REE) in zwitter and Li–F granite of the Verkhneurmisky ore cluster, where fergusonite, samarskite, euxenite, wolframioxiolite, aeschynite, columbite, minerals of the pyrochlore supergroup, and Nb-bearing wolframite have been identified. In areas of mineralization revealed by geochemical mapping, representative samples of granite and zwitter without relics and superimposed mineralization have been collected. An expert field sampling in spots of mineralization finished with a office study of samples by petrographic analysis (Zeiss Axioplan, Leica DM2500 M, Olympus BX51 optic microscopes), emission spectral and X-ray

spectral fluorescent analyses (ED-2000, XRF-1800), mass spectrometry with inductively coupled plasma (ICP-MS) (ICPE-9000), and atomic absorption spectrometry (AAS) (AA6300, AAS5EA) at the Center for Collective Use of Scientific Equipment of St. Petersburg Mining University. In samples with elevated contents of rare elements, we carried out optic and electron microscopic studies of the minerals enriched in rare elements (JSM-6460LV, JSM-7001F, JIB-4500, Cameca MS-46 at the St. Petersburg Mining University and Russian Geological Research Institute in St. Petersburg). Analytical interpretation was performed with INCA Energy software (Oxford). The micromineralogical methods were elaborated at the Department of Analytical Research, Center for Collective Use of the St. Petersburg Mining University: profiling of microminerals, probing of their contacts with matrix minerals, etc.

When niobium minerals were studied, the main focus was the structure of individuals, their relationship to rock-forming minerals, the composition of trace elements, and the distribution of mineral inclusions in crystals. The chemical composition of wolframite was measured in monomineralic fractions using wet chemistry, ICP-MS, and AAS. The composition of niobates represented by microscopic individuals was studied with X-ray spectral microanalysis on microprobes with wave spectrometers (CamScan MV2300 at Geological Institute and JXA-8230 at Mining University).

NIOBIUM MINERALS IN LITHIUM–FLUORINE GRANITE AND ZWITTER

Nb-bearing wolframite with fergusonite inclusions in quartz–topaz and quartz–muscovite greisens after biotite granite of the Verkhneurmisky massif and after felsic volcanic rocks in near the exomorphic contact were described earlier in the Verkhneurmisky ore cluster (Gavrilenko et al., 1995). Unfortunately, the authors of the find did not indicate to which stage of the hydrothermal process the studied greisen with wolframite is related: preore sericite or ore siderophyllite–quartz–topaz, after (Gavrilenko et al. 1992). In the Dozhdiliv Li–F granite stock, accessory rare metal (Nb, Ta, Zr, Hf, W, Bi, Sc, Y, REE) mineralization has been established: yttrifluorite, cyrtolite, niobium ilmenite, monazite-(Ce), ilmenorutile, niobium wolframite, allanite-(Y), wolframioxiolite, samarskite-(Yb), ishikawaite, fergusonite-(Y), columbite-(Fe), Bi-bearing pyrochlore, aeschynite-(Y), polycrase-(Y), etc. (Alekseev, 2014). Niobium minerals, the species composition of which is close to that of accessory minerals in Li–F granite—fergusonite, euxenite-(Y), and Nb-bearing wolframite—were revealed in zwitter in the Verkhneurmisky ore cluster by the St. Petersburg Mining University expedition (Marin et al., 1990; Alekseev and Marin, 2015).

Fergusonite-(Y) from Li–F granite of the Verkhneurmisky massif is represented by single dipyrnidal individuals a few microns in size (see panel (a) in Fig. 1). The mineral contains Ca, Ti, Ce admixtures; yttrium is substantially replaced by heavy REE: Dy, Yb, Er, and niobium are replaced with tantalum; the $\text{Nb}_2\text{O}_5/\text{Ta}_2\text{O}_5$ ratio is 5–10 (Table 1). Dysprosium and ytterbium maximums and the presence of cerium in REE spectrum are characteristic of accessory fergusonite in rare metal granite and pegmatite (Gorzhevskaya et al., 1974). A typomorphic feature of fergusonite from granite is isomorphous substitution of niobium with tungsten. The empirical formula is $(\text{Y}_{0.66}\text{Ca}_{0.12}\text{Dy}_{0.12}\text{Yb}_{0.09}\text{Er}_{0.08}\text{Ce}_{0.08})_{0.96}(\text{Nb}_{0.78}\text{W}_{0.12}\text{Ti}_{0.08}\text{Ta}_{0.06})_{1.04}\text{O}_4$.

