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Age and Isotope-Geochemical Characteristics of Ta, Nb, W, Sn Mineralization Associated with Rare-Metal Granites (Khangilay Ore District, Eastern Transbaikalia)

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Abstract—The age relations between the formation of the parent massif and the crystallization time of the associated ore mineralization were established based on isotope-geochronological study of the massif-deposits of the Khangilay ore cluster with various metallogenic specialization in Eastern Transbaikalia. In the Orlovka Li–F granite massif, the crystallization time of columbite–tantalite (145 ± 1 Ma) and cassiterite (144.2 ± 0.3 Ma) (U-Pb, ID-TIMS) is almost identical to the crystallization time of zircon (140.6 ± 2.9 Ma (U-Pb, SHRIMP) and 145 ± 1 Ma (U-Pb, CA-ID-TIMS)), which is an age marker of the formation of massifs. This fact testifies to the magmatogenic nature of rare-metal mineralization. In the Spokojnoye massif—the "standard type" of rare-metal peraluminous granites—a 0.6–3.8 Ma time gap was revealed between the time of massif formation (141.3 ± 1.8 Ma, U-Pb, SHRIMP, 146.9 ± 0.7 Ma, Rb-Sr isotopic system) and crystallization of wolframite (141.8 ± 0.6, Rb-Sr isotopic system and 140.1 ± 1.4 Ma, Sm-Nd isotopic system). This interval likely corresponds to the life time of the hydrothermal system, which produced tungsten mineralization.

Keywords: rare-metal granites, ore-mineralization, columbite–tantalite, cassiterite, wolframite, Eastern Transbaikalia, isotopic-geochronological investigations

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INTRODUCTION

Deciphering the duration of formation of ore deposits is one of the key tasks in solving for the modern problems of ore formation. Of special interest are isotope-geochronological and isotope-geochemical studies of complex ore-bearing magmatogenic-hydrothermal systems (OMS) related to the differentiated massifs of rare-metal plumasite granites (RPG). Such systems are characterized by the diversity of metallogenic specialization (Li, Ta, Nb, W, Sn, Be) and genetic types. In the most complete model variant, such type of ore formation corresponds to OMS with systematic spatial localization of mineralization relative to the parent massif: Ta, Nb, Li (±Sn) within parent massif → Li, W, Sn, (±Mo, Be) in the outer and inner contact zones (greisens, metasomatites) → Sn and W (±Mo) in quartz-vein framework of the RPG massif → Pb and Zn (sulfide mineralization). Tantalum mineralization is formed within massif as fine-grained Ta–Nb mineralization (columbite–tantalite, microlite). It is known that the Ta and Nb concentrations in melt do not reach saturation limits required to crystallize the columbite–tantalite at the magmatic stage (Chevychelov, 2013), which suggests their crystallization from Al–Na–F melt at the late magmatic stage (Badanina et al., 2010) or during metasomatic redistribution (Zaraisky, 2004). Some amounts of tin and tungsten are accumulated within RPG massifs, but saturation required to crystallize wolframite and cassiterite at the magmatic stage is not attained (Badanina, 2008; Syritso et al., 2018). However, unlike tantalum and niobium, these elements are characterized by the high fluid–melt partition coefficients (Chevychelov, 2013). This facilitates their partitioning into fluid and escape into host rocks, where tin and tungsten form two types of accumulations: in the outer–inner contact greisens and metasomatites and in quartz–vein mineralization in host rocks of the RPG massifs. The occurrence of spatial zoning of mineralization with diverse metallogenic specialization around RPG massifs could be explained by the evolution of physicochemical state of fluid-saturated melt with a change of P-T conditions, acidity–basicity regime, and, as a result, a sequence of separation of

