

Article

Geochemistry and Genesis of Rare Metal (Sn-W) Cherdoyak Deposit, Eastern Kazakhstan

Oxana N. Kuzmina ^{1,*}, Sergey V. Khromykh ², Maria D. Tsareva ², Arseniy D. Senko ¹, Maria O. Shapovalova ² and Marina A. Mizernaya ¹

¹ School of Geosciences, D. Serikbayev East Kazakhstan Technical University, Ust'-Kamenogorsk 070000, Kazakhstan; krump_94@mail.ru (A.D.S.); mmizernaya@edu.ektu.kz (M.A.M.)

² V.S. Sobolev Institute of Geology, Mineralogy Siberian Branch of the Russian Academy of Sciences, Novosibirsk 630090, Russia; serkhrom@igm.nsc.ru (S.V.K.); tsarevamd@igm.nsc.ru (M.D.T.); shapovalovam@igm.nsc.ru (M.O.S.)

* Correspondence: okuzmina@edu.ektu.kz; Tel.: +7-(777)155-92-25

Abstract

This study presents new data on the Cherdoyak Sn–W deposit in Eastern Kazakhstan. The deposit is spatially associated with the northeastern contact of the Cherdoyak granite intrusion and comprises a stockwork of quartz veins and greisen bodies developed within the earlier-emplaced Kunush granite intrusion. Three granite varieties were distinguished: (1) biotite plagiogranites of the Kunush massif, (2) first-phase biotite granites of the Cherdoyak intrusion, and (3) second-phase muscovite granites and leucogranites of the Cherdoyak intrusion. The Kunush granites underwent extensive graphitization and greisenization, resulting in the development of stockwork-type Sn–W–As mineralization composed of cassiterite, scheelite, and arsenopyrite. The crystallization ages of the granites were determined by U–Pb zircon geochronology and yielded ages of 296 Ma for the Kunush intrusion, 290 Ma for the first-phase Cherdoyak intrusion, and 289 Ma for the second-phase intrusion. Muscovite from the Cherdoyak greisens yielded an Ar/Ar age of 280 ± 5 Ma. The available geochronological and geochemical evidence suggest a genetic relationship of Cherdoyak deposit with the emplacement and magmatic evolution of the Cherdoyak intrusion. Ore formation was driven by advanced fluid–magma differentiation during the evolution of the Cherdoyak magmatic system.

Keywords: Cherdoyak deposit; Sn–W mineralization; rare metal; genesis; Kalba–Naryn belt; Eastern Kazakhstan



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1. Introduction

Tin (Sn) and tungsten (W) are critical raw materials for modern high-technology industries because of their widespread applications in electronics, metallurgy, and advanced materials manufacturing. Consequently, both metals are included on the lists of critical raw materials compiled by many countries [1,2]. More than 90% of primary tin deposits are associated with greisens or hydrothermal veins which in turn are genetically related with granitoids [3]. Similarly, the majority of occurrences of the main tungsten minerals, wolframite and scheelite, are also associated with metasomatic rocks which are in turn spatially and genetically related to granitic intrusions. Also, felsic igneous rocks including granites, pegmatites, rhyolites, alkaline syenites, etc., commonly constitute the principal source of rare metal mineralization, including Li, Cs, Be, Nb, Ta, Sn, W, and Mo [4–15]. The mechanisms controlling the ore potential of granitoids depend on numerous factors

that govern the concentration of rare metals during the evolution of granitic magmas. Geological and structural factors that provide pathways for ore-bearing fluids and promote the development of geochemical barriers also play a key role in the formation of economic mineral deposits. In this paper, we present new geological, geochemical, mineralogical, and geochronological data on the Cherdoyak Sn–W rare metal deposit in Eastern Kazakhstan.

Eastern Kazakhstan is a well-known rare metal province hosting numerous rare-element pegmatite deposits with Li–Cs–Ta–Be mineralization [9,12,15–18]. These ore deposits form the Kalba–Narym rare metal belt, which is genetically associated with the granites of the Kalba–Narym Batholith (Figure 1). The Kalba–Narym Batholith was emplaced in the Early Permian during the post-collisional stage of the regional geodynamic evolution [19]. Two major granitoid associations have been distinguished within the batholith: (1) the Kalba granodiorite–granite complex, which accounts for approximately 80–85% of the batholith volume and formed between 297 and 287 Ma [20]; and (2) the Monastery granite–leucogranite complex, represented by several large, isolated plutons that account for approximately 15–20% of the batholith volume and formed between 283 and 276 Ma [20]. The granites intrude the Devonian–Carboniferous terrigenous sedimentary rocks of the Takyr Formation (D_3 – C_1), composed predominantly of siltstones, mudstones, and black shales.

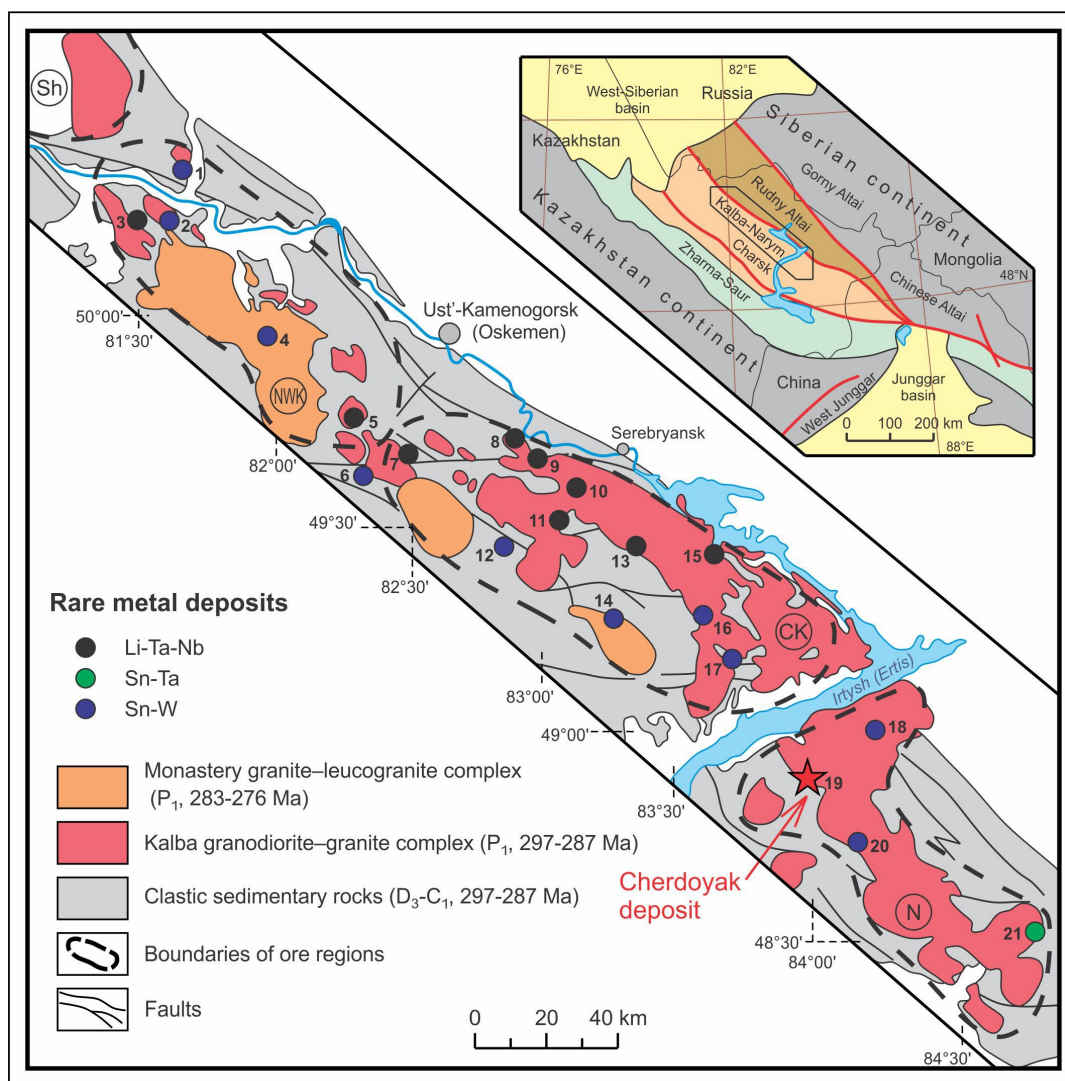


Figure 1. Scheme of the geological structure of Kalba–Narym metallogenic belt [18]. The main ore districts are shown: Sh—Shulbinsk, NWK—North-Western Kalba, CK—Central Kalba and N—Narym.

Rare metal deposits: 1—Mokhnatukha; 2—Malo-Kaindy; 3—Kvartsevoye; 4—Zelenoye; 5—Novo-Saryozek; 6—Kanaika; 7—Medvedka; 8—Ognevka; 9—Bakennoye; 10—Yubileynoye; 11—Belaya Gora; 12—Karagoin; 13—Komarovskoye; 14—Kozlovskoye; 15—Shebuntai; 16—Komsomolskoye; 17—Palatsy; 18—Kasatkinskoye; 19—Cherdoyak; 20—Burabai; 21—Karasu.

