The Aksug Porphyry Cu–Mo Deposit (Northeastern Tuva): Chronology of Magmatism and Ore Formation Processes (U–Pb and Re–Os Isotope Data) and Metallogenic Implications

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Abstract—The Aksug porphyry Cu-Mo deposit is located in a region of long-lasting magmatic activity. Gabbroids of the Khoito-Oka complex are the earliest intrusive rocks, in which the Aksug granitoid pluton hosting ore-bearing small porphyry intrusions is localized. The intrusive activity was terminated with emplacement of late leucogranite dikes. There are different viewpoints on the age of magmatism and mineralization of the Aksug deposit, with the concept of their Devonian age prevailing. To solve the debatable issue, we performed isotope geochronological studies and analyzed new results of U-Pb (SHRIMP-II) zircon dating and previously published Re-Os molybdenite dates $(518 \pm 2, 516 \pm 2, and 511 \pm 2 Ma)$. The concordant U–Pb zircon ages for igneous rocks are younger than the Re–Os age for mineralization. New U–Pb dating of Khoito-Oka gabbro-diorites has yielded an age of 503 ± 2 Ma. The U–Pb SHRIMP zircon age of tonalites from the Aksug pluton has been estimated at 504 ± 5 Ma. The U–Pb zircon ages for ore-related tonalite porphyry I and tonalite porphyry II are 500 ± 6 and 499 ± 6 Ma, respectively. The obtained SHRIMP age for leucogranite dike is 509 ± 4 Ma. Two groups of U–Pb dates have been obtained for each of the analyzed zircon samples: close to the Re–Os dates $(518-511 \pm 2 \text{ Ma})$ and younger (507-486 Ma). The weighted average zircon ages calculated for early and late populations from post-ore leucogranites are 515 ± 4 and 500 ± 4 Ma, respectively. We suggest that zircons with an age close to the Re-Os dates found in post-ore leucogranites were assimilated from the underlying substrate and zircons with an age of 500 ± 4 Ma crystallized from melt. The oldest U–Pb dates (509–515 Ma) of individual zircon grains from ore-bearing tonalite porphyry are consistent with the Re-Os molybdenite ages. Zircons from tonalite, tonalite porphyry, and Khoito-Oka gabbroids sometimes show internal textures indicating secondary alteration. The younger U-Pb concordia zircon ages relative to the Re-Os dates might be due to the influence of late thermal processes on the U-Pb isotopic system. The younger dates (486-507 Ma) of individual zircon grains probably reflect the time of the impact of a thermal fluid process. The weighted average of these younger dates $(502 \pm 2 \text{ Ma})$ falls within the weighted average age of post-ore leucogranites (500 ± 4 Ma). According to the Re–Os dates, the Aksug deposit formed at the end of the early Cambrian. Ore occurrences similar in magmatism and mineralization to the Aksug ore deposit are widespread in Tuva and in the Lake Zone in Mongolia. Therefore, it is necessary to reassess the role of the Cambrian and Devonian magmatism in the development of porphyry Cu-Mo mineralization both in Tuva and in the Altai-Sayan orogenic area.

Keywords: porphyry Cu-Mo deposits, Re-Os dating, U-Pb dating, Aksug deposit, Tuva

INTRODUCTION

Aksug is a large porphyry Cu–Mo deposit. Its ores contain Au, Pt, Pd, and Re. The deposit was discovered during a geological survey in 1952. At present, it is prepared for development. The deposit is located in northeastern Tuva, less studied than other Tuva regions. The main attention of researchers was always focused on the Aksug ore district. However, the degree of its geological exploration is insufficient to understand the geologic environment and reconstruct the conditions favoring the formation of large-scale mineralization.

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One of the most debatable issues is the age of igneous rocks and mineralization of the Aksug deposit. There are different views on this point. Sotnikov et al. (2003) dated the deposit at a wide interval (from Ordovician–Silurian to Devonian). Popov et al. (1988) recognized two stages of ore mineralization (Silurian and Devonian) and did not rule out the presence of Late Cambrian ores in the deposit. The oremagmatic system of the deposit formed in a long time span (Zabelin, 1992): The formation of intrusive rocks, metasomatites, and ores was initiated before the Devonian and ended not earlier than the Middle Devonian. On the geological maps (Mironyuk et al., 2012), the Aksug igneous rocks and ore occurrences of the Aksug type in northeastern Tuva are recognized as the Aksug complex of Early Devonian age.

Earlier we performed Re–Os and 40 Ar/ 39 Ar geochronological studies to refine the age of magmatism and mineralization of the Aksug deposit. Three Re–Os analyses of molybdenite yielded the following dates: 511 ± 2 , 516 ± 2 , and 518 ± 2 Ma (Berzina et al., 2003). The latter two dates are close to the Re–Os ages of molybdenite (517.3 ± 3 and 517.4 ± 3 Ma) obtained recently by Pollard et al. (2017). The above Re–Os ages correspond to the upper half of the early Cambrian.

The ⁴⁰Ar/³⁹Ar dating of amphibole, plagioclase, and sericite showed a wide time interval of magmatism in the Aksug deposit and the young age of its mineralization. Granitoids hosting ore-bearing porphyry intrusions formed in the period ~532-462 Ma. The endogenous activity during the formation of small intrusions and mineralization was in the interval ~404-324 Ma (Sotnikov et al., 2003). The above authors report the younger ⁴⁰Ar/³⁹Ar age of igneous rocks upon superposition of late processes. The older Re-Os dates for the mineralization relative to the ⁴⁰Ar/³⁹Ar age of these rocks suggest the influence of late processes on the ⁴⁰Ar/³⁹Ar isotopic system of small porphyry intrusions and the host granitoids. The disturbance of the isotopic system might have been related to the intrusion of dike-like granites and aplites within the deposit and of large intrusions of similar composition beyond it. These intrusive rocks are recognized as the Bren' complex of controversal age (Early Devonian or Late Ordovician) (Mironyuk et al., 2012). Leucogranite and aplite dikes cross the main porphyry Cu-Mo stockwork

mineralization and bear poor veinlet and nest pyrite–chalcopyrite mineralization (Sotnikov et al., 2003). The 40 Ar/ 39 Ar dates for K-feldspar and plagioclase of the leucogranites are in the interval ~336–324 Ma, which overlaps with the interval of the youngest dates for metasomatized porphyry of the small intrusions.

In this paper we present the first results of U–Pb geochronological studies of zircons from igneous rocks of the Aksug deposit. The obtained U–Pb dates, including those for igneous rocks with later developed mineralization, are somewhat younger than the Re–Os dates for molybdenite, which contradicts the geologic evolution. According to the results of U–Pb isotope dating, the calculated concordant age of zircon from granitoids of the Aksug pluton corresponds to the middle Cambrian, and the concordant age of zircon from ore-bearing porphyries, to the middle–late Cambrian boundary. These data indicate that the large-scale porphyry Cu–Mo mineralization in Tuva is related to the Cambrian magmatism. Below we consider the possible causes of the "rejuvenation" of U–Pb dates for igneous rocks of the Aksug pluton and small ore-bearing porphyry intrusions.

