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The latest Aptian/earliest Albian age of the Kekura gold deposit, Western Chukotka, Russia: implications for mineralization associated with post-collisional magmatism

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Abstract

The Kekura gold deposit (76.2 t Au at 8.1 g/t) is situated in Western Chukotka, a region that hosts several Au, Ag, Cu, and Mo deposits and prospects. The Kekura deposit is related to the eponymous granite intrusion that is cut by porphyry dikes. The U-Pb zircon age of one of these dikes is 112 ± 1 Ma (2σ) that corresponds to the latest Aptian/earliest Albian. Both intrusion and dikes are hydrothermally altered and are cut by gold-quartz and molybdenite-quartz veins and stringers. Two molybdenite samples yield Re-Os model ages of 112.5 ± 0.6 and 112.3 ± 0.6 Ma (2σ). These Re-Os ages indicate the close temporal relationship between the molybdenite mineralization and the porphyry dikes. The age of the Kekura mineral system is similar to that of the post-collisional granitic plutons of the Anyui zone spatially scattered, between 140 and 210 km northwest of Kekura. We suggest that this temporal relationship may increase the likelihood of further discoveries of economic gold mineralization related to the currently underexplored Aptian post-collisional magmatic complexes of the Western Chukotka area.

Keywords Zircon · U-Pb geochronology · Molybdenite · Re-Os geochronology · Kekura deposit · Western Chukotka

Introduction

The Western Chukotka region of Russia is host to several gold, silver, copper, and molybdenum deposits and prospects.

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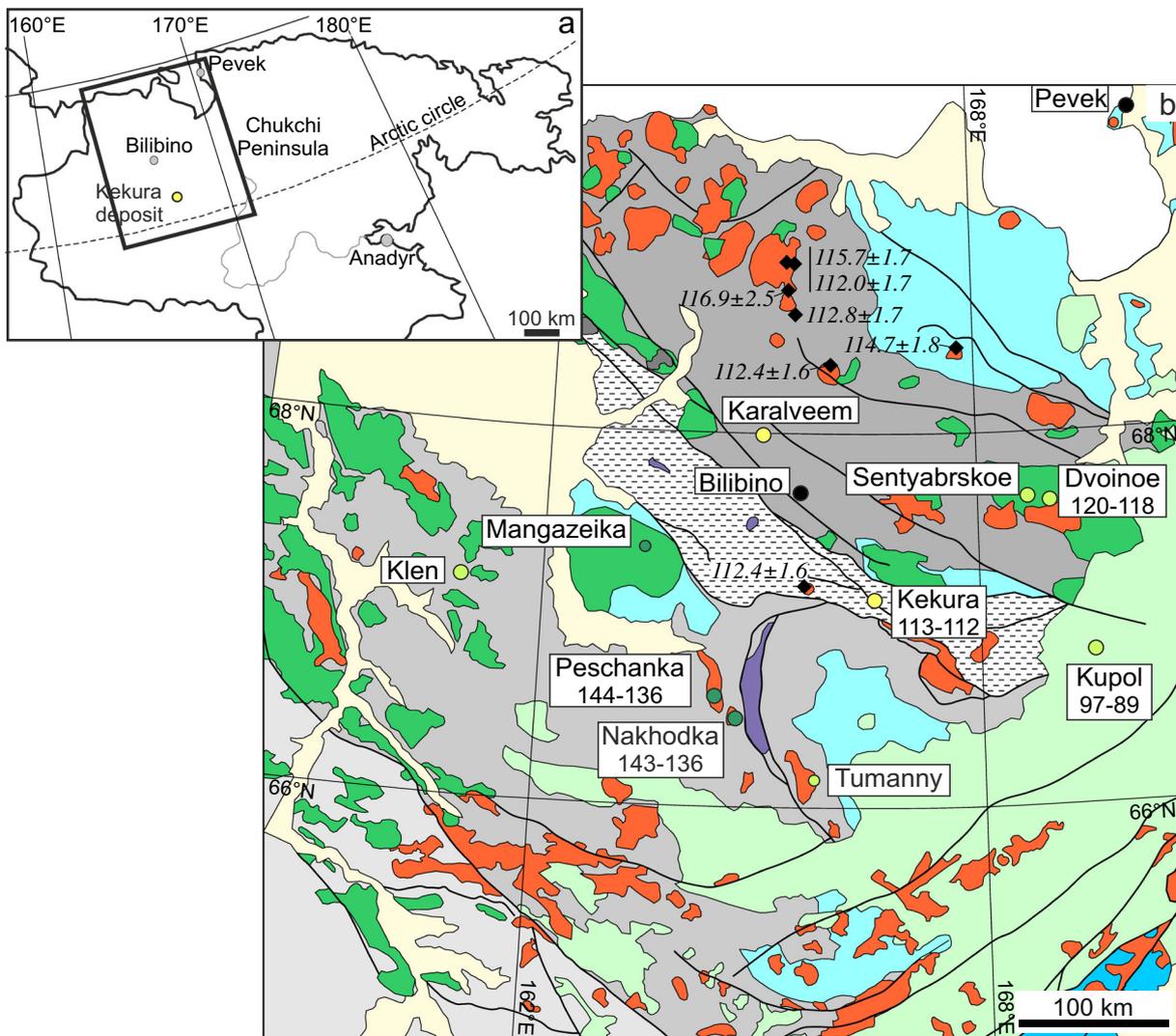
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Among them are the Kupol (55.3 t Au at 36.4 g/t, 752 t Ag at 485.7 g/t; Vasil'kova et al. 2018) and Dvoinoe (28.1 t Au at 2.3 g/t; Vasil'kova et al. 2018) epithermal gold-silver deposits, the Karalveem intrusion-related gold deposit (9.1 t Au at 14.1 g/t; Akimova et al. 2016), the Klen intermediate sulfidation epithermal gold deposit (18.6 t Au at 5 g/t; www.russdragmet.ru), and the Peschanka (3.7 Mt Cu at 0.83%, 98 kt Mo at 230 g/t, 234 t Au at 0.57 g/t, 2002 t Ag at 4.6 g/t; Vasil'kova et al. 2018) and Nakhodka (3.1 Mt Cu at 0.34%, 50 kt Mo at 54 g/t, 278 t Au at 0.30 g/t, 1130 t Ag at 1.2 g/t; Chitalin et al. 2013) porphyry copper deposits.