Rare metal mineralization is mainly associated with granites of the Kalba complex. Most ore occurrences are concentrated in the apical parts and endocontact zones of granite intrusions. Mineralization occurs as pegmatite veins and pegmatite fields, greisen bodies, and quartz-vein systems. Four major ore districts have been recognized within the belt (Figure 1): Sh—Shulbinsk, NWK—North-Western Kalba, CK—Central Kalba, and N—Narym [21].

Most well-studied Li–Cs–Ta–Be pegmatite deposits, including Tochka, Yubileynoye, Belogorskoye, and Bakennoye, are located within the Central Kalba ore district [9,12,16,17,21,22]. These deposits were extensively mined during the second half of the twentieth century. In the North-Western Kalba district, the large Kvartsevoye deposit [18] and several smaller pegmatite deposits have been identified. In addition, both the Central and North-Western Kalba districts host numerous small Sn–W deposits and occurrences [15,22]. Compared with the well-investigated Central Kalba and North-Western Kalba ore districts, the Narym ore district, located in the southeastern part of the Kalba–Narym metallogenic belt, remains comparatively poorly explored. Fewer deposits and mineral occurrences have been discovered there, and no economically significant rare-element pegmatite deposits have been identified. The known ore occurrences are characterized by Sn–W and Sn–Ta mineralization.

2. Geological Background

The largest and best-known deposit of the Narym district was discovered in the 1930s. The Cherdoyak deposit is situated within the western exocontact zone of the Cherdoyak intrusion [23]. Mineralization is confined to the relatively small Kunush massif (Figure 2), which consists of plagiogranites intruding the siltstone–shale sequence of the Takyr Formation. The Cherdoyak intrusion lies immediately east of the Kunush massif. The two intrusive bodies are not in direct contact and are separated by a narrow (<15 m) strip of host rocks; no direct intrusive contacts have been observed. The Cherdoyak intrusion is surrounded by a contact metamorphic aureole characterized by hornfels and mica-rich schists derived from sandstones and siltstones. The plagiogranites of the Kunush massif are pervasively fractured and cataclazed, probably as a result of tectonic deformation associated with the emplacement of the Cherdoyak intrusion. Numerous quartz veins and greisen bodies cut the Kunush plagiogranites. Quartz veins also occur in the surrounding sedimentary rocks; however, economically significant Sn-bearing veins are restricted to the Kunush massif.

Three principal ore zones can be distinguished within the Cherdoyak ore field (Figure 2). Each zone consists of clusters of quartz veins and quartz-greisen stockwork bodies hosting Sn–W mineralization. These ore clusters contain numerous thin quartz veins, commonly intersecting to form dense vein networks distributed irregularly throughout the mineralized areas. The plagiogranites are also extensively cut by and impregnated with thin quartz and ore-bearing veinlets. According to exploration data, the mineralized bodies are lens-shaped, ranging from 30 to 110 m in length and from several metres to several tens of metres in thickness. In some ore zones, mineralization has been traced to depths of up to 250 m. Mining at the Cherdoyak deposit commenced in the 1950s and ceased in the 1990s. During 2017–2019, the “Topaz exploration company” (Ust-Kamenogorsk, Kazakhstan) conducted additional exploration and evaluation of rare metal mineralization at the deposit. However, these investigations failed to identify economically significant resources sufficient

to support renewed mining [24]. Consequently, conventional exploration methods have proved insufficient for assessing the metallogenic potential of this area.

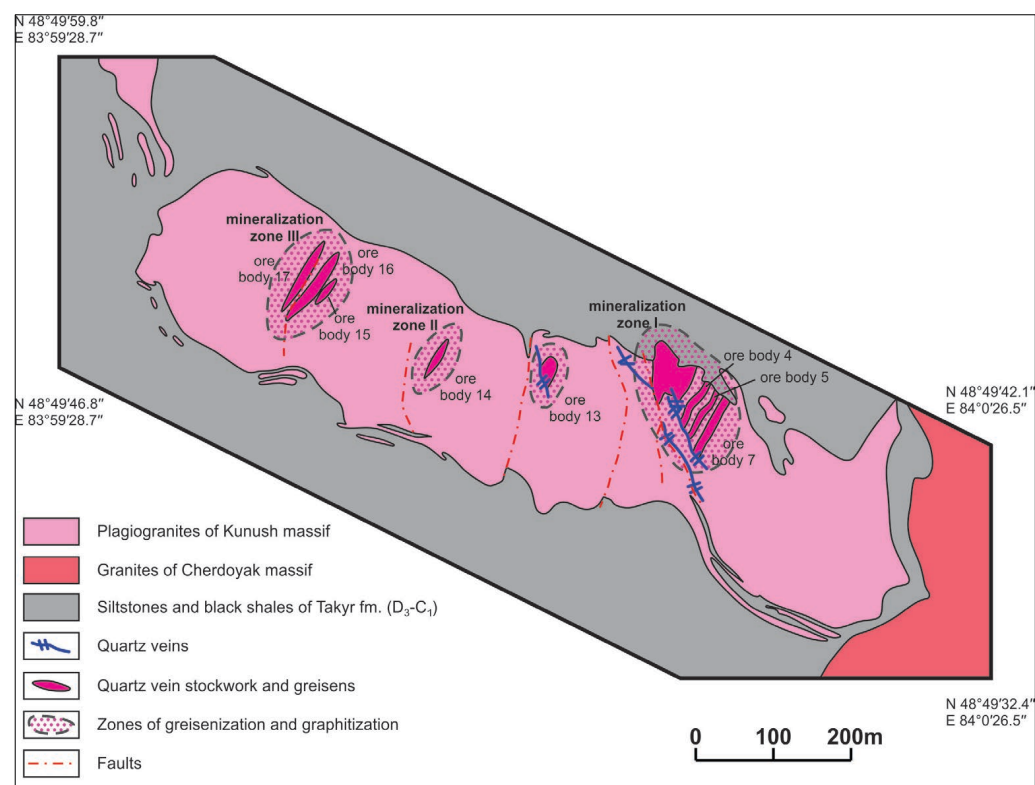


Figure 2. Geological scheme of the Cherdoyak deposit after B.A. D'yachkov [22].

3. Materials and Methods

Geochemical and geochronological analyses were conducted on rocks from the Cherdoyak deposit. More than 40 samples of granitic and ore-bearing rock samples were collected from outcrops and quarry walls. The samples were photographed and described at D. Serikbayev East Kazakhstan Technical University (EKTU) (Ust-Kamenogorsk, Kazakhstan). Analytical work was conducted at the VERITAS Laboratory of EKTU and the V.S. Sobolev Institute of Geology and Mineralogy of the Siberian Branch of the Russian Academy of Sciences (IGM) (Novosibirsk, Russia). Petrographic examination of polished thin sections was performed with a Carl Zeiss AxioScope.A1 (ZEISS, Oberkochen, Germany) polarizing light microscope equipped with a Canon PowerShot A640 digital camera (Canon, Tokyo, Japan). The chemical compositions of ore minerals were determined at IGM with a Tescan MIRA 3 LMU scanning electron microscope (Tescan, Brno, Czech Republic) equipped with an energy-dispersive X-ray spectrometer (EDS, Oxford, Abingdon, UK). Analyses were performed at a beam current of 1 nA and a scanned area of $5 \times 5 \mu\text{m}$. The live spectrum acquisition time was 60 s. The stability of the analytical conditions was monitored by periodic measurements of the $K\alpha$ line intensity of pure cobalt. The detection limit was 0.1 wt % for both major and trace elements.

Whole-rock compositions were determined by XRF and ICP-MS. Major-element oxides were analyzed at IGM by X-ray fluorescence (XRF) with an Applied Research Laboratories ARL-9900-XP analyser (Thermo Fisher Scientific, Waltham, MA, USA) following the standard procedure. Trace elements were determined at EKTU by inductively coupled plasma mass spectrometry (ICP-MS) with an Agilent 7500cx instrument (Agilent Technologies, Santa Clara, CA, USA), which enables the determination of 73 elements with high sensitivity. Prior to geochemical analyses, the samples were digested using a multi-acid

digestion procedure. During digestion, standard aqueous solutions with known elemental concentrations were used for calibration, after which the prepared solutions were analyzed. Calibration solutions were prepared by diluting certified reference solutions (CMS-1, IV-Stock-21, and IV-Stock-29 manufactured by Inorganic Ventures, Christiansburg, VA, USA) with 2% or 5% nitric acid, 10% hydrochloric acid, or distilled water. A 5% nitric acid solution was used as an analytical blank.

