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Evolution of Zircons from Postorogenic Intrusive Series with Li–F Granites, Russian Far East

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Abstract—The paper discusses the morphology, anatomy, and geochemistry of zircons from granitic rocks of postorogenic intrusive series with Li–F granites in the Russian Far East. The multiphase Upper Urmi pluton in the Amur region and the Severny pluton in the Chukchi Peninsula have been chosen as reference objects. The directed variations of zircon morphology and geochemistry in the history of Pacific postorogenic granitic magmatism reflect decrease in depth of magma generation and crystallization temperature along with an increase in alkalinity, fluid saturation, and rare-metal potential of granitic melts.

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INTRODUCTION

Many problems concerning the genesis and formation conditions of the granites that complete evolution of regional magmatism and related mineral deposits can be resolved by studying the accessory minerals (Marin, 2004). Zircon is one of the most informative accessories. The morphology and anatomy of zircon crystals reflect the formation conditions of rocks and are typomorphic for various types of granites (Brodskaya, 1986; Krasnobaev, 1986). Owing to updated technology and methods of local analysis, new possibilities have appeared for studying the structural and chemical heterogeneities of this mineral (Zircon, 2003; Harley and Kelly, 2007; Fedotova et al., 2008). A combination of microgeochemical and ontogenetic techniques proved especially efficient (Alekseev and Marin, 2012). In this paper, we discuss the results of a comparative analysis of the morphology, anatomy, and composition of zircons from granitic rocks of the Upper Urmi and Severny plutons in the Russian Far East. The choice of the objects with complete succession of Late Mesozoic granite complexes and intrusive phases in the Amur region and Chukchi Peninsula is dictated by the interest they have attracted over many decades, and by prospectivity of the Badzhai and Pyrkai districts for tin (Zagruzina, 1977; *Geologiya* ..., 1986; Dudkin et al., 1994; Grigor'ev, 1997; Efremov et al., 2000; Gonevchuk, 2002; Tibilov, 2005; Alekseev, 2011, 2012).

GEOLOGY OF STUDIED OBJECTS

The studied plutons belong to the Khingan–Okhotsk magmatic area of the Sikhote-Alin orogenic

belt and the Chukchi plutonic belt. The Upper Urmi pluton is referred to the Late Cretaceous Miao Chang Series and occurs in the Badzhai volcanic–plutonic zone developing on the Jurassic accretionary prism of the eponymous terrane (*Geodinamika* ..., 2006). The late orogenic igneous complexes of the Badzhai Terrane are comagmatic to the intrusive rocks of the Khungari and Lower Amur series. Postorogenic granitic rocks are related to the Silino Complex of monzonitoids and the Badzhai Complex of biotite granites (*Geologiya* ..., 1986; Grigor'ev, 1997; Gonevchuk, 2002). We also recognize the Right Urmi Complex of zinnwaldite (Li–F) granites and ongonites (Alekseev, 2012). The rocks of all three stages of postorogenic magmatism are represented in the Upper Urmi pluton, which is a domal jut of the Badzhai cryptobatholith exposed over an area of 350 km². The Late Cretaceous postorogenic granitic series of the Middle Amur region comprises (1) massifs of biotite granite and leucogranite of the Badzhai Complex; (2) monzodiorite, monzogranite, and elvan dike swarms and stocks of the Silino Complex; and (3) stock and dikes of rare-metal zinnwaldite granite and ongonite pertaining to the Right Urmi Complex. The U–Pb (SHRIMP II) zircon age is estimated at (1) 96.3 ± 1.0 , (2) 95.9 ± 0.8 , and (3) 95.5 ± 0.9 Ma (zinnwaldite granite) and 89.6 ± 1.5 Ma (ongonite).

The Chukchi plutonic belt is situated in the central part of the eponymous terrane of the Olloi–Chukchi orogenic belt. Five intrusive complexes are distinguished in the Chukchi belt: the Late Jurassic–Early Cretaceous gabbro–diorite–granodiorite and granodiorite–granite (monzonite–granite) complexes; the Early to Late Cretaceous granite–leucogranite complex; the Late Cretaceous leucogranite (rare-metal granite) complex; and the gabbro–syenite complex

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(*Geodinamika* ..., 2006). The first three postorogenic complexes are spatially combined into the Chukchi granodiorite–granite complex (Zagruzina, 1977; Tibilov, 2005). In the northern Chukchi Peninsula, Late Cretaceous postorogenic granitic rocks make up the Chaun granite–leucogranite complex and the Ichuveem complex of potassic and ultrapotassic monzonitoid and lamprophyre minor intrusions (*Geologiya* ..., 1986; Kozlov et al., 1995; Efremov et al., 2000; Tibilov, 2005; Efremov, 2012). We also recognize the Pyrkakai Complex of rare-metal topaz–zinnwaldite Li–F granite and ongonite (Alekseev, 2011).

Rocks pertaining to all three stages of postorogenic magmatism occur in the Severny pluton situated in the Shelag Ridge of the Chukchi Highland. This pluton is a slightly eroded jut of the East Chaun cryptobatholith occupying an area of 308 km² at the surface. The pluton consists of numerous intrusive sheets of various granitic rocks with diffuse contacts within the main-phase body, which impart expression of layering (Alekseev, 2011). Based on the geochemistry of leucogranites (high Al content and elevated Li, F, and Sn concentrations), they are referred to the Li–F type of rare-metal granites bearing cassiterite–quartz mineralization (Dudkinsky et al., 1994; Efremov et al., 2000). This, however, contradicts the cassiterite–silicate mineralization hosted in the Severny massif (*Geologiya* ..., 1986); this discrepancy also exists between the large area occupied by topaz granite (>250 km²) and the idea of typical minor size of such intrusions (Kovalenko, 1977; Beskin et al., 1999). The extensive occurrence of Li–F granites in the Severny pluton is explained by widespread metasomatic alteration of older intrusive rocks cut by minor intrusions of topaz–zinnwaldite Li–F granite proper in association with ongonite (Alekseev, 2011). The Late Cretaceous postorogenic series of northern Chukchi Peninsula comprises: (1) massifs of biotite granite and leucogranite of the Chaun Complex, (2) dike swarms and minor stocks of quartz monzonite, monzodiorite, and monzogranite of the Ichuveem Complex, and (3) stocks, sills, and dikes of zinnwaldite granite and ongonite of the Pyrkakai Complex. The U–Pb SHRIMP II age of these complexes are (1) 89.4 ± 0.7 , (2) 84.3 ± 0.7 , and (3) 88.0 ± 0.7 (zinnwaldite granite), and 84.1 ± 1.1 Ma (ongonite).

Thus, the postorogenic granitic series are composed of the following petrographic species (listed in the succession of emplacement): porphyritic biotite granite and leucogranite (further called biotite granite)—biotite and amphibole—biotite sharply porphyritic quartz monzonite, granosyenite, and monzogranite (further called monzogranite)—zinnwaldite granite, leucogranite, and ongonite (further called zinnwaldite granite and ongonite).

RESEARCH METHODS

Zircons were studied with optical, electron microscopic, and microprobe methods using monomineralic fractions selected from nonelectromagnetic fractions of gravity concentrates, as well as thin and polished sections of granitic rocks. In total, 39 zircon monofractions and 63 thin polished preparations of zircons, and 450 preparations of granitic rocks from the Amur region and Chukchi Peninsula have been studied; 1320 electron and 202 ion microprobe analyses have been carried out, including 107 SHRIMP II analyses; 70 SEM and SIMS profiles and zircon crystal maps, 866 optical, 476 electron, and 170 cathodoluminescent images of zircons have been obtained.

The technique of investigating the morphology, anatomy, and geochemistry of zircons is based on principles of genetic mineralogy and ontogenetic analysis elaborated by D.P. Grigor'ev, N.P. Yushkin, A.G. Zhabin, and other researchers (Pupin, 1980; Brodskaya et al., 1986; Alekseev and Marin, 2012). Selections of 50 to 120 grains more than 70 μm in size and electron and cathodoluminescent images of zircon crystals less than 70 μm in size were used for measurements. Morphological estimations were performed by comparison of measured and calculated angles between faces of simple forms in projections to the (110) and (100) prism planes. The distribution of zircon morphotypes reflecting the formation conditions of mineral generations was studied using Pupin's diagrams.

Information on the anatomy and composition of zircons have been obtained using cathodoluminescence (CL), optical and SEM microscopy, X-ray microprobe instrumentation of the National University of Mineral Resources, and the Russian Geological Research Institute in St. Petersburg: JSM-6460LV, JSM-7001F with a Schottky cathode, CamScan MV2300, CamScan MX2500S, Zeiss Axioplan, Olympus GX71, and Polam-211. Microadmixture were studied using the SIMS technique at the Center of Isotopic Research, Russian Geological Research Institute (SHRIMP II), and at the Yaroslavl Branch, Physicotechnological Institute, Russian Academy of Sciences (RAS) (Cameca IMS-4f, TOF.SIMS 5).