The available U-Pb zircon data (Akinin et al. 2015; Nikolaev et al. 2016) indicate that magmatism associated with mineralization highlights three major magmatic-hydrothermal events at 144–138 Ma (represented by the Peschanka and Nakhodka porphyry Cu-Au-Mo systems), 120–118 Ma (e.g., Dvoinoe epithermal deposit), and 97–92 Ma (e.g., Kupol epithermal deposit). However, both magmatic evolution and mineralization of Western Chukotka remain poorly studied, especially in terms of precise geochronology.

The Kekura hydrothermal gold deposit is situated approximately 120 km southwest of the town of Bilibino, Chukotka Autonomous Okrug, Russia (Fig. 1a). Kekura was discovered in 1990 by the Anyui Exploration Expedition team. Further



Tectonic zones of the Verkhoyansk-Chukotka province

- | | | | |
|---|--|---|--|
|  | Omolon (a slightly deformed cover of Paleozoic and Mesozoic clastic and volcanic strata over the Precambrian crystalline basement) |  | Post-collisional volcanic complexes (Aptian) |
|  | Oloy (tectonic collage of Paleozoic and Mesozoic active margin complexes) |  | Uda-Murgal belt (Late Jurassic through Early Cretaceous) |
|  | South Anyui (suture zone formed after the closure of an oceanic basin; strongly deformed Mesozoic clastic and volcanic strata) |  | Okhotsk-Chukotka belt (Albian through Campanian) |
|  | Anyui (Late Permian(?) through Triassic clastic complexes of the passive margin of Chukotka continental block) |  | Quaternary sediments |
|  | Late Jurassic through Early Cretaceous syn-collisional and post-collisional basins filled with clastic sediments |  | Major faults |
|  | Massifs of Paleozoic ophiolitic gabbro and peridotites |  | Cu-Mo-Au porphyry deposit |
|  | Granitic plutons, dominantly Cretaceous |  | Au granitoid-related deposit |
|  | Approximate location and U-Pb age ($\pm 2\sigma$) of granitic samples from Anyui and South Anyui zones (Miller et al. 2009) |  | Au-Ag IS / LS epithermal prospect and deposit |

Fig. 1 Location of the Kekura gold deposit and tectonic map of Western Chukotka, modified after Tikhomirov et al. (2017). Numbers with the names of the deposits depict the time span of deposit formation in Ma determined by radiometric dating (data from Akinin et al. 2015, Nikolaev et al. 2016 and references therein, this study)

assessment of the mineralization at Kekura was carried out by the Sibir Mining company between 2004 and 2010. The deposit is currently owned by Highland Gold Mining Limited and is set to go into production in 2023. According to Highland Gold Mining, Kekura hosts a large JORC-compliant resource base of 76.2 t at a grade of 8.1 g/t (www.highlandgold.com).