Geochronological study was performed at IGM using U–Pb and $^{40}\text{Ar}/^{39}\text{Ar}$ dating methods. U–Pb ages of individual zircon grains from granites (40–50 grains per sample) were determined by LA–SF–ICP–MS following the procedure described by Semenova et al. [25]. Zircon grains were mounted in epoxy resin and polished to approximately half of their thickness prior to analysis. Laser-ablation spots were selected based on optical and cathodoluminescence (CL) images. Measurements were performed on a Thermo Fisher Scientific Element XR magnetic sector-field ICP mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) coupled with an Analyte Excite (Teledyne CETAC Technologies, Omaha, NE, USA) excimer laser ablation system. All measurements were conducted using electrostatic scanning (E-scan) at masses of ^{202}Hg , $^{204}(\text{Hg} + \text{Pb})$, ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{232}Th , and ^{238}U . Signals were acquired in counting mode for all isotopes except ^{238}U and ^{232}Th . Zircons were analyzed with a laser spot diameter of 25–35 μm , a fluence of 2–3 J/cm^2 , and a repetition rate of 10 Hz for 30 s. Plešovice with the age of 337 Ma [26] was used as the external standard to correct for mass bias, instrument drift, and downhole fractionation of Pb from U during laser drilling. Temora with the age of 417 Ma [27] was used as the secondary standard. During one sample, six Plešovice standards and six Temora standards were measured. Age was calculated, not including a common Pb correction. Data reduction was performed with the Glitter software package [28]. Concordia diagrams and ages were calculated using Isoplot-3 [29]. All uncertainties are reported at the 2σ level.

The $^{40}\text{Ar}/^{39}\text{Ar}$ ages of mica from greisens were determined by the step-heating technique [30]. The analytical procedure is described in detail by Travin et al. [31]. The sample was irradiated in a BWR nuclear reactor at Tomsk Polytechnic University (Tomsk, Russia). A standard biotite sample, MSA-11 (OSO No. 129-88), with an age of 311.0 ± 1.5 Ma, was used for calibration against the international standards Bern-4M (muscovite) and LP-6 (biotite). The ages of the Bern-4M and LP-6 standards were assumed to be 18.51 Ma and 128.1 Ma, respectively [30]. The argon isotopic composition of the irradiated samples was measured with a Noble Gas 5400 (Micromass, Wilmslow, UK) mass spectrometer. Argon extraction by stepwise heating and isotopic measurements were performed over a temperature range of 500–1200 $^{\circ}\text{C}$. Ages were calculated from the measured $^{40}\text{Ar}/^{39}\text{Ar}$ ratios. The raw data were corrected for procedural blanks, instrumental mass discrimination based on atmospheric Ar measurements, radioactive decay of irradiation-produced ^{37}Ar and ^{39}Ar , and interference corrections for ^{36}Ar , ^{39}Ar , and ^{40}Ar produced from ^{40}Ca , ^{42}Ca , and ^{40}K , respectively. The following correction factors were applied: $(^{39}\text{Ar}/^{37}\text{Ar})\text{Ca} = 0.001279 \pm 0.000061$, $(^{36}\text{Ar}/^{37}\text{Ar})\text{Ca} = 0.000613 \pm 0.000084$, and $(^{40}\text{Ar}/^{39}\text{Ar})\text{K} = 0.0191 \pm 0.0018$. The amount of ^{40}Ar in the procedural blank did not exceed 0.5 ng.

4. Results

4.1. Lithology

4.1.1. Granitoids

The Kunush massif is composed of biotite plagiogranites. These granites are commonly affected by late metasomatic alteration; however, relatively weakly altered rocks are preserved in some areas (Figure 3a). These rocks exhibit an inequigranular texture. Approximately 55 vol.% of the rock consists of subhedral plagioclase grains with zoned interiors.

The interstices between plagioclase grains are filled with fine-grained recrystallized quartz (up to 30 vol.%) and fine flakes of recrystallized biotite (up to 15 vol.%). This texture indicates that the plagiogranites underwent deformation after magma crystallization. Most of the granites of the Kunush massif have undergone post-magmatic metasomatic alteration, with two processes being especially well-developed: (a) graphitization and (b) greisenization. Graphitization is characterized by the pervasive distribution of fine-flake graphite throughout the granite (Figure 3b). This process is accompanied by the recrystallisation of biotite and muscovite (sericite), whereas quartz is the only primary mineral preserved. Greisenization is characterized by the replacement of plagioclase by sericite (Figure 3c), the widespread development of muscovite, and the appearance of ore minerals, including cassiterite, scheelite and arsenopyrite. Graphitization and greisenization commonly occur simultaneously in the Kunush granites, particularly near ore bodies.

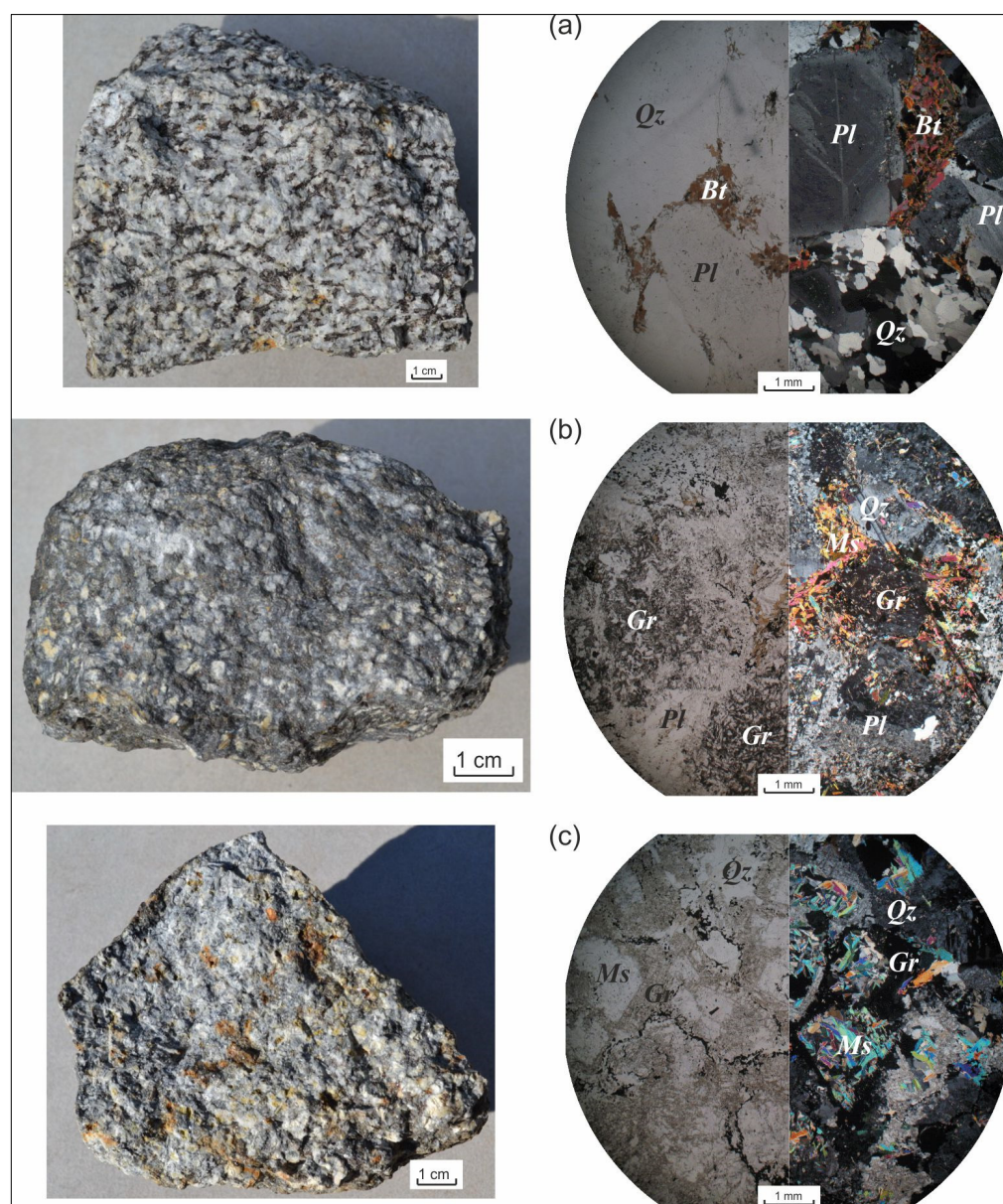


Figure 3. Photo (samples on a left) and photomicrographs (thin sections on a right) of Kunush granites. (a) Slightly weathered Bt plagiogranite, (b) graphitized Bt plagiogranite, (c) greisenized Bt plagiogranite. Qz—quartz, Pl—plagioclase, Bt—biotite, Ms—muscovite, Gr—graphite.

The Cherdoyak intrusion, located east of the Cherdoyak deposit, comprises two intrusive phases. The first-phase granites constitute most of the intrusion. They are weakly altered medium- to coarse-grained biotite granodiorites containing approximately 30 vol.% sodic plagioclase, 30 vol.% K-feldspar, 20 vol.% quartz, and up to 20 vol.% biotite (Figure 4a). The second-phase granites occur as small bodies and numerous dykes that cut the first-phase granites. They are fine-grained muscovite granites containing 30–40 vol.% quartz, approximately 50 vol.% feldspar, and up to 10 vol.% muscovite (Figure 4b). Garnet and tourmaline were identified in some second-phase granites.

