



Mineralizations of Nb-Ta-Rb-Zr and rare-earth elements in Boziguoer, South Tianshan, NW China: Geochronology and geochemistry of monazite and bastnäsite

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ABSTRACT

The Boziguoer alkaline intrusion is located in the South Tianshan Orogenic Belt on the northern margin of the Tarim Craton. The intrusion is entirely mineralized and forms a super-large rare metal (RM) and rare-earth element (REE) deposit dominated by Nb-Ta-Rb, accompanied by Zr-REE. The primary RM minerals include pyrochlore, astrophyllite, and zircon, while the main REE minerals consist of fluocerite, monazite, xenotime, and bastnäsite, which are commonly present as granular aggregates or singularly filling the interstices between gangue minerals. Through a combination of geochronological and geochemical analyses of different types of monazite and bastnäsite in the mineralized alkaline rocks, this study elucidates the role of magmatic-hydrothermal evolution on the Boziguoer RM-REE mineralization and reconstructs the geochronological framework of alkalic magmatic-hydrothermal evolution and mineralization processes, as well as establishing mechanisms responsible for RM-REE enrichment. Petrographic observations and back-scattered electron (BSE) imaging revealed several types of monazite and bastnäsite with different characteristics as follows: (1) type Ia monazite (Mnz-Ia) experienced intense hydrothermal alteration, forming residual cores of monazite mantled by apatite and allanite coronas; (2) type Ib monazite (Mnz-Ib) was partially eroded, forming concentric zoning patterns with a core of monazite, a mantle of apatite, and an outer rim of allanite coronas; (3) type II monazite (Mnz-II) is slightly modified, and commonly associated with fluorite; (4) bastnäsite and fluocerite exhibit a core-rim structure, with the core of fluocerite being brighter than the rim of bastnäsite in BSE images. According to the paragenetic relationships and compositional variations, all two types of monazite are of primary magmatic origin, while bastnäsite is of hydrothermal origin. In addition, principal component analysis (PCA) and partial least squares-discriminant analysis (PLS-DA) results indicate that Mnz-Ia and Mnz-Ib belong to the same group, different from Mnz-II. The latter has higher (Ce/Gd)_N and (Th/U)_N ratios, indicating relatively low-temperature crystallization of Mnz-II at late stages. In-situ LA-ICP-MS U-Th-Pb dating of monazite and bastnäsite show that Mnz-Ia and Mnz-Ib have ages of ca. 290 Ma, consistent with the zircon age of the intrusion, whereas the Mnz-II and bastnäsite have younger ages of ca. 280 Ma, representing a post-magmatic hydrothermal mineralization event at Boziguoer. These new ages indicate that both magmatic and subsequent hydrothermal processes played critical roles in the RM-REE mineralization in this deposit. The latest findings also support the model that the formation of the alkaline belt where the Boziguoer ore-bearing intrusion was temporally and spatially linked to the Tarim Large Igneous Province that is genetically related to a mantle plume.

1. Introduction

As the world shifts towards a low-carbon, high-tech lifestyle, there is

increasing attention on alkaline rocks due to their association with numerous cutting-edge issues in solid earth sciences. These include but are not limited to, lithospheric evolution, crust-mantle interactions,

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mantle metasomatism, material cycling, and particularly critical metal mineralization (Markl et al., 2010; Schilling et al., 2011; Goodenough et al., 2016; Smith et al., 2016; Dostal, 2016, 2017; Sokół et al., 2021; Beard et al., 2023). Among these alkaline rocks, are highly evolved peralkaline igneous rocks [molar $(\text{Na} + \text{K})/\text{Al}$ ratio > 1] that are generally enriched in large ion lithophile elements (LILEs; e.g., Li, Na, Rb, and Cs), rare earth elements (REEs), and high field strength elements (HFSEs; e.g., Zr, Hf, Nb, Ta, and U), exhibiting enormous ore-forming potential (Kogarko, 1990; Sørensen, 1992; Bailey et al., 2001). However, the origin of rare metal (RM) and REE deposits associated with the alkaline rocks is still controversial. There exists three main perspectives, attributing the mineralization to magmatic processes, hydrothermal activity, or a combination of both (e.g., Salvi et al., 2005; Huang et al., 2014; Vasyukova and Williams-Jones, 2014, 2016; Yang et al., 2014a, 2020; Siegel et al., 2018; Bernard et al., 2020; Su et al., 2021). The lack of reliable geochronometers to constrain the sequence of magma fractionation and melt-fluid interaction might be an essential factor contributing to these controversies (Černý et al., 2005; London and Morgan, 2012). Furthermore, understanding the genesis of the RM/REE minerals is crucial in investigating the mechanisms of magmatic-hydrothermal processes in RM/REE mineralization related to alkaline rocks.

The northern margin of the Tarim Craton (TC) and its adjacent area (South Tianshan Orogen Belt (STOB)) are distributed with a roughly 1100 km long alkaline igneous belt, which hosts several significant RM-REE ore deposits (occurrences) (Xie et al., 2022). The Boziguero deposit is a super large RM-REE polymetallic ore deposit in this alkaline rock belt, characterized by dominant Nb-Ta-Rb mineralization and associated with Zr and REE mineralization (Xu et al., 2011). Based on petrological and geochemical features, Huang et al. (2014) pointed out that in although almost all mineralization associated with alteration (e.g., greisenization and albitization), the post-magmatic hydrothermal alteration did not play a critical role in the Nb, Ta, and REE mineralization at Boziguero. However, Rb-rich mineral astrophyllite mainly formed during the post-magmatic stage, with its grade satisfying industrial utilization requirements (Xu et al., 2011; Huang et al., 2014). Due to the lack of robust age data for the alkaline magmatic-hydrothermal evolution at Boziguero, the geochronological framework of mineralization is still debated. Although the Boziguero alkaline rock intrusion contains abundant zircon grains, most have undergone post-magmatic hydrothermal alteration (Huang et al., 2018). Radiation damage caused by high U content is generally shown as black in CL images (Liu et al., 2014a; Huang et al., 2018), making the obtained U-Pb age results less reliable (White and Ireland, 2012). Monazite and bastnäsite are the main REE mineral phases in the Boziguero deposit, and both are considered promising U (Th)-Pb geochronological tools with widespread geological applications (e.g., Sal'nikova et al. 2010; Yang et al. 2014b, 2019; Gonçalves et al., 2016; Ling et al., 2016; Piechocka et al., 2017; Itano et al., 2018; Weng et al., 2022). Additionally, monazite can form during both magmatic and low-temperature hydrothermal stages, providing helpful information on petrogenesis and thermal evolution (Williams et al., 2007; Rusiecka and Baker, 2019), while bastnäsite is generally considered a typical hydrothermal mineral, commonly forming during hydrothermal stage (Bau and Dulski, 1995; Agangi et al., 2010; Migdisov and Williams-Jones, 2014). Therefore, studying the composition and U-Th-Pb geochronology of monazite and bastnäsite can reveal the magmatic-hydrothermal evolution and metallogenic processes related to RM-REE mineralization.

In this study, based on our petrological and whole-rock geochemical analysis of the Boziguero mineralized alkaline rock samples, as well as microstructural analysis of REE minerals (monazite and bastnäsite), we presented the structural characteristics, geochronology, and chemical composition of bastnäsite and different types of monazite. We reconstructed the geochronological framework of alkaline magmatic-hydrothermal evolution and mineralization and explored the potential RM-REE enrichment and mineralization mechanism. Finally, the

implications of our studies on the regional RM-REE mineralization related to alkaline rocks were also discussed.

2. Geological background

Tarim Craton (TC) is one of the oldest cratons in China and is mainly composed of Precambrian crystalline basement and overlying thick layer sedimentary sequences (Xinjiang Bureau of Geology and Mineral Resources (XJBGM), 1993; Lu et al., 2008). An approximately 1100 km long alkaline igneous belt lies at the junction between the northern margin of the TC and the southern margin of the Central Asian Orogenic Belt (CAOB; Fig. 1a). The CAOB is considered to be one of the most extensive and longest-lasting accretionary orogenic belts in the world, with significant Neoproterozoic and Phanerozoic crustal growth (Jahn et al. 2004; Cawood et al., 2009; Xiao et al., 2013), containing considerable tectonic units like microcontinents, island arcs, marine plateaus, seamounts, ophiolites and accretionary complexes (Huang et al., 2014; Jahn et al., 2004; Kröner et al., 2013; Sengör et al., 1993; Windley et al., 1990, 2007; Xiao et al., 2013). In this study, we focus on the STOB, where the Boziguero alkaline intrusion is exposed, and provides a summary of the geological setting of this tectonic unit.

The STOB is bounded by the South Central Tianshan Suture Zone as the northern boundary and the North Tarim Fault in the south (Fig. 1b, Gao et al., 2009; Qian et al., 2009). The suture zone is composed of discontinuous late Neoproterozoic to Carboniferous ophiolitic mélange, high-pressure (HP)/ultra-high-pressure (UHP) metamorphic terranes, and oceanic plate stratigraphic elements (Alexeiev et al., 2015; Gao et al., 2009; Hegner et al., 2010; Jiang et al., 2014; Mühlberg et al., 2016; Safonova et al., 2016; Xiao et al., 2013; Wang et al., 2018). Besides, the STOB is considered to be a widely distributed fore-arc accretionary complex, which formed in southward accretions during northward subduction (Xiao et al., 2013). In other words, it is closely related to the subduction closure of the South Tianshan Ocean (STO) and the subsequent continent–continent collision orogeny of the Yili-Central Tianshan Block and the TC, being the northernmost part of the TC before the continent–continent collision occurred (Sengör et al., 1993; Gao et al., 2009; Zhang et al., 2010b; Han et al., 2011, 2020). The tectonic unit mainly comprises the Late Ordovician–Carboniferous clastic-carbonate series with intense deformation, superimposed with a medium–low degree of metamorphism, and accompanied by interbedded volcanic rocks (Wang et al., 2018). The Precambrian basement rocks are rarely exposed, only part of the area is exposed (Alexeiev et al., 2015). The basement rocks are similar in age and composition to the Tarim and Central Tianshan Block (e.g., Paleoproterozoic Xingditagh Formation; Midproterozoic Akesu Formation; Huang et al., 2014). Locally, the terrestrial volcano-clastic series of the Early Permian unconformably the underlying strata (Huang et al., 2015; Liu et al., 2014b). The STOB has experienced two magmatism periods, which occurred at ~ 440–338 and 310–270 Ma (Huang et al., 2013; Konopelko et al., 2007; Lin et al., 2013; Seltmann et al., 2011; Zhao et al., 2015).

A current residual of nearly 250,000 km² of Early Permian Tarim Large Igneous Province (TLIP) is exposed to the west and southwest of the TC and consists mainly of volcanic series (mostly continental flood basalts) and associated intrusive rocks, ranging from 600 to 800 m thick (Fig. 1b; Tian et al., 2010; Yang et al., 2013). Early Permian mafic–ultramafic, intermediate-acid intrusions, and A-type granites are widely distributed in the South Tianshan region. The age of their formation is close to that of flood basalt, and they are mostly considered to be the products of TLIP events and are related to the activities of mantle plume (e.g., Yang et al., 2007; Zhang et al., 2008, 2010a, b; Li et al., 2011; Zou et al., 2015; Qin et al., 2011; Huang et al., 2012; Ma et al., 2016). The magmatic activity of the TLIP spanned approximately 30 Ma, initiated by the emplacement of the Tarim mantle plume, leading to large-scale magmatic events ranging from ca. 300 Ma to ca. 270 Ma (Yang et al., 2007; Zhang et al., 2008, 2013; Zhou et al., 2009; Li et al., 2011, 2014; Tian et al., 2010; Xie et al., 2022).

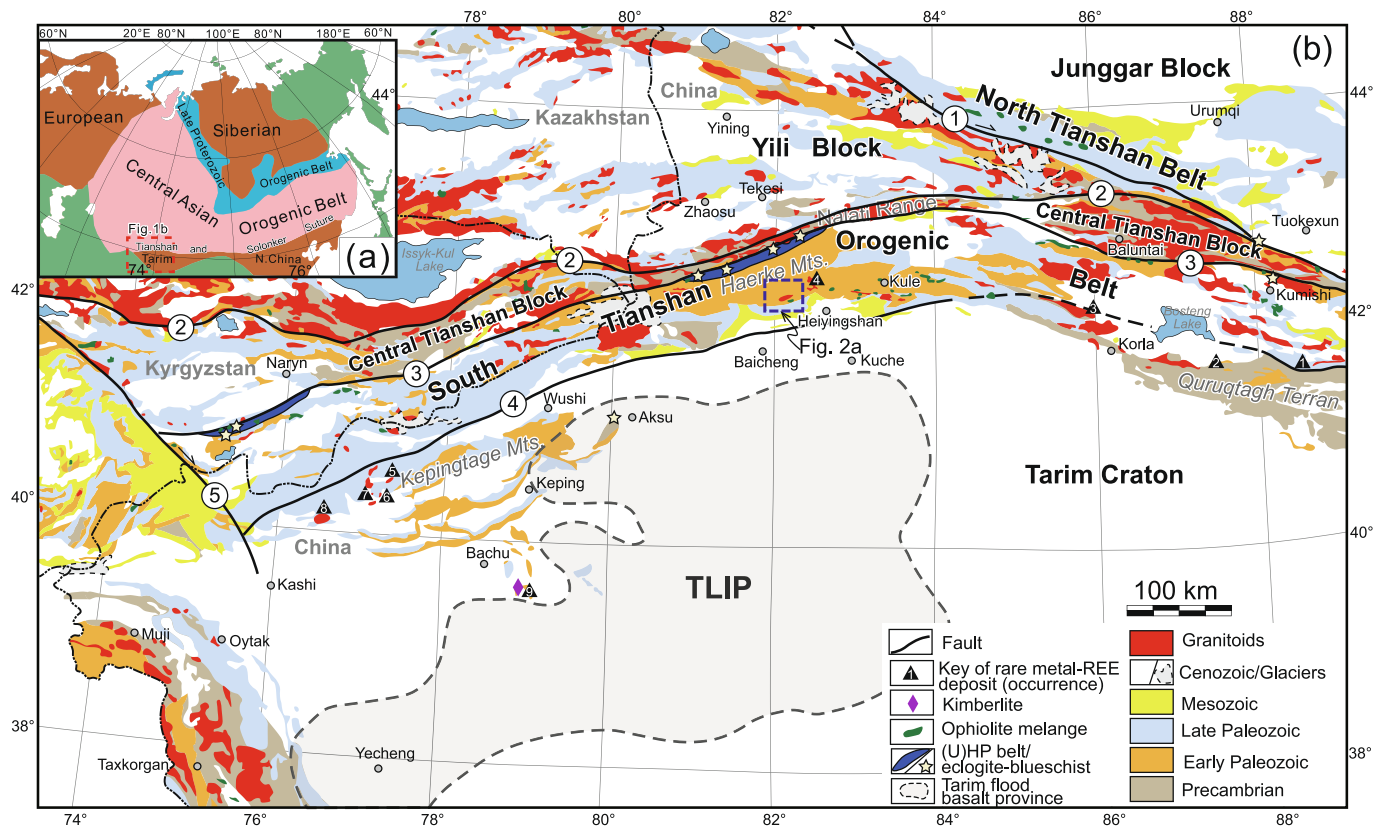


Fig. 1. (a) Tectonic sketch map of the Central Asian Orogenic Belt showing the position of Tarim Craton (modified from Gao et al., 2011; Huang et al., 2014). (b) Simplified geological map showing the tectonic map of the northern Tarim Craton and western Tianshan regions (modified after Gao et al., 2009; Xiao et al., 2013; Han et al., 2019) and the distribution of the Tarim Large Igneous Province (TLIP) (modified from Yang et al., 2007), ①–⑤: North Tianshan Fault, Nikolaev Line–North Nalati Fault, Atbashi–Inylchek–South Nalati Fault, North Tarim Fault, and Talas–Ferghana Fault. Key to rare metal-REE deposits (occurrences): 1 = Kuoktag, 2 = Qieganbulak, 3 = Shanghu, 4 = Yilanlik, 5 = Huoshibulake, 6 = Tamu, 7 = Tamuxi, 8 = Bashisuogong, 9 = Wajilitag.