Available information on the geology and mineralization at Kekura is limited and to date has only been published in abstract form at various conferences (Dvurechenskaya et al. 2007; Baksheev et al. 2015, 2019). Currently there are no published data on the age of igneous rocks and mineralization at Kekura. Here, we present the first dating of magmatism and mineralization of the Kekura deposit via U-Pb zircon geochronology of a hydrothermally altered granodiorite porphyry dike and Re-Os molybdenite dating of disseminated molybdenite and quartz-molybdenite veinlets hosted by the granodiorite porphyry. We demonstrate that the Kekura deposit formed during the latest Aptian/earliest Albian is associated with post-collisional magmatic activity, which postdates the formation of the South Anyui suture. The results also provide a scientific basis for future mineral exploration in this region.

Geology and mineralization

The West Chukotka area comprises four major tectonic zones (from SW to NE; see Fig. 1b): (1) the marginal part of the Omolon cratonic terrane; (2) the Oloy zone, dominated by Jurassic and Early Cretaceous continental (?) arc magmatism; (3) the South Anyui suture zone, formed in the Early Cretaceous, after the closure of an oceanic basin and subsequent collision between the Chukotka block and the Siberian continent, and (4) the Anyui zone, the former passive margin of the Chukotka block (Parfenov 1991; Nokleberg et al. 2001). All four zones have been overprinted by a post-collisional magmatic event at ca. 121–112 Ma (Tikhomirov et al. 2017; Kara et al. 2019) and later by subduction-related volcanism of the Okhotsk-Chukotka volcanic belt (106–74 Ma; Akinin and Miller 2011; Tikhomirov et al. 2012).

The Oloy zone hosts the large Peschanka and Nakhodka porphyry Cu-Au-Mo deposits, the small minor Mangazeika porphyry Cu-Mo-Au, and the Klen intermediate sulfidation epithermal gold deposit. The large Karalveem intrusion-related gold deposit is situated in the Anyui tectonic zone. The Kekura deposit, the subject of this study, is located in the South Anyui zone.

The South Anyui zone stretches for ~600 km and has a width of 15 to 40 km. It is characterized by a series of NW-SE trending tectonic slices composed of intensely folded clastic rocks that are occasionally intercalated with basalts and cherts. The age of the volcanic and sedimentary rocks of the South Anyui zone ranges from Late Triassic to Early Cretaceous (Sokolov et al. 2009). The youngest detrital zircons extracted from the clastic rocks of the zone yield U-Pb ages of ca. 125 Ma (Amato et al. 2015), suggesting that the final orogenic collision occurred during the early Aptian.

The Kekura deposit area (Fig. 2; ESM Fig. 1) comprises a Late Triassic highly deformed flysch-like sequence composed of folded and fractured intercalated mudstone, siltstone, and sandstone. This sequence is intruded by the Kekura three-phase granitic pluton that is considered part of the Early Cretaceous Gvardeisky igneous complex. Mineralization of the deposit is spatially related to intrusive rocks. Bulk rock K-Ar age determinations for the Gvardeisky complex range from 124 to 94 Ma (Furman 1999), suggesting a likely Early Cretaceous age for magmatism. The outcrop area of the Kekura stock is about 13 km² and is represented by three phases of magmatism. Based on crosscutting relationships, these are (oldest to youngest) medium-grained diorite, medium- to coarse-grained quartz monzodiorite and syenite, and medium- to coarse-grained granodiorite. The igneous rocks contain xenoliths of gabbro. The Kekura pluton has not been affected by any considerable compressional tectonic event but is cut by numerous and multi-directional dikes of pre-ore granodiorite and granite porphyries, and spessartite, and a post-ore diorite porphyry.