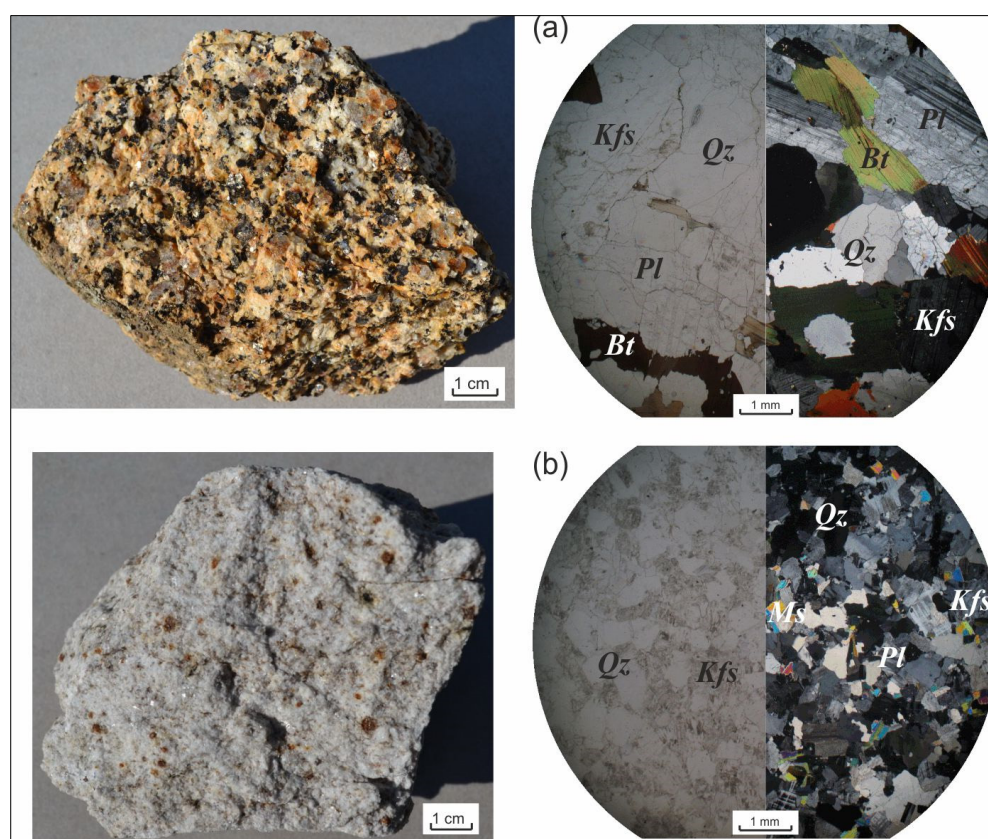


Figure 4. Photo (samples on a left) and photomicrographs (thin sections on a right) of Cherdoyak granites. (a) Bt granite of 1st phase, (b) Ms granite of 2nd phase. Qz—quartz, Pl—plagioclase, Kfs—K-feldspar, Bt—biotite, Ms—muscovite.

4.1.2. Ore-Bearing Rocks

The ore-bearing rocks are represented by greisens, graphite-bearing microgreisens, tourmaline–quartz veins, and quartz veins. Greisens and microgreisens form laterally extensive zones within the Kunush granites (Figure 2). Microgreisens are typically dark-grey rocks with a cryptocrystalline texture, and their colour is determined by abundant greenish muscovite and graphite (Figure 5a). In contrast, greisens have a crystalline texture and contain well-developed flakes of light-grey to light-green muscovite up to 1 cm in size (Figure 5b). The metasomatically altered rocks are cut by numerous small veins of two types. The first and most common type comprises quartz–tourmaline veins, in which massive tourmaline is abundant and may constitute more than 70 vol.% of the vein material (Figure 5c). The second, less common type comprises veins of relatively pure light-orange quartz containing large crystals (up to 3 cm) of hematite, goethite, and cassiterite (Figures 5d and 6a). Well-formed cassiterite crystals occasionally occur, showing well-developed faces of tetragonal prisms and bipyramids (Figure 6b).

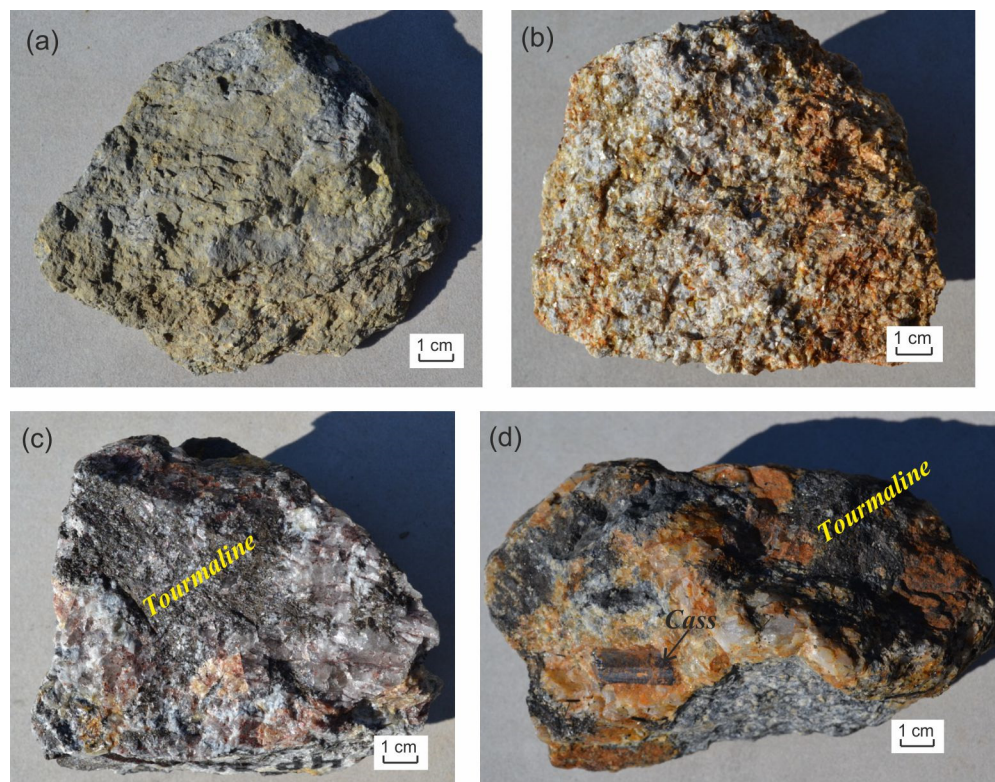


Figure 5. Photo of ore-rocks from Cherdoyak deposit. (a) Microgreisen, (b) greisen, (c) quartz vein with tourmaline, (d) quartz vein with cassiterite and tourmaline.

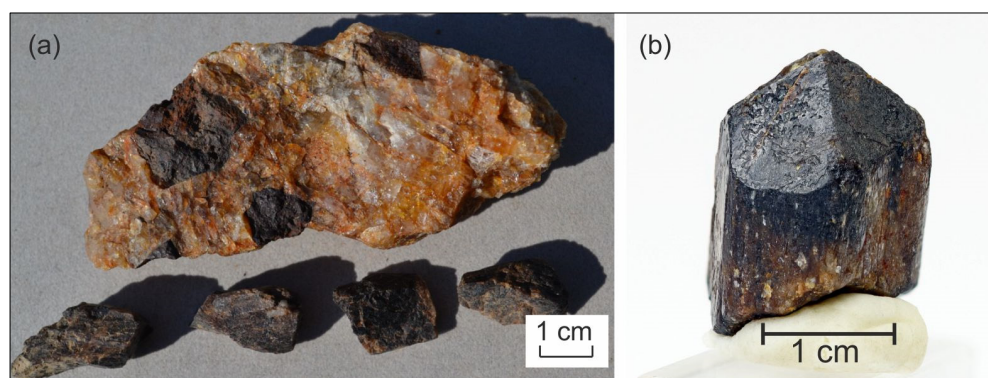


Figure 6. Photo of cassiterite crystals from Cherdoyak deposit. (a) Crystals in the quartz vein, (b) well-faceted crystal.

4.2. Ore Minerals

According to previous mineralogical investigations of the Cherdoyak deposit [22,24], the ore assemblage comprises cassiterite, scheelite, arsenopyrite, pyrite, and chalcopyrite.

Cassiterite occurs predominantly in quartz veins, where it is commonly associated with tourmaline. It typically forms isolated euhedral crystals up to 2–3 cm in size and, less commonly, crystal clusters. Well-developed crystals are numerous and exhibit distinct tetragonal prism and bipyramid faces (Figure 6b). The internal textures of selected cassiterite grains were examined using scanning electron microscopy (SEM). Cassiterite contains relatively large tourmaline inclusions together with abundant microcrystalline rutile inclusions, generally not exceeding 3–5 μm in size (Figure 7a). Representative electron-microprobe compositions of cassiterite and rutile are given in Table S1. Rutile contains up to 2.17 wt.% Nb_2O_5 , 3.14 wt.% WO_3 , and 0.94 wt.% V_2O_3 .

