Geochronology and Geochemistry of Granitic Pegmatites from Tashidaban Li Deposit in the Central Altun Tagh, Northwest China

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Abstract: The Central Altun orogenic system is a result of the amalgamation of multiple microcontinental blocks and island arcs. This complex system originated from subduction–accretion–collision processes in the Proto-Tethys Ocean during the Early Paleozoic. Research has reported the discovery of several Li–Be granitic pegmatite deposits in the Central Altun Block, including the North Tugeman granitic pegmatite Li deposit, Tugeman granitic pegmatite Be deposit, Tashisayi granitic pegmatite Li deposit, South Washixia granitic pegmatite Li deposit, and Tamuqie granitic pegmatite Li deposit. The Tashidaban granitic pegmatite Li deposit has been newly discovered along the northern margin of the Central Altun Block. Field and geochemical studies of the Tashidaban granitic pegmatite Li deposit indicate: (1) Spodumene pegmatites and elbaite pegmatites, as Li-bearing granitic pegmatites that form the Tashidaban granitic pegmatite Li deposit, intrude into the two-mica schist, and marble of the Muzisayi Formation of the Tashidaban Group. (2) Columbite–tantalite group minerals and zircon U–Pb dating results indicate that the mineralization age of Tashidaban granitic pegmatites is 450.2 ± 2.4 Ma with a superimposed magmatic event at around 418–422 Ma later. (3) Whole-rock geochemical results indicate that the Kumudaban rock sequence belongs to the S-type high-K to calc-alkaline granites and the Tashidaban Li granitic pegmatites originated from the extreme differentiation by fractional crystallization of the Kumudaban granite pluton.

Keywords: Altun Tagh; rare-metal granitic pegmatite; CGMs and zircon U–Pb dating; magma evolution

1. Introduction

Lithium is an essential metal in modern technologies with indispensable applications [1–3], which is widely used in various industries such as glass ceramics, non-ferrous metallurgy, high-energy batteries, nuclear fusion (reactors), and aerospace [1,4]. As an essential source of lithium, petrological studies of the granitic pegmatites is of paramount importance [5–7].

Several large-scale rare-metal mineralization belts have been discovered in China with distributions in the West Kunlun-Songpan-Ganzi orogenic belt, Tianshan orogenic belt, Altai orogenic belt, Qinling-Dabie orogenic belt, Himalaya orogenic belt, Sanjiang...
orogenic belt, Wuyi-Yunkai orogenic belt, and Jiangnan orogenic belt in recent years [8,9]. Extensive work has been carried out by previous researchers on the formation age of pegmatites [10–17], petrogenesis [18–21], mineralogical characteristics [22–25], magma evolution [26–31], ore-forming fluids [32–34], and genesis mechanisms of granitic pegmatites [35–40], which significantly enhanced the understanding of rare-metal pegmatites in China.

The Altun Orogenic Belt (AOB) has undergone a complex tectonic evolution from the Archean to Paleoproterozoic with several stages: the formation of the craton and crystalline basement, stable continental margin sedimentation (Middle Paleoproterozoic), continental expansion (Late Neoproterozoic to Early Paleozoic), multiple microcontinents subduction–collision (Palozoic), and intra-plate evolution (Late Paleozoic to Mesozoic) [41,42]. Tectonic collisions and continental accretion have led to a thickening of the crust in the region, creating conditions that favor the generation of significant magma volumes. Consequently, this has facilitated the formation of highly differentiated pegmatitic magmas [9,37,43]. In recent years, multiple survey results pointed out the significant rare-element mineralization potential in the area. Currently, there are nine rare-metal granitic pegmatite deposits of medium to large scale that have been discovered in the region with mineralization age in 499–445 Ma. These deposits are categorized from southwest to northeast as the Washixia district, the Ayake district, the Kumusayi district, and the Tashidaban district [44–49]. The Washixia district and the Tashidaban district have been preliminarily identified as large to super-large scale. In the northern margin of the AOB, the Tashidaban granitic pegmatite Li deposit is newly discovered in the Tashidaban district with little relevant reports available, currently.

In this study, we firstly presented the geological characteristics of the Tashidaban granitic pegmatite Li deposit and constrained the mineralization age of the Li granitic pegmatites through columbite group minerals (CGMs) and zircon U-Pb dating. The whole-rock geochemical elucidates the petrogenesis of the Kumudaban granitoids and the origin of the Li granitic pegmatites in the Tashidaban granitic pegmatite Li deposit. This study provides a better understanding of the tectonic evolution of the region and facilitates exploration campaigns for Li in the study area.

2. Regional Geological Background

The AOB is a complex tectonic belt subjected to extensive magmatic activity and formed by multiple episodes of subduction–collision in the Early Paleozoic, which traverses the northern margin of the Qinghai-Tibet Plateau in the NE–SW direction. It is sandwiched between the Tarim Block, the Qaidam Block, and the Qilian-Kunlun Orogenic Belt. The tectonic units of the Altun are divided into the Dunhuang block, the North Altun subduction–accretion complex belt (NASB), the Central Altun Block (CAB), the South Altun subduction–collision complex belt, and the Apa-mangya Ophiolitic Mélange Belt from north to south (Figure 1) [50–55].

The Tashidaban granitic pegmatite Li deposit is located on the northern margin of the CAB. The exposed stratigraphy in this area includes the Mesoproterozoic Changcheng System Bashikuergan Group (ChB), Jixian System Taxidaban Group Muzisayi Formation (Jxm) and Jinyanshan Formation (Jxj), Qingbaiou System Suoerkuli Group (QbS.), and Quaternary sediments. The Bashikuergan Formation consists of a suite of meta-clastic rocks, carbonate, and basic volcanic rocks. Whole-rock Sm-Nd isotopic data from plagioclase amphibolite indicate a Mesoproterozoic age [56]. The Taxidaban Group is a continental clastic–carbonate formation formed at the edge of the marine basin during the tectonic stability period after the consolidation of the transitional basement of the Changcheng System. The U-Pb age of detrital zircons constrains the sedimentary age from the Late Mesoproterozoic to Early Neoproterozoic [57]. The main lithology of the Muzisayi Formation is composed of two-mica schist, quartzite, phyllite, dolomite and garnet-bearing granulite. The main lithology of the Jinyanshan Formation is composed of dolomite, limestone, and marble. The Suoerkuli Group consists of a suite of littoral-to-
shallow clastic rocks, carbonate, and volcanic sedimentary rocks. The depositional age indicated by the TIMS U–Pb age of meta-rhyolite (930 Ma) is Neoproterozoic [58].

