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Geology, Mineralogy, and Age of Li-Bearing Pegmatites: Case Study of Tochka Deposit (East Kazakhstan)

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Abstract: New geological, mineralogical, geochemical, and geochronological data have been obtained for Li-bearing pegmatites from the Tochka deposit located within the Karagoin–Saryozek zone in East Kazakhstan. Earlier, the exploration works in this zone were carried out to detect only Ta and Sn mineralization, but other ores (including Li) were not considered. The estimation of lithium resources in pegmatites from the area was methodologically imperfect. Previously, it was believed that the formation of rare-metal pegmatite veins was associated with Late Carboniferous Na-granites. The obtained geological observation confirms that the ore-bearing rare-metal pegmatites at the Tochka deposits cut the Late Carboniferous Na-granites and do not cut the Early Permian Kalba granites. The associations of the accessory minerals in host hornfels, Na-granites, and rare-metal pegmatites are different and the accessory minerals in pegmatites are similar to the accessory minerals in the Kalba granites. Geochemical data show that the behavior of rare elements (Ba, Th, HFSE, and REE) and the levels of accumulation of rare metals prove that pegmatites are similar to the product of the differentiation of the granitic magmas of the Kalba complex. The $^{40}Ar/^{39}Ar$ muscovite age of the Tochka pegmatites (~292 Ma) fits the age range of the Kalba granite complex. Based on the main principles of the generation of rare-metal pegmatites, the Tochka pegmatites formed during the fluid–magmatic fractionation of magma in large granitic reservoirs of the Kalba complex. The Karagoin–Saryozek zone—located between several large granite massifs of the Kalba complex where host rocks play a role as a roof—may be very promising for rare-metal pegmatite mineralization.

Keywords: rare-metal pegmatite; granite; lithium resources; development of Li pegmatite deposits; Ar-Ar dating; East Kazakhstan

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1. Introduction

The Central Asian Orogenic Belt (also known as the Altaids) accommodates voluminous Phanerozoic granitoid batholiths [1–9]. Granitic magmatism hosts Rb, Be, Mo, and W metals [10–13], including especially valuable Li, Cs, Ta, Nb, and Sn. Many rare-metal pegmatite bodies (first of all the lithium–cesium–tantalum (LCT) pegmatite family) are spatially and genetically associated with large granitoid intrusions and often occur as fields or swarms of veins, commonly along the margins or above the roofs of plutons [11,12,14–17].

Rare-metal pegmatite mineralization (LCT family) related to granitic magmatism is abundant in East Kazakhstan, which is part of a Late Paleozoic collisional suture between Siberia and Kazakhstan [18,19]. Magmatic activity in the region was the most active in the Early Permian [20–22] and produced, among others, the large Kalba and Zharma granitoid batholiths [21,22]. Large-scale magmatism occurred in a setting of post-collisional extension and was maintained by heat from the Tarim plume [23–27]. The area—with multiple and diverse juxtaposed igneous complexes—stores extremely rich resources of base, noble, and rare metals [28–33]. Rare-metal deposits cluster mainly within the Kalba–Narym belt bound by the West Kalba and Irtysh shear zones (Figure 1). A great part of rare-metal mineralization of pegmatite, albitite–greisen, greisen–quartz vein, and hydrothermal types is hosted by Early Permian granitoids of the Kalba batholith, including spodumene pegmatites bearing economic grades of Ta, Nb, Be, Li, Cs, and Sn located in the Asubulak ore district along intrusion margins in the Kalba granite complex [14]. Some sites of rare-metal mineralization in the area are located outside the Kalba complex: F-rich granite porphyry (ongonites) dikes in the northwestern end of the Kalba–Narym belt [34,35] and the Novoakhmirovo porphyry granite stock [36,37].

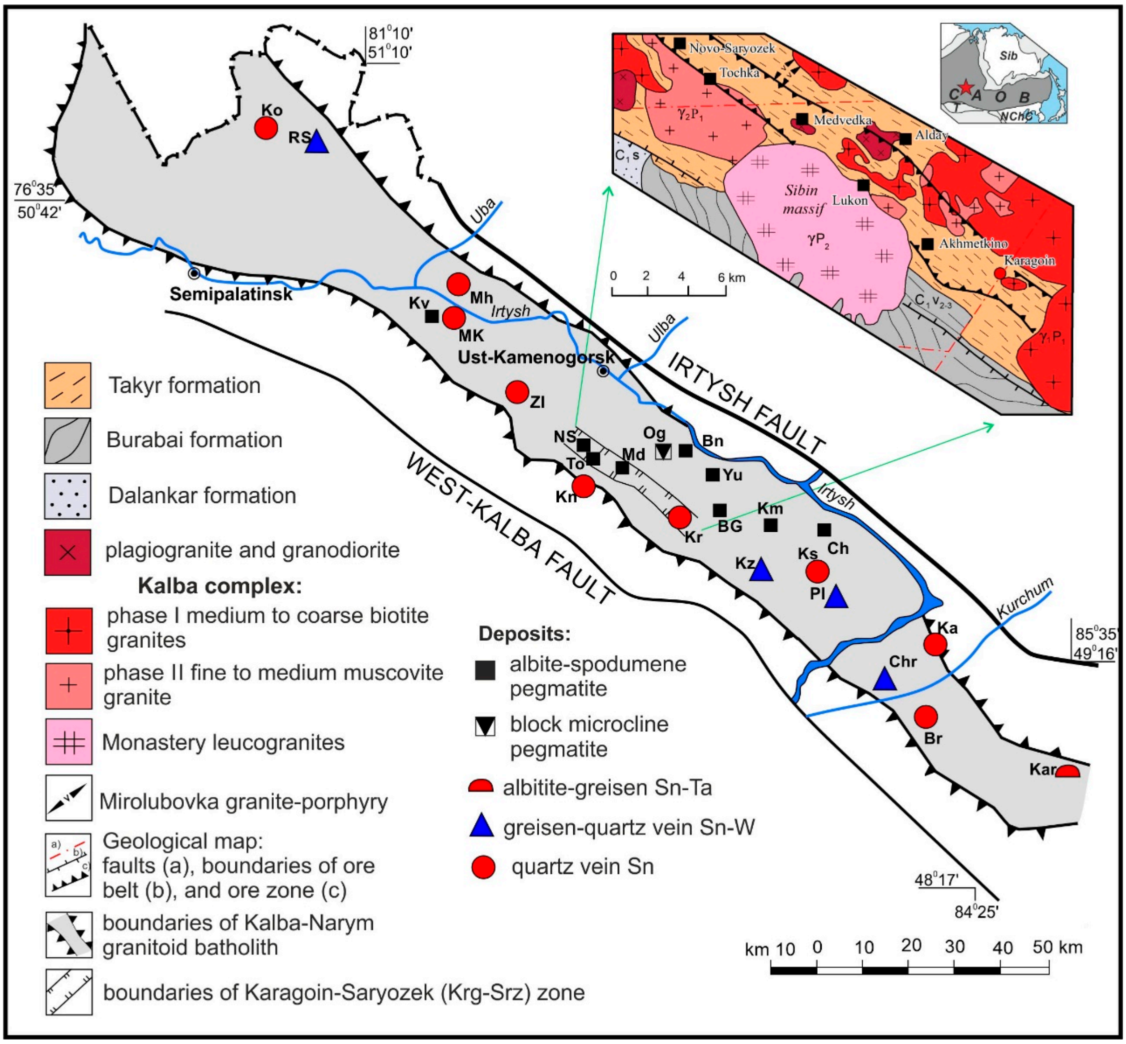

Figure 1. Location map of rare-metal deposits and occurrences in the Kalba–Narym belt [30]. Abbreviations stand for names of mineral deposits: Ko—Korosteli; RS—Rzhavaya Sopka; Mh—Mokhnatukha; MK—Malaya Kainda;, Kv—Kvartz; Zl—Zelenoye; Kn—Kanaika; NS—Novo-Saryozek; Md—Medvedka; To—Tochka; Kr—Karagoin; Og—Ognevka; Bn—Bakennoye; Yu—Yubileinoye; BG—Belaya Gora; Kz—Kozlovskoye; Km—Komarovskoye; Ks—Komsomolskoye; Ch—Chebuntay; Pl—Palatsy; Chr—Cherdoyak; Ka—Kasatka; Br—Burabay; Kar—Karasu. Sibiny pluton.