Mineralization is represented by several stages. Stage 1 is characterized by Ni-Co-Fe arsenides and sulfoarsenides (nickeline, safflorite, cobaltite, löllingite) and native bismuth. Stage 2 is represented by molybdenite, bornite, chalcopyrite, and pyrite I. The bulk of the economic mineralization (Stage 3) includes two substages. The first substage is represented by scheelite, arsenopyrite, pyrite II, chalcopyrite II, sphalerite, galena, tennantite-tetrahedrite, maldonite, and native gold (fineness approximately 850). The second substage of Stage 3 mineralization is characterized by Bi tellurides and sulfotellurides, native bismuth, bismuthinite, and gold with fineness of 920–995 as a decomposition product of maldonite. The final mineralization stage, Stage 4, is characterized by chalcopyrite III, galena II, boulangerite, bournonite, Ag-rich tetrahedrite, Sb-bearing sphalerite, stibnite, low-fineness Au-Ag alloy, and native silver. Each mineralization stage is characterized by a distinct hydrothermal alteration assemblage. A propylitic assemblage of quartz-oligoclase-actinolite-clinocllore-calcite is common to Stage 1 mineralization. An albite-quartz-muscovite-tourmaline assemblage is associated with Stage 2 mineralization. The Stage 3 mineralization episode is associated with an alteration assemblage of quartz-dolomite-muscovite and arsenopyrite. The Stage 4