The regional magmatic activity is characterized by multiple episodes and diverse types of processes exhibiting a northeast to east–northeast trend. The early Paleozoic magmatic rock types are biotite granite and muscovite granite, with the emplacement age between 522 and 432 Ma [42,44,46–48,59–62].

3. Geology of the Tashidaban Granitic Pegmatite Li Deposit

The Tashidaban Li district includes the Tamuqie granitic pegmatite Li deposit, the North Tashidaban granitic pegmatite Li deposit, and the Tashidaban granitic pegmatite Li deposit. An inferred resource of over 400,000 tons of Li₂O in the district was assessed by the No. 3 Geological Party, Xinjiang Bureau of Geology and Mineral Exploration and Development. The exposed strata in the Tashidaban granitic pegmatite Li deposit include the Bashikuergan Group in the Mesoproterozoic Changcheng System, Jixian System Taxidaban Group in the Muzisayi Formation, and the Jinyanshan Formation. Early Paleozoic Kumudaban pluton is located in the Northwest of the Tamuqie granitic pegmatite Li deposit and intruded the Changcheng System Bashikuergan Group. The pluton consists of fine- to medium-grained biotite monzogranite with the crystallization age of 451–445 Ma [59,62]. The Kumudaban granite facies also includes muscovite granite, albite granite, and tourmaline granite (Figure 2).

The biotite granite (sample 23TD07-5/6) is grey-black and fine- to medium-grained. Quartz (25–30%), plagioclase (30–35%), K-feldspar (20–25%), and biotite (10%) are the primary components with accessory zircon and ilmenite. Biotite occurs as flakes between feldspar and quartz grains and exhibits weak chlorite alteration (Figure 3a). The muscovite granite (sample 21TD22-4/5) is grey-white and medium-grained. Quartz (20–25%), plagioclase (30–35%), K-feldspar (20–25%), and muscovite (10%) are the primary components with accessory garnet (3%), biotite (3%), zircon, and ilmenite. The photomicrograph of Figure 3b depicts muscovite occurring in the form of flakes interspersed between feldspar and quartz grains, exhibiting weak sericite alteration along its edges. The albite granite (sample 23TD06-6/7) is grey-white and fine- to medium-grained. Quartz (30–35%), plagioclase (35–40%), K-feldspar (5–10%), and muscovite (15%) are the primary components with accessory garnet and zircon (Figure 3c). The tourmaline granite (sample 23TD03-1/2) is grey-white and fine- to medium-grained. Quartz (30–35%),
plagioclase (30–35%), K-feldspar (5–10%), muscovite (15%), and tourmaline (10%) are the primary components with accessory garnet and zircon. The tourmaline exhibits weak zoning (Figure 3d).

The Early Paleozoic Suwushijie complex pluton is located in the South of the Tashidaban granitic pegmatite Li deposit and intruded the Jixian System Jinyanshan Formation. The Suwushijie pluton is composed of gabbro–diorite–porphyritic granodiorite fine-grained monzogranite and porphyritic medium-grained monzogranite from early to late [66]. The zircon U-Pb age of monzogranite is 463.6 ± 9.1 Ma and 474.7 ± 5.7 Ma [67]. The muscovite 40Ar-39Ar age is 413.8 ± 7.4 Ma [68], which may represent later hydrothermal events. Several faults cut the metasedimentary rocks in the district with the same direction of the regional deep faults [69].

Figure 2. Geological map of (a) Kumudaban-Tashidaban area and (b) the Tashidaban granitic pegmatite Li deposit.

There are over 50 pegmatite hosted in the Tamuqie granitic pegmatite Li deposit which are located on the northern edge of the district. Among them, more than 40 dykes have a Li2O grade that meets the standard for industrial mining. The Li-bearing pegmatites represented by spodumene pegmatite contrast with most Li-barren tourmaline-bearing albite pegmatites. The pegmatites concordant with the schist foliation are primarily tabular or lens-shaped intrusions within two-mica schists of the Bashikuergan Group. The main ore-bearing pegmatite dyke, τ13 spodumene pegmatite, as a whole is approximately 400 m long and is comprised of ten sub-dykes arranged in a left-stepped fashion. CGMs U-Pb dating studies indicated that the τ13 spodumene pegmatite formed at 448 Ma [64], while ρ8 tourmaline-bearing albite pegmatite formed at 418 Ma [64]. The τ13 dyke can be classified into the fine-grained albite zone, muscovite–albite–quartz (Mus-Ab-Qz) zone, muscovite–spodumene–albite–quartz (Mus-Spd-Ab-Qz) zone, and Quartz core from outer to inner. The fine-grained albite zone mainly includes muscovite (5–10 vol%), quartz (15–25 vol%), albite (50–60 vol%), and with accessory amounts of apatite, CGMs, and cassiterite (Figure 3e,f).
Figure 3. Photographs of the Kumudaban granite facies and pegmatites from the Tamuqie granitic pegmatite Li deposit. (a) Photomicrograph of biotite granite from Kumudaban. (b) Photomicrograph of muscovite granite from Kumudaban. (c) Photomicrograph of albite granite from Kumudaban. (d) Photomicrograph of tourmaline granite from Kumudaban. (e) Field photograph of the t\textsubscript{g}13 spodumene pegmatite from the Tamuqie granitic pegmatite Li deposit. (f) Photomicrograph of the t\textsubscript{g}13 spodumene pegmatite from the aplite zone. Abbreviations: Qz: quartz; Pl: plagioclase; Kfs: K-feldspar; Ab: albite; Mus: muscovite; Grt: garnet; Tur: tourmaline; Spd: spodumene.