The timing of the collision between the Tarim and Yili-Central Tianshan Block remains a topic of considerable debate. There is a general consensus that the collision occurred during the Late Carboniferous (Gao et al., 2011; Wang et al., 2018; Han et al., 2019 and references therein). We propose that the collision between the Tarim and Yili-Central Tianshan Block occurred ca. 310 Ma. The upwelling Tarim mantle plume occurred shortly after the Tarim and Yili-Central Tianshan Block collision. However, the formation of the Boziguoer alkaline magma is evidently unrelated to the collisional orogeny, as the presence of alkaline rocks indicates an extensional tectonic setting (Collins et al., 1982; Eby, 1992; Turner et al., 1992). Thus, some scholars propose that the formation of the Boziguoer alkaline rocks resulted from post-collision extensional processes (Huang et al., 2014).

3. Deposit geology

The ore-bearing Boziguoer alkaline intrusion is located 43 km north of Baicheng County with geographical coordinates of 81°54'30" East and 42°13'30" North. The strata exposed in this area include the Upper Silurian Qiongkushitai Formation, the Lower Carboniferous Gancaohu Formation and the Lower Permian Xiaotikanlik Formation, while the alkaline pluton is mainly intruded in the Qiongkushitai Formation marbles (Fig. 2a). The nearly east–west oriented Akya Ilyaktage fault cuts through the whole area and is characterized by multi-stage activity, with several NE–SW secondary faults. Folds are generally located south of the main fault and are poorly distributed within the mine area. The magmatic activity in this area is vigorous. It can be broadly divided into three eruptive cycles: Silurian, Early Carboniferous, and Early Permian, which form numerous volcanic rocks. Still, the intrusive rocks are only exposed in the central part, and the lithology is mainly alkaline rocks.

The Boziguoer pluton is an east–west fish-like strain, which intrudes *cis-layer* into the Upper Silurian Qiongkushitai Formation marbles, and the relationship between them is clear through fault contact (Fig. 2). It has overall strike of 295°, dipping towards NNE with the dip angle of ~70°, and is ~4.4 km in length and 0.4–1.2 km in width (average ~0.8 km), covering an area of about 3.56 km². The intrusion is divided into two sections by the fault, consisting of aegirine-arfvedsonite alkaline rocks (granite) in the west and biotite alkali-feldspar granite in the east (Fig. 2b). The eastern part of the pluton hasn't been investigated in detail due to glacier coverage. This study focuses on the western part of the pluton, which is described in detail.

From field observations, it is evident that the intrusion is either in direct contact or fault contact with the marble (Fig. 3a). The outcrops consist primarily of dark-colored banded or banded-like alkaline rocks (Fig. 3b, h, i), followed by fine-grained or coarse-grained dark-colored alkaline rocks (Fig. 3c, f), and finally mass dark-colored alkaline rocks (Fig. 3g). The intrusion consists of various lithological units that exhibit a gradual transition tendency, lacking distinct boundaries between them. Banded alkaline rocks typically shift to coarse-grained/pegmatitic alkaline rocks (Fig. 3i), while fine-grained alkaline rocks transform into coarse-grained/pegmatitic alkaline rocks but lacking clear boundaries (Fig. 3c, f). The pegmatitic alkaline rocks form during the later stages of magma evolution and are often found as veins within marbles (Fig. 3d). Biotite alkali feldspar granite, which has a gray-white to light gray color and medium to coarse-grained granitic structure (Fig. 3e), is not commonly exposed in the western part of the Boziguoer intrusion.

Ore minerals are often present as granular aggregates or singularly filling the interstices between gangue minerals, forming distinct sparsely disseminated structures, occasionally exhibiting fine-vein disseminated structures (Fig. 4f–k). The ore minerals are predominantly pyrochlore

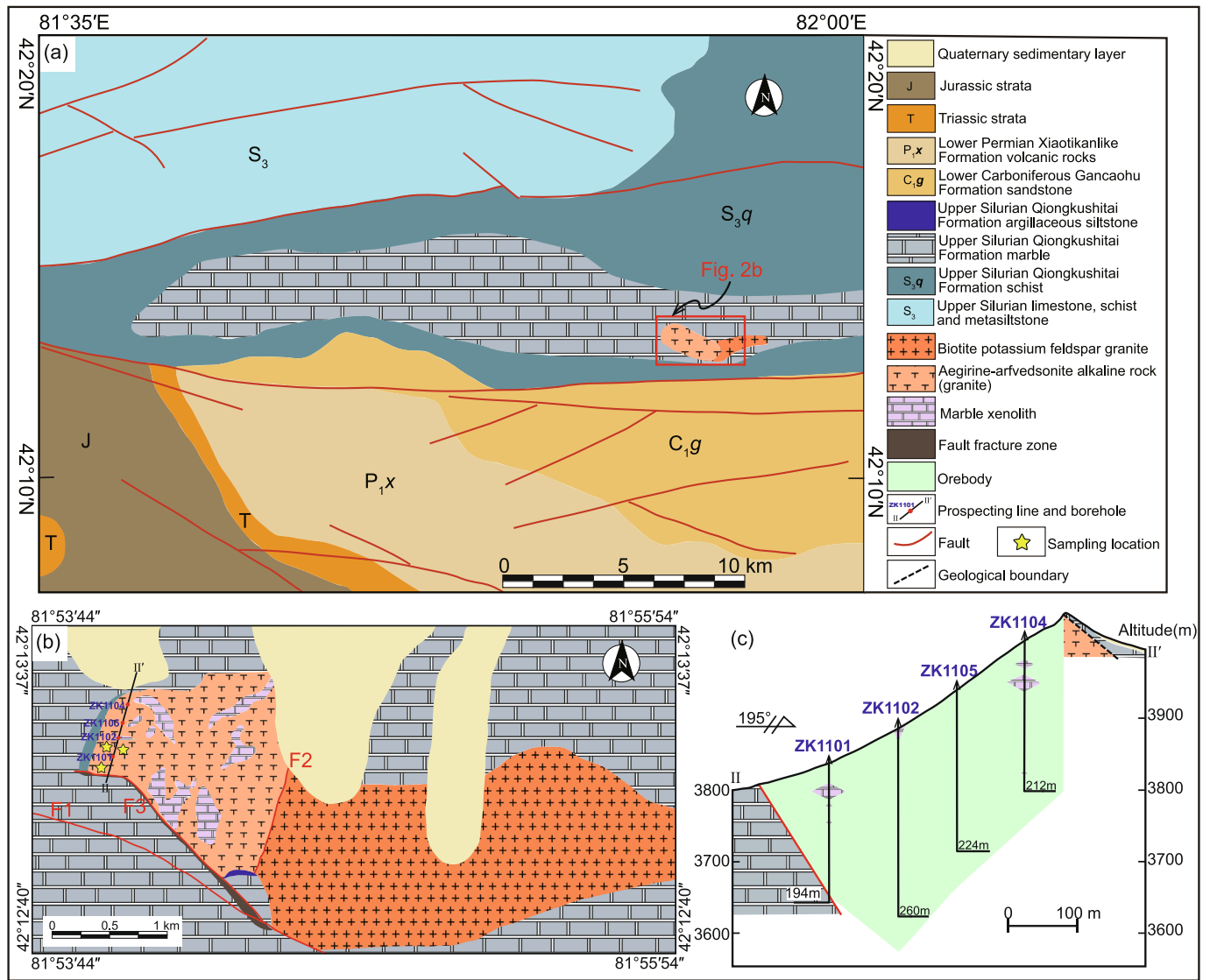


Fig. 2. (a) Regional geological map of the Boziguoer area (modified from Liu et al., 2014a). (b) Geological sketch map of the Boziguoer alkaline intrusion (modified from Xu et al., 2011). (c) The orebody section along II-II' line of the Boziguoer Nb-Ta-Rb-Zr-REE deposit (modified from Xu et al., 2011).

and astrophyllite, with secondary monazite, zircon, thorite, xenotime, bastnäsite, fluocerite and parisite. The gangue minerals are mainly albite, microcline, orthoclase and quartz, with minor amounts of aegirine, arfvedsonite and traces of fluorite and apatite (Fig. 4). The pyrochlore is the main carrier of Nb, Ta and U ore mineral. Rubidium and Cs are hosted in astrophyllite, Zr and Th (U) are derived from zircon and thorite, respectively, while monazite, bastnäsite, fluocerite and xenotime are the main REE minerals. The K-feldspar is one of the major rock-forming minerals, including orthoclase and microcline. Orthoclase shows a first-order interference color of gray to gray-white (Fig. 4c, d), while microcline exhibits subhedral to anhedral granular and well-developed grid twinning (Fig. 4b, d). The albite content is relatively high, exhibiting subhedral short columnar to tabular crystals, clustered twinning or perthitic intergrowth, with a gray-white color and a turbid surface (Fig. 4c, d). The biotite occurs in sheet, with a brownish-red to dark green color, exhibiting extremely strong pleochroism and distributed in clusters (Fig. 4d). The arfvedsonite is subhedral tabular, with obvious polychromatism, dark blue, co-occurring with aegirine and astrophyllite to form oriented dark bands (Fig. 4a–c). Aegirine exhibits long columnar to tabular, typically euhedral to subhedral, with strong pleochroism and a clinopyroxene-type cleavage (Fig. 4a–c). Some aegirine and arfvedsonite have been deformed by hydrothermal

alteration, resulting in poor preservation of their crystal shape (Fig. 4e). Tabular, bladed, or acicular astrophyllite with well-developed cleavage and an antique bronze yellow color exhibiting strong pleochroism coexists with aegirine and arfvedsonite (Fig. 4a–c). The pyrochlore occurs as yellow, semi-transparent, euhedral octahedral or subhedral granular of varying grain sizes, appearing in clusters or individually, and often coexisting with zircon (Fig. 4f, g, f, k). Zircon appears colorless to flesh-red and mostly as semi-transparent, euhedral tetragonal prisms and occasionally as subhedral granules, exhibiting a wide range of grain sizes, often coexisting with pyrochlore or xenotime in clusters or individually, and containing numerous slight inclusions (Fig. 4a, g–j). Monazite appears bright yellow, brown, or brownish and mostly as subhedral granules and occasionally as euhedral plates (Fig. 4i). Thorite is typically brown or tan and appears as subhedral- anhedral, with grains of varying sizes filling in between other mineral grains, often occurring together with zircon (Fig. 4j). Fluorite is colorless or purple, and its color distribution is uneven, with a notable rough surface, often occurring together with pyrochlore, xenotime and bastnäsite (Fig. 4k). In alkaline pegmatite veins, abundant titanite with euhedral to subhedral granular shapes coexists with aegirine (Fig. 4l). The alkaline rocks are essentially magmatic minerals with relatively few hydrothermal minerals dominated by apatite.

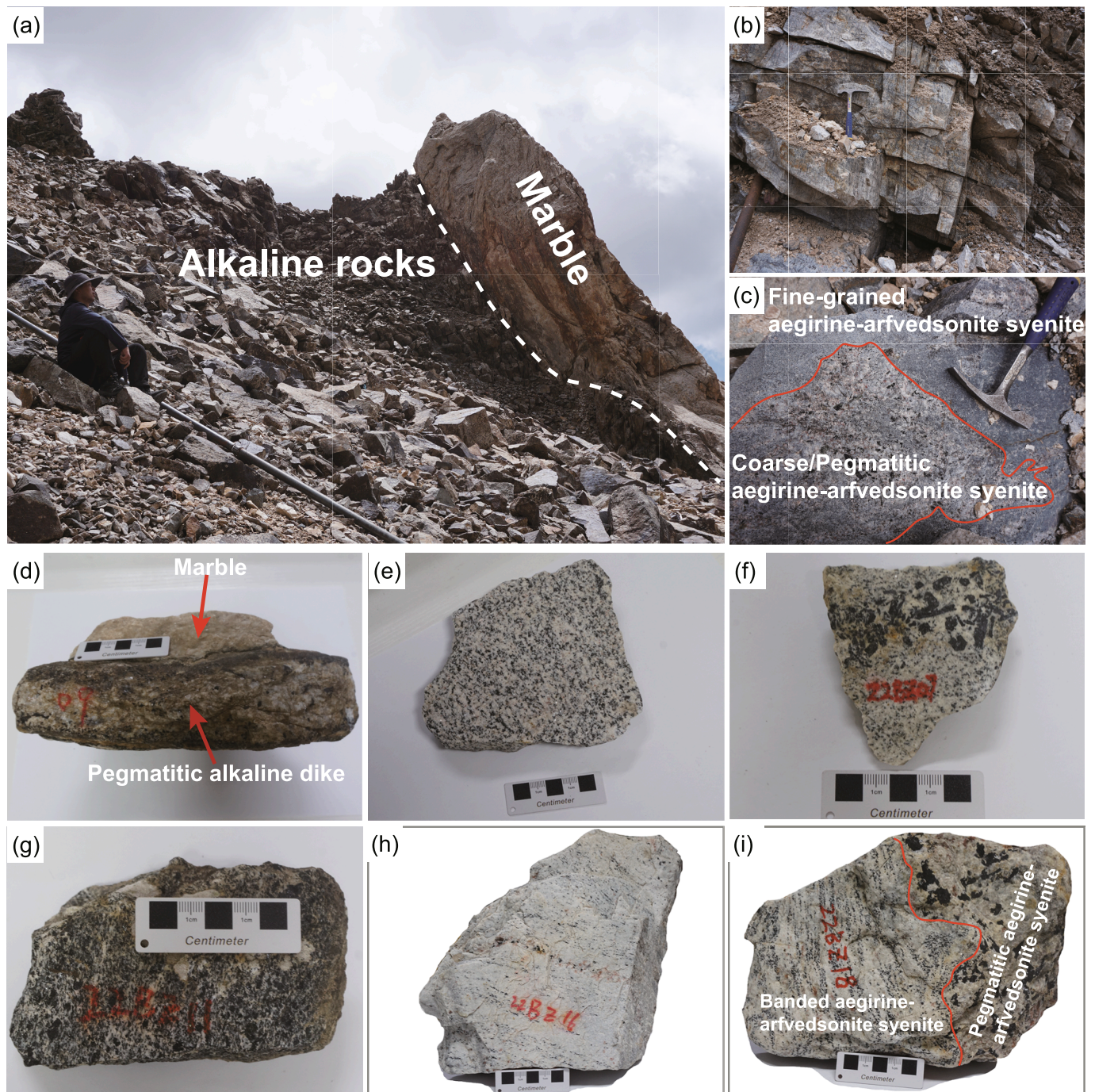


Fig. 3. Field photos and hand specimen photographs of the Boziguoer alkaline rocks. (a) Outcrop photograph showing fault contact between alkaline rock intrusion and marble. (b) Outcrop of dark-banded alkaline rocks. (c) Outcrop photograph showing transition from fine-grained aegirine-arfvedsonite syenite to coarse-grained/pegmatitic aegirine-arfvedsonite syenite. (d-i) Hand specimens of representative alkaline rock of different types. (d) Alkaline pegmatite vein in marble. (e) Biotite alkali feldspar granite. (f) Transition from fine-grained aegirine-arfvedsonite syenite to pegmatitic aegirine-arfvedsonite syenite. (g) Dark-massive aegirine-arfvedsonite syenite. (h) Light-banded aegirine-arfvedsonite syenite. (i) Transition from banded aegirine-arfvedsonite syenite to pegmatitic aegirine-arfvedsonite syenite.