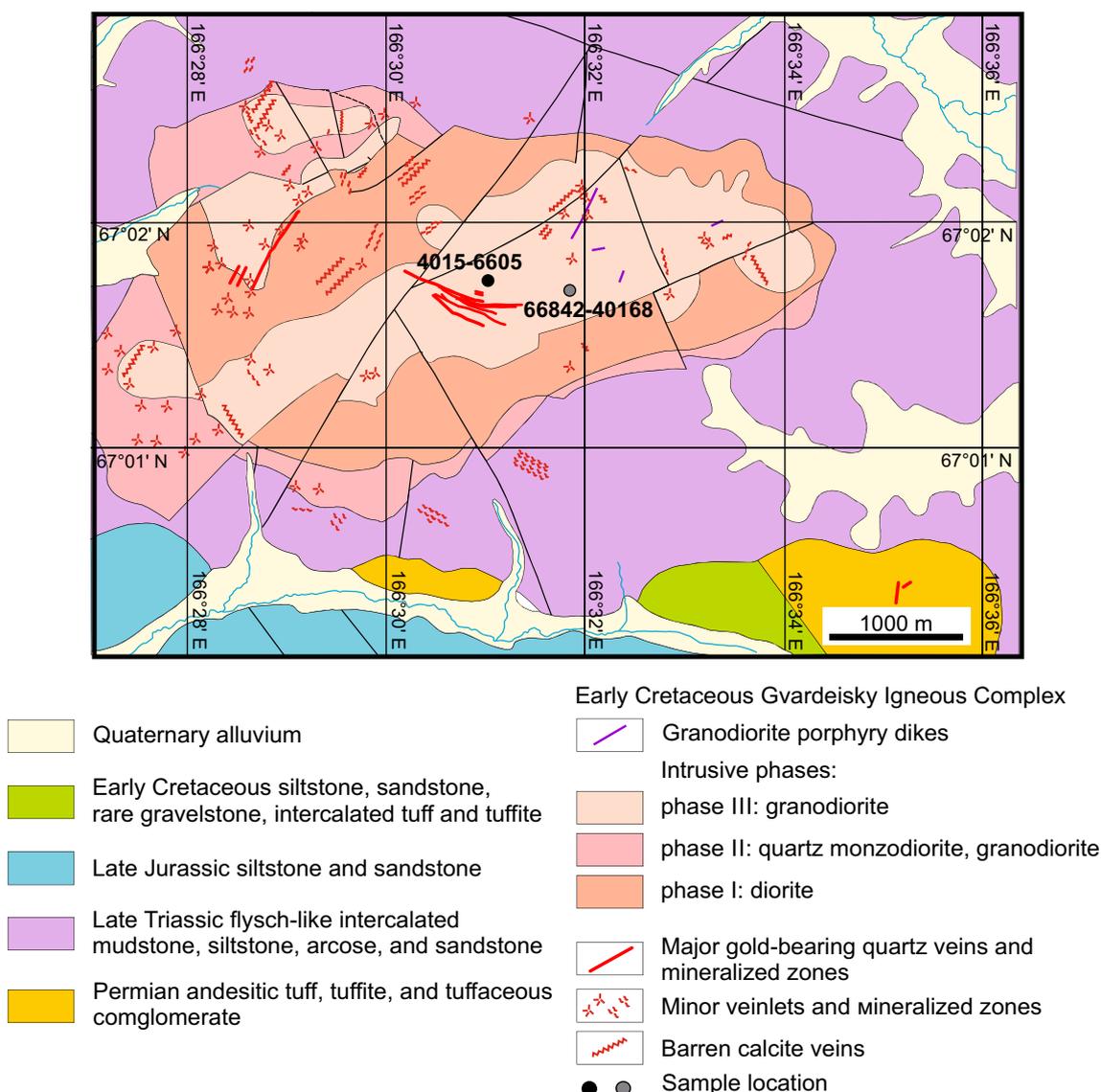


Fig. 2 Geological map of the Kekura gold deposit and sample locations. Solid gray circle corresponds to granodiorite sample 66842-40168 for U-Pb zircon dating and Re-Os molybdenite dating; solid black circle represents sample 4015-6605 for Re-Os molybdenite dating

mineralization is associated with a muscovite-illite-siderite-quartz assemblage.

Sample description

Two samples of granodiorite porphyry dikes were collected from surface exposures (Fig. 2). The outcropping porphyry is altered to a yellowish, medium-grained quartz-carbonate-muscovite rock. The porphyry dike is cut by Stage 2 quartz-molybdenite veinlets up to 1 cm wide and hosts disseminated molybdenite as rosettes up to a few centimeters in size (ESM Fig. 2).

Sample 66842-40168 is massive granodiorite porphyry with a fine-crystalline matrix that is cut by numerous

carbonate and quartz stringers. Phenocrysts of primary magmatic minerals are plagioclase (60%), quartz (20%), potassium feldspar (10%), and biotite and highly altered amphibole (10%). Apatite, zircon, and ilmenite are accessory minerals. Phenocrysts of primary plagioclase and potassium feldspar occur as up to 2-mm tabular crystals. Plagioclase is partly replaced by saussurite and albite. Potassium feldspar exhibits weak argillic alteration. Rounded subhedral to anhedral quartz phenocrysts of up to 2 mm are not altered. Primary biotite of up to 0.5 mm is completely replaced by an assemblage of rutile-muscovite-chlorite and carbonate. The groundmass (65% of the sample) is composed of potassium feldspar, primary magmatic quartz, plagioclase, biotite, and hornblende and is partially replaced by albite, muscovite, dolomite, and chlorite. This sample also contains a Stage 2 10-mm-wide

quartz-molybdenite vein (ESM Fig. 2a), with the molybdenite being a few hundred microns in length. The sample was utilized for both U-Pb zircon and Re-Os molybdenite dating.

Sample 4015-6605 is massive granodiorite porphyry with a fine-crystalline matrix. Phenocrysts are predominantly plagioclase (70%), quartz (20%), and potassium feldspar and biotite (10%). Zircon, apatite, and ilmenite are accessory minerals. Plagioclase phenocrysts up to 2.5 mm are partly replaced by sericite and albite. Subhedral quartz, up to 2 mm, is unaltered. Anhedral potassium feldspar up to 2 mm exhibits argillic alteration. Biotite phenocrysts (up to 1 mm) are altered to sericite and rutile. The fine-grained groundmass (60% of the sample) of quartz, plagioclase, potassium feldspar, biotite, and hornblende is significantly altered to albite, muscovite, and dolomite. Thin (5–10 mm) quartz-carbonate-sericite stringers also cut the rock. Fine-grained (few hundred microns in length) molybdenite is present as disseminated rosettes (up to a few centimeters in size) throughout the groundmass of the granodiorite porphyry (ESM Fig. 2b). Molybdenite from this sample was utilized for Re-Os dating.

Methods

U-Pb zircon dating. Zircons from sample 66842-40168 were analyzed at the Centre of Isotopic Research of the Russian Geological Institute, St. Petersburg, Russia. Separated grains of zircon were handpicked, mounted in epoxy resin randomly oriented together with mineral standards, and polished until the crystal centers of the grains were exposed. Potential target sites for isotope analyses were chosen using a CamScan-2500 electron microprobe together with reflected and transmitted light microscopy. Backscattered electron (BSE) and cathodoluminescence (CL) images of grains were obtained in order to assess internal compositional variation and their textures; moreover, SEM-EDX information about mineral inclusions was ascertained.