There are 42 pegmatite dikes hosted in the Tashidaban granitic pegmatite Li deposit, eleven of which have a Li\textsubscript{2}O grade that meets the standard for industrial mining (Figure 2). Four types of pegmatite were distinguished in the Tashidaban granitic pegmatite Li deposit, including tourmaline-bearing albite pegmatite, elbaite pegmatite, and spodumene pegmatite. These pegmatites with EW or SE trend intruded into the two-mica schist and marble of the Jixian System Taxidaban Group in the Muzisayi Formation and had a sharp contact with the host rock. For this study, samples were collected from \text{\textsubscript{\rho}}\text{26}, \text{\textsubscript{\rho}}\text{36}, and \text{\textsubscript{\rho}}\text{40} pegmatite dykes. The pegmatite (\text{\textsubscript{\rho}}\text{40}) show a simple internal zoning structure; from the border inward, it can be divided into the elbaite–albite–quartz (Elb-Ab-Qz) zone and aplite zone (Figure 4b). Unlike other zoned pegmatites, aplite zones are not always found in the outer zones of pegmatite [70]. Instead, the aplite zones are dispersed inside pegmatitic dykes, possibly due to multiple episodes of magmatic–hydrothermal developments [71]. The Elb-Ab-Qz zone is characterized by coarse-grained texture (0.3–0.8 cm) and mainly includes quartz (15–20 vol%), albite (30–35 vol%), K-feldspar (5–10 vol%), muscovite (5–10 vol%), elbaite (5–10 vol%), and tourmaline (2–5
vol%), with CGMs and cassiterite as accessory mineral phases (Figures 4e and 5b,c). Coarse-grained quartz with undulose extinction and moderate subgrain orientation displays variable degrees of recrystallization (Figure 5b). The coarse-grained elbaite is replaced by a later fine-grained albite granite (Figure 5c). The aplite zone mainly includes quartz (10–20 vol%), albite (60–70 vol%), apatite (5–10 vol%) and with accessory of CGMs (Figure 5a). The replacement of aplite zone by late-stage fine-grained albite granite can be observed in Figure 5a, and both the aplite zone and albite granite have CGMs intergrown with albite and quartz (Figure 5d,e). The ρ26 tourmaline-bearing albite pegmatite is exposed as a disc-shaped structure on a steep slope with extension in the SE and SW directions with multiple branches. The lithology of the disc-shaped dyke gradually transitions from tourmaline granite to tourmaline-bearing albite pegmatite, a transition marked by a variation in grain size. The tourmaline granite is grey-white and fine- to medium-grained. Quartz (30–35%), plagioclase (30–35%), K-feldspar (5–10%), muscovite (5%), and tourmaline (10%) are the primary components with accessory zircon and CGMs (Figures 4f and 5f). The ρ36 spodumene pegmatite is 5–8 m wide and 70 m long in an intermittent outcrop. Internal zonation of the aplite zone, muscovite–albite–quartz (Mus–Ab–Qz) zone, spodumene–albite–quartz (Spd–Ab–Qz) zone from border to core characterizes the outcrop (Figure 4c,d). The aplite zone mainly includes quartz (25–35 vol%), albite (30–35 vol%), and muscovite (15–25 vol%) with accessory of CGMs (Figure 5g). The Spd–Ab–Qz zone mainly includes quartz (20–30 vol%), albite (25–30 vol%), spodumene (15–20 vol%), microcline (5–10 vol%), muscovite (5 vol%), and apatite (5–10 vol%) with accessory of CGMs (Figure 5g–i). The coarse-grained quartz intergrown with spodumene has undulose extinction. Recrystallization into granoblastic quartz is observed at the edges of the coarse-grained crystals (Figure 5h,i). Moreover, the replacement of the Spd–Ab–Qz zone by late-stage fine-grained muscovite–albite–granite can be observed (Figure 5i). Distinguished from the aplite zone at the edge of the ρ36 spodumene pegmatite, the content of muscovite in fine-grained muscovite–albite–granite is usually less than 10% by volume.
Figure 4. Field photographs of the Tashidaban granitic pegmatite Li deposit and representing hand specimens of the studied pegmatites. (a–d) Field photographs of the studied pegmatites. (e–g) Hand specimens of the ρ40 elbaite pegmatite, ρ26 tourmaline granite, and the ρ36 spodumene pegmatite. Abbreviations: Qz: quartz; Ab: albite; Spd: spodumene; Tur: tourmaline; Elb: elbaite.
Figure 5. Photographs of the Tashidaban granitic pegmatite Li deposit representing photomicrographs of the studied pegmatites. (a–e) Photomicrographs of the ρ40 elbaite pegmatite. (f) Photomicrograph of the ρ26 tourmaline granite. (g) Photomicrograph of the ρ36 spodumene pegmatite from the aplite zone. (h,i) Photomicrographs of the ρ36 spodumene pegmatite from the Spd-Ab-Qz zone. Abbreviations: Qz: quartz; Ab: albite; Mc: microcline; Ms: muscovite; Spd: spodumene; Tur: tourmaline; Elb: elbaite; CGMs: columbite group minerals; Cst: cassiterite.

4. Sample Selection and Analytical Methods

The samples selection and description are listed in Table 1. The U-Pb dating samples are from the Tashidaban granitic pegmatite Li deposit (Figure 2). Sample 21TD12-1 was collected from the ρ40 tourmaline granite, sample 21TD10-5 was collected from the fine-grained aplite zone of the ρ40 elbaite pegmatite, and sample 21TD16-1 was collected from the fine-grained aplite zone of the ρ36 spodumene pegmatite. The whole-rock geochemical samples are from the vicinity area of the Kumdaban pluton, the Tamuqie granitic pegmatite Li deposit, and the Tashidaban granitic pegmatite Li deposit area.