GEOLOGIC SETTING

The Aksug Cu–Mo deposit is located on the southern slope of the East Sayan Ridge in the zone of its junction with the West Sayan Ridge along the Kandat Fault. Its area



Fig. 1. Schematic geological map of northeastern Tuva, after Mironyuk et al. (2012), simplified (*a*), and location of the Aksug deposit (*b*). *a*, Stratified deposits: *1*, terrigenous rocks of the Atakshil Formation (D₂), *2*, volcanosedimentary rocks of the Kendei Formation (D₁:O₃), *3*, volcanosedimentary rocks of the Khamsara Formation (ε_1), *4*, sedimentary/metamorphic rocks of the Bilin Formation (RF₃); intrusions: *5*, Bren' syenite–granosyenite–granite complex (D₁:O₃), *6*, Tannu-Ola granodiorite–plagiogranite complex (ε_2), *7*, Aksug gabbro–plagiogranite–diorite complex (ε_{1-2}), *8*, Khoito-Oka pyroxenite–gabbro complex (ε_{1-2}); *9*, faults, *10*, location of the Aksug deposit. Numerals mark Cu and Mo ore occurrences probably assigned to the Aksug complex: 1, Kadyr-Oi, 2, Upper Dashtygoi, 3, Biche-Kadyr-Os, 4, Dashtyg, 5, Ulug-Kadyr-Os. *b*, Position of the study area (a rectangle) on the schematic tectonic map of the eastern Altai–Sayan area, after Obolenskii et al. (1999), simplified: *1*, Siberian craton, AR–PR₂, *2*, Derbina terrane of passive continental margin, PR₃, *3*, accretion–subduction zones, PR₃; *4*, island arc, V– ε , *5*, deep-water trough of continental margin, V–PZ₁, 6, shallow-water back-arc troughs, PR₃– ε_2 , 7, clastic carbonate deposits (including turbidites of continental margins), V–PZ₂; 8, volcanosedimentary rocks of continental margin, PZ₂; 9, metamorphic terrane.



Fig. 2. Schematic geological map of the Aksug porphyry Cu–Mo deposit, after Dobryanskii et al. (1992), simplified. *1*, Quaternary deposits; *2*, Middle Devonian terrigenous deposits; *3*, granodiorite, leucogranite, and aplite dikes; *4*, tonalite porphyry II; *5*, tonalite porphyry I; *6*, porphyritic tonalites; *7*, tonalites; *8*, hornblende quartz diorites; *9*, pyroxene–hornblende quartz diorites; *10*, diorites; *11*, gabbro; *12*, faults; *13*, ore stockwork outlines; *14*, location of boreholes; *15*, locality of sampling of molybdenite for Re–Os dating; *16*, locality of sampling for U–Pb dating.

is part of the Khamsara zone, a segment of a long belt of Vendian-Early Cambrian island-arc complexes formed in the Altai-Sayan area under subduction of the Paleoasian Ocean (Berzin and Kungurtsev, 1996). The ore district lies at the junction of the Kandat suture (fault) and the Dashtygoi rift graben and makes contact with this graben along the Cheldezrik regional fault (Fig. 1). The graben is formed by volcanics of the Kendei Formation of controversial age (O₃ or D₁) and unconformably overlying terrigenous deposits of the Atakshil Formation (D₂) (Mironyuk et al., 2012). The Kendei Formation is made up of effusive rocks mostly of intermediate and mafic compositions. Its subvolcanic rocks are gabbro and quartz porphyry, rhyolite porphyry, and rhyodacite porphyry, forming dikes, stocks, and extrusions. Some researchers regard them as ore field rocks (Glukhov, 2000). East of the ore district, there is the large Kadyr-Os granitoid pluton of the Tannu-Ola complex (\mathcal{C}_2), which formed at the accretion-collision stage of the regional evolution (Rudney, 2013).

The Aksug deposit is localized within the Aksug pluton of the Aksug gabbro–plagiogranite–diorite complex associated with a number of porphyry Cu–Mo ore occurrences. The Aksug pluton (~12 km² in area) crosses pyroxenite– gabbro intrusion of the Khoito-Oka complex. The Khoito-Oka igneous rocks intrude volcanosedimentary strata of the lower Cambrian Khamsara Formation and are cut by granitoids of the Tannu-Ola complex of middle Cambrian age (according to radiological data). The above geological data permit dating the Khoito-Oka complex at the early or middle Cambrian (Mironyuk et al., 2012). The ⁴⁰Ar/³⁹Ar date (532 Ma) obtained for the Aksug gabbroids (Sotnikov et al., 2003) corresponds to the early Cambrian.

The Aksug pluton is located at the intersection of the Dashtygoi graben of NW strike with an intense-fracturing zone of the Aksug Fault of EW strike. The pluton (plutonic complex) is formed by holocrystalline, predominantly medium-grained rocks hosting small stocks and dikes (orebearing complex) of porphyritic rocks spatially and temporally associated with Cu–Mo mineralization (Fig. 2).

The rocks of the pluton belong to two associations, gabbroid and granitoid. The gabbroid association comprises gabbro, gabbro-diorites, and pyroxene–amphibole diorites. The granitoid association involves quartz diorites, tonalites, and plagiogranites. The rocks commonly show propylitic alteration and contain disseminated pyrite and chalcopyrite. The content of sulfides increases toward the center of the deposit.

Small porphyry intrusions of the ore-bearing complex are localized at the center of the deposit. They are composed of fine- to medium-grained quartz diorite porphyrites, porphyraceous tonalites, and tonalite porphyry. Two stages of intrusion of tonalite porphyry are recognized: early (porphyry I) and late (porphyry II). The rocks were affected by intense quartz–sericite alteration and host the major amount of commercial mineralization. Small porphyry intrusions show occasional propylitic alteration.

Magmatism in the deposit terminated with the intrusion of late leucogranite and aplite dikes, which cut major stockwork porphyry Cu–Mo mineralization. Minor veinlet and nest pyrite–chalcopyrite mineralization is associated with these dikes.

The rocks of the Aksug pluton and ore-bearing small intrusions are calc–alkalic, of low alkalinity, with domination of Na over K. The late igneous rock association comprises high-K calc-alkalic leucogranites and aplites.

Two types of hydrothermal alteration of rocks are recognized: quartz–sericite and quartz–K-feldspar. The first type is related to ore-bearing small intrusions, which underwent the most considerable alteration. The widespread second type is related to the intrusion of numerous dikes of the late igneous rock association. Overprinting of this hydrothermal alteration on gabbroids and tonalites was accompanied by the formation of streaky syenite- and granodiorite-like rocks. Superposition of quartz–K-feldspar alteration on the ore-bearing small intrusions led to leaching of metals followed by their deposition and the formation of poor noncommercial mineralization (Sotnikov et al., 2003).

We studied zircons from the least altered rocks. In all rocks of the pluton and small intrusions, plagioclase is locally altered to saussurite and hornblende is partly replaced by chlorite, sericite, and carbonate.

METHODS

For geochronological studies we used monomineral fractions of zircon from the most representative rocks of the Aksug pluton, small porphyry intrusions, and the host gabbroids of the Khoito-Oka complex. The studies were carried out at the Center of Isotope Studies of the All-Russian Geological Institute, St. Petersburg (analyst N.V. Rodionov). The U-Pb isotope compositions were measured for individual zircon grains on a SHRIMP-II high-resolution secondary-ion mass spectrometer, following the standard technique (Williams, 1998; Larionov et al., 2004). The TEMORA (Black et al., 2003) and 91500 (Wiedenbeck et al., 1995) zircons were used as standards. The current of a primary beam of molecular negative oxygen ions was 4 nA. The obtained data were processed using the SQUID and ISOPLOT programs (Ludwig, 2009, 2012). The errors of singular analyses were at the 1σ level, and the errors of calculated concordant and weighted average 206 Pb/ 238 U ages were at the 2σ level. Cathodoluminescence images were obtained on a CamScan MX2500S scanning electron microscope.

The results of U–Pb zircon dating are given in Table 1.

