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Accessory Mineralization of Rocks from Late Cretaceous Intrusive Series with Li–F Granites in the Far East

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Abstract—Accessory mineralization of the Late Cretaceous intrusive series in the Far East was investigated on the basis of published data and the author's original evidence. The composition of accessory minerals from leucogranite, monzonitoid rocks, and Li–F granites has been established. The trend in the evolution of Late Cretaceous granitoids is characterized by an increase in the mineral-forming role of iron and rare elements. Diverse accessory minerals and their typomorphic assemblages have been identified for Li–F granites and ongonites. The regional specificity of accessory mineralization in rare-metal granites consists in the leading role of the minerals W, Ta, Nb, Bi, Y, REE, and As. The uniformity of mineral species and mineral assemblages and the typomorphism and evolution of accessory minerals are inherent to the Far East belt of Li–F granites.

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INTRODUCTION

Accessory minerals are one of the forms in which the concentration of rare elements in rocks is realized. Sobolev (1949) and Ginzburg (1954) were the first to connect the mineralogy of igneous rocks with concentration of rare elements in silicate melt. Further mineralogical and geochemical study of granitic rocks has shown that the obvious importance of rock-forming mineral indicators does not rule out a significant body of genetic and mineragenic information derived from speciation and typomorphism of accessory minerals (Lyakhovich, 1967; Ginzburg, 1972; Marin, 1976; Vladyskin, 1983). The discovery of rare-metal granites containing economic concentrations of rare elements in their minerals (columbite, fergusonite, tantalite, etc.), was an important event in petrology (Ginzburg, 1972; Kovalenko, 1977; Beskin et al., 1979, 1999).

In the last decades, following the tin provinces of Europe, Australia, Africa, North and South Americas, and Central Asia, rare-metal Li–F granites were discovered in the Far East of Russia¹ and the adjacent regions of Alaska and China known for their large and unique deposits of tin, tungsten, and other mineral resources (Nedosekin, 1988; Gavrilenko and Panova, 2001; Gonevchuk, 2002; *Geodinamika* ..., 2006; A.K. Rub and M.G. Rub, 2006; Alekseev, 2011; Huang et al., 2002; Trunilina et al., 2008; data of *Gosgeolokarta-1000*, -200, etc.). These findings furnish

evidence for the validity of the ideas of S.S. Smirnov, E.A. Radkevich and their followers, who emphasized the geological and genetic conformity of ore districts at the Pacific continental margins (*Geodinamika* ..., 2006), and allow us to suggest that the Far East belt of Li–F granites actually exists as a superprovince of rare-metal magmatism (Alekseev, 2012). In this connection, it is important to provide insights into mineralogy of Late Cretaceous granitoid series and their position in history of magmatism and ore formation in the Far East. In this paper, we present new data on the accessory minerals of rare-metal Li–F granites obtained by application of the technique of electron petrography.

LATE CRETACEOUS GRANITIC SERIES OF THE FAR EAST

The Mesozoic plutonic magmatism of this region developed from Jurassic–Early Cretaceous calc-alkaline I-granites making up the Kolyma, Miao-Chang, Khungari, and other diorite–granodiorite and granitic series to the Late Cretaceous (100–85 Ma) subalkaline series of IS- and A-granites and leucogranites, including minor intrusions (often dikes) of rare-metal Li–F granites (Pyrkakai, Omchikanda, Nyut, Right Urmi complexes). The Late Cretaceous series comprise not only rare-metal granitic rocks, but also, immediately preceding the Chaun, the Omsukchan, Badzhal–Dusse-Alin leucogranites and the Ichuveem, Kongali, and Silin monzonitoid complexes (Zagruzina, 1977; Gonevchuk, 2002; *Geodinamika* ..., 2006; Trunilina et al., 2008; Alekseev, 2011; *Gosgeolokarta-1000*).

The spatiotemporal juxtaposition of rare-metal granites and ore-bearing zwitterites with earlier leucog-

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¹ The Far East is the easternmost territory of Russia, including the basins of rivers influent into the Pacific Ocean and the eastern Arctic seas. In terms of administrative regionalization, this territory corresponds to the Far East Federal okrug (district).

ranites, alaskites, and monzonitoid rocks is a typical feature of many tin areas: Kazakhstan, Mongolia, China, Germany, Transbaikalia, etc. (Kovalenko, 1977; Beskin et al., 1979; Gavrilenko and Panova, 2001; A.K. Rub and M.G. Rub, 2006). All three complexes of the Late Cretaceous intrusive series feature the following: (i) relatively large (50–300 km²) multiphase intrusions of biotite leucogranites; (ii) minor monzonitoid intrusions (monzogranite, granosyenite, quartz monzonite) close in time, and (iii) the youngest intrusions of Li–F granites and ongonites are exposed in deeply eroded areas of the Far East occupied by granitic rocks (Kuiviveem–Pyrkakai, Omsukchan, Badzhal districts). Monzonitoid rocks and rare-metal granites are spatially associated with leucogranites or localized within them. In turn, leucogranites and alaskites may be situated within Early Cretaceous–Jurassic granitic batholiths or nearby, making up complex assemblies of multiphase plutons. In the slightly eroded Central Polousny, Khingan–Olonoi, and Armi areas, the leucocratic batholiths are not exposed, and only separate or partly combined in space minor leucogranitic, monzonitoid, and rare-metal granitic intrusions crop out. Thus, *a typical Late Cretaceous intrusive series in the Far East consists of leucogranites, monzonitoids, and Li–F granites*. The intrusive complexes are listed in order of their formation. The Li–F granites are always accompanied by zwitter with W and Sn mineralization, tourmalinites, and other melanocratic metasomatic rocks (Zagruzina, 1977; Nedosekin, 1988; Gavrilenko and Panova, 2001; Gonevchuk, 2002; A.K. Rub and M.G. Rub, 2006; Alekseev, 2011).

ACCESSORY MINERALS IN LATE CRETACEOUS GRANITIC SERIES: A REVIEW OF PUBLISHED DATA

Accessory minerals from the Late Cretaceous granitic rocks have been studied nonuniformly in space and by rock types. The speciation and typomorphic features of accessory minerals have been investigated rather thoroughly for leucogranites and monzonitoid rocks, where zircon, ilmenite, apatite, and allanite are mentioned most frequently. Monazite, xenotime, magnetite, titanite, rutile, garnet, and cassiterite almost always occur, whereas fluorite, topaz, tourmaline, and sulfides are noted sporadically. Monazite, fergusonite, wolframite, and arsenopyrite are more abundant in the late intrusive phases of leucogranitic complexes; the accessory minerals become enriched in Y, REE, U, and Th (Radkevich, 1971; Bolotnikov et al., 1975; Ipat'eva, 1976; *Geologiya* ..., 1986; Finashin, 1986; Sobolev, 1989; Gonevchuk, 2002; Gvozdev, 2010).

In leucogranites and alaskites of the *Novosibirsk–Chukchi province* (Severnny, Yanranai, Pevek, East Iul'tin, Gyrgychan, Left Kainvaam plutons), anatase, wolframite, scheelite, and arsenopyrite have been

described in addition to the aforementioned mineral species. Abundant accessory cassiterite, topaz, and tourmaline were pointed out in granites of the Pevek and Kuiviveem–Pyrkakai ore districts (Severnny, Pevek, Lootaipyn, Pyrkanayan, Palyan, Right Ichuveem, and Yandrapaak plutons) (Zagruzina, 1977; *Geologiya* ..., 1986; Sobolev, 1989; *Gosgeolkarta-200*). Leucogranites of the Central Polousny, Central Yana, Indigirka–Kolyma, and Ayan–Yuryakh districts of the *Yana–Kolyma province* (Omchikanda, Arga–Ynnah–Khay, Khayargastakh, Left Eriket, Chuguluk, Left Arangas, Tobychan, Kurum, and Kyutep plutons) contain fergusonite, pyrochlore, uraninite, cyrtolite, and columbite in addition to the above-mentioned accessory minerals (Ipat'eva, 1976; Zagruzina, 1977; Sobolev, 1989). The complex of accessory minerals in leucogranites from the Badzhal, Dusse-Alin, and Komsomol'sk districts of the *Sikhote-Alin province* (Upper Urmi, Dusse-Alin, and Chalba plutons and minor intrusions) contains (in addition to the type set) fluorite, tourmaline, fergusonite, wolframite, cassiterite, thorite, scheelite, arsenopyrite, chalcopryrite, anatase, and brookite. Leucogranites of the Armi district (Biserny, Izluchinsky, Priiskovy, Ognevsky, Benevsky plutons) contain topaz, fluorite, cassiterite, scheelite, monazite, garnet, rutile, betafite, tourmaline, chalcopryrite, bismuthinite, and axinite. A number of rare chemical elements have accumulated in the main accessory minerals without forming a special mineral, e.g. Nb in ilmenite, rutile, titanite, and cassiterite; Y in zircon, fluorite, allanite, apatite, and titanite; Sn in allanite, titanite, ilmenite, pyrite, tourmaline, and axinite; W in zircon and cassiterite (Radkevich et al., 1971; Bolotnikov et al., 1975; Levashev, 1991; *Geodinamika* ..., 2006; *Gosgeolkarta-200, -1000*) (Table 1).