The separation of CGMs and zircon was carried out at the Hebei Regional Geological Survey Institute, China. The samples were crushed to particles with sizes of 40 mesh. Based on differences in mineral physical and chemical properties, zircon was separated using gravity separation, while CGMs were separated using magnetic separation.
Subsequently, manual handpicking was performed under a binocular microscope to select appropriate mineral grains.

Textural and mineralogical investigations were conducted using a TM4000plus scanning electron microscopy system at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). Back-scattered electron (BSE) images were obtained at an accelerating voltage of 15 kV to illustrate texture features of CGMs minerals. Cathodoluminescence (CL) imaging was conducted for zircon grain using a JEOL scanning electron microscope at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS).

U–Pb dating of columbite was conducted using an ASI RESOlution S-155 193nm ArF Excimer laser coupled to a Thermo Scientific iCAP Qc quadrupole ICP-MS at the State Key Laboratory for Mineral Deposits Research, Nanjing University, China. The diameter of the laser beam was 43 µm, and the laser energy and the repetition rate of laser pulses were set at ~4 mJ/cm² and 4 Hz, respectively. The Coltan 139 standard from Madagascar documented U–Pb ages of 505.4 ± 1.0 Ma (BGR, Hannover, Germany; ID–TIMS), 506.6 ± 2.4 Ma (ID–TIMS), and 506.2 ± 5.0 Ma (LA–ICP–MS; Goethe University Frankfurt, Germany) [72,73]. The obtained concordant U–Pb ages of Coltan 139 are 505.5 ± 2.1 Ma (1σ; MSWD = 0.0078) and 505.1 ± 2.3 Ma (1σ; MSWD = 0.055) for samples 21TD10-5 and 21TD16-1, respectively.

U–Pb dating and trace element analysis of zircon was simultaneously conducted by LA-ICP-MS at the Beijing GeoAnalysis CO., LTD, Beijing, China. The NWR193UC model laser ablation system (Elemental Scientific Lasers LLC, Bozeman, MT, USA) was coupled to an Agilent 7900 ICPMS (Agilent, Santa Clara, CA, USA). Detailed tuning parameters can be seen in [74]. The spot size and frequency of the laser were 30 µm and 6 Hz, respectively. Zircon 91,500 (TIMS 207Pb/206Pb age = 1065.4 ± 0.3 Ma, 1σ, n = 11) was used as external standards for U–Pb dating and trace element calibration, respectively. An Excel-based software ICPMSDataCal was used to perform off-line selection and integration of background and analyzed signals, time-drift correction, and quantitative calibration for trace element analysis and U–Pb dating. Concordia diagrams and weighted mean calculations were performed using Isoplot/Ex_ver3 [75].

Whole-rock major and trace elements were determined at ALS Minerals-ALS Chemx, Guangzhou, China. The rock powder was fused with lithium–lithium metaborate flux which also includes an oxidizing agent (Lithium Nitrate), and then poured into a platinum mold. The concentrations of major elements were analyzed by XRF spectrometry. A prepared sample (0.100 g) was added to lithium metaborate/lithium tetraborate flux and fused in a furnace at 1025 °C. The resulting melt was then cooled and dissolved in an acid mixture containing nitric, hydrochloric, and hydrofluoric acids. Trace element concentrations were analyzed by inductively coupled plasma–mass spectrometry. For lithium analysis, a ~0.4 g sample undergoes an initial digestion process using HClO₄, HF, and HNO₃ until complete dryness is achieved. Following this, the residue is further processed through a secondary digestion in concentrated HCl, cooled down, and diluted to the desired volume. Finally, the samples are examined for lithium content using ICPAES spectroscopy.

Table 1. Sample location, rock type, and analytical method for granites and pegmatites.

<table>
<thead>
<tr>
<th>No.</th>
<th>Location</th>
<th>Sample</th>
<th>Rock Type</th>
<th>Major Trace Elements</th>
<th>Zircon U–Pb Dating</th>
<th>CGM U–Pb Dating</th>
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<td>Kumudaban</td>
<td>23TD07-5/6</td>
<td>biotite granite</td>
<td>√ (2)</td>
<td></td>
<td></td>
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<tr>
<td>2</td>
<td></td>
<td>21TD22-4/5</td>
<td>muscovite granite</td>
<td>√ (2)</td>
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<td></td>
<td>23TD03-1/2</td>
<td>tourmaline granite</td>
<td>√ (2)</td>
<td></td>
<td></td>
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<tr>
<td>5</td>
<td>Tamuqie Li granitic pegmatite deposit</td>
<td>23TD01-6-1/2</td>
<td>spodumene pegmatite</td>
<td>√ (2)</td>
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</tr>
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</table>
5. Results

5.1. CL Features and U-Pb Dating Results

The CGM grains in the Tashidaban granitic pegmatite Li deposit from ρ40 elbaite pegmatite are mainly black and subhedral (Figures 5d,e and 6a). Seven analyzed points (Sample number 21TD10-5) varying from 452 to approximately 448 Ma with a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 450.2 ± 2.4 Ma (1σ; MSWD = 0.37) are shown. Thirteen measured points have a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 413.0 ± 3.6 Ma (1σ; MSWD = 0.21), varying from 417 to 407 Ma (Figure 7a,b; Table 2).

The CGM grains from ρ36 spodumene pegmatite are mainly black and subhedral (Figures 5g and 6b). Four analyzed points (Sample number 21TD16-1) vary from 458 to 450 Ma, and five analyzed points have a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 418.1 ± 6.6 Ma (1σ; MSWD = 0.023), varying from 420 to approximately 416 Ma (Figure 7c; Table 2).

The zircon grains from ρ26 tourmaline granite are predominantly black and subhedral to anhedral with a blurred and sponge texture in few inclusions, while the rims have little oscillatory zoning (Figure 6c). One analyzed point has an older $^{206}\text{Pb}/^{238}\text{U}$ age of 445 Ma, and four points have a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 411.6 ± 9.8 Ma (1σ; MSWD = 1.06), varying from 421 to 402 Ma (Figure 7d; Table 3).

