



Age and geochemistry of the intrusive rocks from the Shaquanzi-Hongyuan Pb–Zn mineral district: Implications for the Late Carboniferous tectonic setting and Pb–Zn mineralization in the Eastern Tianshan, NW China



Wan-Jian Lu ^{a,b}, Hua-Yong Chen ^{a,c,*}, Li Zhang ^a, Jin-Sheng Han ^a, Bing Xiao ^a, Deng-Feng Li ^d, Wei-Feng Zhang ^e, Cheng-Ming Wang ^{a,b}, Lian-Dang Zhao ^{a,b}, Hong-Jun Jiang ^a

^a Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

^b Graduate University of Chinese Academy of Sciences, Beijing 100049, China

^c Guangdong Provincial Key Laboratory of Mineral Physics and Materials, 511 Kehua Street, Guangzhou 510640, China

^d School of Marine Sciences, Sun Yat-sen University, Guangzhou 510006, China

^e Wuhan Institute of Geology and Mineral Resources, China Geological Survey, Wuhan 434205, China

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ABSTRACT

The Central Tianshan Terrane (CTT) in the Eastern Tianshan (Xinjiang, NW China) is an important Pb–Zn metallogenic belt and played a pivotal role in crustal evolution and collisional tectonics of the southern Central Asian Orogenic Belt. The Shaquanzi gabbro and Hongyuan granodiorite are located in the northern margin of the CTT and associated with Pb–Zn mineralization. Zircon U–Pb dating yielded weighted mean ages of 307.2 ± 1.5 Ma and 301.2 ± 1.5 Ma for the Shaquanzi gabbro and the Hongyuan granodiorite, respectively. These rocks are medium-K calc-alkaline series and enriched in large ion lithophile elements (LILEs; e.g., K, Rb, Ba) and depleted in high field strength elements (HFSEs; e.g., Nb, Ta, Ti), displaying typical arc affinities. The Shaquanzi gabbro shows low Nb/Ta (11.0–14.2), a high $Mg^\#$ range (56–59), positive zircon $\varepsilon_{Hf}(t)$ (+3.30 – +7.26) and whole rock $\varepsilon_{Nd}(t)$ (+0.70 – +1.38) values, and low I_{Sr} ratios (0.704858–0.705137), which indicate that the protolith was probably derived from the sub-continental lithospheric mantle that had been metasomatized by subduction-related fluids. The Hongyuan granodiorite contains hornblende but lack of Al-rich minerals and has low I_{Sr} ratios (0.704769–0.706211 < 0.707), suggesting an I-type origin. Moreover, the Hongyuan granodiorite has positive $\varepsilon_{Hf}(t)$ (+1.12 – +5.57) and $\varepsilon_{Nd}(t)$ (+0.38 – +1.86) values, with high $Mg^\#$ (52), variable Nb/Ta ratios (12.6–12.9), low contents of Ni, Cr and Co and Pb isotopes ($^{206}Pb/^{204}Pb = 17.461\text{--}18.299$, $^{207}Pb/^{204}Pb = 15.541\text{--}15.581$, $^{208}Pb/^{204}Pb = 37.456\text{--}38.129$), suggesting the Hongyuan granodiorite was generated by partial melting of juvenile crust sources mixed with some mantle-derived materials. Combined published works with our new geochronological, geological, geochemical and isotopic data, we propose that the CTT may have evolved from a continental arc to a syn-collisional setting during the period of ca. 307–301 Ma. The continuing southward subduction of the Junggar oceanic slab beneath the CTT in the Late Carboniferous resulted in extensive arc-related volcanic rocks emplacement that had indirect links to the Pb–Zn mineralization (e.g., reworked/upgraded).

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1. Introduction

Located between the European and Siberia Cratons to the north and the Tarim and North China cratons to the south (Fig. 1A), the Central Asian Orogenic Belt (CAOB) has experienced a long-lived evolution of

multiple accretion of continents, microcontinents, arc systems and accretionary complexes in the Paleo-Asian Ocean (Jahn et al., 2000; Sengör et al., 1993; Sengör and Natal'in, 1996; Windley et al., 2007; Zhang et al., 2016a, 2016b, 2016c, 2017; Xiao et al., 2012, 2015).

The Junggar Ocean, situated between the Junggar terrane to the north and the Central Tianshan Terrane (CTT) and Yili block to the south (Fig. 1B), represents a major southern segment of the Paleo-Asian Ocean, making its subduction and closure crucial to the understanding of the accretionary and collisional processes of the southern

* Corresponding author at: Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China.
E-mail address: huayongchen@gig.ac.cn (H.-Y. Chen).

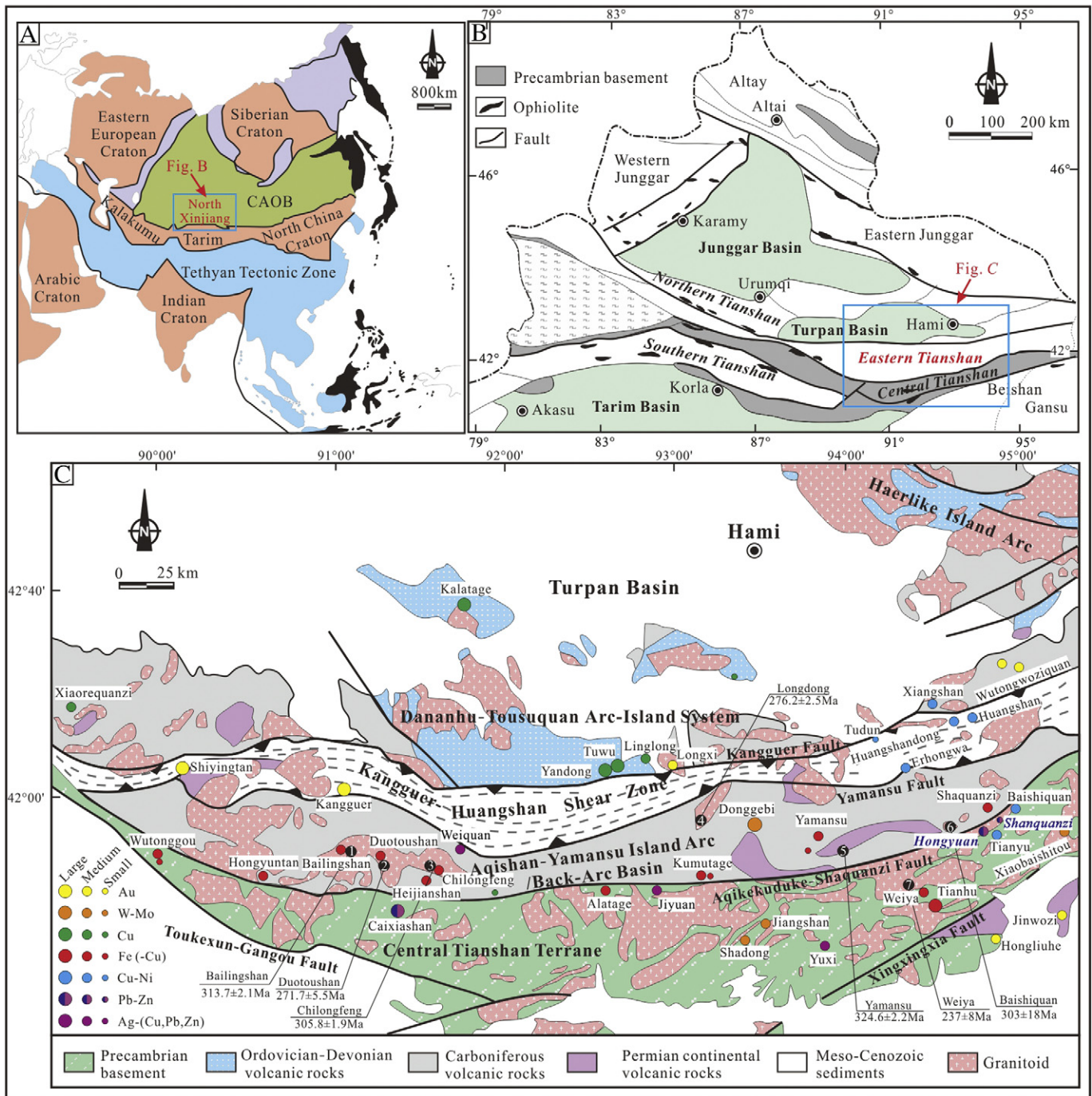


Fig. 1. (A) Simplified geological map of the Central Asian Orogenic Belt (CAOB; modified after Sengör and Natal'in, 1996), (B) Sketch map showing the tectonic framework of North Xinjiang (after Xiao et al., 2008; Y.J. Chen et al., 2012) and (C) Geologic map of the Eastern Tianshan Orogenic Belt, showing the distribution of major ore deposits (modified after Deng et al., 2014; Wang et al., 2006). Chronological data from: W.F. Zhang et al. (2016), Zhang et al. (2005), Zhang et al. (2015b), Zhao et al. (2017) and Zhou et al. (2010).

CAOB (Windley et al., 1990; Xiao et al., 2012, 2015). However, the timing of its closure is still hotly debated, with suggestions ranging from the Early Carboniferous (Gao et al., 1998), through the Late Carboniferous–Early Permian (Charvet et al., 2007; Chen et al., 2011; Zhang et al., 2015a, 2015, 2016a), to the Permian–Triassic (W.J. Xiao et al., 2009), leading to various competing models proposed for the Paleozoic evolution of the Eastern Tianshan (an important component of the southern CAOB).

The oldest basement rocks in the Eastern Tianshan occur in the CTT, which is one of the most important Pb–Zn metallogenic provinces in northwestern China, including the giant Caixiashan, Hongyuan, Shaquanzi, Hongxingshan, Jiyuan and Yuxi Pb–Zn (–Ag) deposits

(Fig. 1C). Previous studies indicated that the Pb–Zn ore-hosting Precambrian basement had undergone various degrees of reworking by the Carboniferous magmatism (Cao et al., 2013; Gao et al., 2007; H.Y. Chen et al., 2012; Lu et al., 2017; Peng et al., 2006, 2007; Q.H. Xiao et al., 2009; Zhong et al., 2008; Zhou et al., 1999). However, the geodynamic setting and genesis of these Pb–Zn deposits and their associated igneous rocks remains unclear.

Representative intrusive rocks were collected from the Shaquanzi and Hongyuan Pb–Zn deposits (located in the CTT), including gabbro and granodiorite, which reworked the Shaquanzi and Hongyuan Pb–Zn orebodies, respectively (Lu et al., 2017; Zhong et al., 2008). In this study, we report whole-rock geochemical and zircon U–Pb and Lu–Hf

isotope data from Shaquanzi and Hongyuan. We then discuss the petrogenesis of these intrusive rocks and the Late Carboniferous tectonic implications for the Eastern Tianshan.