The techniques of structural–chemical observations included optical selection of zircon individuals, electron scanning with the obtaining of electron and cathodoluminescent images, and electron and ion microprobing. Identification of mineral inclusions is the most important element of observations. To coordinate optical and electron images, preparation maps were used. Scanning was performed in the SEM, TOPO, and COMPO regimes with a progressive increase in magnification from 100–300 to 5000–20000. High-resolution SEM with thermal-field emission and JSM-7001F, JEOL microprobes made it possible to

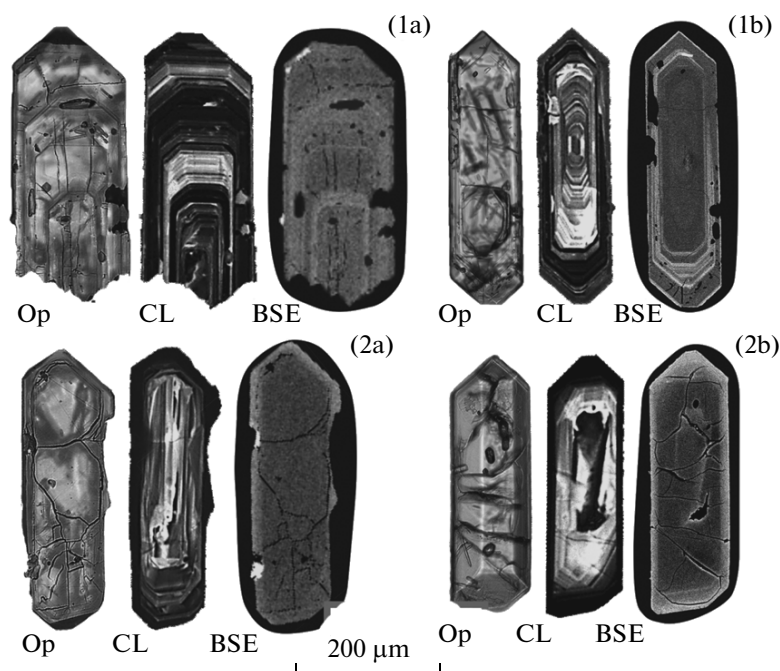


Fig. 1. Types of zircons from Late Cretaceous biotite granites of Russian Far East: (1) primary oscillatory zoned zircon, (2) partly recrystallized zircon with secondary rim (dark in CL) containing inclusions of Y–U–Th phases (white in BSE); (1a, 2a) Severny massif, Chukchi Peninsula; (1b, 2b) Upper Urmi massif, Amur region. Op, optical; CL, cathodoluminescent; BSE, back-scattered electron images.

examine grain heterogeneities with a resolution of 1 nm. Electron probing of zircons and associated minerals was implemented with a semiconducting INCA detector (Oxford Instruments, Great Britain) operating at 15–25 kV and an analytical spot of 3 μm . The matrix effect was minimized by the following procedures: (1) convolution of peaks by computing the best coincidence with standard peaks using the least squares method; (2) electron profiling of phases with trapping of matrix fragments and analysis of spectral intensity variations in the contact zone; (3) simplification of the spectral background by analyzing phases in homogeneous zircon blocks; (4) combined use of energy dispersive and wave spectrometry of X-ray radiation. The ion microprobe technique has been described by (Sergeev et al., 2007; Fedotova et al., 2008). The microprobe area was 15–20 μm ; the measurement uncertainty is 10–15%; the mean detection limit is 10 ppb. The chondrite-normalized REE patterns are based on the composition of C1 chondrite (McDonough and Sun, 1995). The geochemical study of zircons was supplemented by mapping of local grain surfaces using time-of-flight SIMS on a TOFSIMS 5 (ION-TOF, Germany) at the Yaroslavl Branch of the Physicotechnological Institute, RAS, with parallel recording of all ions (Skublov and Simakin, 2009). Complete mass spectrometry over the grain area made it possible to construct maps and sections of compo-

nent distribution with a resolution reaching 300 nm and a detection limit at the ppm level.

ZIRCON MORPHOLOGY AND ANATOMY

Zircon from biotite granite is characterized by a high isomorphism, prismatic habit (the elongation coefficient (EC) is 2–4), predominance of the {110} and {111}, as well as the {100} and {311} faces, and relatively large size (50–200 μm across and 150–500 μm in length). Two types of grains are distinguished by morphology and anatomy: (1) almost colorless euhedral crystals with fine oscillatory zoning and (2) brown and reddish brown euhedral crystals with rough zoning (Fig. 1). Zircons of the first type have smooth shining faces occasionally complicated by low (0.1–0.5 μm) crystallographically undirected growth steps. Sporadic and relatively large (up to 50 μm) mineral and melt inclusions are seen in almost transparent crystals. CL images show a contrasting rhythmically zoned structure of two levels: the finest growth zones 2–3 μm thick and differing in degree of lattice unsoundness are grouped in thicker (20–50 μm) zones with variable luminescence intensity and admixture composition (Figs. 1-1a, 1-1b). Many grains reveal growth sectors, growth channels, and chains of defects in overgrowth pyramids.

Zircon of the second type is distinguished by rounded edges and uneven topography of dull faces

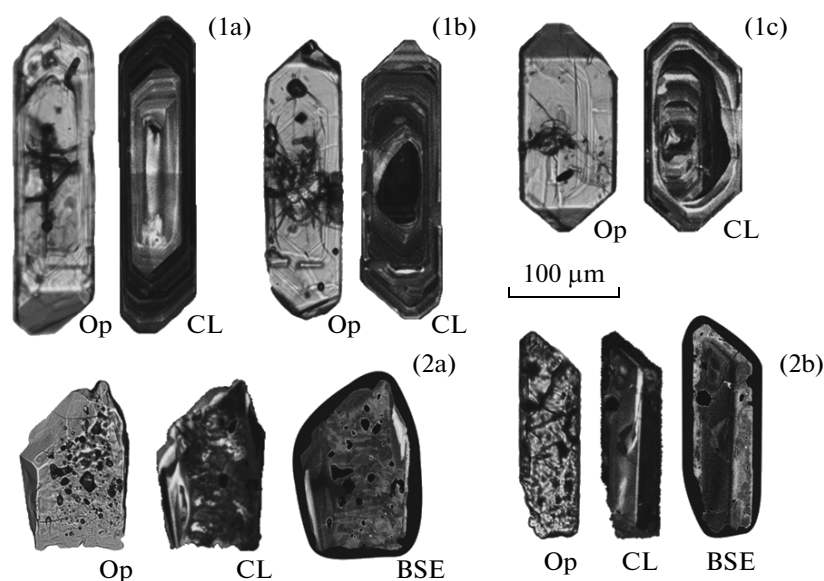


Fig. 2. Types of zircons from Late Cretaceous biotite monzogranites of Russian Far East: (1) crystals with cores of (a) recrystallized, (b) rounded, and (c) polyzonal zircon from source and three growth zones; (2) with recrystallized porous core and rare-metal rim; (1a, 1b, 2b) Ichuveem dike swarm, Chukchi Peninsula; (1c, 2a) Orokot belt, Amur region. See Fig. 1 for symbols.

complicated by high (1–10 μm) growth steps, irregular projections, and pits. The crystals are surrounded by the discontinuous dark-in-CL rim enriched by isomorphic admixtures and microinclusions of Y, HREE, U, and Th minerals. Abundant mineral inclusions are accompanied by metamictization of the outer part of zircon, and they make it opaque. The thickness of such a rim is variable (5–30 μm); the short-prismatic individual crystals are surrounded by an outer rim up to 40–50 μm thick. The crystal cores are light in CL, markedly recrystallized, and composed of azonal and curved zonal blocks that intersect and cut off growth zoning. The recrystallized domains retain shadow textures in the form of blocks with primary concentric and sectorial zoning. Due to the sharp structural inconsistency between crystal cores and rims, heterometric fractures develop in the cores (Figs. 1-2a, 1-2b). About 60–70% of zircon crystals are related to the second type.

Zircons from monzogranites yield to zircons of biotite granite in size and are faced by {100}, {311}, and {211} forms in addition to {110} and {111}, and are characterized by diverse morphology and anatomy, which are reduced to two types. The first type of crystals are light-colored from colorless to pale brown, euhedral, columnar ($EC = 3.5\text{--}9.1$), zircon and hyacinth in habit with a {311} dipyramid (Figs. 2-1a–2-1c). Prismatic {110} faces are stepwise, whereas {100} faces are ideally smooth. The first type of zircon is characterized by multistage crystallization of individuals in combination with a recrystallized xenogenic core in form of a rounded fragment or polyzonal zircon derived from a source. The dark-colored metamict

seed crystal with weakened CL is rimmed by the recrystallization zone and the outer oscillatory zone. The first type of zircons are characterized by relatively large apatite and REE–U mineral inclusions.

Up to 20–40% of samples fall on euhedral brown grains of the second type, cyrtolitic in appearance with rounded vertices and edges often making up intergrowths. They are dark-colored in CL and include the porous core with curved blocks and recrystallized zones and abundant inclusions of Th–U minerals. The outer zone is distinguished by concentric zoning. The second type of zircon is especially characteristic of rocks pertaining to the Silino Complex in the Amur region (Figs. 2-2a, 2-2b).

Zircons from zinnwaldite granite are relatively small (20–100 μm), short-columnar ($EC = 1.5\text{--}3.0$), with obtuse dipyrnidal vertices and uneven topography of faces. The {100} and {111} forms are supplemented by {311}, {331}, and {131} dypyrnides that create hyacinth appearance of crystals. The complex internal structure is their main feature. Individual grains more than 50 μm across consist of a core and a thick rim enriched in heavy elements and clearly discernible in BSE images. Two types of zircon differing in structure have oscillatory zoned and recrystallized cores (Fig. 3). The first type was formed by regeneration of an ancient zircon and mimics its outlines. The second type is a product of recrystallization of the first-type grains or crystallization from a fluid-saturated melt. The second type of zircon is distinguished by a shortened shape, oppressed development of the prism, and a cyrtolite appearance.

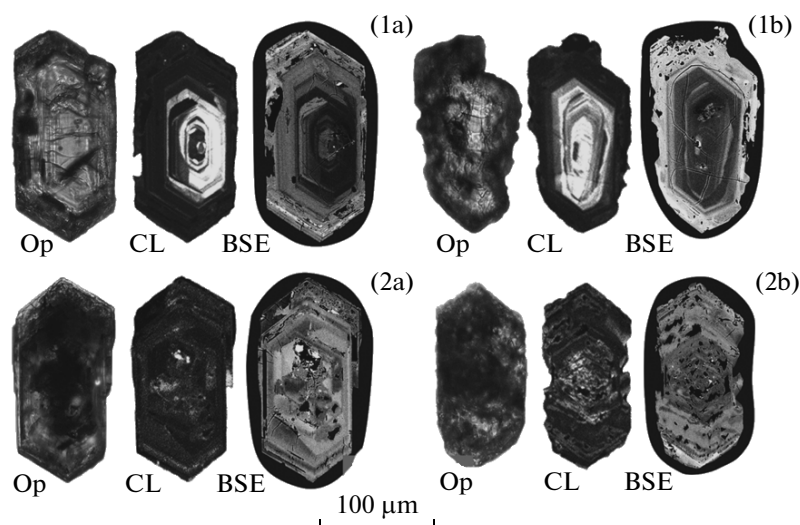


Fig. 3. Types of zircons from Late Cretaceous zinnwaldite granites of Russian Far East: (1) crystal with oscillatory zoned protocystal as core and porous rare-metal rim; (2) porous crystal with recrystallized core and inclusions of Y–U–Th phases (white in BSE); (1a, 2a) Severny massif, Chukchi Peninsula; (1b, 2b) Upper Urmi massif, Amur region. See Fig. 1 for symbols.