In zwitter, fergusonite-(Y) has been revealed as inclusions in wolframite crystals, like in topaz–muscovite greisen (Gavrilenko et al., 1995). Fergusonite in zwitter is also represented by euhedral dipyrnidal individuals 10–40 μm in size with crooked faces (see panel (b) in Fig. 1). These individuals are localized at the margins and junctions of wolframite grains. Inter-growths of fergusonite with euxenite are characteristic (see panel (d) in Fig. 1). The chemical composition of the mineral is unstable, with variable Ca, Ti, and REE contents. The REE composition is distinguished by the presence of LREE (Nd, Sm) and a Dy maximum. As compared with fergusonite in granite, this mineral in zwitter stands out with lower HREE and Ti contents, as well as a lack of Ta and W admixtures (Table 1). The appearance of neodymium in fergusonite from zwitter and the predominance of dysprosium are characteristic of hydrothermal varieties of the mineral (Gorzhevskaya et al., 1974): $(\text{Y}_{0.69}\text{Yb}_{0.08}\text{Dy}_{0.06}\text{Er}_{0.04}\text{Gd}_{0.03}\text{Ca}_{0.03}\text{Sm}_{0.01}\text{Ho}_{0.01})_{0.96}\text{Nb}_{1.03}\text{O}_4$.

It is noteworthy that no tungsten admixture occurs in fergusonite from zwitter, although such an admixture was earlier recorded as a regional feature of accessory minerals from rare metal granites in the Russian Far East (Alekseev, 2014). The rare metal magmas were specialized in tungsten, which is contained in the ore minerals wolframite, scheelite, and russellite.

In some cases, the euxenite-(Y) found in zwitter forms grains where euxenite zones (2–5 μm) intercalate with thin (1 μm) fergusonite zones (see panel (d) in Fig. 1). Compared with niobates from Li–F granite, euxenite is close to accessory samarskite-(Yb) (see panel (c) in Fig. 1). Being enriched in Ta, U, Th, Fe, euxenite resembles samarskite at the type locality of rare metal pegmatites in the Ilmeny Mountains of the Urals (Semenov, 2001) and at the Little Patsy Pegmatite quarry in Colorado, United States (Simmons et al., 2006): $(\text{U}_{0.17}\text{Fe}_{0.09}\text{Mn}_{0.08}\text{Yb}_{0.06}\text{Ca}_{0.05}\text{Sc}_{0.03}\text{Th}_{0.03}\text{Pb}_{0.01}\text{REE}_{0.01})_{0.53}(\text{Nb}_{0.72}\text{Ta}_{0.28}\text{W}_{0.23})_{1.24}\text{O}_4$. The similarity of euxenite to aeschynite-(Y) from Li–F granite is also noteworthy. This euxenite is characterized by W, Th, Pb, and U admixtures (Table 2). The empirical formula of aeschynite is

