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EDITED BY

Songjian Ao,
Chinese Academy of Sciences (CAS),
China

REVIEWED BY

Gaoxue Yang,
Chang'an University, China
Wei-Qiang Ji,
Chinese Academy of Sciences (CAS),
China

*CORRESPONDENCE

Kai Weng,
✉ kaikaino1@qq.com

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Petrogenesis, tectonic setting and geodynamic implications of keziergayin granites in the kelan basin (Chinese Altai): constraints from geochemistry, zircon U-Pb geochronology and Nd-Hf-Pb-O isotopes

Kai Weng^{1*}, Wenbin Kang², Xiaojian Zhao¹, Zhongping Ma¹, Jifei Cao¹ and Qinglin Sui³

¹Key Laboratory for the Study of Focused Magmatism and Giant Ore Deposits MNR, Xi'an Center of Geological Survey, Xi'an, China, ²School of Coal Engineering, Shanxi Datong University, Datong, China, ³School of Resource Environment and Safety Engineering, University of South China, Hengyang, China

The Chinese Altai is characterized by abundant granitoids, which not only are indicators of the interaction between crust and mantle but also provide critical constraints on the tectonic evolution of the orogen. This study presents zircon U-Pb-O isotopes, whole-rock major and trace element and Nd-Hf-Pb isotopes data for granite porphyries from the Keziergayin region in the Kelan Basin. The granite porphyries intrude in the Kangbutiebao Formation with zircon U-Pb dating of 394 ± 3 Ma. They have the characteristics of subalkaline and metaluminous to weakly peraluminous and show geochemical affinity with I-type granite. The granite porphyry samples display negative $\epsilon_{Nd}(t)$ (-1.9 to -1.4), positive $\epsilon_{Hf}(t)$ (+4.3 to +11.4) values, with Nd-Hf decoupling; low Pb isotope compositions; $\delta^{18}O_{V-SMOW}$ (6.38‰–8.45‰) is less than 10‰, within the range of O isotopes of medium-basic igneous rocks. These geochemical signatures indicate that the granite porphyries originated from lower crust medium-basic igneous rocks extracted from the lithospheric mantle metasomatized by subducted melt. They are characterized by high SiO₂ contents and Rb/Sr ratios; low CaO contents and K/Rb ratios, hinting that they were formed by highly evolved magmas, with fractionation crystallization of feldspar, apatite, garnet, allanite and/or monazite. The granite porphyries possess positive Rb, Th, U, Nd, Zr, Pb and light rare Earth elements (LREEs) anomalies with strong negative Ba, Nb, Ta, Sr, P, Ti and Eu anomalies, implying that their formation were related to an island arc. Combined with previous studies, it is suggested that the existence of the Early Devonian arc-basin system associated with subducting slab rollback in the Chinese Altai, which belongs to the Siberian active continental margin system.

KEYWORDS

I-type granite, early devonian, slab rollback, Chinese Altai, continental growth

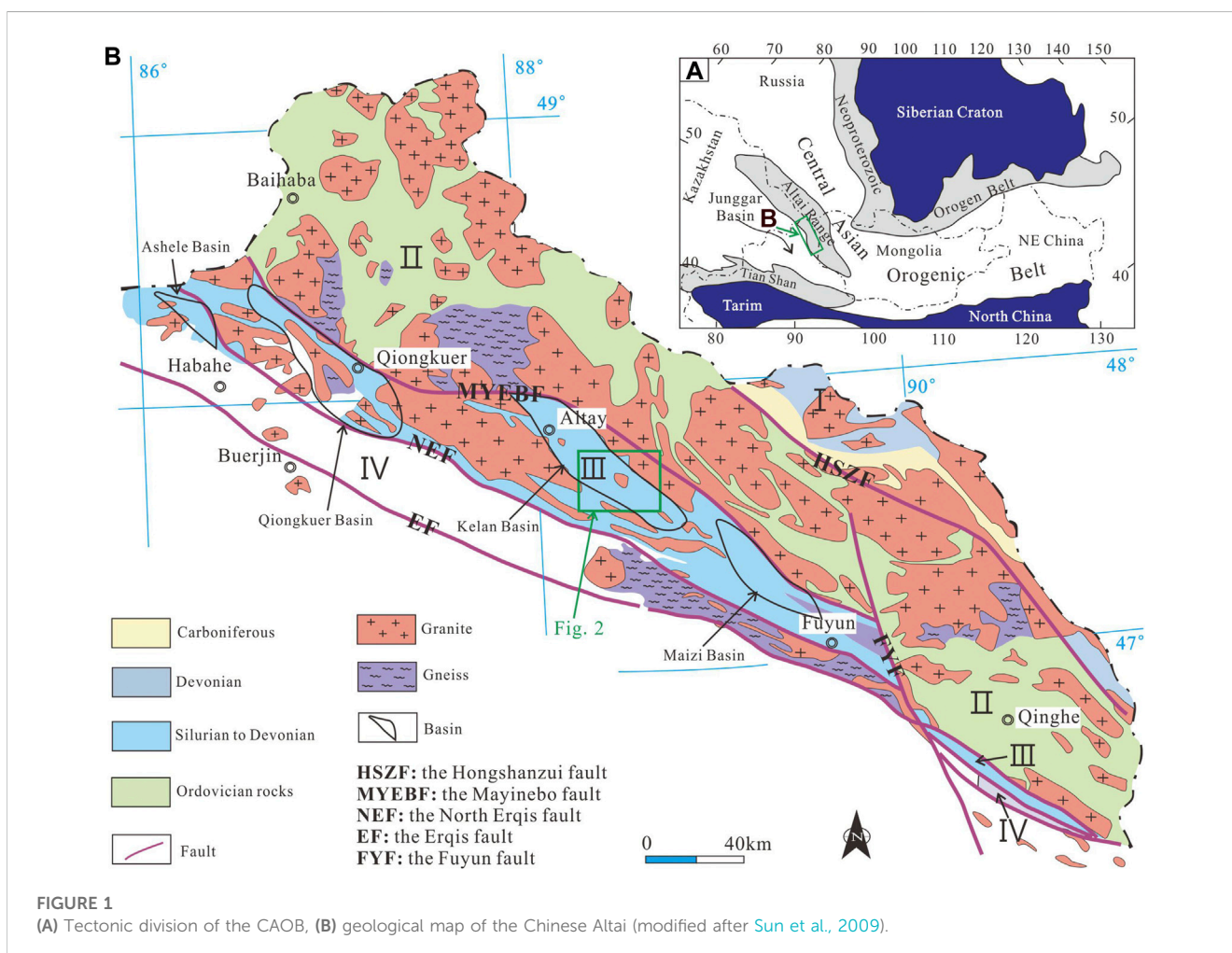
1 Introduction

The Central Asian Orogenic Belt (CAOB; Mossakovsky, 1993; Jahn et al., 2000b; Windley et al., 2007; Kröner et al., 2014; Zheng et al., 2015) is the largest Phanerozoic accretionary orogen in the world (Figure 1A; Zonenshain, 1990; Mossakovsky, 1993; Şengör et al., 1993; Jahn et al., 2000a, Jahn et al., 2000b; Windley et al., 2002; Windley et al., 2007). The CAOB extends from the Urals in the west to the Pacific in the east and from Siberia in the north to the North China and Tarim cratons in the south (Figure 1A; Zonenshain, 1990; Mossakovsky, 1993; Jahn et al., 2000a; Windley et al., 2007). It mainly developed from ca. 1,000 Ma to 250 Ma by the continuous, long-term subduction and accretion of multiple blocks of different origins, including island arcs, ophiolitic complexes, oceanic islands, seamounts, accretionary wedges, and oceanic plateaus (Coleman, 1989; Badarch et al., 2002; Khain et al., 2002; Zhu and Ogasawara, 2002; Xiao et al., 2004; Wilhem et al., 2012; Yang et al., 2015; 2022; Zhu et al., 2015), and substantial vertical addition of juvenile material derived from the upper mantle (Han et al., 1997; Jahn et al., 2000a; 2000b; Chen and Jahn, 2002; Jahn, 2004). Vertical crustal growth is supported by the study of isotopic geochemistry for the positive whole-rock $\epsilon_{\text{Nd}}(t)$ and zircon $\epsilon_{\text{Hf}}(t)$ values of granitoids in the CAOB (Han et al., 1997; Chen and Jahn, 2002; Jahn, 2004; Long et al., 2007; 2010; Yuan et al., 2007; Sun et al., 2008; Wang et al., 2009; Cai et al., 2011a; Cai et al., 2011b; Wang et al.,

2023). These granitoids provide important constraints on the tectonic evolution of the CAOB and critical information on crustal growth (Jahn et al., 2000b; Jahn, 2004; Geng et al., 2009).

As a southwestern portion of the CAOB, the Chinese Altai is situated in the northern Xinjiang Uygur Autonomous Region of China and is composed of volcanic rocks, high-grade metamorphic rocks, sedimentary sequences, and voluminous granitoids (Windley et al., 2002; 2007). Granitoids and granitic gneisses occupy approximately 70% of the Chinese Altai (Windley et al., 2002), which is also an important rare metal and Fe-Cu-Ni metallogenic belt in China. The mineralization was closely related to the granitoids (Zhu et al., 2006; Chai et al., 2009). Recent zircon U–Pb isotopic dating results show that granitic magmatism continued from the Ordovician to Jurassic in the Chinese Altai and peaked ca. 400 Ma in the Early Devonian (Weng et al., 2023). The range of tectonic interpretations for these Early Devonian rocks is contradictory (Xiao et al., 2004; Long et al., 2007; Zhou et al., 2007), including an island arc related to subduction (Windley et al., 2002; Xiao et al., 2004), an active continental margin (Wang et al., 2006; Long et al., 2007; Liu et al., 2008; Yang et al., 2008), and a continental margin rift (Zhou et al., 2007).

Here, we carried out a detailed study on the major and trace elements, zircon U–Pb dating, zircon O isotope and whole-rock Nd–Hf–Pb isotopes for granite porphyries from the Kelan Basin in



the Chinese Altai to unravel their petrogenesis and tectonic setting during the Early Devonian.