![Figure 6](https://example.com/figure6.png)

**Figure 6.** SEM-back-scattered electron (BSE) and Cathodoluminescence (CL) images of CGMs and zircons from the Tashidaban granitic pegmatite Li deposit. (a) CGMs from the aplite zone of ρ40 elbaite pegmatite; (b) CGMs from the aplite zone of ρ36 spodumene pegmatite; (c) Zircons from ρ26 tourmaline granite. The orange circles denote the U-Pb dating sites.
Figure 7. Diagrams of CGMs and zircons from the Tashidaban granitic pegmatite Li deposit. (a,b) CGMs from the zone of ρ40 elbaite pegmatite; (c) CGMs from the zone of ρ36 spodumene pegmatite; (d) Zircons from the zone of ρ26 tourmaline granite; (e) Chondrite-normalized [76] discrimination plots of (Sm/La) vs. La; (f) Chondrite-normalized REE concentrations for magmatic and hydrothermal zircon [77].

Table 2. Concentrations of U, Th, and Pb, and U-Pb isotopes of CGMs from the ρ40 elbaite pegmatite and the ρ36 spodumene pegmatite in the Tashidaban granitic pegmatite Li deposit.

| No.     | Pb (ppm) | Th (ppm) | U (ppm) | Th/U | 206Pb/207Pb | Error (1σ) | 207Pb/206Pb | Error (1σ) | 208Pb/206Pb | Error (1σ) | 206Pb/238U | Error (1σ) | 206Pb/238U | Error (1σ) | Age (Ma) | 1σ Age |
|---------|----------|----------|---------|------|-------------|------------|-------------|------------|-------------|------------|-------------|------------|-------------|------------|----------|
| 21TD10-5-1 | 28       | 10       | 367     | 0.03 | 0.0556      | 0.0009     | 0.5566      | 0.0108     | 0.0726      | 0.0010     | 451.8       | 6.3        | 413.0±3.6Ma | 21, n=13   |          |
| 21TD10-5-2 | 23       | 9        | 302     | 0.03 | 0.0557      | 0.0010     | 0.5551      | 0.0129     | 0.0722      | 0.0011     | 449.4       | 6.3        | 418.1±6.6Ma | 23, n=5    |          |
| 21TD10-5-3 | 25       | 11       | 322     | 0.03 | 0.0562      | 0.0011     | 0.5609      | 0.0123     | 0.0726      | 0.0011     | 451.6       | 6.8        | 420.2±2.4Ma | 37, n=7    |          |
| 21TD10-5-4 | 24       | 9        | 323     | 0.03 | 0.0555      | 0.0010     | 0.5500      | 0.0117     | 0.0721      | 0.0011     | 448.6       | 6.6        | 420.3±2.7Ma | 21, n=3    |          |
| 21TD10-5-5 | 27       | 8        | 381     | 0.02 | 0.0589      | 0.0010     | 0.5910      | 0.0137     | 0.0726      | 0.0011     | 451.8       | 6.8        | 420.1±2.8Ma | 11, n=7    |          |
| 21TD10-5-6 | 22       | 10       | 306     | 0.03 | 0.0560      | 0.0012     | 0.5609      | 0.0130     | 0.0722      | 0.0011     | 449.1       | 6.7        | 414.9±5.9Ma | 10, n=10   |          |
| 21TD10-5-7 | 23       | 8        | 322     | 0.03 | 0.0565      | 0.0011     | 0.5603      | 0.0120     | 0.0720      | 0.0011     | 448.4       | 6.6        | 412.0±5.9Ma | 22, n=4    |          |
| 21TD10-5-8 | 22       | 8        | 323     | 0.02 | 0.0548      | 0.0011     | 0.5002      | 0.0115     | 0.0665      | 0.0011     | 414.9       | 6.7        | 414.9±5.9Ma | 22, n=9    |          |
| 21TD10-5-9 | 25       | 9        | 372     | 0.03 | 0.0576      | 0.0012     | 0.5236      | 0.0122     | 0.0660      | 0.0010     | 412.0       | 5.9        | 414.9±5.9Ma | 25, n=10   |          |
| 21TD10-5-10| 25      | 10       | 378     | 0.03 | 0.0573      | 0.0012     | 0.5234      | 0.0127     | 0.0665      | 0.0011     | 414.9       | 6.7        | 414.9±5.9Ma | 25, n=10   |          |
5.2. Mineral Chemistry of Zircon

The Th/U ratios of both zircons from q26 tourmaline granite are 0.01 (Table 3). In the chordrite-normalized REE (rare-earth element) diagrams of tourmaline granite, the samples are distinguished by their enrichment in both LREE (light rare-earth elements) and HREE (heavy rare-earth elements) (Figure 7f, Table 4). These samples exhibit positive Ce anomalies and negative Eu anomalies. In the (Sm/La)N vs. La magmatic and hydrothermal zircon discrimination plot [77], one zircon grain was plotted in the magmatic zircon field, and three grains were plotted between the magmatic and hydrothermal zircon fields (Figure 7e).