The pluton is almost entirely mineralized, with Nb, Ta and Rb mineralization predominantly accompanied by Zr, U, Th, Cs and REE mineralization. The industrially significant primary minerals in this deposit include pyrochlore and astrophyllite. Other economically valuable minerals comprise monazite, zircon, thorite, xenotime, bastnäsite, and fluocerite. Pyrochlore, zircon, monazite, xenotime, fluocerite, and some bastnäsite often occur as coexisting or aggregates, suggesting that these metallic minerals may have formed during the same period of magmatic activity, while astrophyllite is the product of post-magmatic hydrothermal processes (Huang et al., 2014). The mineralization is

particularly rich in aegirine-arfvedsonite alkalic pegmatites at the top of the strain, and in dikes or veins that cut into the marble of the outer contact zone (Fig. 3d), and more marble captures are also present within the pluton (Fig. 2c). The proven resources of Nb₂O₅, Ta₂O₅ and Rb₂O are 320,000 tons, 20,000 tons and 640,000 tons respectively, with average grades of 0.0418 %, 0.0028 % and 0.0831 % for Nb, Ta and Rb respectively. The estimated associated REE resource (grade: 0.058 % to 0.1453 %) is approximately 210,000 tons, and the Zr resource is 710,000 tons. While Nb mineralization dominates, Boziguoer is considered a super-large Nb-Ta-Zr-Rb-REE deposit (Xu et al., 2011;

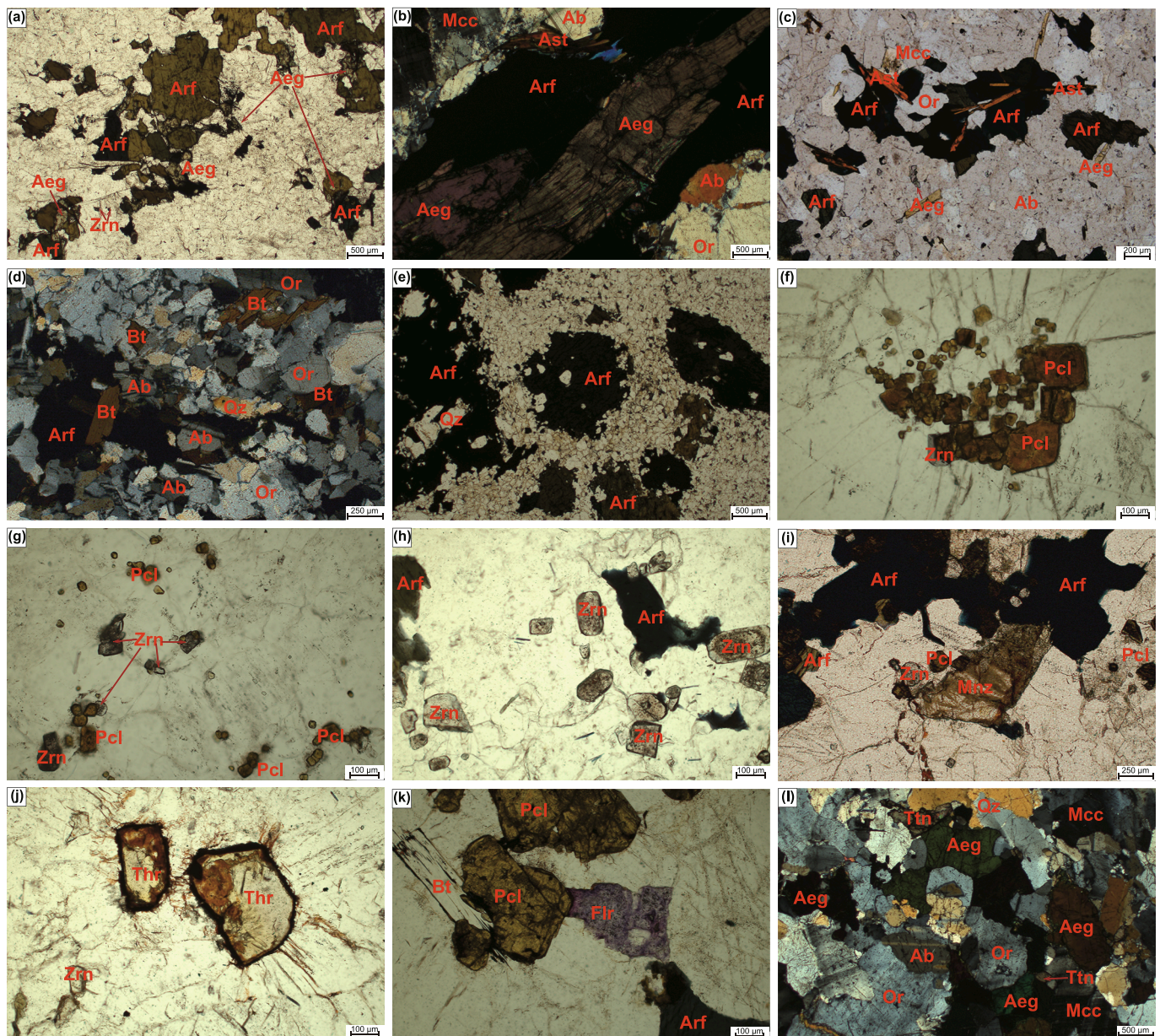


Fig. 4. Petrographic images of the Boziguoer alkaline rocks. (a) Photomicrograph (plane-polarized light) showing oriented distribution of aegirine and arfvedsonite coexisting in felsic minerals. (b) Photomicrograph (crossed-polarized light) showing the co-occurrence of pegmatitic aegirine, arfvedsonite and astrophyllite distributed between grains of pegmatitic felsic minerals. (c) Acicular or short columnar astrophyllite coexisting with arfvedsonite and aegirine. (d) Clustered distribution of sheeted biotite in biotite alkali feldspar granite. (e) Altered pegmatitic arfvedsonite in a matrix of fine-grained felsic mineral. (f) Euhedral to subhedral distribution of clustered pyrochlore in coexisting zircon. (g) Clustered distribution of euhedral-subhedral zircon and pyrochlore. (h) Zircon grains coexist with arfvedsonite, with abundant inclusions inside the zircon. (i) Platy monazite co-occurring with zircon, pyrochlore and arfvedsonite. (j) Variable sizes of brown thorite often coexist with zircon. (k) Purple fluorite coexisting with pyrochlore. (l) Titanite with euhedral to subhedral granular shapes coexists with aegirine in alkaline pegmatite vein. Mineral abbreviations: Ab-albite, Aeg-aegirine, Arf-arfvedsonite, Ast-astrophyllite, Bt-biotite, Flr-fluorite, Mcc-microcline, Mnz-monazite, Or-orthoclase, Pcl-pyrochlore, Qz-quartz, Thr-thorite, Ttn-titanite, Zrn-zircon. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Huang et al., 2014).

According to Liu et al., (2014a), the zircon LA-ICP-MS U-Pb ages of the western alkaline intrusion range from 287.7 to 291.6 Ma, and they were modified by late hydrothermal fluids at ca. 280 Ma. Huang et al. (2014) divided the western intrusion into porphyritic albite granite (unit I) and equigranular, medium-grained biotite- aegirine-arfvedsonite granite (unit II), with no apparent boundary between the two units, implying that they formed simultaneously, and emplaced during Early Permian at ca.290 Ma. The eastern pluton biotite alkaline granites can be visible in the field as thin veins cut through the western pluton (Yin

et al., 2014). It can be assumed that the eastern rocks were formed later than the western rocks, and they are contemporary but different sequences. Therefore, the Boziguoer alkaline rock intrusion was formed in the Early Permian.

4. Sampling and analytical methods

4.1. Samples

Given the entire mineralization of the Boziguoer pluton, there is no

difference in the formation time of the different types of rocks (Huang et al., 2014; Liu et al., 2014a). Here, we collected twenty alkaline rock samples from the western orebody, including fine-grained, banded, massive and coarse-pegmatitic alkaline rocks. Polished thin sections were made from some representative samples, and the fresh interior pieces of the samples were crushed into 200 mesh powders using an agate disintegrator at the Institute of Regional Geology and Resource Survey, Langfang, Hebei Province, China. Polished thin sections of each sample were investigated first by a petrographic microscope. Then, monazite and bastnäsite grains were observed under backscattered electron (BSE) imaging using a TM4000 desktop scanning electron microscope at the Key Laboratory of Mineral Resources, Institute of Geology and Geophysics, Chinese Academy of Sciences, prior to elemental and isotopic analysis.

Monazite is the most common REE-bearing mineral phase in the Boziguoer intrusion, ranging in size from 10 to 300 μm , and occurring as euhedral to subhedral grains or platelets (Fig. 5a–d). It exists not only as interstitial minerals but also as inclusions in the major rock-forming minerals. The BSE images show that monazite exhibits different

structures, which can be roughly classified into two types based on their morphology and internal structure (Fig. 5a–d). The type I monazite (Mnz-I) can be divided into two subtypes, Mnz-Ia and Mnz-Ib. The Mnz-Ia is relatively scarce, occurring only in massive aegirine-arfvedsonite syenite, which contains a large amount of arfvedsonite (Fig. 3g), and the Mnz-Ia is closely associated with arfvedsonite in most cases. The Mnz-Ia grains are strongly modified by hydrothermal fluids, with a small remnant of monazite, internally altered to apatite and some slight thorite inclusions, and externally dominated by allanite, forming a ring band (Fig. 5a). The Mnz-Ib occurs mainly in fine-grained aegirine-arfvedsonite syenite, and has an apparent core-mantle-rim structure (Fig. 5b). Compared with the Mnz-Ia the Mnz-Ib is less modified by hydrothermal fluid, with a narrower mantle and rim. The core-mantle-rim is monazite, apatite and limonite, respectively, and the modified monazite occasionally forms an irregularly metasomatic residual structure (Fig. 5b). The majority of monazite grains are unaltered or weakly altered and can be classified as type II monazite (Mnz-II), which occur in all types of alkaline rocks in Boziguoer, mainly banded aegirine-arfvedsonite syenite. Compared with the previous two subtypes of

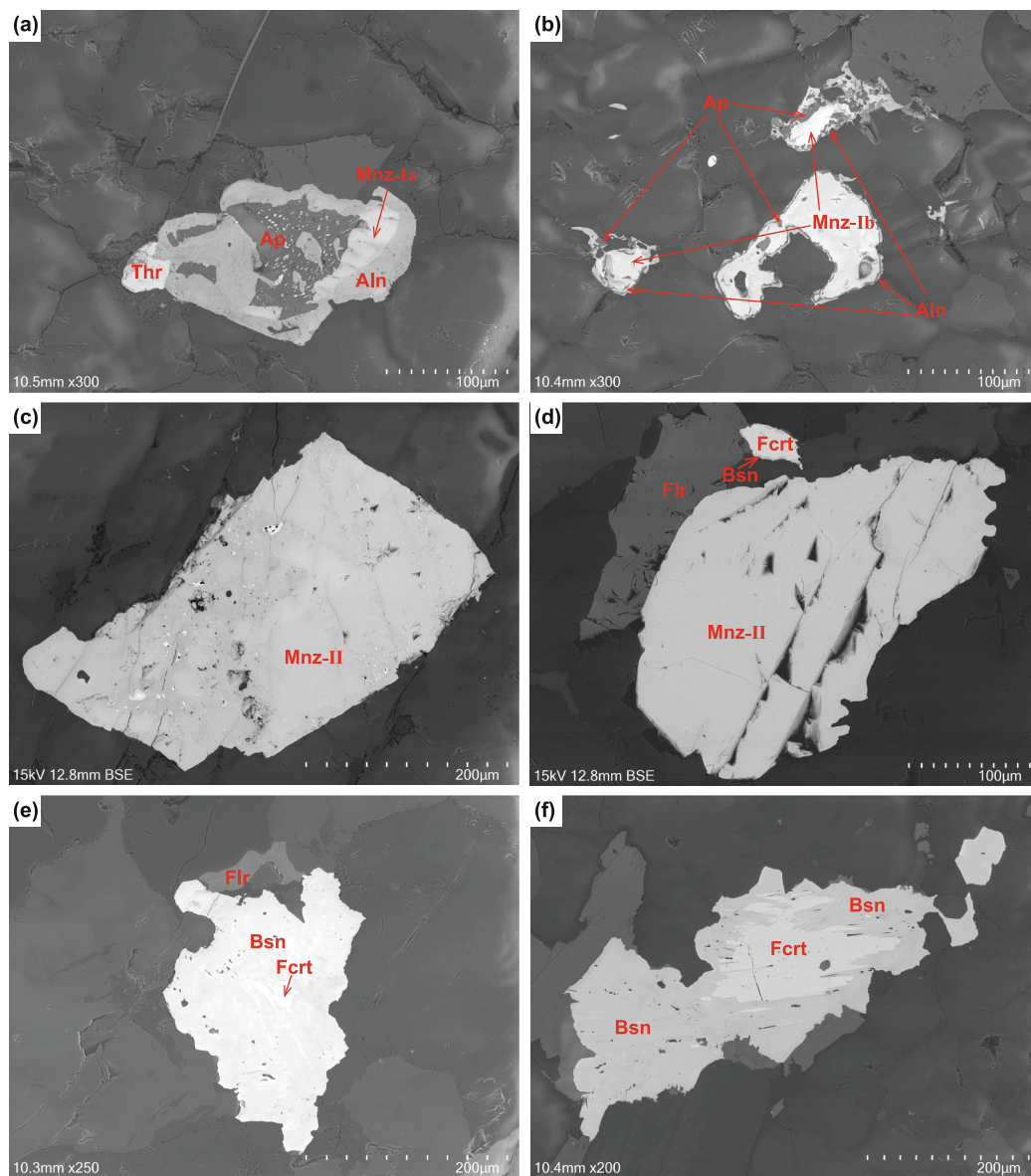


Fig. 5. Representative scanning electron microscope (SEM) back-scattered monazite and bastnäsite grains images. (a–d) Different types of monazite grains, (a) type Mnz-Ia, (b) type Mnz-Ib, (c) and (d) type Mnz-II. (e) and (f) Images showing the core of the residual fluorite with bastnäsite rim to form a light-dark core-rim structure. Mineral abbreviations: Aln-allanite, Ap-apatite, Bsn-bastnäsite, Fcrt-fluocerite, Flr-fluorite, Mnz-monazite.

monazite, the Mnz-II is relatively fresh or weakly altered, with occasional thorite inclusions within, generally occurring as intergranular phases alone or in groups, in co-occurrence with fluorite and fluocerite (Fig. 5c, d).