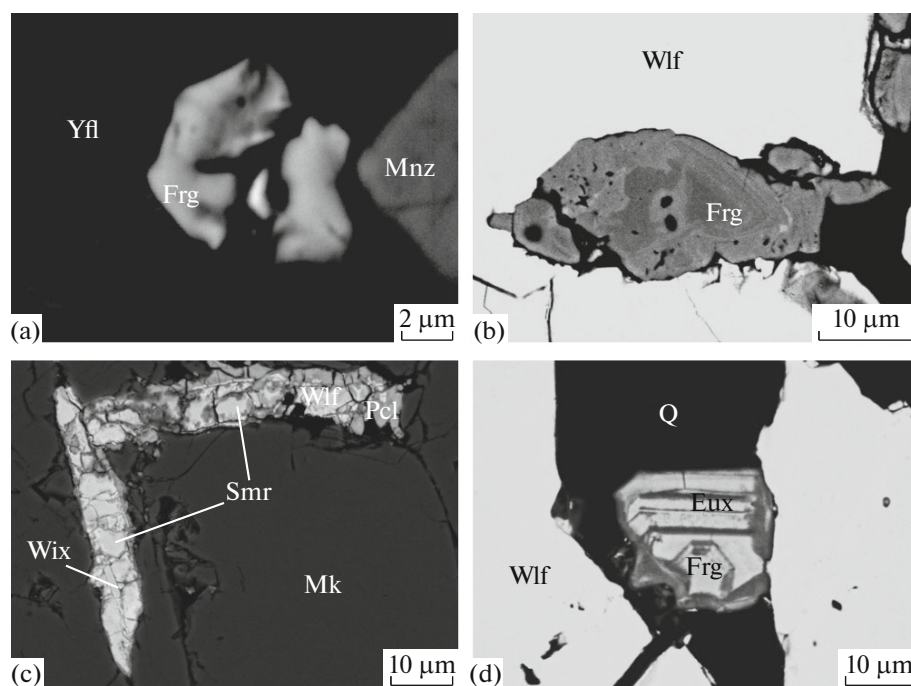


Fig. 1. Accessory niobium minerals from rare metal granites and zwitter in Verkhneurmitsky massif, Amur River Region. BSE images prepared on JSM-7001F SEM at Center for Collective Use of Scientific Equipment, St. Petersburg Mining University. Panels: (a) fergusonite-(Y) and monazite-(Ce) in yttrifluorite from Li–F granite; (b) fergusonite-(Y) in niobium-bearing wolframite from zwitter; (c) samarskite-(Yb) with inclusions of niobium wolframite, wolframoixiolite, and pyrochlore from Li–F granite; (d) euxenite-(Y) intergrown with fergusonite-(Y) in niobium-bearing wolframite. Eux, euxenite; Frg, fergusonite; Mk, microcline; Mnz, monazite; Pcl, pyrochlore; Smr, samarskite; Wix, wolframoixiolite; Wlf, wolframite; Q, quartz; Yfl, yttrifluorite.

$(Y_{0.34}Fe_{0.11}Dy_{0.04}Gd_{0.03}Pb_{0.03}Th_{0.03}Er_{0.02}Yb_{0.02}Nd_{0.01}Sm_{0.01}Ca_{0.01}U_{0.01})_{0.99} \cdot (Ti_{1.84}W_{0.06}Nb_{0.10}Ta_{0.01})_{2.00}(O,OH)_6$. Our observations (Alekseev, 2014) and the published data (Vasil'ev et al., 2008; Duran et al., 2016) show that the relative enrichment of niobium minerals from granite and zwitter in Ca, Ti, Ce, U, Pb is explained in certain cases by their replacement with minerals of the pyrochlore supergroup.

Euxenite from zwitter differs from samarskite and aeschynite from granite by excess Nb and lack of Ta and Ti in position *B*, and a lack of REE, Th, Mn, Ca in position *A* (Table 2). This was noted earlier as a feature of hydrothermal euxenite (Gorzhevskaya et al., 1974). The typomorphic trait of pneumatohydrothermal euxenite, which makes it similar to niobates from Li–F granite, is a substantial admixture of W, Fe, Pb, U: $(Y_{0.47}Fe_{0.40}Pb_{0.10}U_{0.06})_{1.03}(Nb_{1.65}W_{0.19})_{1.83}O_6$.

Accessory wolframite in Li–F granite occurs as thin lamellar crystals 15–100 μm in length and xenomorphic micrograins (a few microns in size) in wolframoixiolite; it also occurs in close association with zinnwaldite and wolframoixiolite (Alekseev, 2014). The mineral is represented by a ferric variety close to ferberite ($MnWO_4$ 0.21–0.36) with a stable admixture of niobium and scandium; an admixture of tantalum has also been recorded (Table 3). The crystal

chemical formula of wolframite is $(Fe_{0.65}Mn_{0.27}Nb_{0.09}Sc_{0.03})W_{0.94}O_4$.