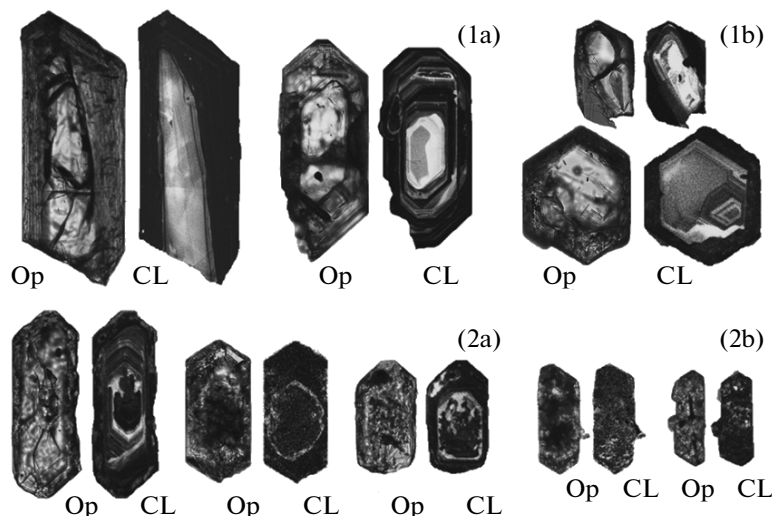


Fig. 4. Types of zircons from Late Cretaceous zinnwaldite ongonites of Russian Far East: (1) crystal with recrystallized protocystal as core and porous rare-metal rim; (2) porous crystal with imperfect crystal lattice (dark areas in CL) and inclusions of Y–U–Th phases; (1a, 2a) Ichuveem dike swarm, Chukchi Peninsula; (1b, 2b) Orokot belt, Amur region. See Fig. 1 for symbols.

The second type of crystals and the outer rim in the first type are characterized by elevated unsoundness of the lattice, expressed as a weak CL. The primary growth zoning is disturbed and gives way to secondary tortuous and wavy zones or homogeneous recrystallized blocks with diffuse boundaries. The elevated brightness of grains in BSE images indicates enrichment in heavy trace elements. The second type of crystals predominate (60–70%) among relatively large grains. Small grains (<50 μm) are poorly faced and do not contain relict cores. Zircons from zinnwaldite granites are characterized by radial fractures of heterometry, as well as by numerous pores irregular in shape

and controlled by growth zones at the crystal margins. Large lenticular cavities are confined to the boundaries of zones. A significant amount of crystalline and fluid inclusions is observed in the outer rim and at its boundary with the core. Separate individuals with darkened cores are crowded with inclusions of Th–U minerals (Fig. 3).

Zircons from ongonites resemble those from rare-metal granites. Two types of crystals are observed: (I) relatively large grains with relict cores light in CL and (II) small porous zircons dark in CL and with rough topography of faces (Fig. 4). The second type of zircons are more abundant: 97 and 85% in ongonites

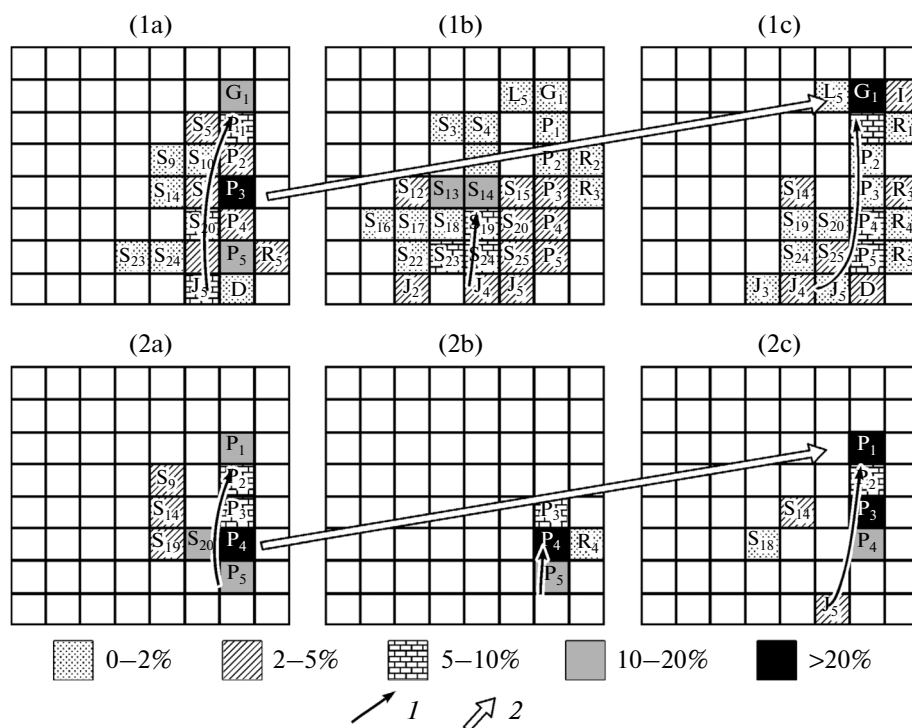


Fig. 5. Evolution of zircon morphotypes from postorogenic intrusive series with Li–F granites of the Russian Far East plotted in Pupin–Turco diagrams (Pupin, 1980): (1) Late Cretaceous granitic series of Middle Amur region; (2) Late Cretaceous granitic series of northern Chukchi Peninsula; (1a, 2a) biotite granite; (1b, 2b) monzogranite; (1c, 2c) zinnwaldite granite. Arrows denote direction of zircon evolution: (1) in intrusive complexes and (2) in intrusive series.

from the Amur region and the Chukchi Peninsula, respectively. The size of protocrusts and corresponding dimensions of first type of zircons are as large as zircons from zinnwaldite granite; variations in grain size are rather wide. The cores of large grains are always recrystallized. The second type of grains are much smaller (often $<10\ \mu\text{m}$) and shorter up to barrel-like cyrtolite appearance. Zircons from ongonites are distinguished by a vaguely zoned domain structure, are metamictic, porous, and enriched in microinclusions. The morphology of zircons from postorogenic granitic rocks was studied by the semiquantitative Pupin–Turco technique (Pupin, 1980, Brodskaya et al., 1986). It has been established that zircons from biotite granite are represented primarily by early magmatic high-temperature ($850\text{--}750^\circ\text{C}$) morphotypes $P_3\text{--}P_5$, S_{20} and J_5 ; the $\{110\}$ prism prevails over the $\{100\}$ prism or both develop in approximately equal amounts (Figs. 5-1a, 5-2a). This category comprises the first type of grains (P_5) and part of the second type of grains (P_3) overgrowing high-temperature individuals and retaining their outlines. The temperature maximum in evolutionary trend of zircons (morphotypes G_1 , P_1) is explained by the late magmatic origin of some second-type crystals. Zircons from biotite granites are distinguished by diverse morphology caused by elevated viscosity and long-term crystallization of the melt. The

evolutionary trends have bends characteristic of peraluminous leucogranites (Pupin, 1980), which mark enrichment of magma in alumina at intermediate temperature. Zircons from monzogranite of the first and second types have high-temperature (S_{23} , S_{24} , $P_5\text{--}850^\circ\text{C}$) and middle-temperature (S_{13} , S_{14} , $P_3\text{--}750^\circ\text{C}$) habits with a $\{311\}$ dipyrmaid characteristic of moderately alkaline conditions. In low-temperature ($750\text{--}700^\circ\text{C}$) varieties, the faces of the acute $\{331\}$ dipyrmaid growing in an alkaline setting (Figs. 5-1b, 5-2b) appears along with the $\{311\}$ and $\{111\}$ forms. The contribution of low-temperature morphotypes (G_1 , L_5 , P_1 , S_4) does not exceed a few percent. A series of morphotypes close to those of biotite granite has been established in zinnwaldite rare-metal granite. The difference is the higher alkalinity of the medium, which rapidly increases at the early stages of the process from 500–600 to 700–800 conventional units. The main feature of the population is expressed in abundant low-temperature ($650\text{--}600^\circ\text{C}$) cyrtolite zircons pertaining to the P_1 , G_1 , I , and R_1 morphotypes. A gap has been established in the stock of the morphotype distribution of zircons from rare-metal granite. Two maxima correspond to early magmatic zircon with relict cores and late magmatic cyrtolite (Figs. 5-1c, 5-2c).

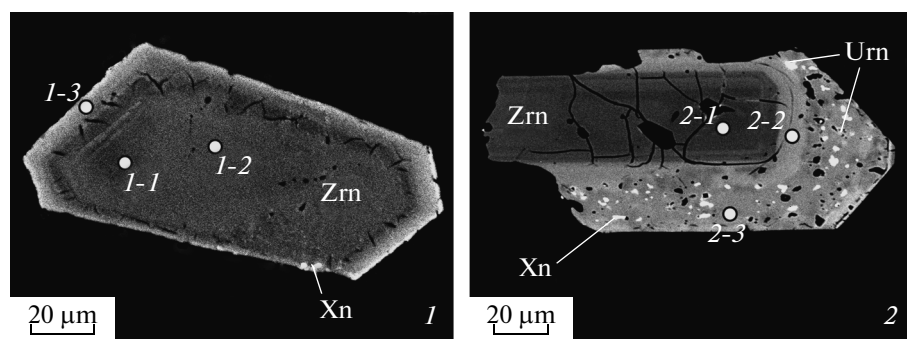


Fig. 6. Zircons from Late Cretaceous biotite granites of Russian Far East. BSE images: (1) zircon of second type with recrystallized core and rare-metal rim, Badzhal Complex, Amur region; (2) zircon with anomalously wide rare-metal rim with abundant mineral inclusions, Chaun Complex, Chukchi Peninsula. Minerals: Urn, uraninite; Xn, xenotime-(Y); Zrn, zircon.