2. Geology background

2.1. Regional geology

The Chinese Tianshan Orogen is bordered between the Tarim Craton to the south and the Junggar terranes to the north (Fig. 1A, B) (Allen et al., 1993; Charvet et al., 2007; Gao et al., 1998; Windley et al., 1990; Xiao et al., 2012), which can be geographically divided into the western and eastern segments roughly along 86°E longitude (Charvet et al., 2007; Gao et al., 2009; Zhang et al., 2016a, 2017; Xiao et al., 2004). This study mainly focuses on the Eastern Tianshan, which can be tectonically subdivided into the North Tianshan (NTS), Central Tianshan Terrane (CTT) and South Tianshan (STS), separated from each other by major strike-slip faults (Charvet et al., 2007; Zhang et al., 2016a, 2017; Xiao et al., 2004). The tectonic framework of the Eastern Tianshan was primarily influenced by the development of two sub-oceans of the Pale-Asian Ocean, namely (a) the Junggar Ocean between the CTT and Junggar terranes and (b) the South Tianshan Ocean between the CTT and Tarim Craton (Ma et al., 1997; Windley et al., 1990; Zhang et al., 2016a, 2017; Xiao et al., 2004).

The NTS accretionary belt is composed dominantly of a series of Devonian–Carboniferous island arcs (Fig. 1B, e.g., Bogda, Dananhu, Yamansu) and Carboniferous–Jurassic imbricated strata, genetically controlled by the subduction and closure of the Junggar Ocean (e.g., Han et al., 2010; Ma et al., 1997). A primarily southward subduction of the Junggar Ocean beneath the Chinese Tianshan has been substantiated by not only detailed kinematic investigations in the region (Charvet et al., 2007; Laurent-Charvet et al., 2002; Shu et al., 1999) but also the findings of Late Ordovician (ca. 450 Ma) thickened lower crust-derived adakitic rocks (Zhang et al., 2016b), high-pressure basic-intermediate granulites (Shu et al., 2004) and Early Paleozoic to Late Carboniferous subduction-related magmatic rocks (e.g., Ma et al., 2014; Shi et al., 2014; Zhang et al., 2015b, 2016a) along the northern margin of the CTT.

As the most essential portion of the Chinese Tianshan, the CTT comprises mainly of Precambrian basement with minor Paleozoic volcanosedimentary formations (Hu et al., 2000; Lei et al., 2011; Li et al., 2007; Liu et al., 2004; Shu et al., 2004; Xiao et al., 2004) and a number of granitoids (Fig. 1C). The basement is consisted of the Mesoproterozoic Xingxingxia and Kawabulag Groups and the Neoproterozoic Tianhu Group, and has been metamorphosed to upper greenschist- to amphibolite-facies (Gao et al., 1993; Luo, 1989). The Xingxingxia Group represents the oldest rocks in the CTT, and comprises mainly amphibolite- to granulite-facies marble, schist, gneiss and migmatite (He et al., 2014; Hu et al., 1986, 2000). The Late Mesoproterozoic Kawabulake Group is composed of meta-carbonatite, schist and granitic gneiss (He et al., 2014; Xiu et al., 2002). The Tianhu Group distributed between the Jianshanzi and Hongliuhe areas comprises mainly schist, quartzite, marble and minor amphibolite, with protoliths of terrigenous clastics intercalated with minor mafic volcanics (Liu et al., 2004).

The STS accretionary belt, characterized by widespread ophiolitic mélanges and a well-studied Carboniferous high-pressure/low-temperature (HP/LT) metamorphic belt (Gao et al., 1998; Gao and Klemd, 2003; Long et al., 2006; Wang et al., 2011), is believed to have been formed by the closure of the South Tianshan Ocean between the CTT and the northern Tarim Craton (Gao and Klemd, 2003; Huang et al., 2015; Wang et al., 2011).

2.2. Deposit geology

2.2.1. Shaquanzi Pb–Zn deposit

The Shaquanzi Pb–Zn deposit is situated at ~170 km southeast of the city of Hami in Xinjiang, NW China (Fig. 1C), and ~4 km south of the Shaquanzi Fault. The exposed strata are the Kawabulake Group silicified marble, marble, banded carbonaceous marble and minor dolomitic marble. Quaternary sediments, situated southwest of Shaquanzi, are dominated by alluvial gravel, sand and clay.

The gabbro presented in the northern part of the Shaquanzi deposit. In the vicinity of the Shaquanzi Pb–Zn deposit, the contact metamorphism generated some calc–silicate skarn. Mafic and felsic dykes and quartz veins are extensively exposed in the district (Fig. 2).

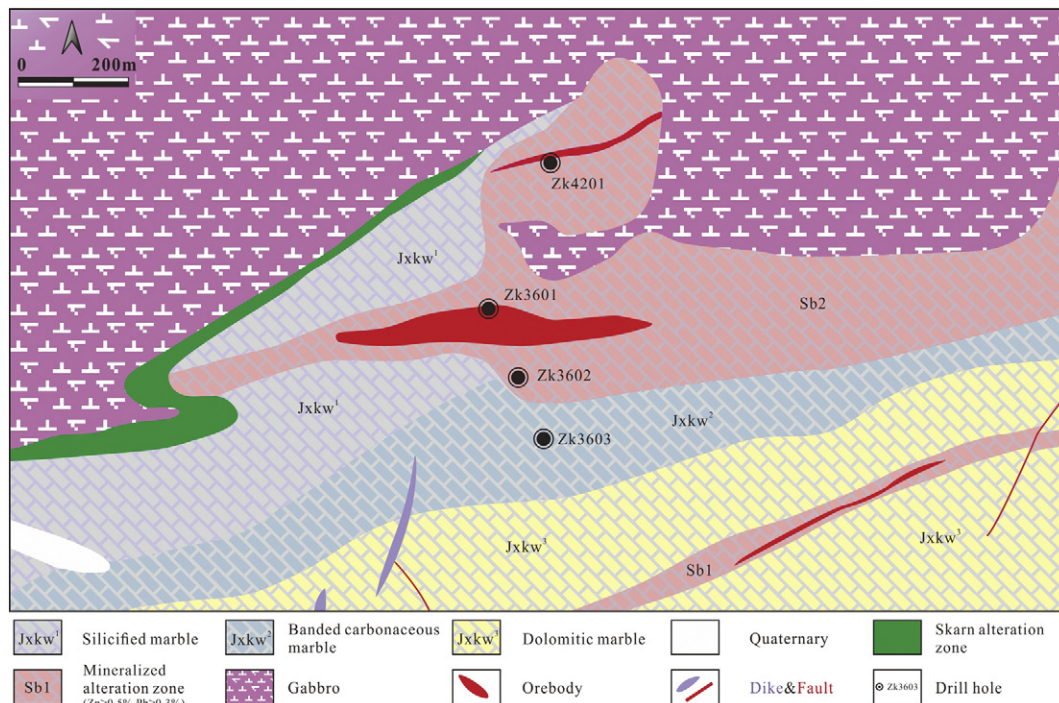


Fig. 2. Deposit geology of the Shaquanzi Pb–Zn deposit (modified after Xinjiang BGMR).

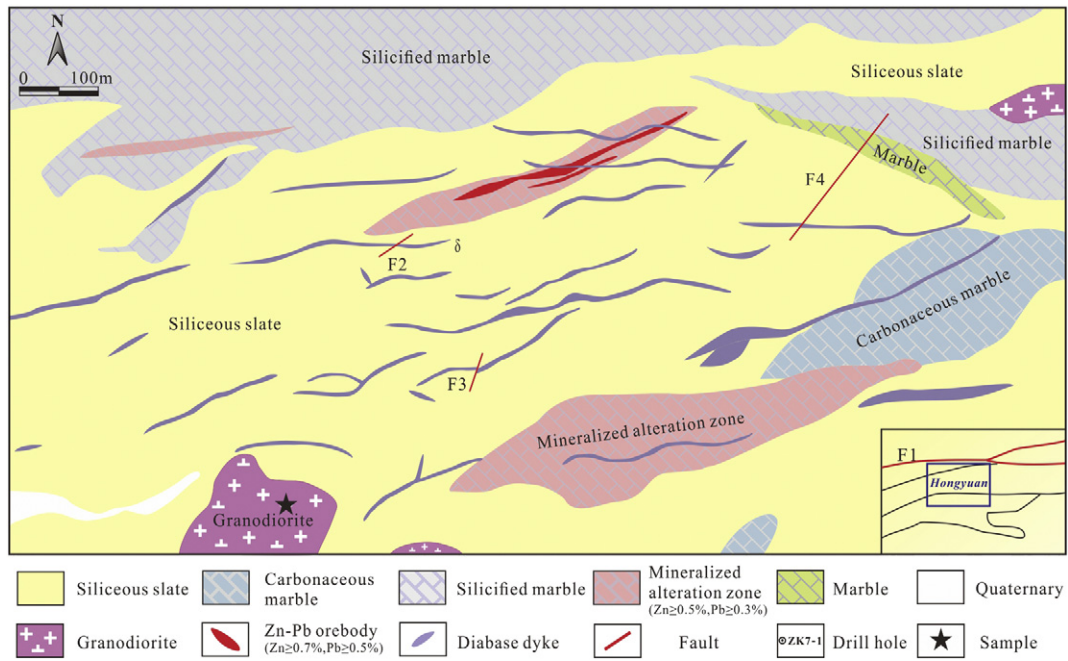


Fig. 3. Deposit geology of the Hongyuan Pb–Zn deposit (modified after Lu et al., 2017).

Nine stratabound orebodies (200–300 m long and 0.7–10.4 m thick) have been delineated at Shaquanzi (Zhong et al., 2008). The major orebodies are hosted by carbonaceous marble and generally have

limonite, tremolite and actinolite alterations. Ore minerals include fine- to medium-grained sphalerite and galena accompanied by abundant pyrite and pyrrhotite.