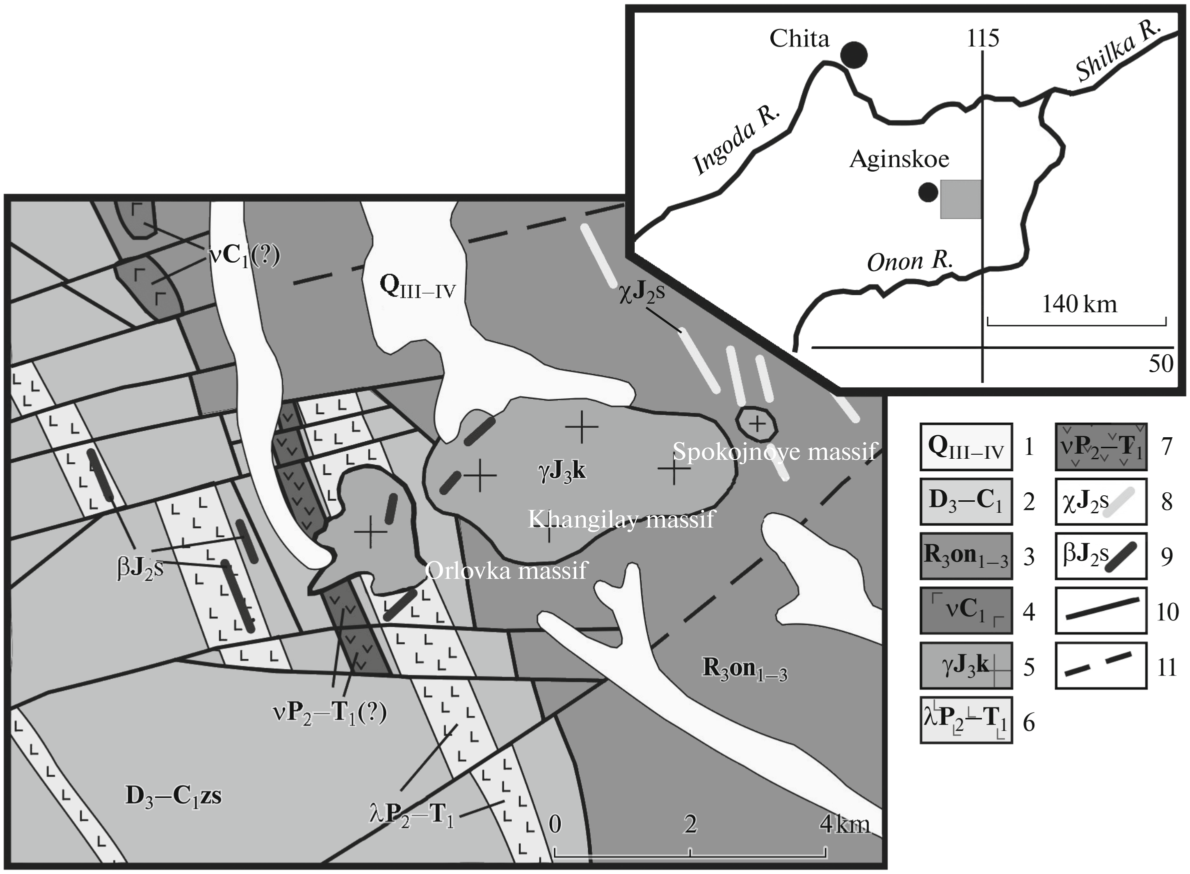

Fig. 1. Schematic geological map of the Khangilay ore cluster after (Abushkevich and Syritso, 2007). (1) Quaternary deposits; (2) Upper Devonian–Lower Carboniferous gravelstones, sandstones, and siltstones; (3) Upper Riphean sandstones and silty pelites; (4) Early Carboniferous (?) subalkaline gabbro (Inkizhin stocks); (5) Late Jurassic granites of the Kukulbei Complex (Khangilay intrusion); (6–9) rocks of dike complex: (6) Late Permian–Early Triassic trachydacites and trachyrhyolites; (7) Late Permian–Early Triassic (?) diabases, (8) Middle Jurassic lamprophyres (kersantites, spessartites); (9) Middle Jurassic dolerites. (10, 11) faults. Dike lamprophyre and dolerite bodies are shown out-of-scale.

diverse volatiles that serve as complexing agents for the transfer of trace elements. The formation of diverse spatially separated genetic types of mineralization within framework of the massifs reflects differences in the crystallization of ore mineralization and provides prerequisites for revealing age differences between formation stages of such OMS. Using known genetic concepts underlain by the direct study of mineral-forming medium, the formation of the indicated minerals reflects the evolution of silicate melt within wide temperature interval, including the magmatogenic–hydrothermal transition: from late-magmatic stage (crystallization of columbite–tantalite from aluminosilicate melt or salt medium) to greisenization (crystallization of cassiterite from fluid), and proper hydrothermal process (crystallization of wolframite from hydrothermal solution). Of special interest is dating of ore minerals—columbite–tantalite, cassiterite, wolframite—and their relations with formation time of host granite.

BRIEF GEOLOGICAL CHARACTERISTICS OF THE MODEL OBJECT

We attempted to estimate the age relations of parental rock and ore mineralization by the example of deposits of the Khangilay ore cluster in Eastern Transbaikalia (Fig. 1), which are represented by satellites of the Khangilay intrusion with different geochemical and metallogenic specialization: Orlovka massif of Li–F amazonite granites with tantalum mineralization and Spokojnoye massif of albitized and greisenized granites with tungsten mineralization.

According to U-Pb geochronological zircon studies (SHRIMP, VSEGEI), all three massifs were formed practically simultaneously: biotite granites of the Khangilay massif are dated at 140.3 ± 2.6 Ma; protolithionite granites of the Orlovka massif define an age of 140.6 ± 2.9 Ma; and muscovite granites of the Spokojnoye massif yield an age of 141.3 ± 1.8 Ma (Abushkevich and Syritso, 2007). Obtained age data are well consistent with results of Rb-Sr dating of rocks of the Khangilay intrusion (Kostitsyn et al., 2004).

Based on these studies, the simultaneous formation of three massifs of the Khangilay ore cluster was revealed for the first time and concept of their genetic relation was proposed.

Since the Khangilay intrusion is confined to a zone of sharp structural unconformity, the indicated satellites are localized in host rocks of different age: the Spokojnoye massif is contained in the Riphean sandy–shaly sequence, while the Orlovka massif is hosted in the weakly metamorphosed Devonian–Carboniferous silty-sandy rocks, which suggests differences in their protolith and source.

According to the isotope-geochemical studies (Dolgopolova and Seltmann, 2005; Abushkevich and Syritso, 2007), the protolith of the Khangilay ore cluster could be host metasedimentary rocks of the Zun–Shiviin Formation, the isotope signatures of which indicate a crustal nature ($^{206}Pb/^{204}Pb = 18.06–19.07$, $^{207}Pb/^{204}Pb = 15.51–15.60$), $\varepsilon_{Nd}(140) = –8.7, –6.9$). Inconsistency in $\varepsilon_{Nd}(T)$ between inferred protolith and three massifs of the Khangilay intrusion (Table 1) could be caused by the melt interaction with fluid, which has mantle characteristics and was derivative of mantle diapir (Abushkevich and Syritso, 2007). Of importance for understanding the genesis of the Orolovka satellite is its spatial association with Paleozoic trachyrhyodacite covers ($\varepsilon_{Nd}(235) = –6.7$), which were produced by melting of host sandy–shaly rocks (Syritso et al., 2001; Badanina et al., 2008), as well as the abundance of 320–149 Ma subalkaline basaltic dikes (lamprophyres, diabases, and dolerites) and subalkaline gabbroid stocks ($\varepsilon_{Nd}(320) = 2.9$, $\varepsilon_{Nd}(149) = –0.1$) around this massif. Specialization of the trachyrhyodacites for lithophile trace elements typical of Li-F granites (Li up to 950 ppm, Rb up to 2400 ppm, and F up to 0.18 wt %) and their enrichment in high-field strength elements (Zr up to 90 ppm, total REE up to 227 ppm, Th up to 43 ppm) typical of basaltic rocks of the dike complex suggest the possible mixing of crustal and deeper mantle matter. The similar geochemical composition (total REE content and their distribution patterns) of inherited zircon cores from the Orlovka massif and zircon from the trachyrhyodacite and the close ages of their crystallization (254 ± 5 and 235 ± 2 Ma, respectively) point to the common source of Li–F melts and rhyolite chambers.

Since the discovery of RPG-related trace metals (1960s) up to the present, this intrusion gained great attention in the Russian and foreign literature, which is mainly determined by the fact that two satellite massifs representing different geochemical types of RPG are restricted to a single parent biotite granite massif. The pathways in the solution of this problem have been determined by progress in methods and approaches to studying ore-bearing granitoid systems: mineral-rock level (Zalashkova, 1969; Syritso, 2002), experimental (Chevychelov, 2013), and numerical (Syritso et al., 2011) modeling, isotope-geochemical studies (Kostitsyn, 2004; Dolgopolova and Syritso, 2007), and examination of mineral-forming medium (Badanina et al., 2010). In recent years, isotope techniques of dating ore minerals have been intensely developed. With allowance for the diversity of ore formation processes at the considered objects, of interest was to reveal their age differences.

The inner structure of the ore-bearing massifs of the intrusion has been repeatedly considered in literature, including above mentioned works. Based on obtained results, the Orlovka massif has the following structure. The deepest horizons of the massif are made up of two-mica porphyritic granites with Li-siderophyllite and muscovite. Upsection, they grade into porphyroblastic microcline–albite granites with "snow-ball" quartz and Li-phengite–muscovite. A sharp contact of these rocks with underlying two-mica granites and their enrichment in lithophile trace elements, including fluorine and lithium (Badanina et a., 2010), give grounds to consider these rocks as independent phase produced by separation of residual fluid-saturated melt from the Khangilay magmatic chamber. Overlying rock varieties, including microcline–albite granites with green muscovite and ore-bearing lithionite–amazonoite–albite granites, represent the result of such late to post-magmatic transformations of melt of porphyroblastic granites as liquid silicate immiscibilities and/or post-magmatic metasomatism.