Two zircon generations occurring in the Late Cretaceous leucogranites of the Far East are distinguished by morphology, color, and admixture contents (Lyakhovich, 1967; Bolotnikov et al., 1975; Sobolev, 1989; *Geologiya* ..., 1986; Gonevchuk, 2002; A.K. Rub and M.G. Rub, 2006). Postmagmatic processes exert a strong effect on the composition of leucogranite and induce, in particular, the deficiency in Ca-bearing minerals (apatite, allanite, titanite) along with appearance of topaz, fluorite, tourmaline, monazite, xenotime, uranothorite, cyrtolite, cassiterite, scheelite, arsenopyrite, loellingite, bismuthine, and chalcopryrite. These facts have been noted in the Yana–Kolyma province (Lyakhovich, 1967; Ipat'eva, 1976; Nedosekin, 1988), Novosibirsk–Chukchi province (*Geologiya* ..., 1986; Sobolev, 1989), and Sikhote-Alin province (Lyakhovich, 1967; Bolotnikov et al., 1975; A.K. Rub and M.G. Rub, 2006; *Gosgeolkarta-200*).

Monzonitoids of the *Novosibirsk–Chukchi province* (monzonite, monzodiorite, subalkali granodiorite of the West Iul'tin, Veshkap, and Metegyn plutons) contain accessory ilmenite, titanite, zircon, apatite, and monazite; cassiterite and tourmaline are rare. Gadolinite, fergusonite, xenotime, and malacon are

Table 1. Accessory minerals of Late Cretaceous intrusive series in the Far East

Mineral	Chukchi Pen.				Yakutia		Amur region				Primorye	
	lg	mnz	lfg	ong	lg	lfg	lg	mnz	lfg	ong	lg	lfg
Zircon	+	+	+	x	+	+	+	+	+	x	+	+
Ilmenite	+	+	+	x	+	x	+	+	+	x	+	
Monazite-(Ce)	+	+	+	+	+	x	+	+	+	x	+	+
Topaz			+	+		+			+	+	x	+
Fluorite	+	+	+	+	x	+	+	+	+	+	x	+
<i>Ce, Y fluorides</i>			+	x			x		x	x		
Cyrtolite		x	+	+		x			+	+		+
Allanite-(Ce)	x	+			+		+	+			+	
Allanite-(Y)*		x	x					x	+			
<i>Tantaloniobates</i>	x		+	+			x		+	+		+
Apatite	+		x		+	+	+	+	x		+	+
Xenotime-(Y)	x	+	x		+	x	x		+	x		+
<i>Li, Al phosphates</i>				x	x	+						
Rutile	+		x	x	+	x	x		x	x	x	x
<i>Ti oxides</i>		x	x		+			x				x
Titanite	+						+					
Ferberite			x	+	x	+		x		+		x
<i>W-minerals</i>	x		x	x	x	+	x		x	x		+
Tourmaline		x	x	x	+	+	x	x		x	x	
Garnet	x				+		x				x	
Thorite	x	x	+	x			x	x	+	+		x
Uraninite			x	x	x	x			x	x		
Cassiterite	x		x	x	x	+					x	+
Chernovite-(Y)*	x		x				x	x	x	x		
<i>Bi, Pb arsenates</i>	x		x	x			x	x	x	x		
Bismuth					x	x				x		x
<i>Sulfides</i>					x	x		x			x	x

* (1) Areas of the Far East: Chukchi Pen. (Kuiviveem–Pyrkakai); Yakutia (Central Polousny and Central Yana); Amur region (Badzhal); Primorye (Armi). (2) Rocks: lg, leucogranite; mnz, monzonitoid; lfg, Li–F granite; ong, ongonite. (3) The author's data on Chukchi Peninsula and Amur region have been used, as well as the data published by V.V. Gavrilenko, V.I. Gvozdev, V.G. and G.A. Gonevchuk, G.A. Goryachev, S.I. Grigoriev, L.Ya. Efremenko, S.V. Efremov, I.A. Zagruzina, I.S. Ipat'eva, V.D. Kozlov, P.G. Korostev, K.K. Levashev, S.F. Lugov, V.V. Lyakhovich, P.G. Nedashkovsky, Yu.D. Nedosekin, I.Ya. Nekrasov, E.V. Polyakova, V.A. and V.I. Popov, E.A. Radkevich, S.M. Rodionov, M.G. and A.K. Rub, V.G. Sakhno, B.I. Semenyak, A.P. Sobolev, V.A. Stepnova, N.I. Tikhomirov, P.L. Tikhomirov, V.A. Trunilina, V.G. Finashin, B.L. Flerov, T.S. Khabibulina, L.N. Khetchikov, V.S. Shkodzinsky; internet resources: www.mindat.org, www.webmineral.com, and Gosgeolkart-1000, 200. (4) Occurrence frequency: (+) main (70–100% of samples), (++) secondary in occurrence (10–70%, and (x) rare minerals (10%); abundances are >50, 1–50, and <1 ppm, respectively. Dash, mineral is not detected. Minerals revealed in granitic rocks of the Far East for the first time are marked by asterisk.

typomorphic minerals of the Chukchi monzonitoids. They are especially characteristic of felsic varieties (*Geologiya ...*, 1986; *Gosgeolkart-200*). Apatite-(CaF), allanite, titanite, titanomagnetite, Mn- and Mg-ilmenite, zircon enriched in U, Th, and Hf, monazite, xenotime, fluorite, chevkinite, and thorite are contained in monzogranites and granosyenites of the *Yana–Kolyma province* (Trunilina et al., 2008). Monzodiorite and monzogranodiorite of the *Sikhote-Alin province* (Silin, Anadzhakan, Left Yarap plutons

and minor intrusions) contain apatite-(CaF), ilmenite, titanite, tourmaline, axinite, zircon, allanite, and garnet (Radkevich et al., 1971; *Gosgeolkart-200, -1000*). Monzonitoids of Primorye (monzonite, monzodiorite, and granosyenite of the Strel'nikovo, Zolotogorsky, Right Valinkui, Berezovsky, and Ararat plutons) contain apatite, zircon, ilmenite, rutile anatase, monazite, allanite, cassiterite, pyrite, magnetite, galena, and chalcopryrite (Finashin, 1986; Levashov, 1991; *Gosgeolkart-200*). Typomorphic accessory

minerals monazite, xenotime, cheralite, and apatite are enriched in REE and Th (Gvozdev, 2010).

The accessory minerals of Li–F granites remain poorly studied. Despite the obvious importance of this line of research, only lists of main accessory minerals have been compiled in most areas. Auxiliary and rare accessory minerals, typomorphic features of accessory minerals, and their evolution in intrusive series are still awaiting study. The regional correlation of accessory mineral assemblages has not been carried out, nor has the topomineralogical study of Pacific rare-mineral granites.

The Li–F granites of the *Novosibirsk–Chukchi province* contain minerals of volatile and rare elements: beryl, fluorite, topaz, tourmaline, apatite, and allanite along with zircon, monazite, xenotime, ilmenite, and anatase inherent to leucogranites. The assemblages of accessory minerals in rare-metal granites of the Iul'tin, Svetly, Solnechny, and Tenkergin stocks in the Iul'tin district comprises topaz, fluorite, zircon, apatite, wolframite, cassiterite, and garnet (*Geologiya* ..., 1986; Kozlov et al. (1995); *Gosgeolkarta-200*). According to Golota (1953) and Karaeva (1967), the Li–F granites of the Severny pluton are markedly enriched in topaz, fluorite, ilmenite, monazite, xenotime, cassiterite, and anatase as compared with leucogranites and monzonitoids and are free of titanite. Fergusonite, pyrochlore, columbite–tantalite, britholite-(Y), thorite, and probably betafite are typomorphic minerals.

Accessory mineral assemblages in Li–F granites of the *Yana–Kolyma province* include topaz, fluorite, tourmaline, ilmenorutile, tantaloniobates, cassiterite, wolframite, scheelite, molybdenite, arsenopyrite, and loellingite. The rare-metal granites of the Central Yana district differ in their occurrence of columbite–tantalite, spodumene, Li-schorl, and allanite. Topaz, monazite, fluorite Mn-ilmenite, columbite, tantaloniobates with high Sn and W contents, amblygonite, triplite, cassiterite enriched in Ta and Nb, Sn-bearing rutile, and molybdenite have been identified among accessory minerals in Li–F granites from the Central Polousny district. Zircon, monazite, xenotime, uraninite, gadolinite, tourmaline, scheelite, as well as postmagmatic cassiterite, wolframite, arsenopyrite, galena, sphalerite, and molybdenite have been described from rare-metal aplite–pegmatites in the Omchikanda Pluton. Topaz, fluorite, magnetite, rutile, zircon, xenotime, and fergusonite have been noted in Li–F granites of the Indigirka–Kolyma district (Ipat'eva, 1976; Nedosekin, 1988; Sobolev, 1989; *Geodinamika* ..., 2006; Trunilina et al., 2008) (Table 1).