Some other rare-metal occurrences have no immediate linkage with large granitic plutons, although are located within their vicinity. They are, namely, the Tochka, Medvedka, Akhmetkino, Lukon, Alday, and other swarms of spodumene pegmatite veins (Figure 1) between the plutons within the Karagoin–Saryozek ore zone [38,39]. From 1955 to 1994, exploration works in this zone were carried out to detect Ta and Sn mineralization, but other ores (including Li) were not considered. The estimation of lithium resources in pegmatites from the area was methodologically imperfect. Pegmatite veins were sampled on 200 m × 150–200 m or 400 m × 200 m grids; however, this spacing is insufficient to pick ore intersections in the short veins, which are highly variable in morphology and composition, and to evaluate the volume of potentially metalliferous albite-spodumene material in individual veins and over the deposit as a whole. Average reported Li_2O contents [38,40–42] were underestimated, because Li grades were averaged over barren and albite–spodumene pegmatites taken together. Moreover, laboratory works, mainly by flame photometry and poorly sensitive semi-quantitative spectral analyses, failed to furnish appropriate information.

Thus, it is relevant to consider the mineralogical and geochemical characteristics of deposits in the Karagoin–Saryozek zone as promising for Li mineralization. We report geological, mineralogical, geochemical, and geochronological data from the Tochka deposit of rare-metal spodumene pegmatites, with implications for the age of mineralization and its relation to the granitoids.

2. Geological Background

The Karagoin–Saryozek ore potential zone—60 km long and 4–6 km wide—strikes in the NW direction along the margins of intrusions within the Kalba–Narym batholith. The batholith comprises the large Shubarshoky, Dvoryansky, Eshkulmes, and Sibiny plutons composed of granites and leucogranites, as well small NW aplitic intrusions and granite porphyry dikes between them, which may belong to a zone of hidden supra–plutonic granitic bodies.

The Tochka deposit is located in the northwestern part of the Karagoin–Saryozek zone, near Bayash-Utepov Village. It is a field of rare-metal pegmatite veins, more than 3 km long and 300 m wide, at the northeastern margin of the Shubarshoky pluton (Figure 2). The area accommodates two small intrusions that consist of granites of two types: (1) the intrusion of Na-rich biotite granites on the east that belong to the Late Carboniferous Kunush complex and have a 299 ± 2 Ma age [43]; (2) the intrusion of K-Na biotite granites that are an apophysis of the Shubarshoky pluton assigned to the Early Permian Kalba complex with ages from 296 to 286 Ma [6,23,24]. The Tochka pegmatite veins crosscut the Kunush Na-granites but do not intrude the Kalba granites (Figure 2).

As it was found out previously [25,27–29,33], the ore bodies of the deposit are mainly localized in deformed and metamorphosed black shales of the Takyr Fm. (D_3–C_1) and in Na-granites (Bariernaya vein, etc.).

Pegmatite veins, 3–5 m thick and 250–300 m long, strike in the NW direction (315–330°) concordantly with the black shale sequence and dip mainly to the NE at 70–85°; later quartz veins are 0.2–1.0 m thick. The pegmatites are of microcline, microcline–albite, albite, and albite–spodumene types. No zonation is observed within the pegmatite veins; each vein is represented by any one mineralogical type. However, in the contact zones of some veins, there are medium-grained or fine-grained quartz–microcline–muscovite greisens. All pegmatite veins are subparallel and have almost no crossing relationships. Thus, it is impossible to unambiguously establish the sequence of intrusion of different pegmatite types; most likely they were introduced synchronously.

The pegmatite veins within the field make up the central and southern zones displaced 380 m one relative to another by sublatitudinal faults. Within the field, three pegmatite formations of the northwestern direction are distinguished, located in a vertical section one under the other: the Eastern Fm. (hanging side), Central Fm., and Western Fm. (recumbent). The Central Fm. is the most promising, composed mainly of albite–spodumene pegmatites, which form two bundles of closely spaced veins, with a total thickness of about 23 m. Each bundle consists of 3–5 closely spaced bodies 170–200 m long and it is considered as a single ore body. The pegmatite veins are exposed on the surface (veins 13, 14, etc.) and exhibit nest-like clusters of spodumene crystals more than 1 m in size, most often in the vein interior. According to drilling evidence, economic albite–spodumene mineralization is unevenly distributed and is traceable to depths of 200–300 m or more [38].

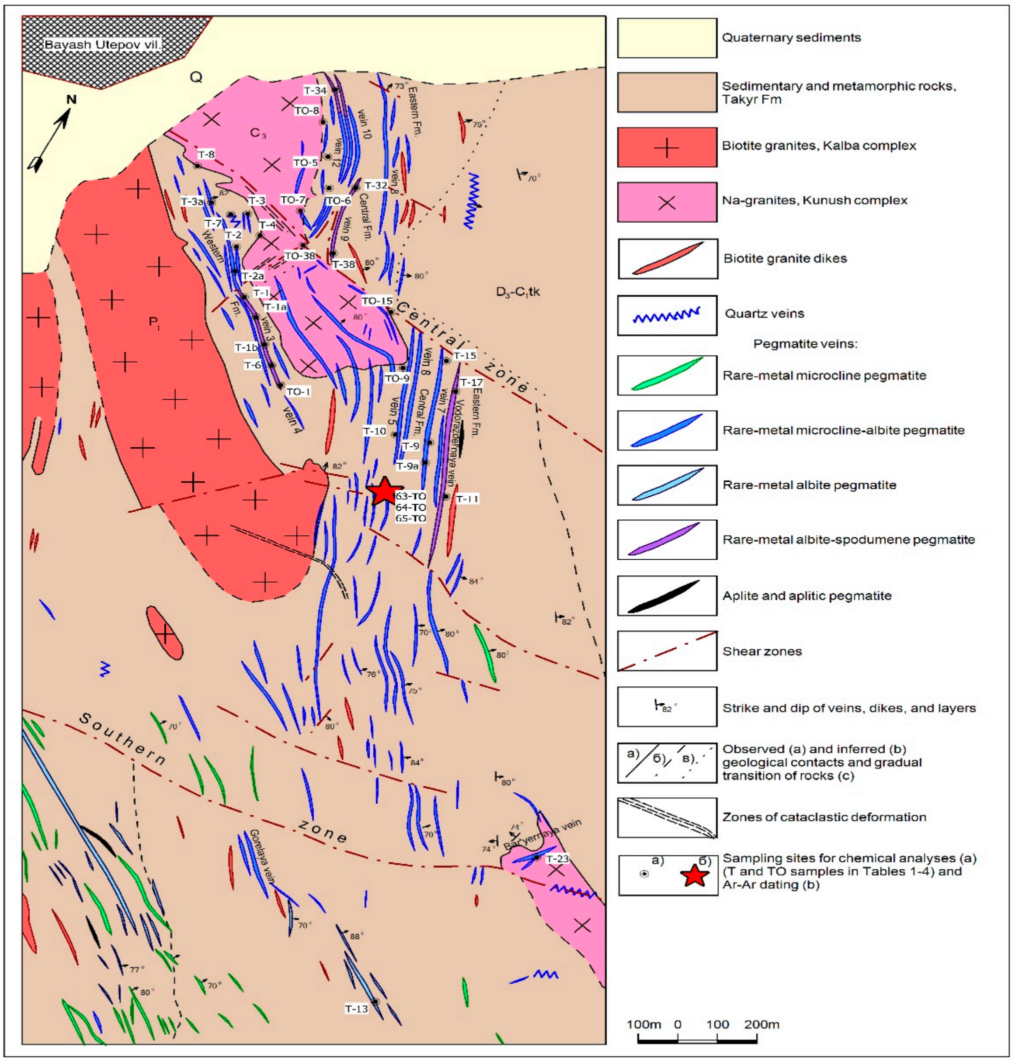

Figure 2. Local geology of the Tochka deposit, from Kashcheev et al. [38].