A Re–Os isotopic age was estimated for two samples of molybdenite from the cores of borehole 23 (BH-23, sample S-0488v, depth of 242 m) and borehole 39 (BH-39, sample

S-0465, depth of ~550 m) drilled in the northern part of the Aksug deposit during prospecting in 1966–1981. The sample S-0465 is molybdenite of early generation from thin (\leq 5 mm) molybdenite–carbonate–quartz veinlets in sericitized tonalites. It was analyzed twice. The sample S-0488v is molybdenite of late generation from monomineral thin (<1 mm) seams in sericitized tonalite porphyry I.

A Re–Os isotope analysis of molybdenite was performed at the AIRIE (Applied Isotope Research for Industry and the Environment) Center at the University of Colorado, USA, guided by H. Stein (analyst A. Zimmerman) (Berzina et al., 2003). The analytical technique was described in detail earlier (Stein et al., 2001). The contents of Re and Os and the ¹⁸⁷Re/¹⁸⁸Os ratios were determined by the isotope dilution method. The 10-40 mg samples together with the calculated quantity of tracer solutions containing ¹⁸⁵Re and ¹⁹⁰Os were placed in Carius tubes. Then a mixture of concentrated acids HCl and HNO₃ (1:3) was added. The samples were decomposed in thick-walled glass ampoules at 230 °C for 12 h. Osmium was recovered from the resulting solution by extraction with bromine and microdistillation. Rhenium was recovered by anion exchange. Rhenium and osmium were loaded onto Pt filaments, and an isotope analysis was carried out by negative thermal ionization mass spectrometry (NTIMS) on an NBS magnetic-sector mass spectrometer. The accuracy of measurements was monitored by two inhouse molybdenite standards calibrated at the AIRIE Center (Markey et al., 1998). The blank samples contained no more than 10 pg Re and 3 pg ¹⁸⁷Os, which did not affect the calculated molybdenite ages.

For comparison we used the Re–Os dates obtained recently for the Aksug molybdenites by NTIMS at the University of Arizona, USA (Pollard et al., 2017). These and our data on the Re–Os age of molybdenites (Berzina et al., 2003; Pollard et al., 2017) are given in Table 2.

RESULTS OF U-Pb ISOTOPE RESEARCH

We studied zircons from tonalites of the Aksug pluton, tonalite porphyry I and tonalite porphyry II of ore-bearing small intrusions, late (post-ore) leucogranites, and gabbrodiorites of the Khoito-Oka complex.

S-0485. Gabbro-diorite of the Khoito-Oka complex. The investigated zircons are light pink transparent and semitransparent subeuhedral and euhedral cracked crystals, crystal fragments, or shapeless grains up to 300 µm in size (Fig. 3*a*). There is a distinct oscillatory zoning in some grains; in others it is unclear or absent. Some transformed grains have a rough contrasting zoning with alternating light and dark bands in cathodoluminescence (CL) (grain 2), wavy borders (grain 3), curvilinear flexuous zoning (grain 7), and veinlets white in CL (grains 4 and 5). Most of the grains are uniformly dark in CL. The contents of U and Th vary from 114 to 1579 and from 25 to 1471 ppm, respectively. The 232 Th/ 238 U ratio is 0.23–0.96. The concordant age estimated over 10 spots is 503 ± 2 Ma; MSWD = 0.03 (Fig. 4*a*).

Spot	²⁰⁶ Pb _c ,	U	Th	- 232 Th /2381 I	²⁰⁶ Pb*,	Age, Ma	²⁰⁷ Pb*/ ²⁰⁶ Pb*	⊥0/	²⁰⁷ Pb*/ ²³⁵ U	⊥0∕₀	206Pb*/238U	+0/2	Pho
	%	ppm		TH/ TO	ppm	(1)	(1)	±/0	(1)	±/0	(1)	±/0	KIIO
Khoito-Oka complex													
Gabbro	-diorite (sample S-	0485)										
1	0.37	176	43	0.25	12.5	510.8 ± 4.8	0.0571	3.2	0.650	3.4	0.0825	1.0	0.288
2	0.16	114	25	0.23	7.93	503.2 ± 4.9	0.0583	3.0	0.653	3.1	0.0812	1.0	0.324
3	0.16	408	180	0.46	28.5	503 ± 3.3	0.0566	1.9	0.633	2.0	0.0812	0.7	0.337
4	0.07	941	524	0.58	65.6	502.7 ± 2.1	0.0572	1.0	0.640	1.1	0.0811	0.4	0.384
5	0.13	877	550	0.65	61.1	502 ± 2.2	0.0568	1.3	0.634	1.3	0.0810	0.5	0.339
6	0.10	384	101	0.27	27.0	505.9 ± 3.4	0.0585	1.7	0.659	1.8	0.0817	0.7	0.390
7	0.05	1579	1471	0.96	110	501.6 ± 2.1	0.0572	0.8	0.638	0.9	0.0809	0.4	0.479
8	0.00	787	538	0.71	54.4	499.2 ± 2.5	0.0577	1.0	0.641	1.2	0.0805	0.5	0.455
9	0.06	423	200	0.49	29.8	507.4 ± 2.8	0.0575	1.5	0.649	1.6	0.0819	0.6	0.363
10	0.00	562	127	0.23	39.5	506.7 ± 2.5	0.0575	1.2	0.649	1.4	0.0818	0.5	0.385
Aksug	oluton												
Tonalite	e (sample	S-0494g))										
1	0.00	563	129	0.24	40.6	519.9 ± 8.5	0.0589	1.7	0.677	2.4	0.0840	1.7	0.709
2	0.10	337	111	0.34	23.2	495.2 ± 8.4	0.0562	2.4	0.619	3.0	0.0799	1.8	0.592
3	0.00	211	63	0.31	14.5	495.8 ± 8.8	0.0566	2.6	0.624	3.2	0.0800	1.9	0.574
4	0.10	365	107	0.30	25.3	500.2 ± 8.4	0.0568	2.2	0.632	2.8	0.0807	1.8	0.626
5	0.24	590	239	0.42	41.0	500.3 ± 8.2	0.0568	2.2	0.632	2.8	0.0807	1.7	0.619
6	0.03	766	212	0.29	54.2	510.3 ± 8.3	0.0566	1.5	0.643	2.3	0.0824	1.7	0.744
7	0.30	861	278	0.33	60.5	505.7 ± 8.1	0.0576	1.7	0.648	2.4	0.0816	1.7	0.693
8	0.16	467	85	0.19	32.7	504.1 ± 8.4	0.0566	2.5	0.634	3.1	0.0813	1.7	0.570
9	0.20	619	182	0.30	43.1	501.3 ± 8.4	0.0570	2.0	0.635	2.6	0.0809	1.7	0.662
10	0.11	996	366	0.38	70.6	510.7 ± 8.2	0.0575	1.5	0.654	2.3	0.0825	1.7	0.741
Ore-bea	aring sma	ll intrusio	ons										
Tonalite	e porphyr	y I (samp	le S-0491	a)									
1	0.32	107	29	0.28	7.47	500.4 ± 9.7	0.0553	5.7	0.616	6.1	0.0807	2.0	0.331
2	0.11	173	27	0.16	12.2	508.7 ± 9	0.0568	3.0	0.643	3.5	0.0821	1.8	0.525
3	0.00	69	13	0.19	4.81	501 ± 11	0.0576	5.2	0.641	5.7	0.0808	2.3	0.412
4.1	0.03	629	227	0.37	43.8	502.5 ± 8.3	0.0578	1.5	0.646	2.3	0.0811	1.7	0.749
4.2	0.30	88	20	0.23	6.2	506 ± 10	0.0554	5.0	0.624	5.5	0.0816	2.1	0.392
5	0.17	410	200	0.50	28.1	494.3 ± 8.2	0.0569	2.3	0.625	2.9	0.0797	1.7	0.604
6	0.00	76	23	0.31	5.28	502 ± 12	0.0596	4.2	0.666	4.8	0.0810	2.4	0.495
7	0.53	114	34	0.31	7.98	504 ± 10	0.0556	5.9	0.623	6.2	0.0813	2.1	0.331
8	0.32	288	95	0.34	19.9	498.4 ± 8.9	0.0569	3.1	0.630	3.6	0.0804	1.9	0.508
9	0.24	195	80	0.42	13.3	492.6 ± 8.9	0.0552	3.5	0.604	4.0	0.0794	1.9	0.471
Tonalite porphyry II (sample S-0494)													
1	0.74	60	11	0.18	4.22	504 ± 11	0.0533	11	0.598	11	0.0813	2.4	0.210
2	0.33	109	15	0.14	7.65	503 ± 11	0.0582	5.2	0.651	5.7	0.0812	2.2	0.395
3	0.00	170	43	0.26	11.7	496.3 ± 9.4	0.0565	3.1	0.623	3.6	0.0800	2.0	0.541
4	0.10	291	149	0.53	20.9	515.3 ± 9	0.0587	2.8	0.674	3.4	0.0832	1.8	0.541
5	0.72	143	38	0.27	10.1	$507\pm\ 9.8$	0.0554	6.8	0.625	7.1	0.0818	2.0	0.284
6	0.24	146	34	0.24	9.82	486.1 ± 9	0.0584	4.1	0.631	4.5	0.0783	1.9	0.429
7	0.52	75	12	0.17	5.13	489 ± 10	0.0550	7.4	0.598	7.7	0.0789	2.2	0.288