The assemblage of accessory minerals from the Li–F granites of the Badzhal district in the *Sikhote-Alin province* comprises ilmenite, monazite, thorite, zircon, and fluorite (Gavrilenko and Panova, 2001). Sub-alkaline granites from the Khingan–Olonoi district include zircon, apatite, monazite, xenotime, magne-

tite, allanite, topaz, fluorite, ilmenite (?), rutile, and cassiterite (Gonevchuk, 2002). In the Li–F granites of the Armi district (Tigriny and Zabyty stocks), topaz, fluorite, zircon, apatite, xenotime, monazite, anatase, columbite, cassiterite, wolframite, thorite, garnet, rutile, scheelite, wolframite, arsenopyrite, molybdenite, and pyrite have been identified (*Geodinamika* ..., 2006; A.K. Rub and M.G. Rub, 2006). As concerns Li–F granites in China, Hf-zircon, apatite, amblygonite–montebrasite, pollucite, fluorite, Cs-beryl, columbite–tantalite, wodginite, tapiolite, Ta-microlite, Ta-cassiterite, sphalerite, magnetite, apatite, ilmenite, and pyrite are mentioned (Huang et al., 2002).

NEW DATA ON ACCESSORY MINERALS IN LATE CRETACEOUS GRANITIC SERIES

Many of the aforementioned data have been obtained using petrographic methods and examination of heavy concentrates, which make it possible to reveal the most abundant accessory minerals; however, they are unfit for study of rare minerals, secondary in abundance, which are frequently represented by grains as small as 0.05 mm, and which have variable composition and complex anatomy. We carried out detailed research on accessory minerals in the Late Cretaceous intrusive series of the Far East combining artificial heavy concentrates (Lyakhovich, 1967) with electron and ion microprobes applied to probing, profiling, and mapping of mineral grains (Alekseev et al., 2013). In doing so, we used the laboratory equipment of the Mining university, Russian Geological Research Institute (St. Petersburg), Yaroslavl Branch of the Physical Technological Institute, RAS, and Technoinfo Ltd. Company (Moscow).

Accessory minerals of leucogranites. According to the results of studying granitic rocks from the reference Kuiviveem–Pyrkakai (Chukchi Peninsula) and the Badzhal (Amur region) districts, accessory minerals of leucogranites proved to be more diverse than seemed earlier. Quantitative microanalysis has shown that parallel with Ti–Fe oxides, zircon, allanite, monazite, xenotime, and other REE phases (up to 70 ppm), fluorite and yttrifluorite (1800–2500 ppm), topaz (0–200 ppm), U-thorite (5–15), Mn and U minerals (up to 50 ppm), wolframates and tantaloniobates occur sporadically; their concentration reaches 70–100 ppm (Fig. 1).

Ilmenite containing Mn (3.94–9.08 wt %, up to 24.34 wt % MnO) and Nb (up to 23.29 wt %) is predominant among *Ti and Fe oxides*; rutile and anatase containing 0.11–1.27 wt % Nb₂O₅ also occur. Some rutile grains as microinclusions in ilmenite correspond to ilmenorutile in composition. Microinclusions (<0.02 mm in size) of long-prismatic apatite-(CaF) with Ce, Nd, Mn, Fe, Sr, and Th (up to 0.1 apfu in total) are frequently observed in rock-forming minerals. Apatite aggregates overgrown by monazite and xenotime are abundant. *Monazite*-(Ce) from

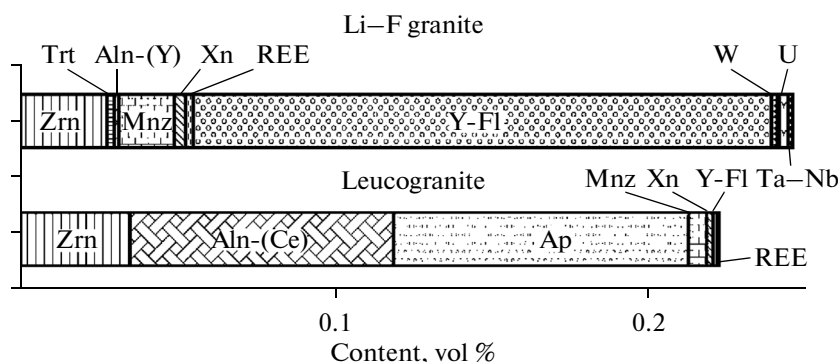


Fig. 1. Comparison of accessory mineralization in Li-F granite and leucogranite of Severny pluton, Chukchi Peninsula: generalized data of electron microprobe analysis of large polished sections. Minerals: Aln, allanite; Ap, apatite; Mnz, monazite; Trt, thorite; Xn, xenotime; Y-Fl, yttrifluorite; Zrn, zircon; Bi, Bi-minerals (bismutopyrochlore, rooseveltite, etc.); Pb, Pb-minerals (phillipsbornite, coronadite, etc.); Mn, Mn-minerals (pyrophanite, triplite, etc.); REE, REE-minerals (fluocerite, tveitite, etc.); Ta-Nb, tantaloniobates (wolframoixiolite, samarskite, etc.); W, W-minerals (ferberite, scheelite, etc.); U, U-minerals (uraninite, asselbornite, etc.).

leucogranites is represented in thin sections and artificial heavy concentrates by tiny (<0.01 mm) yellow xenomorphous grains commonly incorporated into biotite. At the mean composition ($\text{Ce}_{0.51}\text{La}_{0.19}\text{Nd}_{0.15}\text{Sm}_{0.01}\text{Gd}_{0.02}\text{Th}_{0.07}\text{U}_{0.01}\text{Ca}_{0.04}\text{PO}_4$), significant variations of major component contents are established in separate grains and on a scale of intrusions. Varieties markedly enriched in brabantite component are met with: their ThO_2 content reaches 21.79 wt %. *Allanite*-(Ce) from leucogranite is distinguished by relatively large dimensions (tenths of mm), euhedral morphology, and zonal structure. *Allanite*-(Y) containing up to 44.23 wt % Y_2O_3 has been identified in the greisenized leucogranite (Aleksiev et al., 2012).

Zircon is contained in leucogranite in the amounts of few hundreds ppm and represented by two generations: almost colorless euhedral crystals with fine oscillatory zoning and brown to reddish brown subhedral individuals with rough zoning. *Zircon* is characterized by low abundance and homogeneous distributions of admixtures except for the outer shells of second-type crystals with anomalously high concentrations of Hf (0.5–3.0, occasionally up to 8.9 wt %), U (0.2–2.4 wt %), Th (0.3–1.2 wt %), P (up to 2137 ppm), Ca (up to 2573 ppm), and H_2O (up to 4310 ppm). Among other isomorphic admixtures, Y and HREE (mainly Yb, Er, Dy) deserve mention. Their contents in core reach 6837 and 2524 ppm, respectively and up to 9693 and 5840 ppm in rim (Aleksiev et al., 2013). *Fluorite* is widespread in leucogranite; thorite, tantaloniobates (wolframoixiolite, columbite-(Fe), less frequent aeschynite-(Y), liandratite) occur occasionally; scheelite and cassiterite are identified. In contrast to deep-rooted opinion, cassiterite occurs in biotite leucogranite rarely as single grains 1–2 μm in size entrapped into Ti oxides. Such rare minerals as chernovite-(Y), cerianite-(Ce), pyrophanite, triplite have been revealed in leucogranites as second-

ary minerals with respect to the major minerals (Table 1). *Pyrophanite* is closely associated with Mn-ilmenite (0.76–4.04 wt %, up to 9.08 wt % MnO_2), replacing the latter. *Cerianite*-(Ce) appears in fractures and leaching voids within allanite-(Ce). *Chernovite*-(Y) replaces xenotime and thorite and occurs as lenticular segregations at the boundaries between silicates (Aleksiev and Marin, 2012). The set of accessory minerals in leucogranites corresponds to the leucogranite–alaskite association (Marin, 1976; Beskin et al., 1979).

Accessory minerals of monzonitoids make up assemblages enriched in F, P, Y, REE, and Th. The leading role of *allanite*-(Ce) and *REE-bearing apatite*-(CaF) containing up to 2.89 wt % Ce_2O_3 , 2.38 wt % Nd_2O_3 , and 0.60 wt % La_2O_3 is characteristic. The rare-metal specialization of monzonitoids is expressed in abundant *fluorite* containing up to 4.93 wt % Ce_2O_3 and 4.30 wt % La_2O_3 ; *zircon* enriched in HfO_2 up to 5.17 wt %, ThO_2 up to 10.01 wt %, and UO_2 up to 5.21 wt %; occurrence of *tourmaline*, *ferberite*, *allanite*-(Y), *As-thorite*, *britholite*-(Y), *chernovite*-(Y), *thorbastnaesite*, and *brockite* (Table 1). *Ti-bearing ferriallanite*-(Ce) has been found in monzonitoid dikes in the Chukchi Peninsula. In composition of accessory minerals, monzonitoids occupy an intermediate position between leucogranites and rare-metal granites. They contain *tourmaline*, *fluorite*, *tveitite*-(Y), *xenotime*-(Y), *allanite*-(Y) along with *apatite*, *monazite*-(Ce), and *allanite*-(Ce).