Bastnäsité is a common accessory mineral in Boziguoer alkaline rocks. It occurs mostly as an intergranular phase in major rock-forming minerals with subhedral to anhedral tabular shapes, ranging in size from 10 to 400 μm . Here, we are concerned with a special bastnäsité, which usually occurs in banded aegirine-arfvedsonite syenite and other rocks and is closely related to fluocerite (Fig. 5e, f). A core-edge structure composed of fluocerite and bastnäsité is occasionally seen, and in the BSE images, the fluocerite core is brighter than the bastnäsité edge (Fig. 5e, f), inferring that the bastnäsité may have formed by the transformation of fluocerite by hydrothermal metasomatism.

4.2. Monazite trace element and U–Th–Pb age analysis

In-situ U–Th–Pb monazite dating was carried out using the LA-ICP-MS method at the Institute of Geology and Geophysics, Chinese Academy of Sciences (IGGCAS). An Agilent 7500a Q-ICP-MS coupled to a 193 nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) was used to determine trace element compositions and U–Th–Pb ages. The analysis was done with a laser beam spot size of 16 μm and frequency of 3 Hz. A matrix matched monazite reference material (RW-1) was used as external standard to correct $^{207}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$, and $^{208}\text{Pb}/^{232}\text{Th}$ ratios. Two RW-1 and multiple groups of standards analyses were measured after every ten samples. All measured $^{207}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$ isotopic ratios of the RW-1 reference material during sample analyses were regressed and corrected following the method of Liu et al. (2012). Trace element concentrations were calibrated using ^{140}Ce as the internal standard (Ce_2O_3 contents were previously measured by EPMA) and ARM-1 (Wu et al., 2019b, 2021) as the external standard material. Isotopic and elemental fractionation plus instrumental mass bias were calibrated using Glitter 4.0 software (Griffin et al., 2008). For multiple groups of standards, we selected the option for the interpolation of linear fit to ratios to perform drift corrections. Signal sections of each analysis were selected independently to get the very similar interval for standards and unknowns. The U–Pb ages and Th–Pb weighted mean ages were calculated using the IsoplotR program (Vermeesch, 2018).

4.3. Bastnäsité trace element and U–Th–Pb age analysis

In-situ U–Th–Pb dating of bastnäsité was carried out using LA-ICP-MS method at the IGGCAS. An Agilent 7500a Q-ICP-MS coupled to a 193 nm ArF excimer laser system (Geolas HD, Lambda Physik, Göttingen, Germany) was used to determine trace element compositions and U–Th–Pb ages, with analyzed laser beam spot of 44 μm and frequency of 5 Hz. A matrix-matched in-house reference material consisting of a crystal of K-9 bastnäsité was used to correct for U–Th–Pb fractionation and instrumental mass discrimination. Two K-9 and LZ1384 analyses were measured after every ten unknown bastnäsité spots. All measured $^{207}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{235}\text{U}$, $^{206}\text{Pb}/^{238}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$ isotopic ratios of the K-9 reference material during sample analyses were regressed and corrected following the method of Yang et al. (2014, 2019). Standard deviations of the calibrated isotope ratios include those from sample, external standard, and deviations from the external reference materials. Considering the lower U content of most bastnäsites, we conducted $^{208}\text{Pb}/^{232}\text{Th}$ age calculation after common ^{207}Pb correction (Yang et al., 2019). Quantitative results for trace elements were obtained via the external calibration of relative elemental sensitivities using the ARM-1 standard (Wu et al., 2019b, 2021) and normalization of each analysis to ^{140}Ce as the internal standard using the Glitter software (Griffin et al., 2008). The Ce_2O_3 content in bastnäsité samples was determined by electron microprobe analysis. The Th–Pb weighted mean ages were calculated using the IsoplotR program (Vermeesch, 2018).

5. Analytical results

5.1. U–Th–Pb ages and geochemistry of monazite

We performed in-situ U–Th–Pb geochronology of different types of monazite grains from the Boziguoer alkaline rocks. The LA-ICP-MS U–Th–Pb data for the monazite is listed in Supplemental Table S1. The U concentrations in monazite grains are too low relative to Th (Th/U ratios range from 42 to 917; Table S1) to derive reliable U–Pb ages, but ^{232}Th are consistently well above the limit of detection.

For the type of Mnz-Ia grains (sample 22BZ11), the U–Pb isotope data on Mnz-Ia define a well-constrained line on the Tera–Wasserburg diagram (Fig. 6a) and yield a lower intercept age of 293.3 ± 3.5 Ma (MSWD = 1.7, 2σ). The analyses of Mnz-Ia show variable abundances of Th (26397–52841 ppm) and U (137–471 ppm) and Th/U ratios of 106–263 (Table S1), which gave a weighted average $^{208}\text{Pb}/^{232}\text{Th}$ age of 291.3 ± 1.3 Ma ($n = 18$, MSWD = 0.50, 2σ) (Fig. 6b). Trace element analysis results of Mnz-Ia show consistent extremely enriched LREE pattern (Fig. 7b), with $(\text{La}/\text{Yb})_N > 10000$ (Table S1). Mnz-Ia also shows significant negative Eu anomalies ($\delta\text{Eu} = 0.09\text{--}0.10$).

The Mnz-Ib grains from sample 22BZ07-2 have Th ranging from 13,993 to 72,727 ppm and U from 87 to 1427 ppm, and Th/U ratios from 42 to 189 (Table S1). Twenty seven analyses on Mnz-Ib grains have defined a well-constrained line on the Tera–Wasserburg diagram (Fig. 6c) and yield a lower intercept age of 287.9 ± 2.9 Ma (MSWD = 3.6, 2σ). Since monazite ^{232}Th – ^{208}Pb age is uniformly distributed, the data yield a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ age of 289.2 ± 1.0 Ma (MSWD = 0.39, 2σ) from the 27 analyses (Fig. 6d). Trace element analysis results of Mnz-Ib grains show that an extremely enriched LREE pattern consistent with that of monazite from sample 22BZ11, with $(\text{La}/\text{Yb})_N > 10000$ and significant negative Eu anomalies ($\delta\text{Eu} = 0.09\text{--}0.10$; Table S1; Fig. 7c).

The Mnz-II grains from sample 22BZ20 have Th and U concentrations ranging from 11,035 to 29,008 ppm and 14 to 145 ppm, respectively, corresponding to the Th/U ratios of 918 to 1282 (Table S1). In the Tera–Wasserburg diagram, sample 22BZ20 obtained lower intercept ages of 280.0 ± 6.4 Ma (MSWD = 4.7, 2σ) (Fig. 6e), as well as weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ ages of 280.5 ± 1.0 Ma ($n = 29$, MSWD = 0.10, 2σ) (Fig. 6f). Trace element analysis results of Mnz-II grains show that they have the same REE pattern, and are strongly enriched in LREE, with $(\text{La}/\text{Yb})_N > 10000$ (only one less than 10000) and significant negative Eu anomalies (22BZ20: $\delta\text{Eu} = 0.08\text{--}0.10$; Table S1; Fig. 7d).

5.2. U–Th–Pb ages and geochemistry of bastnäsité

The LA-ICP-MS U–Th–Pb data for the bastnäsité are listed in Supplemental Table S2. The U concentrations in bastnäsité grains are too low relative to Th (Th/U ratios range from 188 to 4580; Table S2) to derive a reliable U–Pb ages, but ^{232}Th are consistently well above the limit of detection, and the ^{232}Th – ^{208}Pb ages of the analyzed points are uniformly distributed.

The bastnäsité grains from sample 22BZ02 have Th concentrations between 20 and 492 ppm, U between 0.004 and 1.256 ppm and Th/U ratios between 188 and 4580 (Table S2). The analyzed grains yield a weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ ages of 281.4 ± 2.2 Ma ($n = 13$, MSWD = 0.48, 2σ) (Fig. 8a). Trace element analysis results of bastnäsité grains show that they have the same REE pattern, and are strongly enriched in LREE, with high $(\text{La}/\text{Yb})_N$ ratios (>10000 , only one less than 10000) and significant negative Eu anomalies ($\delta\text{Eu} = 0.10\text{--}0.46$; Table S2; Fig. 8b). In addition, in the chondrite-normalized REE patterns for bastnäsité, displays obvious negative Dy anomaly, which indicates that it may have hydrothermal affinity (Fig. 8b).

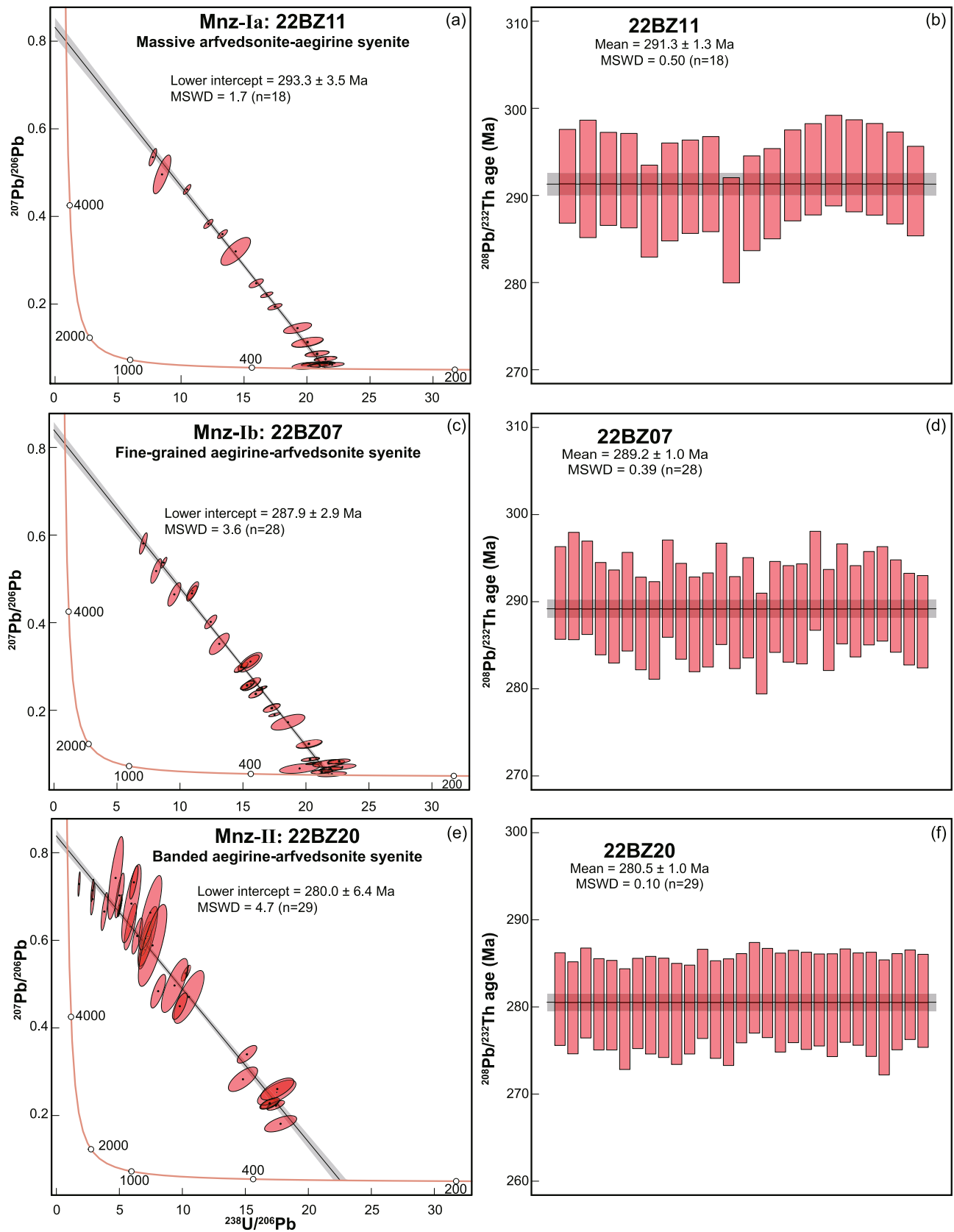


Fig. 6. Tera-Wasserburg concordia diagrams and weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ ages of three types of monazite from the Boziguoer alkaline rocks. MSWD: mean square weighted deviation.

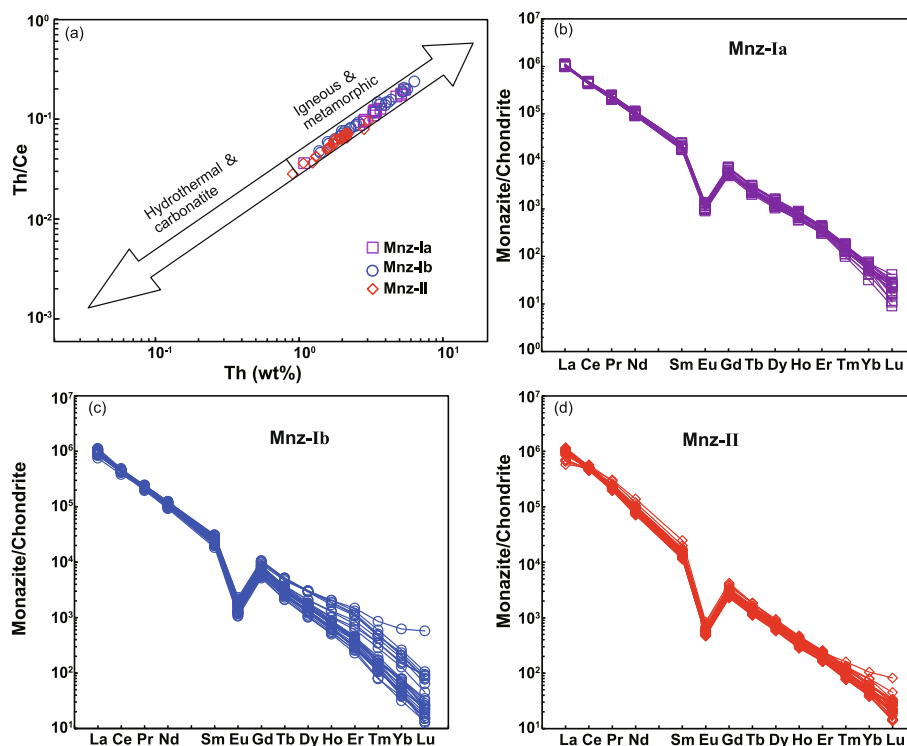


Fig. 7. (a) Monazite origin discrimination plot (modified after Wu et al., 2019a). (b-d) Chondrite-normalized REE distribution pattern diagrams of different types of monazite from Boziguoer alkaline rocks: (b) Mnz-Ia, (c) Mnz-Ib, (d) Mnz-II. Chondrite values are after Sun and McDonough (1989).