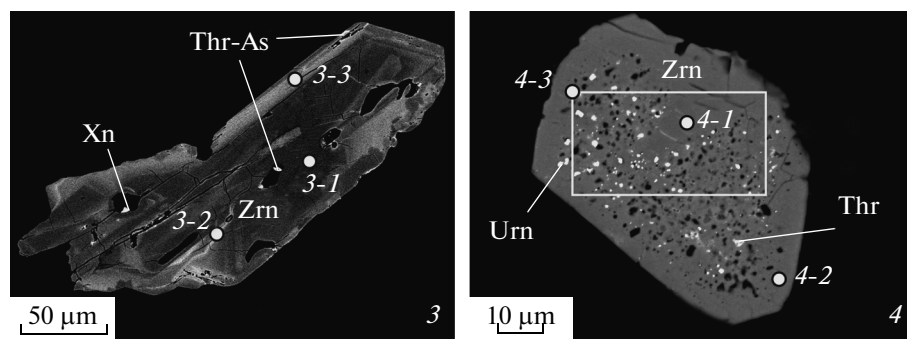


Fig. 7. Zircons from Late Cretaceous biotite monzogranites of Russian Far East. BSE images: (1) recrystallized zircon with rare-metal rim, Silino Complex, Amur region; (2) rare-metal zircon with poikilitic inclusions, Ichuveem Complex, Chukchi Peninsula. Minerals: Thr, thorite; Urn, uraninite; Xn, xenotime-(Y); Zrn, zircon.

ZIRCON GEOCHEMISTRY

Consideration of the chemical composition and distribution of trace elements in zircons and their behavior during origination, growth, and mineral alteration is important for studying the evolution of zircon in postorogenic intrusive series. Our investigation has shown that zircons from various granitic complexes differ in geochemistry.

Zircon from biotite granite is characterized by low contents and a similar distribution of trace elements irrespective of the degree of recrystallization, except for the outer rims of second-type crystals, where anomalous Hf contents (up to 0.5–3.0 and occasionally up to 8.9%), U (0.2–2.4%), and Th (0.3–1.2%) are detected (Fig. 6; Table 1), as well as P (up to 2137 ppm), Ca (up to 2573 ppm), and H₂O (up to 4310 ppm). Y and HREE (especially Yb, Er, Dy) are also noteworthy (Table 2). The concentrations of these elements in cores reach 6837 and 2524 ppm, respectively, as opposed to 9693 and 5840 ppm in the outer rims. Zircon from the Badzhal volcanic–plutonic zone is enriched in Fe up to 0.3–1.23%. In the rare-metal rim of zircon, rather large (up to 5–15 μm) grains of xenotime, monazite, and uraninite have been identified.

Small secondary grains (1–3 μm) of this mineral occur in pores and heterometric fractures of cores. The REE minerals are not characteristic of growth channels in cores, where thorite occurs in association with uraninite.

Zircons from monzogranite devoid of relict cores are characterized by elevated concentrations of trace elements in the inner and especially in the outer zone, wt %: 0.10–0.95 and 0.4–6.4 Hf; 0.1–0.7 and 0.5–3.3 U; 0.05–0.5 and 0.1–1.0% Th (Fig. 7; Table 1). Zircons from monzogranite differ from those in biotite granite by substantially higher concentrations of most trace elements and by lower concentrations of P and Ti (Table 2). For example, 847–4601 ppm Y, 499–3034 ppm HREE, 12–78 ppm Nb; 1.3–85.5 ppm F, and 385–4296 ppm H₂O. All admixtures are distributed extremely nonuniformly. Inclusions of secondary As-thorite and xenotime are hosted in pores and fractures. As-thorite microveinlets are 0.2–0.5 μm thick. Imperfectly faced zircon grains with poikilitic uraninite and thorite inclusions stand out in their elevated Hf and U contents.

Zircons from zinnwaldite granite consist of three zones: the core as a recrystallized and partly dissolved

Table 1. Chemical composition of zircons from postorogenic intrusive series with Li–F granites in Russian Far East, wt %

Point	Si	Ca	Fe	Zr	Yb*	Hf	Th	U	O
<i>1-1</i>	15.76	—	—	49.07	—	—	—	—	35.17
<i>1-2</i>	14.89	—	0.79	49.26	—	—	—	0.39	34.67
<i>1-3</i>	15.38	—	0.83	47.17	—	0.74	0.59	0.54	34.75
<i>2-1</i>	15.20	—	—	49.47	—	0.40	0.16	—	34.77
<i>2-2</i>	14.94	—	—	47.70	—	0.74	1.17	1.17	34.28
<i>2-3</i>	14.71	—	—	48.25	—	1.70	0.33	0.82	34.20
<i>3-1</i>	14.55	—	—	49.80	—	0.79	0.24	0.32	34.29
<i>3-2</i>	14.94	—	—	46.40	—	4.22	0.35	—	34.10
<i>3-3</i>	14.77	—	—	44.08	—	6.25	0.12	1.14	33.65
<i>4-1</i>	15.27	—	—	47.34	—	2.88	—	—	34.51
<i>4-2</i>	15.15	—	—	47.19	—	2.30	—	0.93	34.42
<i>4-3</i>	15.29	—	—	44.38	—	1.69	1.89	2.65	34.09
<i>5-1</i>	15.11	—	—	49.48	—	0.71	—	—	34.70
<i>5-2</i>	15.34	—	—	46.27	—	0.58	1.12	2.28	34.42
<i>5-3</i>	14.90	—	—	46.85	0.42	2.75	—	0.93	34.15
<i>6-1</i>	15.01	—	—	49.55	—	0.80	—	—	34.63
<i>6-2</i>	14.05	—	0.39	45.44	—	3.24	2.29	1.33	33.27
<i>6-3</i>	14.93	—	—	42.87	—	7.67	—	0.92	33.61
<i>7-1</i>	15.05	—	—	48.35	—	1.70	0.43	—	34.47
<i>7-2</i>	15.14	—	—	45.87	—	2.06	0.45	2.27	34.22
<i>7-3</i>	14.58	—	—	43.60	—	6.19	0.64	1.57	33.42
<i>8-1</i>	14.75	—	—	48.78	—	1.87	—	0.29	34.31
<i>8-2</i>	14.84	0.76	1.15	37.34	0.75	5.70	4.09	2.40	32.97
<i>8-3</i>	14.84	0.33	1.01	35.11	—	13.24	1.37	1.45	32.65
<i>9-1</i>	15.42	1.00	0.83	36.38	6.29	5.34	1.58	—	33.16
<i>9-2</i>	15.11	0.22	0.65	34.75	—	14.37	0.57	1.58	32.75
<i>10-1</i>	15.31	0.74	0.77	40.18	1.22	3.87	2.68	1.53	33.71
<i>10-2</i>	15.25	—	0.22	38.45	—	12.21	0.03	0.58	33.26
<i>11-1</i>	14.77	1.20	1.06	39.38	1.40	3.38	2.11	3.38	33.34
<i>11-2</i>	14.78	—	—	40.42	1.35	3.79	0.99	5.53	33.14
<i>12-1</i>	15.74	—	—	41.77	—	7.79	0.18	0.43	34.09
<i>12-2</i>	14.56	—	—	40.98	—	9.05	—	2.35	33.06

Representative electron microprobe analyses were carried out at points indicated in Figs. 6–9 (4–3, composition of scanning site). Yb* = Yb + Er + Dy + Tb. Concentrations of elements are shown in wt % recalculated to 100%; dash, below detection limit. SEM EDS analyses were performed at Center of Sharing Use, National University of Mineral Resources, St. Petersburg.

protocrystal (20–50 vol %); thick intermediate zones of accumulation of U, Th, REE, and other incompatible elements; and an outer rim 5–20 μm thick saturated with Hf. Various relationships of the aforementioned zones, which demonstrate the microgeochemical evolution of zircon from zinnwaldite granite with gradual transformation of the core and expansion of rare-metal rims, are considered in Fig 8. The zircon cores are characterized by relatively low concentra-

tions of Hf (0.36–2.24%), U (0.01–1.0%), Th (0.01–0.9), and REE (<0.01%). The U–Pb SHRIMP II age of one such core in zircon from the Severny massif has been estimated at 2427 ± 22 Ma, whereas the majority of zircons are dated at 89.4 ± 7 Ma. In the intermediate zone, the concentrations of trace elements increase: U (0.1–3.7%), Th (0.1–2.3), and HREE, including Yb, Dy, Er, Tb (0.01–1.2%) (Table 1). The increase is accompanied by crystallization of abundant

Table 2. Trace element contents (ppm) in zircons from postorogenic intrusive series with Li–F granites in Russian Far East, wt %

Component	Biotite granite			Biotite monzogranite			Zinnwaldite granite		
	1	2	3	4	5	6	7	8	9
Li	0.1	0.3	1.5	0.4	0.5	0.6	2.8	1.8	5.7
P	n.a.	333	404	212	209	255	2242	1433	1288
Ca	0.4	9.7	42	6.1	5.4	22	344	601	246
Ti	17	169	28	4.3	2.9	7.0	28	45	69
Sr	0.7	1.5	1.0	1.3	1.1	1.2	16	20	10
Y	637	3075	2348	2939	1973	2581	5567	13421	7742
Nb	21	26	26	25	28	26	808	974	826
Cs	n.a.	0.9	0.8	0.8	0.6	0.7	8.3	6.0	84
Ba	1.4	1.8	2.9	1.1	1.1	1.8	5.0	3.6	13
Hf	7136	8208	7587	10679	11705	11596	26587	13884	16396
Th	69	334	485	532	628	877	671	4605	2156
U	230	928	863	1824	2490	2196	11896	22377	10800
La	0.1	0.5	1.8	1.2	0.7	6.9	3.8	6.4	7.2
Ce	5.4	24.2	24.0	16.3	16.4	45.5	30.2	72.2	61.2
Pr	0.1	0.5	1.3	0.4	0.4	4.5	4.2	3.6	5.0
Nd	1.2	4.3	9.8	3.5	4.3	26.5	28.9	21.8	27.9
Sm	2.0	9.4	11.3	5.4	6.2	21.0	39.7	32.2	35.7
Eu	0.02	0.23	0.30	0.20	0.40	0.98	0.30	0.24	0.35
Gd	11	55	41	39	33	56	106	130	112
Dy	47	227	167	209	150	203	592	805	646
Er	98	528	349	534	378	447	1811	2180	1556
Yb	173	868	619	1001	779	884	6493	4975	3805
Lu	28	123	93	159	126	142	1036	741	563
H ₂ O	n.a.	728	775	1009	832	1646	2075	4411	3323
F	"	9	25	23	8	29	97	169	241
Th/U	0.30	0.36	0.42	0.29	0.25	0.43	0.06	0.21	0.22
Eu/Eu*	0.02	0.03	0.04	0.04	0.08	0.08	0.01	0.01	0.02
Ce/Ce*	14.2	11.7	11.9	5.5	7.2	4.8	1.8	3.6	7.3
ΣREE	365	1840	1317	1970	1495	1838	10146	8968	6820
ΣLREE	7	29	37	21	22	83	67	104	101
ΣHREE	357	1801	1268	1942	1466	1732	10039	8832	6683

SIMS analyses were performed on a Cameca IMS-4f5 at Yaroslavl Branch, Physicotechnological Institute, RAS; n.a., not analyzed. Representative ion microprobe analyses of zircons from (1) Chaun, (2) Badzhal, (4) Ichuveem, (5) Silino, (7) Right Urmi, (8) Pyrkakai granitic complexes. Average composition of zircons from (3) biotite granite (35 samples), (6) monzogranite (35 samples), (9) zinnwaldite granite (40 samples).

thorite, uraninite, xenotime-(Y), and monazite-(Ce) microphases. Hafnium accumulates at crystal margins up to 1.4–14.7%; the Zr/Hf ratio reaches 2.7. Hierarchical concentric zoning is noted: microzones enriched in heavy admixtures make up series within thicker zones.