Wolframite from zwitter in the Verkhneurmitsky ore cluster is represented by faceted tabular crystals 0.5–10 mm in length along (100), with inclusions of fergusonite and euxenite. The mineral is defined as ferberite ($MnWO_4$ 0.08–0.27); the Mn, Nb, and Sc contents are lower than in the magmatic generation. The mineral is devoid of Ta admixture: $(Fe_{0.79}Mn_{0.18}Nb_{0.02}Sc_{0.01})W_{0.99}O_4$ (Table 3).

DISCUSSION

Genetic Significance of Niobium Mineralization in Zwitter

The fact that niobium minerals were revealed in combination with earlier known REE mineralization in zwitter of the Verkhneurmitsky massif (Alekseev and Marin, 2015) allows us to specify the origin of these rocks. The available data display similar species of niobium minerals hosted in zwitter: fergusonite-(Y), euxenite-(Y), samarskite-(Yb), aeschynite-(Y), and niobium-bearing wolframite (see Fig. 1). The same-named and allied niobium minerals of the aeschynite–euxenite supergroup in zwitter and granite formed under similar geochemical conditions and are

Table 1. Chemical composition, wt % of fergusonite from Li–F granite and zwitter in Verkhneurmitsky massif

Component	Li–F granite			Zwitter		
	1	2	aver. (11)	3	4	aver. (18)
CaO	2.77	1.57	2.44	1.12	0.25	0.73
TiO ₂	3.69	2.05	2.38	0.00	0.73	0.08
FeO*	—	—	—	0.00	0.12	0.01
Nb ₂ O ₅	33.33	40.25	37.60	49.27	51.66	52.24
Ta ₂ O ₅	6.76	4.97	4.63	—	—	—
WO ₃	9.87	10.34	10.11	—	—	—
Y ₂ O ₃	20.76	23.65	22.66	29.75	28.68	29.73
Ce ₂ O ₃	0.00	0.02	0.07	—	—	—
Nd ₂ O ₃	—	—	—	0.38	0.13	0.22
Sm ₂ O ₃	—	—	—	1.04	0.07	0.53
Gd ₂ O ₃	—	—	—	3.22	2.49	2.19
Tb ₂ O ₃	—	—	—	0.00	0.69	0.09
Dy ₂ O ₃	9.35	7.00	8.34	4.88	4.90	4.47
Ho ₂ O ₃	—	—	—	0.00	2.33	0.33
Er ₂ O ₃	6.98	4.59	5.86	5.03	2.92	2.87
Tm ₂ O ₃	—	—	—	0.00	0.24	0.03
Yb ₂ O ₃	6.48	5.59	6.13	5.29	5.29	6.36
Lu ₂ O ₃	—	—	—	0.00	0.22	0.02
Total	100.00	100.03	100.00	99.99	100.70	99.91
Cation coefficients in formulas (O = 4)						
Ca	0.14	0.08	0.12	0.05	0.01	0.03
Ti	0.13	0.07	0.08	0.00	0.02	0.003
Fe	—	—	—	0.00	0.004	0.000
Nb	0.70	0.82	0.78	0.99	1.02	1.03
Ta	0.09	0.06	0.06	—	—	—
W	0.12	0.12	0.12	—	—	—
Y	0.52	0.57	0.66	0.70	0.66	0.69
Ce	0.00	0.00	0.001	—	—	—
Nd	—	—	—	0.01	0.002	0.003
Sm	—	—	—	0.02	0.001	0.01
Gd	—	—	—	0.05	0.04	0.03
Tb	—	—	—	0.00	0.01	0.001
Dy	0.14	0.10	0.12	0.07	0.07	0.06
Ho	—	—	—	0.00	0.03	0.005
Er	0.10	0.06	0.08	0.07	0.04	0.04
Tm	—	—	—	0.00	0.003	0.000
Yb	0.09	0.08	0.09	0.07	0.07	0.08
Lu	—	—	—	0.00	0.003	0.000

Representative (1–4) and average (aver., number of samples) microprobe analyses of mineral. Analytical procedures carried out at Center for Collective Use of Scientific Equipment, St. Petersburg Mining University. Dash, element not detected; FeO* = FeO + Fe₂O₃.