Table 3. Concentrations of U, Th, and Pb, and U-Pb isotopes of zircons from q26 tourmaline granite in the Tashidaban granitic pegmatite Li deposit.

| No.  | Pb (ppm) | Th (ppm) | U (ppm) | Th/U | 207Pb/206Pb | Error (1σ) | 207Pb/206U | Error (1σ) | 208Pb/206U | Error (1σ) | 208Pb/206U Age (Ma) | 1σ
|------|----------|----------|---------|------|-------------|------------|------------|------------|------------|------------|-----------------|------
| 21TD12-1-1 | 745      | 89       | 11,102  | 0.01 | 0.0587      | 0.0013     | 0.5457     | 0.0143     | 0.0675     | 0.0017     | 420.9          | 10.2
| 21TD12-1-2 | 441      | 51       | 6628    | 0.01 | 0.0622      | 0.0013     | 0.5511     | 0.0140     | 0.0643     | 0.0016     | 401.6          | 9.8
| 21TD12-1-3 | 690      | 153      | 10,479  | 0.01 | 0.0592      | 0.0012     | 0.5282     | 0.0136     | 0.0648     | 0.0016     | 404.5          | 9.8
| 21TD12-1-4 | 777      | 131      | 11,434  | 0.01 | 0.0559      | 0.0011     | 0.5194     | 0.0129     | 0.0674     | 0.0017     | 420.7          | 10.2
| 21TD12-1-5 | 374      | 27       | 5140    | 0.01 | 0.0585      | 0.0014     | 0.5762     | 0.0163     | 0.0714     | 0.0018     | 444.8          | 10.9

5.3. Whole-Rock Geochemical Data

Whole-rock geochemical data are listed in Supplementary Table S1. The granite rock facies in the Kumudaban area are composed of biotite granite, muscovite granite, albite granite, and tourmaline granite, with relatively elevated SiO2 (69.59–75.03%), Al2O3 (14.80–15.49%), and Na2O (3.69–5.75%) contents, and lower TiO2 content ranging from 0.01% to 0.39%. The A/CNK values range from 1.11 to 1.40 with differentiation index (DI) ranging from 81.87 to 93.62 increasing from biotite granite to tourmaline granite. In the chondrite-
normalized diagram (Figure 8a), biotite granite exhibits a rightward-shaped pattern of light rare-earth element (LREE) enrichment ((La:Yb)_N = 46.88 to 50.21), while the others show relatively flat distribution trends ((La:Yb)_N = 0.20 to 3.76). All samples except biotite granite exhibit significant negative Eu anomalies (δEu = 0.07 to 0.40), and the total rare-earth element (REE) content decreases from biotite granite (average ΣREE = 177.88) to tourmaline granite (average ΣREE = 10.77). In the spider diagram (Figure 8b), all samples except biotite granite show depletions in Ba and Ti.

The fine-grained aplite sample of the spodumene pegmatite (448 Ma) in the Tamuqie granitic pegmatite Li deposit has relatively low SiO₂ content (average 68.58%), higher Al₂O₃ (average 17.89%), and Na₂O content (average 9.39%), with an average A/CNK value of 1.12 and average DI value of 95.70. The total REE content is lower than that of the Kumudaban granite (average ΣREE = 3.02) (Figure 8a).

The tourmaline granite samples compared to the aplite samples of elbaite pegmatite and spodumene pegmatite in the Tashidaban granitic pegmatite Li deposit have relatively high SiO₂ content (average 73.36%) and low Al₂O₃ content (average 15.34%), with an average A/CNK value of 1.20. The fine-grained aplite zone of the ρ36 spodumene pegmatite exhibits the highest A/CNK values (average 1.57) and the lowest total REE content (average ΣREE = 0.54) (Figure 8a). The average DI value of tourmaline granite, elbaite pegmatite, and spodumene pegmatite ranged from 95.09 to 98.13. Furthermore, in the spider diagram, the pegmatitic granite samples exhibit similar distribution patterns (Figure 8b).

![Figure 8](image_url)

**Figure 8.** (a) Chondrite-normalized REE patterns [78] and (b) primitive mantle-normalized trace element diagrams [76]. Kumudaban biotite granite are from [65].
6. Discussion

6.1. Formation Times of the Tashidaban Li Granitic Pegmatites

The CGMs found in the granitic pegmatite contain relatively low common Pb contents and exhibit suitable Th and U contents for U-Pb geochronology [79,80]. Reflected light and BSE images show that most samples of CGMs are homogeneous. Only a few images exhibit bright Ta-Mn oscillatory zoning within dark Mn-rich cores, which indicates that these samples have not undergone hydrothermal metasomatism [81,82]. The ages of CGMs of ρ40 elbaite pegmatite are primarily distributed in two intervals with ranges from 452 to 448 Ma and 417 to 407 Ma. Additionally, those of ρ36 spodumene pegmatite range from 458 to 450 Ma and 420 to 416 Ma. Since the restriction of CGMs stability, the problem of inheritance from precursor rocks can be ruled out [79]. A similar phenomenon showing in a single pegmatite was reported by Melcher et al. [83] and Konzett et al. [84], which have a large age spread of 150–309 Ma in Passeier Valley (Italy) and 70–172 Ma age spread in Eastern Alpine (Italy). Konzett et al. [84] suggested that the oldest CGMs age represents the emplacement age and the age spread due to Cretaceous resetting involves multiple tectono-magmatic events. However, the two distribution interval ages in the single pegmatite of the Tashidaban granitic pegmatite Li deposit possibly represent two independent tectonic thermal events. In the Tashisayi granitic pegmatite Li deposit, three-stage age distribution was found in a composited aplite–pegmatite dike at 472 Ma, 440 Ma, and 416 Ma, with the oldest age originating from the Lep-Ab-Qz pegmatite and the middle age from the Spd-Ab-Qz pegmatite [65]. Additionally, Li-Be mineralization events were found to occur during 472–455 Ma in the North Tugeman granitic pegmatite Li-Be deposit and superimposed by 436–435 Ma and 415 Ma fine-grained granite [46].

In this study, only five age data points are considered reliable, among which the oldest age is 445 Ma, and the other four ages range between 421 and 402 Ma with weighted average age of 411.6 ± 9.8 Ma (MSWD = 1.06). Cores of zircon grains in the ρ26 tourmaline granite are predominantly black and exhibit a blurred and sponge texture with few inclusions, while the rims have little oscillatory zoning (Figure 6c), which indicates that the zircon grains originated from magmatic sources but underwent later recrystallization or metamorphic events [85]. Furthermore, the Th/U ratios of four zircons are 0.1, which are lower than typical magmatic zircons [86]. In the chondrite-normalized REE diagrams, the samples exhibit a similar pattern to hydrothermal zircons (Figure 7f). In the (Sm/La)N vs. La magmatic and hydrothermal zircon discrimination plot [77], three grains were plotted between the magmatic and hydrothermal zircon fields (Figure 7e). Combined with the CL features, these geochemical characteristics suggest that the zircons have undergone late-stage metamorphic alteration.