6. Discussion

6.1. Genesis of monazite and bastnäsite

Monazite grains in the Boziguoer alkaline rocks are typically present as interstitial minerals in rock-forming minerals (e.g., K-feldspar, albite, aegirine, and arfvedsonite) or occur as inclusions within biotite. In BSE images, monazite exhibits a homogeneous texture, displaying distinct internal features of typical magmatic monazite (Fig. 5a–d; Itano et al., 2018). The difference between magmatic and hydrothermal monazite is that the former has a higher Th content ($\text{ThO}_2 > 1 \text{ wt\%}$; Schandl and Gorton, 2004) and lack of Eu anomalies or only slight Eu anomaly in the latter (Liang et al., 2022). According to geochemical discrimination diagrams in Wu et al., (2019a), all monazite samples in this study fall in the fields defined by rock of igneous and metamorphic origin (Fig. 7a). In addition, monazite from Boziguoer shows elevated Th content (average greater than 27,000 ppm) and pronounced negative Eu anomalies (Fig. 7b–d; $\delta\text{Eu} = 0.08\text{--}0.10$), thereby distinguishing it from metamorphic monazite ($\delta\text{Eu} = 0.1\text{--}0.6$) (Zhu et al., 2019). Hence, all the monazite samples in this study are classified as magmatic monazite.

Bastnäsite typically contains a significant amount of volatile elements (e.g., F and CO_2) that are enriched in late-stage alkalic-hydrothermal fluids, making it a typical hydrothermal mineral (Bau and Dulski, 1995; Agangi et al., 2010; Migdisov and Williams-Jones, 2014). In Boziguoer, the bastnäsite samples commonly partially to completely replace the fluorite as pseudomorphism (Fig. 5e, f). This is generally attributed to a dissolution-reprecipitation mechanism resulting from superimposed fluid processes (Putnis, 2009; Zhang et al., 2023). Fluorite is relatively rare in nature, and it readily reacts with CO_2 to form REE-fluorocarbonate minerals (Strzelecki et al., 2022). Moreover, all analyzed bastnäsite grains exhibit low Th/U ratios (mostly < 1000) and δEu values (Fig. 8c, d), as well as negative Dy anomalies (Fig. 8b), which are markedly different from magmatic bastnäsite (Weng et al., 2022). Therefore, bastnäsite is of hydrothermal origin, and its formation age can represent the timing of hydrothermal activity.

6.2. Geochronological framework of the Boziguoer magmatism-hydrothermal activity and mineralization

Huang et al. (2014) pointed out that rare metal minerals (pyrochlore and zircon) and monazite all crystallized in the magmatic stage and commonly co-existed together, and the post-magmatic hydrothermal process was unlikely to have been crucial in developing REE's economic concentrations. In nature, apatite, allanite, and thorite are the typical products of magmatic-hydrothermal or metamorphic fluid breakdown of monazite, often forming concentric corona surrounding residual monazite cores (e.g., Mnz-Ia and Mnz-Ib; Fig. 5a, b) (Finger et al., 1998; Budzyń et al., 2021). During hydrothermal alteration, monazite may experience variable degrees of Pb-loss, resulting in discordant ages (Budzyń et al., 2021). In this study, both hydrothermally altered Mnz-Ia and Mnz-Ib and relatively fresh Mnz-II exhibit inconsistent concordant ages (Fig. 6a, c, e), indicating limited disturbance of monazite ages by hydrothermal processes, with elevated common Pb content being the main cause of age discordance. Conversely, regardless of the Th content, all types of monazite samples exhibit consistent Th-Pb ages, suggesting that monazite is not affected by deformation or metamorphic overprinting that would affect Pb migration (Song et al., 2017; Fig. 6b, d, f). Therefore, different types of monazite with high Th/U ratios in the Boziguoer alkaline rocks (Table S1) can provide ages representing the timing of the alkalic magma evolution and Nb-Ta-REE mineralization.

Using MetaboAnalyst 5.0 software, the different types of monazite geochemical data (chondrite-normalized REEs, Th and U) in the Boziguoer alkaline rocks, were subjected to various statistical analysis, including Principal Component Analysis (PCA) and Partial Least Squares Discriminant Analysis (PLS-DA). The results indicate that Mnz-Ia and Mnz-Ib can be classified into the same type, exhibiting significant differences from Mnz-II (Fig. 9a, b). The $(\text{Ce}/\text{Gd})_N$ values from Mnz-Ia and Mnz-Ib to Mnz-II initially show a slight decrease followed by a significant increase (Fig. 9c). The decrease in $(\text{Ce}/\text{Gd})_N$ values can possibly be attributed to the fractional crystallization of monazite which can lead to a decrease in Ce content in the melt and thus a lower $(\text{Ce}/\text{Gd})_N$ value

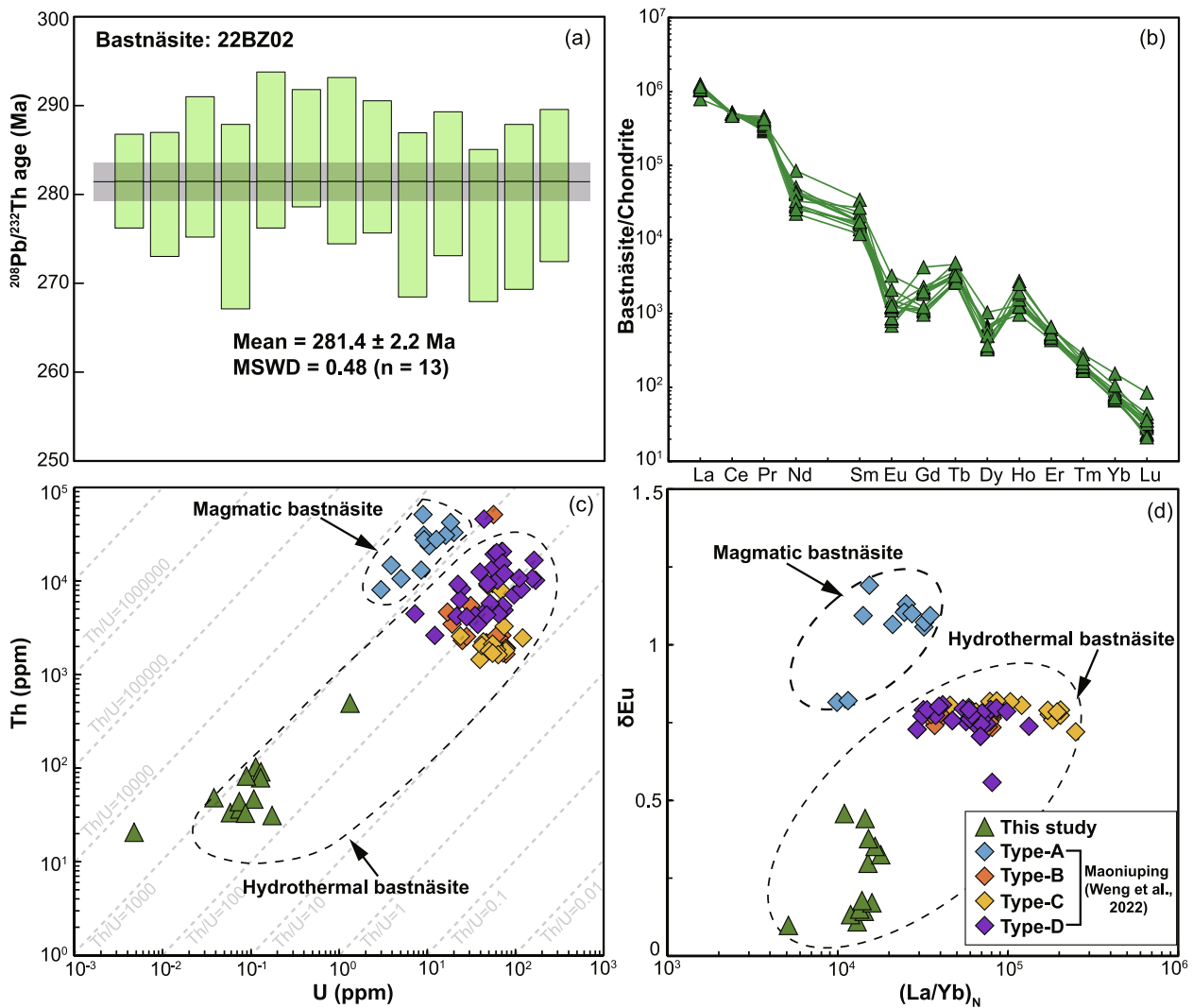


Fig. 8. (a) Diagrams of weighted mean $^{208}\text{Pb}/^{232}\text{Th}$ ages, (b) chondrite-normalized REE distribution patterns diagram, (c) Th (ppm) vs. U (ppm), and (d) δEu vs. $(\text{La}/\text{Yb})_N$ of bastnäsite from the Boziguoer alkaline rocks. Bastnäsite data). MSWD: mean square weighted deviation, chondrite values are after . Source: REE mineralized Maoniuping syenite-carbonatite complex (Weng et al., 2022; Sun and McDonough (1989))

(Stepanov et al., 2012; Fisher et al., 2017; Liu et al., 2022). However, Mnz-II exhibits a significant increase in $(\text{Ce}/\text{Gd})_N$ values (Fig. 9c), which can be attributed to a substantial decrease in melt temperature causing a lower partition coefficient of Gd between monazite and melt (Stepanov et al., 2012; Liu et al., 2022). The $(\text{Th}/\text{U})_N$ values show a similar variation trend from Mnz-Ia and Mnz-Ib to Mnz-II (Fig. 9d). The significant increase in $(\text{Th}/\text{U})_N$ values is also related to the substantial drop in temperature, leading to a decrease in the partition coefficient of Th and U between monazite and melt, but more pronounced effect on U (Beattie et al., 1993; Stepanov et al., 2012; Liu et al., 2022). Therefore, Mnz-Ia and Mnz-Ib can be products of the same crystallization stage, occurring sequentially, while Mnz-II represents late-stage crystallization during magma cooling.

Based on the comprehensive monazite Th-Pb age results, the obtained Th-Pb ages for Mnz-Ia and Mnz-Ib are 291.3 ± 1.3 Ma and 289.2 ± 1.0 Ma, respectively (Fig. 6b, d). These results are consistent with the zircon U-Pb ages of alkaline rocks obtained by Liu et al., (2014a) and Huang et al. (2014), which are ca. 290 Ma. Generally, Mnz-Ia may have crystallized slightly earlier than Mnz-Ib, so Mnz-Ia underwent a relatively higher degree of hydrothermal alteration (Fig. 5a, b). The Th-Pb age of Mnz-II is 280.5 ± 1.0 Ma (Fig. 6f), significantly younger than those of Mnz-Ia and Mnz-Ib. Therefore, it can be inferred that the evolution of the Boziguoer alkalic magma spanned a long duration. The

presence of common fluorite in the Boziguoer alkaline rocks (Fig. 3k, 5d, e) indicates the enrichment of volatiles in alkalic magma, and the presence of volatiles could extend the crystallization time to lower temperature stages (Markl et al., 2001) and inhibit the premature crystallization of the HFSE and REE minerals until the crystallization of the RM (e.g., pyrochlore) and REE minerals (e.g., monazite) (Halter and Webster, 2004). This explains the prolonged evolution of the Boziguoer alkalic magma and demonstrates that the significant increase in $(\text{Ce}/\text{Gd})_N$ and $(\text{Th}/\text{U})_N$ values in Mnz-II is attributed to a substantial decrease in melt temperature (Fig. 9c, d).

The Th-Pb age of hydrothermal bastnäsite in the Boziguoer alkaline rocks is 281.4 ± 2.2 Ma (Fig. 8a), which is close to the age of Mnz-II within the error range. Additionally, Liu et al., (2014a) reported hydrothermal activity in the rock formation during a period of 279–282 Ma. These pieces of evidence suggest that the hydrothermal activity during that period may correspond to late-stage hydrothermal processes following magma evolution, wherein the superimposed hydrothermal effects led to the dissolution-precipitation formation of bastnäsite along previously formed fluorite.

In summary, integrating previous studies on the age of the Boziguoer alkaline rocks and our newly obtained data can effectively reveal the fundamental framework of magma-hydrothermal evolution and mineralization in the Boziguoer deposit. From approximately 290–280 Ma, the

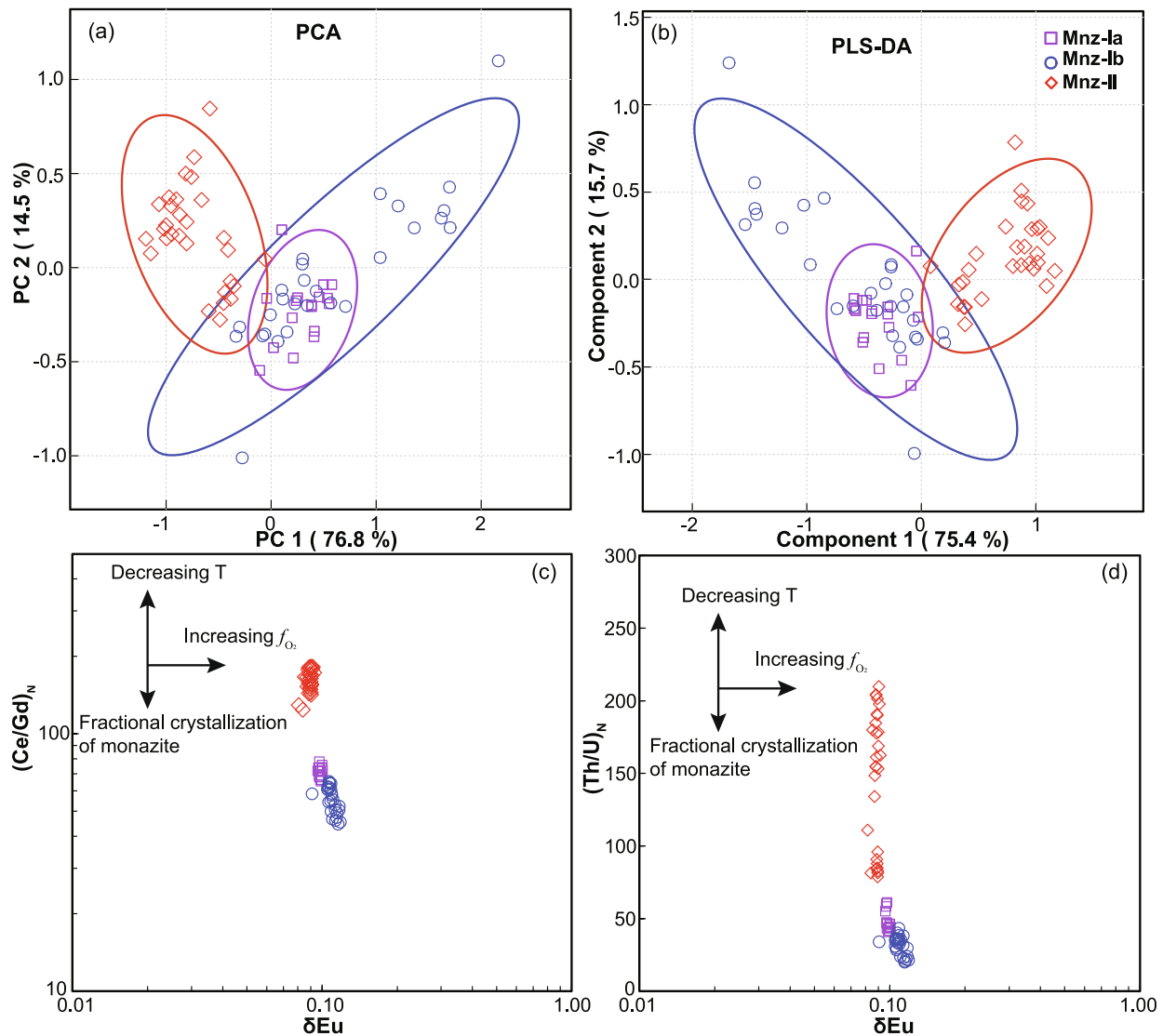


Fig. 9. (a-b) Diagrams of principal component analysis (PCA) and partial least squares-discriminant analysis (PLS-DA) of the different types of monazite REE-Th-U content, after chondrite normalization and logarithmic transformation (Table S1) with the program MetaboAnalyst 5.0. (c-d) Plots of (Ce/Gd)_N and (Th/U)_N vs. δEu for different types of monazite. Chondrite values are after Sun and McDonough (1989).