Nb, LREE, F, Ti, Cs, and Li are typomorphic trace elements of zinnwaldite granites (Table 2). LREE

(69–206 ppm) accumulate primarily in the uranium zone, whereas Nb (137–2280 ppm), Ti (5.1–308 ppm), Cs (1.6–101 ppm), and Li (2.1–18 ppm) are detected in the hafnium zone. It is noteworthy that elements atypical of zircon, such as Fe (0.31–2.4 to 4.81%), Ca (0.1–1.25 to 3.22%), Al (0.04–1.87 to 6.33%), and As (up to 2.41%), constantly appear in zones enriched in U and Hf (Fig. 8; Table 1); Ba, Sr, F, and H₂O accu-

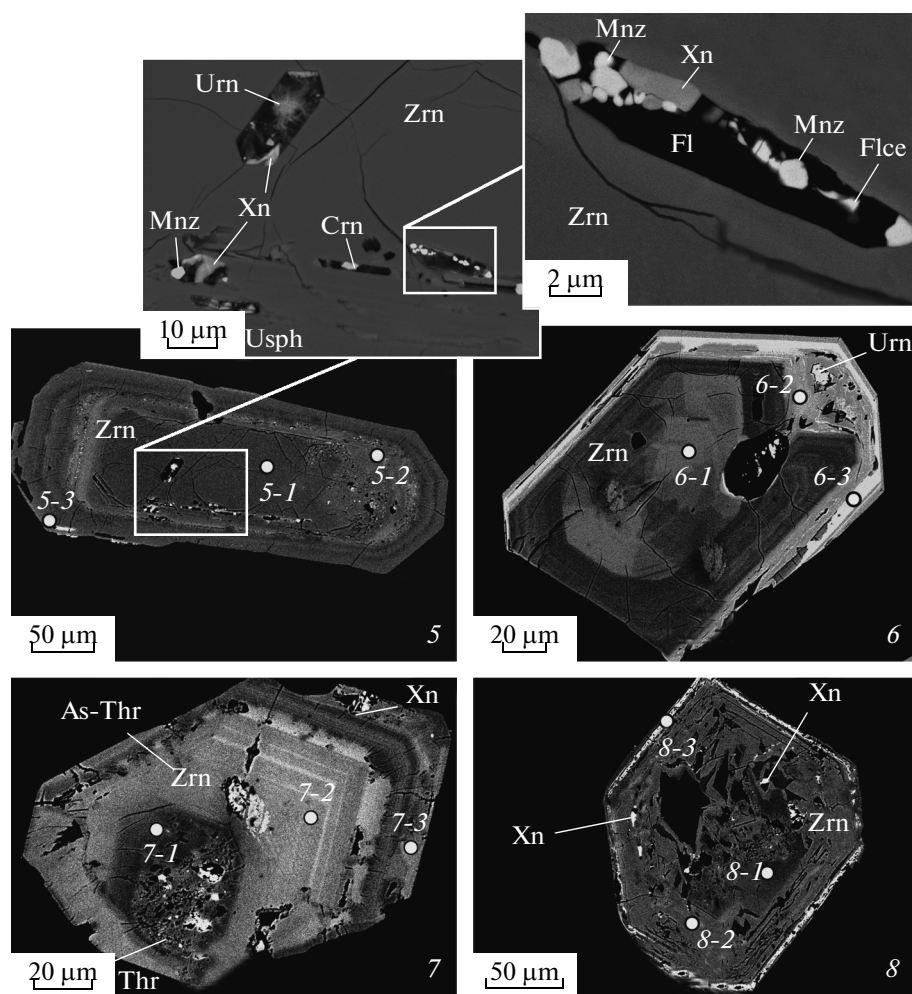


Fig. 8. Zircons from Late Cretaceous zinnwaldite granites of Russian Far East. BSE images: (5) recrystallized zircon (5-1) with uranium (5-2) and hafnium (5-3) rims and mineral inclusions, Pyrkakai Complex, Chukchi Peninsula; (6) zircon with large, slightly transformed core as an intergrowth of protocrystals (6-1) and relatively thin secondary rims (6-2, 6-3); (7) rare-metal zircon with intensely transformed core (7-1), thick uranium (7-2) and hafnium (7-3) rims and mineral inclusions; (8) porous cyrtolite with relics of core (8-1), thick rare-metal-uranium (8-2) and thin hafnium (8-3) rims, Right Urmi Complex, Amur region. Minerals: As-Thr, As-thorite; Crn, cerianite; Fl, fluorite; Flce, fluocerite; Mnz, monazite-(Ce); Thr, thorite; Urn, uraninite; Usph, uranospherite; Xn, xenotime-(Y); Zrn, zircon.

mulate as well. A Th/U ratio markedly low in zircons from rare-metal granites becomes even lower in the outer rims (down to 0.06–0.11 against to 0.24–1.25 in biotite granite) (Table 2). Isometric pores (0.05–5.0 μm) and elongated caverns (up to 10, occasionally up to 50 μm) develop in zones of accumulation of trace elements, extending along fractures of heterometry and the boundaries of concentric growth zones. Pores concentrate in the core and hafnium rim, where their total volume reaches 1–5%, ensuring elevated permeability for fluids. Fluorite, topaz, U, Th, and HREE minerals have been identified within pores: As-thorite, monazite-(Ce), xenotime-(Y), cerianite, fluocerite, and uranospherite (Fig. 8, inset).

The highest levels of accumulation of trace elements are characteristic of relatively small (<50 μm)

recrystallized porous and cavernous zircon crystals with a thick rare-metal outer rim and uneven faces. The core almost disappears, and the difference between uranium and hafnium zones is obliterated (Fig. 9). The composition of microadmixtures is as follows (wt %): 1.5–14.4 Hf; 0.5–6.3 U; 0.5–4.5 Th; 0.3–6.9 HREE (Yb, Dy, and to a lesser degree, Er, Tb); 1.61–4.55 Y (Table 1); in addition to common incompatible admixtures (Fe, Ca, Al), cyrtolite contains up to 3.5% Bi. The Zr/Hf ratio in the outer zone of cyrtolite is 2.4–5.6. Trace elements are distributed extremely nonuniformly. Their content varies by several times along growth zones distorted by secondary blocks of concentration–deconcentration of admixtures. Cyrtolite is characterized by a spotty–zonal structure of grains with elements of primary concentric zoning (Fig. 9).

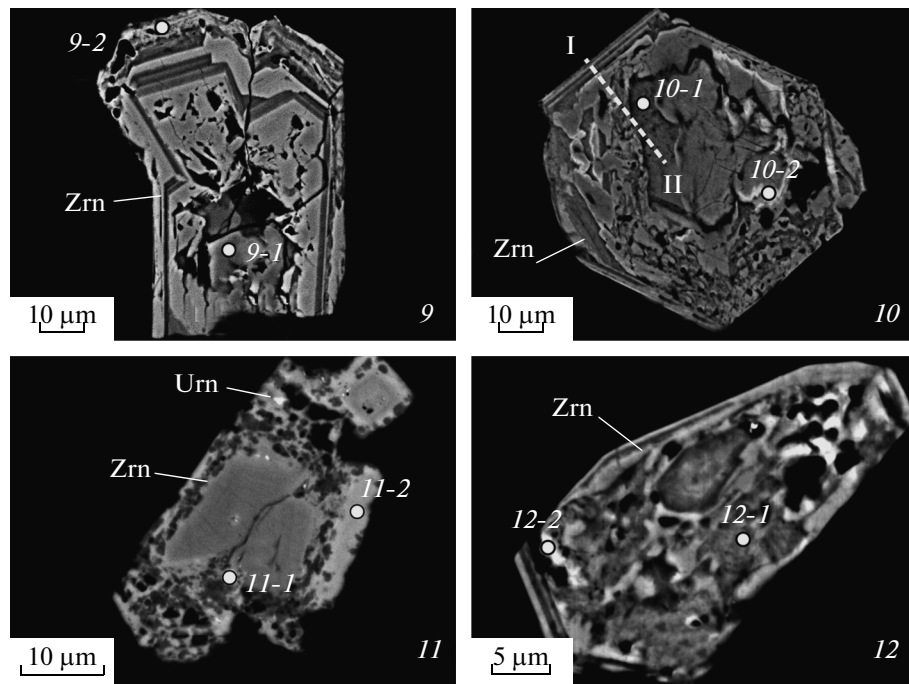


Fig. 9. Cyrtolite from Late Cretaceous zinnwaldite granites (9, 10) and ongonites (11, 12). BSE images: (9) recrystallized zircon with uranium (9-1) and hafnium (9-2) rims and mineral inclusions, Pyrkakai Complex, Chukchi Peninsula; (10) zircon with large transformed core in form of protocystal (10-1) and relatively thin secondary rims (10-2); (11) rare-metal zircon with intensely transformed core (11-1), thick uranium and hafnium rims and mineral inclusions (11-2); (12) porous cyrtolite with relics of core (12-1), thick uranium and thin hafnium rims (12-2), Right Urmi Complex, Amur region. I–II, line of electron scanning. Minerals: As-Thr, As-thorite; Crn, cerianite; Fl, fluorite; Flce, fluocerite; Mnz, monazite-(Ce); Thr, thorite; Urn, uraninite; Usph, uranospherite; Xn, xenotime-(Y); Zrn, zircon.