2 Regional geological setting

The Chinese Altai is in the central part of the CAOB, which separates the Kazakhstan and Junggar Blocks to the south and Siberian Craton to the north (Figure 1A; Wang et al., 2009; Zhang et al., 2017). Four domains bounded by faults can be identified in the Chinese Altai based on the analysis of magmatic activity, deformation, metamorphism and stratigraphy history (Figure 1B; Windley et al., 2002). Unit I (North Altai Domain) lies in the north of Altai, consisting of the upper Devonian to Carboniferous limestones and terrigenous clastic sediments, incorporating minor metamorphosed arc-related volcanic rocks; Unit II (Central Altai Domain) is located in the central Altai and bounded by the Hongshanzui fault from Unit I, consisting of a thick turbiditic and pyroclastic succession, middle to upper Silurian metasediments and upper Ordovician volcanic molasse and clastic deposits of the Habahe Group; Unit III (Qiongkuer Domain) is separated from Unit II by the Mayinebo fault and located in the south of Altai, composed of arc-type volcano-sedimentary rocks of the lower Devonian Kangbutiebao Formation and an overlying middle-upper Devonian turbiditic sandstone–shale of the Altai Formation (Windley et al., 2002). The Kuerti mafic rocks are exposed at 30 km north of Fuyun County, which represent a suite of meta-basalts and meta-gabbros. The southern and northern blocks are separated by migmatitic gneiss belonging to the Kangbutiebao Group. In the north Kuerti block, layered meta-basalts dominate with a few gabbro and diabase dike or sheets intruding into the volcanic rock layers. In the south Kuerti block, the mafic rocks consist of an intrusive complex of gabbro and dolerite dikes and a few pillow basalts (Xu et al., 2003). Zircon SHRIMP U–Pb age of plagioclase granitic dikes in the gabbro unit of south Kuerti block is 372 ± 19 Ma (Zhang et al., 2003). Unit IV (Irtys Domain) lies in the south of Altai and is separated from Unit III by the North Irtys fault, composing a sequence of Devonian sediments and late Carboniferous volcanoclastic rock, with metamorphism at greenschist- to amphibolite-facies. Further south, the Chinese Altai is separated from the Junggar blocks by the Irtys Fault (Figure 1B).

The granitoids in the Chinese Altai mainly occurred in the Paleozoic. These granitoids are classified into orogenic (462–375 Ma) and anorogenic (281–256 Ma) groups based on chemical compositions (Xiao et al., 2009). Geochemical studies have revealed that mantle-derived components as well as continental sources have both contributed to the generation of these granitoid magmas (Chen and Jahn, 2002; Wang et al., 2006; 2009; Yuan et al., 2007; Sun et al., 2008), and some magma chambers experienced composite assimilation and fractional crystallization processes (Liu et al., 1997).

3 Study area geology and sample collection

The granite porphyry samples were collected from the Kezieryayin region in the Kelan Basin and intrude into the Kangbutiebao Formation. (Figure 2; Yang et al., 2017; Yang et al., 2019). The Kelan Basin lies in the Qiongkuer Domain (Figure 1B).

The metamorphosed late Cambrian–early Ordovician rocks (495–481 Ma, Yang et al., 2017) and middle–late Silurian Kulumuti Group consist of migmatites, gneisses, granulite, schists and metasandstones and are exposed in the basement of the Kelan Basin (Figure 2A). The metamorphosed basement has a fault contact with arc-type volcano-sedimentary rocks of the lower Devonian Kangbutiebao Formation and an overlying middle–upper Devonian turbiditic sandstone–shale of the Altai Formation (Windley et al., 2002). The intrusions are widely distributed in and around the Kelan Basin and were emplaced during the middle Ordovician–late Triassic (462–202 Yang et al., 2021).

The granite porphyries are light red to dark gray in color and generally ~2 m wide and ~10 m long (Figure 2B; Figures 3A, B). The granite porphyries exhibit a gneissic structure (Figures 3A, B) and typical porphyritic texture (Figures 3C, D), and the mineral grains are mostly medium and fine. The phenocrysts (~15–20 vol%) mainly consist of alkaline feldspar (~5–10 vol%) and quartz (~10–15 vol%); the matrix (~80–85 vol%) with a fine-grained granitic texture contains a similar mineral assemblage of quartz (~33 vol%), K-feldspar (~27 vol%), plagioclase (~14 vol%), a small amount of biotite (~5.5 vol%), muscovite (~1 vol%), amphibole (~1 vol%) and opaque minerals (~1 vol%; Figures 3C, D). Accessory minerals are zircon and apatite. The alkaline feldspar phenocrysts are generally lath-shaped and form euhedral-subhedral grains with sizes up to 5 mm across. Abundant inclusions, such as biotite, can be locally observed in the alkaline feldspar (Figures 3C, D). The quartz phenocrysts are subhedral-anhedral in shape with sizes of ~0.1–7.5 mm in diameter (Figures 3C, D). Five granite porphyry samples were collected for this major and trace element, Nd–Hf–Pb–O isotopes and zircon U–Pb dating study.

4 Analytical methods

Zircon U–Pb geochronology, whole-rock geochemistry, Nd–Hf–Pb isotopes and zircon O isotope analyses were conducted on the samples collected in this study. Zircon U–Pb dating and O isotope have been completed at the Beijing Sensitive high-resolution ion microprobe (SHRIMP) Center. Whole-rock major and trace elements were determined at the Key Laboratory for the Study of Focused Magmatism and Giant Ore Deposits, the Xi'an Center of China Geological Survey, MNR. The whole-rock Nd and Pb isotope ratios were analyzed at the Beijing Research Institute of Uranium Geology, and the Hf isotope ratios were determined at the Institute of Geochemistry, Chinese Academy of Sciences.

4.1 Zircon U–Pb dating

After crushing, zircons were separated from 80 mesh sieved samples by standard heavy liquid and magnetic techniques. The representative zircons were handpicked and mounted with adhesive tape under a binocular microscope, enclosed in epoxy resin and polished to approximately half of their thickness. After being photographed under reflected and transmitted light, transmitted electron, backscattered electron (BSE) and cathodoluminescence (CL) images were obtained for zircons, revealing their internal structures.

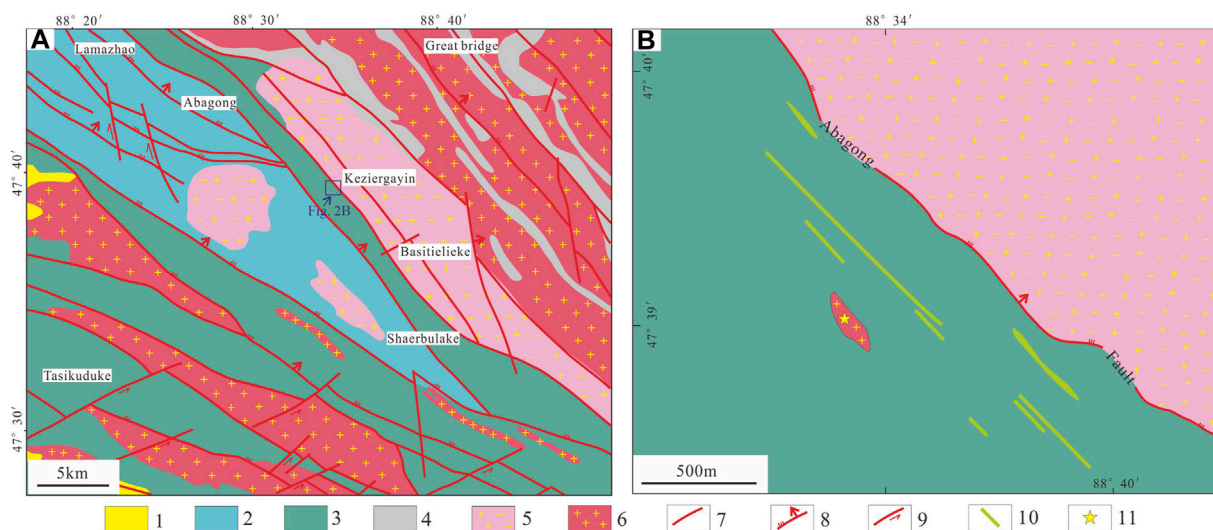


FIGURE 2
Simplified regional geological map of the Kelan basin (A) and Keziergayin region (B) in the Chinese Altai (after Yang et al., 2019; Bao et al., 2021). 1- Quaternary sediments; 2-Metasedimentary rocks of the Altay Formation; 3-Metavolcanosedimentary rocks of the Kangbutiebao Formation; 4-Late Cambrian-early Ordovician metamorphic rocks; 5-Permian granite; 6-Ordovician-Devonian granite; 7-Fault; 8-Compressoshear fault; 9-Shear fault; 10-Tungsten polymetallic ore body; 11-Location of sample.

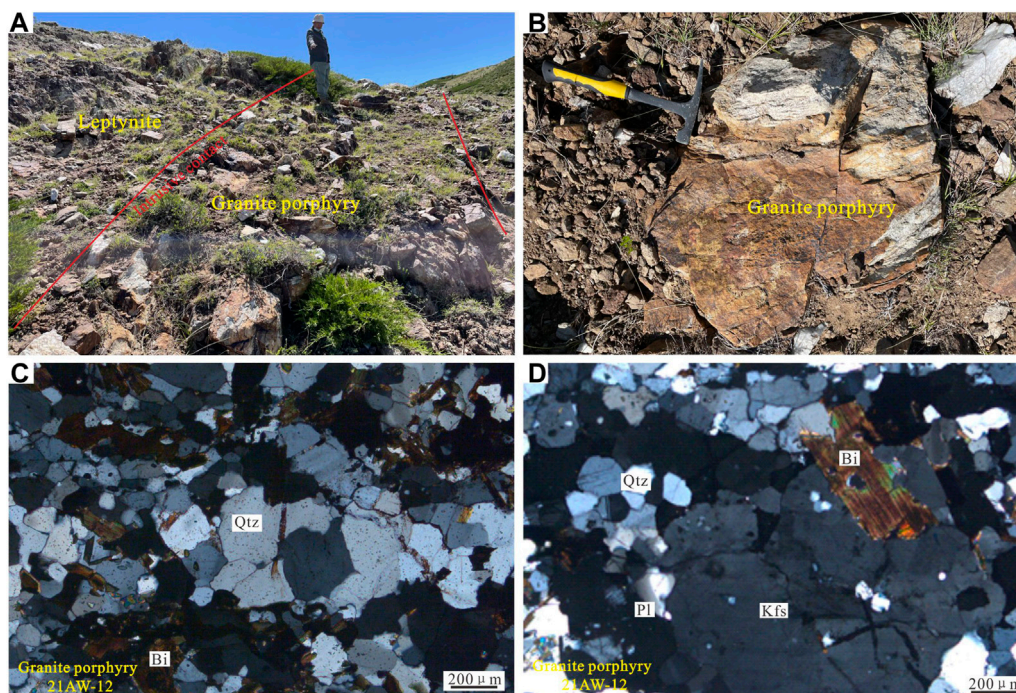


FIGURE 3
Field and microscopic photos of the granite porphyries from the Keziergayin region of the Kelan basin. (A) The leptynite of the Devonian Kangbutiebao Formation was intruded by granite porphyry. (B) Hand specimen of granite porphyry. (C,D) Mineral compositions and texture of granite porphyry (sample 21AW-12). Qtz=quartz, Pl=plagioclase, Kfs=K-feldspar, Bi= biotite.