Table 2. Chemical composition, wt % of tantalum-niobate from Li–F granite and zwitter in Verkhneurmitsky massif

Component	Samarskite-(Yb) in Li–F granite			Aeschynite-(Y) in Li–F granite			Euxenite-(Y) in zwitter		
	1	2	ave. (17)	3	4	ave. (10)	5	6	ave. (7)
CaO	3.60	0.00	0.83	0.00	0.00	0.09	—	—	—
Sc ₂ O ₃	1.55	0.00	0.60	—	—	—	—	—	—
TiO ₂	—	—	—	42.49	31.61	43.30	—	—	—
MnO	3.34	2.69	1.98	—	—	—	—	—	—
FeO*	0.00	9.01	2.09	0.00	11.24	2.26	5.53	9.22	7.49
Y ₂ O ₃	—	—	—	19.05	28.17	22.80	22.12	10.07	13.69
Nb ₂ O ₅	34.58	26.61	31.79	12.72	0.00	7.58	62.81	54.00	56.97
Ta ₂ O ₅	19.83	29.15	20.77	0.00	0.00	0.75	—	—	—
WO ₃	14.63	18.34	17.71	0.00	22.22	4.42	9.52	13.20	11.31
PbO	0.00	0.00	0.47	4.55	0.00	1.85	0.00	7.09	6.00
ThO ₂	0.00	5.92	2.72	4.61	2.28	2.55	—	—	—
UO ₂	15.05	1.71	15.55	2.54	0.00	0.90	0.00	6.05	4.28
Nd ₂ O ₃	0.00	0.00	0.04	0.97	0.80	1.35	—	—	—
Sm ₂ O ₃	—	—	—	0.55	0.00	0.53	—	—	—
Gd ₂ O ₃	—	—	—	3.41	0.00	2.75	—	—	—
Dy ₂ O ₃	0.00	1.37	0.27	3.95	2.43	4.01	—	—	—
Er ₂ O ₃	0.00	1.12	0.22	2.88	0.00	2.50	—	—	—
Yb ₂ O ₃	6.54	4.01	4.04	2.13	0.00	2.31	—	—	—
Total	99.11	99.91	99.08	99.84	98.76	99.96	99.99	99.63	99.74
Cation coefficients in formulas									
Ca	0.19	0.00	0.05	0.00	0.00	0.01	—	—	—
Sc	0.07	0.00	0.03	—	—	—	—	—	—
Ti	—	—	—	1.83	1.44	1.84	—	—	—
Mn	0.14	0.11	0.08	—	—	—	—	—	—
Fe	0.00	0.37	0.09	0.00	0.57	0.11	0.28	0.50	0.40
Y	—	—	—	0.58	0.91	0.34	0.70	0.35	0.47
Nb	0.76	0.60	0.72	0.33	0.00	0.10	1.69	1.60	1.65
Ta	0.26	0.39	0.28	0.00	0.00	0.01	—	—	—
W	0.18	0.24	0.23	0.00	0.35	0.06	0.15	0.22	0.19
Pb	0.00	0.00	0.01	0.07	0.00	0.03	0.00	0.12	0.10
Th	0.00	0.07	0.03	0.06	0.03	0.03	—	—	—
U	0.16	0.02	0.17	0.03	0.00	0.01	0.00	0.09	0.06
Nd	0.00	0.00	0.001	0.02	0.02	0.01	—	—	—
Sm	—	—	—	0.01	0.00	0.01	—	—	—
Gd	—	—	—	0.06	0.00	0.03	—	—	—
Dy	0.00	0.02	0.004	0.07	0.05	0.04	—	—	—
Er	0.00	0.02	0.003	0.05	0.00	0.02	—	—	—
Yb	0.10	0.06	0.06	0.04	0.00	0.02	—	—	—

Cation coefficients in formulas calculated for four (samarskite) and six (aeschynite, euxenite) oxygen atoms.