The U-Th-Pb isotope analyses were conducted by secondary ion microprobe (SHRIMP-II) instrument with pit diameter ca. 40 μm , corresponding primary O^{2-} beam intensity was about 9 nA. The zircon ages were calculated from $^{206}\text{Pb}/^{238}\text{U}$ measured ratios which have been normalized relative to a value of 0.0668 for the $^{206}\text{Pb}/^{238}\text{U}$ ratio of the TEMORA reference zircons, equivalent to an age of 416.75 Ma (Black et al. 2003). Individual analysis consisted of five cycles (150 s per cycle), each cycle representing one pass through the mass stations: $^{196}(\text{Zr}_2\text{O})$, ^{204}Pb , $^{204}\text{background}$, ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{238}U , $^{248}(\text{ThO})$, and $^{254}(\text{UO})$. The U-Pb data were processed in a manner described by Baldwin and Ireland (1995). Assuming concordance of ages, the mixing line between common and radiogenic portions was plotted. The lower interception of this line with concordia gives an age of the zircons. The Th-Pb ages were determined

from $^{208}\text{Pb}/^{232}\text{Th}$ ratios through the common U-Th-Pb SHRIMP procedure (Williams 1998), corrected for any common lead content detected from ^{204}Pb . The U and Th contents were normalized relative to the 91500 zircon reference standard. The obtained isotope data were processed using the SQUID-1 program (Ludwig 2000), with concordia diagrams plotted using ISOPLOT/EX (Ludwig 2003).

Re-Os molybdenite dating. Two molybdenite samples, obtained from samples 66842-40168 and 4015-6605, were analyzed in the Source Rock and Sulfide Geochemistry and Geochronology and Arthur Holmes Laboratories at Durham University (UK) to establish the Re-Os age of molybdenite mineralization. Molybdenite separation was achieved through using traditional methods (crushing to 70 to 200 mesh, magnetic separation, heavy liquids, and finally handpicking to remove any impurities). For both samples, no other ore minerals are present together with the molybdenite. An aliquant of the molybdenite separate (~20 mg) together with a known amount of tracer solution ($^{185}\text{Re} + \text{Os}$ bearing a normal isotope composition) were placed into a carius tube and digested with 3 mL HCl and 6 mL HNO_3 at 220 $^\circ\text{C}$ for 23 h. Osmium was isolated and purified using solvent extraction (CHCl_3) and microdistillation methods, with the resulting Re-bearing fraction purified using NaOH-acetone solvent extraction and anion chromatography (Selby and Creaser 2004; Li et al. 2017). Although negligible in comparison with the Re and Os abundance in the molybdenite, the final Re-Os data are blank corrected. A full analytical protocol blank run parallel with the molybdenite analysis yields 4.1 pg Re and 0.7 pg Os, the latter possessing a $^{187}\text{Os}/^{188}\text{Os}$ composition of 0.20 ± 0.2 . Data treatment follows that outlined in Li et al. (2017). All Re-Os data are given with 2σ absolute uncertainties (Table 1). Re-Os molybdenite ages are calculated using a ^{187}Re decay constant of $1.666 \times 10^{-11} \text{ y}^{-1}$ with an uncertainty of 0.31% (Smoliar et al. 1996; Selby et al. 2007). The Henderson molybdenite reference material (RM8599) analyzed during the course of this study yields a Re-Os age of $27.78 \pm 0.11 \text{ Ma}$ (2σ ; $n=1$), which is in good agreement with the recommended value of $27.66 \pm 0.10 \text{ Ma}$ (Markey et al. 2007; Zimmerman et al. 2014) and that reported by Li et al. (2017) ($27.695 \pm 0.038 \text{ Ma}$, $n=9$) and previous analyses at Durham (e.g., $27.65 \pm 0.12 \text{ Ma}$; Lawley and Selby 2012 and references therein).