In SHRIMP zircon U–Pb analyses, spot sizes were 25–30 μm, and the intensity of the primary particle flow was approximately 4 nA. Each data point measurement consisted of five scans. The

interelement fractionation correction was carried out using standard zircon TEM (417 Ma). The standard zircon SL13 (572 Ma) was used to calibrate the contents of U, Th and Pb of the standard TEM

(417 Ma) and the analyzed zircons. The detailed analysis process followed that described by Song (2002). Ludwig SQUID 1.0 and Isoplot (Ludwig, 2003) were used for processing the original data and drawing the zircon U–Pb concordia diagrams.

4.2 Major and trace element analyses

Fresh samples for whole-rock analyses were collected and crushed to 200 mesh using an agate mill. Major elements were obtained by a Phillips PW 240 X-ray fluorescence (XRF) spectrometer on fused glass beads. The analytical precision was better than 1%. Trace elements were analyzed by an inductively coupled plasma mass spectrometry (ICP–MS) using an Agilent 7,700×ICP–MS system, and the accuracies for minor element content were better than 5%. For a detailed analytical process, please refer to those described by Ma et al. (2012) and Gao et al. (2008).

4.3 Whole-rock Nd–Hf–Pb isotopic analyses

About 0.1 g powder sample was accurately weighed in a low-pressure sealed sample dissolving tank, diluent Sm–Nd was accurately added, and dissolved with mixed acid (HF+HNO₃+HClO₄) for 24 h. After the sample was completely dissolved, it was steamed and dried by adding 6 mol/L hydrochloric acid into chloride. The solution was dissolved in 0.5 mol/L hydrochloric acid solution and centrifuged. The clear solution was placed in cation-exchange column (φ0.5×15 cm, AG50W×8 (H⁺) 100–200 mesh). The matrix elements and other elements were rinsed with 1.75 mol/L hydrochloric acid solution and 2.5 mol/L hydrochloric acid solution. The rare Earth elements were washed with 4 mol/L hydrochloric acid solution and then dried. Sm–Nd were separated using P507 extraction resin, evaporated to dryness, and converted into nitrate for mass spectrometry analysis. Nd isotopic analysis was performed using an ISOPROBE-T thermal ionization mass spectrometer. The mass fractionation correction of Nd isotopes was based on a ¹⁴⁶Nd/¹⁴⁴Nd ratio of 0.7219, and the JMC standard ¹⁴³Nd/¹⁴⁴Nd=0.512109 ± 3 was used by an experimental monitor. The background Sm and Nd concentrations of the whole analytic process are less than 50 pg.

About 0.1 g powder sample was accurately weighed in a savillex sample dissolving tank, 3 mL of mixed acid solution of HF:HNO₃:3:1 was added. The samples were heated on an electric heating plate using a temperature of 120°C for 3 days to dry the sample. Then, 3 mL HNO₃ was added, followed by evaporation to dry the sample, then 3 mL 6N HCl was added, then evaporation to dry again, and finally 2N HF was added to dissolve the sample, loaded on an ion-exchange column for separation, and prepared for analyses. Hf isotope analysis was performed by Neptune Plus type MC-ICP-MS. The instrumental fractionation of Hf isotopes was monitored by measuring the Hf standard solution JMC475 every 15 samples. The Hf isotope data was normalized to ¹⁷⁹Hf/¹⁷⁷Hf=0.7325 using the exponential law. The mean ¹⁷⁶Hf/¹⁷⁷Hf for JMC 475 solutions in this study was 0.282163 ± 13 (2δ, n=7).

About 0.1–0.2 g powder sample was accurately weighed in a low-pressure sealed sample dissolving tank, and dissolved with mixed

acid (HF+HNO₃+HClO₄) for 24 h. After the sample was completely dissolved, it was steamed and dried by adding 6 mol/L hydrochloric acid into chloride. The solution was dissolved in 1 mL 0.5 mol/L HBr solution and centrifuged. The clear solution was placed in anion-exchange column (250 μL AG1×8,100–200 mesh). The impurities were washed with 0.5 mol/L HBr, and the lead was parsed with 1 mL 6 mol/L HCl in a Teflon beakers, then dried for use. Pb isotopic analysis was performed using an ISOPROBE-T thermal ionization mass spectrometer. Pb isotopic analysis was corrected using NBS981 as the reference material, and its uncorrected results was ²⁰⁸Pb/²⁰⁶Pb=2.164940 ± 15, ²⁰⁷Pb/²⁰⁶Pb=0.914338 ± 7, ²⁰⁴Pb/²⁰⁶Pb=0.0591107 ± 2 and the whole process background Pb<100 pg.

4.4 Zircon O isotopic analyses

In situ zircon O isotope analyses were conducted on the same zircon spots as U–Pb laser ablation with a 25 μm spot. The zircon TEMORA 2 (δ¹⁸O=8.20‰) standard was measured as an unknown to monitor the external precision, and the analysis point ratio of the standard sample and analysis sample was 1:3. The measured values of a single point are the calculated mean value of ¹⁸O/¹⁶O with 10 groups of scans, and the accuracy of single point ¹⁸O/¹⁶O data is generally better than 0.2‰–0.3‰. Details of the instrumental conditions and data acquisition procedures were similar to those described by Ávila et al. (2020).

5 Results

5.1 Zircon morphology and U–Pb geochronology

Zircon grains from the granite porphyry (21 AW-12) were selected for U–Pb dating, as summarized in Table 1. Zircon grains in the sample display colorless and transparent grains in plane-polarized light, exhibiting euhedral–subhedral shapes. Their lengths range from 75–135 μm, and the length/width ratios range from 2:1–3:1. Under CL images, most zircon grains are prismatic and weakly to moderately luminescent with typical oscillatory zoning, hinting at a magmatic origin (Figure 4A). Twelve spots were analyzed on 12 zircon grains from sample 21AW-12. They have high Th/U ratios greater than 0.46 (Table 1). Twelve analyses with better concordant ²⁰⁶Pb/²³⁸U ages ranging from 385 Ma to 404 Ma yield a weighted mean age of 394 ± 3 Ma (2σ, MSWD=1.14; Figures 4B,C), which is Early Devonian, representing the emplacement age of magma.

5.2 Whole-rock major and trace elements

Five samples of the granite porphyry were analyzed to acquire their major and trace element compositions, as summarized in Table 2 and illustrated in Figures 5, 6. The granite porphyry samples are characterized by high SiO₂ (74.69–82.08 wt%) and Na₂O (3.59–6.12 wt%) concentrations, moderate Al₂O₃ (10.13–14.99 wt%), and low FeO^T (0.44–0.88 wt%), MgO (0.05–0.2 wt%) and CaO (0.42–3.8 wt%) with low K₂O/Na₂O

TABLE 1 SHRIMP U–Pb geochronological data of single zircons from granite porphyries.

Sample/ zircon number	$^{206}\text{Pb}_c$ (%)	U (ppm)	Th (ppm)	Th/ U	$^{206}\text{Pb}^*$ (ppm)	$^{206}\text{Pb}/$ ^{238}U	% err	$^{207}\text{Pb}/$ ^{206}Pb	% err	$^{206}\text{Pb}/$ ^{238}U age (Ma)	1 σ err	$^{207}\text{Pb}/$ ^{206}Pb age (Ma)	1 σ err	% Dis
21AW-12 (Sample number)														
Zr.1	0.00	581	303	0.54	31.7	0.06341	1.3	0.05455	1.4	396	5	394	32	-1
Zr.2	0.53	680	328	0.50	37.5	0.06382	1.3	0.05230	2.6	399	5	297	59	-34
Zr.3	0.07	461	322	0.72	25.1	0.06331	1.3	0.05499	1.8	396	5	412	39	4
Zr.4	0.10	517	278	0.56	27.9	0.06277	1.3	0.05544	1.8	393	5	430	40	9
Zr.5	0.24	551	269	0.50	29.3	0.06163	1.3	0.05450	2.2	386	5	391	49	1
Zr.6	--	481	226	0.49	26.7	0.06474	1.3	0.05549	1.6	404	5	432	35	6
Zr.7	0.10	586	347	0.61	31.7	0.06292	1.3	0.05416	1.5	393	5	378	33	-4
Zr.8	0.00	670	403	0.62	35.4	0.06151	1.3	0.05358	1.4	385	5	354	31	-9
Zr.9	0.89	722	323	0.46	39.2	0.06263	1.3	0.05490	2.8	392	5	407	63	4
Zr.10	0.19	441	224	0.53	24.1	0.06359	1.4	0.05390	2.3	397	5	366	51	-8
Zr.11	0.16	498	250	0.52	27.1	0.06338	1.3	0.05420	2.5	396	5	378	57	-5
Zr.12	0.20	560	313	0.58	30.6	0.06334	1.4	0.05408	1.7	396	5	375	38	-6

Errors are 1-sigma; Pbc and Pb* indicate the common and radiogenic portions, respectively.
Common Pb corrected using measured ^{204}Pb .