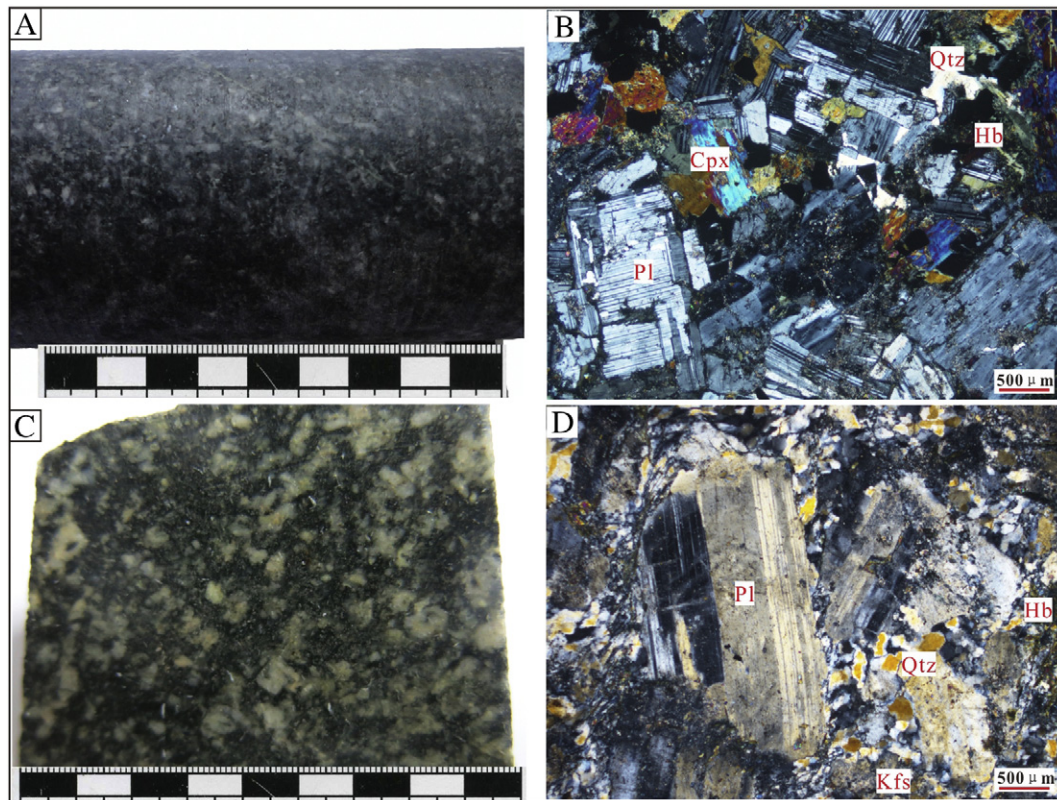


Fig. 4. Hand specimen and thin sections of the Shaquanzi and Hongyuan intrusive rocks. (A–B) Shaquanzi gabbro; (C–D) Hongyuan granodiorite. Abbreviations: Pl = plagioclase; Qtz = quartz; Hb = hornblende, Kfs = K-feldspar; Cpx = clinopyroxene.

2.2.2. Hongyuan Pb–Zn deposit

The Hongyuan Pb–Zn deposit (~5 km southwest of Shaquanzi) (Fig. 1C) is located to the south and tectonically controlled by the Shaquanzi Fault. Outcropping strata at Hongyuan are the Mesoproterozoic Kawabulake Group carbonaceous marble and siliceous slate. Late Paleozoic intrusions (dominantly Carboniferous granodiorite) are mainly distributed in the northern and southern parts of Hongyuan (Fig. 3).

The major Hongyuan orebodies are hosted by siliceous slate and carbonaceous marble, commonly epidote and diopside altered. Thirteen EW-trending stratabound orebodies (ca. 50–500 m long and tens of meters thick) (Fig. 3) were delineated. Major metallic minerals include fine- to medium-grained sphalerite and galena, which are accompanied by abundant pyrite, pyrrhotite and minor chalcopyrite. Alteration types at Hongyuan include mainly silicic, carbonate, diopside, tremolite and chlorite alterations (Lu et al., 2017).

3. Sampling and analytical methods

3.1. Sampling

Following detailed geological sampling, three least altered gabbro samples from Shaquanzi (drill hole Zk4201; Fig. 2) and three granodiorite samples from Hongyuan (Fig. 3) were collected.

The Shaquanzi gabbro (SZ1–30; Fig. 4A, B) and the Hongyuan granodiorite (HY-N; Fig. 4C, D) intruded the Mesoproterozoic Kawabulake Group. The dark-grayish gabbro displays fine- to medium-grained hypidiomorphic texture, and is composed mainly of subhedral tabular plagioclase (40–45 vol%), clinopyroxene (10–20 vol%), irregularly-shaped hornblende (20–25 vol%) and quartz (15–25 vol%). Some plagioclase grains are potassic and argillic altered. The granodiorite is a dark-grayish and medium- to coarse-grained, and contains plagioclase (40–56 vol%), quartz (15–25 vol%), K-feldspar (10–20 vol%), hornblende (3–8 vol%) and biotite (2–5 vol%). Some hornblende grains are slightly chlorite altered.

3.2. Analytical methods

Whole-rock major element analyses were performed at the ALS Chemex Company in Guangzhou (Guangzhou, China), analyzed by X-ray fluorescence spectrometry (XRF) for major elements, with the analysis precision better than $\pm 2\%$. Trace element concentrations were measured at the State Key Laboratory of Ore Deposit Geochemistry, Guiyang Institute of Geochemistry (Guiyang, China), with analytical uncertainties generally $< 5\%$. Zircons were separated from Shaquanzi gabbro (SZ1–30) and Hongyuan granodiorite (HY-N) samples, using standard density and separation magnetic techniques. Then, the selected zircons were conducted for cathodoluminescence (CL) imaging, U–Pb dating and in situ Lu–Hf isotope analyses at the Guangzhou Institute of Geochemistry (Guangzhou, China). Whole-rock Sr–Nd–Pb isotope analysis was performed using a Micromass Isoprobe MC-ICP-MS at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry (Guangzhou, China). Detailed analytical procedures are given in online Appendix A.

4. Results

4.1. Whole-rock major and trace elements

Whole-rock major and trace element compositions of the Shaquanzi and Hongyuan rocks are listed in Table A.1.

The Shaquanzi gabbro samples contain $\text{SiO}_2 = 48.5\text{--}49.5$ wt%, $\text{Al}_2\text{O}_3 = 16.0\text{--}18.3$ wt%, $\text{CaO} = 8.6\text{--}9.1$ wt%, $\text{K}_2\text{O} = 0.9\text{--}1.1$ wt%, $\text{Na}_2\text{O} = 2.7\text{--}2.9$ wt%, with $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios of 2.4–3.1. Their Fe_2O_3 and MgO contents range 9.6–10.4 wt% and 5.2–6.3 wt%, respectively, corresponding to the $\text{Mg}^\#$ values of 56–59. Three gabbro samples fall inside

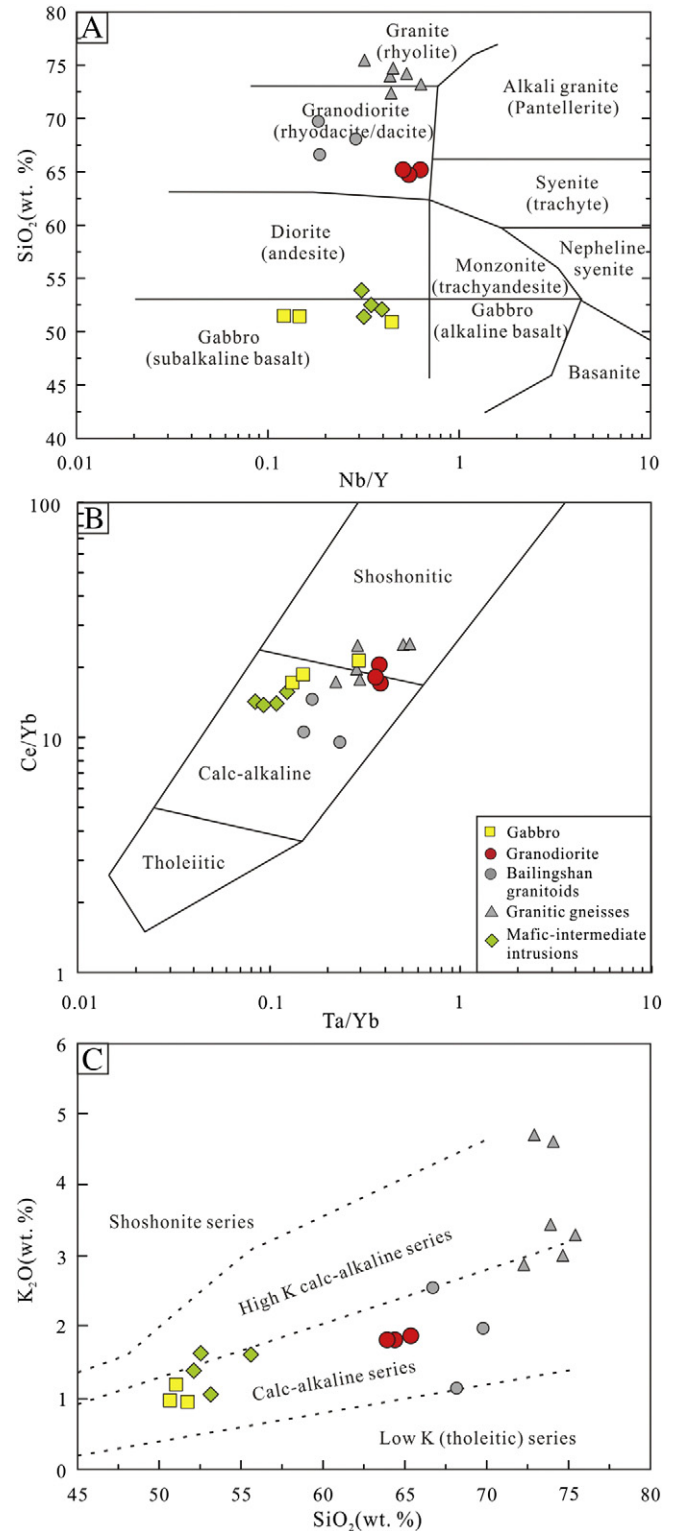


Fig. 5. (A) SiO_2 vs. Nb/Y diagram (modified after Winchester and Floyd, 1977), (B) Ce/Yb vs. Ta/Yb diagram (after Müller et al., 1992) and (C) K_2O vs. SiO_2 diagram (after Peccerillo and Taylor, 1976) for the Shaquanzi and Hongyuan intrusive rocks. Late Carboniferous Bailingshan granitoids, granitic gneisses and mafic-intermediate intrusions data are from W.F. Zhang et al. (2016), Zhang et al., 2015b, 2016a).

the gabbro field in the SiO_2 vs. Nb/Y diagram (Fig. 5A), similar with the Late Carboniferous mafic rocks from the CTT (Zhang et al., 2016a). The gabbro rocks generally show medium-K calc-alkaline