Boziguoer alkalic magma underwent evolution from early to late stages, during which the RM minerals (e.g., pyrochlore, zircon) primarily formed. Some REE minerals, such as monazite, fluocerite, xenotime and bastnäsite, also formed during this stage. Subsequently, around 280 Ma, magmatic-hydrothermal fluids were exsolved, containing a significant amount of volatiles (e.g., F, CO₂). These fluids interacted with previously crystallized minerals such as zircon, monazite, fluocerite, and arfvedsonite (Fig. 3e, 5a, b, e, f). Through the dissolution-precipitation mechanism, these minerals, especially REE minerals, underwent alteration and gave rise to hydrothermal minerals (e.g., allanite, bastnäsite, and apatite). Therefore, the primary monazite and hydrothermal bastnäsite in the Boziguoer deposit indicate a continuous RM-REE mineralization process during the alkalic magma and hydrothermal evolution.

6.3. Tectonic setting and metallogenetic model

As mentioned above, the Boziguoer alkaline magmatic evolution lasted for at least 10 Ma, from ca. 290 Ma to ca. 280 Ma, consistent with the timing of TLIP magmatic activity and spatially adjacent, indicating a strong genetic connection with mantle plume (Fig. 1b). Additionally, the

formation of alkaline rocks is generally associated with rift or intraplate extensional settings caused by mantle plume or hotspot (Dostal, 2016). Liu et al., (2014a) plotted the Boziguoer alkaline rock samples in Nb-Y-Ce and Nb-Y-3 Ga ternary diagrams, indicating that they belong to A1-type alkaline granite, which forms in non-orogenic continental rift or mantle plume setting (Eby, 1992). Therefore, the Boziguoer mineralized alkaline pluton formed in a tectonic setting of intraplate extension induced by mantle plume, disrupting the normal sequence of collisional orogeny event (Han et al., 2019; Zhang et al., 2019). The Boziguoer, together with other alkaline plutons on the northern margin of the TC (e.g., Yilanlik, Bashisuogong, Halajun), forms an alkaline belt dominated by early Permian ages (Xie et al., 2022; Sun et al., 2022). These alkaline plutons, distributed in the STOB, adjacent to the TLIP, with periods close to that of Boziguoer, mainly formed between 280–270 Ma, are both products of mantle plume activity (Xie et al., 2022).

Regarding the incompatibility of HFSEs and REEs, these elements are incorporated into the crystal structures of early-crystallized minerals with difficulty but undergo significant enrichment as magma evolves (Vasyukova and Williams-Jones, 2020). Therefore, prolonged fractional crystallization is a crucial factor in the substantial enrichment and mineralization of these incompatible elements (Linnen and Cuney,

Due to the entire pluton mineralization of the Boziguoer alkaline rock intrusion, the pluton formation controlled the formation of the Boziguoer Nb-Ta-Rb-Zr-REE deposit. Based on the above discussion, the following is a proposed RM-REE metallogenic model for the Boziguoer deposit: (1) Ca. 300–290 Ma, an upwelling mantle plume was present beneath the TC, triggering large-scale magmatic activities. The South Tianshan belt, situated in the tectonically active zone influenced by the mantle plume, experienced low-degree partial melting of sub-continental lithospheric mantle (SCLM) which had previously undergone metasomatism and reworking by subduction-related sediments and recycled oceanic crust, leading to form enriched in HFSEs (Nb, Ta, Zr, Hf), REEs, and volatiles primitive Boziguoer magma. (2) The primitive magma further evolved and differentiated as it ascended along deep fault into the middle crustal magma chamber. High contents of volatile components (e.g., F) increased the solubility of HFSEs and REEs, enriching these elements in the late, evolved melt (Fig. 10a). (3) The residual melt in the magma chamber intruded into the Upper Silurian marble along structurally weak zones (Fig. 10a). Sufficient magmatic

evolution and fractional crystallization (crystallization of minerals like albite, K-feldspar, magnetite, and arfvedsonite) have significantly concentrated HFSEs and REEs in the residual magma. (4) Subsequent cooling of the melt resulted in the gradual crystallization of RM-REE complexes saturated in the magma, RM minerals (e.g., pyrochlore, zircon) and REE minerals (e.g., fluocerite, monazite, bastnäsite) that usually exist as interstitial minerals of early crystallizing phases (Fig. 10b). (5) Ca. 280 Ma, the Bozigueroer alkalic magma evolved to the late stage, and Mnz-II was formed during this period. Post-magmatic hydrothermal fluid exsolution and astrophyllite (Rb) were basically formed at this stage. Fluoride- and CO₂-enriched hydrothermal fluid interacted with and subsequently modified the early-crystallized ore minerals (e.g., bastnäsite, fluocerite, zircon, and pyrochlore), forming a series of hydrothermal minerals (e.g., apatite, allanite, bastnäsite, and fluorite) and finally forming the Bozigueroer Nb-Ta-Rb-Zr-REE deposit (Fig. 10c).

The study demonstrates that monazite and bastnäsite can serve as potential indicators of magmatic-hydrothermal evolution and related RM-REE mineralization processes. In the Boziguoe Nb-Ta-Rb-Zr-REE

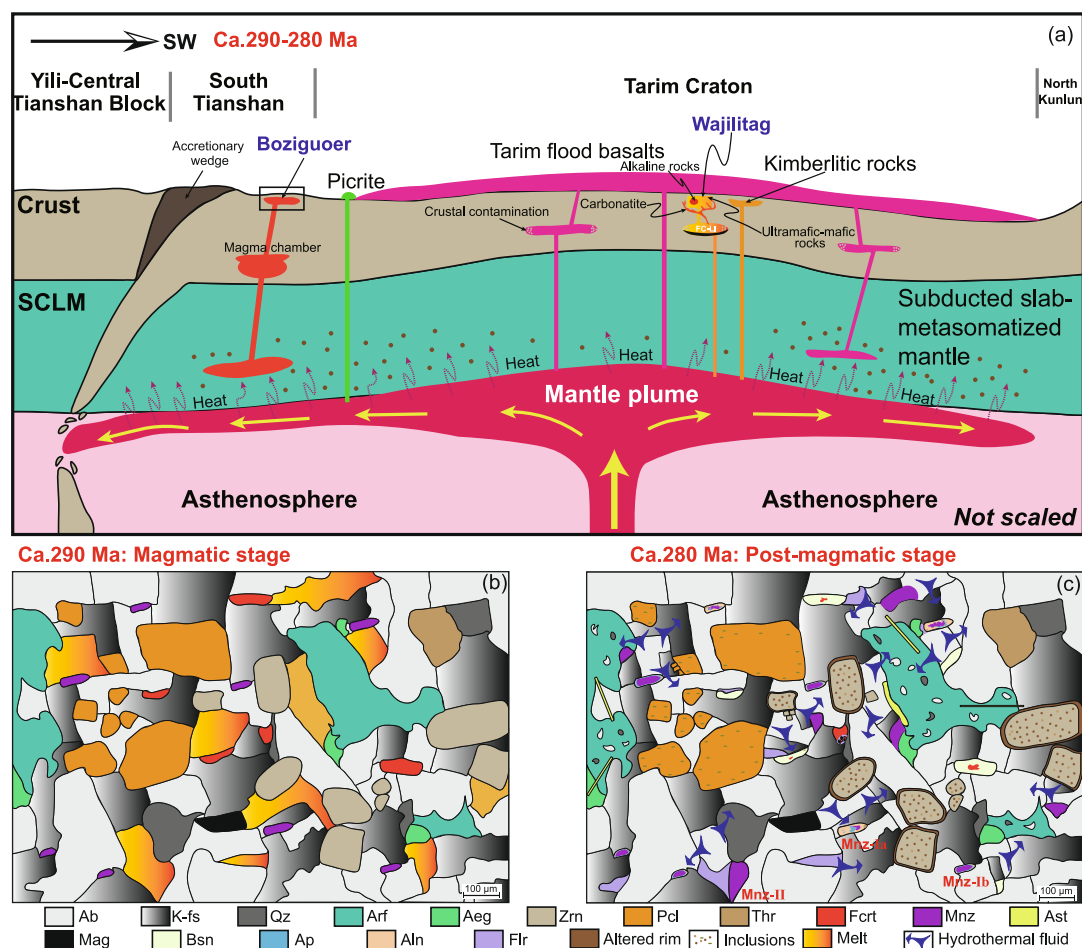


Fig. 10. Schematic metallogenetic model illustrating the formation of the Boziguouer Nb-Ta-Rb-Zr-REE deposit related to mantle plume. (a) Early Permian low-degree partial melting of previously metasomatized SCLM, triggered by the upwelling mantle plume which interrupted the collision orogeny, giving rise to the rare metal-REE ore-bearing Boziguouer alkaline intrusion in the STOB, north TLIP (modified from [Zhang et al., 2016](#); [Han et al., 2019](#)). (b) At ca. 290 Ma, temperature decreases and saturation of metallogenetic elements in the magma, resulting in the gradual crystallization of rare metal minerals (e.g., pyrochlore, zircon) and REE minerals (e.g., fluorocrite, monazite), usually existing as interstitial minerals of early crystallizing phases. (c) At ca. 280 Ma, late-stage evolution of alkalic magma, accompanied by the formation of Mnz-II, exsolution of hydrothermal fluid and formation of astrophyllite (enriched in Rb). Interaction of F- and CO₂-enriched hydrothermal fluid with and subsequent modification of the early-crystallized ore minerals (e.g., bastnäsite, fluorocrite, zircon, and pyrochlore), forming a series of hydrothermal minerals (e.g., apatite, allanite, bastnäsite, and fluorite). Mineral abbreviations: Ab-albite, Aeg-aegirine, Aln-allanite, Ap-apatite, Arf-arfvedsonite, Ast-astrophyllite, Bsn-bastnäsite, Fcrt-fluocrite, Flr-fluorite, Kfs-K-feldspar, Mag-magnetite, Mnz-monazite, Pcl-pyrochlore, Qz-quartz, Thr-thorite, Zrn-zircon.

deposit, monazite and bastnäsite are the main REE minerals, with monazite divided into two types based on microstructure and geochemistry. Combining their paragenetic relationships and compositional variations, all two types of monazite are considered to have originated from primary magmatic processes, while bastnäsite is of hydrothermal origin. In-situ LA-ICP-MS U-Th-Pb geochronology of monazite and bastnäsite indicates that the ages of Mnz-Ia and Mnz-Ib are ca. 290 Ma, indicating that the crystallization of Mnz-Ia and Mnz-Ib is in sequence but consistent with zircon age. On the other hand, the ages of Mnz-II, which crystallized after significant cooling is close to that of bastnäsite, about 280 Ma, indicating a continuous RM-REE mineralization during the magmatic-hydrothermal evolution at Boziguoer. Therefore, post-magmatic hydrothermal processes play an important role in the mineralization process at Boziguoer.

The magmatic-hydrothermal evolution of the Boziguoer alkaline rocks occurred during the same period as the peak magmatic activity of the TLIP (290–280 Ma). Therefore, the upwelling mantle plume in the Early Permian triggered low-degree partial melting of the SCLM, which had previously undergone metasomatism and reworking due to subduction-related sediments and recycled oceanic crust. This process led to forming the Boziguoer primitive magma enriched in HFSEs (Nb, Ta, Zr, Hf), REEs, and volatiles. Through a series of magmatic evolution and hydrothermal fluid processes, the ore-forming elements were further activated, migrated, enriched, and precipitated in tectonically weak zones, forming the Boziguoer RM-REE ore deposit.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.oregeorev.2024.106034>.

References

Agangi, A., Kamenetsky, V.S., McPhie, J., 2010. The role of fluorine in the concentration and transport of lithophile trace elements in felsic magmas: insights from the Gawler Range Volcanics, South Australia. *Chem. Geol.* 273, 314–325.
 Alexeiev, D.V., Biske, Y.S., Wang, B., Djenchuraeva, A.V., Getman, O.F., Aristov, V.A., Kroener, A., Liu, H., Zhong, L., 2015. Tectono-Stratigraphic framework and Palaeozoic evolution of the Chinese South Tianshan. *Geotectonics* 49, 93–122.