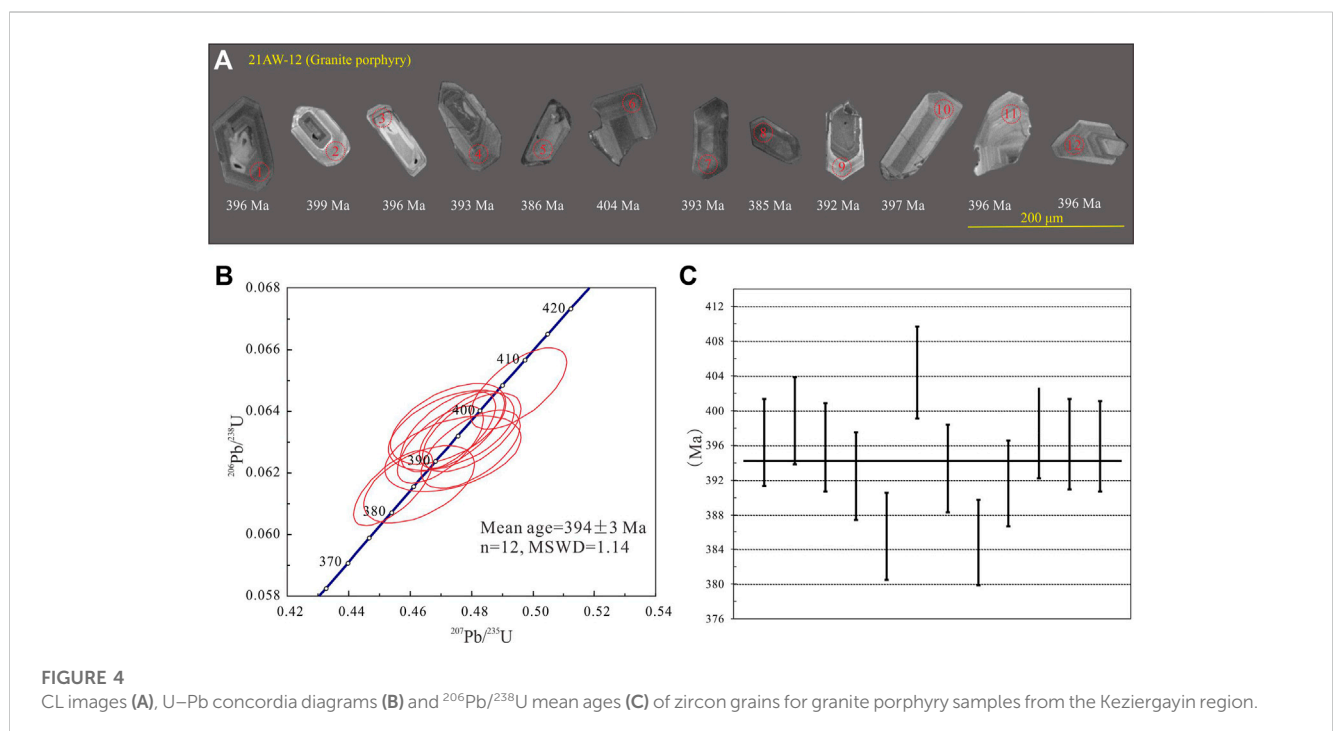


FIGURE 4 CL images (A), U–Pb concordia diagrams (B) and $^{206}\text{Pb}/^{238}\text{U}$ mean ages (C) of zircon grains for granite porphyry samples from the Keziergayin region.

ratios between 0.04 and 1.03, and $\text{Mg}^\#$ ($\text{Mg}^\# = 100 * (\text{MgO}/40.3044) / (\text{MgO}/40.3044 + \text{FeO}^{\text{T}}/71.844)$) values of 9–32 (Figure 5; Table 2). The granite porphyries have low alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O} = 4.91\text{--}7.29$ wt%); on a total alkalis vs. silica (TAS) diagram, they plot in the granite field with a subalkaline signature (Figure 6A); on a K_2O vs. SiO_2 diagram,

the granitic rock samples show an evolution trend from a low-K (tholeiite) series to a high-K calc-alkaline series (Figure 6B). They show weakly peraluminous and metaluminous signatures with aluminum saturation indices of A/CNK and A/NK ranging from 0.98 to 1.02 and from 1.06 to 1.88, respectively (Figure 6C).

TABLE 2 Whole-rock major and trace element compositions of granite porphyries.

Samples elements	21AW-12	21AW-13	21AW-14	21AW-15	21AW-16
SiO ₂	77.10	80.29	82.08	74.69	77.67
Al ₂ O ₃	12.76	11.42	10.13	14.99	12.36
Fe ₂ O ₃	0.50	0.16	0.31	0.62	0.26
FeO	0.30	0.30	0.31	0.32	0.25
CaO	1.31	0.48	0.42	3.80	1.38
MgO	0.20	0.08	0.09	0.05	0.10
K ₂ O	1.66	0.63	1.42	0.19	3.70
Na ₂ O	5.37	6.12	4.66	4.72	3.59
TiO ₂	0.19	0.11	0.11	0.13	0.13
P ₂ O ₅	0.03	0.02	0.02	0.02	0.02
MnO	0.06	0.02	0.02	0.04	0.02
LOI	0.45	0.32	0.33	0.35	0.41
Cu	90.7	66.2	35.8	66.6	80.1
Pb	10.9	3.57	3.36	9.24	9.52
Zn	27.0	8.61	11.1	38.2	322
Ni	6.05	2.88	3.12	4.10	3.86
Co.	2.32	0.880	0.660	0.820	0.850
Li	9.59	2.15	2.11	2.85	5.83
Rb	65.1	18.5	29.4	10.3	139
Cs	1.47	0.540	0.520	0.410	5.20
W	19.7	3.12	2.45	5.24	8.39
Mo	4.98	1.33	1.44	7.00	6.81
Sr	70.5	33.9	33.5	315	243
Ba	169	56.6	101	59.7	383
V	6.07	0.860	2.04	2.77	2.65
Sc	7.42	6.13	5.72	5.25	1.81
Nb	11.6	9.53	8.18	6.93	9.78
Ta	1.46	1.01	0.960	0.910	1.03
Zr	123	109	94.2	108	134
Hf	5.05	4.04	3.48	3.69	4.71
Ga	12.8	10.4	11.2	20.8	11.2
Sn	3.98	3.03	3.98	6.04	4.55
U	4.80	3.17	2.42	1.75	2.00
Th	12.8	12.9	13.4	16.6	13.2
La	40.3	21.7	60.8	12.0	6.62
Ce	96.1	48.7	131	22.8	13.8
Pr	11.1	6.31	16.6	3.05	1.81

(Continued in next column)

TABLE 2 (Continued) Whole-rock major and trace element compositions of granite porphyries.

Samples elements	21AW-12	21AW-13	21AW-14	21AW-15	21AW-16
Nd	42.4	23.9	61.6	11.5	7.18
Sm	9.70	5.62	11.4	2.84	1.92
Eu	1.17	0.740	1.42	0.370	0.290
Gd	7.73	5.26	8.10	2.85	1.95
Tb	1.17	0.980	1.22	0.550	0.390
Dy	6.18	6.20	5.98	3.65	2.74
Ho	1.27	1.36	1.16	0.760	0.640
Er	3.89	3.94	3.22	2.34	2.12
Tm	0.640	0.590	0.480	0.330	0.360
Yb	4.35	3.83	3.26	2.18	2.55
Lu	0.670	0.560	0.480	0.330	0.450
Y	31.8	31.3	30.6	19.1	15.5

The granite porphyries have low total rare Earth elements (REEs) contents of 42.82–306.72 ppm Table 2. In the chondrite-normalized REEs distribution diagram (Figure 7A), the granite porphyry samples display enrichments in light REEs (LREEs) ((La/Yb)_N = 1.86–13.38) and flat heavy REEs (HREEs) ((Dy/Yb)_N = 0.72–1.23) with obviously negative Eu anomalies ($\delta\text{Eu} = 0.40\text{--}0.46$). On the primitive mantle-normalized multielement diagram, the granite porphyry samples show negative Ba, Sr, Nb, Ta, P and Ti and positive Rb, Th, U, Nd, Zr and Pb anomalies (Figure 7B).

5.3 Whole-rock Nd–Hf–Pb isotopes

Four samples of the granite porphyry were further chosen to acquire their Nd–Hf–Pb isotopes, as listed in Tables 3–5. The results of initial ¹⁴³Nd/¹⁴⁴Nd ratios, $\epsilon_{\text{Nd}}(t)$, $\epsilon_{\text{Hf}}(t)$, initial ²⁰⁶Pb/²⁰⁴Pb, initial ²⁰⁷Pb/²⁰⁴Pb, and ²⁰⁸Pb/²⁰⁴Pb were calculated at $t = 394$ Ma based on the results of zircon U–Pb dating. The granite porphyries exhibit low initial ¹⁴³Nd/¹⁴⁴Nd (0.512033–0.512059), negative $\epsilon_{\text{Nd}}(t)$ (–1.9 to –1.4) values, with $T_{2\text{DM}}$ Nd model ages of 1,438–1,774 Ma ($n = 4$; Table 3; Figure 8A), positive $\epsilon_{\text{Hf}}(t)$ (+4.3 to +11.4) values, $T_{2\text{DM}}$ Hf model ages of 661–1,112 Ma ($n = 4$; Table 4; Figure 8B), and low (²⁰⁶Pb/²⁰⁴Pb)_i (17.363–18.408), (²⁰⁷Pb/²⁰⁴Pb)_i (15.515–15.557) and (²⁰⁸Pb/²⁰⁴Pb)_i (36.953–37.696) values ($n = 4$; Table 5; Figure 8D).

5.4 Zircon O isotope

Twelve zircon grains for granite porphyry that were used for U–Pb dating were further chosen to determine their $\delta^{18}\text{O}_{\text{V-SMOW}}$ values. The results are summarized in Table 6 and presented in