Ore mineralization of the Orlovka massif is represented by columbite–tantalite and less common microlite, which form fine-grained dissemination in the amazonite granites of the apical part of the massif. Close sizes and paragenetic association of columbite–tantalite with accessory minerals (zircon, monazite) served as prerequisite for concept of their magmatogenic genesis. Cassiterite, in addition to dissemination, also forms large segregations in quartz veinlets and in zinnwaldite–topaz greisen. The largest cassiterite aggregates (up to 7 kg) were found in the zinnwaldite–topaz–amazonite dikes in the outer contact. Wolframite is scarcer in the granite, forms the Ferberitovoe vein-greisen stockwork occurrence in the northeastern outer contact.

In the Spokojnoye massif, the ore is mainly represented by fine-grained wolframite in highly albitized and greisenized granites and greisens, and only small part (4%) of ores is accumulated in quartz veins in the inner and outer contacts.

It was interesting to determine the crystallization age of main ore minerals of both massifs, their time relations with host rocks and, in general to estimate, the duration of ore-forming system. For correct comparison of age data, it was planned to analyze rocks and minerals based on U-Pb isotopic system. Unlike Rb-Sr dating, this technique placed constraints on the possible errors related to the superimposed metasomatic processes.

Table 1. Age and isotope-geochemical characteristics of ore minerals and host rocks in the deposits of the Khangilay ore cluster, East Transbaikalia

Massif, deposit	Rock, granite	Object	Age, Ma/method	Isotope-geochemical parameters		Reference
				$^{87}Sr/^{86}Sr$	ε_{Nd}	
	Host sequences of the Zun–Shiviin Formation D–C_1 (zs)	rock		0.709485	–8.7; –6.9	Abushkevich and Syritso, 2007
	Trachyrhyodacites	zircon	235 ± 2.4 (U-Pb, SHRIMP)			
		rock		0.70465	–6.1	
Khangilay	biotite	rock	145 ± 3 (Rb-Sr)	0.7067 ± 4		Kostitsyn et al., 2004
					–2.6	Abushkevich and Syritso, 2007
		zircon	140.3 ± 2.6 (U-Pb, SHRIMP)			
Orlovka	Protolithionite	zircon	140.6 ± 2.9 (U-Pb, SHRIMP)			
	Porphyroblastic microcline-albite		145 ± 1 (U-Pb, ID-TIMS)			Original data
	Amazonite	rock	145.2 ± 1.8 (Rb-Sr)	0.706 ± 5		Kostitsyn et al., 2004
					–1.7	Abushkevich and Syritso, 2007
		Columbite–tantalite	145 ± 1 (U-Pb, ID-TIMS)			Anisimova et al., 2013
	Zinnwaldite–topaz–greisens	cassiterite	144.2 ± 0.3 (U-Pb, ID-TIMS)			Original data
Spokojnoye	Muscovite	rock	146.9 ± 0.7 (Rb-Sr, rock-mineral isochron)	0.70658 ± 28	–3.4	Abushkevich and Syritso, 2007
		zircon	141.3 ± 1.8 (U-Pb, SHRIMP)			
		muscovite	144.6 ± 1.6 (Ar-Ar)			Original data
	Quartz–wolframite veins, pegmatoids, greisens	wolframite	141.8 ± 0.6 (Rb-Sr)	0.710832 ± 42	–2.2 –2.3	Syritso et al., 2018
			140.1 ± 1.4 (Sm-Nd)	0.711048	–2.5	
Uval'noe	Quartz–wolframite vein in shales	Mineral isochron (K-Fsp, muscovite, fluorite)	146.4 ± 1.47 (Rb-Sr)	0.708598 ± 35		

Table 2. Localities of sampling for analytical studies presented in this paper.

Massif	Rock, granite	Studied object (sample number)	Description	Sampling localities
Orlovka	Porphyroblastic microcline–albite	Zircon (O-2299)	Accessory zircon	Hole 628, depth of 170–176 m
	Zinnwaldite–topaz greisen	Cassiterite (O-306)	Cassiterite monofraction	Quarry, 1000 horizon
Spokojnoye	Muscovite	Muscovite (C-190)	Monofraction of gray muscovite	Hole 176, depth of 348 m

ANALYTICAL TECHNIQUES

Zircon was extracted using conventional heavy-liquid technique. Unfortunately, ore-bearing amazonite granites lack zircon required for dating. The underlying porphyroblasic granites replaced by lepidolite–amazonite assemblage contain high-U zircon (up to 10 wt % UO_2), which is not suitable for dating by local U-Th-Pb method (SHRIMP). In this relation, the U-Pb geochronological studies of zircon involved preliminary high-temperature annealing and acid treatment (CA-ID-TIMS).

Zircon crystals selected for U-Pb geochronological studies were subjected to multistage removal of surface contamination by alcohol, acetone, and 1 M HNO_3. After each stage, zircon grains (or their fragments) were washed with extra-pure water. The chemical decomposition of zircon and extraction of U and Pb were carried out using a modified Krogh technique (Krogh, 1973). The discordance was reduced by chemical abrasion (acid treatment with a mixture of 35% HF + 15% HNO_3 in proportion 5 : 1 at 220°C) with preceding high-temperature annealing for 48 h at 850°C (Mattinson, 2005). The isotope studies were performed using $^{235}U–^{202}Pb$ spike. Blank was no more than 15 pg Pb and 1 pg U. The isotope studies were conducted at the Institute of Precambrian Geology and Geochronology of the Russian Academy of Sciences (IPGG RAS, St. Petersburg) on a multichannel TRITON TI mass spectrometer in static and dynamic regimes (using electron multiplier). The measurement accuracy of U/Pb ratio and U and Pb contents was 0.5%. Experimental data were processed using PbDAT and ISOPLOT softwares (Ludwig, 1991, 2003). Ages were calculated using values of the uranium decay constants (Steiger and Jager, 1976). Correction for common lead was introduced according to the Stacey–Kramers model (Stacey and Kramers, 1975).