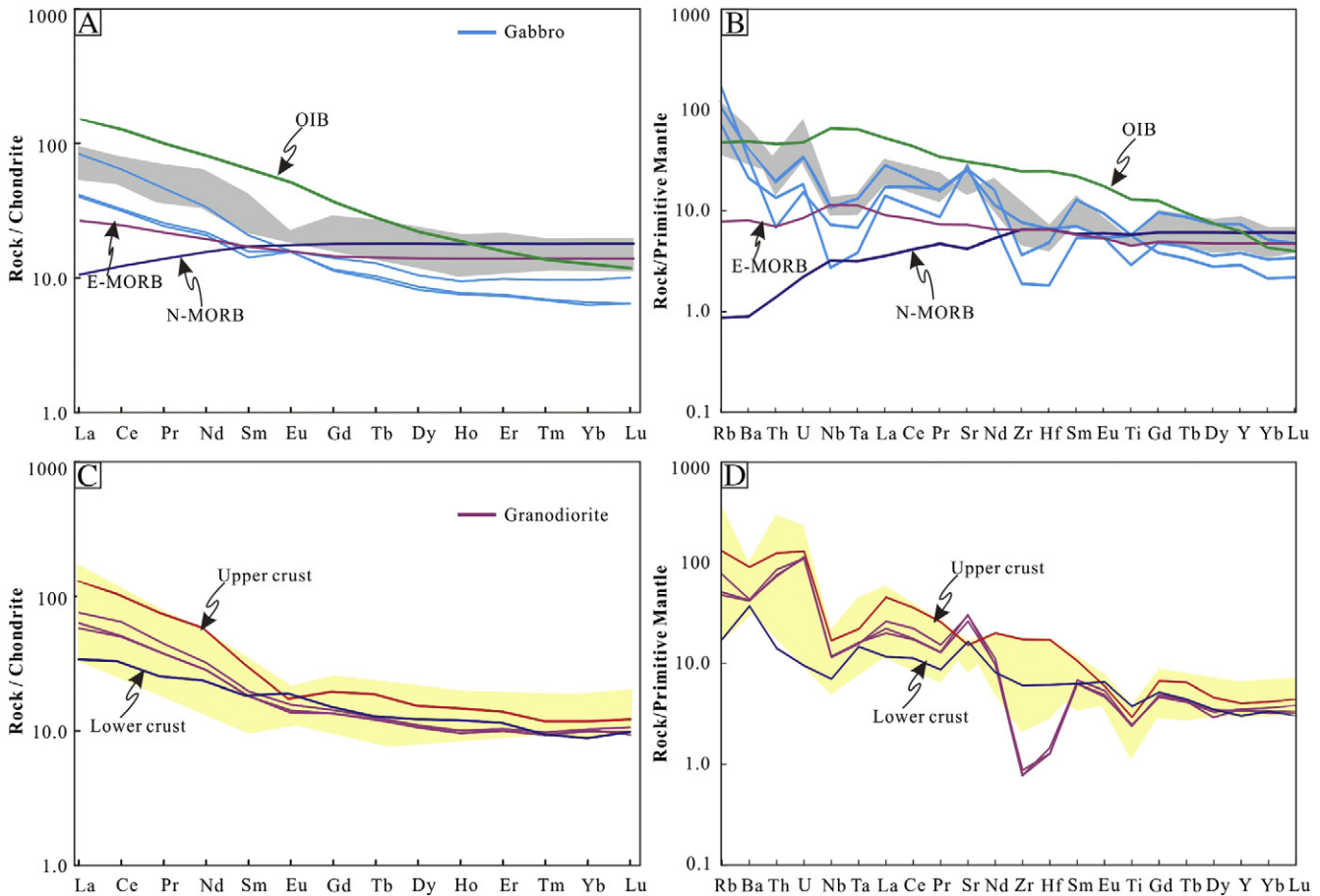


Fig. 6. Chondrite-normalized REE patterns and Primitive mantle-normalized multi-element diagrams for the representative samples. (A–B) Shaquanzi gabbro; (C–D) Hongyuan granodiorite. The gray shaded areas denote the Late Carboniferous CTT mafic-intermediate intrusions (W.F. Zhang et al., 2016) and the yellow shaded areas denote the Late Carboniferous granites from CTT and Bailingshan (W.F. Zhang et al., 2016; Zhang et al., 2015b). Data of the average chondrite, primitive mantle, E-MORB, N-MORB and OIB are from Sun and McDonough (1989). Data of the upper and lower crust are from Rudnick and Gao (2003).

affinities (Fig. 5) and have low total REE contents (52–94 ppm), exhibiting slightly right-inclined REE patterns ($(La/Yb)_N = 6.06–8.61$, $(Tb/Yb)_N = 1.34–1.57$, $\delta Eu = 0.93–1.22$; Fig. 6A). In the primitive-mantle normalized trace element diagram, the gabbro samples show enrichments in large ion lithophile elements (LILEs; e.g., Rb, Ba and Sr) and depletions in high field strength elements (HFSEs; e.g., Nb, Ta and Ti) (Fig. 6B).

The Hongyuan granodiorite samples contain SiO_2 (62.7–63.0 wt%), Al_2O_3 (16.3 wt%) and CaO (4.3–5.1 wt%), lower TiO_2 (0.5 wt%), K_2O (1.7–1.8 wt%) and Na_2O (3.8–3.9 wt%), with Na_2O/K_2O ratios of 2.2. With $Fe_2O_3^T$ (4.8–4.9 wt%) and MgO (2.2–2.3 wt%), the three granodiorite samples have average $Mg^\#$ values of 52, belonging to medium-K calc-alkaline series (Fig. 5). The rocks have total REE contents of 75–91 ppm, and display right-inclined REE patterns ($(La/Yb)_N = 5.62–7.64$, $(Tb/Yb)_N = 1.17–1.27$, $\delta Eu = 0.87–0.93$ (Fig. 6C). In the primitive-mantle normalized trace element diagram, the granodiorite samples show enrichments in large-ion lithophile elements (LILEs; e.g., Rb and Sr) and strong depletions in high field strength elements (HFSEs; e.g., Nb, Ta and Ti) (Fig. 6D).

4.2. Zircon U–Pb ages and Lu–Hf isotopic compositions

Representative CL images, U–Pb ages and $\varepsilon_{Hf}(t)$ values of the analyzed zircons are shown in Fig. A.1. Most zircon grains are euhedral to subhedral, transparent to semi-transparent and light brown or

colorless, with lengths of 50 to 100 μm and aspect ratios between 1:1 and 4:1. Most crystals show well-developed oscillatory zoning in CL images, together with their relatively high Th/U ratios (0.41–1.02; Table A.2), suggesting an igneous origin (Rubatto, 2002), consistent with the HREE enrichment, positive Ce anomalies and negative Eu anomalies (Fig. 7B, D; Table A.3) in zircon REE patterns (Hoskin and Schaltegger, 2003; Rubatto, 2002).

Twenty zircons from the Shaquanzi gabbro (SZ1–30) yielded $^{206}Pb/^{238}U$ ages of 311–302 Ma and a weighted mean age of 307.2 ± 1.5 Ma (1σ ; MSWD = 0.67), which can be used to represent the formation age of the Shaquanzi gabbro (Fig. 7A; Table A.2). Thirty-one analyses were undertaken on zircons from the Hongyuan granodiorite (HY-N). Excluding one old inherited zircon (332 Ma), the remaining 30 zircons yielded $^{206}Pb/^{238}U$ ages of 307–295 Ma and a weighted mean age of 301.2 ± 1.5 Ma (1σ ; MSWD = 0.53) that can be considered as the formation age for the Hongyuan granodiorite (Fig. 7C; Table A.2).

Results of the Lu–Hf isotope analysis are given in Table A.4 and shown in Fig. 8. Twelve zircons from the Shaquanzi gabbro yielded $^{176}Hf/^{177}Hf$ ratios of 0.282683 to 0.282795, corresponding to $\varepsilon_{Hf}(t)$ values of +3.30 to +7.26 and T_{DM2} model ages of 1107–855 Ma (Table A.4). Eleven zircons from the Hongyuan granodiorite yielded initial $^{176}Hf/^{177}Hf$ ratios of 0.282302 to 0.282745, corresponding to $\varepsilon_{Hf}(t)$ values of –10.26 to +5.57 and T_{DM2} model ages of 1965–966 Ma (Table A.4).

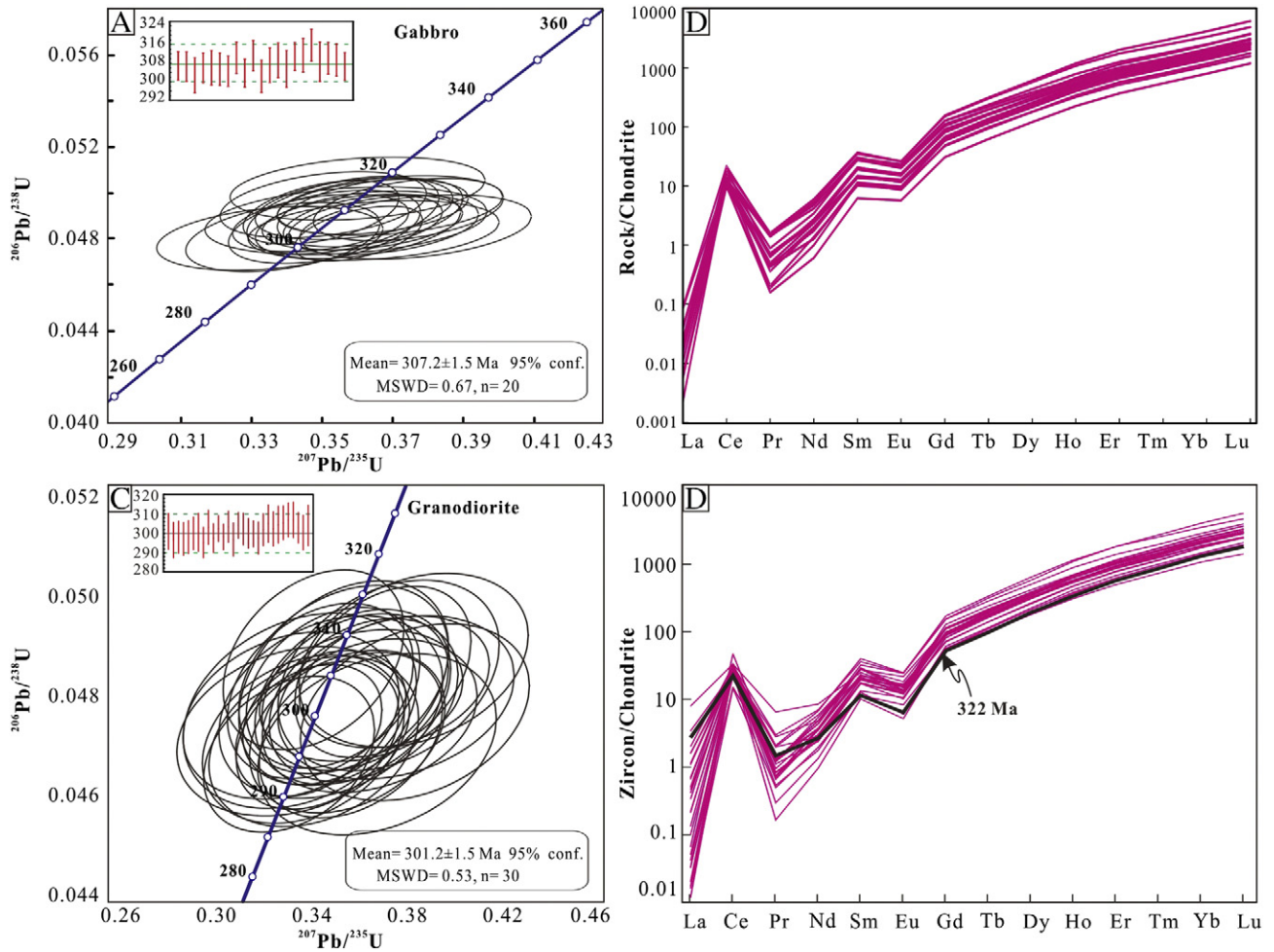


Fig. 7. Zircon U-Pb concordia diagram and weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages and chondrite-normalized REE patterns of zircon grains from the representative samples. (A–B) Shaquanzi gabbro; (C–D) Hongyuan granodiorite. Data of the average chondrite are from Sun and McDonough (1989).