3. Materials and Methods

The study included field and analytical work and was made with reference to the available published evidence and survey reports of different years [38,40–42,44]. Fifty samples of rare-metal pegmatites and country rocks were collected for analyses. Large-volume samples of pegmatites weighing up to 10 kg were taken. Chemical analyses were carried out for bulk rocks and, in some cases, for the spodumene monomineral fraction. Additionally, to assess the effect of pegmatite veins on the host rocks, the host rocks samples (hornfelses and Na-granites) were taken and analyzed.

The samples were dried at a temperature of 105 °C and then ground to a fraction of less than 71 mkm. Before geochemical measurements, the samples were transferred into a solution using polyacid decomposition. During acid decomposition, standard samples of the composition of aqueous solutions of elements were used as calibration solutions. Calibration solutions were prepared by diluting standard samples with a solution of nitric acid with a molar concentration of 1 mol/dm^3, a mass concentration of 2% or 5%; hydrochloric acid solution with a mass concentration of 10% or water. A solution of nitric acid with a mass concentration of 5% was used as a background solution.

The analyses were performed at the VERITAS Laboratory of the D. Serikbaev East Kazakhstan Technical University (Ust'-Kamenogorsk, Kazakhstan). The compositions of rocks and minerals were determined, respectively, by mass spectrometry with inductively coupled plasma (ICP-MS) on an Agilent 7500cx (Agilent Technologies, Santa Clara, CA, USA) spectrometer and by electron probe microanalysis (EPMA), under standard operation conditions, on a Cameca MS-46 analyzer (Cameca, Gennevilliers, France) that allowed detection and precise measurements of seventy-three elements (Au, Ag, Pt, Cd, In, Ir, Y, Cd, REE, U, etc.). Scanning electron microscopy and energy dispersive spectrometry (SEM-EDS), with a Jeol-100C microscope with a Kevex-Ray detector and a Jeol ISM-6390 LV microscope (JEOL, Tokyo, Japan) with an Oxford INCA Energy system, were applied to study micrometer inclusions of metallic and gangue minerals and to analyze impurity elements (Au, Ag, Sb, As, Pt, In, U, etc.).

The $^{40}Ar/^{39}Ar$ dating of muscovite was carried out using the stepwise heating technique [45,46]. The samples were irradiated in a nuclear BWR-reactor at the Tomsk Polytechnic University (Tomsk). A standard biotite sample MSA-11 (OSO No. 129-88) with an age of 311.0 $\pm$ 1.5 Ma, validated against international standard samples Bern-4M (muscovite) and LP-6 (biotite), was used as the fluence monitor. The ages of the Bern 4M and LP-6 standard samples were assumed to be 18.51 and 128.1 Ma, respectively. The Ar isotopic composition in the irradiated samples was measured using a Noble Gas 5400 (Micromass) mass spectrometer [45,46]. The separation of gas fractions and the isotopic analysis of argon were carried out in a temperature range from 500 to 1200 °C. The raw data were corrected for procedural blank mass discrimination by analysis of atmospheric Ar, decay of radioactive ^{37}Ar and ^{39}Ar isotopes produced by irradiation, and interferences of ^{36}Ar, ^{39}Ar, and ^{40}Ar produced from ^{40}Ca, ^{42}Ca, and ^{40}K, respectively. The corrections were applied using the following coefficients: $(^{39}Ar/^{37}Ar)_{Ca}$ = 0.001279 $\pm$ 0.000061, $(^{36}Ar/^{37}Ar)_{Ca}$ = 0.000613 $\pm$ 0.000084, $(^{40}Ar/^{39}Ar)_{K}$ = 0.0191 $\pm$ 0.0018. The amount of ^{40}Ar in the blank did not exceed 0.5 ng.

4. Results

4.1. Mineralogy

4.1.1. Host Rocks

Rare-metal mineralization in the area is hosted by the Late Devonian–Early Carboniferous (D_3–C_1) Takyr Fm. of carbonaceous shales, fine sandstones, and mudrocks. The rocks at the contacts with pegmatite veins include hornfelsed shales (Figure 3a) and muscovitized hornfels with $\leq$0.5 cm flaky and platy muscovite (Figure 3b,d). The shales bear signatures of contorted bedding with small thin folds delineated by 0.5–1.0 cm thick veins (Figure 3c) [47,48].

The hornfels rocks enclose micrometer grains of ilmenite, magnetite, zircon, monazite, and xenotime (Figure 4a–d). A pyrite microcrystal with inconspicuous faces was also revealed (Figure 4e). In addition, a micro-inclusion of cassiterite was found in a microcrack (Figure 4f), reflecting the overlay of ore-bearing fluids on hornfelses. The composition of accessory minerals from hornfels are given in Supplementary Table S1. Ilmenite contains Mn (from 0.69% to 2.07%); monazite contains La (from 2.37% to 5.49%), Nd (from 2.77% to 6.02%), Th (from 1.12% to 1.79%); xenotime contains 3.2% of Dy.

4.1.2. Na-Granites

Na-granites are heavily cracked on the surface and enclose xenoliths of the Takyr Fm. (Figure 5a). They are deformed and metamorphosed in fault zones with chloritization of biotite, quartzitization, etc. Core samples are light grey, inequigranular, with distinct grains of white plagioclase (Figure 5b). Dikes are composed of quartz porphyry and quartz albitophyre (Figure 5c,d). Of special interest is a dike of quartz albitophyre with spherulites and streaks of fine albite enclosing acicular schorl tourmaline (Figure 5d), which indicates quite high concentrations of boron in granitic melts.

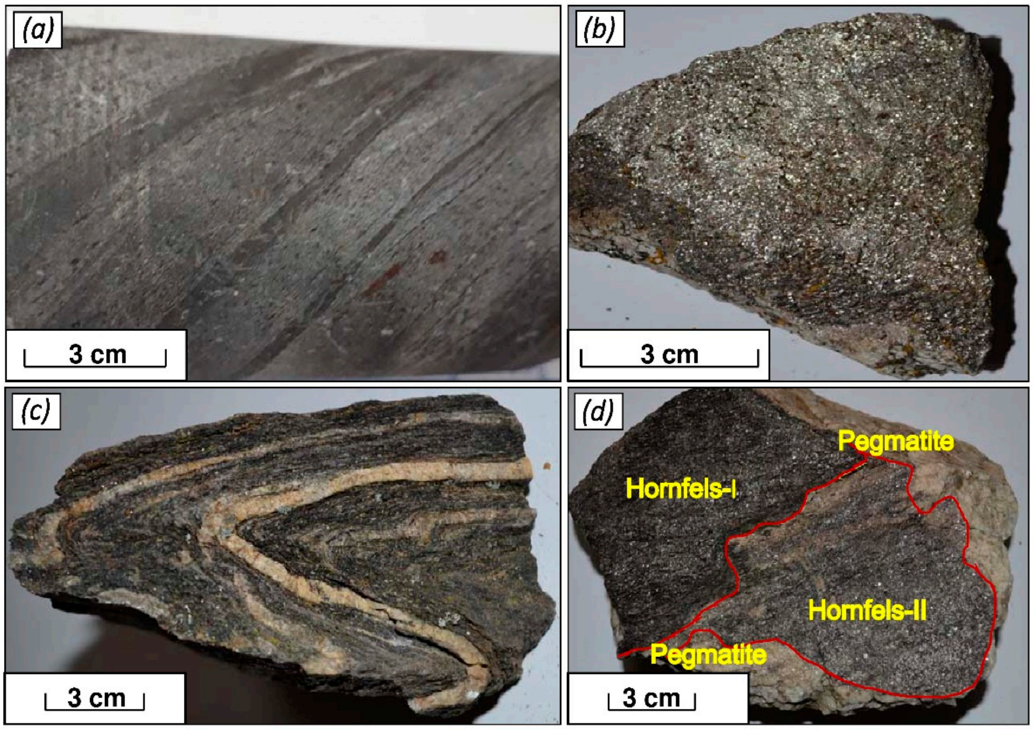

Figure 3. Takyr Fm. shales and hornfels from the Tochka area: black shale (**a**), muscovitized hornfels (**b**), folded hornfels with quartz veinlets (**c**), quartz–biotite–muscovite (I) and quartz–feldspar–muscovite (II) hornfels and pegmatite (**d**).