Zircons from monzonitoids yield to zircons from leucogranites in size and are characterized by diverse morphology and anatomy. The most frequent are light-colored euhedral prismatic crystals with dark metamict cores and brown subhedral short-prismatic grains with numerous microinclusions of Th–U minerals. They differ from zircons in leucogranites in higher admixture concentrations (wt %): 0.1–6.4 Hf, 0.1–3.3 U, 0.05–1.0 Th, as well as (ppm) 847–4601 Y, 499–3034 HREE, 12–78 Nb, 1.3–85.5 F, 385–4296 H_2O

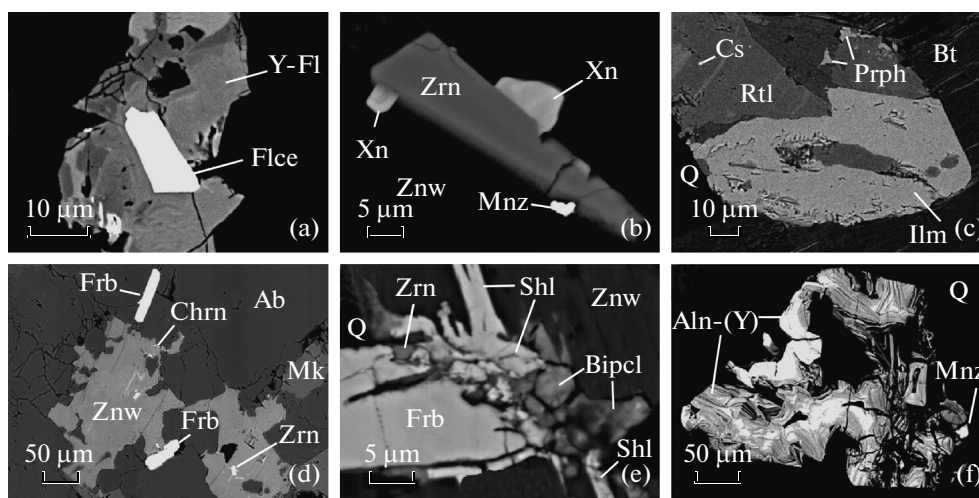


Fig. 2. Main and secondary in abundance accessory minerals in Li–F granites and ongonites of the Far East: (a) fluocerite in zonal yttrifluorite; (b) zircon overgrown by xenotime and monazite; (c) intergrowth of Mn-ilmenite, pyrophanite, and Sn–Nb-rutile with cassiterite inclusions; (d) Nb-ferberite, cyrtolite, and chernovite-(Y); (e) intergrowth of ferberite, scheelite, and cyrtolite with secondary bismutopyrochlore; (f) skeletal allanite-(Y) crystal with monazite-(Ce) inclusion; (a, c) Li–F granites of Chukchi Peninsula; (b, f) Li–F granites of Amur region; (d, e) ongonites of Amur region. Minerals: Ab, albite; Aln-(Y), allanite-(Y); Bipcl, bismutopyrochlore; Bi, biotite; Chrn, chernovite; Cs, cassiterite; Frb, ferberite; Y-Fl, yttrifluorite; Flce, fluocerite; Mk, microcline; Mnz, monazite; Prph, pyrophanite; Q, quartz; Rtl, rutile; Shl, scheelite; Xn, xenotime; Znw, zinnwaldite; Zrn, zircon. See also Table 2. BSE images.

and in lower P and Ti contents (Alekseev et al., 2013). The set and typomorphic features of accessory minerals from monzonitoids indicate that these rocks belong to a granite–granosyenite association (Beskin et al., 1979).

Accessory minerals of Li–F granites make up assemblages characterized by the absence of titanite and garnet, as well as an insignificant amount of apatite. The major and auxiliary accessory minerals are topaz, fluorite, altered zircon and cyrtolite, ilmenite, monazite-(Ce), W–Nb rutile, Nb-ferberite, tantaloniobates, and allanite-(Y) (Table 1). The mean phase composition of accessory minerals is as follows (ppm): topaz (15800), fluorite (3900), yttrifluorite (1900), Ti–Fe oxides (800), cyrtolite (300), monazite (200), tantaloniobates (100), xenotime (30), and other Y–REE phases (50), thorite and Th-phases (25), U and U–As phases (25), ferberite and other W-phases (15), Ag-phases (2), Bi-phases (1), and unspecified phases (6) (Fig. 1). *Fluorite* contains 0.25–8.45 wt % Y_2O_3 , Yb (no higher than 0.96 wt %), occasional Ce and Nd (no higher than 1.90 wt %). Fluorite is steadily associated with fluocerite, especially in granites of the Chukchi Peninsula. In addition to LREE, Y and Th (up to 2.50–11.28 wt % Y_2O_3 , 2.86–9.81 ThO_2) are incorporated into the latter mineral. *Monazite*-(Ce) is enriched in a huttonite component and La as compared with its analog from leucogranite. A share of relatively large (50–70 µm) *xenotime* grains intergrown with zircon and monazite increases in Li–F granites. *Ilmenite* always contains Mn (3.67–8.83 wt % and up to 21.51 wt % MnO). *Rutile* and *anatase* are enriched in Nb, W, Ta, and Sn (usually 1–3 wt % of each com-

ponent, less frequently up to 10 wt % and higher) and contain microsegregations (0.5–5.0 µm) of cassiterite, wolframite, and fergusonite (Fig. 2).

Zircon from Li–F granites is characterized by small (20–100 µm) size, relatively low (200–400 ppm) abundance, and a complex internal structure. Two types of zircon crystals with oscillatory zoning and recrystallized cores are distinguished. The first type is formed by means of recrystallization of older zircons, and the second type is a product of recrystallization of the first-type grains or crystallization from fluid-saturated melt. Crystals of the second type and outer rim of the first-type crystals are distinguished by defects in lattice structure, porosity, fracturing, and abundant Th–U mineral inclusions. Zircons of rare-metal granites sharply differ from zircons in leucogranites and monzonitoids, having high concentrations of rare elements and being represented by a typical Y–U–Hf cyrtolite. The core is a recrystallized protocystal surrounded by a thick zone of U, Th, and REE accumulation (wt %): 0.1–3.7 U, 0.1–2.3 Th, and 0.01–1.2 HREE (Yb, Dy, Er, Tb), as well as by abundant thorite, uraninite, xenotime-(Y), and monazite-(Ce) microinclusions. Hf accumulates in the outer rim (1.4–14.7 wt %); the Zr/Hf ratio reaches 2.7. Typomorphic admixtures in zircons from Li–F granites are Nb, LREE, F, Ti, Cs, Li. Atypical of zircon, Fe, Ca, Al, As steadily appear in zones enriched in U and Hf; Ba, Sr, F, and H_2O accumulate as well. A marginal accumulation and extremely nonuniform distribution of the above-mentioned elements is detected in the second-type cyrtolite with Zr/Hf ratio reaching 2.4–5.6. Zircon from ongonite resembles this mineral from

Table 2. Typomorphic accessory minerals from Li–F granites and ongonites of the Far East