4.3. Whole-rock Sr–Nd–Pb isotopes

Whole-rock Sr, Nd and Pb isotope compositions of the Shaquanzi and Hongyuan rocks are listed in Table A.5 and shown in Fig. 9. Initial

isotopic ratios were calculated back to the crystallization ages of the studied rocks.

The gabbro samples show I_{Sr} ratios of 0.704858–0.705137, $\epsilon_{\text{Nd}}(t)$ values of +0.70 – +1.38 and T_{DM} model ages of 1.22–1.04 Ga. The

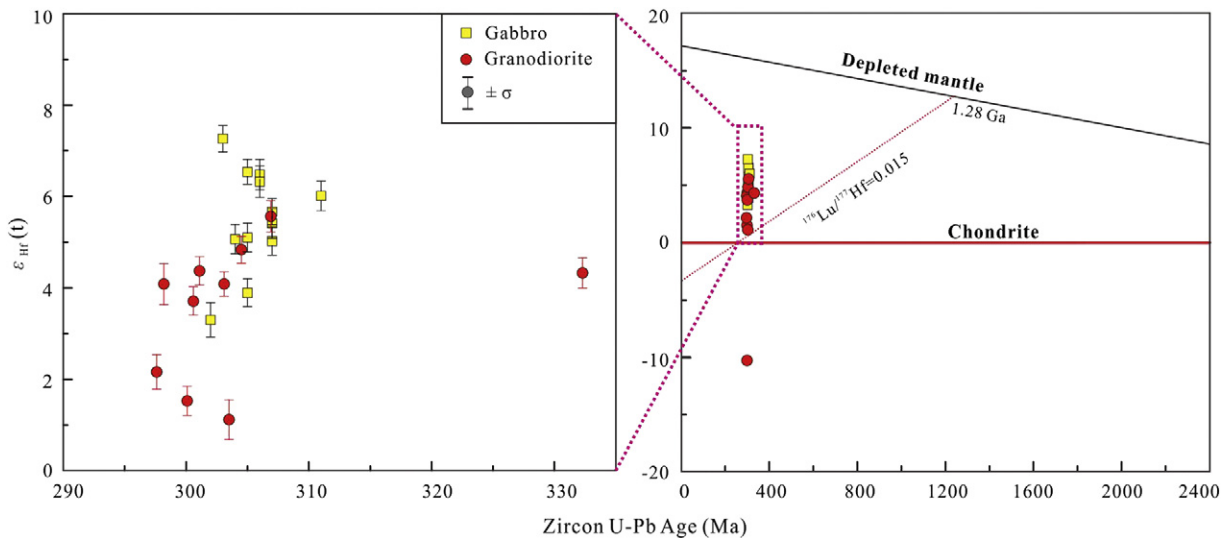


Fig. 8. Zircon Hf isotopes for the Shaquanzi and Hongyuan intrusive rocks.

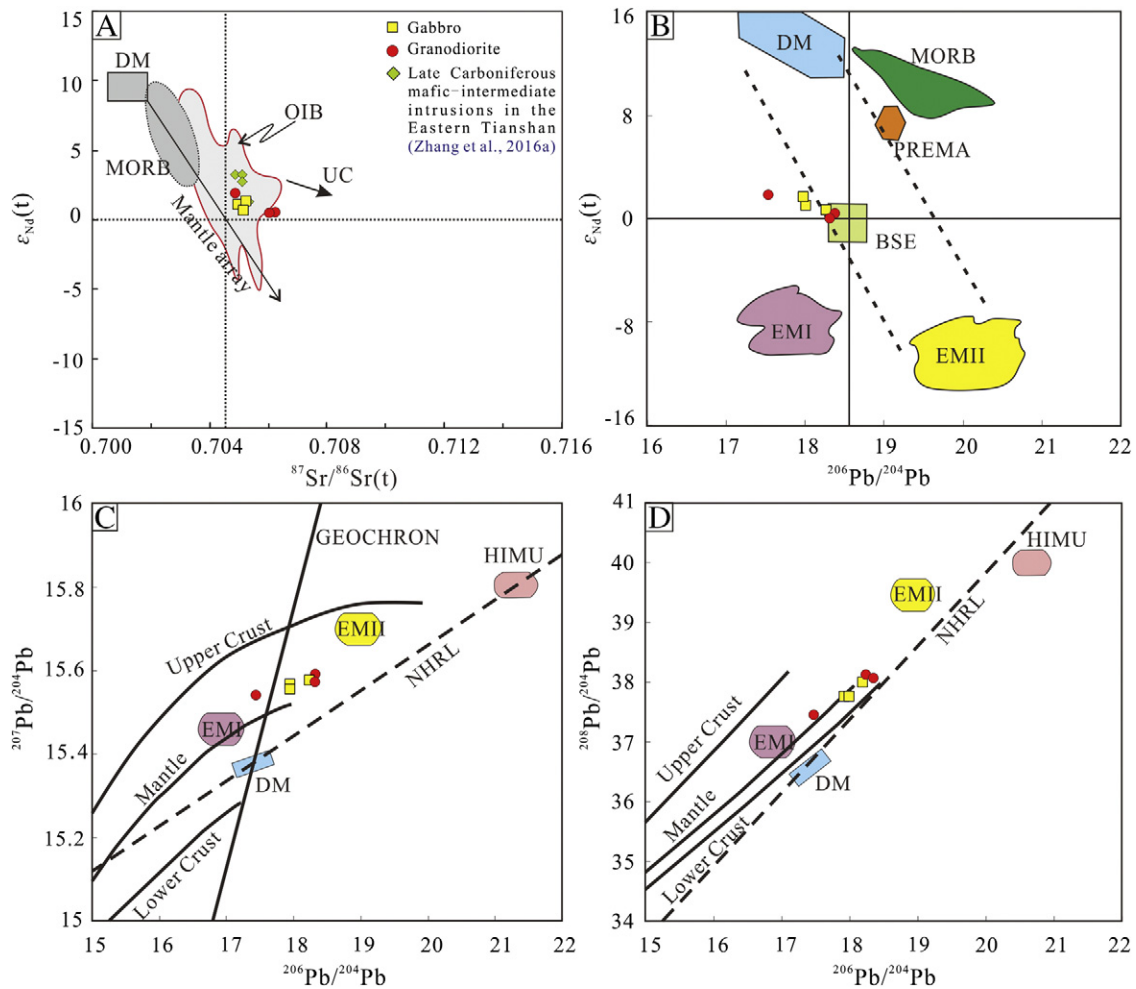


Fig. 9. Radiogenic isotopes for the Shaquanzi and Hongyuan intrusive rocks: (A) $\epsilon_{\text{Nd}}(t)$ vs. $^{87}\text{Sr}/^{86}\text{Sr}(t)$ diagram ($t = 307.2$ Ma for the Shaquanzi gabbro and $t = 301.2$ Ma for the Hongyuan granodiorite), (B) $\epsilon_{\text{Nd}}(t)$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram after Zindler and Hart (1986), (C) $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram and (D) $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram after Li et al. (2001). Data for the Late Carboniferous CTT mafic-intermediate rocks are from Zhang et al. (2016a). NHRL = Northern Hemisphere reference line (Hart, 1984); BSE = bulk silicate earth, UC = upper crust, DM = depleted mantle, MORB = mid-oceanic ridge basalts, EMI = enriched mantle with low $^{87}\text{Sr}/^{86}\text{Sr}$, EM II = enriched mantle with high $^{87}\text{Sr}/^{86}\text{Sr}$, HIMU = high U/Pb mantle component (Zindler and Hart, 1986).

granodiorite samples have I_{Sr} ratios of 0.704769–0.706211, $\epsilon_{\text{Nd}}(t)$ values of +0.38 – +1.86 and T_{DM} ages of 1.11–0.97 Ga. The initial $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of these samples are 17.461–18.299, 15.541–15.581 and 37.456–38.129, respectively

(Table A.5). The Pb isotope compositions of these samples are generally uniform and plot between the mantle and the upper crustal growth curves, or close to the mantle line in the Pb isotope diagrams (Fig. 9C, D; Li et al., 2001).