Picked up purest cassiterite grains after multiple treatment in an ultrasonic bath in H_2O were thoroughly ground in mill. Then aliquot taken for analysis was treated with a mixture of 6 N HCl + 6 N HNO_3 for two hours on heater at 100°C, and was subjected to triple washing in extrapure water at 100°C, 15 min at each stage. The samples were decomposed in 10 N HCl within temperature range of 230–235°C in thermostat for two days in steel bombs with Teflon liners. The lead and uranium contents were determined by isotope dilution using mixed $^{235}U/^{208}Pb$ spike. The chromatographic extraction of Pb and U was carried out using technique (Manhes et al., 1978) in bromoform with subsequent extraction of U on an UTEVA ion exchange resin in nitrate form. The laboratory blank was 25 pg Pb and 5 pg U. The isotope studies were performed at the IPGG RAS on a TRITON TI multicollector mass spectrometer in static mode.

The $^{40}Ar/^{39}Ar$ dating of muscovite was conducted at the Institute of Geology and Mineralogy of the Siberian Branch of the Russian Academy of Sciences (IGM SB RAS, Novosibirsk, analyst D.S. Yudin) using technique (Travin et al., 2009). For dating, gray muscovite monofraction was extracted using conventional electromagnetic separation technique from the least altered muscovite granites from the deep horizons of the Spokojnoye massif.

RESULTS OF ISOTOPE-GEOCHRONOLOGICAL STUDIES

To solve given task, the previous U-Pb geochronological studies of zircons from rocks of three massifs of the Khangilay intrusion (Abushkevich and Syritso, 2007) and analysis of tantalite from granites of the Orlovka massif (Anisimova et al., 2013) were supplemented by U-Pb dating of zircon from ore-bearing porphyroblastic granites and cassiterite from the ore zone of the Orlovka massif. In addition, $^{40}Ar/^{39}Ar$ method was used to estimate the age of muscovite from granites of the Spokojnoye massif. Geochronological sampling localities are presented in Table 2.

U-Pb geochronological studies of zircon from porphyroblastic granites were performed using modified technique with preliminary high-temperature annealing and acid treatment (CA-ID-TIMS) (Mattinson, 2005), which, as was shown in (Ivanova et al., 2021), can be successively applied even for high-U metamict zircon. Concordant age estimate of zircon from por-

Table 3. Results of U-Pb geochronological studies of zircon from porphyroblastic microcline–albite granites of the Orlovka massif (sample O-2299)

Ordinal no.	Number of grains, characteristics, size fraction, preliminary treatment	U/Pb	Isotope ratios					Rho	Age, Ma		
			$^{206}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb^a$	$^{208}Pb/^{206}Pb^a$	$^{207}Pb/^{235}U$	$^{206}Pb/^{238}U$		$^{207}Pb/^{235}U$	$^{206}Pb/^{238}U$	$^{207}Pb/^{206}Pb$
1	35 gr., transp., brown., 50–150 μm, prism. and long-prism., HA, acid tr.=2.0	41.9	1271	0.0498 ± 1	0.1056 ± 1	0.1576 ± 2	0.0230 ± 1	0.88	149 ± 1	146 ± 1	186 ± 2
2	65 gr., transp., brown., 50–150 μm, Prism. and long-prism., HA, acid tr.=4.0	43.3	1858	0.0490 ± 1	0.1071 ± 1	0.1539 ± 3	0.0228 ± 1	0.73	145 ± 1	145 ± 1	149 ± 3
3	15–20 gr., transp., brown., 50–150 μm, long.-prism., BO, acid tr.=4.0	34.0	206	0.0490 ± 1	0.1425 ± 1	0.1541 ± 5	0.0228 ± 1	0.52	146 ± 1	145 ± 1	148 ± 6

[a] Isotope ratios corrected for blank, fractionation, and common lead; Rho is the error correlation coefficient of $^{207}Pb/^{235}U$–$^{206}Pb/^{238}U$; (HA) high-temperature annealing of zircon; acid tr. = 3.0—acid treatment of zircon with exposure time (hours). The error values (2σ) correspond to last digits after comma.

phyroblastic granites corresponds to 145 ± 1 Ma (MSWD = 0.76) (Table 3, Fig. 2a) and coincides with the lower intercept age of discrodia plotted for all analytical points of zircon (145 ± 1 Ma, MSWD = 0.19).

U-Pb age of cassiterite from the quartz–topaz greisen in the inner contact of the Orlovka massif was determined by isotope dilution (ID-TIMS) using a new technique (Rizvanova and Kuznetsov, 2020) and corresponds to 144.2 ± 0.3 Ma (Table 4, Fig. 2b).

The $^{40}Ar/^{39}Ar$ age of gray muscovite from muscovite granites of deep horizons of the Spokojnoye massif was determined by a stepwise heating. As seen in Table 5 and Fig. 3, this muscovite defines a conditional plateau with age values of 144.6 ± 2.2 Ma at relatively even stepwise spectrum. Based on this analysis, the closure of isotope system of muscovite occurred 144.6 ± 2.2 Ma.

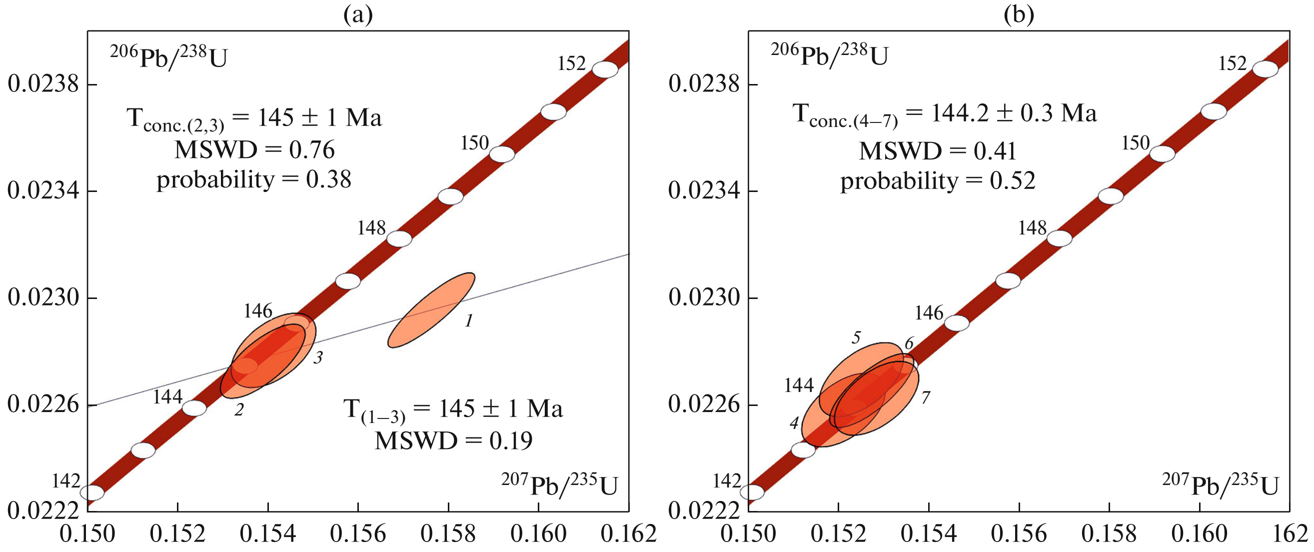

Fig. 2. Concordia diagram for zircon from porphyroblastic microcline–albite granites (a) and cassiterie from zinnwaldite–topaz greisen (b) of the Orlovka massif. Sample numbers in the diagrams correspond to the ordinal numbers in Tables 3 and 4.