Mineral	Empirical formula
Allanite-(Y)	$\text{Ca}_{0.35}(\text{Y}_{1.55}\text{Ree}_{0.66}\text{Th}_{0.01})\text{Al}_{0.18}\text{Fe}_{1.09}\text{Mn}_{0.02}(\text{Si}_{3.62}\text{O}_{11})\text{O}(\text{OH})$
Bismutopyrochlore	$(\text{Bi}_{0.13}\text{Fe}_{0.64}\text{Ca}_{0.11}\text{Th}_{0.1}\text{U}_{0.05}\text{As}_{0.05}\text{Mn}_{0.02}\text{Ce}_{0.01}\text{Sc}_{0.01})(\text{Nb}_{0.37}\text{Ta}_{0.2}\text{P}_{0.18}\text{W}_{0.08})\text{O}_4$
Wolframoixiolite	$(\text{Fe}_{0.43}\text{Nb}_{0.30}\text{Mn}_{0.14}\text{Sc}_{0.05})(\text{Nb}_{0.40}\text{W}_{0.31}\text{Ta}_{0.15}\text{Ti}_{0.14})\text{O}_4$
Gahnite	$\text{Zn}_{1.00}\text{Al}_{1.51}\text{Fe}_{0.73}\text{O}_4$
Gananite	$\text{Bi}_{0.94}\text{Fe}_{0.08}\text{F}_3$
Zavaritskite	$\text{Bi}_{1.00}\text{OF}$
Ilmenite	$\text{Fe}_{0.70}^{2+}\text{Mn}_{0.29}^{2+}\text{Ti}_{1.01}\text{O}_3$
Ilmenorutile	$(\text{Ti}_{0.72}\text{Nb}_{0.12}\text{Fe}_{0.11}\text{Ta}_{0.05})\text{O}_2$
Yttriaite-(Y)	$(\text{Y}_{1.48}\text{Yb}_{0.16}\text{Dy}_{0.15}\text{Er}_{0.13}\text{Cd}_{0.07})_{1.99}\text{O}_3$
Ishikawaite	$(\text{U}_{0.25}^{4+}\text{Ca}_{0.1}\text{Mn}_{0.07}\text{Fe}_{0.05}\text{Th}_{0.04}\text{Yb}_{0.04}\text{Y}_{0.01}\text{Dy}_{0.01}\text{Sc}_{0.03})(\text{Nb}_{0.77}\text{Ta}_{0.23}\text{W}_{0.18})\text{O}_4$
Columbite-(Fe)	$(\text{Fe}_{0.75}\text{Mn}_{0.28})(\text{Nb}_{1.67}\text{W}_{0.15}\text{Ti}_{0.13}\text{Sc}_{0.03})\text{O}_4$
Xenotime-(Y)	$(\text{Y}_{0.57}\text{Cd}_{0.03}\text{Dy}_{0.06}\text{Er}_{0.05}\text{Yb}_{0.10}\text{Si}_{0.03})\text{PO}_4$
Monazite-(Ce)	$(\text{Ce}_{0.49}\text{La}_{0.18}\text{Nd}_{0.17}\text{Sm}_{0.02}\text{Gd}_{0.01}\text{Th}_{0.04}\text{U}_{0.001}\text{Ca}_{0.001})\text{PO}_4$
Rutile	$(\text{Ti}_{0.93}\text{Fe}_{0.02}\text{Nb}_{0.03}\text{Ta}_{0.01}\text{W}_{0.002})\text{O}_2$
Samarskite-(Yb)	$(\text{Ca}_{0.1}\text{Sc}_{0.02}\text{U}_{0.2}^{4+}\text{Ti}_{0.01}\text{Mn}_{0.1}\text{Fe}_{0.2}\text{As}_{0.03}\text{Pb}_{0.01}\text{Yb}_{0.1}\text{Th}_{0.04})(\text{Nb}_{0.7}\text{Ta}_{0.3}\text{W}_{0.2})\text{O}_4$
Strüverite	$(\text{Ti}_{0.70}\text{Sn}_{0.10}\text{Ta}_{0.08}\text{Fe}_{0.07}\text{Nb}_{0.05})\text{O}_2$
Thorutite	$(\text{Th}_{0.54}\text{U}_{0.33}\text{As}_{0.26})(\text{Ti}_{1.83}\text{Fe}_{0.22})_{2.05}(\text{O}, \text{OH})_6$
Uranopolycrase	$(\text{U}_{0.55}\text{Ca}_{0.27}\text{Th}_{0.09}\text{Y}_{0.04})(\text{Ti}_{1.42}\text{Nb}_{0.34}\text{Ta}_{0.20})_{1.96}(\text{O}, \text{OH})_6$
Ferberite	$(\text{Fe}_{0.62}\text{Mn}_{0.20}\text{Nb}_{0.12}\text{Sc}_{0.04})_{0.98}(\text{W}_{0.71}\text{Nb}_{0.23}\text{Ti}_{0.06})_{1.00}\text{O}_4$
Fergusonite-(Y)	$(\text{Y}_{0.55}\text{Dy}_{0.12}\text{Er}_{0.08}\text{Yb}_{0.04}\text{Ca}_{0.12}\text{Ti}_{0.08})(\text{Nb}_{0.78}\text{Ta}_{0.06}\text{W}_{0.12})\text{O}_4$
Fluorite	$(\text{Ca}_{0.97}\text{Y}_{0.02})\text{F}_2$
Fluocerite	$(\text{Ce}_{0.49}\text{La}_{0.22}\text{Nd}_{0.11}\text{Ca}_{0.22}\text{Th}_{0.04})\text{F}_3$
Cyrtolite	$(\text{Zr}_{0.76}\text{Hf}_{0.15}\text{Ca}_{0.02}\text{Fe}_{0.04}\text{Th}_{0.01}\text{U}_{0.01})\text{Si}_{1.04}\text{O}_4$
Euxenite-(Y)	$(\text{Y}_{0.27}\text{U}_{0.20}\text{Fe}_{0.42})(\text{Nb}_{1.76}\text{W}_{0.20})_{2.96}\text{O}_6$

Li–F granite and is characterized by predominance of the second-type cyrtolite with the highest contents of Hf (2.3–11.9 wt %; Zr/Hf = 3.2–8.6), Yb (up to 1.2–3.5 wt %), U (0.2–5.5 wt %), and Th (0.03–2.74 wt %) (Alekseev et al., 2013).

Tantaloniobates with W, Bi, Y, REE, and Th, as well as W, Bi, Y, REE, and Th minerals have been identified in Li–F granites and ongonites (Alekseev et al., 2011, 2012, 2013). Tantaloniobates amount to 6–12% of total accessory minerals (except for fluorite and topaz), or 40–120 ppm. In addition, 100–800 ppm ilmenite, rutile, and anatase containing significant Nb, W, Ta, and Sn admixtures and 15 ppm Nb-ferberite should be noted (Fig. 1; Table 1). Tantaloniobates from rare-metal granites of the Far East are distinguished from other groups of minerals by wide species diversity. Wolframoixiolite, samarskite-(Yb), and other REE-bearing tantaloniobates from euxenite group with U and Th admixtures (ishikawaite, bismu-

topyrochlore) are widespread. Aeschynite-(Y), fergusonite-(Y), pyrochlore, columbite-(Fe), ixiolite, and microlite are constantly identified. Liandratite and euxenite-(Y) in association with samarskite-(Y) along with W-columbite-(Fe), wodginite, betafite, and petschekite should be mentioned among the rare tantaloniobates. A similar mineral assemblage is characteristic of Paleozoic rare-metal granites of the Voznesenka district in Primorye (Tables 3, 4).

Ferberite and scheelite are closely associated with tantaloniobates often making regular intergrowths with the latter (Fig. 2). Wolframoixiolite–Nb-ferberite paragenesis is characteristic of Far East Li–F granites and ongonites. *Wolframoixiolite* occurs as relatively large long-prismatic crystals and intergrowths in zinnwaldite, quartz, topaz, and fluorite. This mineral corresponds in composition to its analogs from rare-metal granites elsewhere. Far East wolframoixiolite is distinguished by elevated $\text{Ta}_2\text{O}_5/\text{Nb}_2\text{O}_5$, FeO/MnO

Table 3. Accessory tantaloniobates from Li–F granites of the Far East

Mineral	Chukchi Pen.		Yakutia	Amur region		Primorye		
	lfg	ong		lfg	lfg	ong	A	V
							lfg	lfg
Wolframoixiolite*	+	+	(x)		x	(x)	x	
Ixiolite*					x	(x)		
Wodginite								
Samarskite-(Yb)*		x	(x)	x	+			
Ishikawaite*	x	x		x	x			
Petschekite	x						+	
Liandratite*	x	x						
Fergusonite-(Y)				x	x			
Columbite-(Fe)		x	+			+		
W-Columbite-(Fe)*	x	x						
Tapiolite-(Fe)			(x)					
Pyrochlore			+					
Bismutopyrochlore	x	x			x			
Betafite						x		
Aeschynite-(Y)*	x			+				
Euxenite-(Y)*					x		+	
Polycrase-(Y)*				(x)				
Uranopolycrase*	(x)							
Microlite								
W–Nb-rutile*	x	x	+	x	x	x		
Strüverite		x						
Ilmenorutile	x	x	+	x				
Nb-ilmenite	x							

* See notes to Table 1. Primorye: A, Armi and V, Voznesenka districts; (x), in zwitter. Minerals revealed in granitic rocks of the Far East for the first time are marked by asterisks.

ratios and low Sn content. Anhedral and less frequent subhedral ferberite inclusions with Nb, Sc, and Ti admixtures are identified within wolframoixiolite crystals.

Regular ixiolite–ferberite intergrowths, where wolframite grows over wolframoixiolite, have been described; russellite along with U-bearing samarskite, ishikawaite, liandratite, and bismutopyrochlore also occur (Fig. 3) (Alekseev et al., 2011).

The specificity of the identified rare-element mineral assemblage consists in isomorphic tungsten admixture in samarskite, ishikawaite, aeschynite, bismutopyrochlore, euxenite, liandratite, fergusonite, ilmenite, rutile, and anatase. The WO_3 content in tantaloniobates varies from 5.50 to 48.44 wt %, reaching a maximum in wolframoixiolite, samarskite, and ishikawaite (17.48, 18.32, and 14.01 wt %, respectively, on the average). This feature is inherited by secondary

accessory minerals: isomorphic tungsten is contained in columbite (up to 9.34 wt % WO_3) and rutile (up to 6.96 wt %) from greisenized Li–F granites and zwitter. W, Sn, and Sc admixtures in tantaloniobates from the Far East were noted by A.K. Rub and M.G. Rub (2006) and Trunilina et al. (2008). Nb prevails over Ta in tantaloniobates; Sc, As, Bi, Pb, Th, and Sn admixtures are frequent; the Sn admixture is the most significant (Tables 4, 5).