Bailey, J.C., Gwozdz, R., Rose-Hansen, J., Sørensen, H., 2001. Geochemical overview of the Ilímaussaq alkaline complex, South Greenland. *Geol. Greenl. Surv. Bull.* 190, 35–53.
 Bau, M., Dulski, P., 1995. Comparative study of yttrium and rare-earth element behaviours in fluorine-rich hydrothermal fluids. *Contrib. Mineral. Petrol.* 119, 213–223.
 Beard, C.D., Goodenough, K.M., Borst, A.M., Wall, F., Siegfried, P.R., Deady, E.A., Pohl, C., Hutchison, W., Finch, A.A., Walter, B.F., Elliott, H.A.L., Brauch, K., 2023. Alkaline-Silicate REE-HFSE Systems. *Econ. Geol.* 118, 177–208.
 Beattie, P., Drake, M., Jones, J., Leeman, W., Longhi, J., McKay, G., Nielsen, R., Palme, H., Shaw, D., Takahashi, E., 1993. Terminology for trace-element partitioning. *Geochim. Cosmochim. Acta* 57, 1605–1606.
 Bernard, C., Estrade, G., Salvi, S., Béziat, D., Smith, M., 2020. Alkali pyroxenes and amphiboles: a window on REE and other HFSE behavior through the magmatic hydrothermal transition of peralkaline granitic systems. *Contrib. Mineral. Petrol.* 175, 81.
 Budzyń, B., Wirth, R., Sláma, J., Birska, L., Tramm, F., Kozub-Budzyń, G.A., Rzepa, G., Schreiber, A., 2021. LA-ICPMS, TEM and Raman study of radiation damage, fluid-induced alteration and disturbance of U-Pb and Th-Pb ages in experimentally metasomatised monazite. *Chem. Geol.* 583, 120464.
 Cawood, P.A., Kröner, A., Collins, W.J., Kusky, T.M., Mooney, W.D., Windley, B.F., 2009. Accretionary orogens through Earth history. *Geol. Soc. Spec. Publ.* 318, 1–36.
 Černý, P., Blevin, P.L., Cuney, M., London, D., 2005. Granite-related ore deposits. In: Hedenquist, J.W., Thompson, J.F.H., Goldfarb, R.J., Richards, J.P. (Eds.), *One Hundredth Anniversary Volume. Soc. Econ. Geol., Littleton*, pp. 337–370.
 Collins, W.J., Beams, S.D., White, A.J.R., Chappell, B.W., 1982. Nature and origin of A-type granites with particular reference to southeastern Australia. *Contrib. Mineral. Petrol.* 80, 189–200.
 Dostal, J., 2016. Rare Metal Deposits Associated with Alkaline/Peralkaline Igneous Rocks. In: Verplanck, P.L., Hitzman, M.W. (Eds.), *Rare Earth and Critical Elements in Ore Deposits. Soc. Econ. Geol., Littleton*, pp. 33–54.
 Dostal, J., 2017. Rare Earth Element Deposits of Alkaline Igneous Rocks. *Resources* 6, 1–12.
 Eby, G.N., 1992. Chemical subdivision of the A-type granitoids: Petrogenetic and tectonic implications. *Geology* 20, 641–644.
 Finger, F., Broska, I., Roberts, M.P., Schermaier, A., 1998. Replacement of primary monazite by apatite-allanite-epidote coronas in an amphibolite facies granite gneiss from the eastern Alps. *Am. Mineral.* 83, 248–258.
 Fisher, C.M., Hanchar, J.M., Miller, C.F., Phillips, S., Vervoort, J.D., Whitehouse, M.J., 2017. Combining Nd isotopes in monazite and Hf isotopes in zircon to understand complex open-system processes in granitic magmas. *Geology* 45, 267–270.
 Gao, J., Long, L.L., Klemm, R., Qian, Q., Liu, D.Y., Xiong, X.M., Su, W., Liu, W., Wang, Y.T., Yang, F.Q., 2009. Tectonic evolution of the South Tianshan orogen and adjacent regions, NW China: geochemical and age constraints of granitoid rocks. *Int. J. Earth Sci.* 98, 1221–1238.
 Gao, J., Klemm, R., Qian, Q., Zhang, X., Li, J.L., Jiang, T., Yang, Y.Q., 2011. The collision between the Yili and Tarim blocks of the Southwestern Tianshan: geochemical and age constraints of a leucogranite dike crosscutting the HP–LT metamorphic belt in the Chinese Tianshan Orogen. *Tectonophysics* 499, 118–131.
 Gonçalves, G.O., Lana, C., Scholz, R., Buick, I.S., Gerdes, A., Kamo, S.L., Corfu, F., Marinho, M.M., Chaves, A.O., Valeriano, C., 2016. An assessment of monazite from the Itambé pegmatite district for use as U-Pb isotope reference material for microanalysis and implications for the origin of the “Moacyr” monazite. *Chem. Geol.* 424, 30–50.
 Goodenough, K., Schilling, J., Jonsson, E., Kalvig, P., Charles, N., Tuduri, J., Deady, E., Sadeghi, M., Schiellerup, H., Müller, A., 2016. Europe's rare earth element resource potential: An overview of REE metallogenetic provinces and their geodynamic setting. *Ore Geol. Rev.* 72, 838–856.
 Griffin, W., Powell, W., Pearson, N.J., O'Reilly, S., 2008. GLITTER: data reduction software for laser ablation ICP-MS. In: Sylvester, P. (Ed.), *Laser Ablation-ICP-MS in the Earth Sciences: Current Practices and Outstanding Issues*, pp. 308–311.
 Halter, W.E., Webster, J.D., 2004. The magmatic to hydrothermal transition and its bearing on ore-forming systems. *Chem. Geol.* 210, 1–6.
 Han, B.F., He, G.Q., Wang, X.C., Guo, Z.J., 2011. Late Carboniferous collision between the Tarim and Kazakhstan-Yili terranes in the western segment of the South Tianshan Orogen, Central Asia, and implications for the Northern Xinjiang, western China. *Earth-Sci. Rev.* 109, 74–93.
 Han, C.M., Xiao, W.J., Su, B.X., Asamoah, S.P., Ao, S.J., Zhang, J.E., Wan, B., Song, D.F., Zhang, Z.Y., Wang, Z.M., Xie, M.C., 2020. Late Paleozoic metallogenesis and evolution of the Chinese Western Tianshan Collage, NW China, Central Asia orogenic belt. *Ore Geol. Rev.* 124, 103643.
 Han, Y.G., Zhao, G.C., Cawood, P.A., Sun, M., Liu, Q., Yao, J.L., 2019. Plume-modified collision orogeny: The Tarim–western Tianshan example in Central Asia. *Geology* 47, 1001–1005.
 Hegner, E., Klemm, R., Kroener, A., Corsini, M., Alexeiev, D.V., Iaccheri, L.M., Zack, T., Dulski, P., Xia, X., Windley, B.F., 2010. Mineral ages and P-T conditions of Late Paleozoic high-pressure eclogite and provenance of mélange sediments from Athasi in the south Tianshan orogen of Kyrgyzstan. *Am. J. Sci.* 310, 916–950.
 Huang, H., Zhang, Z., Kusky, T., Santosh, M., Zhang, S., Zhang, D., Liu, J., Zhao, Z., 2012. Continental vertical growth in the transitional zone between South Tianshan and Tarim, western Xinjiang, NW China: Insight from the Permian Halajun A1-type granitic magmatism. *Lithos* 155, 49–66.
 Huang, H., Zhang, Z.C., Santosh, M., Zhang, D.Y., Zhao, Z.D., Liu, J.L., 2013. Early Paleozoic Tectonic Evolution of the South Tianshan Collisional Belt: Evidence from Geochemistry and Zircon U-Pb Geochronology of the Tie'oke Monzonite Pluton, Northwest China. *J. Geol.* 121, 401–424.

- Huang, H., Zhang, Z.C., Santosh, M., Zhang, D.Y., 2014. Geochronology, geochemistry and metallogenic implications of the Boziguo'er rare metal-bearing peralkaline granitic intrusion in South Tianshan. NW China. *Ore Geol. Rev.* 61, 157–174.
- Huang, H., Zhang, Z.C., Santosh, M., Zhang, D.Y., Wang, T., 2015. Petrogenesis of the Early Permian volcanic rocks in the Chinese South Tianshan: Implications for crustal growth in the Central Asian Orogenic Belt. *Lithos* 228, 23–42.
- Huang, H., Wang, T., Zhang, Z.C., Li, C., Qin, Q., 2018. Highly differentiated fluorine-rich, alkaline granitic magma linked to rare metal mineralization: A case study from the Boziguo'er rare metal granitic pluton in South Tianshan Terrane, Xinjiang. NW China. *Ore Geol. Rev.* 96, 146–163.
- Itano, K., Iizuka, T., Hoshino, M., 2018. REE-Th-U and Nd isotope systematics of monazites in magnetite-and ilmenite-series granitic rocks of the Japan arc: Implications for its use as a tracer of magma evolution and detrital provenance. *Chem. Geol.* 484, 69–80.
- Jahn, B., 2004. Phanerozoic continental growth in Central Asia. *J. Asian Earth Sci.* 23, 599–603.
- Jiang, T., Gao, J., Klemd, R., Qian, Q., Zhang, X., Xiong, X.M., Wang, X.S., Tan, Z., Chen, B.X., 2014. Paleozoic ophiolitic melanges from the South Tianshan Orogen, NW China: Geological, geochemical and geochronological implications for the geodynamic setting. *Tectonophysics* 612, 106–127.
- Kogarko, L., 1990. Ore-forming potential of alkaline magmas. *Lithos* 26, 167–175.
- Konopelko, D., Biske, G., Seltmann, R., Eklund, O., Belyatsky, B., 2007. Hercynian post-collisional A-type granites of the Kokshaal Range, Southern Tien Shan, Kyrgyzstan. *Lithos* 97, 140–160.
- Kovalenko, V., Yarmolyuk, V., Kozlovsky, A., Kovach, V., Sal'nikova, E., Kotov, A., Vladyskin, N., 2007. Two types of magma sources of rare-metal alkali granites. *Geol. Ore Depos.* 49, 442–466.
- Kröner, A., Alexeev, D., Rojas-Agramonte, Y., Hegner, E., Wong, J., Xia, X., Belousova, E., Mikolaichuk, A., Seltmann, R., Liu, D., 2013. Mesoproterozoic (Grenville-age) terranes in the Kyrgyz North Tianshan: zircon ages and Nd-Hf isotopic constraints on the origin and evolution of basement blocks in the southern Central Asian Orogen. *Gondwana Res.* 23, 272–295.
- Li, Z.L., Chen, H.L., Song, B., Li, Y.Q., Yang, S.F., Yu, X., 2011. Temporal evolution of the Permian large igneous province in Tarim Basin in northwestern China. *J. Asian Earth Sci.* 42, 917–927.
- Li, Y.Q., Li, Z.L., Yu, X., Langmuir, C.H., Santosh, M., Yang, S.F., Chen, H.L., Tang, Z.L., Song, B., Zou, S.Y., 2014. Origin of the Early Permian zircons in Keping basalts and magma evolution of the Tarim Large Igneous Province (northwestern China). *Lithos* 204, 47–58.
- Liang, X., Xu, Y.J., Zi, J.W., Zhang, H.C., Du, Y.S., 2022. Genetic Mineralogy of Monazite and Constraints on Interpretation of U-Th-Pb Ages. *Earth Sci.* 47, 1383–1398 in Chinese with English abstract.
- Lin, W., Chu, Y., Ji, W.B., Zhang, Z.P., Shi, Y.H., Wang, Z.Y., Li, Z., Wang, Q.C., 2013. Geochronological and geochemical constraints for a middle Paleozoic continental arc on the northern margin of the Tarim block: Implications for the Paleozoic tectonic evolution of the South Chinese Tianshan. *Lithosphere* 5, 355–381.
- Ling, X.X., Li, Q.L., Liu, Y., Yang, Y.H., Tang, G.Q., Li, X.H., 2016. In situ SIMS Th-Pb dating of bastnaesite: constraint on the mineralization time of the Himalayan Mianning-Dechang rare earth element deposits. *J. Anal. at. Spectrom.* 31, 1680–1687.
- Linnen, R.L., Cuney, M., 2005. Granite-related rare-element deposits and experimental constraints on Ta-Nb-W-Sn-Zr-Hf mineralization. In: Linnen, R.L., Samson, I.M. (Eds.), *Rare-Element Geochemistry and Mineral Deposits*, Geological Association of Canada. GAC, Short Course.
- Liu, D.D., Guo, Z.J., Jolivet, M., Cheng, F., Song, Y., Zhang, Z.Y., 2014b. Petrology and geochemistry of Early Permian volcanic rocks in South Tian Shan, NW China: implications for the tectonic evolution and Phanerozoic continental growth. *Int. J. Earth Sci.* 103, 737–756.
- Liu, X.H., Li, B., Xu, J.W., He, B., Liao, J., Peng, H.W., Wang, Y.H., Lai, J.Q., 2022. Monazite geochronology and geochemistry constraints on the formation of the giant Zhengchong Li-Rb-Cs deposit in South China. *Ore Geol. Rev.* p. 150.
- Liu, Z.C., Wu, F.Y., Yang, Y.H., Yang, J.H., Wilde, S.A., 2012. Neodymium isotopic compositions of the standard monazites used in U-Th-Pb geochronology. *Chem. Geol.* 334, 221–239.
- Liu, C.H., Wu, C.L., Gao, Y.H., Lei, M., Qin, H.P., Li, M.Z., 2014a. Zircon LA-ICP-MS U-Pb dating and Lu-Hf isotopic system of A-type granitoids in South Tianshan, Baicheng County. Xinjiang. *Acta Petrol. Sin.* 30, 1595–1614 in Chinese with English abstract.
- London, D., Morgan, G.B., 2012. The pegmatite puzzle. *Elements* 8, 263–268.
- Lu, S.N., Li, H.K., Zhang, C.L., Niu, G.H., 2008. Geological and geochronological evidence for the Precambrian evolution of the Tarim Craton and surrounding continental fragments. *Precambrian Res.* 160, 94–107.
- Ma, Y., Zhang, Z.C., Huang, H., Santosh, M., Cheng, Z.G., 2016. Petrogenesis of the Bashisuogong bimodal igneous complex in southwest Tianshan Mountains, China: Implications for the Tarim Large Igneous Province. *Lithos* 264, 509–523.
- Markl, G., Marks, M., Schwinn, G., Sommer, H., 2001. Phase equilibrium constraints on intensive crystallization parameters of the Ilímaussaq Complex, South Greenland. *J. Petrol.* 42, 2231–2257.
- Markl, G., Marks, M.A.W., Frost, B.R., 2010. On the Controls of Oxygen Fugacity in the Generation and Crystallization of Peralkaline Melts. *J. Petrol.* 51, 1831–1847.
- Migdisov, A.A., Williams-Jones, A.E., 2014. Hydrothermal transport and deposition of the rare earth elements by fluorine-bearing aqueous liquids. *Miner. Depos.* 49, 987–997.
- Müehlberg, M., Hegner, E., Klemd, R., Pfaender, J.A., Kaliwoda, M., Biske, Y.S., 2016. Late Carboniferous high-pressure metamorphism of the Kassin Metamorphic Complex (Kyrgyz Tianshan) and assembly of the SW Central Asian Orogenic Belt. *Lithos* 264, 41–55.
- Piechocka, A.M., Gregory, C.J., Zi, J.-W., Sheppard, S., Wingate, M.T., Rasmussen, B., 2017. Monazite trumps zircon: applying SHRIMP U-Pb geochronology to systematically evaluate emplacement ages of leucocratic, low-temperature granites in a complex Precambrian orogen. *Contrib. Mineral. Petrol.* 172, 1–17.
- Putnis, A., 2009. Mineral replacement reactions. *Rev. Mineral. Geochem.* 70, 87–124.
- Qian, Q., Gao, J., Klemd, R., He, G.Q., Song, B., Liu, D.Y., Xu, R.H., 2009. Early Paleozoic tectonic evolution of the Chinese South Tianshan Orogen: constraints from SHRIMP zircon U-Pb geochronology and geochemistry of basaltic and dioritic rocks from Xiata. NW China. *Int. J. Earth Sci.* 98, 551–569.
- Qin, K.Z., Su, B.X., Sakyi, P.A., Tang, D.M., Li, X.H., Sun, H., Xiao, Q.H., Liu, P.P., 2011. SIMS zircon U-Pb geochronology and Sr-Nd isotopes of Ni-Cu-Bearing Mafic-Ultramafic Intrusions in Eastern Tianshan and Beishan in correlation with flood basalts in Tarim Basin (NW China): Constraints on a ca. 280 Ma mantle plume. *Am. J. Sci.* 311, 237–260.
- Rusiecka, M.K., Baker, D.R., 2019. Monazite and xenotime solubility in hydrous, boron-bearing rhyolitic melt. *Am. Mineral.* 104, 1117–1130.
- Safonova, I., Biske, G., Romer, R.L., Seltmann, R., Simonov, V., Maruyama, S., 2016. Middle Paleozoic mafic magmatism and ocean plate stratigraphy of the South Tianshan. *Kyrgyzstan. Gondwana Res.* 30, 236–256.
- Sal'nikova, E., Yakovleva, S., Nikiforov, A., Kotov, A., Yarmolyuk, V., Anisimova, I., Sugorakova, A., Plotkina, Y.V., 2010. Bastnaesite: a promising U-Pb geochronological tool. Springer Nature BV, Doklady earth sciences, p. 134.
- Salvi, S., Williams-Jones, A.E., Linnen, R., Samson, I., 2005. Alkaline granite-syenite deposits. *Geological Association of Canada Short Course Notes* 17, 315–341.
- Schandl, E.S., Gorton, M.P., 2004. A TEXTURAL AND GEOCHEMICAL GUIDE TO THE IDENTIFICATION OF HYDROTHERMAL MONAZITE: CRITERIA FOR SELECTION OF SAMPLES FOR DATING EPIGENETIC HYDROTHERMAL ORE DEPOSITS. *Econ. Geol.* 99, 1027–1035.
- Schilling, J., Wu, F.Y., Mccammon, C., Wenzel, T., Marks, M.A.W., Pfaff, K., Jacob, D.E., Markl, G., 2011. The compositional variability of eudialyte-group minerals. *Mineral. Mag.* 75, 87–115.
- Seltmann, R., Konopelko, D., Biske, G., Divaev, F., Sergeev, S., 2011. Hercynian post-collisional magmatism in the context of Paleozoic magmatic evolution of the Tien Shan orogenic belt. *J. Asian Earth Sci.* 42, 821–838.
- Şengör, A., Natal'In, B., Burtman, V., 1993. Evolution of the Altaid tectonic collage and Palaeozoic crustal growth in Eurasia. *Nature* 364, 299–307.
- Siegel, K., Vasyukova, O.V., Williams-Jones, A.E., 2018. Magmatic evolution and controls on rare metal-enrichment of the Strange Lake A-type peralkaline granitic pluton, Québec-Labrador. *Lithos* 308, 34–52.
- Smith, M.P., Moore, K., Kavecsánszki, D., Finch, A.A., Kynicky, J., Wall, F., 2016. From mantle to crustal zone: A review of large and giant sized deposits of the rare earth elements. *Geosci. Front.* 7, 315–334.
- Sokó, K., Finch, A.A., Hutchison, W., Cloutier, J., Borst, A.M., Humphreys, M.C.S., 2021. Quantifying metasomatic high-field-strength and rare-earth element transport from alkaline magmas. *Geology* 50, 305–310.
- Song, W.L., Xu, C., Chakhmouradian, A.R., Kynicky, J., Huang, K.J., Zhang, Z.L., 2017. Carbonates of Tarim (NW China): First evidence of crustal contribution in carbonates from a large igneous province. *Lithos* 282–283, 1–9.
- Sørensen, H., 1992. Apatitic nepheline syenites: a potential source of rare elements. *Appl. Geochem.* 7, 417–427.
- Stepanov, A.S., Hermann, J., Rubatto, D., Rapp, R.P., 2012. Experimental study of monazite/melt partitioning with implications for the REE, Th and U geochemistry of crustal rocks. *Chem. Geol.* 300, 200–220.
- Strzelecki, A.C., Migdisov, A., Boukhalfa, H., Sauer, K., McIntosh, K.G., Currier, R.P., Williams-Jones, A.E., Guo, X., 2022. Fluocerite as a precursor to rare earth element fractionation in ore-forming systems. *Nat. Geosci.* 15, 327–333.
- Su, H.M., Jiang, S.Y., Zhu, X.Y., Duan, Z.P., Huang, X.K., Zou, T., 2021. Magmatic-hydrothermal processes and controls on rare-metal enrichment of the Baerzhe peralkaline granitic pluton. Inner Mongolia, Northeastern China. *Ore Geol. Rev.* p. 103984.
- Sun, S.S., McDonough, W.F., 1989. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. *Geol. Soc. Spec. Publ.* 42, 313–345.
- Sun, Z.H., Qin, K.Z., Mao, Y.J., Tang, D.M., Wang, F.Y., Evans, N.J., Zhou, Q.F., 2022. Mineral Chemistry of Pyrochlore Supergroup Minerals from the Boziguo'er Nb-Ta-Zr-Rb-REE Deposit, NW China: Implications for Nb Enrichment by Alkaline Magma Differentiation. *Minerals* 12, 785.
- Tian, W., Campbell, I.H., Allen, C.M., Guan, P., Pan, W.Q., Chen, M.M., Yu, H.J., Zhu, W. P., 2010. The Tarim picrite-basalt-rhyolite suite, a Permian flood basalt from northwest China with contrasting rhyolites produced by fractional crystallization and anatexis. *Contrib. Mineral. Petrol.* 160, 407–425.
- Turner, S., Sandiford, M., Foden, J., 1992. Some geodynamic and compositional constraints on "postorogenic" magmatism. *Geology* 20, 931–934.
- Vasyukova, O., Williams-Jones, A.E., 2014. Fluoride-silicate melt immiscibility and its role in REE ore formation: Evidence from the Strange Lake rare metal deposit, Québec-Labrador. *Canada. Geochim. Cosmochim. Acta* 139, 110–130.
- Vasyukova, O., Williams-Jones, A., 2016. The evolution of immiscible silicate and fluoride melts: Implications for REE ore-genesis. *Geochim. Cosmochim. Acta* 172, 205–224.
- Vasyukova, O., Williams-Jones, A., 2020. Partial melting, fractional crystallisation, liquid immiscibility and hydrothermal mobilisation – A 'recipe' for the formation of economic A-type granite-hosted HFSE deposits. *Lithos* 356–357, 105300.
- Vermeesch, P., 2018. IsoplotR: A free and open toolbox for geochronology. *Geosci. Front.* 9, 1479–1493.
- Wang, X.S., Klemd, R., Gao, J., Jiang, T., Li, J.L., Xue, S.C., 2018. Final Assembly of the Southwestern Central Asian Orogenic Belt as Constrained by the Evolution of the