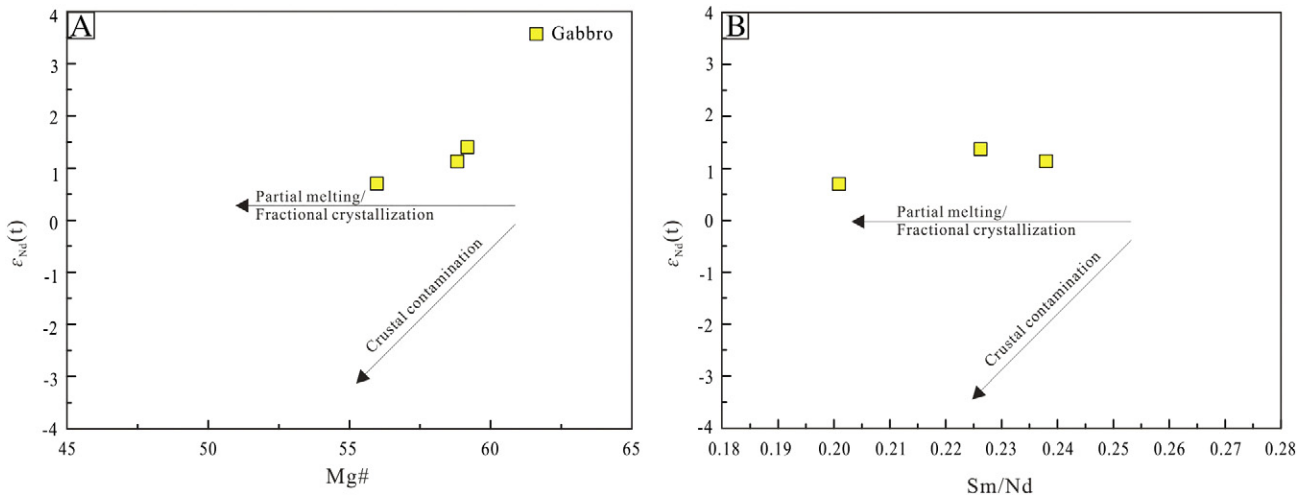


Fig. 10. (A) $\epsilon_{\text{Nd}}(t)$ vs. $\text{Mg}^\#$ and (B) $\epsilon_{\text{Nd}}(t)$ vs. Sm/Nd diagrams for the Shaquanzi gabbro.

5. Discussion

5.1. Petrogenesis and magma sources

Considering that rocks from the Shaquanzi and Hongyuan Pb–Zn deposits are partially altered, we focus largely on the immobile elements (e.g., Th, REEs and HFSEs) and transition elements (e.g., Sc, V, Ni and Cu) (Chen et al., 2013; Condie, 2005; Said and Kerrich, 2009; Winchester and Floyd, 1977) in our petrogenetic discussion.

5.1.1. Shaquanzi gabbro

The Shaquanzi gabbro samples contain MgO of 5.2–6.3 wt%, with $Mg^\#$ values of 56–59, Ni of 7–24 ppm and Cr of 23–29 ppm, which are much lower than those of typical mantle-derived primary melts ($Mg^\# = 73–81$, Ni > 400 ppm and Cr > 1000 ppm; Wilson, 1989), indicating the presence of crystal fractionation. Fractionation of clinopyroxene and olivine is evidenced by the positive correlations between $Mg^\#$ values and Cr and Ni contents (Table A.1). Plagioclase fractionation is limited, as suggested by the lack of negative Sr and Eu anomalies (Fig. 6B). The distinct negative Nb, Ta and Ti anomalies of the gabbro rocks (Fig. 6B) may have been inherited from their sources that had been affected by crustal contamination or metasomatized by subduction-related fluids or Ti-minerals (such as rutile and spinel) fractionation (e.g., Hawkesworth et al., 1993; Lana et al., 2004; Saunders and Tamey, 1984).

Crustal contamination is common to the basaltic magmas that ascend through thick continental crust (Castillo et al., 1999; Watson, 1982). As shown in Fig. 6B, the Shaquanzi gabbro samples are enriched in LILEs (e.g., Rb, Ba, Pb) and depleted in HFSEs (e.g., Nb, Ta, Ti), which can be caused either by subduction or crustal contamination (Rudnick and Gao, 2003; Shinjo et al., 1999; Wang et al., 2013). Nevertheless, rocks formed by crustal contamination generally do not show distinct negative Zr–Hf anomalies because of the abundances of Zr and Hf in the crust (Qian et al., 2014). Because the Th/Nb ratio of basaltic magmas is independent of olivine, clinopyroxene and feldspar fractionation (Aldanmaz et al., 2000), mantle-derived mafic rocks tend to show diagnostic Th/Nb ratios, which can differentiate the relative input of crustal materials vs. subduction-related fluids (Li et al., 2013; Pearce, 2008). However, the absence of correlations between $Mg^\#$ and $\varepsilon_{Nd}(t)$ (Fig. 10A), or between $\varepsilon_{Nd}(t)$ and Sm/Nd (Fig. 10B), suggesting crustal contamination was not significant for the Shaquanzi gabbro samples. As shown in Fig. 11A, the gabbro samples have Th/Nb ratio of 0.23–1.00, plotting in the continental arc field, but far from the average upper continental crust (UCC). In addition, the gabbro samples have relatively high Ti/Zr (42.2–335.5) and Ti/Y (207.4–537.7) ratios, much higher than those (Ti/Zr < 30, Ti/Y < 200) of the typical crustal rocks (Wedepohl, 1995), precluding significant crustal contamination. This inference is further supported by the lack of correlations between the Sr–Nd isotopes and MgO (or SiO₂, Th/Nb, Ce/Nb) (Pearce and Cann, 1973; Sun and McDonough, 1989; Wood, 1980). As a strongly incompatible element, Th is enriched in sediments and the middle/upper crust (average middle and upper crust Th contents are ~6.5 and 10.5 ppm, respectively; Rudnick and Gao, 2003). However, thorium content is relatively low in the gabbro (average = 1.55 ppm), precluding significant involvement of crustal materials in the genesis of the gabbro samples.

Due to their similar crystal/melt partition coefficients, Nb and U are not significantly fractionated during crystallization (Hofmann, 1988; Sun and McDonough, 1989), and thus the Nb/U ratios can be used to identify mantle sources, e.g., oceanic basalts (Nb/U = ~50) (McDonough and Sun, 1995), continental crust (Nb/U = ~9) (Rudnick and Fountain, 1995) and arc volcanics (Nb/U = 0.3–9.0) (Chung et al., 2001). In the Nb vs. Nb/U diagram, three gabbro samples (Nb/U = 3.2–6.3) fall inside the arc volcanic field (Fig. 11B; Chung et al., 2001). In addition, the gabbro samples show selective enrichment of LILEs and LREEs and positive Sr anomalies in the primitive mantle-

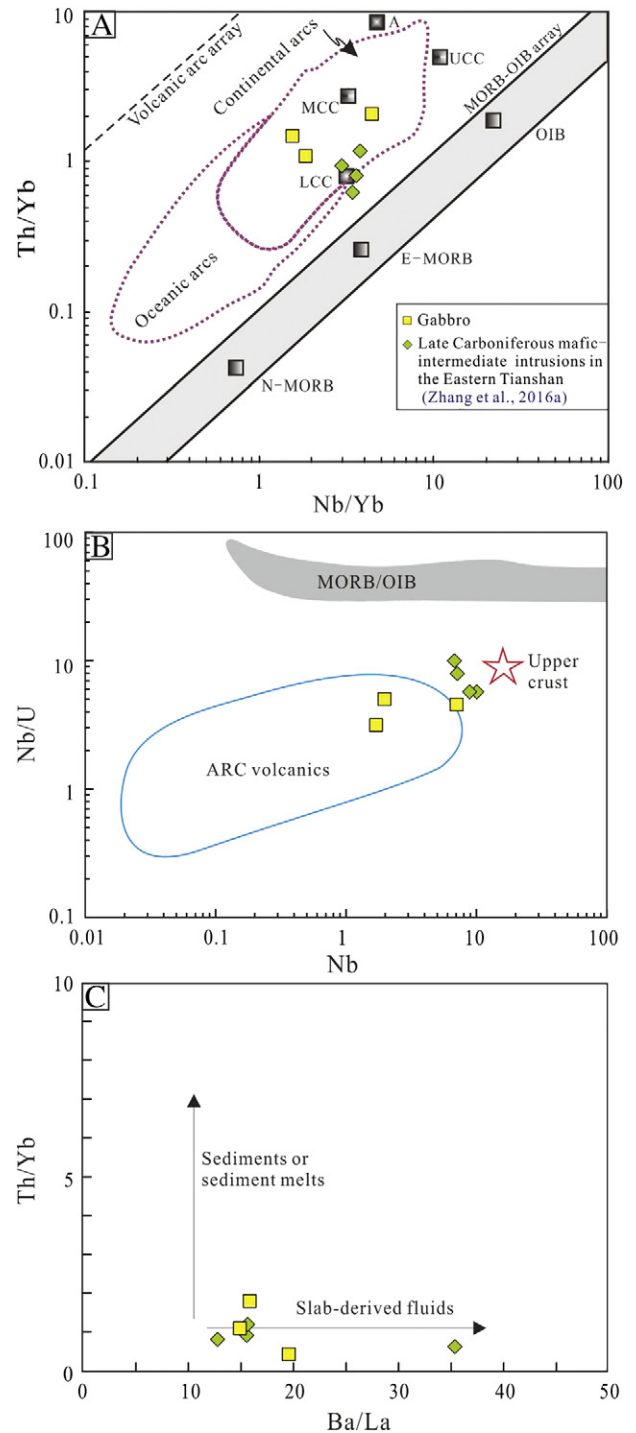


Fig. 11. (A) Th/Yb vs. Nb/Yb (Li et al., 2013; Pearce, 2008), (B) Nb/U vs. Nb (Chung et al., 2001) and (C) Th/Yb vs. Ba/La (Woodhead et al., 2001) diagrams for the CTI mafic-intermediate samples (Zhang et al., 2016a). Trace elements are plotted in ppm. Data source: MORB/OIB field are from McDonough and Sun (1995); the arc volcanic field is from Chung et al. (2001); Archean (A) crust is from Rudnick and Fountain (1995); LCC, MCC and UCC are from Rudnick and Gao (2003).

normalized multi-element diagram (Fig. 6B), which suggests that their magma sources may have been metasomatized before the partial melting (Wang et al., 2013). Hydrous melts and slab-derived fluids are generally considered to be the two major metasomatic sources in subduction zones. Hydrous melts are capable to transport both water-soluble and water-insoluble materials, whereas slab-derived fluids are generally more capable to transport water-soluble materials (Zheng,