Table 4. Results of U-Pb isotope studies of cassiterite from zinnwaldite–topaz greisen in the inner contact of the Orlovka massif (sample O-306)

Ordinal no.	Characteristics of mineral, conditions of preliminary treatment	Weight, mg	U, ppm	Pb, ppm	Isotope ratios					Rho	Age, Ma		
					$^{206}Pb/^{204}Pb$	$^{207}Pb/^{206}Pb^{a}$	$^{208}Pb/^{206}Pb^{a}$	$^{207}Pb/^{235}U$	$^{206}Pb/^{238}U$		$^{207}Pb/^{235}U$	$^{206}Pb/^{238}U$	$^{207}Pb/^{206}Pb$
4	Dark brown cryst. 1–3 mm, on heater, in 6 N HCl ± 6 N HNO_3	24.08	8.8	0.23	257	0.0489 ± 1	0.0002 ± 1	0.1521 ± 4	0.0226 ± 1	0.52	143.8 ± 0.4	144.0 ± 0.2	141.2 ± 5.3
5	Dark brown cryst. 1–3 mm, on heater, in 6 N HCl ± 6 N HNO_3	19.24	7.8	0.18	617	0.0487 ± 1	0.0006 ± 1	0.1525 ± 4	0.0227 ± 1	0.56	144.1 ± 0.3	144.7 ± 0.2	135.4 ± 4.4
6	Dark brown cryst. 1–3 mm, on heater, in 6 N HCl ± 6 N HNO_3 twice	25.95	8.4	0.20	376	0.0489 ± 1	0.0002 ± 1	0.1528 ± 4	0.0227 ± 1	0.77	144.3 ± 0.4	144.4 ± 0.3	143.2 ± 4.4
7	Dark brown cryst. 1–3 mm, on heater, 6 N HCl ± 6 N HNO_3 twice	20.59	8.7	0.19	1075	0.0490 ± 1	0.0005 ± 1	0.1529 ± 4	0.0226 ± 1	0.55	144.4 ± 0.4	144.2 ± 0.2	147.9 ± 5.0

[a] Isotope ratios corrected for blank, fractionation, and common lead; Rho is the error correlation coefficient of $^{207}Pb/^{235}U$–$^{206}Pb/^{238}U$. Errors (2σ) correspond to last digits after comma.

Table 5. Results of $^{39}Ar/^{40}Ar$ dating of muscovite from muscovite granite of the Spokojnoye massif (sample C-190)

T, °C	t, min	^{40}Ar, 10^{-9} cm^3	$^{40}Ar/^{39}Ar$	±1σ	$^{38}Ar/^{39}Ar$	±1σ	$^{37}Ar/^{39}Ar$	±1σ	$^{36}Ar/^{39}Ar$	±1σ	Ca/K	$\Sigma^{39}Ar$, %	Age, Ma	±1σ
Muscovite, J=0.003955±0.000041, weight 26.66 mg														
600	10	19.6	88.1	3.858	0.306	0.01440	14.0	1.0538	0.2196	0.04471	50.5	1.0	158.7	84.6
700	10	22.6	29.5	0.148	0.067	0.00306	3.2	0.2020	0.0211	0.00501	11.5	4.3	158.7	9.8
800	10	53.2	23.1	0.072	0.043	0.00114	1.7	0.1296	0.0072	0.00311	6.3	14.5	143.6	6.2
900	10	190.5	21.6	0.025	0.018	0.00011	0.2	0.0202	0.0007	0.00092	0.6	53.3	146.3	2.3
975	10	67.7	21.6	0.017	0.023	0.00045	0.5	0.0400	0.0019	0.00037	2.0	67.0	144.5	1.6
1050	10	123.5	21.7	0.050	0.018	0.00028	0.3	0.0275	0.0014	0.00207	1.1	92.0	145.9	4.3
1130	10	40.0	21.9	0.029	0.034	0.00096	1.0	0.1775	0.0035	0.00091	3.7	100.0	142.9	2.3

1σ—standard deviation.

DISCUSSION

The isotope-geochronological studies of rare-metal granites and ore minerals of the Khangilay ore cluster led us to discuss separately the analytical data obtained by different methods. As seen from Table 1, the ages of the studied rocks obtained by local U-Pb dating (SHRIMP, VSEGEI) clearly differ from those obtained using U-Pb (ID-TIMS), Rb-Sr, and Ar-Ar geochronological methods. There is a systematic difference between these data, which demonstrates a stable rejuvenation (about 5 Ma, based on average values) of ages obtained by local U-Pb method on zircon compared to the analytical studies performed by other aforementioned methods. At the same time, it is noteworthy that analytical studies performed by U-Pb (ID-TIMS), Rb-Sr, and Ar-Ar methods yield well consistent results. Thus, as seen from Table 1, two variants of age intervals can be distinguished for the formation of the Khangilay intrusion. The local dating yielded 140.3 ± 2.6 Ma for the Khangilay massif, 140.6 ± 2.9 Ma for the Orlovka massif, and 141.3 ± 1.8 for the Spokojnoye massif. The Rb-Sr dating gave 145 ± 3 Ma for the Khangilay massif, 145.2 ± 1.8 Ma for the Orlovka massif (Kostitsyn, 2004), and 146.9 ± 0.7 Ma for the Spokojnoye massif (Abushkevich and Syritso, 2007). With allowance for the intensity of superimposed metasomatic processes in rocks of ore-bearing

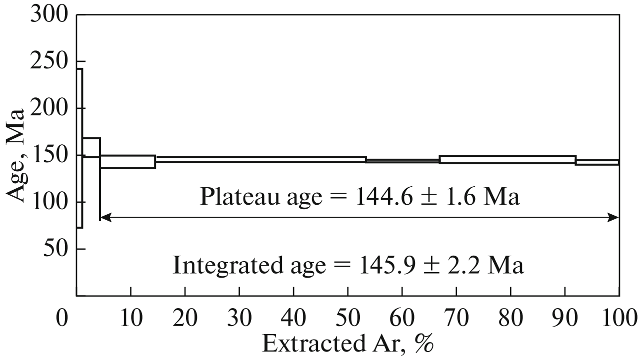

Fig. 3. Results of $^{40}Ar/^{39}Ar$ dating of gray muscovite from muscovite granite of the Spokojnoye massif (sample C-190).

satellites, the isotope-geochronological studies of minerals were performed to control whole-rock ages estimates. In particular, the U-Pb (CA-ID-TIMS) age of zircon from porphyroblastic granites of the Orlovka massif corresponds to 145 ± 1 Ma. The Ar-Ar age of gray muscovite from the Spokojnoye massif was determined as 144.6 ± 1.6 Ma. Thus, in both cases, obtained data are well consistent with results of Rb-Sr dating.