Results

U-Pb dating of granodiorite porphyry. Ten zircon grains from porphyry granodiorite dike sample 66842-40168 analyzed in this study are colorless to possessing a yellowish tint. All zircons are transparent, euhedral to subhedral, and elongate

Table 1 Re-Os data of molybdenite from the Kekura gold deposit and the molybdenite reference material RM8599

Sample	Weight (g)	Re (ppm)	±	¹⁸⁷ Re (ppm)	±	¹⁸⁷ Os (ppb)	±	Age (Ma)	± [^]	± [*]	± [#]
66842-40168	0.021	98.0	0.4	61.6	0.2	115.4	0.4	112.3	0.1	0.5	0.6
4015-6605	0.022	104.7	0.4	65.8	0.2	123.4	0.4	112.5	0.1	0.5	0.6
RM8599	0.100	11.01	0.0	6.9	0.0	3.2	0.0	27.8	0.0	0.1	0.1

All uncertainties quoted are 2σ absolute

[^]Uncertainty including only mass spectrometry uncertainty

^{*}Uncertainty including all sources of analytical uncertainty

[#]Uncertainty including all sources of analytical uncertainty plus decay constant

and contain minor fractures. The zircons also contain melt and unidentified mineral inclusions (ESM Fig. 3a). The zircon grains show magmatic fine oscillatory zoning parallel to the crystal faces (ESM Fig. 3b). Evidence for zircon inheritance is absent.

The U and Th concentrations in the zircon grains range from 231 to 652 ppm and from 98 to 472 ppm, respectively. The Th/U ratios are between 0.34 and 0.82. Their common Pb concentrations vary from being below the detection limit to 1.57 ppm (ESM Table 1). All U-Pb data plot near the concordia line and yield a ²³⁸U/²⁰⁶Pb age of 111.0 ± 2.0 Ma (MSWD = 6.6, 2σ) (Fig. 3a). ²³⁸U/²⁰⁶Pb ages yield a weighted average of 112.0 ± 1.0 Ma (MSWD = 0.46; Fig. 3b). These ages correspond to the latest Aptian/earliest Albian and are taken to be the best estimate for timing of emplacement of the porphyry granodiorite.

Re-Os molybdenite dating. The Re and ¹⁸⁷Os concentrations of the two molybdenite samples studied are similar: Re = 98.0 and 104.7 ppm and ¹⁸⁷Os = 115.4 and 123.4 ppb, respectively (Table 1). The Re-Os model ages for both samples are identical within uncertainty: sample 4015-6605 = 112.5 ± 0.6 Ma; sample 66842-40168 = 112.3 ± 0.6 Ma.

Discussion

The dated granodiorite porphyry is host to the dated quartz-molybdenite-bearing vein and disseminated molybdenite. The Re-Os molybdenite ages of 112.5 ± 0.6 and 112.3 ± 0.6 Ma are identical within uncertainty to the ²³⁸U/²⁰⁶Pb zircon weighted average age of the granodiorite porphyry (112.0 ± 1.0 Ma). These ages indicate that the molybdenum (Stage 2) mineralization of the Kekura deposit is temporally related to the magmatism associated with the granodiorite porphyry dike. Further it constrains magmatism and mineralization to the Late Aptian/Early Albian likely being related to the third intrusion phase of the Kekura pluton.

The isotopic age of the Kekura deposit does not correspond to any of the three known mineralization epochs in the Western Chukotka area (144–138, 120–118, and 97–94 Ma; Akinin et al. 2015; Nikolaev et al. 2016). U-Pb zircon ages of 117 to 112 Ma have been reported for several post-collisional granitic plutons of the Anyui zone (Miller et al. 2009), which occur between 140 and 210 km northwest of Kekura (Fig. 1b). These plutons are considered to be part of an Aptian post-collisional magmatic event present in the West Chukotka area