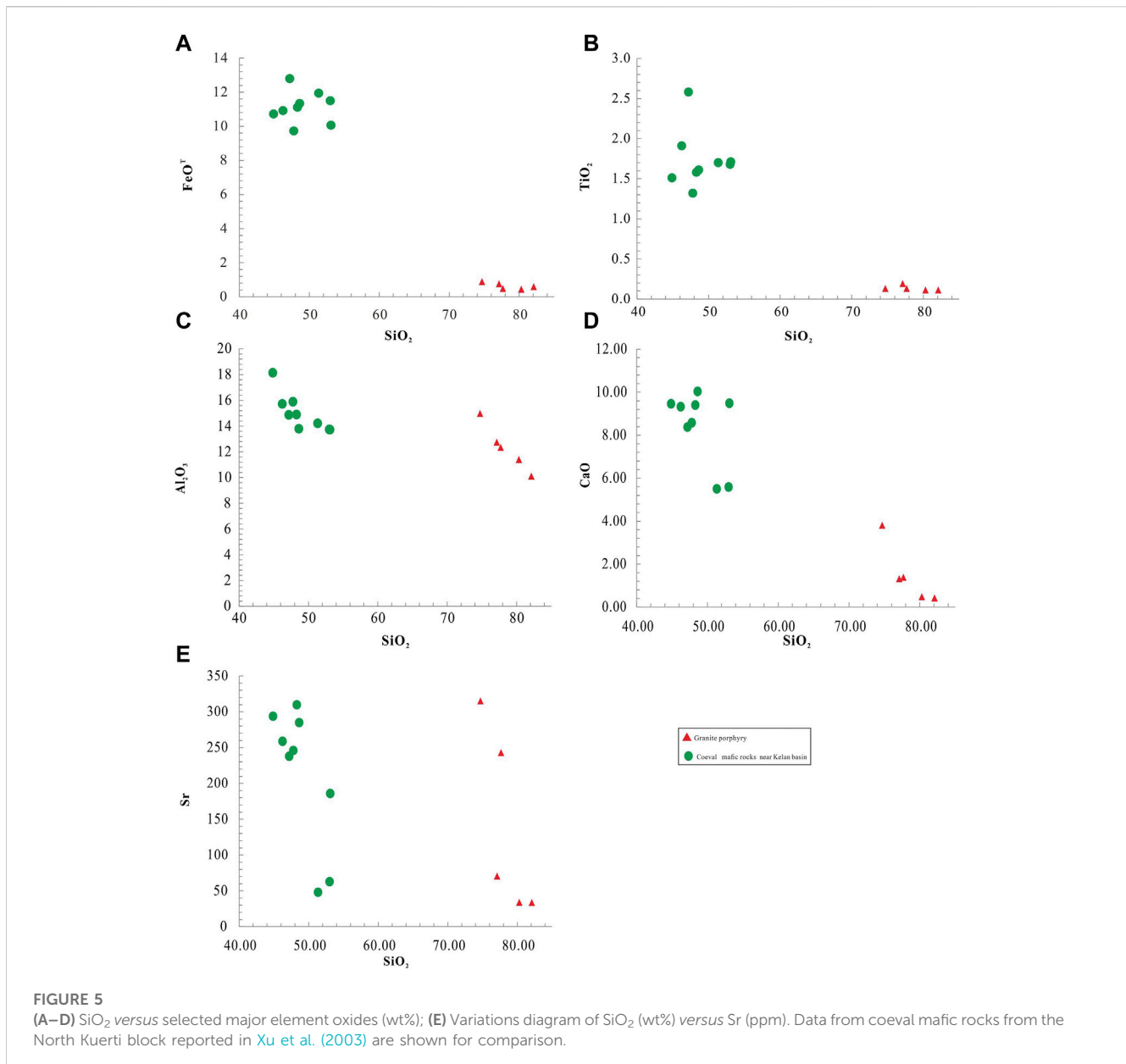


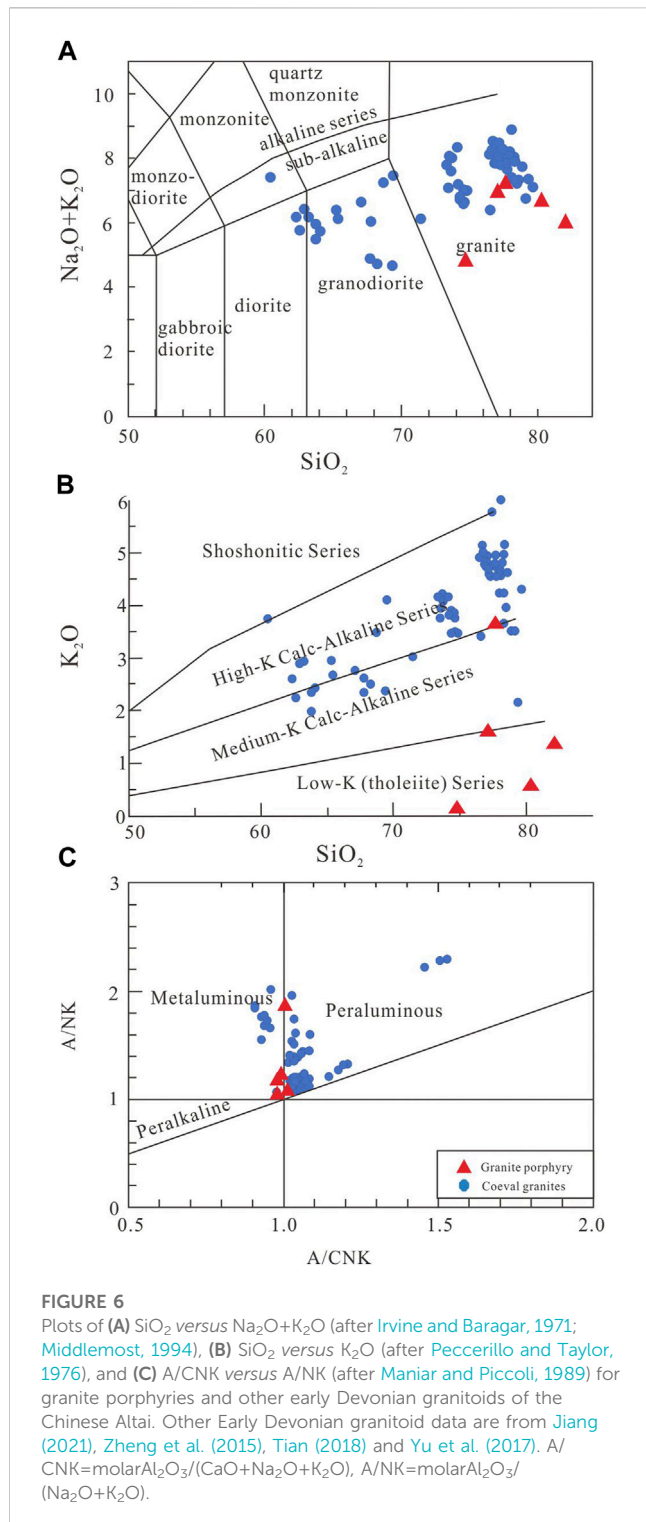
Figure 8E. The magmatic zircons from granite porphyry display $\delta^{18}\text{O}_{\text{V-SMOW}}$ values of 6.38‰–8.45‰, with an average of 7.14‰.

6 Discussion

6.1 Genetic classification

In general, granites can be divided into S-, I- and A-types according to their mineralogical and geochemical characteristics and the nature of their protoliths (Collins et al., 1982; Whalen et al., 1987; Chappell and White, 1992; Wang S J et al., 2020). I-type granites are metaluminous to weakly peraluminous and commonly contain amphibole as a diagnostic phase (Chappell et al., 2012); S-type granites are strongly peraluminous and contain cordierite, muscovite and other aluminum-rich

minerals. Chappell (1974) proposed that the boundary between S-type and I-type granites can be drawn at an A/CNK ratio of 1.1. There is a small amount of muscovite in the petrographic observations of granite porphyry samples. In contrast, the extremely low P₂O₅ content (0.002–0.003 wt%), weakly peraluminous and metaluminous signatures with the moderate A/CNK content in geochemical analysis indicate that S-type granites can be excluded (Chappell, 1974; King et al., 1997; Bonin, 2007). Geochemically, the granite porphyries show lower Zr (94.2–134.0 ppm), Nb (6.9–11.6 ppm), total REEs (42.8–306.7 ppm), Zr+Nb+Y+Ce (156.8–264.0 ppm) and Ga/Al ratio (10,000×Ga/Al ratios of 1.71–2.62) values than typical A-type granite (Collins et al., 1982; White and Chappell, 1983; Whalen et al., 1987; Zhao et al., 2018). In the discrimination diagrams of FeO^T/MgO, Zr, Ce vs. 10,000 Ga/Al (Figures 9A–C), they plot in the fields



straddling between I- and S-types and A-type granite. In the FeO^T/MgO vs. $(\text{Zr}+\text{Nb}+\text{Ce}+\text{Y})$ diagram (Figure 9A), they plot in the fields straddling fractionated and unfractionated I- and S-type granites. Therefore, the granite porphyries are not typical A-type granites but fractionated I-type granites.

6.2 Magmatic source

I-type granitic melts can originate from different source (Holden et al., 1987; Han et al., 1997; Griffin et al., 2002; Bonin, 2007; Zhong et al., 2007; Yang et al., 2008; Ahmed et al., 2018; Chen et al., 2018; Wang J et al., 2020), including mantle-derived magma, magma mixing or mingling of mafic and felsic magmas, and mafic to intermediate igneous rocks (Li et al., 2007; Chappell et al., 2012; Wang S J et al., 2020). The granite porphyries in this study contain low contents of MgO , FeO^T , $\text{Mg}^\#$ and Ni (Table 2), and no mafic-ultramafic cumulates occur in association with granitic intrusions as synplutonic dikes (Gao et al., 2016). In Figure 5, they show no linear trends with coeval mafic igneous rocks from the North Kuerti area (Xu et al., 2003; Shen et al., 2017), indicating different origins between the granitic and mafic rocks. These geochemical characteristics argue against the formation of granite porphyries originated from mantle-derived magma. The granite porphyries have a narrow range of whole-rock Nd compositions (Figure 8A; Table 3). Mafic magmatic enclaves that commonly occur as indicators of magma mixing or mingling are also not observed in the granite porphyries. Thus, a model of crust and mantle mixing is not favored for the origin of the magma. In contrast, their $\delta^{18}\text{O}_{\text{V-SMOW}}$ values are 6.38‰–8.45‰, less than 10‰, within the range of O isotope of medium-basic igneous rocks (Figure 8E), suggesting that the magma of the granite porphyries was derived from mafic to intermediate igneous rocks (Li et al., 2007; Chappell et al., 2012; Wang J et al., 2020).

These samples show geochemical signatures of negative $\varepsilon_{\text{Nd}}(t)$ (−1.9 to −1.4) and positive $\varepsilon_{\text{Hf}}(t)$ (+4.3 to +11.4) values (Figures 8A,B). In the diagram of $\varepsilon_{\text{Nd}}(t)$ and $\varepsilon_{\text{Hf}}(t)$, they plot in the fields straddling ocean island basalt (OIB) and global lower crust and mainly in the fields of global lower crust, supporting a lower crust origin (Figure 8C). Significant Nd-Hf isotope decoupling was shown by all samples in this study (Figure 8C), which may have resulted from disequilibrium melting processes or inherited from the magma source (Yu et al., 2017). However, the poor correlation between the Hf and $\varepsilon_{\text{Hf}}(t)$ values rule out the former model (Farina et al., 2014; Figure 10A). Therefore, the decoupled Nd-Hf isotopic features of the granite porphyries should be inherited from the magma source and may reflect the previous subduction process (Jiang et al., 2006), consistent with the geochemical characteristics of enrichment of Rb, Th and U and depletion of Nb, Ta, P and Ti in the primitive mantle-normalized trace element spider diagrams (Figures 7A,B). Because subduction slab-derived melts possessing high Nd/Hf ratios may add to the lithospheric mantle and result in Nd-Hf isotopic decoupling in the mantle (Pearce et al., 1999; Spandler et al., 2007; Todd et al., 2010), magma sources might be extracted from the lithospheric mantle and inherited Nd-Hf isotopic decoupling features of the mantle (Yu et al., 2017). This crust-mantle interconnection is further supported by the Pb isotope compositions of the granite porphyries that plot between the orogenic and mantle lines near the orogenic line (Figure 8D). Thus, the granite porphyries are interpreted to originate from lower crust medium-basic igneous rocks extracted from the lithospheric mantle metasomatized by subducted melt.