Table 1. Results of U-Pb isotope dating of zircons from igneous rocks of the Khoito-Oka complex, Aksug pluton, ore-bearing small intrusions,and post-ore dike

(continued on next page)

Table 1 (continued)

Spot	²⁰⁶ Pb _c , %	U ppm	Th	²³² Th/ ²³⁸ U	²⁰⁶ Pb*, ppm	Age, Ma ²⁰⁶ Pb/ ²³⁸ U (1)	²⁰⁷ Pb*/ ²⁰⁶ Pb* (1)	±%	²⁰⁷ Pb*/ ²³⁵ U (1)	±%	²⁰⁶ Pb*/ ²³⁸ U (1)	±%	Rho
Tonalite porphyry II (sample S-0494)													
8	0.57	90	16	0.18	6.24	498 ± 11	0.0526	7.2	0.582	7.5	0.0804	2.2	0.293
9	0.00	109	25	0.24	7.47	493 ± 11	0.0591	4.2	0.647	4.8	0.0794	2.3	0.472
10	0.45	122	27	0.23	8.53	$501\pm\ 9.7$	0.0546	5.2	0.609	5.6	0.0808	2.0	0.362
Post-or	e dike												
Leucogranite (sample S-0474b)													
1	0.15	120	29	0.25	8.66	520 ± 5	0.0562	3.0	0.651	3.1	0.0840	1.0	0.318
2	0.07	451	166	0.38	32.2	513.7 ± 2.8	0.0570	1.5	0.651	1.6	0.0829	0.5	0.353
3	0.41	115	25	0.23	8.23	514.2 ± 5.1	0.0566	4.0	0.648	4.2	0.0830	1.0	0.248
4	0.55	147	42	0.29	10.4	509.7 ± 5.2	0.0555	4.0	0.629	4.1	0.0823	1.1	0.257
5	0.33	184	56	0.32	12.7	499.1 ± 3.9	0.0553	3.7	0.614	3.8	0.0805	0.8	0.217
6	0.00	71	12	0.17	5.11	518.1 ± 6.3	0.0576	3.3	0.665	3.6	0.0837	1.3	0.355
7	0.45	94	21	0.23	6.77	514.8 ± 5.7	0.0561	5.1	0.643	5.3	0.0831	1.2	0.221
8	0.38	126	38	0.31	8.74	496.9 ± 4.7	0.0561	3.6	0.620	3.8	0.0801	1.0	0.263
9	0.22	186	59	0.33	13.1	505.6 ± 3.9	0.0585	2.4	0.658	2.5	0.0816	0.8	0.322
10	0.19	99	20	0.21	6.81	497.4 ± 5.2	0.0555	5.0	0.614	5.1	0.0802	1.1	0.211

Note. Pb_c and Pb^{*}, common and radiogenic lead, respectively. (1), correction for common lead using measured ²⁰⁴Pb. The error of calibration of the TE-MORA standard does not exceed 0.4% for the samples S-0485 and S-0474b and 0.65% for the samples S-0494g, S-0491a, and S-0494. The errors are at the 1 σ level. RHO, coefficient of correlation between ²⁰⁷Pb^{*/235}U and ²⁰⁶Pb^{*/238}U.

S-0494g. Tonalite of the Aksug pluton. Zircons are present mostly as semitransparent fragments of pale pink crystals up to 250 µm in size (Fig. 3*b*). The growth zoning is often unclear, of low luminosity, or is absent. The zircon exhibits weak cathodoluminescence. Some zircon grains have altered sites with high CL intensity (grains 3, 5, and 7). The contents of U and Th are 211–966 and 63–366 ppm, respectively. The ²³²Th/²³⁸U ratio varies from 0.19 to 0.42. The age of individual grains varies from 495 ± 8 to 520 ± 9 Ma. The concordant age estimated over 10 spots is 504 ± 5 Ma, MSWD = 0.37 (Fig. 4*b*).

S-0491a. Tonalite porphyry I, ore-bearing small intrusions. Zircons are transparent light pink prismatic and bipyramid-prismatic crystals up to 300 μ m in size (Fig. 3*c*). There are also crystals showing complex internal structures, with dark nonzoned cores and light (in CL) rims with un-

 Table 2. Re-Os isotope data for molybdenite samples from ores of the

 Aksug deposit

Sample	Re, ppm	¹⁸⁷ Os, ppb	Age, Ma	Reference			
S-0488v	214.4	1151.6	511 ± 2	(Berzina et al., 2003)			
S-0465	59.46	322.8	516 ± 2	(Berzina et al., 2003)			
S-0465	62.54	340.9	518 ± 2	(Berzina et al., 2003)			
8-5 256.9	100.77	548.59	517.3 ± 3	(Pollard et al., 2017)			
5-3 440.5	204.16	1110.126	517.4 ± 3	(Pollard et al., 2017)			

Note. Age = $(1/\lambda)[\ln(^{187}\text{Os}/^{187}\text{Re} + 1)]$. λ , decay constant, $\lambda(^{187}\text{Re}) = 1.666 \times 10^{-11} \text{ yr}^{-1}$ (Smoliar et al., 1996). The calculated age includes all analytical errors and the $\lambda(^{187}\text{Re})$ error.

clear (Fig. 3*c*, grain 2) or weak (Fig. 3*c*, grains 4 and 8) zoning. The zircons contain mineral inclusions (not analyzed) with luminescent rims (grains 1, 5, and 6). Grain 5 is a crystal fragment with a dark, nonuniformly spotted (in CL) and apparently altered core. The BSE images show cracks spreading from the edge of the crystal to its dark core, which might have been the fluid paths. Grain 9 has a disturbed zoning, which is unconformably overlapped by luminescent light sites in the lower part of the grain. Dating of these two grains (5 and 9) yielded the youngest ages.

The ages determined for the core and rim of the zircon with a complex internal structure (spots 4.1 and 4.2, respectively) are close; their difference is within the analytical error.