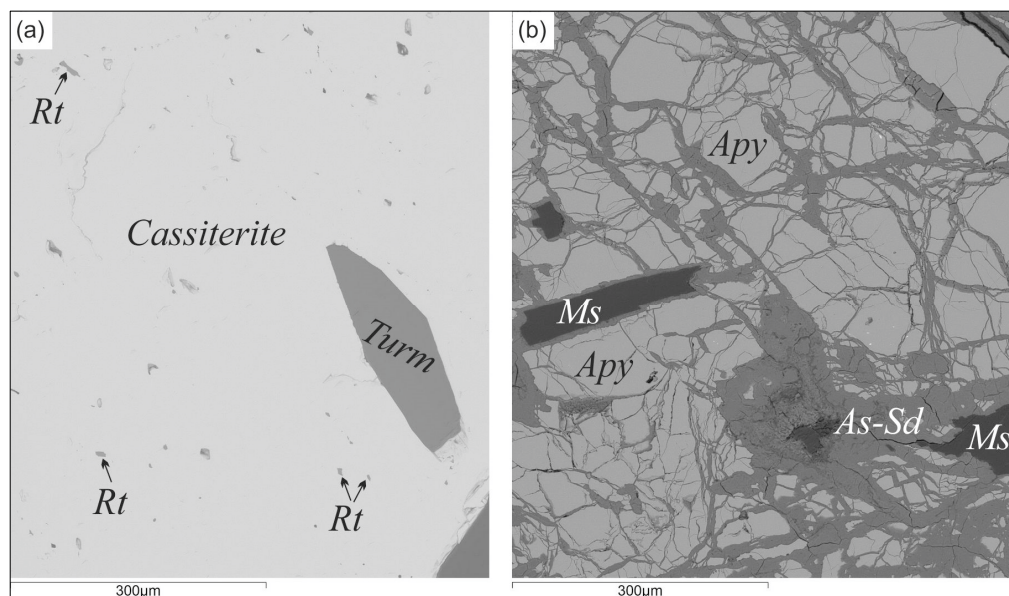


Figure 7. BSE-images of ore minerals from Cherdoyak deposit. (a) Cassiterite with rutile (Rt) and tourmaline (Turm) inclusions; (b) arsenopyrite (Apy) with muscovite (Ms) inclusions and veins of late arseniosiderite (As-Sd).

Scheelite is hosted mainly in quartz veins and veinlets as yellowish-white granular aggregates, whereas well-formed bipyramidal crystals are rare. It is generally associated with fluorite.

Arsenopyrite is present in quartz veins, greisens, and greisenized plagiogranites. It typically occurs as aggregates of anhedral to subhedral grains and, less commonly, as euhedral crystals up to 3 mm in size. Several arsenopyrite grains were investigated by SEM to examine their internal textures. Inclusions of pyrite and muscovite, together with microinclusions of native bismuth, are present in arsenopyrite. The mineral is commonly affected by oxidation, resulting in the formation of secondary mineral phases and numerous veinlets of scorodite and arseniosiderite (Figure 7b). Representative electron-microprobe analyses of arsenopyrite are presented in Table S2. Arsenopyrite contains up to 0.82 wt.% Co and 0.44 wt.% Ni.

Pyrite is found in quartz veins as well as in greisens and greisenized plagiogranites, where it is closely associated with arsenopyrite. It is frequently replaced by secondary iron oxides, including goethite and limonite.

Chalcopyrite is a minor ore mineral and occurs as irregular anhedral grains in quartz veins.

4.3. Geochemistry

The analytical data are provided in Table S3. For geochemical study of granitoids, only samples that show no visible secondary alteration and contain only paragenesis of primary igneous minerals were selected. This was verified by petrographic observations.

The Kunush granites are plagiogranites characterized by Na_2O contents exceeding those of K_2O ($\text{Na}_2\text{O}/\text{K}_2\text{O} = 5.4\text{--}6.7$). In the altered plagiogranites, the K_2O content increases, resulting in a lower $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio of 2.4. The 1st-phase Cherdoyak rocks are high-K diorites and granodiorites ($\text{SiO}_2 = 62.4\text{--}67.9$ wt.%; $\text{Na}_2\text{O}/\text{K}_2\text{O} = 0.95\text{--}1.14$), whereas the 2nd-phase granites are represented by high-K leucogranites ($\text{SiO}_2 = 72.4\text{--}75.5$ wt.%; $\text{Na}_2\text{O}/\text{K}_2\text{O} = 0.7\text{--}1.4$). On the TAS diagram [32], the Kunush granites plot near the boundary between the granodiorite and granite fields, the 1st-phase Cherdoyak granitoids plot within the diorite and granodiorite fields, whereas the 2nd-phase Cherdoyak granites plot within the granite field (Figure 8a). On the $\text{SiO}_2\text{--K}_2\text{O}$ discriminant diagram [33], the

Kunush granites belong to the tholeiitic series, whereas the Cherdoyak grantoids fall within the high-K calc-alkaline series (Figure 8b). According to the granitoid classification of Frost et al. [34], the Kunush plagiogranites are magnesian, belong to the calcic to calc-alkalic series, and are peraluminous. In contrast, the Cherdoyak granitoids are ferroan, belong to the calc-alkalic to alkali-calcic series, and are also peraluminous (Figure 8c–e).

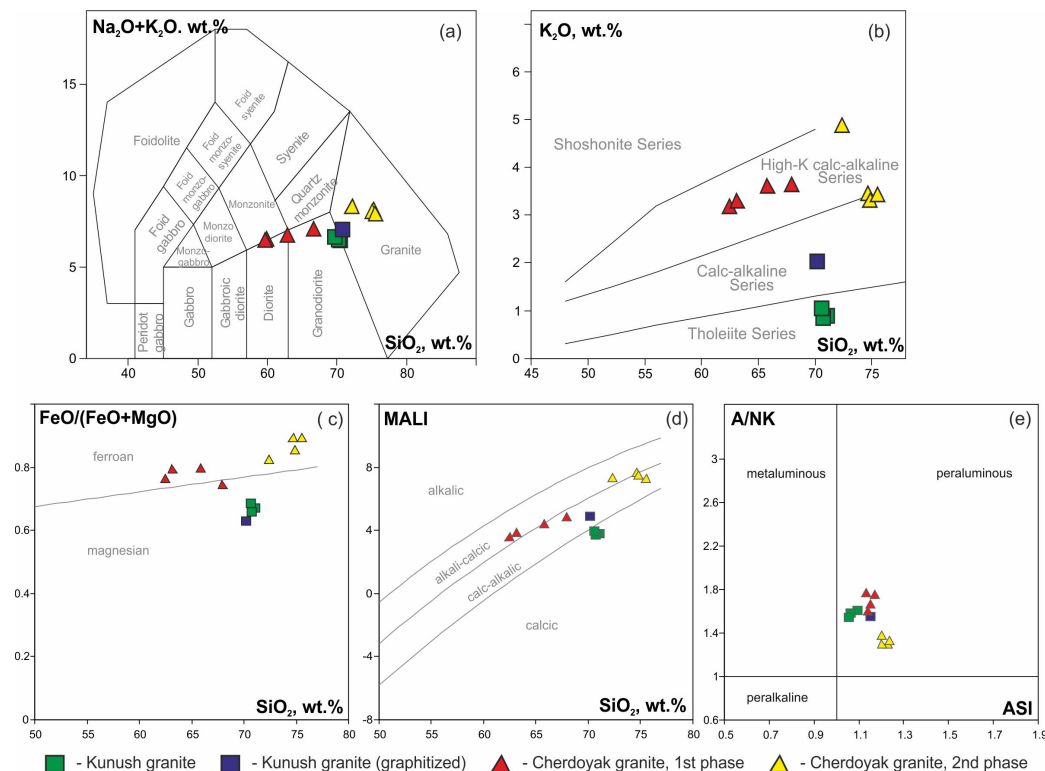


Figure 8. Composition of granites on a classification diagrams. (a) TAS diagram [32]; (b) SiO₂ vs. K₂O [33]; (c) SiO₂ vs. FeO/(FeO_{tot} + MgO) [34]; (d) SiO₂ vs. MALI [34]; (e) ASI vs. A/NK [34].

The Kunush granites are enriched in light rare earth elements (LREE) relative to heavy rare earth elements (HREE), with (La/Yb)_N values of 41–42, and have a weakly positive Eu anomaly: the Eu/Eu* ratio is 1.06–1.24 (Figure 9a). The REE pattern of the graphitized Kunush granite is nearly identical to that of the least altered granites but they have a weakly negative Eu anomaly: the Eu/Eu* ratio is 0.94. Primitive mantle-normalized trace-element patterns indicate relative depletion in both large-ion lithophile elements (LILE) and high-field-strength elements (HFSE), with pronounced negative Th and Nb anomalies and a positive Sr anomaly (Figure 9b). The 1st-phase Cherdoyak granitoids contain higher total REE abundances than the Kunush granites. They are also enriched in LREE relative to HREE, with (La/Yb)_N values of 10–18 and have a weakly negative Eu anomaly: the Eu/Eu* ratio is 0.8–1.12 (Figure 9a). Their primitive mantle-normalized trace-element patterns are characterized by LILE enrichment, pronounced negative Nb and Zr anomalies, and positive K and Hf anomalies (Figure 9b). The 2nd-phase Cherdoyak granites are characterized by lower total REE abundances, lower (La/Yb)_N ratios (2–7), and a pronounced negative Eu anomaly: Eu/Eu* = 0.27–0.58 (Figure 9a), that indicate a possible fractionation of plagioclase. Their trace-element patterns (Figure 9b) exhibit distinct negative anomalies in Ba, Eu (that indicate a possible fractionation of plagioclase and feldspar) Th, Nb, and Ti (that indicate a possible fractionation of accessory oxides), accompanied by a pronounced positive Hf anomaly.