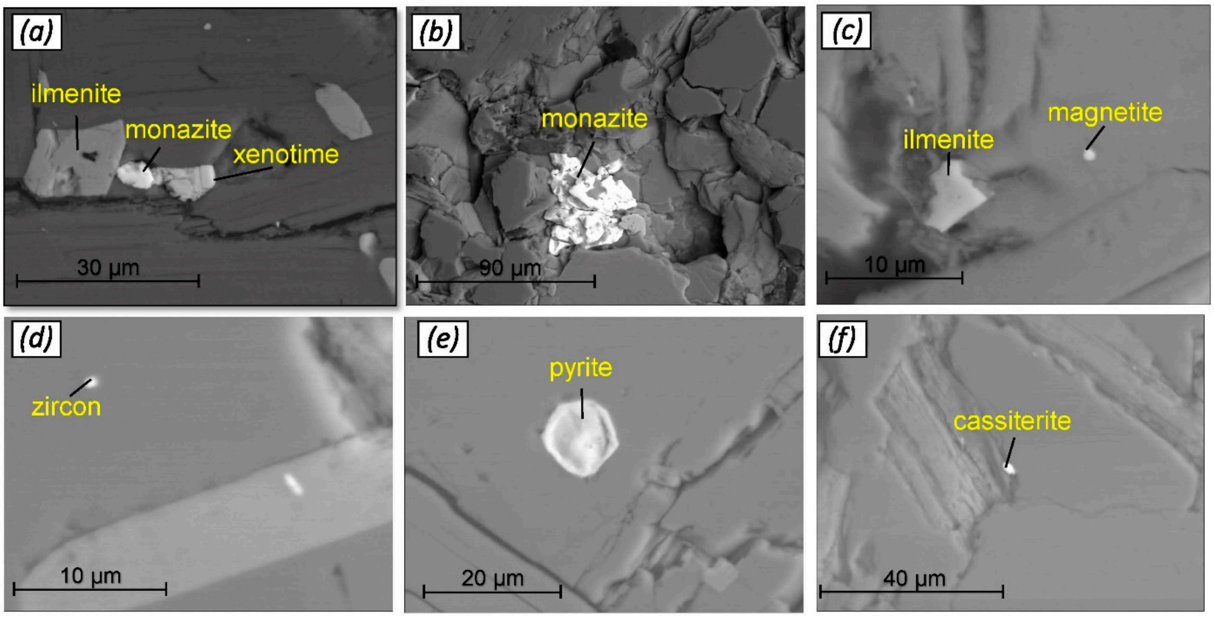

Figure 4. Micrometer accessory minerals in hornfels from the Tochka area (vein 2, sample TO-11, TO-5). (**a**) Nests of ilmenite, monazite, and xenotime; (**b**) a nest of monazite; (**c**) ilmenite and magnetite; (**d**) sub-micrometer zircon in hornfels and tourmaline; (**e**) oval pyrite; (**f**) cassiterite in a crack.

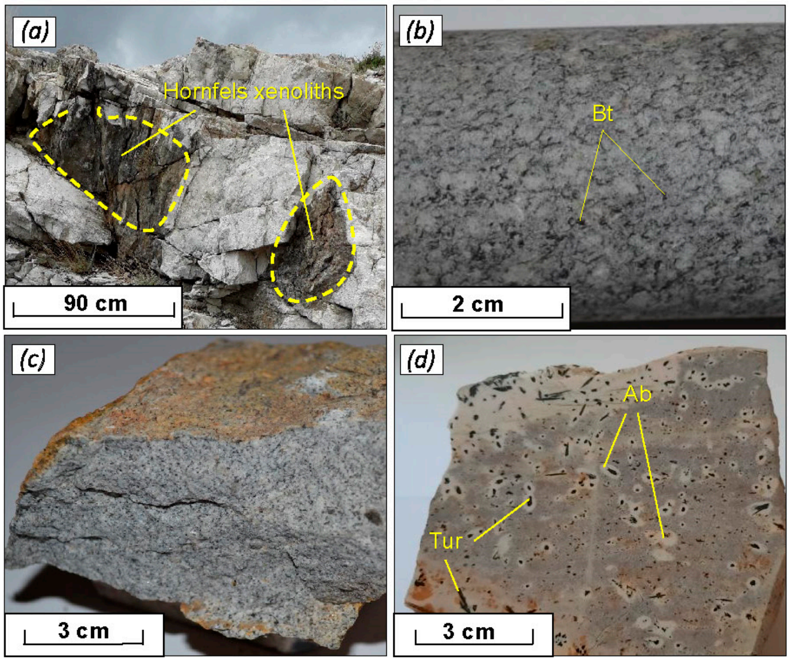

Figure 5. Na-granites from the Tochka area. (**a**) Outcrop of Na-granites with hornfels xenoliths; (**b**) core samples of medium-grained biotite (Bt) Na-granite; (**c**) quartz porphyry dike with albite and quartz phenocrysts; (**d**) quartz albitophyre dike with albite (Ab) spherulites that enclose tourmaline (Tur) (schorl).

Scanning electron microscopy of Na-granite revealed accessory minerals: zircon, titanite, monazite, sphalerite and apatite (Figure 6a,b), tungstite ($WO_3 \cdot H_2O$) (Figure 6c), as well as a gersdorffite (NiAsS) (Figure 6d) with an admixture of Co (5.24 wt.%) and Fe (3.54 wt.%). The composition of accessory minerals from hornfels are given in Supplementary Table S2. Apatite contains 0.38 wt.% of La, 0.89 wt.% of Ce, and 0.38 wt.% of Nd; monazite contains 5.66 wt.% of La, 13.12 wt.% of Ce, and 6.06 wt.% of Nd.

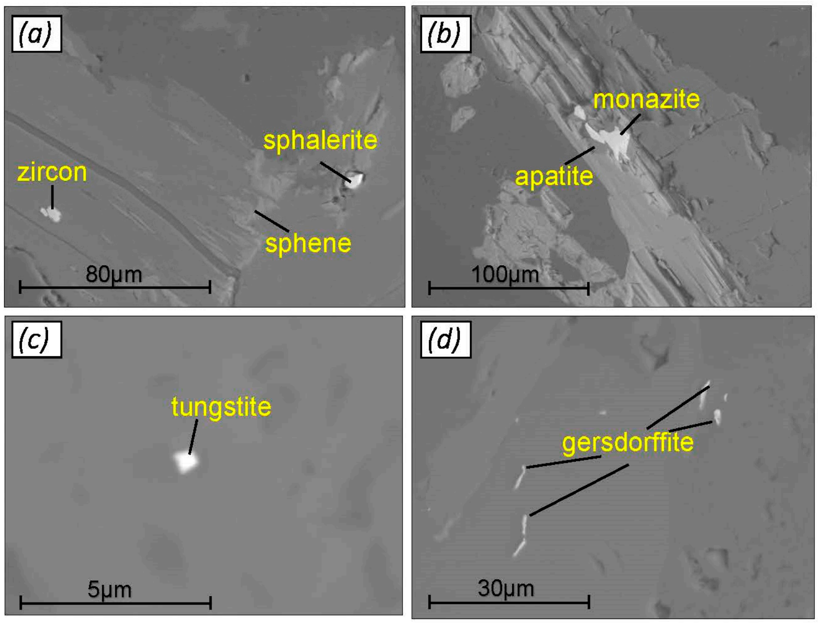

Figure 6. Micrometer accessory minerals in Na-granite (samples TO-4 and TO-10). (**a**) Zircon (spectrum 1) and sphalerite (spectrum 2) in a matrix defect; (**b**) nests of monazite in apatite; (**c**) tungstite; (**d**) gersdorffite streaks.