The contents of U in ten analyzed zircons vary from 69 to 629 ppm (the average is 215 ppm), and the contents of Th, from 13 to 227 ppm (the average is 75 ppm). The 232 Th/ 238 U ratio is 0.16–0.50 (the average is 0.31). The central zones and cores of the crystals are characterized by higher Th/U ratios (0.16–0.50) as compared with the edges (0.19–0.31). In the central zones and cores, the contents of U and Th are 173–629 and 27–227 ppm, respectively, and at the edges they decrease to 69–114 and 13–34 ppm.

The age of single grains varies from 493 ± 9 to 509 ± 9 Ma. The concordant age estimated over ten spots is 500 ± 6 Ma; MSWD = 0.07 (Fig. 4*c*).

S-0494. Tonalite porphyry II, ore-bearing small intrusions. Zircons are present as transparent pale pink prismatic and bipyramid-prismatic crystals and their fragments up to



Fig. 3. CL images of zircons from gabbroids of the Khoito-Oka complex (*a*), tonalites of the Aksug pluton (*b*), ore-bearing small intrusions—tonalite porphyry I (*c*) and tonalite porphyry II (*d*), and post-ore leucogranites (*e*). The 206 Pb/ 238 U age (Ma) is shown. Spot numbers follow Table 1.



Fig. 4. U–Pb isotope diagrams with a concordia for zircons from gabbroids of the Khoito-Oka complex (a), tonalites of the Aksug pluton (b), ore-bearing small intrusions—tonalite porphyry I (c) and tonalite porphyry II (d), and post-ore leucogranites (e).

300 μ m in size (Fig. 3*d*). The crystals show a zoning; some of them have large isometric cores >150 μ m in size with sectorial zoning (Fig. 3*d*, grains 1, 2, and 3) or smaller elongate cores dark in CL (grains 6 and 9), whose ages, with

regard to the dating error, overlap with the age of the crystal edge. In grain 7 in the pyramidal part of the crystal, there is a site of probably newly formed nonzoned zircon light gray in CL, which cuts off the growth zoning of the primary zir-



Fig. 5. Histogram and probability density plot displaying the age distribution for individual zircon grains from the leucogranite sample S-0474b, constructed with the Isoplot 3.75 software (Ludwig, 2012). *n*, number of samples.

con. This site is dated at 489 ± 10 Ma. Similar light nonzoned sites cutting off the growth zoning are observed in the lower edge zones of grains 6 and 8. The rim of grain 6 shows a coarse contrasting zoning in CL, with unclear blurred zone boundaries. The formation of structureless dark and light (in CL) shells around the core in grain 2 is probably due to the fluid impact.

The contents of U and Th vary from 60 to 291 and from 11 to 149 ppm, respectively, and 232 Th/ 238 U = 0.14–0.53. As in tonalite porphyry I, this sample has crystals with higher contents of Th and U and Th/U ratios in the inner zones as compared with the edges. The Th/U ratio in the inner and edge zones is 0.14–0.53 and 0.17–0.18, respectively. The contents of U and Th in the inner zones are within 109–291 and 15–149 ppm, respectively, and those in the edge zones are 60–90 and 11–16 ppm. The ages of ten grains of this sample vary from 486 ± 9 to 515 ± 9 Ma, the calculated concordant age is 500 ± 6 Ma, and MSWD = 0.01 (Fig. 4*d*).

S-0474b. Post-ore leucogranite. Zircons are present as prismatic and bipyramidal transparent and semitransparent pale pink crystals and their fragments 100–400 μ m in size (Fig. 3*e*). The ²⁰⁶Pb/²³⁸U age shows a significant spread in values, from 497 ± 5 to 520 ± 5 Ma. The concordant age estimated over ten spots is 509 ± 4 Ma, MSWD = 1.5, and the concordance probability is 0.22 (Fig. 4*e*). This sample probably contains both magmatic zircon formed during the crystallization of leucogranite and assimilated zircon. The ²⁰⁶Pb/²³⁸U age histogram shows a bimodal distribution for zircons from this leucogranite (Fig. 5). The weighted average age over six oldest grains is 515 ± 4 Ma. In morphology, the kind of luminescence, and U and Th contents these grains are similar to zircons from the tonalites and tonalite porphyry hosting leucogranites. Their contents of U and Th

vary from 71 to 451 and from 12 to 166 ppm, respectively, and their 232 Th/ 238 U ratio varies from 0.17 to 0.38. The weighted average age over four youngest grains is 500 ± 4 Ma and probably reflects the time of crystallization of leucogranites. These grains are characterized by U = 99–186 ppm, Th = 20–59 ppm, and 232 Th/ 238 U = 0.21–0.33.

DISCUSSION

Isotope geochronology and the effect of later overprinting processes on dating results

In the legends of geological maps (Glukhov, 2000; Mironyuk et al., 2012), the Aksug pluton is presented as Early Devonian. This age is reported by most researchers. It is substantiated by the presence of pebble of mineralized porphyritic granodiorites in Middle Devonian conglomerates of the Atakshil Formation and by porphyritic granodiorites intruding Middle Ordovician rocks of the Bellyk complex (Mironyuk et al., 2012). The Early Devonian age of the orebearing small porphyry intrusions agrees with the ⁴⁰Ar/³⁹Ar dates (404–401 Ma) (Sotnikov et al., 2003). According to these authors, the ⁴⁰Ar/³⁹Ar age of plutonic rocks formed before the emplacement of small porphyry intrusions is 500–460 Ma. Popov et al. (1988) reported porphyry copper mineralization in Lower Cambrian volcanic rocks in the Aksug ore district.

The Devonian age of the small intrusions and the Aksug mineralization disagrees with the Re–Os molybdenite dates of 518, 516, and 511 Ma (Berzina et al., 2003) and 517 Ma (Pollard et al., 2017) (Table 2) and with the U–Pb zircon dates (this paper).

The U-Pb dates for igneous rocks of the Aksug deposit and the Re-Os dates for its mineralization are rather close within the analytical error (Berzina et al., 2017). Nevertheless, the concordant U-Pb ages of zircons from these rocks (both pre-ore and intra-ore ones) are somewhat younger than the Re-Os age of the mineralization. For example, the concordant U-Pb age of zircon from gabbro-diorites of the Khoito-Oka complex (S-0485), hosting the Aksug pluton, is 503 ± 2 Ma (Fig. 4a). It does not agree with the older 40 Ar/ 39 Ar date for amphibole (532 ± 3 Ma) from the same sample (Sotnikov et al., 2003) and with the Re-Os age of the overprinting mineralization. The concordant U-Pb ages of zircons from the Aksug pluton and porphyry intrusions are as follows: tonalites— 504 ± 5 Ma and tonalite porphyry— $500 \pm$ 6 and 499 \pm 6 Ma (Fig. 4*b*-*d*). That is, the U–Pb ages of the Aksug pluton rocks and ore-bearing small porphyry intrusions are younger than the Re-Os age of the mineralization, which contradicts their geologic age relationship.

The similar Re–Os ages of different samples of the Aksug molybdenites of early generation estimated in different laboratories (Table 2) serve as a criterion for the reliability of the obtained results. The younger concordant U–Pb ages of zircons from gabbro-diorites of the Khoito-Oka complex and from tonalites and tonalite porphyry as compared with the Re–Os dates, along with the presence of secondary alteration textures in zircon crystals, suggest that the rejuvenation of the U–Pb dates might be due to overprinting of late thermofluid processes on the igneous rocks.