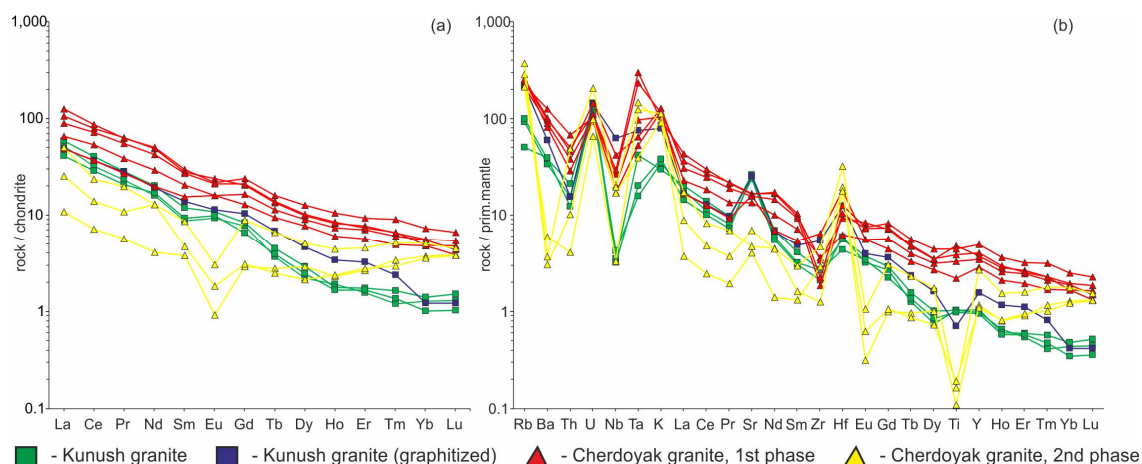


Figure 9. Chondrite-normalized rare earth element patterns (a) and primitive mantle-normalized spider diagrams (b) for granites of Kunush and Cherdoyak massifs. Normalizing values are from Sun and McDonough [35].

Trace-element concentrations in the greisens and quartz veins are generally lower than those in the granites (Table S3). However, rare metal abundances provide a more informative basis for comparison. Figure 10 shows average-continental crust-normalized rare metal patterns for the Cherdoyak rocks [36]. Compared with the least altered granites, the graphitized Kunush granite is markedly enriched in Rb, Be, Ta, Nb, Sn, W, Bi, Zn, Pb, As, and Ag. Greisens are enriched in Li, Cs, Be, Sn, and As relative to the granites. Their Rb, Cs, Nb, and Ag contents are comparable to those of the Kunush plagiogranites, whereas their Ta, W, and Bi contents are similar to those of the Cherdoyak granitoids. Relative to the granites, the greisens show the strongest enrichment in Sn, As, and W. Two scheelite-bearing greisen samples contain up to 3945 ppm W (these are probably areas of local accumulation of scheelite). Quartz veins are depleted in most rare metals relative to both granites and greisens, with the exception of Ta, W, Bi, and As. Among the analyzed elements, W and As reach the highest concentrations in the quartz veins.

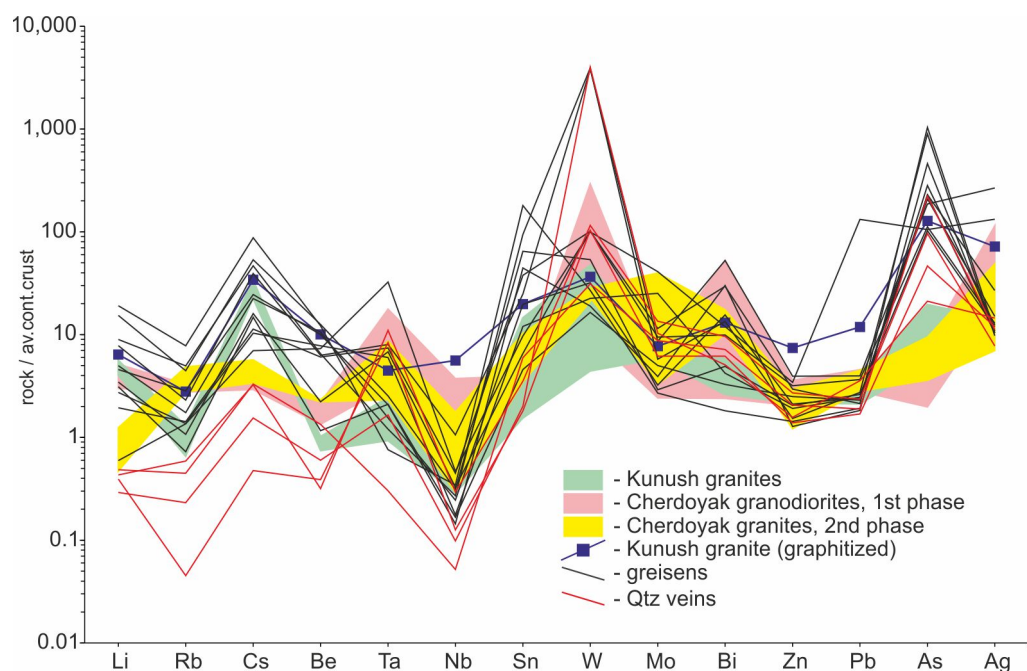


Figure 10. Average continental crust-normalized rare metal element patterns for rocks of Cherdoyak deposit. Normalizing values are from Rudnick and Gao [36].

4.4. Geochronology

The crystallization ages of the granitoids were determined by U–Pb dating of magmatic zircon (Figure 11).

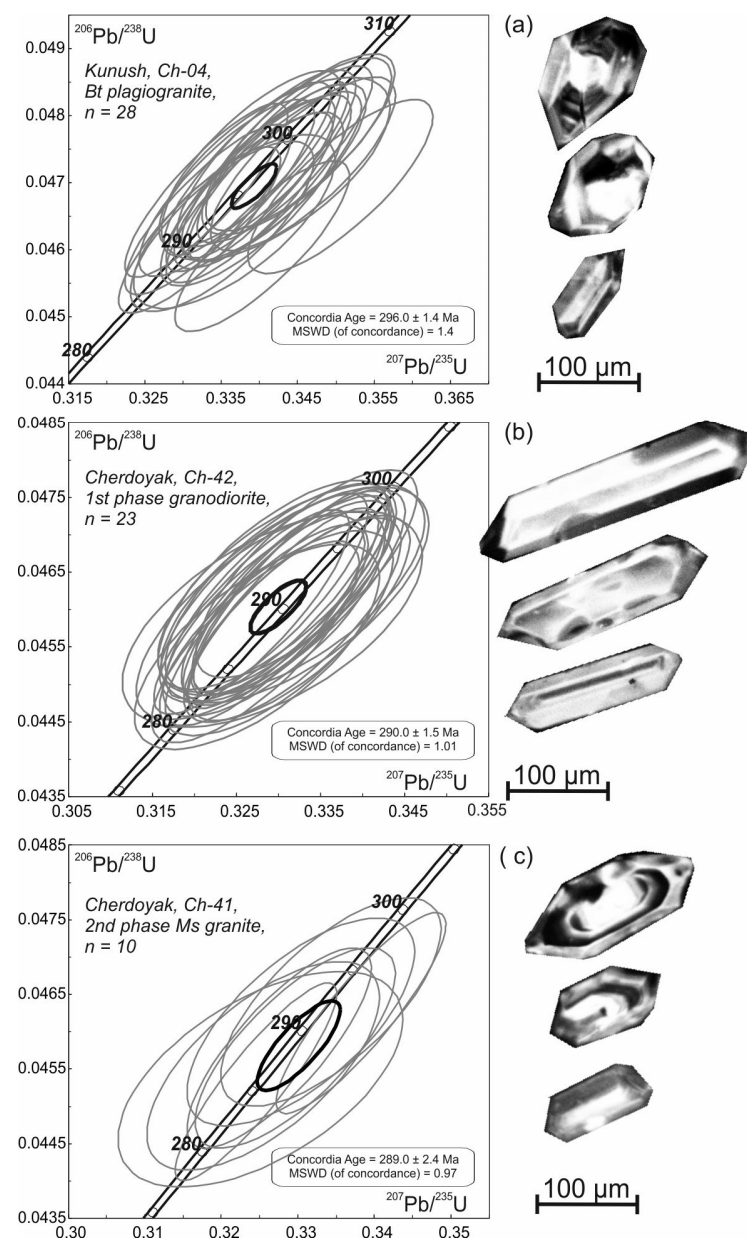


Figure 11. Results of U–Pb dating (concordia Wetherill diagrams) of magmatic zircon grains from Kunush (a) and Cherdoyak (b,c) granitoids. Errors of single analyses and calculated concordant ages are given at the level of 2σ. At the right are CL-images of the most typical zircon grains.