The alteration phenomena observed in this study indicate that the pegmatites in the Tashidaban granitic pegmatite Li deposit have undergone a later magmatic–hydrothermal event. The undulose extinction coarse-grained quartz intergrown with spodumene and albite undergoes recrystallization at the edges into granoblastic quartz, which is commonly observed in ρ40 elbaite pegmatite and ρ36 spodumene pegmatite (Figure 5b, h, i). These characteristics represent the synkinematic emplacement of the pegmatites, which are restricted to the shear zones [87]. The Altun region was undergoing simultaneous compression and amalgamation of three micro-continental blocks, resulting in intense compression and the formation of shear zones from the north and south at ~450 Ma (see Section 6.3). Moreover, elbaite was observed being replaced by a later fine-grained albite granite (Figure 5c). The replacement of aplite zone by late-stage fine-grained albite granite can be observed in Figure 5a, and both the aplite zone and albite granite have CGMs intergrown with albite and quartz, while the Spd-Ab-Qz zone is replaced by late-stage fine-grained muscovite albite granite in the ρ36 spodumene pegmatite (Figure 5i). All indicate that the pegmatites in the Tashidaban granitic pegmatite Li deposit have undergone the superimposition of a later magmatic–hydrothermal event. Therefore, the
Li-mineralization age of the Tashidaban granitic pegmatite Li deposit is 450.2 ± 2.4 Ma, with superimposing of a late-stage magmatic–hydrothermal event during 418–412 Ma.

Multiple episodes of subduction–collision events occurred on both the northern and southern sides of the CAB due to a complex tectonic evolution in the Early Paleozoic. Statistical results indicate that Early Paleozoic magmatic granitoids in the North Altun Block (NAB) were formed between 514 and 411 Ma, while granitoids in the CAB are concentrated between 522 and 432 Ma. Furthermore, Wang et al. [88] obtained an age of 417 Ma from leucosome in garnet-bearing biotite gneiss of the Altun Group. An age of 413.8 ± 7.4 Ma from muscovite Ar-Ar dating of the Suwushijie monzogranite [68] as well as ages of 406–405 Ma from diorite and granite dykes in the Tashsayi area [89] were obtained. It indicates that contemporaneous magmatic activities exist in the Central Altun during 417–405 Ma. The ages of rare-metal pegmatite in CAB are shown in Figure 9. Ages obtained from the Tashidaban Li granitic pegmatites range in two intervals: 450.2 ± 2.4 Ma and 418–412 Ma, which are consistent with the regional magmatic and mineralization events.

Figure 9. Formation times of granites and granitic pegmatite Li–Be deposits in the CAB. The granite ages of the NAB are from [90–101]; the granite ages of the CAB are from [46–48,60,62,88–90,102–105]. Igneous crystallization and mineralization ages of Li–Be deposits are consistent with the literature in Figure 1.

6.2. Petrogenesis of the Kumudaban Granitoids and Origin of Tashitaban Granitic Pegmatites

6.2.1. Petrogenesis of the Kumudaban Granitoids

An S-type granitoid is generally considered as a peraluminous granitoid, which is mainly formed by the partial melting of crustal materials [106,107]. The Kumudaban granitoid samples, with Alumina saturation index (ASI) values exceeding 1.1, are classified as peraluminous granite (Figure 10a). The content of corundum in granitoid samples in Cross, Iddings, Pirrson, and Washington (CIPW) norm calculation are more than 1%. Muscovite and garnet are identified under the microscope observation (Figure 3b–d). In addition, apatite commonly crystallizes early in I- and A-type granitic magma, resulting in a decrease in the P2O5 content of the residual magma. This decrease establishes a strong negative correlation with the SiO2 content, while, P2O5 in S-type granite increases or basically remains unchanged with the increase in SiO2 [108–110]. P2O5 values in these samples are basically unchanged with increased SiO2 (except for tourmaline granite, with P2O5 in the range 0.07–0.09). The Kumudaban granitoids were characterized as S-type
high-K to calc-alkaline granite plotting in the area of the high-K to calc-alkaline series (biotite granites to muscovite granites to albite granites, tourmaline granites) (Figure 10b) [111,112].

6.2.2. Origin of the Tashidaban Li Granitic Pegmatites

Two petrogenetic processes were proposed to explain the formation of rare-element pegmatites: (1) extensive fractionation of fertile parental granitic magma [115–118], and (2) partial melting of rare-element-rich source rocks [119–121]. The large granite plutons near the Tashidaban granitic pegmatite Li deposit are the Kumudaban granite pluton (with zircon U-Pb ages 445–451 Ma) and the Suwushijie intermediate-acidic pluton (with zircon U-Pb ages 464–475 Ma). In this study, the Li-mineralization age in the Tashidaban granitic pegmatite Li deposit is 450.2 ± 2.4 Ma. The Tashidaban Li granitic pegmatites should originate from the highly crystallized differentiation of the Kumudaban biotite granite pluton (Suwushijie intermediate-acidic pluton is excluded due to the presence of a >6 Ma age gap). The Tamuqie granitic pegmatite Li deposit is located north of the Tashidaban granitic pegmatite Li deposit and has a Li-mineralization age of 448 Ma with occurrence of a 418 Ma tourmaline-bearing albite pegmatite. Since pegmatites accentuate the trace element signatures of their granitic sources [24,25], the chemical evolution of Tashidaban Li granitic pegmatites should be similar to the Tamuqie spodumene pegmatite.