Zircon is chemically and physically stable in most of the crustal and upper-mantle conditions. For this reason, it is one of the most important tools to determine the age and genesis of igneous rocks. Many studies, however, showed that the impact of residual melts and water-salt fluids causes local alterations in the mineral (Bomparola et al., 2007; Geisler et al., 2007; Kusiak et al., 2009; Ayers et al., 2012; Schneider et al., 2012; Alekseev et al., 2013; Sal'nikova et al., 2014; Van Lankvelt et al., 2016). At the same time, secondary textures can be developed in magmatic zircons under fluid impact. Studies of zircons showed replacement of the primary growth zoning by nonzoned domains, a blurred unclear oscillatory or curvilinear zoning, bright patches in CL, and homogeneous (dark in CL) and luminescent zones around the cores (Pidgeon, 1992; Vavra et al., 1996, 1999; Pidgeon et al., 1998; Schaltegger et al., 1999; Hoskin and Black, 2000; Van Lankvelt et al., 2016). Such textures are specific to zircons of igneous rocks of the Aksug deposit.

The chemical and structural alteration of zircon crystals might be the result of solid-state diffusion (Geisler et al., 2007) or dissolution–reprecipitation process (Pidgeon et al., 1998; Geisler et al., 2007) in the presence of fluids or melts. Secondary modifications are often observed in magmatic zircon from granitoids and are treated as a result of fluid impact at the postmagmatic stage (Pidgeon, 1992; Pidgeon et al., 1998). As evidenced by experimental results, the primary oscillatory magmatic zoning can be preserved in zircons altered by moderate-temperature (>600 °C) fluids (Geisler et al., 2007). Similar structures with preserved magmatic zoning are also observed in zircons altered by low-temperature fluids (Geisler et al., 2003).

Modern petrological research has established that zircon not always behaves as a closed system and that changes in its internal texture and chemical composition are usually accompanied by disturbance of the U–Pb isotopic system. Therefore, dating of some zircon grains yields different ages, which suggests the impact of later endogenous processes on the mineral. In this case, the U–Pb ages can be erroneously interpreted. The disturbance of the U–Pb isotopic system is not always accompanied by "erasure" of the morphological and chemical signatures of magmatic zircon, which also complicates the interpretation of isotope dates (Bomparola et al., 2007; Kempe et al., 2015).

Magmatic zircons that were subjected to fluid impact usually have a younger U–Pb age, which does not show the time of their formation but reflects the loss of lead during a superposed process. For example, Kempe et al. (2015) studied the geochronology of zircons from intensely altered late Paleozoic granitoids of the Muruntau gold district (Uzbekistan). They concluded that the U–Pb age obtained from the least altered sites of zircon crystals with oscillatory zoning reflects the age of a later process (albitization) rather than the age of the granitoids.

Vakh et al. (2011), studying the Berezitovoe Au-polymetallic deposit in the upper-Amur area, performed a U-Pb isotope dating of zircons from ore-bearing metasomatites overprinted on porphyritic granites and from unaltered porphyritic granites sampled beyond the ore zone. The U-Pb isotopic age of the latter granites is 344 ± 3 Ma. The calculated concordant age of zircons from metasomatites is slightly younger $(335 \pm 5 \text{ Ma})$ and, probably, reflects the age of metasomatic processes. The authors note that the zircons from unaltered granites and metasomatites are similar in morphology and color and have a fine rhythmic zoning typical of magmatic zircons. Zircons from metasomatized rocks of the Berezovskoe gold field (Middle Urals) and Ryabinovoe gold-sulfide field (Central Aldan) (Pribavkin et al., 2013; Shatova et al., 2017) also show a several million years younger U-Pb age as compared with zircons from similar but unaltered rocks of these fields. At the same time, zircon crystals from metasomatites have preserved the morphology and zoning typical of magmatic zircons.

The U–Pb isotopic system in individual zircon crystals might record several separate events including growth of new zircon and chemical and/or structural modification of existing zircon (Grant et al., 2009).

The simultaneous decrease in U and Th contents and the Th/U ratio in the edge zones of zircon crystals from tonalite porphyry I and II of the Aksug deposit does not fit the classical concepts of crystallization differentiation. During differentiation, the distribution of U and Th in the zoned grain is almost in accord with the change in their contents in the melt. The decrease in U and Th contents toward the edge of the crystal might have been due to its interaction with an aqueous fluid. Experimental studies showed (Geisler et al., 2007) that a fluid impact can cause the replacement of primary zircon by a chemically purer one containing less trace nonformula elements (U, Th, Y, P, and Ti). The Th/U ratio also decreases, because U enters the zircon structure more easily than Th. This process, like pseudomorphism, does not change the crystal shape and leads to the loss of U, Th, and Pb and the complete rearrangement of the isotopic system. As a result, the age of zircon corresponds to the time of its modification under interaction with fluid (Geisler et al., 2007).

Most of the analyzed zircons from igneous rocks of the Aksug deposit are characterized by ${}^{206}Pb/{}^{238}U$ dates close to the Re–Os age (518–511 ± 2 Ma) and younger ones. In general, taking into account all ${}^{206}Pb/{}^{238}U$ geochronological data on five analyzed Aksug zircon samples, we see several age groups in the summary histogram (Fig. 6): 520, 514–518, 509–511, and 487–507 Ma. Most of the obtained dates (38 zircon spots) fall in the last interval. The other intervals include a few dates.

The oldest date (520 Ma) was obtained for zircon from the tonalite S-0494g (Fig. 3*b*, grain 1) and for assimilated zircon grain from the leucogranite S-0474b (Fig. 3*e*, grain 1). These zircons are similar in morphology and CL. They are



Fig. 6. Summary histogram of the 206 Pb/ 238 U (SHRIMP-II) dates for zircons from igneous rocks of the Aksug pluton, ore-bearing small intrusions, and gabbro-diorites of the Khoito-Oka complex and the Re–Os age of molybdenite. Numerals mark the weighted average 206 Pb/ 238 U age of zircon (Ma). *n*, number of analyses. Dashed line marks the dates for magmatic zircon from post-ore leucogranites.

also characterized by close 232 Th/ 238 U values (0.24 and 0.25 in zircons from tonalite and leucogranite, respectively). The weighted average age over two grains, 520 ± 9 Ma (Fig. 6), seems to reflect the time of formation of the pluton tonalites more exactly.

The age of 514–518 Ma of individual zircon grains, mostly assimilated crystals from leucogranite, is the closest to the age of tonalite porphyry I and associated early ore mineralization (Re–Os age is ~516–518 Ma). Inherited zircon grain 6 (518 Ma) from the leucogranite S-0474b (Fig. 3*e*) is close in age to the grain from the tonalite S-0494g (520 Ma) but is more similar in morphology and CL to tonalite porphyry I. The weighted average age over five grains of this age group is 515 ± 4 Ma (Fig. 6).

The interval 509–511 Ma in Fig. 6 contains five zircon grains from different rocks (gabbro-diorite, tonalite, tonalite porphyry I, and leucogranite (inherited grain)). These dates might reflect the time of formation of tonalite porphyry II and associated hydrothermal processes. The weighted average age over five grains is 510 ± 6 Ma (Fig. 6). It agrees with the Re–Os age of late ore mineralization (511 ± 2 Ma) associated with the formation of tonalite porphyry II.

The maximum number of the measured ages falls in the interval 486–507 Ma (Fig. 6), which includes zircons from all analyzed samples. We think that this interval probably corresponds to the time of the event that caused re-equilibration of zircon, disturbance of its U–Pb isotopic system, and "rejuvenation" of its age. Two grains from tonalite porphyry II have the minimum ages, 486 and 489 Ma, which apparently reflect the loss of lead. Rejection of these grains negligibly affects the weighted average age, which is 502 ± 2 Ma

over 34 grains. The obtained date is consistent with the weighted average age (over four measurements) of magmatic zircon from leucogranites (500 ± 4 Ma).