Three varieties of the least altered granitoids representing the main intrusive phases were selected for geochronological study: (a) biotite plagiogranite from the Kunush massif (sample Ch-04), (b) first-phase biotite granodiorite from the Cherdoyak intrusion (sample Ch-42), and (c) second-phase muscovite leucogranite from the Cherdoyak intrusion (sample Ch-41). The U–Pb isotope data are presented in Table S4. Zircon grains from the Kunush biotite plagiogranite are weakly elongated crystals, generally approximately 100 μm in length and 50–60 μm in width, with prismatic and bipyramidal morphologies. Magmatic oscillatory zoning is clearly visible in cathodoluminescence (CL) images (Figure 11a) and supported by the Th/U ratios in 0.12–0.65. Forty analytical spots were analyzed. The

concordia age calculated from 28 concordant analyses is 296.0 ± 1.4 Ma (MSWD = 1.4) (Figure 11a).

Zircon grains from the Cherdoyak first-phase biotite granodiorite are strongly elongated crystals, generally 150–200 μm in length and approximately 50 μm in width, with prismatic morphology and well-developed bipyramidal faces. Magmatic oscillatory zoning is clearly visible in CL images (Figure 11b) and supported by the Th/U ratios in 0.14–0.56. Forty analytical spots were analyzed. The concordia age calculated from 23 concordant analyses is 290.0 ± 1.5 Ma (MSWD = 1.01) (Figure 11b).

Zircon grains from the Cherdoyak second-phase muscovite leucogranite are elongated crystals, generally 100–150 μm in length and 50–60 μm in width, with prismatic and bipyramidal morphologies. Magmatic oscillatory zoning is clearly visible in CL images (Figure 11c) and supported by the Th/U ratios in 0.08–0.59. Twenty analytical spots were analyzed. The concordia age calculated from 10 concordant analyses is 289.0 ± 2.4 Ma (MSWD = 0.97) (Figure 11c). Thus, the crystallization ages of the Kunush and Cherdoyak granites correspond to the Early Permian. However, a distinct age gap of approximately 6 Myr separates the emplacement ages of the Kunush and Cherdoyak intrusions.

The timing of greisen formation at the Cherdoyak deposit was further constrained by $^{40}\text{Ar}/^{39}\text{Ar}$ dating of greisen muscovite (sample Ch-30). The Ar-Ar isotope data are presented in Table S5. The calculated age of muscovite in 280.2 ± 4.7 Ma corresponds to a plateau encompassing 97.4% of the cumulative ^{39}Ar release (Figure 12). The obtained greisen age is significantly younger (by approximately 6–10 Myr) than the crystallization ages of the granites. As zircon is a high-temperature mineral, its age can reflect the time of magma crystallization onset in chamber. But the greisenization and hydrothermal events could have occurred some Ma after emplacement of granites. At the same time, the difference in 9 Myr may be explained by the lower closure temperature of the K–Ar isotope system in mica (about 300 °C) compared with the U–Pb isotope system in zircon, resulting in younger apparent ages for mica. Thus, for granites of the Kalba batholith [9,37] and granites of the Ol'khon region [31], a systematic difference of 10–15 Myr was revealed between the U–Pb zircon age (the time of the onset of magma crystallization) and the Ar–Ar biotite or muscovite age (the time of cooling of the granite body to a temperature of about 300 °C). Therefore, we have reason to believe that the Cherdoyak deposit greisens formation is associated with the intrusion and cooling of Cherdoyak granites.

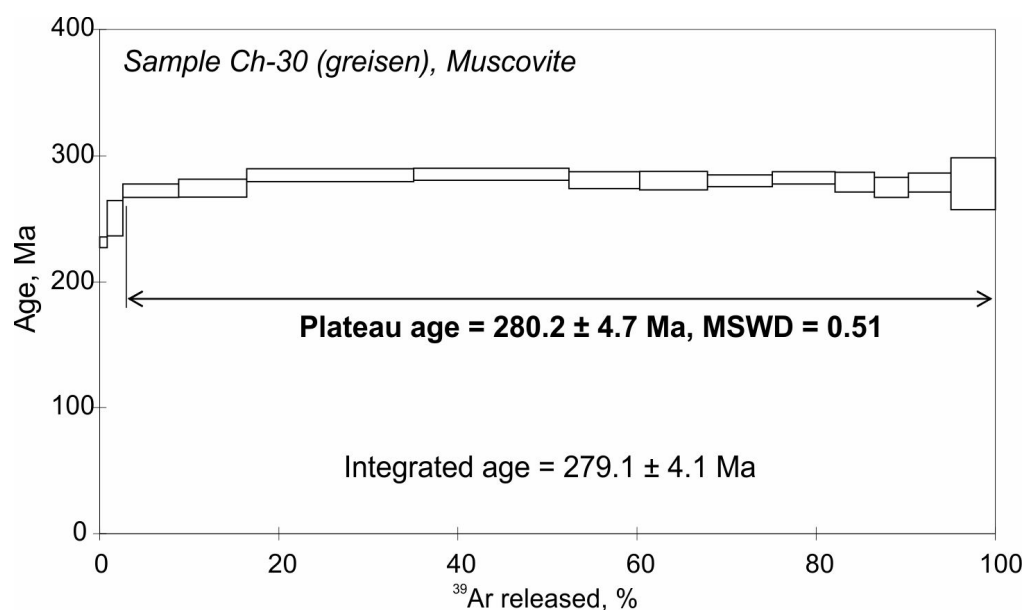


Figure 12. $^{40}\text{Ar}/^{39}\text{Ar}$ age spectra of muscovite from the greisen from Cherdoyak deposit.

5. Discussion

5.1. Origin of the Granitoids

The geological framework of Eastern Kazakhstan was formed during the Middle–Late Palaeozoic through the collision of the Siberian and Kazakhstan continents and the closure of the Ob–Zaisan Ocean [19,38]. During the Late Carboniferous–Early Permian, the region experienced post-orogenic extension, and subsequent magmatism was closely associated with the Tarim Large Igneous Province and the activity of the Tarim mantle plume [39–41].

Kunush and Cherdoyak granitoids were derived from different crustal sources, as indicated by their contrasting geochemical characteristics. The Kunush plagiogranites contain 70–71 wt.% SiO_2 and are characterized by Na_2O predominance over K_2O , high Sr concentrations, and relatively low Rb and Y contents. These features are consistent with I-type plagiogranites derived from the partial melting of metabasic amphibolitic lower- to middle-crustal sources [42]. The first-phase Cherdoyak granitoids contain 63–67 wt.% SiO_2 , have broadly comparable Na_2O and K_2O contents, relatively low Sr concentrations, elevated Rb contents, and belong to the ferroan series. These characteristics are consistent with K-rich I-type granites generated by the partial melting of amphibole–biotite-bearing metasedimentary rocks at middle-crustal levels, such as [42].

The coexistence of amphibolitic and metasedimentary source rocks within the crust was probably a consequence of Carboniferous collisional deformation and crustal thickening. One possible interpretation is that the deeper amphibolitic source underwent partial melting first, producing the Kunush plagiogranites at ca. 296 Ma. Partial melting of the shallower metasedimentary source followed approximately 6 Myr later, resulting in the emplacement of the Cherdoyak intrusion at ca. 290 Ma.

The second phase Cherdoyak granites are depleted in LREE, Ba, Sr, Eu, Th, P_2O_5 , and Ti, compared to the first-phase granodiorites. This indicates fractionation of plagioclase, as well as accessory oxides (e.g., ilmenite and orthite) and phosphates (e.g., monazite) during the evolution of the granitoid magma. These differences could also theoretically be due to partial melting of another source or assimilation processes. However, no other geological formations are known in the region other than Takyr Formation metagraywackes, the melting of which most likely formed the primary magmas of the Kalba granitoids [20]. This allows us to suggest fractional crystallization of the first-phase Cherdoyak granodiorites as the most likely mechanism for the formation of the second-phase Cherdoyak granites. The fractional crystallization resulted in the enrichment of second-phase Cherdoyak granites in silica and alkalis. Continued magmatic differentiation promoted the accumulation of volatile components, as also indirectly indicated by the abundance of muscovite in the second-phase granites. The exsolved magmatic fluids were probably enriched in rare metals, which were subsequently concentrated within the hydrothermal system and ultimately gave rise to greisen mineralization.

5.2. Genetic Model for the Cherdoyak Deposit

Studies of analogous Sn–W deposits in the Sikhote-Alin region (Russia) [11,43,44], China [45,46], and Portugal [47] indicate that Sn–W mineralization is genetically associated with rare metal granitic magmatism. During magma evolution, fluid–melt differentiation within the magma chamber produces late-stage granitic melts enriched in alkalis and rare metals. Continued differentiation subsequently leads to the exsolution of a volatile-rich magmatic fluid enriched in F, K, and rare metals. Migration of these fluids into the apical part of the intrusion ultimately results in the development of greisen-type mineralization.