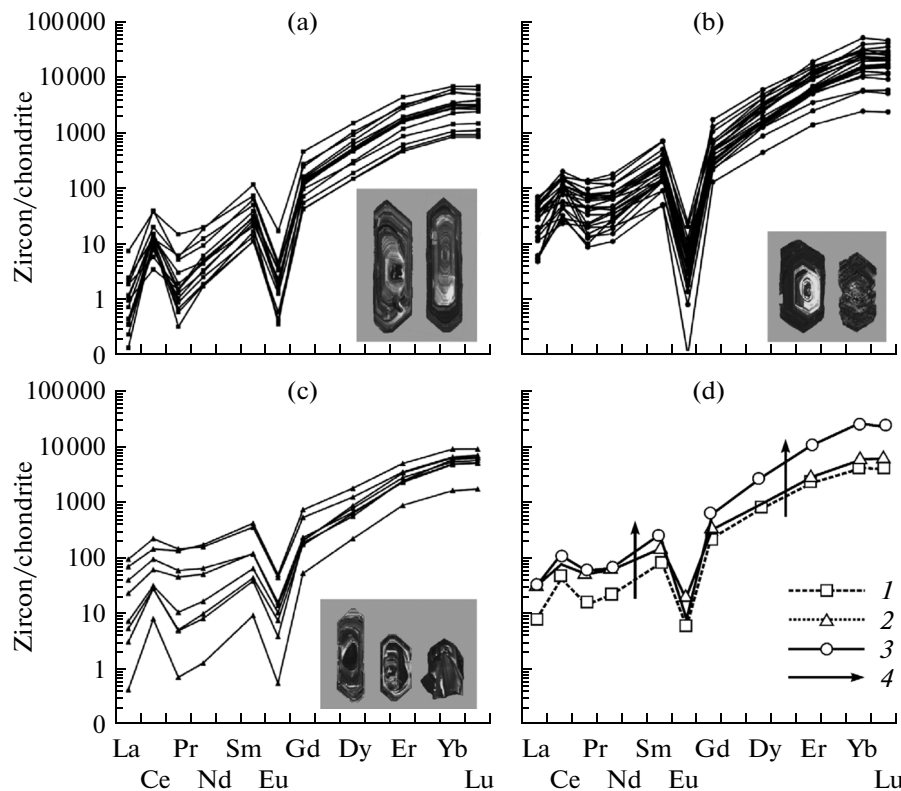


Fig. 10. Chondrite-normalized REE patterns of zircons from postorogenic intrusive series with Li–F granites of the Russian Far East: (a) biotite granite, (b) zinnwaldite granite, (c) monzogranite, (d) evolution of REE patterns. (1) average REE concentrations in zircon from biotite granite; (2) monzogranite, (3) zinnwaldite granite, (4) direction of REE pattern evolution.

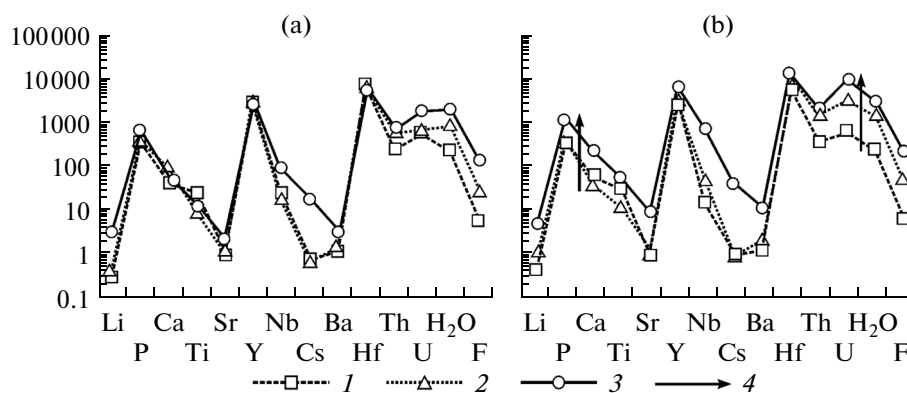


Fig. 11. Average concentrations of trace elements (ppm) in (a) protocrystals and (b) rare-metal rims of zircons from postorogenic intrusive series with Li–F granites of the Russian Far East. (1) Biotite granite, (2) monzogranite, (3) zinnwaldite granite; (4) direction of zircon composition evolution.

Zircons of ongonites are similar in composition to cyrtolite from zinnwaldite granites. Crystals of the first type include severely reworked relict cores depleted in admixtures; cyrtolite of the most abundant second type differs from cyrtolite in zinnwaldite granite by a more heterogeneous structure (Figs. 9–11, 9–12) and a limited set of admixtures. Cyrtolite from ongonite contains 2.3–11.9% Hf, 0.2–5.5% U, and 0.03–2.74% Th. Sporadic admixtures of Yb (up to 1.2–3.5%), up to 0.4–1.1% Fe, and up to 0.2–1.2% Ca are also noted (Table 1). Cyrtolite from ongonite is distinguished by a poor set and small size of mineral inclusions. These are tiny (0.1–1.0 μm) spherical inclusions of Th uraninite and xenotime.

The REE patterns of zircon from biotite granite have a configuration typical of magmatic zircons with a characteristic positive slope ($\text{Lu}_\text{N}/\text{La}_\text{N} = 3034$) comparable to heavy branch ($\text{Lu}_\text{N}/\text{Gd}_\text{N} = 21.3$) and light branch ($\text{Sm}_\text{N}/\text{La}_\text{N} = 35.3$) and with distinct Ce and Eu anomalies (Fig. 10a). Zircons from zinnwaldite granite reveal a substantial increase in the total REE content, including HREE (6358 and 6229 ppm against 1317 and 1268 ppm in biotite granite), deeper Eu minimum (Eu/Eu^* down to 0.001), and smoothing of Ce anomaly (7.98 against 11.87 in biotite granite). Accumulation of LREE and an increase and smoothing of the La–Sm branch ($\text{Sm}_\text{N}/\text{La}_\text{N} = 15.9$ as opposed to 35.3 in biotite granite) are characteristic (Fig. 10b). Zircons from monzogranite have intermediate parameters of REE patterns and a wide range of REE contents (Fig. 10c). Thus, the REE contents increase, the Eu minimum becomes deeper, and the Ce anomaly is smoothed; the REE patterns slightly flatten from biotite to zinnwaldite granites (Fig. 10d).

Comparison of the first and second types of zircons has shown that they obviously differ in chemical composition and volumetric proportions of the relict core and rare-metal rim. The first type of zircon grains, which include protocrystals, are similar in all granitic

complexes and characterized by low concentrations of trace elements. Protocrystals in monzogranite are somewhat enriched in Th, Ca, H_2O , and F, whereas in zinnwaldite granite they are enriched in Li, Cs, Nb, Th, U, F, and H_2O (Fig. 11a). The second type of grains is distinguished by accumulation of trace elements, which increases from biotite to zinnwaldite granites (Fig. 11b) (Alekseev et al., 2011).

MORPHOLOGICAL AND ANATOMIC EVOLUTION OF ZIRCONS

Zircons from postorogenic granitic rocks in the Russian Far East change their morphology, internal structure, and chemical composition in the series of populations pertaining to the complexes of biotite granites, monzogranites, and zinnwaldite granites (Figs. 1–4).

Zircons from biotite granite have the typical zircon appearance and belong to the magmatic type (Figs. 1–1a, 1–1b) (Zircon, 2003). Trends of zircon morphotypes show that postorogenic biotite granites in the Far East are cognate to the leucogranite–alaskite association. The zircon morphotypes S_{11} – S_{14} , S_{16} – S_{18} , S_{21} – S_{22} characteristic of low-silicic granitoids are infrequent or do not occur at all in biotite granite. At the same time, the shortened stock of *P* morphotypes inherent to leucogranite–alaskite association with prevalence of high-temperature crystals dominates in biotite granites (Brodskaia et al., 1986, 1989). At the initial stage of the evolution of zircon, the alkali/alumina index is lowered and increases in medium-temperature morphotypes (Figs. 5–1a, 5–2a). Lack of detrital seeds along with composition of zircons suggest that they crystallized in primary magmatic reservoirs depleted in trace elements. The two-member structure, indications of dissolution and recrystallization, and the sharply different compositions of a core and rim in the second type of zircons are evidence of

postmagmatic transformation in the rare-metal fluid medium (Figs. 1-2a, 1-2b; Fig. 6) (Zircon, 2003; Geisler et al., 2007). Injection of rare-metal granitic melts probably was the cause of alteration.

Zircons from monzogranite with habits transitional from zircon to hyacinth are mostly related to the magmatic type. Subordinate crystals of cyrtolite appearance (Fig. 2) indicate the substantial role of fluids (Brodska et al., 2006). The peculiar morphology of zircons from monzogranite implies special crystallization conditions. The first type of magmatic zircon with polyzonal structure was formed over at least three stages: (1) formation of protocystal (crystal core), (2) recovery of zircon from a source, regeneration in the primary magmatic reservoir, and subsequent recrystallization during ascent of melt, and (3) regeneration of altered zircon in the secondary magma chamber (Figs. 2-1a–2-1c). Zircon of the second type is apparently syngenetic (Figs. 2-2a, 2-2b; Fig. 7) and crystallizes in monzogranite dikes from a melt with an elevated alkalinity and water content (Pupin, 1980). Its common attribute is a thin rare-metal rim (Fig. 7-3). The set and distribution of zircon morphotypes (Figs. 5-1b, 5-2b) are characteristic of monzogranite pertaining to the granite–granosyenite association (Pupin, 1980; Brodska et al., 1986, 1989). The variable zircon morphotypes in monzogranite dikes suggest that the Ichuveem Complex in the Chukchi Peninsula formed over a long time, whereas the Silino Complex in Amur region had a short formation history.

Zircons from zinnwaldite granite and ongonite sharply stand out in morphology: small size and elongation, uneven and cellular topography of faces, and hyacinth or cyrtolite appearance of crystals are typical (Figs. 3, 4). The structure of the first type of zircons shows that crystals similar to those from biotite granite initially occurred in the mineral-forming melt (Figs. 3-1a, 3-1b; Figs. 4-1a, 4-1b). Zircons from rare-metal granite are a product of deep transformation and recrystallization of these protocystals in a fluid-saturated melt with partial dissolution and growth of uranium and hafnium cyrtolite rims (Fig. 8). Morphological and anatomic diversity are controlled by the degree of protocystal transformation. Cores in the first type of zircon crystals from ongonite do not differ from zircon cores in zinnwaldite granite in morphology, size, and internal structure. This assumes that both were probably derived from the same source.