Obtained age determinations indicate a practically simultaneous formation of the parent Khangilay massif and its satellites. Thus, our studies confirmed previous Rb-Sr data by Kostitsyn et al. (2004), who for the first time revealed their simultaneous formation and assumed their genetic relationship.

The comparison of obtained age values and initial Sr isotope ratios for the Khangilay ore cluster with those of similar objects of the Etyka ore cluster and the Ary-Bulak ongonites of the Argun terrane served as evidence for the concept of their formation during a single magmatic stage of crustal granite formation under the influence of powerful mantle energetic source (Kostitsyn et al., 2004). At the same time, it is known that the Kukulbei Complex ascribed to a single RPG geochemical type (Tauson, 1977) comprises two granitoid subtypes, which at close petrogeochemical composition of "parental" biotite granites sharply differ in the trend of crystallization differentiation and metallogenic specialization of mineralization. These subtypes are known for the majority of the Phanerozoic rare-metal provinces and are distinguished as independent leucogranite–alaskite formations (Marin and Beskin, 1983), geochemical types (Li-F and standard, Kovalenko, 1977), or derivatives of intrusive series of different alkalinity (Syritso, 2002). In foreign literature, they are distinguished as peraluminous high fluxing and peraluminous low fluxing RPG subtypes, which well reflects the sense of differences of the Khangilay satellites in the contents of fluxing components (F and Li) in their melts. In the studied region, the rocks of these RPG subtypes known as tantalum- and tungsten-bearing types are spatially separated. The tungsten-bearing massifs are typical of the Aga terrane (Sakhanai, Durulgui, and Khangilay intrusions) with numerous satellites and greisen–vein tungsten mineralization. The tantalum-bearing massifs of Li-F amazonite granites are located in the Argun terrane (Etyka and Achikan massifs, Turga intrusion). Such tendency suggested the differences between these RPG types in magma formation conditions, first of all, in protolith and melting degree. Available materials, including geochemical data, testify the involvement of indicated possible reasons of spatial separation of above mentioned RPG types. This assumption is verified by the Khangilay intrusion, which produced both RPG types within a single intrusion, including manifestation of Li–F type that is not typical of the Aga Zone. However, the solution of these questions is beyond the scope of this work. Our study has been focused on the consideration of genetic relationship of satellites assuming the common parental melt corresponding to the melt of the Khangilay massif and revealing the conditions and mechanisms of formation of two geochemically different ore-bearing granites with rare-metal and tungsten mineralization. This led us to the need for study of mineral-forming media in the derivatives of the satellite massifs (Badanina et al., 2010; Syritso et al., 2021).

These studies were used to develop concepts of the possible different evolution paths of the melt of the Khangilay intrusion depending on differences in the local geological position of minor massifs. As seen from Fig. 1, the Orlovka massif is confined to the deep-seated fault zone, which marks the sharp structural unconformity between Devonian–Carboniferous and Riphean deposits. This fault is traced by thick dike-cover of trachyrhyodacites, diabase dike, and small stocks of the Inkizhin subalkaline gabbroids. Based on $\varepsilon_{Nd}(144) = -1.7$, such setting for the rocks of the Orlovka massif suggests the higher contribution of mantle component in its formation compared to the Spokojnoye massif with $\varepsilon_{Nd}(144) = -3.5$.

The indicated differences in the geological position of satellites could modify the evolution trends of fluid-saturated melt, which, in addition to crystallization fractionation, also reveals liquid immiscibility and postmagmatic metasomatism (Badanina et al., 2010). The possibile derivation of both types of ore-bearing RPG from a single parental melt is expressed in the trace-element composition of main ore minerals of the Khangilay ore cluster: the wolframites of the Spokojnoye deposit are characterized by the high contents of Nb (1.5 wt % Nb_2O_5) and Ta (0.8 wt % Ta_2O_5), whereas columbite–tantalites of the Orlovka deposit with 2.2 wt % WO_3 contain wolframite–columbite isomorphic series, with formation of minerals of intermediate composition such as qitianlingite.

The above mentioned data indicate that the crystallization age of zircon from porphyroblastic granites, the main rock variety of the Orlovka massif, was determined by U-Pb (CA-ID-TIMS) method at 145 ± 1 Ma (MSWD = 0.76), which is comparable with 145.2 ± 1.8 Ma obtained by Rb-Sr dating for ore-bearing lepidolite–amazonite granites (Kostitsyn et al., 2004). Obtained data revealed no significant difference in age estimates within complete differentiation series of the Orlovka massif: from protolithionite granites of deep horizons to the porphyroblastic granites composing the main volume of the massif and further to the ore-bearing lepidolite–amazonite granites of the apical part of the massif. Thus, the differentiation from barren (5.55 ppm Ta) to ore-bearing (162 ppm Ta) melt was too rapid process to be determined by isotope-geochronological methods.

Columbite–tantalite defines an age of 145 ± 1 Ma (Anisimova and Abushkevich, et al., 2013), which seemed to be practically identical to the crystallization age of zircon from porphyroblastic granites. The revealed simultaneous crystallization of columbite–tantalite and zircon is consistent with magmatogenic concept of the genesis of the Ta–Nb mineralization.

The crystallization age of cassiterite from zinnwaldite–topaz greisen in the inner contact zone of the Orlovka massif determined by U-Pb ID-TIMS method using a new technique (Rizvanova and Kuznetsov, 2020) corresponds to 144.2 ± 0.3 Ma. With allowance for the paragenesis, cassiterite was likely formed at the postmagmatic stage. Unfortunately, the precision of the existing dating methods is insuffcent to reveal the interval between the magmatic and postmagmatic stages, which is related to the evolution of ore-magmatic system during ore accumulation. Difference in isotope systems and methods applied to date ore minerals (U-Pb age determination of columbite–tantalite and cassiterite at the Orlovka massif and Rb-Sr dating of wolframite at the Spokojnoye massif) complicates correct comparison of the formation time of rare-metal and tin–tungsten mineralization. Nevertheless, obtained data indicate a very short-term formation of RPG granites of both types and accumulation of trace elements in them. It is not occasional that ore minerals, cassiterite and columbite–tantalite, are widely used in recent publications on China as geochronometers for estimating the age of rare-metal granites, pegmatites, and greisens (Che et al., 2019).