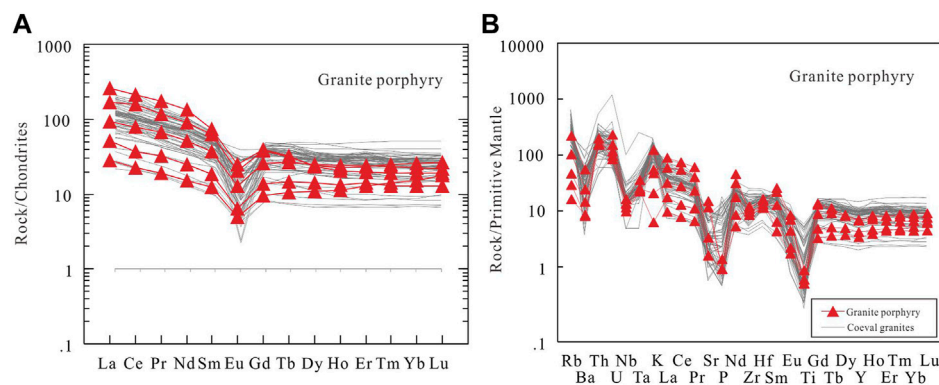


FIGURE 7 (A) Chondrite-normalized rare Earth elements (REEs) patterns and (B) primitive mantle-normalized multielement variation diagrams for granite porphyries. The chondrite values and primitive mantle values are after Taylor and McLennan (1985) and Sun and McDonough (1989), respectively. Other Early Devonian granitoid data are from Jiang (2021), Zheng et al. (2015), Tian (2018) and Yu et al. (2017).

TABLE 3 Whole-rock Nd isotope composition of granite porphyries.

Samples	Sm (ppm)	Nd (ppm)	¹⁴⁷ Sm/ ¹⁴⁴ Nd	¹⁴³ Nd/ ¹⁴⁴ Nd	t (Ma)	(¹⁴³ Nd/ ¹⁴⁴ Nd) _i	ε _{Nd} (t)	T _{DM} (Ma)	T _{2DM} (Ma)
21AW-12	9.70	42.40	0.1392	0.512394	394	0.512035	-1.9	1,545	1,446
21AW-13	5.62	23.90	0.1431	0.512428	394	0.512059	-1.4	1,556	1,438
21AW-15	2.84	11.50	0.1503	0.512443	394	0.512055	-1.5	1,696	1,526
21AW-16	1.92	7.18	0.1628	0.512453	394	0.512033	-1.9	2078	1774

The ¹⁴⁷Sm/¹⁴⁴Nd ratios of samples were calculated based on Sm and Nd content. T_{DM} = 1/λln[(¹⁴³Nd/¹⁴⁴Nd)_s - (¹⁴³Nd/¹⁴⁴Nd)_{DM}] / [(¹⁴⁷Sm/¹⁴⁴Nd)_s - (¹⁴⁷Sm/¹⁴⁴Nd)_{DM} + 1]; T_{2DM} = T_{DM} - (T_{DM} - t) * (f_{cc} - f_{DM}) / (f_{cc} - f_{DM}); In the formula, the subscript s and DM represent the analytical values of samples and the values of depleted mantle, respectively (¹⁴³Nd/¹⁴⁴Nd)_{DM} = 0.51315, (¹⁴⁷Sm/¹⁴⁴Nd)_{DM} = 0.2137, λ = 6.54 × 10⁻¹² a⁻¹, f_s = (¹⁴⁷Sm/¹⁴⁴Nd)_s / (¹⁴⁷Sm/¹⁴⁴Nd)_{CHUR} - 1, (¹⁴⁷Sm/¹⁴⁴Nd)_{CHUR} = 0.1967, f_{cc} = -0.4, f_{DM} = 0.08592.

TABLE 4 Whole-rock Hf isotope composition for granite porphyries.

Samples	Lu (ppm)	Hf(ppm)	¹⁷⁶ Lu/ ¹⁷⁷ Hf	¹⁷⁶ Hf/ ¹⁷⁷ Hf	t (Ma)	(¹⁷⁶ Hf/ ¹⁷⁷ Hf) _i	ε _{Hf} (t)	T _{DM} (Ma)	T _{2DM} (Ma)
21AW-12	0.67	5.05	0.01880	0.282909	394	0.282770	8.6	925	838
21AW-13	0.56	4.04	0.01964	0.282921	394	0.282776	8.8	932	825
21AW-15	0.33	3.69	0.01267	0.282942	394	0.282848	11.4	638	661
21AW-16	0.45	4.71	0.01354	0.282748	394	0.282648	4.3	1,072	1,112

T_{DM} = 1/λln[(¹⁷⁶Hf/¹⁷⁷Hf)_s - (¹⁷⁶Hf/¹⁷⁷Hf)_{DM}] / [(¹⁷⁶Lu/¹⁷⁷Hf)_s - (¹⁷⁶Lu/¹⁷⁷Hf)_{DM} + 1]; T_{2DM} = T_{DM} - (T_{DM} - t) * (f_{cc} - f_{DM}) / (f_{cc} - f_{DM}); In the formula, the subscript s and DM represent the analytical values of samples and the values of depleted mantle, respectively (¹⁷⁶Lu/¹⁷⁷Hf)_{DM} = 0.0384, (¹⁷⁶Hf/¹⁷⁷Hf)_{DM} = 0.28325, λ = 1.867 × 10⁻¹¹ a⁻¹, f_s = (¹⁷⁶Lu/¹⁷⁷Hf)_s / (¹⁷⁶Lu/¹⁷⁷Hf)_{CHUR} - 1, (¹⁷⁶Lu/¹⁷⁷Hf)_{CHUR} = 0.0332, f_{cc} = -0.55, f_{DM} = 0.16.

TABLE 5 Whole-rock Pb isotope composition for granite porphyries.

Samples	Pb(ppm)	U (ppm)	Th (ppm)	t (Ma)	²⁰⁶ Pb/ ²⁰⁴ Pb	±2σ	²⁰⁷ Pb/ ²⁰⁴ Pb	±2σ	²⁰⁸ Pb/ ²⁰⁴ Pb	±2σ	(²⁰⁶ Pb/ ²⁰⁴ Pb) _i	(²⁰⁷ Pb/ ²⁰⁴ Pb) _i	(²⁰⁸ Pb/ ²⁰⁴ Pb) _i
21AW-12	10.90	4.80	12.80	394	19.331	0.063	15.622	0.474	39.347	0.020	17.363	15.515	37.696
21AW-13	3.57	3.17	12.90	394	21.765	0.063	15.765	0.474	42.586	0.020	17.797	15.549	37.505
21AW-15	9.24	1.75	16.60	394	19.015	0.063	15.603	0.474	39.479	0.020	18.169	15.557	36.953
21AW-16	9.52	2.00	13.20	394	19.347	0.063	15.608	0.474	39.178	0.020	18.408	15.557	37.228

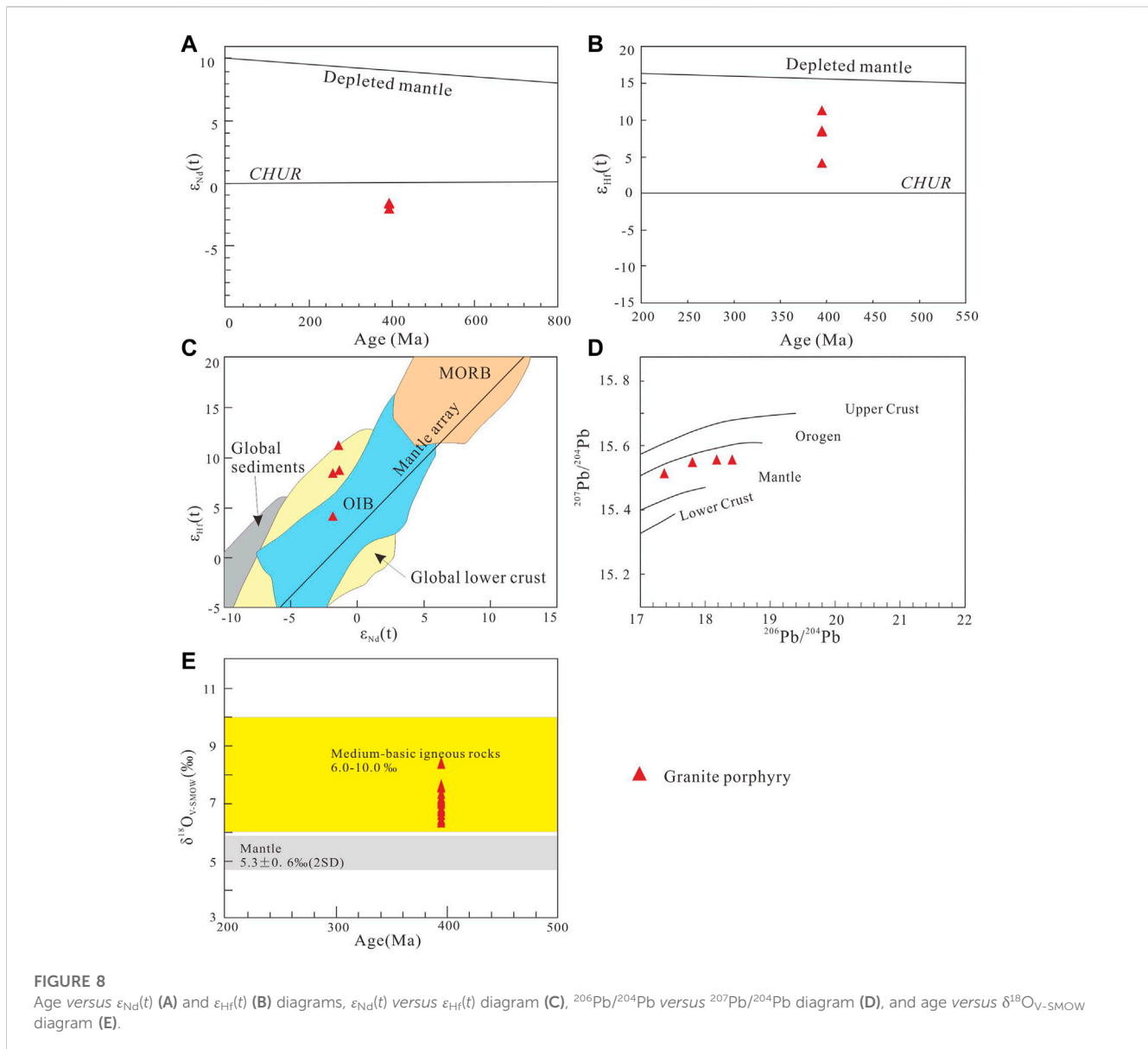


FIGURE 8 Age versus $\epsilon_{Nd}(t)$ (A) and $\epsilon_{Hf}(t)$ (B) diagrams, $\epsilon_{Nd}(t)$ versus $\epsilon_{Hf}(t)$ diagram (C), $^{206}Pb/^{204}Pb$ versus $^{207}Pb/^{204}Pb$ diagram (D), and age versus $\delta^{18}O_{v-SMOW}$ diagram (E).