Zircons from Li–F granite partly inherit the morphology of relict crystals entrapped from their source. Rare-metal rims distort their shape but do not create a new habit. This constrains the ability of crystal morphology in studying the first type of zircons. The main morphotypes are grouped in the Pupin–Turco diagram as a vertical stock D, P₅–P₁, G₁ (I.A. = 700,

I.T. = 900–600°C) (Figs. 5-1c, 5-2c). A similar distribution has been established for ore-bearing subalkali and alkali granite associations (Brodska et al., 1986; Brodska and Marin, 2004). The disturbance of the continuous trend inherent to ore-bearing subalkali and alkali granite complexes indicates fluid phase release during crystallization (Brodska et al., 1989). The outer rare-metal rims formed under conditions of increasing alumina concentration in melt. At the final stage, when a fluid of elevated alkalinity appears in granite, Hf-rich zircon is dissolved (Linnen and Keppler, 2002). The intense transformation of rare-metal zircon in the process of its growth prevents reliable separation of the ontogenetic features related to primary growth and secondary alteration. In particular, it is difficult to estimate the relative amounts of the crystals grown on seeds or as primary cyrtolite. The question of the origin of pores in the second type of zircon and minerals captured therein remains open. It cannot be ruled out that they were partly formed by entrapment of fluid bubbles from rare-metal melt (Figs. 3, 8).

Thus, the decrease in size and elongation of zircon crystals together with increasing role of {111} and {331} dipramids and complication of the face topography are traced from biotite to zinnwaldite granites. The size of mineral inclusions decreases regularly from early to late populations (Figs. 1, 4). *The main tendency of the morphological evolution* of zircons is expressed in substitution of high-temperature (900–800°C) P₅, P₄, J₅, and S₂₀ morphotypes inherent to biotite granites of the Badzhai and Chaun complexes for the low-temperature P₁ and G₁ cyrtolite morphotypes (650–600°C) of rare-metal granite and ongonite of the Right Urmi and Pyrkakai complexes (Fig. 5). The drop in the crystallization temperature is explained by an increase in the fluid saturation of granite melts with time. The stocks of distribution of zircon morphotypes in early granitic and late rare-metal complexes are broken in the temperature interval of 650–750°C. This break is caused by fluid release from melt and the onset of crystallization of the second type of late magmatic zircon generation (Brodska et al., 1989). The crystallization conditions of zircon in Late Cretaceous granites of the Far East are distinguished by elevated alkalinity (I.A. = 600–700) increasing up to 800 in zinnwaldite granite. The increase in alkalinity in consecutive granitic complexes occurs at still earlier high-temperature stages of crystallization (Pupin, 1980). The morphology of zircons suggests that the depth of initial crystallization decreases from biotite granite and monzogranite to rare-metal granite and ongonite (Krasnobayev, 1986). Zircons from the Chukchi Peninsula are distinguished by diversity of morphotypes in all populations, and this reflects the elevated heterogeneity of sources and the significant depth of magma or fluid generation (Khabibulina et al., 1999).

In late populations of zircons, including the rare-metal variety, individual zircon crystals with relict cores inherent to a source have been identified. The first type of zircon was formed by regeneration and metasomatic alteration of protocrytals derived from primary magma chambers, and they inherited some features of the ancient zircon. Cyrtolite with a complex spotty and zonal structure, enriched in pores and mineral inclusions, has been established in monzogranite, Li–F granite, and ongonite. *The main tendency in the anatomic evolution of zircon* is expressed in complication of its structure in a series of consecutive intrusive complexes of postorogenic granites. The appearance in late zircon generations of such attributes as secondary structural–chemical zones or domains, in particular, rare-metal rims, imperfect crystal structure, mineral microinclusions, pores and fractures, peculiar morphology of faces, etc., indicates that the intensity of recrystallization, metasomatism, heterometric deformation, and crystallization of entrapped minerals increases with time (Brodskaya et al., 1986, Krasnobaev, 1986). The transformation of zircons in early biotite granite was related to the influence of late rare-metal granites (Alekseev, 2011, 2012). Late zircons in zinnwaldite granite are formed and transformed in the low-temperature alkaline water-saturated rare-metal melt (Kovalenko, 1977; Linnen and Keppler, 2002; Marin, 2004; Pettke et al., 2005; Alekseev et al., 2011).

GEOCHEMICAL EVOLUTION OF ZIRCONS

Zircons from biotite granite, as follows from their composition and morphology, crystallized from a melt depleted in trace elements (Tables 1, 2; Figs. 1, 10a, 11) (Zircon, 2003; Harley and Kelly, 2007; Fedotova et al., 2008). These zircons have a magmatic REE pattern with characteristic Ce and Eu anomalies and a tendency to gain HREE (Zircon, 2003; Pelleter et al., 2007). The high Yb/La ratio indicates a high degree of REE fractionation by the moment of zircon crystallization. The substantial metasomatic alteration of biotite granite under the action of rare-metal intrusions so characteristic of ore districts in the Far East (Alekseev, 2011, 2012) gave rise to transformation of zircon, its recrystallization, and overgrowth by rare-metal rims (Table 1; Figs. 1, 6). This could have taken place at the stage of monzonitoid magmatism with elevated rare-metal potential.

Zircons from monzogranite are enriched in Hf, Th, U, other admixtures, and mineral inclusions (Table 2; Figs. 7, 11), which indicate rare-metal specialization of monzogranite melts. The zoning of zircons reflects accumulation of rare elements at the late stage of crystallization, and a wide range of REE concentration (Fig. 10c) indicates heterogeneous sources of dike complexes in the Far East (Alekseev et al., 2013).

Zircons from zinnwaldite granite and ongonite evolve depending on their belonging to certain morphological types (Fig. 3). The first type comprises zircons with relics of high-temperature magmatic zircons pertaining to S₉–S₂₀ and P₄–P₅ series (Pupin, 1980), which formed over two stages: (1) dissolution and recrystallization of primary crystals; formation of the rim with U, Y, HREE, P, Th, incompatible Ca, Al, Ba, Sr, etc.; uraninite, thorite, and xenotime microinclusions; (2) crystallization of the outer rim with admixtures of Hf, HREE, Nb, Cs, Li, F, H₂O and incompatible Fe, LREE, As, Bi; redistribution of admixtures and crystallization monazite, As-thorite, fluorite, etc., in pores in association with fluorite and topaz (Figs. 8, 9). Stratification of admixtures in rare-metal zircon is explained by magma fractionation, in particular, its enrichment in alumina with time and the changing partition of rare elements between zircon and melt (Linnen and Keppler, 2002; Kempe et al., 2004). The composition of rims reflects the geochemical evolution of the initial melt: U, Y, HREE, P, Th → Hf, Nb, Cs, Li, F, H₂O (Table 1). The second type, represented by low-temperature short-prismatic cyrtolite (P₁–P₄ morphotypes), is a product of late magmatic crystallization or transformation of the first type of zircon (Figs. 8, 9). The content of rare elements reaches 10% and becomes even higher (Table 1). The contribution of isomorphic components (Hf, Nb, Ti, as well as Cs, Ba, Li, F, and H₂O) abruptly increases from the core to the marginal zone; Th/U ratio decreases from 1.0 to 0.06 in this direction. U, Y, HREE, Th, P, Ca, and Sr accumulate in the intermediate zone. Yb, Er, and Dy play an important role among REEs; the Ce anomaly is smoothed from the core toward the periphery (Ce/Ce* varies from 19.0 to 1.5); the Eu minimum deepens down to Eu/Eu* = 0.003 (Fig. 10 b).

An invariable manifestation of fine growth zoning in the outer hafnium rim (Figs. 8, 9) rules out the possibility of the secondary hydrothermal origin of the rare-metal zones surrounding zircon. At the same time, zircons from zinnwaldite granite and ongonite exhibit an inhomogeneous distribution of isomorphic components (Fig. 9) and accumulation of admixtures not typical of zircon, as well as fluorine and water (Table 1; Figs. 8, 9, 11), indicating late magmatic crystallization from a fluid-saturated melt (Zircon, 2003; Pettke et al., 2005). The increase in concentration and the configuration of REE patterns—an increase and flattening of the La-branch, smoothing of the Ce anomaly, and deepening of the Eu minimum (Fig. 10b)—also reflect the late magmatic origin of cyrtolite (Pelleter et al., 2007). The enrichment of the subalkaline granitic melt pertaining to magmatic systems with Li–F derivatives in alumina is accompanied by a decrease in the D_{Hf}/D_{Zr} ratio to 0.5–0.2 and by a gain in Hf in the residual melt and the outer zircon zones (Linnen and

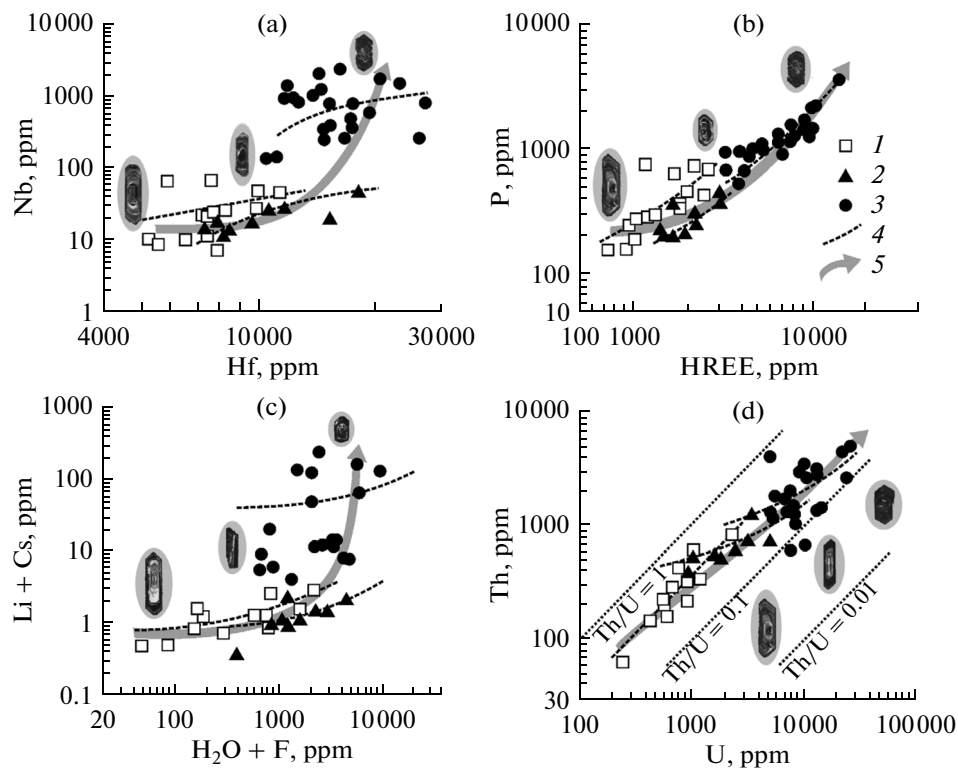


Fig. 12. Geochemical evolution of zircons from postorogenic intrusive series with Li–F granites of Russian Far East: (a) rare-metal, (b) xenotime, (c) alkaline-fluid and (d) actinoid. (1) Biotite granite, (2) monzogranite, (3) zinnwaldite granite; (4) correlation trend of intrusive complexes; (5) direction of zircon composition evolution.