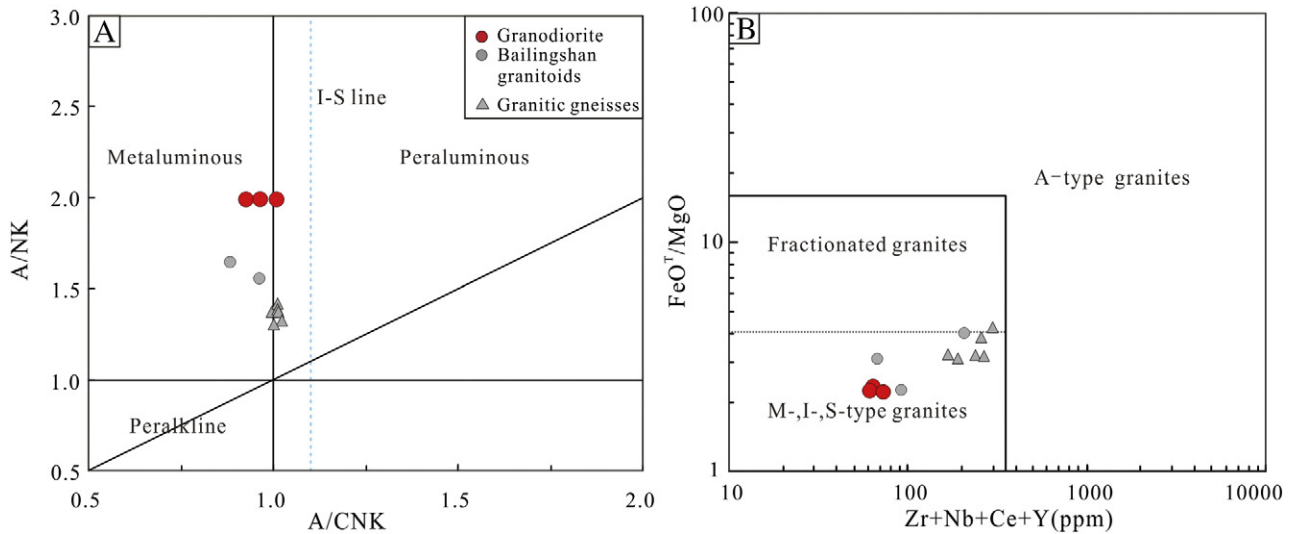


Fig. 12. (A) A/NK vs. A/CNK diagram (Maniar and Piccoli, 1989) and (B) FeO^T/MgO vs. (Zr + Nb + Ce + Y) diagram (Whalen et al., 1987). Data of the Late Carboniferous granites from CTT and Bailingshan are from Zhang et al. (2015b) and W.F. Zhang et al. (2016). A/CNK = molar Al₂O₃ / (Na₂O + K₂O + CaO), A/NK = molar Al₂O₃ / (Na₂O + K₂O).

2012). In subduction zones, Ba/La fractionation can only be reasonably achieved by element mobility in hydrous fluids, while Th and LREEs are less mobile in slab-derived fluids but more mobile in melts (cf. HREEs and LILEs) (Woodhead et al., 2001). Therefore, element ratios such as Ba/La and Th/HREE are useful tracers of sediment inputs or fluid contributions (Woodhead et al., 2001). Our gabbro samples are characterized by variable Ba/La but uniform Th/Yb (Fig. 11C), indicating that the mantle sources may have been previously enriched by slab-derived fluids.

Geochemical signatures of the Shaquanzi gabbro, e.g., low TiO₂ (0.6–1.2 wt%) and enriched Sr–Nd isotopes argue against an asthenospheric mantle source, which generally produce magmatic rocks with high TiO₂ (average TiO₂ in OIB: 2.86 wt%) and depleted Sr–Nd isotopes (Han et al., 2015; Lightfoot et al., 1993; Wu et al., 2014). Thus, we suggest that the gabbro was probably derived from the sub-continental lithospheric mantle (SCLM) metasomatized by subduction-related fluids.

5.1.2. Hongyuan granodiorite

According to different magma sources, granites are genetically divided into M-, I-, S- and A-types (Chappell, 1999; Chappell and White, 1974; Frost et al., 2001). The Hongyuan granodiorite samples belong to medium-K calc-alkaline series (Fig. 5), which is geochemically comparable to the Late Carboniferous alkali-rich granitoids in the Eastern Tianshan (W.F. Zhang et al., 2016; Zhang et al., 2015b). The Hongyuan granodiorite is metaluminous (A/CNK = 0.93 to 1.01) (Fig. 12A; Table A.1), and can be classified as I-type according to Chappell and White (1974). In the (Zr + Nb + Ce + Y) vs. FeO^T/MgO diagram (Fig. 12B), the Hongyuan granodiorite and most Early Permian CTT granitoids fall in the M-, I-, S-type granites field (Chappell and White, 1992). Moreover, S-type granites contain Al-rich biotite and other Al-rich minerals, whereas I-type granites contain mainly hornblende; S-type granites commonly contain ilmenite rather than magnetite, whereas I-type granites contain mainly magnetite, although ilmenite-bearing varieties are also present (Chappell, 1999). Petrographic analysis shows that the Hongyuan granodiorite contains hornblende (Fig. 4D), but lack cordierite, garnet, monazite or ilmenite, suggesting that the samples are most likely I-type. Furthermore, the relatively low *I*_{Sr} ratios of the Hongyuan granodiorite (0.704769–0.706211 < 0.707) also suggest an I-type origin (Chappell and White, 2001; Han and Ma, 2003).

Calc-alkaline I-type granitoids can be generated via (1) partial melting of mafic to intermediate (meta-) igneous rocks without sediment involvement (Chappell and White, 2001) or by (2) mixing of juvenile crustal-derived and mantle-derived magmas (Kemp et al., 2007). The Hongyuan granodiorite samples have Nb/Ta ratios of 12.6–12.9 and low contents of Ni, Cr and Co, indicating a crustal source (Green, 1995). Recent studies indicate that Hf isotopic compositions in zircons are useful in determining possible magma sources (e.g., Kemp et al., 2007; Woodhead et al., 2001; Wu et al., 2006). The Hongyuan granodiorite samples yielded $\epsilon_{\text{Hf}}(t)$ values ranging from –10.26 to +5.57 (average of 1.34; Table A.4), suggesting that the magmas may have derived from a more juvenile source with contributions of older crustal sources (Kemp et al., 2007). In addition, the positive $\epsilon_{\text{Nd}}(t)$ (+0.38 – +1.86) values (Table A.5) of the Hongyuan granodiorite also show juvenile source characteristics. Meanwhile, the Hongyuan granodiorite samples have relatively high Mg[#] (52), implying the involvement of mantle-derived magmas. The initial ²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, and ²⁰⁸Pb/²⁰⁴Pb ratios of the Hongyuan granodiorite samples are 17.461–18.299, 15.541–15.581 and 37.456–38.129, respectively (Table A.5), plotting between the upper crust and the mantle, generally interpreted as a mixing between a fairly homogenized mantle- and upper crust reservoir (Fig. 9C, D). In conclusion, mingling of juvenile crust-derived magmas and mantle-derived magmas can account for the formation of the Hongyuan granodiorite.

5.2. Tectonic and metallogenic implications

5.2.1. Tectonic implications for the Latest Carboniferous Eastern Tianshan

Ophiolites in the northwestern Tianshan (Bayingou: ca. 325 Ma) (Dong et al., 2006; Xu et al., 2006) and West Junggar (Dabalar and Dalabuter: 531–332 Ma) (Jian et al., 2005) have been interpreted to represent remnants of the Junggar Ocean, which was a southern branch of the Paleo-Asian Ocean. The presence of ca. 325–320 Ma arc-related granitic gneiss (Zhang et al., 2015b) and ca. 312 Ma gabbros (Tang et al., 2012) in the northern margin of the CTT and ca. 317–307 Ma I-type Bailingshan granitoids (W.F. Zhang et al., 2016), 317–306 Ma Heijianshan-Chilongfeng intermediate–felsic rocks (Zhao et al., 2017) in the Aqishan-Yamansu Belt could be attributed to the south-dipping subduction of the Junggar oceanic plate. The Late Carboniferous (ca. 307 Ma) Shaquanzi gabbro is calc-alkaline and enriched in LILEs (e.g., K, Rb, Ba) and depleted in HFSEs (e.g., Nb, Ta, Ti) (Fig. 6), displaying

typical subduction-related arc geochemical signatures and mostly plotting into the arc-related fields in the Hf/3–Th–Ta (Wood, 1980), Zr vs. TiO₂ (Pearce, 1982), and Zr vs. Ti (Pearce, 1996) discrimination diagrams (Fig. 13). These features may indicate a Late Carboniferous continental arc system along the northern margin of the CTT, formed by the southward subduction of the Junggar oceanic plate.

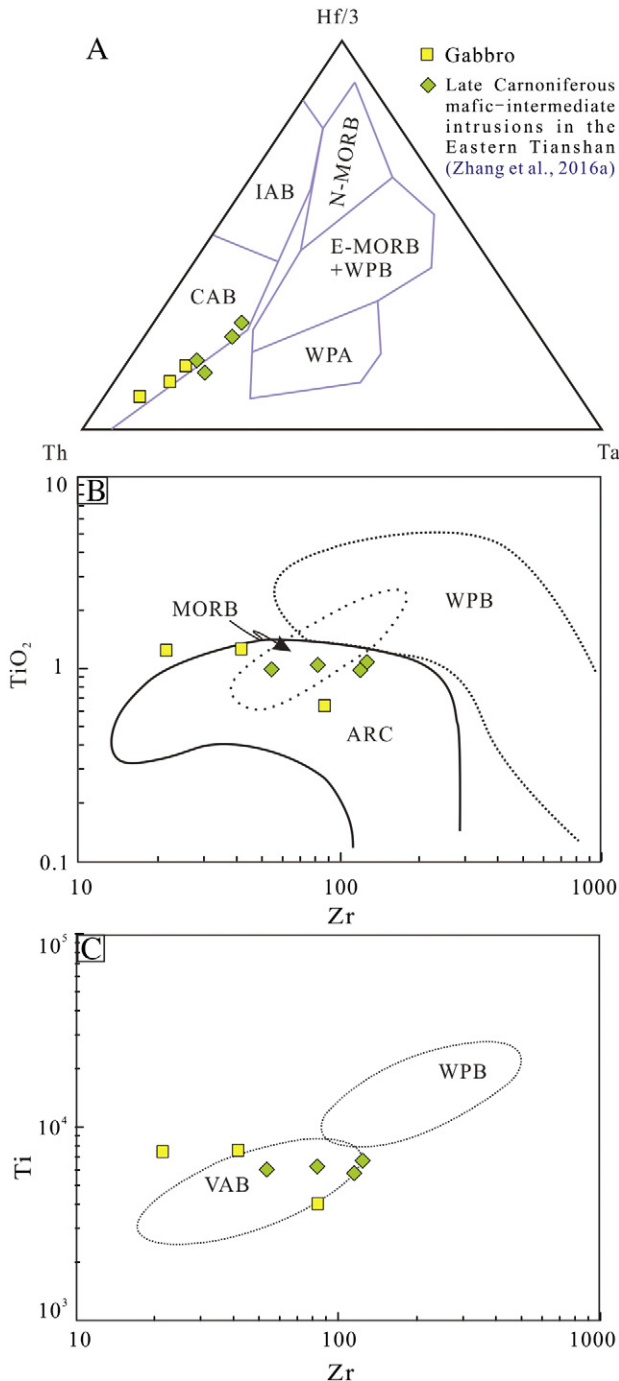


Fig. 13. Tectonic discrimination diagrams for the Shaquanzi gabbro. (A) Hf/3–Th–Ta diagram (Wood, 1980), (B) TiO₂ vs. Zr diagram (Pearce, 1982) and (C) Ti vs. Zr diagram (Pearce, 1996). Data for the Late Carboniferous CTT mafic-intermediate rocks are from Zhang et al. (2016a). CAB = continental arc calc-alkaline basalt, E-MORB = enriched mid-ocean ridge basalt, IAB = island arc calc-alkaline basalt, N-MORB = normal MORB, OIB = ocean island basalt, VAB = volcanic arc basalt, WPA = within plate alkaline basalt, WPB = within plate basalt, WPT = within plate tholeiites.