4.1.3. Pegmatites

The systematics of rare-metal pegmatites are given in the works of Aytaliev Zh.A., Smirnov I.A., Shcherba G.N., Shavlo S.G., Ginzburg A.I., Solodov N.A., Kuznetsov V.I., Rodionov G.G., Dyachkov B.A., and other researchers [48–53].

Traditionally, based on the model of formation of rare-metal pegmatites of the Kalba region, graphic and oligoclase–microcline (ore-free), microcline block (with beryl and columbite), microcline–albite, albite, and albite–spodumene with rich complex ores (Ta, Nb, Li, Cs, Be, Sn) occurred. During their staged formation from early to late, an increasing concentration of rare-metal mineralization occurred with the formation of unique minerals (tantalite–columbite, lepidolite, pollucite, spodumene, petalite, amblygonite, colored and polychrome tourmalines, etc.).

Pegmatites from three type veins: microcline–albite, albite, and albite–spodumene pegmatites were sampled. In addition, the albite–muscovite greisens from contact zones of microcline–albite pegmatite veins were studied.

Microcline–albite pegmatites occur mainly as quartz–albite–muscovite veins with tantalite–columbite, beryl, cassiterite, and sporadic spodumene crystals. They are of several varieties: coarse-grained weakly albitized quartz–microcline, greisenized albite–muscovite, mainly quartz–albite with nests of iron phosphate and manganese, and albite pegmatites (Figure 7) [54,55].

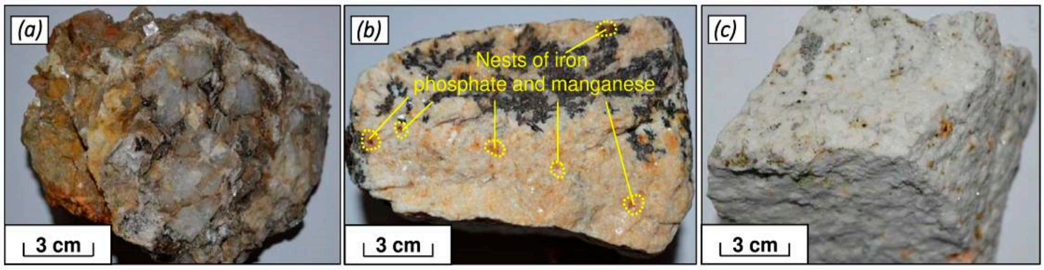

Figure 7. Pegmatites from the Tochka area. (**a**) Coarse-grained weakly albitized quartz–microcline pegmatite; (**b**) albitized pegmatite with nests of iron phosphate and manganese (dark inclusions); (**c**) albite pegmatite with disseminated metallic minerals.

Albite–muscovite greisens bear REE phases of monazite and xenotime (Figure 8a–c), as well as acicular zircon (Figure 8d).

Albite pegmatites with spodumene enclose fluid-derived lumpy cassiterite (Figure 9a) and submicrometer native tin (Figure 9b), a Ni phase, presumably bunsenite (NiO?) discovered for the first time (Figure 9c), and rutile micro-inclusions (Figure 9d). Another sample of albitized pegmatite with cymatolite and garnet bears rare-metal phases of columbite, tantalite–columbite, and cassiterite (Figure 9a), as well as micrometer grains of accessory apatite, zircon, and pyrolusite (Figure 9e). In this respect, cymatolite, which is a pseudomorph after spodumene, can be considered an indicator mineral of Li-bearing albite–spodumene pegmatites. The SEM images (Figure 9f) reveal an ultramicroscopic-zoned grain of radioactive zircon with a disseminated white U mineral (9.7 wt.% Zr and 11.2 wt.% U).

Albite–spodumene pegmatites provide economic Li resources, mainly in spodumene, occurring as flat prismatic crystals. Spodumene crystals (up to 25%–50%) are often oriented across the veins (Figure 10) or cluster in nests, where they are overgrown with fibrous cymatolite and garnet crystals (Figure 10).

The composition of accessory minerals from hornfels are given in Supplementary Table S3. Apatite contains 0.42% of Mn and 0.38% of Nd; monazite contains La (from 1.93% to 2.92%) and Nd (from 2.64% to 3.85%); xenotime contains 1.41% of Dy; pyrolusite contains 0.60% of Cu; rutile contains 1.1% of Nb; columbite contains Mn (from 1.54% to 4.27%).

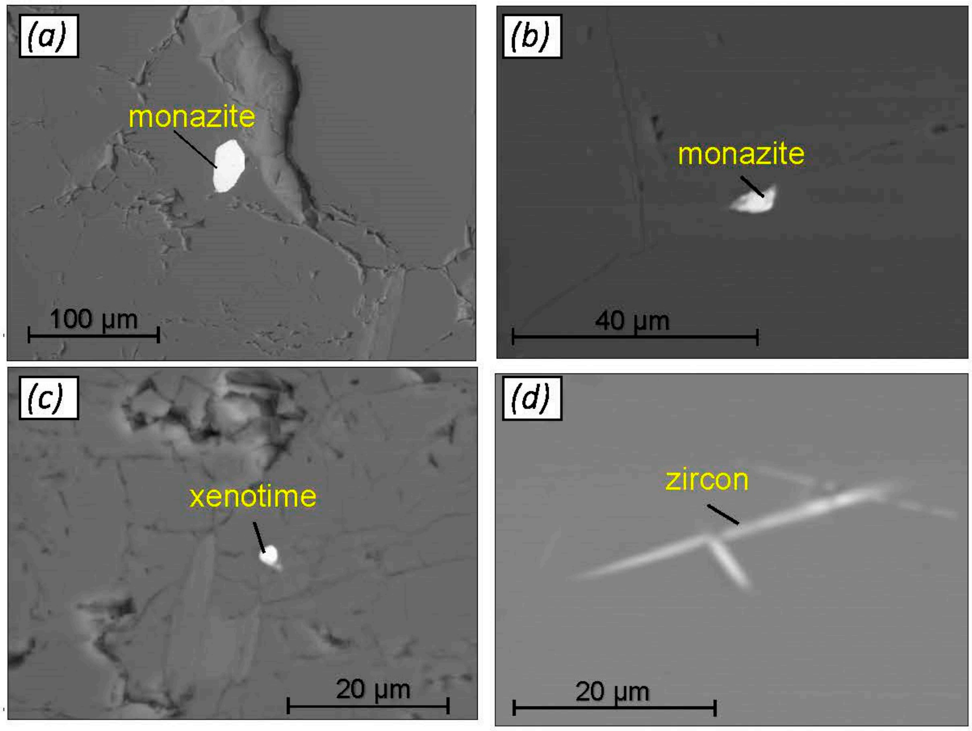

Figure 8. Inclusions of fluid-derived minerals in albite–muscovite greisens (sample TO-9). (**a**,**b**) Monazite crystals (**a**) and lumps (**b**); (**c**) droplet-shaped xenotime; (**d**) zircon in a microcrack.