Keppler, 2002; Kempe et al., 2004). The peaks of trace element accumulation and crystallization of microinclusions in zircon are related to an abrupt change in the crystallization conditions at the moment of emplacement of rare-metal magma and decompression degassing of the fluid-saturated melt. The high fluorine and water concentrations in rims of Far East zircon are indicative of this (Table 1). The concentrations of trace elements in zircon from evolved granitic complexes reach a level characteristic of hydrothermal mineral formation (Zircon, 2003; Pettke et al., 2005). It should be noted that the chemical composition of late magmatic zircon from rare-metal granites at a high activity of mineralizers resembles the composition of hydrothermal zircon. The imperfect structure of cyrtolite arising in the presence of fluids and reflected in weak cathode luminescence facilitates entrapment of incompatible elements (Figs. 3, 4) (Geisler et al., 2007). Thereby, the viewpoint of Fedotova et al. (2008) is supported: two types of magmatic zircon with perfect and primarily disordered crystalline structure corresponding to early biotite and late zinnwaldite granites actually exist. In composition, zircons from zinnwaldite granite and ongonite correspond to zircons from ore-bearing subalkali–alkali granitic associations (Brodskaya, 1986; Huang et al.,

2002; Brodskaya and Marin, 2004; Marin, 2004; Kempe et al., 2004).

As follows from the aforesaid, zircon populations from the studied intrusive complexes are sharply distinct in the concentration levels of major and minor admixtures, which makes it possible to align them into evolutionary geochemical series. In each complex, the protocystals in zircon cores are depleted in admixtures, reflecting the geochemistry of their sources. An appreciable starting specialization for Li, Cs, Nb, Th, U, and F is characteristic of zircon cores from zinnwaldite granite (Fig. 11a). The existence of relict cores should be taken into account by geochemical study of zircons: the conventional collection of mineral grains for the study of heavy concentrates leads to an increased contribution of large (>100 μm) zircon grains containing protocystals and, as a result, to a distorted composition of zircon populations.

The second type of zircon is richer in isomorphic admixtures of trace elements, water and fluorine, and this emphasizes the fact that such zircon formed in the process of magma fractionation and its saturation with fluid. Zircon crystals of consecutive intrusive complexes reveal an abrupt increase in concentrations of isomorphic trace elements, water, fluorine, and admixtures not inherent to zircon (Li, Cs, Sr, Ba) (Fig. 11b), as well as REE (Fig. 10; Tables 1, 2). Evolutionary

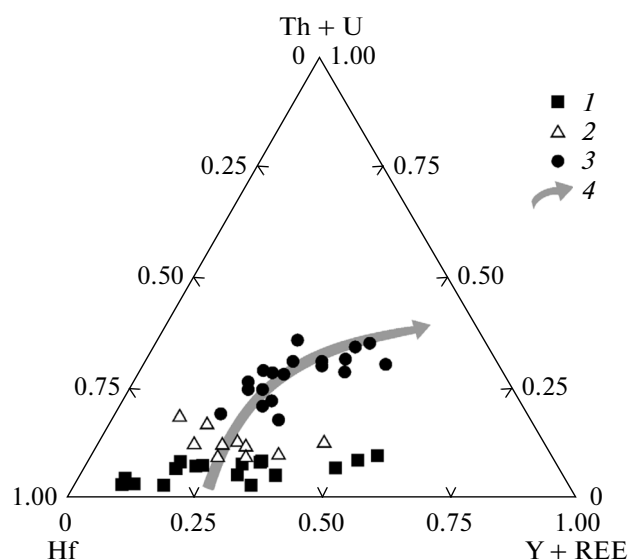


Fig. 13. Crystal chemical evolution of zircons from postorogenic intrusive series with Li–F granites of Russian Far East. (1) Biotite granite, (2) monzogranite, (3) zinnwaldite granite; (4) direction of evolution of zircon composition.

smoothing of the Ce anomaly and deepening of the Eu anomaly characteristic of late and postmagmatic zircons have been established (Pettke et al., 2007; Balashov and Skublov, 2011). It is noteworthy that a tendency toward a gain in LREE in late zircon generations (Pelletier et al., 2007) is relatively weakly expressed in Far East granites (Fig. 10d). Major incompatible elements (Ca, Fe, Al) accumulate in late zircons but reveal sharp variations in both individual crystals (Fig. 9) and populations related to each complex. The relationship of these elements to hydrothermal processes is reflected in a more intense gain in Ca in hydrothermal rims of zircon from biotite granite as compared with outer rims of rare-metal zircon from monzogranite (Fig. 11b).

Despite the compositional evolution, various populations reveal similar trends in correlation of admixtures controlled by the crystal chemical properties of zircon (Fig. 12). These trends developing in different directions are called rare-metal, xenotime, alkaline fluid, and actinoid. The rare-metal evolution proceeds moderately at the early stages due to the accumulation of Hf, U, Th, and volatile components. During crystallization of rare-metal zinnwaldite granite, all established admixtures accumulate violently up to the formation of cyrtolite in ongonite (Fig. 12a). The xenotime evolution of zircon develops by way of the REE and P concentration with retention of the corresponding scheme of isomorphism. A deficiency in phosphorus is typical of monzogranite (Fig. 12b). The alkaline fluid alteration of zircon at the early stage of evolution is expressed as a gradual enrichment in water and fluorine, which gives way to an abrupt increase in the

concentration of mineralizers and rare alkali metals (Fig. 12c). The actinoid transformation of zircons is related to a uniform gain in uranium and a gradual increase in the gradient of accumulation, expressed as a change in correlation between Th and U by passing to rare-metal granite (Fig. 12d). Thus, the history of Late Cretaceous postorogenic magmatism of the Far East directed to an increase in the rare-metal potential of granitic rocks is reflected in the evolution of accessory zircon.

The relationships of tendencies in the geochemical evolution of zircons are determined by the degree of melt fractionation and the isomorphic capacity of the mineral lattice. The granitic series of the Far East are characterized by consecutive development of actinoid and xenotime tendencies of zircon crystallization, expressed as an advanced increase in the relative amounts of U and Th in monzogranite followed by enrichment of zinnwaldite granite and ongonite in Y, REE, and P (Fig. 13). *The main tendency in the geochemical evolution of zircon* is a staged abrupt increase in concentrations of isomorphic trace elements (Hf, U, Y, Th, Nb, Cs, Li, F), REE, water, fluorine, and incompatible admixtures (Ca, Fe, Al, Sr, Ba).

During the evolution of postorogenic intrusive series, zircon accumulates trace elements, which become ore components at the postmagmatic stage (REE, Hf, Nb, U, Th, Li). Because of this, cyrtolite can be a prospecting guide of productive ore–magmatic systems (Alekseev et al., 2011). The release of admixtures by breakdown of zircon and mineral inclusions therein at the postmagmatic stage results in enrichment of hydrothermal solutions in trace elements. Thus, zircon in rare-metal granite works as a transitional concentrator of ore elements and a prospecting guide for ore-bearing granites.

CONCLUSIONS

(1) Zircons contained in postorogenic intrusive series with Li–F granites in the Russian Far East are characterized by a wide range of crystallomorphological, anatomical, and chemical properties. Zircon from granitic complexes is a primary magmatic mineral that bears indications of hydrothermal influence. Zircon in monzonitoid and rare-metal granitic complexes is formed during crystallization of the evolved melts or by means of transformation of zircon retained during partial melting of crustal sources.

(2) Zircons from Late Cretaceous granitoids reveal systematic variations in morphology, internal structure, and chemical composition in series of consecutive intrusive complexes. The main tendency of morphological evolution is expressed as replacement of high-temperature (900–800°C) zircon and hyacinth P_5 , P_4 , J_5 , and S_{20} morphotypes with low-temperature (650–600°C) cyrtolite P_1 and G_1 morphotypes. This

trend is accompanied by a decrease in dimensions and elongation of crystals. The main tendency in the evolution of zircon anatomy is characterized by complication of its internal structure: formation of rare-metal rims, secondary zones with imperfect structure, mineral inclusions, pores, and fractures. Zircons from monzogranite, Li–F granite, and ongonite contain identical relict cores indicating a common source of rare-metal magmas.

(3) The main tendency in the geochemical evolution of zircon is progressive accumulation of Hf, U, Y, Th, Nb, Cs, Li, REE (Yb, Er, Dy), water, fluorine, and incompatible admixtures (Ca, Fe, Al, Sr, Ba, As). Zircons of rare-metal granites reveal consecutive development of actinoid (U, Th) and xenotime (Y, REE, P) tendencies of geochemical evolution.

(4) The established variations in the composition and properties of zircons reflect the evolution of Pacific postorogenic magmatism directed toward a decrease in the depth of origination and crystallization temperature, as well as an increase in alkalinity, fluid saturation, and rare-metal potential of granitic magmas. Cyrtolite is a transitional concentrator of ore elements and serves as a forecasting and prospecting guide of productive ore–magmatic systems.

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