Table 3. Chemical composition, wt % of wolframite from Li–F granite and zwitter in Verkhneurmisky massif

Component	Li–F granite			Zwitter		
	1	2	aver. (55)	3	4	aver. (18)
Sc ₂ O ₃	1.18	0.83	0.63	0.09	1.41	0.15
MnO	6.86	6.92	6.29	3.42	6.91	4.19
FeO*	14.69	15.13	15.61	19.05	19.63	18.51
Nb ₂ O ₅	4.12	3.40	3.82	0.66	2.16	0.86
Ta ₂ O ₅	0.48	0.00	0.01	—	—	—
WO ₃	73.15	72.05	72.47	74.77	68.32	74.27
Total	100.48	98.33	98.82	97.97	98.44	98.06
Cation coefficients in formulas (O = 4)						
Sc	0.05	0.04	0.03	0.004	0.06	0.01
Mn	0.29	0.30	0.27	0.15	0.29	0.18
Fe	0.61	0.64	0.65	0.82	0.82	0.79
Nb	0.09	0.08	0.09	0.02	0.05	0.02
Ta	0.01	0.00	0.00	—	—	—
W	0.92	0.94	0.94	1.00	0.89	0.99

Cation coefficients in formulas calculated for four (samarskite) and six (aeschnite, euxenite) oxygen atoms.

characterized by a similar complex of trace elements: W, REE, Mn, Fe, Pb, U, and Sc (Tables 1–3). The similarity of species and chemical compositions of niobium minerals in zwitter and Li–F granite allows us to suggest a genetic link between tin-bearing metasomatic rocks and granite of the Pravourmiysky Complex. This conclusion corroborates the notions on tin-ore-bearing Li–F granites of the Verkhneurmisky massif (Marin et al., 1990; Brusnitsyn et al., 1993; Gonevchuk, 2002; Alekseev, 2014).

The compositional difference of niobium minerals in granite and zwitter reflects a change in the mineral formation conditions upon transition from magmatic to pneumatohydrothermal stages. The diverse species compositions and complex anatomy of niobates are related to their multistage formation, accompanying transformations, and metasomatic alteration (Alekseev, 2014; Alekseev and Marin, 2015). Postmagmatic niobium minerals are characterized by an increased role of Y, Pb, U, Fe and a decrease in W, Ta, REE, Ti, Sc, and Th concentrations (Tables 1–3). The compositional evolution of mineral compositions is controlled by variation of the physicochemical properties of the mineral-formation medium and the crystal chemistry properties of niobates (Kuz'menko and Es'kova, 1968; Aleksandrov, 1973; Gavrilenko and Sakhonenok, 1986; Voloshin, 1993; Yurgenson, 2003; M.G. Rub and A.K. Rub, 2006; Yang et al., 2013; Harlaux et al., 2015; Duran et al., 2016).

The rare metal-tin-bearing ore–magmatic systems of the Amur River region formed under reductive conditions typical of ilmenite granite crystallization of the Badzhal–Dussealin Complex (Gonevchuk, 2002). It

has been suggested that reductive conditions facilitated enrichment of magma in yttrium, HREE, and niobium (Watanabe et al., 2017) during the evolution of the Verkhneurmisky massif and the formation of accessory yttrium, HREE, and niobium minerals in Li–F granite. This is corroborated by the composition of wolframite, the evolution of which is expressed as decreasing Nb, Ta, Sc, Mn contents similar to the evolution of wolframite deposits in Hunan province of southeastern China, the Kalguty deposit at Mt. Altai, and many others, with a drop in temperature and pH of fluids and an increase in reductive properties and the participation of CO₂ (Yurgenson, 2003; Borovikov et al., 2016; Xiong et al., 2017).