Different age relations between ore-bearing rocks and wolframite mineralization were found for “standard” RPG type with low lithium and fluorine contents. The study of two isotope systems (Rb-Sr and Sm-Nd) of wolframites from different assemblages (scattered dissemination in granites, greisens, quartz veins, and pegmatoids) in the Spokojnoye massif revealed the gap between crystallization time of wolframite and host granite. Based on Rb-Sr data, this age gap corresponds to 3.8 Ma. Close age interval was traced between the formation of the Pervomaisky massif and tungsten-ore greisenization (≈1.3 Ma) within the Dzhida W–Mo deposit in Western Transbaikalia (Chernyshev et al., 1998), which in our opinion suggests a “tight temporal proximity of initial and final processes of ore formation”. It is possible that the revealed age gap between crystallization of ore minerals and host rock could correspond to the duration of hydrothermal activity, which was responsible for the generation of Sn–W mineralization in the “standard-type” RPG. This concept is confirmed by the indifference of the melt of the Spokojnoye massif to the tungsten accumulation at the magmatic stage, which was established from study of melt inclusions in quartz in the differentiated series of rocks of the tungsten-bearing Spokojnoye massif (Syritso et al., 2018). Noteworthy are the results of Rb-Sr dating of tungsten-bearing paragenesis (K-feldspar, muscovite, fluorite) from quartz–wolframite vein of the Uval’noe deposit in the host rocks of the Spokojnoye massif. The Uval’noe deposit is located 1.5 km north of the Spokojnoye deposit and represents a stockwork with quartz-vein tin–tungsten mineralization lying in the host shales. Its position is shown in the schematic geological map of the Khangilay ore cluster in (Syritso et al., 2018, Fig. 4). The established age of these tungsten-bearing veins of 146.4 ± 1.5 Ma (Rb-Sr isotope system) shows that, unlike the Spokojnoye wolframite (141.8 ± 0.6 Ma), their age is identical to the age of granite massif of 146.9 ± 0.7 Ma (Rb-Sr isotope system). Thus, the quartz-vein tungsten mineralization in the framework of rare-metal granite massifs could be produced by hydrothermal vaporization of host rocks during emplacement of ore-bearing melt, which was accompanied by the removal of tungsten from magma chamber or its mobilization from host rocks.

A specific nature of Sn–W ore matter follows from revealed isotope heterogeneity between composition of wolframite and host granites. As seen from Table 1, wolframite is depleted in radiogenic neodymium, and, in contrast, has the greater content of radiogenic strontium (Abushkevich et al., 2010; Syritso et al., 2018). The isotope heterogeneity of radiogenic Nd and Sr can serve as sign of influence of deep-seated juvenile source. Based on Sr and Nd isotope data, the wolframite and cassiterite sources fall in the composition field of EMII-type enriched mantle source. These data are well consistent with concept on the mixed mantle–crustal nature of melts of rare-metal granites formed under the influence of plume-related mantle magmas (Yarmolyuk and Kovalenko, 2003).

CONCLUSIONS

Isotope-geochronological studies (U-Pb, Rb-Sr, Ar-Ar isotope systems) of age relations between the massifs of the Khangilay intrusion in Eastern Transbaikalia confirmed previous Rb-Sr data by Kostitsyn et al. (2004), who revealed for the first time the simultaneous formation of three intrusive massifs.

It was established that the formation ages of the studied granites (average values exclusive of errors) estimated by local U-Pb isotope zircon dating (SHRIMP) are younger compared to dates obtained by other isotope methods, including the Rb-Sr whole-rock and mineral dating, U-Pb zircon dating with chemical decomposition, and Ar-Ar muscovite dating. A stable difference of ~5 Ma is observed between these values.

The formation of a full differentiation sequence of Li-F granites of the Orlovka massif from barren protolithionite granites via predominant porphyroblasic granites to the ore-bearing lepidolite–amazonite apical granites is too rapid process to be determined by isotope geochronological studies.

The crystallization ages of ore mineralization of Li–F granites of the Orlovka massif determined by U-Pb (ID-TIMS) method (columbite–tantalite age of 145 ±

1 Ma and cassiterite age of 144.2 ± 0.3 Ma) are comparable to the crystallization age of zircon from ore bearing granite at 145 ± 1 Ma (U-Pb method, CA-ID-TIMS), which confirms the magmatogenic nature of rare-metal mineralization. In the standard-type RPG of the Spokojnoye massif, a time interval of 3.8 Ma was revealed between the age of the massif (Rb-Sr system) and wolframite crystallization (Rb-Sr system), which could correspond to the duration of hydrothermal system responsible for the production of tungsten mineralization.

Simultaneous formation of RPG massifs of the Khangilay intrusion, including the satellite massifs with rare-metal and tungsten mineralization, is caused by the short-term manifestation of magmatism, according to which "the age duration of the rare-metal melt was no more than 10^4–10^5 years" (Kostitsyn, 2004).

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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REFERENCES

Abushkevich, V.S. and Syritso, L.F., *Izotopno-geokhimicheskaya model' formirovaniya Li-F granitov Khangilaiskogo rudnogo uzla v Vostochnom Zabaikal'e* (Isotope-Geochemical Model of the Formation of Li–F Granites of the Khangilay Ore Cluster in the Eastern Transbaikalia), Sankt-Peterburg: Nauka, 2007.

Abushkevich, V.S., Badanina, E.V., and Syritso, L.F., Wolframite and cassiterite: age of forming and isotope characteristics Sr and Nd, *The 20-th General Meeting of the International Mineralogical Association.* Budapest, 2010, p. 419.

Anisimova, I.V., Abushkevich, V.S., Syritso, L.F., et al., U-Pb and Pb-Pb studies of tantalite as non-traditional mineral geochronometer of rare-metal granites (Orlovka Deposit, Eastern Transbaikalia), *Tr. XX simpoziuma po geokhimii izotopov* (Proc. 20th Symposium on Isotope Geochemistry), M.: IGEM RAN, 2013, pp. 30–32.

Badanina, E.V., First data on the wolframite content in highly specialized granitoid melts: evidence from melt inclusion study in quartz, *Voprosy geokhimii i tipomorfizm mineralov* (Questions of Geochemistry and Typomorphism of Minerals), St. Petersburg: *SPbGU*, 2008, vol. 6, pp. 42–49.

Badanina, E.V., Syritso, L.F., Abushkevich, V.S., et al., Geochemistry of ultra-potassic rhyodacite magmas from the area of the Orlovka Massif of Li–F granites in Eastern Transbaikalia: evidence from study of melt inclusions in quartz, *Petrology,* 2008, vol. 16, no. 3, pp. 299–311.