Compared with the least altered Kunush plagiogranites, the graphitized plagiogranite contains markedly higher concentrations of Rb, Be, Ta, Nb, Sn, W, Bi, Zn, Pb, As, and Ag. This enrichment indicates that these elements were introduced by hydrothermal fluids

derived from the differentiated Cherdoyak magmatic system rather than from the Kunush granites themselves. This interpretation is supported by the elevated concentrations of Rb, Be, Ta, Nb, Sn, W, Bi, Zn, Pb, and Ag in the Cherdoyak granites relative to those of the Kunush granites. At the same time, the graphitized Kunush plagiogranite is enriched in B, As, and C. Boron concentrations in the least altered granites of both intrusive bodies do not exceed 371 ppm and average 74–85 ppm. The graphitized plagiogranite contains 143 ppm B, whereas the greisens and quartz veins contain average B concentrations of 135–144 ppm (Table S3). Arsenic concentrations in the least altered of Kunush and Cherdoyak granitoids do not exceed 49 ppm and average 11–32 ppm. By comparison, the graphitized plagiogranite contains 320 ppm As, whereas the quartz veins and greisens contain average concentrations of 241 and 876 ppm As, respectively. Carbon concentrations were not determined directly; however, the macroscopic characteristics of the samples indicate that graphitized plagiogranites, greisens, and some quartz veins contain abundant graphite. Because granitic magmas are unlikely to have been the principal source of B, C, and As, these elements were most probably derived from the carbonaceous metasedimentary rocks of the Takyr Formation. These geological relationships and geochemical observations form the basis of the conceptual genetic model for the Cherdoyak deposit proposed in Figure 13.

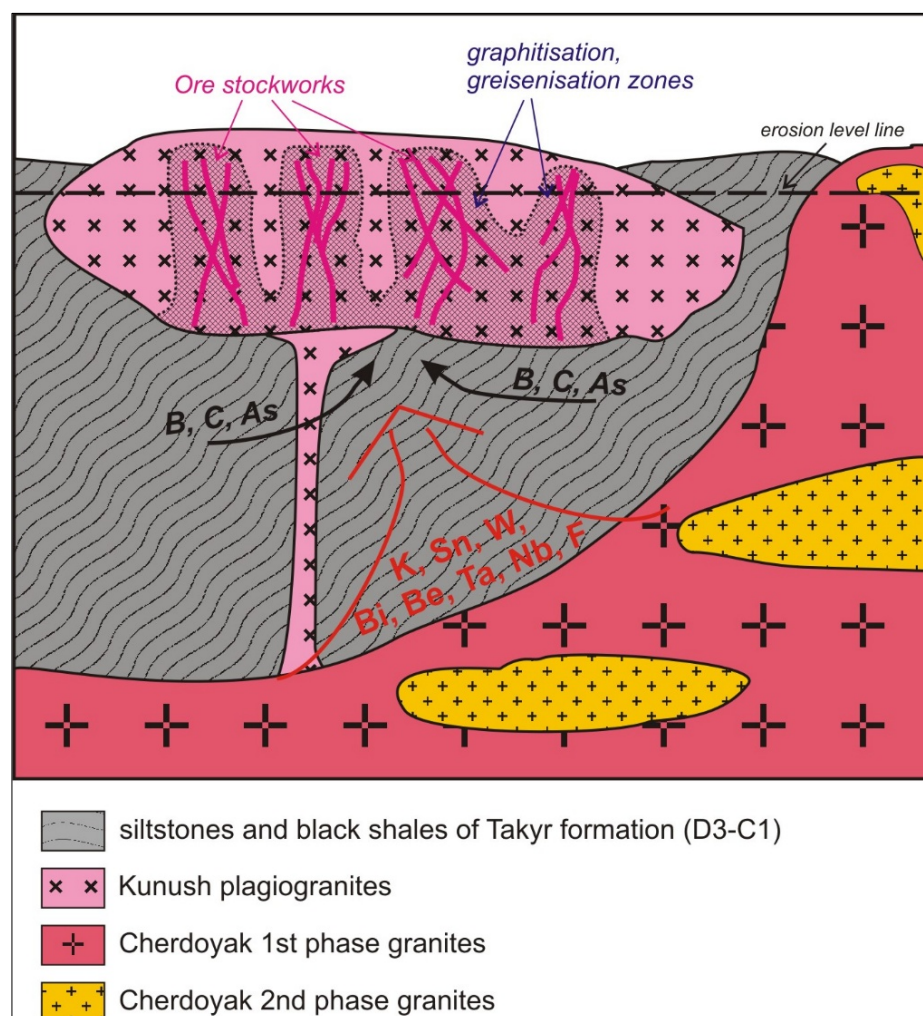


Figure 13. A conceptual model of the Cherdoyak deposit formation.

The first stage of deposit evolution involved the emplacement of the Kunush intrusion at ca. 296 Ma following partial melting of an amphibolitic lower-crustal source. Because the intrusion was relatively small, its thermal influence on the surrounding rocks of the

Takyr Formation was limited. The second stage commenced with emplacement of the much larger Cherdoyak intrusion at ca. 290 Ma. Emplacement of this magma generated an extensive fracture network within the surrounding rocks. The folded carbonaceous metasedimentary siltstones and shales are strictly anisotropic so their fractures caused difficulties, whereas the comparatively brittle Kunush granites may have experienced intensive fracturing [48]. At the same time, progressive crystallization of the Cherdoyak magma chamber was accompanied by magmatic differentiation, producing volatile-rich, alkali-rich, and rare metal-enriched granites of the second intrusive phase. Continued evolution of the magma ultimately resulted in the exsolution of an even more highly enriched magmatic fluid.

Unfortunately, we do not have direct data on the fluid inclusions in granites or in ore samples from the Cherdoyak deposit, which does not allow us to know exactly the fluid composition of the formed deposit. We also lack any isotopic data for Cherdoyak deposit rocks. However, the Nd isotope composition data presented in [20] indicate that the Nd features of Takyr Formation metasedimentary rocks and Kalba granites are very similar ($\epsilon(\text{Nd})_T$ is from -4 to $+1$ for the metasedimentary rocks and from 0 to $+3$ for the Kalba granites). This precludes a reliable distinction between the sources of ores using isotopic data. Therefore, we can only rely on geochemical data in our analysis. They allow us to assume that magmatic fluids enriched in K, Sn, W, Bi, F, Be, Ta, and Nb migrated upward from the Cherdoyak magma chamber.

Interaction between the high-temperature magmatic fluids and the carbonaceous metasedimentary rocks induced contact metamorphism and promoted mobilization of externally derived aqueous fluids enriched in C, B, and As. These components are usually present in significant quantities in metasedimentary rocks—clay shales and black shales [49–51]. In addition, none of the studied granites show enrichment in these components, and therefore only Takyr formation is the possible source.

The resulting mixed magmatic–hydrothermal fluids subsequently migrated through the fracture network developed within the Kunush granite body, where they produced greisen alteration, quartz veining, and stockwork-type mineralization. Consequently, the ore system became strongly enriched in Sn, W, and As, with Sn representing the principal economic commodity.

6. Conclusions

The results of this study indicate that the formation of the Cherdoyak deposit was controlled by the combined influence of three principal factors: structural–geological, magmatic, and geochemical.

The structural–geological factor reflects the emplacement of the relatively small Kunush granite intrusion within the tightly folded and mechanically competent rocks of the Takyr Formation. This structural configuration promoted the development of an extensive fracture network within the more brittle Kunush granites, providing favourable pathways and structural traps for ore-forming fluids.

The magmatic factor is represented by the emplacement of the large Cherdoyak granodiorite intrusion, which acted as the principal source of heat and rare metal-bearing magmatic fluids.

The geochemical factor reflects progressive fractionation of the Cherdoyak magma, resulting in the generation of rare-metal-enriched magmatic fluids together with mobilization of B, C, and As from the surrounding rocks of the Takyr Formation during fluid–rock interaction.

Taken together, these observations suggest that the Early Permian granitoid intrusions of the Kalba Complex throughout the Narym ore district represent promising sources of

Sn–W–As mineralization. Future explorations should focus on the apical and contact zones of large granitic intrusions, particularly where they intrude older granitoid bodies that may provide favourable host rocks for stockwork-type mineralization.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min16090958/s1>, Table S1: Cassiterite and rutile composition; Table S2: Arsenopyrite composition; Table S3: Rocks of Cherdoyak deposit composition; Table S4: U–Pb data on analysis of zircon grains from Kunush and Cherdoyak granites; Table S5: The results of $^{40}\text{Ar}/^{39}\text{Ar}$ dating.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

A/NK	Molar $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O} + \text{K}_2\text{O})$ ratio
ASI	Aluminum saturation index
BSE	Backscattered-electron
BWR	Boiling water reactor
CL	Cathodoluminescence
EDS	Energy-dispersive X-ray spectroscopy
EKTU	D. Serikbayev East Kazakhstan Technical University
E-scan	Electrostatic scanning
HFSE	High-field-strength elements
HREE	Heavy rare earth elements
ICP–MS	Inductively coupled plasma mass spectrometry
IGM	V.S. Sobolev Institute of Geology and Mineralogy
LA–SF–ICP–MS	Laser ablation–sector-field inductively coupled plasma mass spectrometry
LILE	Large-ion lithophile elements
LREE	Light rare earth elements
MALI	Modified alkali–lime index
MSWD	Mean square of weighted deviates
REE	Rare earth elements
SB RAS	Siberian Branch of the Russian Academy of Sciences
SEM	Scanning electron microscopy
TAS	Total alkali–silica
XRF	X-ray fluorescence

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