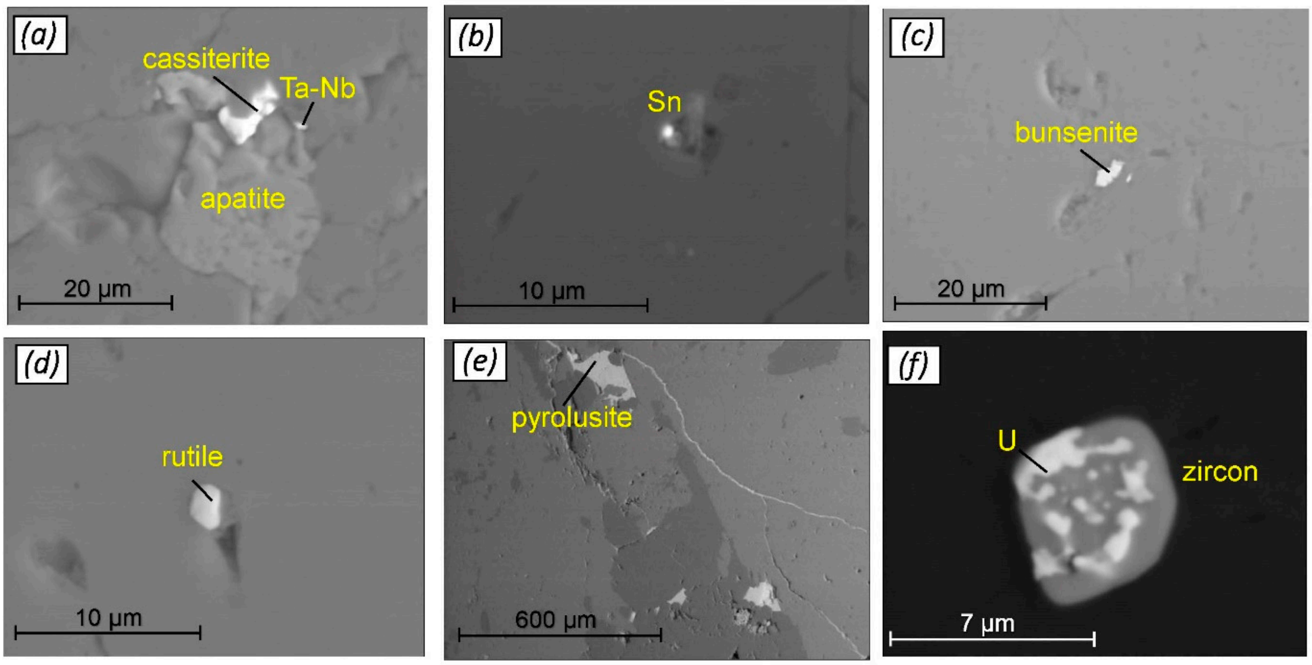

Figure 9. Micrometer mineral inclusions in albite pegmatites with spodumene (sample TO-13, TO-12). (**a**) Cassiterite and tantalite–columbite in apatite; (**b**) native tin; (**c**) Ni phase (bunsenite?); (**d**) rutile; (**e**) Mn phase (pyrolusite); (**f**) zircon with disseminated U phase (uraninite).

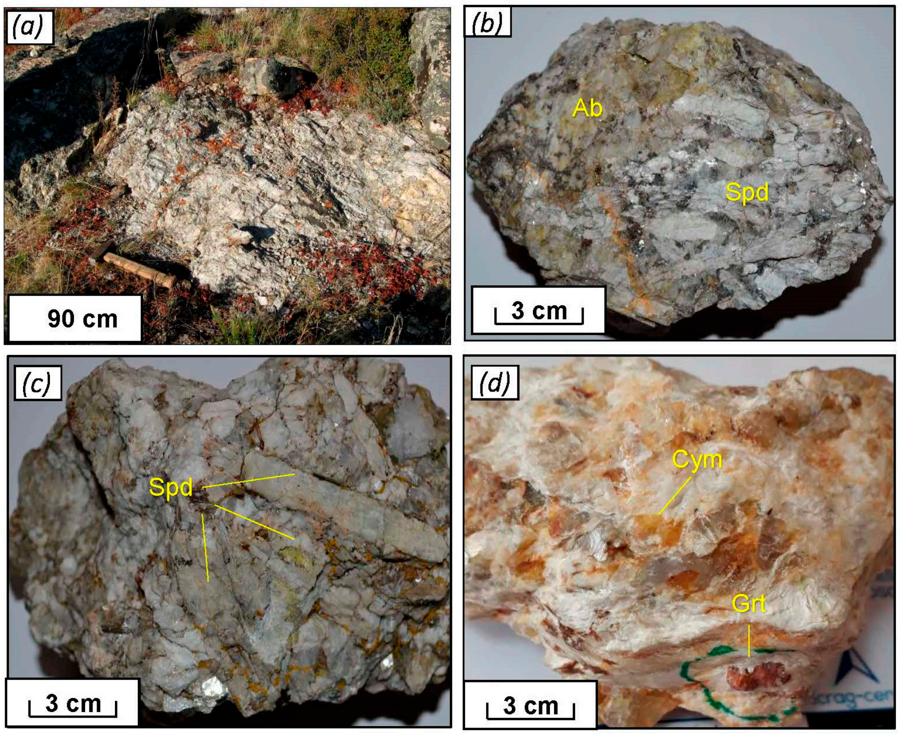

Figure 10. Albite–spodumene pegmatites from the Tochka area. (**a**) Nest of albite–spodumene pegmatite; (**b**) albite–spodumene pegmatite; (**c**) nest of flat spodumene crystals; (**d**) albitized pegmatite with cymatolite nests and garnet crystals.

4.2. Geochemistry

Trace elements in rare-metal pegmatites and their hornfels and Na-granite hosts were analyzed by ICP-MS. The results of the analyses are given in Supplementary Table S4. Unfortunately, we have no analyses from the intrusion of Kalba granites located within the studied area (see Figure 2). Thus, we had to take the data on the composition of Kalba granites from early publications [24,47]. These granites are from Shubarshoky, Dvoryansky, Sibiny, and Asubulak plutons located near the Karagoin–Saryozek zone. The rocks of these plutons are Bt granites and Bt(±Ms) leucogranites. Their compositions are also given in Supplementary Table S4.

Hornfels are similar to each other, according to the contents of the main elements. They have higher concentrations of Ti, Fe, Mg, and P and lower concentrations of Na than all granites and pegmatites. Pegmatites and Na-granites show similar concentrations of the main elements; they contain less Ti, Fe, Na, and K than the Kalba granites (Figure 11).

Hornfels can be divided into two groups, according to the distribution of rare metal. Hornfels without muscovite (analyses 1 and 2 in Table S4) have generally low rare-metal concentrations. The Na-granites show a similar behavior to rare metals (Figure 12).

However, muscovite hornfelses (analyses 3 and 4 in Table S4) show elevated concentrations of Li, Be, Rb, Cs, Sn, and W. The behavior of rare metals in pegmatites is generally close to the Kalba granites, although the pegmatites contain higher concentrations of Li, Rb, Nb, and Ta (Figure 12).

The trace element (Ba, Th, HFSE, REE) behavior in the hornfelses is similar to the Kalba granites, whereas Na-granites and pegmatites show lower concentrations of these elements relative to the Kalba granites (Figure 13).