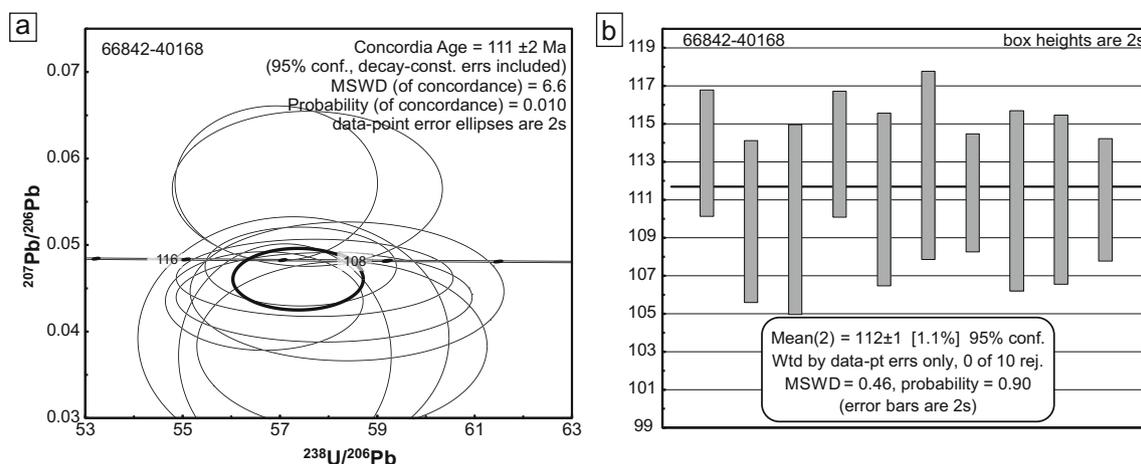


Fig. 3 SIMS U-Pb zircon isotope plots from porphyry granodiorite sample 66842-40168: (a) ²³⁸U/²⁰⁶Pb vs. ²⁰⁷Pb/²⁰⁶Pb concordia plot and (b) weighted average ²³⁸U/²⁰⁶Pb age plot

(Tikhomirov et al. 2017; Kara et al. 2019). Linking the Kekura deposit to the Aptian magmatic event increases the duration of the Aptian metallogenic epoch (120–118 Ma) and implies that both epithermal and intrusion-related gold deposits were formed during this time period.

Alternatively, the Kekura pluton and related gold mineralization could be linked to the next magmatic pulse of Albian age. U-Pb zircon dates of 109 to 105 Ma have been obtained for granitic batholiths and smaller plutons of North Chukotka (Miller and Verzhbitsky 2009; Tikhomirov et al. 2011; Luchitskaya et al. 2019). Similar U-Pb ages (109.3 ± 1.2 Ma, 108.5 ± 2.7 Ma, and 100.9 ± 0.8 Ma) have been reported for post-tectonic plutons and dikes of the South Anyui zone (Miller et al. 2009; Amato et al. 2015). The earliest formations of the huge subduction-related Okhotsk-Chukotka volcanic belt return $^{40}\text{Ar}/^{39}\text{Ar}$ and U-Pb ages of ca. 106 Ma (Akinin and Miller 2011; Tikhomirov et al. 2012). Further, plutons in the northern Chukotka region host several large tin deposits (Flerov 1976), but any genetic relationship between gold mineralization and Albian magmatism is yet to be shown.

The hypothesis linking the Kekura deposit to the Aptian magmatic event looks more plausible because the isotopic age of the Kekura deposit is somewhat closer to the age of Aptian magmatic pulse than that known for the Albian event. Besides, the formation of intrusion-related gold deposits is commonly restricted to the relatively late stages of major magmatic events (Lang and Baker 2001). In addition, the new ages for the post-tectonic Kekura pluton indicate that the late stages of major deformation in the South Anyui zone took place prior to ca. 112 Ma.

Conclusions

This study reports the first U-Pb and Re-Os ages for zircon of a porphyry granodiorite dike and molybdenite disseminated within the dyke and hosted by quartz veins crosscutting the dike, respectively, from the Kekura gold deposit, Chukchi Peninsula, Russia. The precise U-Pb zircon age of 112 ± 1 Ma and Re-Os molybdenite ages of 112.5 ± 0.6 and 112.3 ± 0.6 Ma are essentially identical within uncertainty and show that hydrothermal molybdenite mineralization is genetically related to the timing of the granodiorite porphyry dike and the gold mineralization. The U-Pb and Re-Os ages reported here document the latest Aptian/earliest Albian age for the granodiorite porphyry and associated molybdenum mineralization at the Kekura gold deposit. The ages obtained are close to some of the post-collisional granite plutons in the Anyui tectonic zone. The spatial relationship between gold mineralization and post-collisional Aptian magmatic rocks in the Western Chukotka implies that there are very likely understudied fragments of magmatic-volcanic fields of presumably Aptian age, which are widespread across the western

Oloy zone and NE Omolon block that could potentially host significant economic mineral systems.

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