F, B, and Cl likely played an important role in niobium gain in the melt. Mineral formation with the participation of niobium was facilitated by the precipitation of fluorides (fluorite, fluocerite, tveitite) and phosphates (monazite, xenotime), which was accompanied by a decrease in the concentration of fluorine and phosphate ions and by partial destruction of corresponding niobium complexes (M.G. Rub and A.K. Rub, 2006; Yang et al., 2013; Harlaux et al., 2015; Hien-Dinh et al., 2017). The increased Nb and Ta concentrations in fluids released from a rare metal melt is partly caused by the high fluid pressure inherent to the final stage of Li–F granite crystallization (Alekseev, 2014). At the magmatic stage of mineral formation, the main properties of Nb and Ta are reinforced and result in favorable conditions for the formation of complex alkali fluoride Nb and Ta compounds; they also increase their migration capability

and gain in residual fluids (Aleksandrov, 1973; Singh et al., 2017).

The presence of tantalum as accessory niobates in granite (fergusonite, samarskite, aeschynite) is explained by the high-temperature and acid conditions at the magmatic stage of mineral formation. The lowered Fe/Mn ratio of the melt (Kuz'menko and Es'kova, 1968; Aleksandrov, 1973; Voloshin, 1993) is reflected in the low Fe/Mn ratio of accessory minerals (Tables 1–3) and facilitates the formation of tantalum-bearing phases. The diversity of HREE in pneumatolytic fergusonite and its enrichment in LREE (Table 1) point to an initial increase in the alkalinity of pneumatolytic solutions, which gives way to a decrease in pH and intense gain of ytterbium and dysprosium due to greisenization (Gorzhevskaya et al., 1974; Gavrilenko and Panova, 2001; M.G. Rub and A.K. Rub, 2006; Vasil'ev et al., 2008). A similar conclusion can be drawn taking into account the decrease in the Fe/Mn ratio and Sc, Nb, Ta contents in wolframite from zwitter as compared to wolframite from granite (Vinogradova et al., 1980).

Thus, H₂O, CO₂, F, Cl, and alkalis pass into fluid from the melt at the pneumatolytic–hydrothermal stage. Such a medium is favorable for gain of niobium and tantalum. The postmagmatic precipitation of Nb, Y, and REE salts started at the early alkaline stage (400–600°C) and at the zwitter stage (300–400°C) from solutions enriched in Na, Li, and Fe. A decrease in temperature and pressure along with the advance of oxidation facilitate the formation of mixed REE–niobium and tungsten–tin mineralization (Aleksandrov, 1973; Gavrilenko and Sakhonenok, 1986; Yang et al., 2013; Harlaux et al., 2015; Hien-Dinh et al., 2017; Singh et al., 2017). In addition, greisenization of granite in the Verkhneurmisky massif was accompanied by the transformation of accessory tantaloniobates and redeposition of niobates bearing Y, REE, U (fergusonite, euxenite, pyrochlore), as well as oxides with Ta, REE, Ti, Sc admixtures (wolframite, scheelite, cassiterite, ilmenorutile, etc.) (Alekseev and Marin, 2015).

Metallogenic Significance of Niobium Mineralization in Zwitter

The genetic link between zwitter and Li–F granite in the Verkhneurmisky massif compels us to take a new look at the promising ore potential off the Badzhal district. As emphasized in the resolutions of the Fifth Far East (2011) and the Eastern (2016) Economic Forums, despite the high mineral potential of the Far East, the degree and rate of its development remains insufficient. The prospects of rare metal mineralization in tin–tungsten districts of the Far East attract attention (*Geodynamics* ..., 2006; Alekseev, 2014; Alekseev and Marin, 2015).