Thus, the U–Pb date interval 486–507 Ma includes the ages of zircons crystallized during the formation of post-ore leucogranites and of zircons from igneous rocks of the pluton and small porphyry intrusions that were subjected to overprinting thermofluid process during the intrusion of late leucogranites. The older U–Pb dates (509–520 Ma) might reflect the time of crystallization of the tonalites and tonalite porphyry of small intrusions and the time of ore-forming process.

The effect of a thermofluid process on the alteration of the gabbro-diorites S-0485 of the Khoito-Oka complex is also supported by 40 Ar/ 39 Ar data. The 40 Ar/ 39 Ar age of these rocks is 532 ± 3 Ma (Sotnikov et al., 2003), and the U–Pb zircon age is 503 ± 2 Ma (Fig. 4*a*). There is also a rejuvenated 40 Ar/ 39 Ar date (494 Ma) for the gabbro-diorites (Sotnikov et al., 2003). The 40 Ar/ 39 Ar age of 532 ± 3 Ma is consistent with their occurrence among the rocks of the Khamsara Formation hosting gabbroids of this age in other parts of the Vendian–early Cambrian volcanosedimentary belt (Mongush et al., 2011; Rudnev et al., 2016), and the U–Pb date of 503 ± 2 Ma probably reflects the alteration of the gabbroids under the impact of a late process.

We have also revealed discrepancy between the U–Pb zircon dates and the Re–Os molybdenite dates in the Sora porphyry Cu–Mo deposit of Middle Ordovician age in Kuznetsk Alatau (unpublished data), whose history is largely similar to that of the Aksug deposit. Multiple ore-metasomatic processes and post-ore magmatism are also widely

manifested there. At the same time, in smaller and younger Mesozoic porphyry Cu–Mo deposits of Siberia, where usually only one porphyry rhythm hosting mineralization is widely expressed, the difference in the above dates is within the analytical errors. At present, there are numerous publications on Cenozoic porphyry Cu–Mo deposits in China which report identical Re–Os and U–Pb geochronological estimates. Thus, we note discrepancy between the Re–Os dates for molybdenites and the U–Pb dates for igneous rocks in the most ancient (Paleozoic) orogenic areas with occurrence of igneous and ore-metasomatic rocks of different ages and wide manifestation of post-ore magmatism. All these factors might have affected the preservation of minerals and, correspondingly, their isotopic systems.

Zircons displaying the ages of several events during magmatic-hydrothermal evolution were also revealed in rock samples from other ore-magmatic systems. For example, study of zircons from three dunite samples from Urals platinum-bearing plutons revealed three groups of zircons in each sample: inherited, magmatic, and postmagmatic. The radiogenic U-Pb age of magmatic zircon from the Kos'va, Sakhara, and East Khabarnoe plutons is 435-432, 378-374, and 407-402 Ma, respectively (Fershtater et al., 2009). The age of zircon crystallized from a fluid at the postmagmatic stage of dunite evolution in these plutons is 370–350, 320, and 397-384 Ma, respectively. The authors believe that the recognition of different age generations of zircon helps to understand better the specifics of dunite petrogenesis. In particular, study of zircons permits one to date the stages of rock alteration and associate them with geologic events. For example, the wide spread of zircons with an age of 360 Ma and younger in the dunite of the Kos'va pluton is probably related to the emplacement of fine-grained gabbro (350 Ma) in the region. Zircons with an age of 397-384 Ma in the dunite of the East Khabarnoe pluton seem to be associated with granites of close age. The wide occurrence of postmagmatic zircons in the dunites is explained by the intense rock recrystallization in the presence of fluids, accompanied by segregation of ore minerals.

The U–Pb dating of magmatic zircons from the Norilsk region yielded two ages, 254 ± 4 and 244 ± 4 Ma (Petrov et al., 2010). In the period 220–230 Ma, there were secondary processes that led to the formation of metasomatic zircons. Contemporaneously, the intrusion of granitoids was emplaced in the Norilsk region (229 ± 0.4 Ma).

Based on the performed studies, we assume that igneous rocks of the Aksug pluton, small porphyry intrusions, and the host gabbroids of the Khoito-Oka complex contain zircon whose U–Pb dates (~500 Ma) reflect the time of later thermofluid processes related to the formation of post-ore leucogranites. This zircon is most widespread in K-feldspathization zones associated with such leucogranites. Zircons of close age are also abundant in rocks free of K-feldspathization. The "rejuvenation" of their age might be due to essentially sodic magmatism, which is manifested as the Kadyr-Os granitoid pluton of the Tannu-Ola complex in the

studied ore district. According to geological data, the Tannu-Ola complex is of middle Cambrian age. The age of zircons is 500–451 Ma (Mironyuk et al., 2012) and 486– 465 Ma (Rudnev, 2013).

Our interpretation of the U-Pb dates for the Aksug igneous rocks is most similar to the treatment of results obtained by Bomparola et al. (2007) for Cambrian-Ordovician intrusions of complex composition in northern Victoria Land (Antarctica). These researchers showed a wide scatter of the ²⁰⁶Pb/²³⁸U ages of zircons arranged along the concordia. For example, the ages of single zircon grains from biotite porphyrite are within 522-435 Ma. At the same time, the probability density plot of the concordant ages shows many peaks without clear gaps between them. Based on a detailed study of the morphology and geochemistry of the mineral, the authors concluded that the wide scatter of U-Pb ages is due to events that caused a disturbance of the isotopic system. They think that these U-Pb dates cannot be used to estimate the age of the intrusion. Most of the young ages reflect different degrees of the incomplete or complete disturbance of the primary isotopic system of magmatic zircon. The authors propose to use the weighted average concordant age of the oldest zircon populations (least affected by resetting of the U-Pb isotopic system) to estimate the age of the intrusion. They suggest that the disturbance of the isotopic system was due to the subsolidus recrystallization of the mineral caused by the circulation of fluids (from high- to low-temperature ones) in a stress regime that varied from transpressional to extensional.

Metallogenic implications

The Khamsara zone is one of the segments of the Vendian-early Cambrian volcanosedimentary belt of the Altai-Sayan folded area. The igneous rocks of the zone are less studied than the rocks of other belt segments because of their poor exposure and the zone inaccessibility. Besides the Aksug deposit rocks, biotite-hornblende gabbro of the Shivilig-I pluton in the Khamsara zone was dated (⁴⁰Ar/³⁹Ar age of hornblende is 498.5 ± 5.9 Ma) (Oidup et al., 2016). Detailed isotope studies were carried out for plagiogranitoids of a Vendian-early Cambrian volcanosedimentary belt south of the Khamsara zone (in the Tannu-Ola zone (Mongush et al., 2011) and Lake Zone (Rudnev et al., 2016)). Figure 7 shows isotope dates for the plagiogranites, close to the Re-Os dates for the Aksug molybdenite, which indicate a wide occurrence of Cu- and Mo-ore-bearing magmatism. The latter is confirmed by revealed Cu mineralization (sericite-quartz veins with chalcopyrite and bornite rich in Mo and Au (up to 100 and 0.2 ppm, respectively)) with an ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ age of 518 \pm 5 Ma (from sericite dating). The mineralization is apparently associated with the Darby pluton plagiogranites with a U–Pb age of 524 ± 10 Ma (Rudnev et al., 2016).