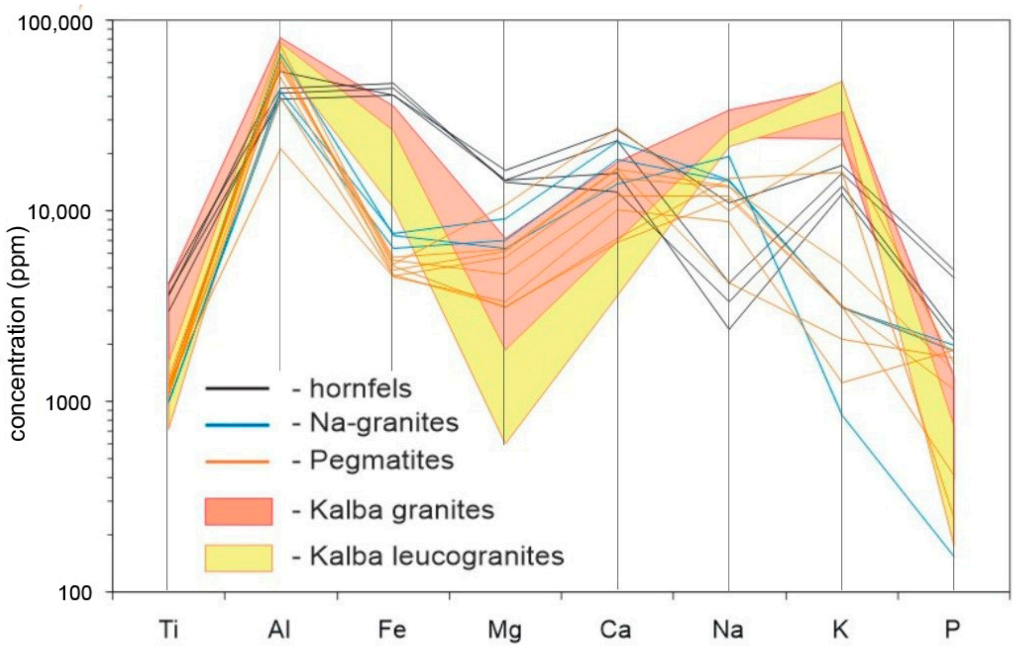

Figure 11. Distribution of main elements (concentrations in ppm) in hornfelses, Na-granites, and pegmatites of the Tochka deposit in comparison with the Kalba granites and leucogranites. The composition of the Kalba granites and leucogranites are taken from [24,47].

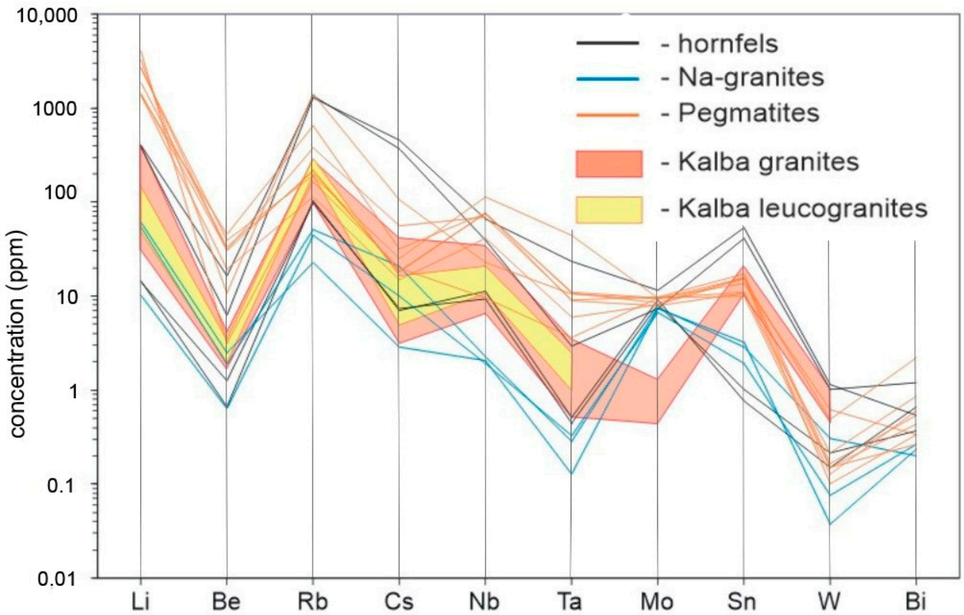

Figure 12. Distribution of rare metals (concentrations in ppm) in hornfelses, Na-granites, and pegmatites of the Tochka deposit in comparison with the Kalba granites and leucogranites. The composition of the Kalba granites and leucogranites are taken from [24,47].

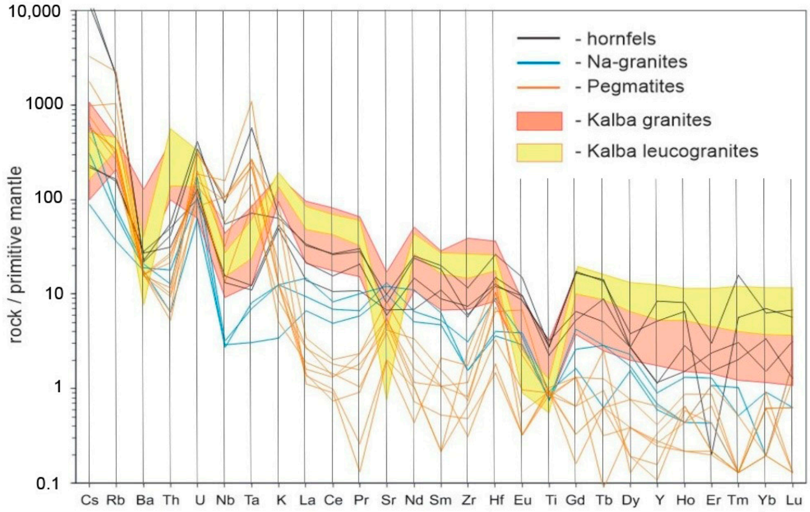

Figure 13. Distribution (spider diagram) of trace elements of rare metals in hornfelses, Na-granites, and pegmatites of the Tochka deposit in comparison with the Kalba granites and leucogranites. The composition of the Kalba granites and leucogranites are taken from [24,47]. The concentrations are normalized to the primitive mantle [56].

4.3. Ar-Ar Age

The age of the Tochka rare-metal pegmatites was estimated in muscovite monofractions from two albite pegmatites (samples 63-TO and 64-TO) from the one vein and from the microcline–albite pegmatite with muscovite (sample 65-TO) from a nearby vein. The measurement results are given in Table S5. All obtained $^{40}Ar/^{39}Ar$ spectra (Figure 14) show distinct plateaus corresponding to 96.8% to 99.3% cumulative fraction of ^{39}Ar released. The resulting plateau ages are 293 ± 4 Ma for 63-TO, 292 ± 4 Ma for 64-TO (albite pegmatite samples), and 290 ± 4 Ma for 65-TO (microcline–albite pegmatite with muscovite). The latter date is slightly younger, but all three determinations are generally similar within the measurement error. Thus, the Tochka pegmatites formed about 292 Ma ago (total age over three samples).

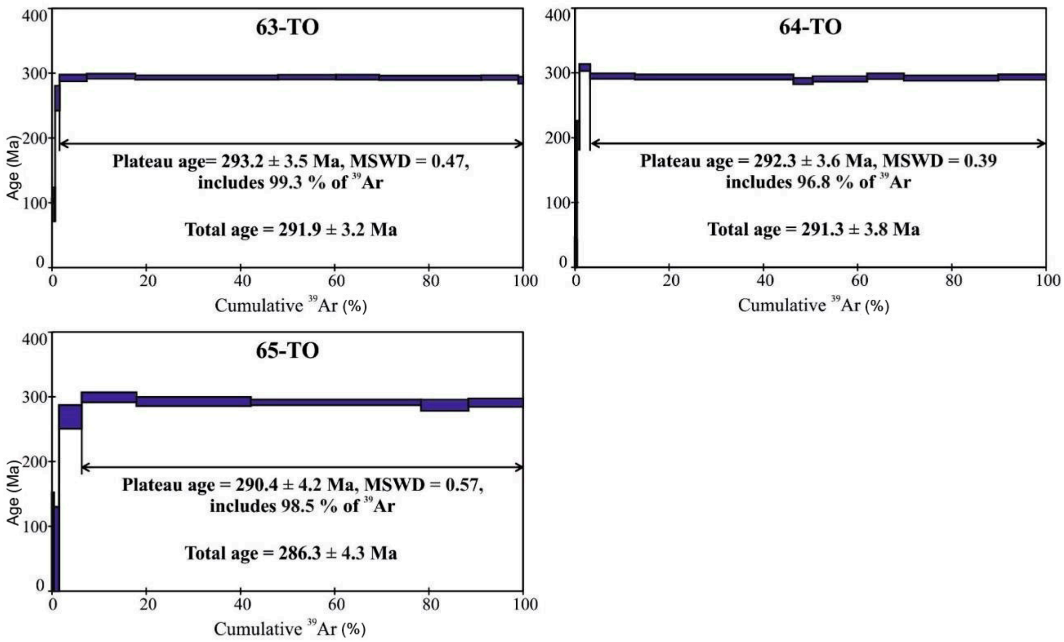

Figure 14. $^{40}Ar/^{39}Ar$ age spectra of muscovite from the Tochka pegmatite.