As is known, peralkaline (Nb, Zr, REE, Y) and subalkaline peraluminous (Ta, Be, Li) pegmatites and rare metal granites are economic sources of rare metals. Postmagmatic rocks related to granite of the aforementioned types markedly differ with respect to the rare metal ore potential. The abundant economic rare metal mineralization (columbite, pyrochlore, zircon, fergusonite, xenotime, etc.) is characterized by feldspathic rocks associated with alkali (riebeckite, aegirine–arfvedsonite, etc.) granite (Katugin, Transbaikalian region; Zashikha, the Eastern Sayan; Ulug-Tanzek, Tuva; Espe, Kazakhstan; Madeira, Brazil; Torlake, Canada; Jos-Bukuru, Nigeria; Haldzan-Buragtag, Mongolian Altai, etc.). Zwitter, which accompanies subalkaline Li–F granite, as a rule bears tin–tungsten (less frequently Be, Li, Rb, fluorite) mineralization: Tigrinoe, Primorye; Odinskoe, Yakutia; Iultin, Chukchi Peninsula; Altenberg, Erzgebirge; Hemerdon, Great Britain; Lost River, Alaska; Xianhualin, China, etc. The main niobium mass at deposits hosted in zwitter is concentrated in cassiterite, wolframite, scheelite, and, extremely rarely, in niobium minerals (columbite–tantalite, pyrochlore–microlite; fergusonite and euxenite are atypical) (Kuz'menko and Es'kova, 1968; Rundqvist et al., 1971; Gorzhevskaya et al., 1974; Beskin et al., 1999; Semenov, 2001; M.G. Rub and A.K. Rub, 2006; Yuan et al., 2008; Alekseev, 2014; Beskin and Marin, 2015; Hien-Dinh et al., 2017).

The presence of rare metal mineralization in zwitter and Li–F granite of the Verkhneurmisky massif described in this paper allows us to recommend the ore occurrences in the western sector of the Verkhneurmisky Cu–W–Sn cluster for Nb, Y, and REE. It is indicative that fergusonite from granite and zwitter of the studied district is close to that from alkali granite and metasomatic rocks at other large rare metal deposits, e.g., Katugin in Transbaikalia; Espe in Kazakhstan; Ayskan in Tuva; Bayanobo in China (Semenov, 2001). The Nb–Ti–Y–HREE–W–U mineral complex at the Puis-Le-Vin in France's Central Massif may be an analog of the studied mineralization. Like in the Verkhneurmisky massif, tungsten-bearing greisen with euxenite mineralization also develops there (Harlaux et al., 2015). Our observations show that nonuniform accommodation of rare metal mineralization in zwitter reflects secondary redistribution of niobium and other rare elements accompanied by alteration of their mineral forms. Niobium minerals hosted in granite and zwitter—fergusonite, samarskite, euxenite, and niobium-bearing wolframite—are indicators of rare metal mineralization.

CONCLUSIONS

(1) The similarity of species and chemical compositions of accessory rare metal mineralization in Li–F granites (samarskite, aeschynite, fergusonite, niobium wolframite) and zwitter (fergusonite, euxenite, nio-

bium-bearing wolframite) of the Verkhneurmisky massif has been established. Niobium minerals from granite and zwitter are characterized by similar compositions of admixtures: W, Y, REE, Mn, Fe, Pb, U, and Sc. The revealed trends reflect the genetic link between zwitter and Li–F granite in the Verkhneurmisky tin-tungsten ore cluster.

(2) The compositional difference between niobium minerals from granite and zwitter reflects a change in the physicochemical conditions of mineral formation upon the transition from magmatic to pneumatolytic–hydrothermal stages. The postmagmatic evolution of the niobium mineral composition is expressed as an increasing contribution of Y, Pb, U, Fe and decreasing concentrations of W, Ta, REE, Ti, Sc, and Th.

(3) The presence of rare metal mineralization in zwitter associated with Li–F granite in the eastern endomorphic zone of the Verkhneurmisky granitic massif allows us to recommend the ore occurrences in the western sector of the Verkhneurmisky tin cluster for Nb, Y, and REE. Mineral indicators of rare metal mineralization are niobium minerals of granite and zwitter: fergusonite, samarskite, euxenite, and Nb-wolframite.

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