6.3 Magmatic evolution

The granite porphyries show geochemical characteristics of high SiO_2 contents and Rb/Sr ratios, low CaO contents and K/Rb ratios, and strong negative Eu anomalies, hinting that they were formed by highly evolved magmas (Table 2) and were mainly controlled by a fractionation crystallization process. The negative P anomaly could be resulting from high differentiation of apatite. Pronounced negative anomalies of Eu, Ba and Sr could result from crystal fractionation of feldspar. Separation of both plagioclase and K-feldspar can be conjectured from the Sr decrease with increasing Rb/Sr ratio (Figure 10B). The TiO_2 and FeO^T contents show a negative correlation with increasing SiO_2 (Figures 5A,B), indicating crystal fractionation of Fe-Ti oxides. Separation of crystallized rutile may be the main cause for the decreasing titanium content in granite porphyries (Figure 10C). Moreover, the granite porphyries have decreasing LREEs contents

corresponding to crystal fractionation of allanite and/or monazite (Figure 10D), consistent with the geochemical characteristics of scattered LREEs in the chondrite-normalized REEs distribution (Jahn et al., 2001).

6.4 Tectonic setting and geodynamic implication

6.4.1 Tectonic setting

The Early Devonian granite porphyries are low-K calc-alkaline and metaluminous to weakly peraluminous in composition (Figure 6), with negative Ba, Sr, Nb, Ta, P, Eu and Ti anomalies and positive light REEs, Rb, Th, U, Nd, Zr and Pb anomalies (Figure 7). Within the element tectonic discrimination diagrams, the granite porphyries plot in the volcanic arc granite (VAG) field (Figure 11). These granites

TABLE 6 The O isotope compositions of zircon grains for granite porphyries.

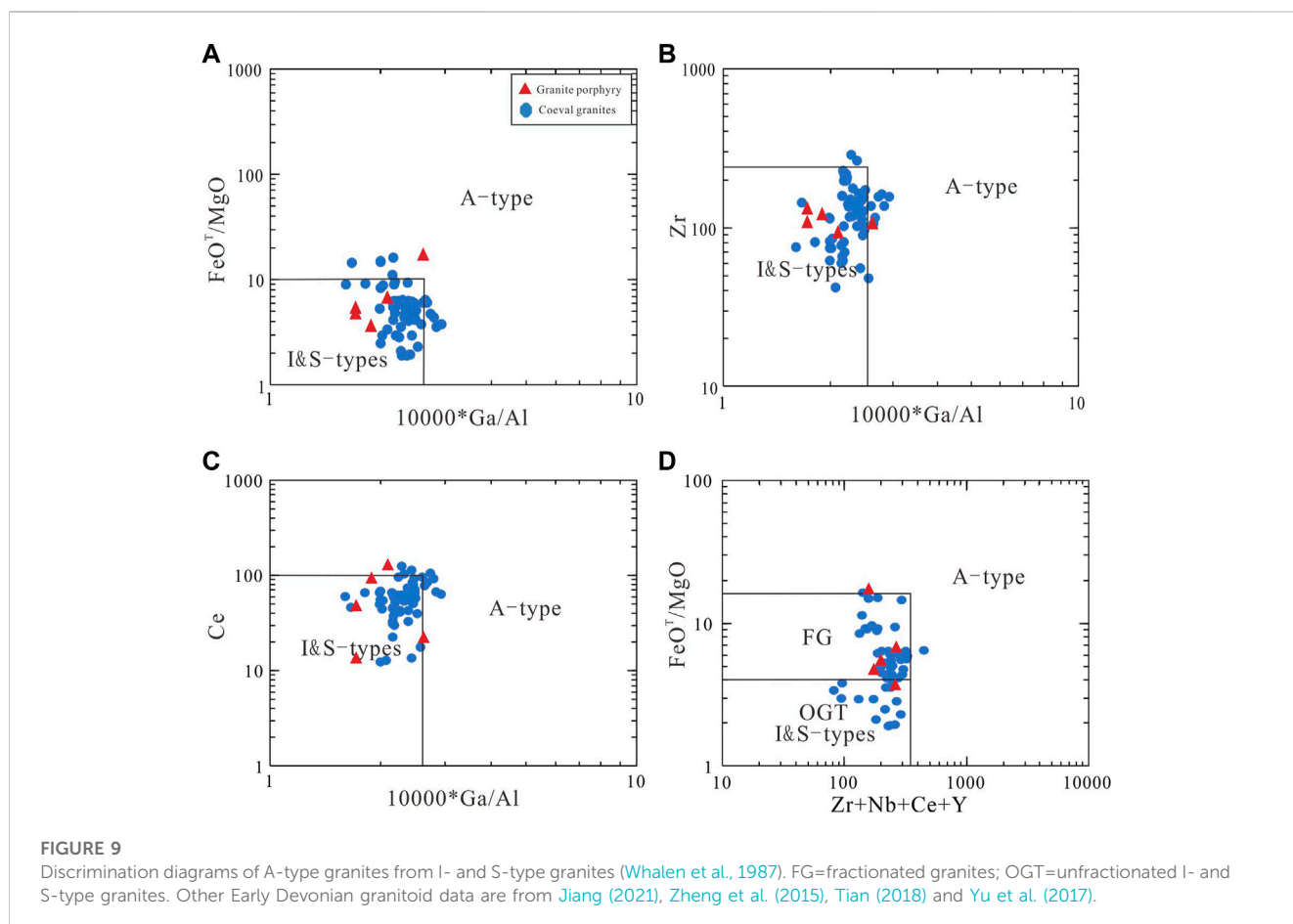
Sample number	Zircon number	$\delta^{18}\text{O}_{\text{V-SMOW}} (\text{‰})$
12AW-12	Zr.1	6.89
	Zr.2	6.38
	Zr.3	6.76
	Zr.4	7.60
	Zr.5	7.65
	Zr.6	6.65
	Zr.7	7.37
	Zr.8	6.48
	Zr.9	7.23
	Zr.10	7.13
	Zr.11	8.45
	Zr.12	7.05

with arc geochemical characteristics suggest that they may have formed in an island arc setting.

The Early Devonian Kangbutiebao Formation, which was invaded by the granite porphyries in the Kelang basin (Figure 2),

is dominated by metasilicic pyroclastic lavas with minor mafic volcanic rocks, including metarhyolite, metabasalt, metatuff, metavolcanic breccias and metavolcanic assemblages, which are consistent with those at active continental margins (Chai et al., 2009). The geochemical features of volcanic rocks from the Kangbutiebao Formation show bimodal geochemical characteristics, indicating a back-arc extensional regime (Xu et al., 2003; Chai et al., 2009; Wan et al., 2011). The coeval high-temperature metamorphic rocks, mafic rocks, adakitic and boninitic units (Xu et al., 2003; Niu et al., 2006; Jiang et al., 2010; Cai et al., 2012a; Cai et al., 2012b) demonstrate that the Early Devonian records the significant transfer of heat and juvenile material from the mantle to the crust. The subhorizontal, possibly extension-related, foliation (ca. 400 to 380 Ma) associated with high-temperature metamorphism occurs (Zhang J et al., 2015; Jiang et al., 2019). The above evidences support that the Chinese Altai was subjected to extensional tectonism during the Early Devonian. This condition could be met in the case of overriding plate crustal extension during trench retreat (Kemp et al., 2009; Collins et al., 2011; Zhang X R et al., 2015; Han et al., 2016; Nelson and Cottle, 2018; Li et al., 2019).

To discuss the Early Devonian tectonic setting, the geochemical data of coeval granitoids from the Chinese Altai are compiled. These granitoids belong to subalkaline granites (Figure 6A), medium-K to high-K calc-alkaline series (Figure 6B)



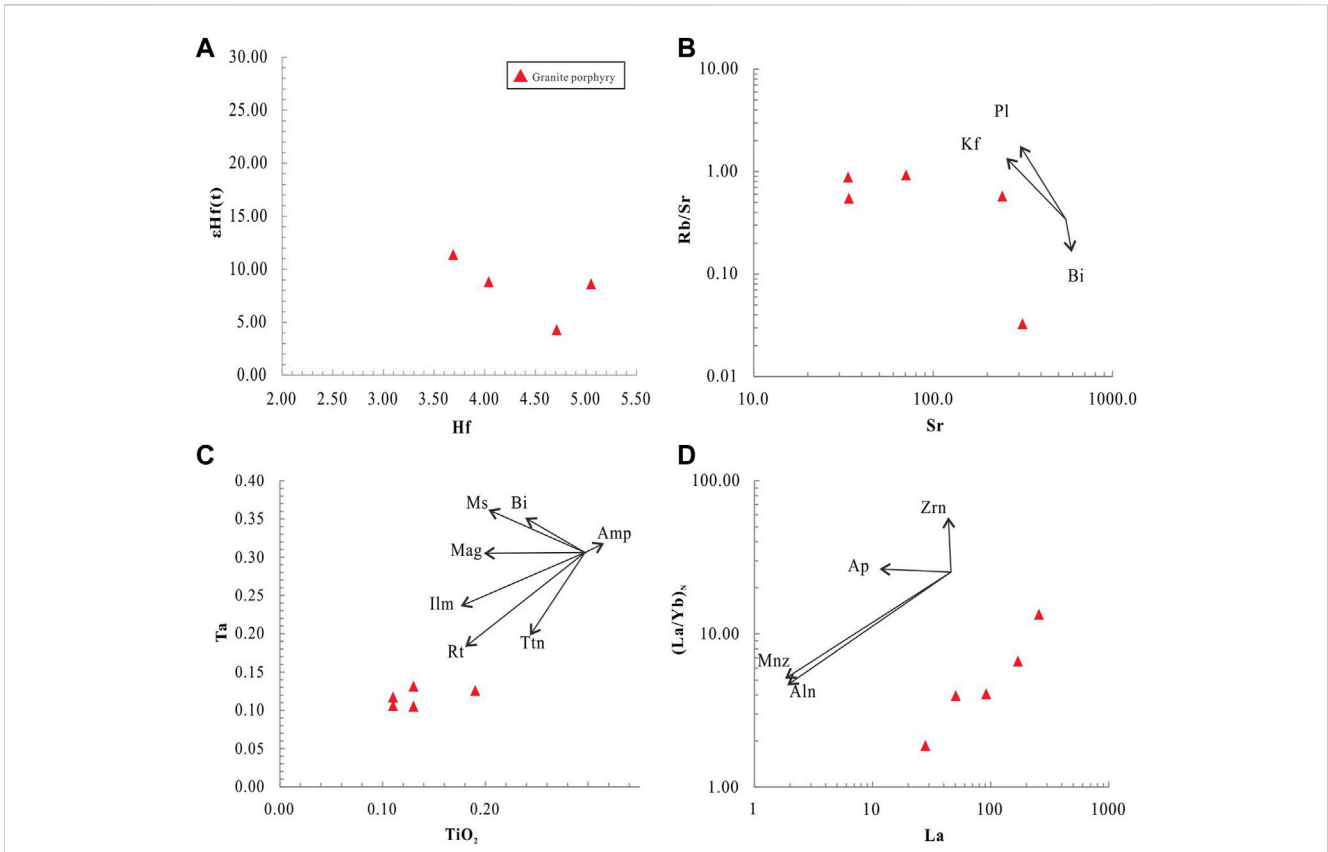


FIGURE 10 Diagrams of (A) $\epsilon_{Hf}(t)$ versus Hf (ppm) contents; (B) Rb/Sr ratios versus Sr (ppm) contents; (C) Ta (ppm) contents versus TiO_2 (wt%) contents; (D) $(La/Yb)_N$ ratios versus La (ppm) contents. Pl=plagioclase; Kf=K-feldspar; Bi=biotite; Ms= muscovite; Amp=amphibole; Mag=magmatite; Ilm=ilmenite; Rt=tutile; Ttn=titanite; Zrn=zircon; Ap=apatite; Mnz=monazite; Aln=allanite.