Strüverite and ilmenorutile containing up to 34.00 wt % Ta_2O_5 and 11.74 wt % Nb_2O_5 are widespread in Li–F granites along with typical tantaloniobates. They are especially characteristic of zinnwaldite granites in the Severny, Upper Urmi, and Voznesenka plutons. Wolframoixiolite, ixiolite, and less frequent cassiterite inclusions are contained in strüverite. Ilmenorutile, ferberite, less frequent fergusonite, and cassiterite inclusions are widespread in W–Nb rutile and ilmenite (Fig. 3). Tungsten minerals were identi-

Table 4. Mean chemical compositions (wt %) and crystal-chemical formulas of tungsten and tungsten-bearing accessory minerals from Li–F granites and ongonites of the Far East

Component	Chukchi Pen.				Amur Region					
	Frb	Wix	Ish	Bipcl	Frb	Wix	Ish	Bipcl	Smrs	Frg
SiO ₂	—	—	—	2.85	—	—	—	—	—	—
CaO	—	—	0.63	0.66	—	—	1.80	2.73	0.95	2.43
Sc ₂ O ₃	0.35	0.41	0.14	0.07	0.63	1.35	0.77	0.22	0.52	—
TiO ₂	0.39	3.22	0.46	1.56	—	1.40	0.05	0.42	0.17	2.34
MnO	3.97	2.95	0.51	1.67	6.29	3.90	1.52	0.65	1.98	—
FeO*	18.11	14.58	4.01	9.53	17.29	15.09	1.28	10.97	4.31	—
As ₂ O ₃	—	—	—	1.39	—	—	—	2.17	0.95	—
Y ₂ O ₃	—	—	—	—	—	—	0.47	—	—	22.60
PbO	—	—	—	1.35	—	—	—	—	0.42	—
Bi ₂ O ₃	—	—	4.45	21.55	—	—	—	13.37	—	—
ThO ₂	—	—	4.61	9.10	—	—	3.30	11.82	3.58	—
UO ₂	—	—	29.06	4.17	—	—	22.11	6.12	14.42	—
REE ₂ O ₃	—	—	—	—	—	—	2.97	0.87	4.05	20.09
Nb ₂ O ₅	10.92	40.46	32.86	21.46	3.72	26.83	33.71	21.47	29.06	37.72
Ta ₂ O ₅	—	9.98	2.44	—	—	32.45	16.84	18.88	20.73	4.77
WO ₃	66.26	27.90	18.67	22.45	72.26	17.48	14.01	7.60	18.32	10.07
SnO ₂	—	—	1.23	—	—	—	—	—	—	—
P ₂ O ₅	—	—	—	3.24	—	—	—	5.55	—	—
<i>n</i>	9	26	7	9	52	4	43	14	19	8
Formula coefficients (O = 4)										
Si				0.12						
Ca			0.04	0.03			0.10	0.12	0.05	0.12
Sc	0.01	0.01	0.01		0.03	0.05	0.03	0.01	0.02	
Ti	0.02	0.09	0.02	0.05		0.05		0.01	0.01	0.08
Mn	0.17	0.11	0.02	0.05	0.26	0.15	0.07	0.02	0.08	
Fe	0.72	0.53	0.18	0.34	0.71	0.58	0.05	0.38	0.18	
As				0.04				0.05	0.03	
Y							0.01			0.55
Pb				0.02					0.01	
Bi			0.06	0.24				0.14		
Th			0.06	0.09			0.04	0.11	0.04	
U			0.34	0.04			0.25	0.06	0.16	
REE							0.05	0.01	0.06	0.29
<i>A</i>	0.92	0.74	0.71	1.02	1.00	0.83	0.60	0.93	0.65	1.04
Nb	0.24	0.77	0.78	0.41	0.08	0.60	0.77	0.40	0.66	0.78
Ta		0.11	0.03			0.40	0.23	0.22	0.29	0.06
W	0.82	0.32	0.25	0.25	0.92	0.21	0.19	0.08	0.24	0.12
Sn			0.02							
P				0.12				0.20		
<i>B</i>	1.06	1.20	1.09	0.78	1.00	1.21	1.19	0.90	1.19	0.96

Minerals: Frb, ferberite; Wix, wolframioxiolite; Ish, ishikawaite; Bipcl, bismutopyrochlore; Smrs, samarskite-(Yb); Frg, fergusonite-(Y). Mean oxide concentrations (*n*, number of analyses) are recalculated to 100% from microprobe analyses (Inca Energy SEM, Mining university, St. Petersburg). FeO* is sum FeO + Fe₂O₃; dash, below detection limit. Formula coefficients are calculated on the basis of four oxygen atoms (*ABO*₄) for minerals from Kuiviveem–Pyrkakai district in Chukchi Peninsula and Badzhal district in Amur region.

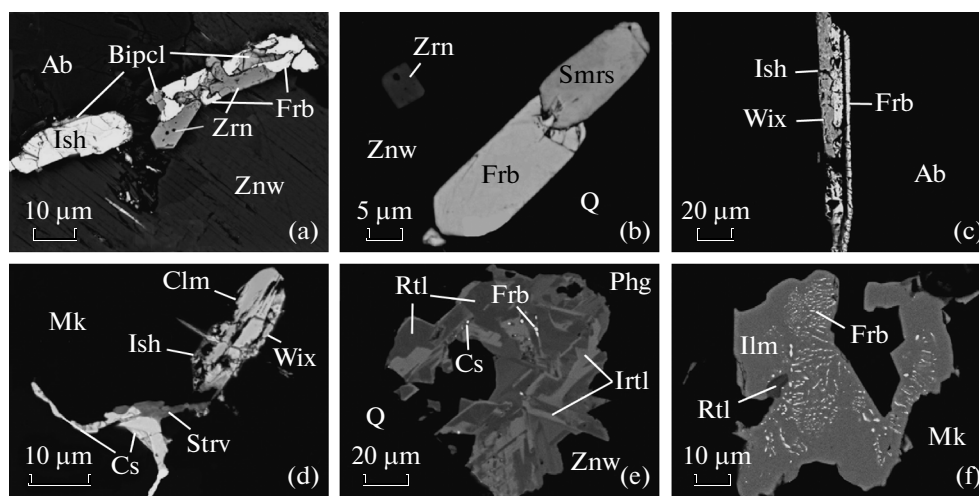


Fig. 3. Accessory tantaloniobates in Li–F granites and ongonites of the Far East: (a) parallel intergrowth of ishikawaite, ferberite, cyrtolite, and bismutopyrochlore; (b) oriented growth of samarskite-(Yb) over ferberite; (c) parallel intergrowth of wolframoixiolite, ferberite, and ishikawaite; (d) intergrowth of columbite-(Fe) with wolframoixiolite and ishikawaite and intergrowth of strüverite and cassiterite; (e) exsolution structure: Sn–Nb–W rutile with inclusions of ilmenorutile, cassiterite, and ferberite; (f) exsolution structure: Mn-ilmenite with inclusions of W–Nb rutile and ferberite; (a, b) ongonites of Amur region; (c) Li–F granites of Amur region; (d) ongonite of Chukchi Peninsula; (e, f) greisenized Li–F granite of Chukchi Peninsula. Minerals: Clm, columbite; Ilm, ilmenite; Irtl, ilmenorutile; Ish, ishikawaite; Phg, phengite; Wix, wolframoixiolite; Smrs, samarskite; Strv, strüverite. See also Fig. 2 and Table 2. BSE image.

fied in rare-metal granites of Primorye by A.K. Rub and M.G. Rub (2006). They described wolframite, wolframoixiolite, W-bearing microlite, and strüverite in the Armi and Voznesenka districts. Sc-ixiolite and Sc-wolframoixiolite were found in zwitter at the Tigriny deposit.

Allanite-(Y) is a subordinate accessory mineral in rare-metal granites of the Far East. This mineral was revealed in monzonitoid rocks of the Silin and Ichu-veem complexes and in leucogranites of the Badzhal–Dusse-Alin Complex altered under effect of the intruded Li–F granites. Allanite-(Y) occurs as chains

Table 5. Mean contents of trace element oxides (wt %) in accessory minerals from Li–F granites and ongonites of the Far East

Oxide	Frb	Wix	Ish	Bipcl	Aesh	Smrs	Frg	Rtl
WO ₃		11.58–48.44	5.50–24.06	0–31.98	0–22.22	7.91–29.71	9.52–10.66	0.48–15.03
SnO ₂		0–2.65						0–2.91
Bi ₂ O ₃					0–5.03			
Ta ₂ O ₅			0–33.33	0–34.60	0–7.46	8.85–39.46	3.42–7.68	0–15.65
Nb ₂ O ₅	0–15.38	10.44–54.92						0–11.74
PbO				0–12.17		0–7.98	0–4.55	
As ₂ O ₃			0–3.85	0–3.85	0–13.69			
Y ₂ O ₃			0–10.78					
Sc ₂ O ₃	0–1.64	0–2.36	0–1.73	0–1.41		0–1.55		
LREE ₂ O ₃				0–3.82	0–5.39	0–0.70		
HREE ₂ O ₃				0–2.91	0–19.21		16.38–27.56	
ThO ₂			0–7.83	5.38–14.78	0–6.80	0–11.82		
UO ₂				0–16.91	0–2.54			
<i>n</i>	61	31	50	23	12	19	8	3

Minerals: Frb, ferberite; Wix, wolframoixiolite; Ish, ishikawaite; Bipcl, bismutopyrochlore; Aesh, aeschynite-(Y); Smrs, samarskite-(Yb); Frg, fergusonite-(Y); Rtl, rutile. Gray cells are constitution components of corresponding mineral; *n*, number of analyses.