- South Tianshan Orogen: Links With Gondwana and Pangea. *J. Geophys. Res.-Solid. Earth* 123, 7361–7388.
- Wang, F.L., Wang, C.Y., Zhao, T.P., 2015. Boron isotopic constraints on the Nb and Ta mineralization of the syenitic dikes in the ~260 Ma Emeishan large igneous province (SW China). *Ore Geol. Rev.* 65, 1110–1126.
- Weng, Q., Yang, W.B., Niu, H.C., Li, N.B., Mitchell, R.H., Zurevinski, S., Wu, D., 2022. Formation of the Maoniuping giant REE deposit: Constraints from mineralogy and in situ bastnäsite U-Pb geochronology. *Am. Mineral.* 107, 282–293.
- White, L.T., Ireland, T.R., 2012. High-uranium matrix effect in zircon and its implications for SHRIMP U-Pb age determinations. *Chem. Geol.* 306, 78–91.
- Williams, M.L., Jercinovic, M.J., Hetherington, C.J., 2007. Microprobe monazite geochronology: understanding geologic processes by integrating composition and chronology. *Annu. Rev. Earth Planet. Sci.* 35, 137–175.
- Windley, B.F., Alexeiev, D., Xiao, W., Kröner, A., Badarch, G., 2007. Tectonic models for accretion of the Central Asian Orogenic Belt. *J. Geol. Soc. London* 164, 31–47.
- Windley, B., Allen, M., Zhang, C., Zhao, Z., Wang, G., 1990. Paleozoic accretion and Cenozoic redeformation of the Chinese Tien Shan range, central Asia. *Geology* 18, 128–131.
- Wu, L.G., Li, X.H., Ling, X.X., Yang, Y.H., Li, C.F., Li, Y.L., Mao, Q., Li, Q.L., Benita, P., 2019a. Further Characterization of the RW-1 Monazite: A New Working Reference Material for Oxygen and Neodymium Isotopic Microanalysis. *Minerals* 9, 583.
- Wu, S.T., Wörner, G., Jochum, K.P., Stoll, B., Simon, K., Kronz, A., 2019b. The preparation and preliminary characterisation of three synthetic andesite reference glass materials (ARM-1, ARM-2, ARM-3) for in situ microanalysis. *Geostand. Geoanal. Res.* 43, 567–584.
- Wu, S.T., Yang, Y.H., Jochum, K.P., Romer, R.L., Glodny, J., Savov, I.P., Agostini, S., De Hoog, J.C., Peters, S.T., Kronz, A., 2021. Isotopic compositions (Li-B-Si-O-Mg-Sr-Nd-Hf-Pb) and Fe²⁺/ΣFe ratios of three synthetic andesite glass reference materials (ARM-1, ARM-2, ARM-3). *Geostand. Geoanal. Res.* 45, 719–745.
- Xiao, W.J., Windley, B.F., Allen, M.B., Han, C.M., 2013. Paleozoic multiple accretionary and collisional tectonics of the Chinese Tianshan orogenic collage. *Gondwana Res.* 23, 1316–1341.
- Xie, M.C., Xiao, W.J., Su, B.X., Sakyi, P.A., Ao, S.J., Zhang, J.E., Song, D.F., Zhang, Z.Y., Li, Z.Y., Han, C.M., 2022. REE mineralization related to carbonatites and alkaline magmatism in the northern Tarim basin, NW China: implications for a possible Permian large igneous province. *Int. J. Earth Sci.* 111, 2759–2776.
- Xinjiang Bureau of Geology and Mineral Resources (XJBGM). 1993. *Regional geology of the Xinjiang Uygur autonomous region*. Geological Publishing House, Beijing, pp.1-843 (in Chinese).
- Xu, H.M., Fang, J.L., Zhang, Z.Y., Wang, J., Fan, L., Zou, T.R., Liu, L.S., Liu, J., Zhang, L., Zhou, Y.X., 2011. Exploration report of Boziguoer niobium and tantalum deposit in Baicheng County, Xinjiang Uygur Autonomous Region. In: *Institute of Mineral Resources, Chinese Academy of Geological Sciences*, pp. 1–197 in Chinese.
- Yang, S.F., Li, Z.L., Chen, H.L., Santosh, M., Dong, C.W., Yu, X., 2007. Permian bimodal dyke of Tarim Basin, NW China: geochemical characteristics and tectonic implications. *Gondwana Res.* 12, 113–120.
- Yang, S.F., Chen, H.L., Li, Z.L., Li, Y.Q., Yu, X., Li, D.X., Meng, L.F., 2013. Early Permian Tarim large igneous province in northwest China. *Sci. China-Earth Sci.* 56, 2015–2026.
- Yang, W.B., Niu, H.C., Shan, Q., Sun, W.D., Zhang, H., Li, N.B., Jiang, Y.H., Yu, X.Y., 2014a. Geochemistry of magmatic and hydrothermal zircon from the highly evolved Baerzhe alkaline granite: implications for Zr–REE–Nb mineralization. *Miner. Depos.* 49, 451–470.
- Yang, W.B., Niu, H.C., Li, N.B., Hollings, P., Zurevinski, S., Xing, C.M., 2020. Enrichment of REE and HFSE during the magmatic-hydrothermal evolution of the Baerzhe alkaline granite. Implications for rare metal mineralization. *Lithos*, NE China, pp. 358–359.
- Yang, Y.H., Wu, F.Y., Li, Y., Yang, J.H., Xie, L.W., Liu, Y., Zhang, Y.B., Huang, C., 2014b. In situ U-Pb dating of bastnaesite by LA-ICP-MS. *J. Anal. at. Spectrom.* 29, 1017–1023.
- Yang, Y.H., Wu, F.Y., Li, Q.L., Rojas-Agramonte, Y., Yang, J.H., Li, Y., Ma, Q., Xie, L.W., Huang, C., Fan, H.R., Zhao, Z.F., Xu, C., 2019. In Situ U-Th-Pb Dating and Sr-Nd Isotope Analysis of Bastnäsite by LA-(MC)-ICP-MS. *Geostand. Geoanal. Res.* 43, 543–565.
- Yin, J.W., Yan, X.G., Piao, T.X., Hou, F.J., Chen, P.P., Nie, X., Xu, H.M., Wang, J., 2014. Mineralogical characteristics of intrusive rocks in Boziguoer east mining area, Baicheng county, Xinjiang. *Earth Sci. J. China Univ. Geosci* 39, 251–260 in Chinese with English abstract.
- Zhang, W., Chen, W.T., Williams-Jones, A.E., 2023. An unique, fluorite-rich REE deposit in Henan province, Central China: the missing link in magmatic-hydrothermal REE mineralizing systems? *Contrib. Mineral. Petrol.* p. 178.
- Zhang, C.L., Li, X.H., Li, Z.X., Ye, H.M., Li, C.N., 2008. A Permian layered intrusive complex in the Western Tarim Block, northwestern China: Product of a ca. 275-Ma mantle plume? *J. Geol.* 116, 269–287.
- Zhang, C.L., Li, Z.X., Li, X.H., Xu, Y.G., Zhou, G., Ye, H.M., 2010a. A Permian large igneous province in Tarim and Central Asian orogenic belt, NW China: Results of a ca. 275 Ma mantle plume? *Geol. Soc. Am. Bull.* 122, 2020–2040.
- Zhang, L.F., Wang, Y., Zhang, L.J., Lü, Z., 2019. Ultrahigh pressure metamorphism and tectonic evolution of southwestern Tianshan orogenic belt, China: a comprehensive review. *Geol. Soc. Spec. Publ.* 474, 133–152.
- Zhang, C.L., Xu, Y.G., Li, Z.X., Wang, H.Y., Ye, H.M., 2010b. Diverse Permian magmatism in the Tarim Block, NW China: Genetically linked to the Permian Tarim mantle plume? *Lithos* 119, 537–552.
- Zhang, D.Y., Zhang, Z.C., Santosh, M., Cheng, Z.G., He, H., Kang, J.L., 2013. Perovskite and baddeleyite from kimberlitic intrusions in the Tarim large igneous province signal the onset of an end-Carboniferous mantle plume. *Earth Planet. Sci. Lett.* 361, 238–248.
- Zhang, D.Y., Zhang, Z.C., Mao, J.W., Huang, H., Cheng, Z.G., 2016. Zircon U-Pb ages and Hf–O isotopic signatures of the Wajilitag and Puchang Fe–Ti oxide-bearing intrusive complexes: Constraints on their source characteristics and temporal-spatial evolution of the Tarim large igneous province. *Gondwana Res.* 37, 71–85.
- Zhao, Z.Y., Zhang, Z.C., Santosh, M., Huang, H., Cheng, Z.G., Ye, J.C., 2015. Early Paleozoic magmatic record from the northern margin of the Tarim Craton: Further insights on the evolution of the Central Asian Orogenic Belt. *Gondwana Res.* 28, 328–347.
- Zhou, M.F., Zhao, J.H., Jiang, C.Y., Gao, J.F., Wang, W., Yang, S.H., 2009. OIB-like, heterogeneous mantle sources of Permian basaltic magmatism in the western Tarim Basin, NW China: Implications for a possible Permian large igneous province. *Lithos* 113, 583–594.
- Zhu, W., Wu, C.D., Wang, J.L., Zhou, T.Q., 2019. Provenance analysis of detrital monazite, zircon and Cr-spinel in the northern Tibetan Plateau: Implications for the Paleozoic tectonothermal history of the Altyn Tagh and Qimen Tagh Ranges. *Basin Res.* 31, 539–561.
- Zou, S.Y., Li, Z.L., Song, B., Ernst, R.E., Li, Y.Q., Ren, Z.Y., Yang, S.F., Chen, H.L., Xu, Y. G., Song, X.Y., 2015. Zircon U-Pb dating, geochemistry and Sr–Nd–Pb–Hf isotopes of the Wajilitag alkali mafic dikes, and associated diorite and syenitic rocks: Implications for magmatic evolution of the Tarim large igneous province. *Lithos* 212, 428–442.