The Latest Carboniferous Hongyuan granodiorite (ca. 301 Ma), characterized by positive $\epsilon_{\text{Nd}}(t)$ values (+0.38 – +1.86), low I_{Sr} ratios (0.704769–0.706211) and high $\text{Mg}^{\#}$ (average of 52), mostly show VAG (volcanic arc granite) affinities in the widely-used trace element discrimination diagrams (Pearce et al., 1984; Fig. 14). Additionally, the Hongyuan granodiorite samples also show some syn-collisional affinities in the Nb vs. Y and Rb/10–Hf–Ta*3 diagrams (Fig. 14C, D; Harris et al., 1986; Pearce et al., 1984). Furthermore, some workers proposed that the 300 Ma shear zone-hosted Au deposits in the Kangguer shear zone were formed in syn-collisional stage (Han et al., 2010; Xiao et al., 2004). Consequently, we consider the ages of Shaquanzi gabbro and Hongyuan Granodiorite may have suggested a tectonic evolution from oceanic subduction to syn-collisional environment during the period of ca. 307–301 Ma in the Eastern Tianshan.

Moreover, previous studies indicate that the collisional regime in the Chinese Tianshan was ceased by the latest Carboniferous to Early Permian (Charvet et al., 2007; Chen et al., 2011; Zhang et al., 2015a, 2015b, 2016a). In addition, voluminous post-collisional magmatic rocks in the CTT were formed in the Early Permian, including ultramafic-mafic intrusions, mafic dyke swarms, granites and bimodal volcanic rocks (Chen et al., 2011; Han et al., 2004; Li et al., 2006; Ma et al., 2015). Zircons from mafic-ultramafic complexes in the Kangguer shear zone are mainly ~300–270 Ma during post-collisional stage and related to magmatic Cu–Ni sulfide mineralization (Mao et al., 2008; Qin et al., 2011; Su et al., 2013; Tang et al., 2011; Wang et al., 2006). The above evidence indicate the final closure of the Junggar Ocean and the subsequent collision and post-collision events between the CTT and Junggar block, occurring at ca. 300 Ma (Zhang et al., 2015b, 2016a, 2016c).

5.2.2. Implication for Pb–Zn mineralization

Regionally, most of the Eastern Tianshan Pb–Zn deposits (e.g., Caixiashan, Hongyuan, Hongxingshan, Jiyuan, Shaquanzi and Yuxi) are hosted in the CTT Precambrian basement rocks. The metals were suggested to have precipitated through a variety of processes, including SEDEX-type (e.g., sedimentary stages of Caixiashan and Hongyuan; e.g. Cao et al., 2013; Gao et al., 2007; Li et al., 2016; Lu et al., 2017; Peng et al., 2006, 2007), sedimentation-hydrothermal reworking (Hongxingshan, Shaquanzi, Yuxi and skarn period of Hongyuan; e.g. Lu et al., 2017; Q.H. Xiao et al., 2009; Zhong et al., 2008; Zhou et al., 1999), and contact metasomatism (Jiyuan; e.g.H.Y. Chen et al., 2012).

Skarn alteration in Jiyuan is extensively developed along the intrusive contact between the Early Carboniferous diorite–granodiorite and the Precambrian marble, and occurred before the main Cu–Ag (–Zn) mineralization stage (H.Y. Chen et al., 2012). The giant Caixiashan Pb–Zn deposit had been modified by the Carboniferous magmatism (ca. 323 Ma; Gao et al., 2007; Cao et al., 2013; Peng et al., 2006, 2007). The Hongxingshan Pb–Zn and Yuxi Ag (–Pb–Zn) deposits have genetic relationships with the Late Carboniferous magmatism (Q.H. Xiao et al., 2009; Zhou et al., 1999). The Shaquanzi Pb–Zn deposit supports a genetic link between Shaquanzi gabbro (307 Ma) and the Pb–Zn mineralization (Zhong et al., 2008). Lu et al. (2017) indicated that the Hongyuan Pb–Zn mineralization may have firstly formed by Mesoproterozoic SEDEX-type processes, and then reworked and upgraded by the Late Carboniferous contact metasomatism during the granodiorite emplacement (ca. 301 Ma).

Regional geochemical characteristics indicate that the abundance of ore-forming elements (e.g. Pb, Zn, Ag) in the Precambrian basement is relatively high, suggesting high fertility in forming Pb–Zn deposits (Peng et al., 2006; Q.H. Xiao et al., 2009; Zhou et al., 1999). During the Early to Latest Carboniferous, S-dipping subduction beneath the CTT may have generated the continental arc magmatism (ca. 353–301 Ma) along the northern margin of the CTT. The associated hydrothermal alteration may have indirect links with the Pb–Zn mineralization (e.g., reworked/upgraded), forming a major Carboniferous Pb–Zn mineralization belt.

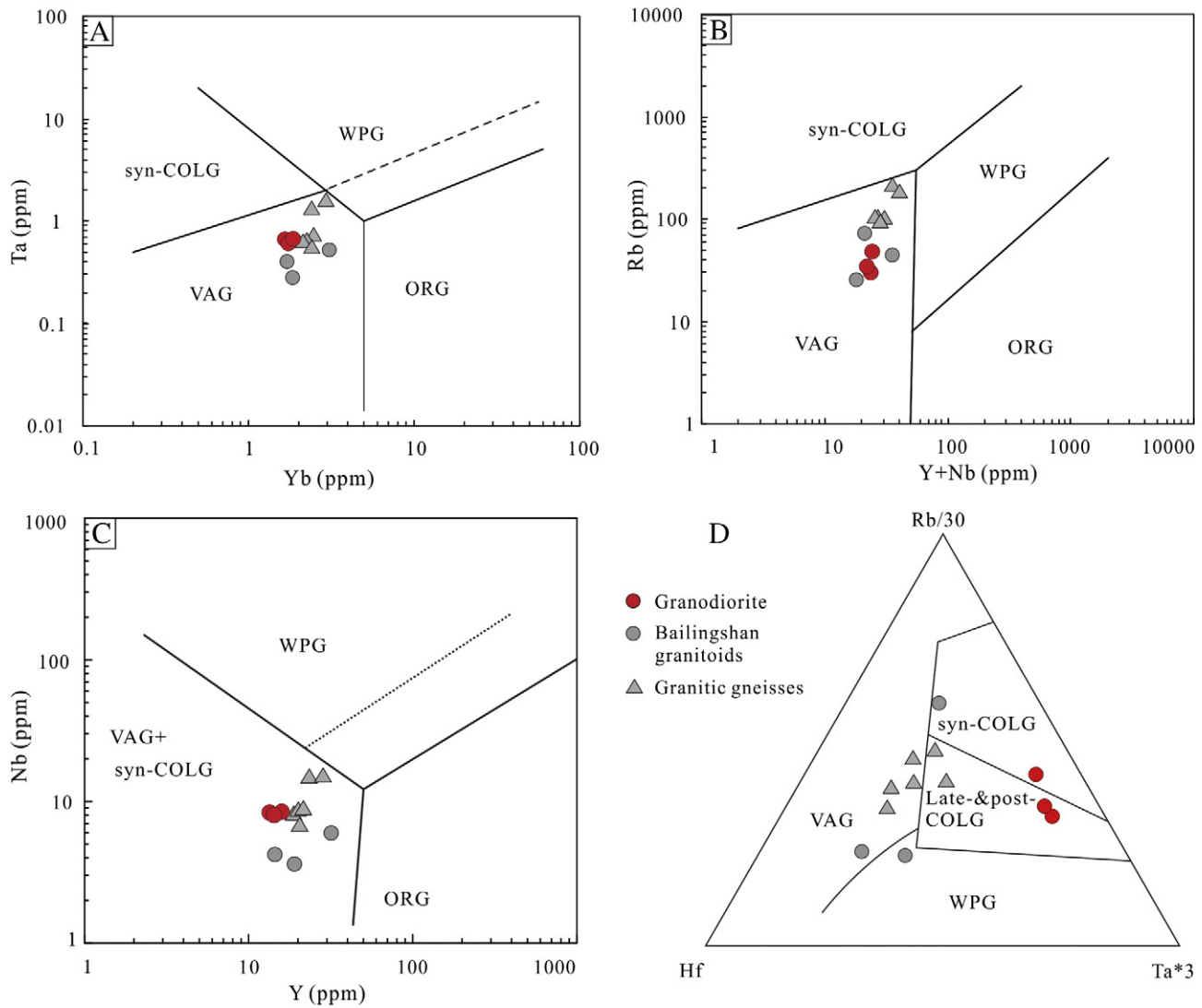


Fig. 14. Tectonic discrimination diagrams for the Hongyuan granodiorite. (A) Ta vs. Yb, (B) Rb vs. Y + Nb and (C) Nb vs. Y diagrams are from Pearce et al. (1984) with (D) Rb/30 – Hf – Ta*3 ternary diagram from Harris et al. (1986). ORG = Ocean Ridge Granite; WPG = Within Plate Granite; VAG = Volcanic Arc Granite; syn-COLG = syn-Collisional Granite.

6. Conclusions

- (1) LA-ICP-MS zircon U–Pb dating of the Shaquanzi gabbro and the Hongyuan granodiorite yielded Late Carboniferous ages of 307.2 ± 1.5 Ma and 301.2 ± 1.5 Ma, respectively.
- (2) Petrological and geochemical data indicate that primary magma of the Shaquanzi gabbro samples may have been derived from the SCLM metasomatized by subduction-related fluids, whereas the Hongyuan I-type granodiorite were likely to be derived from partial melting of juvenile crust sources mixed with some mantle-derived materials.
- (3) Combined our geochemical study of the Shaquanzi gabbro and Hongyuan granodiorite with previous investigations, we suggest a tectonic evolution from oceanic subduction to syn-collisional extension during the period of ca. 307–301 Ma in the Eastern Tianshan.
- (4) Most of the Eastern Tianshan Pb–Zn deposits had indirect (reworked/upgraded) links with the Carboniferous magmatism.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.lithos.2017.10.009>.

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