5. Discussion

Granite magmatism in the Kalba–Narym zone, according to recent studies, occurred in the Early Permian in a post-collision geodynamic setting as a result of the effect of Tarim mantle plume on the lithosphere during its extension [6,22,24,43,57,58]. It was determined that the granites of the Kunush complex have Na specialization, similar to I-type granites. It is believed that they occurred during the melting of lower crustal metabasite substrates [43,58]. Granites of the Kalba complex have a K-Na specialization, similar to S-type granites but, according to some geochemical characteristics, similar to A-type granites. It is believed that they occurred during the melting of medium-crustal substrates of mixed composition (mainly metapelites with a small proportion of metabasites) [24].

The origin of the Tochka rare-metal pegmatites was previously attributed to the Na-granite magmatism of the Kunush complex [38,40–42], proceeding their spatial proximity to and intrusion into a Na-granite body. There was a point of view that pegmatites emplaced within the field of Na-granites, possibly because the ascending pegmatitic magma followed the same paths as the older Na-granite magma [59]. However, our results show the invalidity of this model.

Firstly, there are the field observations and the age data. It has been established that, at the Tochka deposit, pegmatite veins cut only the Na-granites of the Kunsh complex and do not cut the granites of the Kalba complex. In addition, the Kalba granites do not cut the pegmatite veins and the arrangement of the pegmatite veins and the Kalba granites' body is sub-according. This is geological evidence that the Kalba granites and the rare-metal pegmatites intruded synchronously. This is confirmed by the results of the Ar-Ar dating of pegmatites from the Tochka deposit (293–290 Ma). They are younger than the 299 $\pm$ 2 Ma Na-granites of the Kunush complex (U-Pb dating of zircons [43]) but fall within the 296–286 Ma interval for the Kalba granites (U-Pb dating of zircons [6,24]). Moreover, the age of the Tochka rare-metal pegmatites is close to the age (approximately between 291 and 286 Ma) of rare-metal pegmatites from the Asubulak ore district located about 40 km east [14].

Secondly, there are the composition data. Mineralogical data show that the typical accessory minerals for gneisses—ilmenite, magnetite, pyrite, zircon, monazite, and xenotime—are present in hornfels. In Na-granites, the typical accessory minerals for granites—apatite, zircon, monazite, and titanite—are present. Pegmatites also contain accessory apatite, zircon, monazite, and xenotime, but these are common minerals for all granitoid rocks. In addition, apatite in pegmatites contains an admixture of Mn. Other accessory minerals in pegmatites are not similar to accessory minerals in hornfelses and Na-granites; these are rutile, cassiterite, sphalerite, pyrolusite, uraninite, and columbite. The Kalba granites and leucogranites, according to published data, contain accessory cassiterite, rutile, columbite, scheelite, and wolframite [47,59–61]. Thus, the mineral associations of pegmatites are more similar to the mineral associations of the Kalba granites than to those in hornfels or Na-granites. Micro-inclusions of cassiterite in cracks in hornfels and micro-inclusions of tungstite in cracks in Na-granites can be explained by the influence of fluids separated from pegmatite magmas on them.

The composition of muscovite hornfelses near the pegmatite veins shows enrichment in rare metals. This indicates that the pegmatites are a source of rare-metal mineralization, but the Na-granites are not. Thus, the location of rare-metal pegmatites among Na-granites at the Tochka deposit seems to be random.

Geochemical data show that the concentrations of Ti, Fe, Na, K, REE, and HFSE in pegmatites are lower than in the Kalba granites (Figures 11 and 13). The concentrations of some elements, such as Fe, Ca, K, Ba, Th, Zr, Hf, and HREE, in pegmatites and Na-granites are at the same level. However, this similarity is not proof of the genetic relationship between pegmatites and Na-granites but, on the contrary, refutes it. It is generally accepted that pegmatitic magmas are formed during the evolution of granitic magmas, often in large chambers [62–66]. During this, the components compatible with silicate minerals have lower concentrations in pegmatites; that is, if pegmatites were associated with Na-granites, the concentrations of the main elements—REE and HFSE—in them would be even lower than in Na-granites. Since this is not the case, the concentrations of these elements in pegmatites allow us to conclude that they are the result of the differentiation of the magmas of the Kalba granites but not the Na-granites. This is also confirmed by the increased concentrations of rare metals (those components that accumulate in residual magmas during differentiation) in pegmatites compared with the Kalba granites (Figure 12).

These conclusions are confirmed by the results of a study of rare-metal pegmatites in the Asubulak ore district [14,47,66]. There are numerous veins of rare-metal pegmatites that cut granites of the first phase but are not cut by granites of the second intrusive phase. According to geological and geochronological data, the Kalba rare-metal pegmatites are related to granites of the Kalba complex, which may be a source of ore material (considering their relative enrichment in F, Li, Ta, and Be). Thus, the rare-metal pegmatite mineralization may have a magmatic origin and may associate with granitic magma differentiation processes in large chambers. It is also important that the pegmatite fields of the Asubulak ore district were formed in the upper (near-roof) part of the granite massif [56,66].

In this respect the Karagoin–Saryozek zone—located between several large granite massifs of the Kalba complex where host rocks play a role as a roof—may be very promising for rare-metal pegmatite mineralization. Specifically, the source of the Shubarshoky pluton may be such a reservoir of fractionating magma that eventually produced the Tochka pegmatites. The new results mean positive prospects for the Karagoin–Saryozek zone as a potentially rich source of Li in albite–spodumene pegmatites.

It should be noted that the earlier assessment of the resources of the Tochka deposit showed concentrations of Li_2O (0.219–1.132 wt.%), even according to the flame photometry. The low-average values in the reports [38,40–42] apparently represent rather the bulk composition of mixed-mineral assemblages in pegmatites and are thus poorly reliable. The present advanced analytical tools, such as mass spectrometry with inductively coupled plasma (ICP-MS) or atomic emission spectrometry (AES), reveal higher Li grades of the Tochka albite–spodumene pegmatites (0.22% to 1.66%–2.87% Li_2O) that are comparable with the estimates for the economic operations, such as Yubileinoye (0.306%), Bakennoye (0.119%), and Akhmetkino (0.76%) in the Kalba–Narym zone, as well as Greenbushes mine in Australia (up to 2.9%), Vishnevskoye in Russia (1.06%), and other pegmatite deposits [11,65,66].

6. Conclusions

The studies in the area of the Tochka Li deposit in East Kazakhstan have provided updates for local geology, mineralogy, geochemistry, and ages of Li-pegmatites and country rocks. The conducted mineralogical, geochemical, and geochronological studies made it possible to link the formation of pegmatite veins of the Tochka deposit not with Na-granites (as previously thought) but with the Kalba granites. A similar relationship of rare-metal pegmatites with the Kalba granites was shown earlier for the deposits of the Asubulak ore region. Considering that the Karagoin–Saryozek zone is located between large granitic plutons of the Kalba batholith, a significant potential for the discovery of rare-metal deposits is probably concentrated within it.

Supplementary Materials: The following supporting information can be downloaded: https://www.mdpi.com/article/10.3390/min12121478/s1, Table S1. The composition of accessory minerals from hornfels, wt. %; Table S2 The composition of accessory minerals from Na-granites, wt. %; Table S3. The composition of accessory minerals from pegmatites, wt. %; Table S4. The composition of rocks (concentrations in ppm) from Tochka deposit (authors data) and from Kalba batolith (data from [24,47]. Table S5. 40Ar-39Ar dating results of muscovite from pegmatite samples of the Tochka deposit.

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