The evolution of magmatism in the Aksug ore field is much similar to that in the Tannu-Ola zone. The ⁴⁰Ar/³⁹Ar date for gabbro-diorite of the Khoito-Oka complex in the



Fig. 7. Schematic map of plagiogranitoid plutons in Vendian–early Cambrian volcanoplutonic belts in eastern Tuva and the Lake Zone in western Mongolia (after Rudnev (2013), simplified), with isotope dates. *1*, Vendian–early Cambrian volcanic belts; *2*, plagiogranitoid massifs (not to scale); *3–5*, localities of sampling for isotope dating (*3*, gabbroids, *4*, granitoids, *5*, molybdenite). Data in rectangles are the age (Ma), dating method, and sample number (in parentheses). 1, 2, Khoito-Oka complex, gabbro-diorite (Sotnikov et al., 2003); 3, 4, molybdenite from ores of the Aksug porphyry Cu–Mo deposit (3, (Berzina et al., 2003); 4, (Pollard et al., 2017)); 5, Irbitei pluton, norite (Mongush et al., 2011); 6, western part of the Tannu-Ola zone, quartz diorite of diorite–tonalite–plagiogranite association (Mongush et al., 2011); 7, East Tannu-Ola batholith, framing of the Irbitei pluton, quartz diorite (Rudnev et al., 2015); 8, East Tannu-Ola batholith, framing of the Khol'-Ozhu pluton, plagiogranite (Rudnev et al., 2015); 9, Sharatologoi pluton, tonalite (Rudnev et al., 2013); 10, Hara Nuur pluton, quartz diorite (Rudnev et al., 2013); 11, Hara Nuur pluton, plagiogranite (Rudnev et al., 2013); 12, granite intrusions of the Bayan-Tsagaan-Nuur Ridge, Three Hills pluton, quartz diorite (Rudnev et al., 2013); 13, Bumbat-Hairhan pluton, plagiogranite (Rudnev et al., 2013); 14, Bumbat-Hairhan pluton, plagiogranite porphyry (Rudnev et al., 2013); 15, Bumbat-Hairhan pluton, Darby pluton, sericite, Cu(Au) vein mineralization (Rudnev et al., 2016); 16, Bayan-Tsagaan gabbroid massif (Khain et al., 1995).

Aksug area (532 \pm 3 Ma) (Sotnikov et al., 2003) is close to the 40 Ar/ 39 Ar date for hornblende from gabbro of the Irbitei pluton in the Tannu-Ola zone (539 \pm 6 Ma) (Mongush et al., 2011). The age spectrum of this hornblende has a low-temperature plateau with a calculated age of 478 \pm 16 Ma (close to the age of the Aksug deposit leucogranites) corresponding to late tectonothermal events related to the intrusion of

Early Ordovician granitoids. The age of quartz diorite from diorite–tonalite–plagiogranite association located near the Irbitei pluton is 518 ± 2 Ma (Mongush et al., 2011) and agrees with the age of ore-forming granitoid magmatism of the Aksug deposit.

On metallogenic maps of the Central Asian Orogenic Belt, the Aksug deposit is part of the Kizhi-Khem metallogenic belt formed in the middle Paleozoic back-arc rift setting (Distanov et al., 2006). This metallogenic interpretation contradicts the Re-Os isotope dates (Berzina et al., 2003; Pollard et al., 2017) pointing to the formation of mineralization in the second half of the early Cambrian. The Aksug pluton occurs within gabbroids of the early Cambrian $({}^{40}\text{Ar}/{}^{39}\text{Ar}$ age is 532 ± 3 Ma (Sotnikov et al., 2003)) Khoito-Oka complex localized among the early Cambrian islandarc volcanics. These gabbroids are apparently analogs of the Irbitei pluton gabbroids of the Tannu-Ola zone and the Hirgis Nuur complex of the Lake Zone (western Mongolia), which are dated at ~531 Ma (Mongush et al., 2011; Rudney et al., 2016). The Irbitei pluton gabbroids belong to an accretion-subduction complex (Mongush et al., 2011), which formed in the Tannu-Ola zone during the first half of the early Cambrian.

Two stages were recognized in the evolution of magmatism in the Tannu-Ola and Khamsara zones (Rudnev, 2013): island arc (540–520 Ma) and accretion–collision (510– 450 Ma). According to the geochronological isotope data, gabbroids of the Khoito-Oka complex intruded in the first half of the early Cambrian. The Aksug pluton formed in the second half of the early Cambrian (no later than 520 Ma), and small porphyry intrusions, at ~520–511 Ma. Taking into account the isotopic ages of the igneous rocks, we assume that the Khoito-Oka gabbroids formed during the island arc evolution, and the granitoids of the Aksug pluton and orebearing small porphyry intrusions originated during the completion of subduction and the transition to the accretion stage, before the formation of accretion–collisional granitoids of the Tannu-Ola complex.

Two mineralization stages were identified from the Re– Os isotope data. We believe that one of them $(518-516 \pm 2 \text{ Ma})$ was related to the intrusion of tonalite porphyry I, and the second $(511 \pm 2 \text{ Ma})$, to the intrusion of tonalite porphyry II. Ore-bearing small porphyry intrusions formed, most likely, during restructuring caused by shear dislocations as a result of the accretion of island arc fragments and other tectonic structures as they approached the Siberian continent. The restructuring led to the rise of the deep-seated pluton to a subsurface horizon favorable for the localization of small porphyry intrusions and the separation of orebearing fluids from the melt.

Taking into account the results of isotope study of zircons, we assume that the metasomatism and chemical alteration of the Aksug igneous rocks was not limited by the influence of ore-bearing fluids, which led to the formation of stockwork mineralization and associated hydrothermal alterations (sericitization and silicification). Magmatic activity and metasomatism resumed with the emplacement of post-ore leucogranites within the deposit and of the Tannu-Ola granitoids on its periphery at ~500 Ma. The emplacement of leucogranites was accompanied by the exsolution of fluids that caused the wide formation of hybrid rocks (syenite-diorite- and granodiorite-like), the re-equilibration of zircon in the igneous rocks of the pluton and small porphyry intrusions, the removal of metals from the preceding igneous rocks, and the redeposition resulting in late poor mineralization.

There are a number of ore occurrences (Biche–Kadyr-Os, Verkhnii Dashtygoi, etc.) with similar mineralization, united into the Aksug ore cluster, near the Aksug deposit (Glukhov, 2000). Similar deposits and ore occurrences were also found in central and eastern Tuva (Bukharov et al., 1981; Gusev et al., 2014). The new isotope dates for the Aksug and Kyzyk-Chadr deposits (Gusev et al., 2014) make it necessary to reassess the role of the Cambrian and Devonian magmatism in the formation of porphyry Cu–Mo mineralization in the Altai–Sayan folded area. The solution of this problem is crucial for effective exploration.

CONCLUSIONS

Most researchers hold the view of the Devonian age of magmatism and mineralization of the Aksug deposit. However, the available Re–Os dates for molybdenite (518 \pm 2, 516 ± 2 , and 511 ± 2 Ma) are inconsistent with this hypothesis. The results of U-Pb (SHRIMP-II) zircon dating have confirmed the Cambrian age of magmatism. We assume that the rejuvenation of U-Pb dates for pre-ore and intra-ore igneous rocks (gabbro-diorites— 503 ± 2 Ma, tonalites— $504 \pm$ 5 Ma, and tonalite porphyry— 500 ± 6 and 499 ± 6 Ma) relative to the Re-Os dates is due to the influence of late thermofluid processes related mainly to the emplacement of post-ore leucogranites. The slightly older U-Pb age of zircon from the post-ore leucogranites (509 \pm 4 Ma) as compared with the preceding igneous rocks is due to the presence of zircon crystals assimilated from the underlying substrate. The geochronological isotope studies have shown the important role of the Cambrian magmatism in the formation of porphyry Cu-Mo mineralization in the Altai-Sayan folded area.

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