Table 6. Rare accessory minerals from Li–F granites and ongonites of the Far East

Mineral	Chukchi Pen.		Yakutia	Amur region		Primorye
	lfg	ong	lfg	lfg	ong	lfg
Fluocerite-(Ce)*	+	x		x	x	
Tveitite-(Y)*				x	x	
Allanite-(Y)*	x			+		
Gadolinite-(Y)			+			
Britholite-(Y)*				x	x	
Spodumene			x			
Amblygonite			+			x
Lithiophilite ?		x				
Augelite			(x)			
Pseudomalachite			(x)			
Brockite*	(x)					
Triplite			(x)			x
Pyrophanite	x			x		
Coronadite*		x				
Yttriaite-(Y)*					x	
Cerianite-(Ce)*	x					
Thorianite*	x			x		
Thorutite*	(x)					
Scheelite			+	x	x	+
Russellite*	x					
Chernovite-(Y)*	x			x	x	
Gasparite-(Ce)				(x)		
Rooseveltite	x	x	(x)			
Bismuth	(x)		x		x	x
Gananite*	(x)					
Zavaritskite*			x	(x)		
Gahnite				(x)		
Moissanite			x			

* See Table 1 for notes. (x), in zwitter; the minerals revealed in granitic rocks of the Far East for the first time are marked by asterisk.

and reticulate segregations of microscopic xenomorphic grains in rock-forming silicates and accessory fluorite-(Y) and tveitite-(Y). The mineral is distinguished by complex anatomy and fine oscillatory zoning. The composition of allanite from Li–F granite is variable in respect to the constitutional components (Y, Fe²⁺, Ca) and the main (Gd, Dy, Er, Yb) and auxiliary (Nd, Ce, Th, Mn) trace elements. In contrast to REE pattern of allanite-(Ce), the REE pattern of allanite-(Y) has a positive slope caused by predominant HREE accumulation and is distinguished by a positive Dy anomaly (Alekseev et al., 2013).

Rare accessory minerals with an occurrence frequency lower than 10% and the content below a ppm have been discovered in Far East Li–F granite. These are accessory minerals abundant in the nature but not

in the studied rocks: anatase, tourmaline, bismuth, thorite, uraninite, etc. (Table 1) and rare minerals proper, many of which have been identified in the Far East for the first time or were not known earlier in Li–F granite, ongonite, and related zwitter (Table 6).

Rare fluorides (fluocerite-(Ce), tveitite-(Y), gananite, zavaritskite), phosphates (amblygonite, lithiophilite, augelite, triplite, brockite), and oxides (cerianite-(Ce), thorianite, thorutite, gahnite, pyrophanite, russellite) occur in the Far East Li–F granites. Yttriaite-(Y) intergrown with monazite-(Ce) has been identified in one sample. Accessory cassiterite is rarely noted in Li–F granites. Numerous findings of cassiterite in heavy concentrates described in the literature are probably related to occurrence of hydrothermally altered granite in samples. Thorutite and

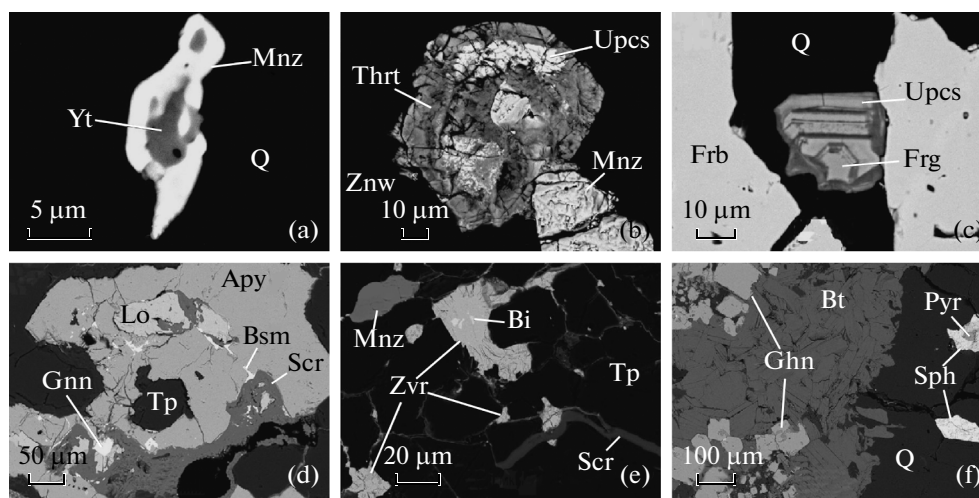


Fig. 4. Rare accessory minerals in Li–F granites and related zwitter of the Far East: (a) yttriaite with monazite rim; (b) thorutite with uranopolycrase growing over monazite; (c) fergusonite-(Y) with uranopolycrase in ferberite; (d) gananite, bismuthinite, and loellingite in arsenopyrite; (e) zavaritskite with bismuth inclusions; (f) gahnite in biotite; (a) Li–F granite of Amur region; (b, c) greisenized Li–F granites of (b) Chukchi Peninsula and (c) Amur region; (d–f) zwitter of Amur region. Minerals: Apy, arsenopyrite; Bsm, bismuthinite; Bt, biotite; Ghn, gahnite; Gnn, gananite; Lo, loellingite; Pyr, pyrrhotite; Scr, scorodite; Sph, sphalerite; Thrt, thorutite; Tp, topaz; Upcs, uranopolycrase; Yt, yttriaite; Zvr, zavaritskite. See also Figs. 2, 3 and Table 2. BSE image.

uranopolycrase identified in greisenized granites are associated with monazite. Euxenite-(Y) and fergusonite in ferberite, gananite in arsenopyrite, zavaritskite with bismuth inclusions, and Zn-spinel (gahnite) were found in zwitter replacing Li–F granite (Figs. 2, 4).

Following German and Czech colleagues who identified *chernovite*-(Y) in association with As-bearing thorite and other REE–Y–Th–U minerals in rare-metal granites of the Erzgebirge, we have discovered *chernovite*-(Y), As-thorite, and rooseveltite in Li–F granites and ongonites in Far East tin districts. As-thorite, rooseveltite, agardite, phillipsbornite, asselbornite have been identified in the zinnwaldite–topaz–quartz greisen (zwitter) genetically related to the rare-metal granites. Arsenates from zwitter are constituents of rare-metal assemblage: cyrtolite, xenotime-(Y), Th-monazite, strüverite, columbite, cassiterite, uranopolycrase, arsenopyrite, loellingite, bismuthinite, gananite, and zavaritskite. Chernovite, As-thorite, and rooseveltite occur as microgranular and ultradispersed veinlets, lenses, and pseudomorphs after xenotime and thorite. They are confined to micromiarolitic vugs with zircon, xenotime, thorite, wolframioiolite in rare-metal granites and zwitter. Chernovite contains variable amounts of U and HREE, P, and Ca; a high thorium content up to 23.9 wt % ThO₂ has been established (Alekseev and Marin, 2012).

The composition of accessory mineral assemblages in Li–F granites of the Far East belt is similar to that in typical rare-metal granites from other tin provinces of Central Asia, Europe, and Africa (Ginzburg, 1972; Marin, 1976, 2004; Kovalenko, 1977; Beskin et al., 1979, 1999; Vladykin, 1983; Alekseev et al., 2011,

2012). In mineral composition, they are related to rare-metal Li–F granites that produce hydrothermal metasomatic Sn, W, Ta, Li, and F mineralization and are localized in supraseismofocal areas of active continental margins and moderately collisional setting (Beskin et al., 1999).