Badanina, E.V., Syritso, L.F., Volkova, E.V., et al., Composition of Li–F granite melt and its evolution during the formation of the ore-bearing Orlovka Massif in Eastern Transbaikalia, *Petrology,* 2010, vol. 18, no. 2, pp. 131–157.

Che, X.-D., Wang, R.-C., Wu, F.-Y., et al., Episodic Nb-Ta mineralization in South China: contraints from in situ LA-ICP-MS columbite–tantalite U-Pb dating, *Ore Geol. Rev.,* 2019, vol. 105, pp. 71–85.

Chernyshev, I. V., Gol'tsman, Yu.V., Bairova, E.D., et al., Rb–Sr geochronometry of sequential granite formation, greisenization, and hydrothermal mineralization: evidence from the Dzhida W–Mo Deposit, Western Transbaikal Region, *Dokl. Earth Sci.,* 1998, vol. 360, no. 4, pp. 613–616.

Chevychelov, V.Yu., Distribution of Volatiles, Rock-Forming, and Ore Components in the Magmatic Systems: Experimental Studies, *Extended Abstract of Doctoral (Geol.-Min) Dissertation,* Chernogolovka: IEM RAN, 2013.

Dolgopolova, A., Seltmann, R., and Stanley, C., Isotope systematics of ore-bearing and host rocks of the Orlovka–Spokojnoe mining district, eastern Transbaikalia, Russia, *Mineral. Deposit Res.,* Jingwen Mao, Frank P. Bierlein, Eds., Springer, 2005, pp. 747–751.

Ivanova, A.A., Sal'nikova, E.B., Kotov, A.B., et al., U-Pb (ID-TIMS) geochronological studies of high-uranium metamict zircons: new opportunities of familiar approaches, *Petrology,* 2021, vol. 29, no. 6, pp. 676–685.

Kostitsyn, Yu.A., Zaraiskii, G.P., Aksyuk, A.M., et al., Rb–Sr evidence for the genetic links between biotite and Li–F granites: an example of the Spokoinoe, Orlovka, and Etyka Deposits, Eastern Transbaikalia, *Geochem. Int.,* 2004, no. 9, pp. 822–829.

Kovalenko, V.I., *Petrologiya i geokhimiya redkometal'nykh granitoidov* (Petrology and Geochemistry of Rare-Metal Granitoids), Novosibirsk: Nauka, 1977.

Krogh, T.E., A low-contamination method for hydrothermal decomposition of zircon and extraction of u and pb for isotopic age determination, *Geochim. Cosmochim. Acta,* 1973, vol. 37, pp. 485–494.

Ludwig, K.R., PbDat for MS-DOS, version 1.21, *U.S. Geol. Surv. Open-File Rept.,* 1991, no. 88-542.

Ludwig, K.R., *Isoplot 3.70. A geochronological toolkit for Microsoft Excel*, *Berkley Geochronol. Center Spec. Publ.*, 2003, Vol. 3.

Manhes, G., Minster, J.E., and Allegre, C.J., Comparative uranium-lead and rubidium-srtontium study of the Severin amphoterite: consequences for early solar system chronology, *Earth Planet. Sci. Lett.,* 1978, vol. 39, no. 1, pp. 14–24.

Marin, Yu.B. and Beskin, S.M., Principles of extraction and systematics of Phanerozoic granitoid formations and associated mineral deposits, *Zap. Leningr. Gorn. Inst.,* 1983, vol. 95, pp. 32–40.

Mattinson, J.M., Zircon U-Pb chemical abrasion “CA-TIMS” method: combined annealing and multi-step partial dissolution analysis for improved and accuracy of zircon ages, *Chem. Geol.,* 2005, vol. 220, pp. 47–66.

Rizvanova, N.G. and Kuznetsov, A.B., A new approach to ID-TIMS U–Pb dating of cassiterite by the example of the Pitkäranta tin deposit, *Dokl. Earth Sci.,* 2020, vol. 491, no. 1, pp. 146–149.

Stacey, J.S. and Kramers, I.D., Approximation of terrestrial lead isotope evolution by a two-stage model, *Earth Planet. Sci. Lett.,* 1975, vol. 26, no. 2, pp. 207–221.

Steiger, R.H. and Jager, E., Subcomission of geochronology: convention of the use of decay constants in geo- and cosmochronology, *Earth Planet. Sci. Lett.,* 1976, vol. 36, no. 2, pp. 359–362.

Syritso, L.F., *Mezozoiskie granitoidy Vostochnogo Zabaikal’ya i problemy redkometal’nogo rudoobrazovaniya* (Mesozoic Granitoids of Eastern Transbaikalia and Problems of Rare-Metal Ore Formation), St. Petersburg: St. Petersb. Univ., 2002.

Syritso, L.F., Tabuns, E.V., Volkova, E.V., et al., Model for the genesis of Li–F pranites in the Orlovka Massif, Eastern Transbaikalia, *Petrology,* 2001, vol. 9. no. 3, pp. 268–290.

Syritso, L.F., Badanina, E.V., Abushkevich, V.S., et al., Fertility of rare-metal peraluminous granites and formation conditions of tungsten deposits, *Geol. Ore Deposits,* 2018, vol. 60, no. 1, pp. 33–51.

Syritso, L.F., Ivanova, A.A., Badanina, E.V., et al., Amazonite Li–F granites with REE–Nb–Zr–Th–U specialization: geochemistry, mineralogy, and isotope geochronology of the Turga Massif, Eastern Transbaikalia, *Petrology,* 2021, vol. 29, no. 1, pp. 54–76.

Tauson, L.V., *Geokhimicheskie tipy i potentsial’naya rudonosnost' granitoidov* (Geochemical Types and Ore Potential of Granitoids), Moscow: Nauka, 1977.

Travin, A.V., Yudin, D.S., Vladimirov, A.G., et al., Thermochronology of the Chernorud granulite zone, Ol’khon Region, Western Baikal Area, *Geochem. Int.,* 2009, no. 11, pp. 1107–1124.

Yarmolyuk, V.V. and Kovalenko, V.V., Deep geodynamics and mantle plumes: their role in the formation of the Central Asian Fold Belt, *Petrology,* 2003, vol. 11, no. 6, pp. 505–531.

Zalashkova, N.E., Zoning of metasomatic alteration of tantalum-bearing granites, *Mineralogo-geokhimicheskie i geneticheskie osobennosti redkometal’nykh apogranitov* (Mineralogical–Geochemical and Genetic Features of Rare-Metal Apogranites), Subbotin, K.D, Eds., Moscow: Nauka, 1969, pp. 5–29.

Zaraiskii, G.P., Conditions of formation of rare-metal deposits related to the granitoid magmatism, *Smirnovskii sbornik*-2004 (Smirnov Collection of Papers-2004), Moscow: Fond im. *Ak. V.I. Smirnova*, 2004, pp. 105–192.

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