Zr/Hf ratio is a useful index of the extent of fractional crystallization of a felsic melt [122,123]. The element pairs K/Rb, K/Cs, and Nb/Ta typically exhibit synergistic behavior, and their variation mechanisms are similar [124]. This also suggests that these ratios could be indicators of the degree of differentiation of felsic melts [27,125]. The pairs mentioned above were plotted against Zr/Hf, which shows a well-defined evolutionary trend in the Kumudaban granite rock facies (Figure 11). The biotite granite exhibits the highest K/Rb, K/Cs, and Nb/Ta ratios. The gradual decrease in these ratios from muscovite granite to albite granite and tourmaline granite shows a clear trend in magmatic evolution. With ongoing of magmatic evolution, the ratios of these incompatible and compatible elements pair decrease successively from tourmaline granite to elbaite pegmatite to spodumene pegmatite in the Tashidaban granitic pegmatite Li deposit (Figure 11). Samples from the aplite zone in spodumene pegmatite (448 Ma) in the Tamuqie granitic pegmatite Li deposit and the aplite zone in q36 spodumene pegmatite in the Tashidaban granitic pegmatite Li deposit almost overlap (Figure 11). The similar distributions of trace elements (Figure 8) indicate a comparable chemical evolution of the granitic magma. The trace element distribution in the normalized chondrite and primitive mantle-normalized diagram have similar patterns, and total REE content shows a continuous decrease trend (Figure 8). All mentioned above indicate that the Tashidaban Li granitic pegmatites have a close

Figure 10. (a) ASI shown by A/NK vs. A/NCNK diagram [113]; (b) the K2O vs. SiO2 diagram with dividing curves from [114].
petrogenetic relationship with Kumudaban granite pluton. Another interpretation suggests that the petrogenetic processes of the Li granitic pegmatites originate from the low-degree partial melting of metamorphic rocks. This mode of origin was confirmed to explain some rare-metal granitic pegmatite deposits worldwide [84,126]. However, no evidence of migmatization was found within the Tashidaban granitic pegmatite Li deposit [102], and no metamorphic minerals such as kyanite and chlorite were discovered in the pegmatite [127,128]. Thus, the evidence above suggests that the Tashidaban Li granitic pegmatites originated from extensive fractionation of the Kumudaban granite pluton.

Figure 11. Selected variation diagrams of granites and pegmatites from the Kumudaban area, Tamuqie granitic pegmatite Li deposit, and Tashidaban granitic pegmatite Li deposit.

6.3. Geodynamic Setting of the Tashitaban Li Granitic Pegmatite Deposit

The Central Altun orogenic system is a product of the amalgamation of multiple micro-continental blocks and island arcs [129]. This complex system originated from subduction–accretion–collision processes in the Proto-Tethys Ocean during the Early Paleozoic [130,131]. The existence of supra-subduction zone (SSZ) ophiolite and plagiogranite are evident of the North Altun ocean subducted from north to south under the CAB with the indication of the initial subduction before ~521–512 Ma [56,132,133]. A series of high-temperature–low-pressure (HT–LT) metamorphic rocks (blueschists, eclogites: ages in 491–520 Ma) [134,135] and related magmatism events (arc volcanic rocks and I- and S-type granites) were formed with ongoing subduction [92–94,136–142]. Zircon age reveals these volcanic rocks and granites were formed between 517 and 459 Ma, which is coeval with the age spectra of detrital zircons in the Early Paleozoic sedimentary rocks from the North Altun [143]. A series of syn-collisional granite formed in the thickened lower crust at 458–431 Ma indicated a collisional regime [92–94,96,97,99]. The transition of the tectonic regime has changed to extension at ~425 Ma with the characterizations of low Sr, Sr/Y and (La/Yb)N granitoids [94,96,99]. The tectonic regime has changed to extension after 432 Ma, which is characterized by intraplate granites (432–418 Ma) [66,150], bimodal volcanic rocks (406 Ma) [151], and A-type granites (432–385 Ma) [152–154].

The Li-mineralization age of the Tashidaban granitic pegmatite Li deposit is 450.2 ± 2.4 Ma with superimposition of the late-stage magmatic–hydrothermal event that occurred at 418 to 412 Ma. The Central Altun block experienced intense continental...
collision between 450 and 445 Ma due to the substantial crustal thickening and regional Barrovian metamorphism [155]. This led to extensive dehydration melting of biotite under granulite facies and generating voluminous granitic magmas, which subsequently crystallized and differentiated to form the Kumudaban to Tatabulake large syn-kinematic biotite granite plutons [60,62,102]. The Tamuqie and Tashidaban Li granitic pegmatites were formed during this period through extreme differentiation by fractional crystallization of granitic magma. The collision ceased on both the northern and southern sides after 432 Ma, and extensional tectonic settings led to lithospheric delamination leading to the lower crust triggered mantle-derived magmatism, resulting in the emplacement of granitic magmas, superimposing the Tashidaban granitic pegmatite Li deposit at 418–412 Ma.

7. Conclusions

Multiple episodes of rare-metal Li-Be mineralization events occurred in the Central Altun during the Early Paleozoic. A newly discovered Tashidaban granitic pegmatite Li deposit, at the northern margin of the Central Altun Block, hosts three distinct types of granitic pegmatites: tourmaline-bearing albite pegmatite, elbaite pegmatite, and spodumene pegmatite. These uniformed pegmatites intruded into the two-mica schist and marble of the Muzisayi Formation of the Tashidaban Group. CGMs and zircon U-Pb dating results reveal the Li-mineralization age of the Tashidaban granitic pegmatite Li deposit is 450.2 ± 2.4 Ma, with a superimposed late-stage magmatic–hydrothermal event occurring at 418 to 412 Ma. The whole-rock geochemical results indicate that the Kumudaban granitoids belongs to the S-type high-K to calc-alkaline granite, and the Tashidaban Li granitic pegmatites have originated from the extreme differentiation by fractional crystallization of the Kumudaban granite pluton.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min14060542/s1, Supplementary Table S1: Major element (wt%) and trace element (ppm) geochemistry of the granites and pegmatites from Kumudaban area, Tamuqie granitic pegmatite Li deposit and Tashidaban granitic pegmatite Li deposit.

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