Accessory mineral assemblages in Li–F granites of the Far East reflect regional geochemical specialization of the Late Cretaceous granitic complexes, which are characterized by intense accumulation of W, Sn, Li, F, Rb, Cs, Ta, Nb, Y, and HREE. Despite a shortage of regional mineralogical information, it may be stated that the composition of accessory mineral assemblages in Li–F granites from various districts and provinces are surprisingly identical along the entire extent of the Pacific continental margin. In all complexes of rare-metal granites, the main minerals are topaz, fluorite (often yttriofluorite), Y–Th–U–Hf cyrtolite, Mn-ilmenite (often Nb-ilmenite), monazite-(Ce), and W-bearing tantaloniobates. The Li–F granites and ongonites from the Far East are distinguished by frequent occurrence of wolframioiolite, Nb-ferberite, samarskite, scheelite, W–Nb rutile, xenotime-(Y), fluocerite, ishihawaite, thorite, uraninite, aeschynite-(Y), bismutopyrochlore, *chernovite*-(Y), and pyrophanite. The similarity of accessory mineralization of the Late Cretaceous Li–F granites of the Far East belt is reflected in similar typomorphism and the same direction of evolution of the main and subordinate accessory minerals: zircon, wolframioiolite, allanite, and *chernovite* (Alekseev et al., 2011, 2013, 2014).

Taking into account chemical composition, the tungsten, tin–tantalum–niobium, niobium–tita-

niun, and bismuthic assemblages of accessory minerals are distinguished. The *tungsten assemblage* comprises (in order of occurrence frequency): ferberite, scheelite, russellite, tungstite, and uranotungstite. The *tin–tantalum–niobium assemblage*: wolframoixiolite, ishikawaite, aeschynite-(Y), strüverite, liandratite, bismutopyrochlore, samarskite-(Yb), columbite, and cassiterite. The *niobium–titanium assemblage*: Nb-ilmenite, aeschynite-(Y), ilmenorutile, W–Nb rutile, fergusonite-(Y), euxenite-(Y), uranopolycrase, and polycrase-(Y). The *bismuth assemblage*: bismuth, bismuthinite, rooseveltite, bismutopyrochlore, russellite, asselbornite, uranosphaerite, bismite, gananite, zavaritskite. The lithium, yttrium, cerium, and thorium groups are secondary in occurrence frequency. The *lithium assemblage*: zinnwaldite, spodumene, lithiophyllite (?), and amblygonite. The *yttrium assemblage*: yttrofluorite, xenotime-(Y), allanite-(Y), chernovite-(Y), fergusonite-(Y), aeschenite-(Y), tveitite-(Y), britholite-(Y), euxenite-(Y), gadolinite-(Y), uranopolycrase, polycrase-(Y), and yttrialite-(Y). The *cerium assemblage*: fluocerite, monazite-(Ce), cerianite, brockite, and thorbastnaesite. The *thorium assemblage*: thorite, thorianite, thorbastnaesite, and As-thorite. The arsenic, uranium–lead, manganese, and zinc assemblages are rare. The *arsenic assemblage*: chernovite-(Y), As-thorite, gasparite-(Ce), rooseveltite, asselbornite, and phillipsbornite. The *uranium–lead assemblage*: phillipsbornite, asselbornite, bismutopyrochlore, ishikawaite, liandratite, coronadite, uranotungstite, uranopolycrase, and thorutite. The *manganese assemblage*: pyrophanite, Mn-ilmenite, wolframoixiolite, wodginite, lithiophyllite (?), and coronadite. The *zinc assemblage*: gahnite and Zn-ilmenite. The role of minerals pertaining to the niobium–titanium assemblage appreciably decreases, whereas occurrence frequency of minerals related to the tungsten, tin–tantalum–niobium, bismuth, arsenic and uranium–lead assemblages increases in ongonites as compared with Li–F granites.

The formation of Li–F granites is a complex process that involves crystallization of rare-metal magma, metasomatism in the presence of a high-temperature fluid responsible for greisenization and followed by medium- and low-temperature hydrothermal solutions. As a result, assemblages of accessory minerals different in age but unified by chemical composition arise: allanite-(Ce), monazite-(Ce), allanite-(Y), and tveitite-(Y); wolframoixiolite, ferberite, ishikawaite, liandratite, bismutopyrochlore, russellite, tungstite, and thorutite; xenotime, thorite, chernovite, As-thorite, rooseveltite, and phillipsbornite; ilmenite, pyrophanite, and coronadite. Groups of syngenetic minerals are recognized. Their coexistence depends on the distribution of rare elements in locally heterogeneous magma, variation of temperature and pressure, e.g., zircon, xenotime, monazite, and uraninite; fluorite and fluocerite; wolframoixiolite, samarskite,

ferberite, and scheelite; ilmenite, rutile, ilmenorutile, strüverite, and cassiterite.

With allowance for the morphology, relationship, and composition of accessory minerals, three stages of mineral formation are outlined. The *early (magmatic) stage*: zircon-1, monazite-(Ce), xenotime-(Y), W–Nb-ilmenite, ferberite, wolframoixiolite, fergusonite-(Y), and aeschynite-(Y); the *medium (late magmatic) stage*: topaz, fluorite, zircon-2 (cyrtolite), fluocerite, ishikawaite, scheelite, W–Nb-rutile, allanite-(Y), samarskite-(Yb), strüverite, thorite, bismuth, and russellite; the *late (late- to postmagmatic) stage*: bismutopyrochlore, chernovite-(Y), britholite-(Y), rooseveltite, tungstite, asselbornite, phillipsbornite, and brockite. Magmatic accessory minerals are represented by faceted crystals with simple anatomy, homogeneous in composition, and uniformly distributed through the host rock. The metasomatic minerals have an irregular or skeletal crystalline shape, occur as lenticular or veined segregations, contain inclusions of rock-forming or accessory minerals, and are characterized by structural and chemical heterogeneity. These data confirm the known tendencies of increasing amount of mineral species, diversity of mineral classes and an appreciably rising contribution of oxides, fluorides, carbonates, phosphates, silicates of rare (including REE) and volatile elements in the course of evolution of rare-metal granitic series (Marin, 1976, 2004).

Further progress in studying accessory minerals in rocks from the Far East rare-metal granitic belt requires additional regional mineralogical research. For example, the anomalous manifestation of accessory mineralization in the Central Yana district of the Yana–Kolyma province (apatite-(F), amblygonite–montebrasite, augelite, pseudomalachite) attracts attention. The abundance of these minerals is explained by assimilation of P-rich black shales known among Paleozoic rocks at the Verkhoyansk continental margin (Trunilina et al., 2008). Anomalous accessory mineralization is also expressed in abundant fluocerite-(Ce) in Li–F granites of the Chukchi Peninsula, allanite-(Y) in Li–F granites of the Priamurye, and other phenomena, which have to be investigated, systematized, and explained.

CONCLUSIONS

(1) The evolution of accessory mineralization in Late Cretaceous rare-metal granitic series is directed toward increase in mineral-forming role of iron and rare elements (W, Ta, Nb, Bi, Sn, F, Li, Y, HREE). The early leucogranites and monzonitoid rocks contain zircon, ilmenite, apatite, allanite-(Ce), monazite, xenotime, titanite, rutile, and garnet. The late and greisenized intrusive phases are characterized by appearance of or enrichment in fluorite, topaz, tourmaline, cassiterite, pyrophanite, thorite, wolframite, pyrochlore fergusonite, and other rare-metal minerals. Monzonitoid rocks are distinguished by elevated

contents of malacon, apatite, Th- and Y-bearing REE-phosphates and silicates. Li–F granites and ongonites as final members of intrusive series are sharply distinguished by abundant rare-metal minerals, primarily, W-bearing tantaloniobates in the absence of apatite and allanite-(Ce).

(2) A rare-metal composition and extremely diverse accessory mineralization have been established for Li–F granites and ongonites of the Far East. The main minerals are topaz, fluorite, cyrtolite, monazite-(Ce), W–Nb-ilmenite, and W–Nb-rutile. The auxiliary mineral species are wolframoixiolite, ferberite, amblygonite, samarskite-(Yb), ishikawaite, bismutopyrochlore, ilmenorutile strüverite, columbite-(Fe), allanite-(Y), etc. The rare minerals are fluocerite-(Ce), tveitite-(Y), gadolinite, gananite, gahnite, bismuth, etc. The tungsten, tin–tantalum–niobium, niobium–titanium, bismuth, and mixed As–Y–REE–U mineral assemblages are typomorphic. Wolframoixiolite, Nb-ferberite, allanite-(Y), and chernovite-(Y) are typomorphic minerals.

(3) The uniform composition of accessory mineralization contained in the Late Cretaceous granitic rocks of the Far East is strikingly expressed in identity of rare-metal mineral assemblages of Li–F granites and ongonites. The speciation, parageneses, main typomorphic features, and tendencies of accessory mineral evolution steadily repeat in rare-metal granites over the entire Far East from Primorye to Chukchi Peninsula, reflecting the genetic and compositional uniformity of the Late Cretaceous rare-metal magmatism. The main regional features of accessory mineralization in Li–F granites are expressed in (i) leading role of W, Na, Nb, and Bi minerals; (ii) W and Sc admixtures in accessory minerals; (iii) prevalence of Nb over Ta; and (iv) obvious contribution of Y, REE, As, Th, and U minerals. The uniform accessory mineralization in Li–F granites over vast territory of the Far East is evidence for existence of the rare-metal granitic subprovince, or the Far-East belt of Li–F granites.

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