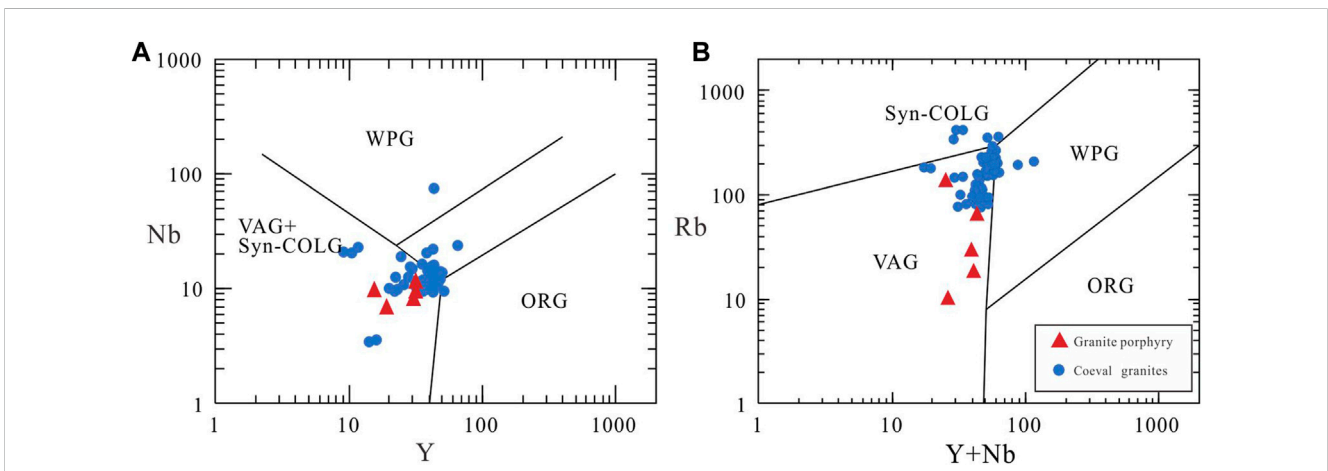
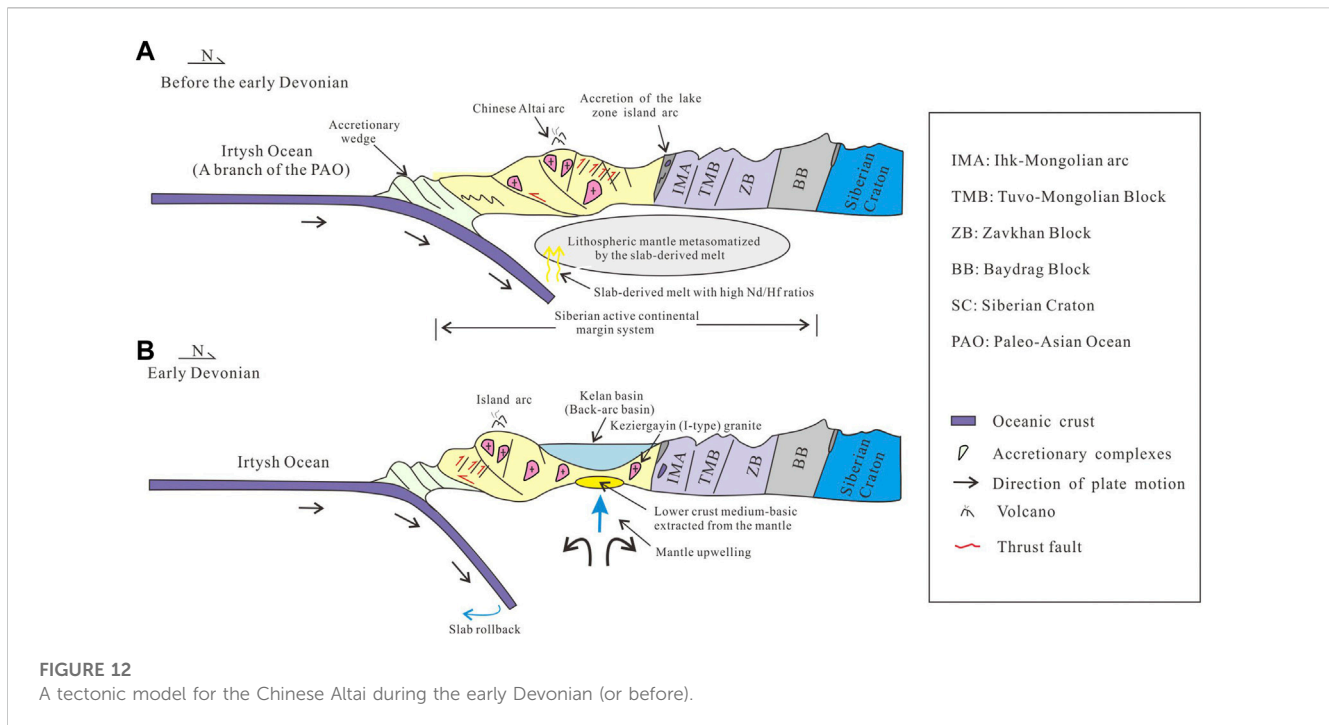


FIGURE 11 Tectonic discrimination diagrams of (A) Y (ppm) versus Nb (ppm) and (B) Y+Nb (ppm) versus Rb (ppm) (Pearce et al., 1984). Fields for Syn-COLG (syncollisional granite), VAG (volcanic arc granite), WPG (within-plate granite), and ORG (ocean-ridge granite) granites are from Pearce et al. (1984). Other Early Devonian granitoid data are from Jiang (2021), Zheng et al. (2015), Tian (2018) and Yu et al. (2017).

and metaluminous to peraluminous in composition (Figure 6C), with negative Eu, Nb, Ta and Ti anomalies and light REEs, Rb, Th and U enrichment (Figure 7). In addition, their compositions

indicate that they are not A-type granites (Figure 9) but mostly I-type granites with $A/CNK < 1.1$ (Figure 6C). The geochemical elements show similar curve characteristics to granite porphyries



(Figure 7). Within the element tectonic discrimination diagrams, most of these granitoids plot in the VAG field (Figure 11), further suggesting that the Early Devonian tectonic setting of the Chinese Altai was related to oceanic subduction.

In summary, we believe that there were island arcs and back-arc basins in the Chinese Altai during the Early Devonian, which belonged to the Siberian active continental margin system.

6.4.2 Implications for the geodynamic evolution of the Chinese Altai

The Chinese Altai experienced subduction, collision and accretion of different types of terrains and built up the current structural framework along with the closure of the Paleo-Asian Ocean (PAO) (Windley et al., 2002; Dobretsov et al., 2003; Xiao et al., 2004; Ni et al., 2006; Wang et al., 2006). Previous studies have shown that the Irtysh Ocean (a branch of the PAO) between the Junggar Block and Chinese Altai began to subduct northward at ~500 Ma, generating a series of blocks from south to north, namely, accretion of the lake zone island arc, Ikh-Mongol arc, Tuvo-Mongolian Block, Zavkhan Block and Baydrag Block in the Siberian continental margin (Li et al., 2019). Therefore, in the early Paleozoic, there was long-term subduction in the Chinese Altai, during which the lithospheric mantle was metasomatized by subducted slab-derived melts and resulted in Nd–Hf isotopic decoupling (Figure 12A).

As the main orogenic and mineralization period of the Chinese Altai, the Early Devonian is an important geological period to study the accretive orogenic process, continental crust growth mode and metallogenic geological background of bulk minerals. During this period, there are regional mutations in zircon isotope values. Two genetic models of mid-ocean ridge subduction (Cai et al., 2010; Jiang et al., 2010) and subducting

slab rollback (Wang S J et al., 2020) have been proposed to explain this phenomenon.

This study reveals that there was a complete arc-basin system in the Chinese Altai. The local extension under the ocean subduction background produced bimodal volcanic rocks, high-temperature metamorphic rocks, mafic rocks, adakitic and boninitic units, indicating the existence of back-arc extension, which supports the subducting slab rollback model. The Chinese Altai experienced subducting slab rollback during the Early Devonian. In this process, early lower crust medium–basic igneous rocks, which were extracted from the lithospheric mantle underneath, are partially melted by the upwelling of the mantle, forming I-type granites after magma evolution, accompanied by pyroclastic deposition and regional deformation metamorphism (Figure 12B).

During the Early Devonian (or before), the $\epsilon_{\text{Nd}}(t)$ and $\epsilon_{\text{Hf}}(t)$ values of granitoids in the Chinese Altai are mostly positive (Wang et al., 2009; Cai et al., 2011c; Yu et al., 2017), and substantial granitoid rocks mainly made of juvenile materials intruded into the Altai orogenic belt, suggesting significant continental crust growth. These granitoids are all related to the subduction of the PAO, suggesting that continental formation was mainly achieved by lateral growth through subduction of multiple small blocks, island arcs, etc., in the CAOB.

7 Conclusion

- 1) Zircon U–Pb dating reveals the presence of Early Devonian granite porphyry intrusions in the Kelan Basin, with a mean age of 394 ± 3 Ma.
- 2) The granite porphyries show geochemical affinity with I-type granite and originate from lower crust medium–basic igneous

rocks extracted from the lithospheric mantle metasomatized by subducted melt.

- 3) The Early Devonian arc-basin system associated with subducting slab rollback exists in the Chinese Altai, which can be attributed to the Siberian active continental margin system. These results reveal that the model of lateral accretion played a leading role in continental crustal growth during the Early Devonian (or before) in the CAOAB.

Data availability statement

The original contributions presented in the study are included in the article/supplementary material, further inquiries can be directed to the corresponding author.

Author contributions

KW: Writing—original draft (lead) and investigation (lead); WK: Writing—original draft (supporting); XZ: Writing—review and editing (supporting); ZM: Investigation (supporting); JC: Investigation (supporting); QS: Writing—review and editing (supporting). All authors contributed to the article and approved the submitted version.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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