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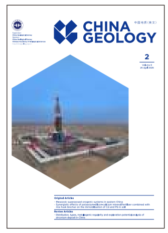

Distribution, types, metallogenic regularity and exploration potential analysis of zirconium deposit in China

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A B S T R A C T

Zirconium, prized for its exceptional corrosion resistance, high melting point, and unique nuclear properties, plays a critical role in multiple industrial sectors globally. Zirconium deposits are categorized into endogenetic and exogenetic types in China. Endogenetic deposits – including alkaline rock-, alkaline granite-, and pegmatite-type mineralizations – predominantly occur along the Tarim Craton's northern margin, the North China Craton, the southern Greater Khingan metallogenic belt, and the Yangtze Craton's western margin. Exogenetic deposits, comprising clastic sedimentary, weathering crust, and fragmentation types, are concentrated in South China's coastal zones. Endogenetic mineralization formed during Permian-Cretaceous magmatic-hydrothermal events linked to evolved alkaline granitic systems, while exogenetic deposits developed in Quaternary periods through weathering of zirconium-rich protoliths. However, economic extraction of endogenetic deposits remains constrained by rare earth element (REE) associations and radioactive complexities. Currently, China's most economically significant reserves derive from clastic sedimentary systems, particularly coastal placer deposits. This study systematically synthesizes the spatial distribution and metallogenic mechanisms of Chinese zirconium deposits, offering strategic insights for resource exploration and sustainable utilization.

1. Introduction

Zirconium, as an essential critical metal renowned for its high melting point, corrosion resistance, and unique nuclear properties (Che D et al., 2016; Liu HY and Ma Z, 2017), is extensively utilized in ceramics, glass, nuclear energy, aerospace, and other high-technology fields (Hao XY and Xiong BK, 2010; Shen ZW et al., 2016; Xue FQ et al., 2016; Che D et al., 2016; Yin LW, 2017). In recent years, its metallogenesis and exploration have garnered significant attention globally. Zirconium resources are distributed worldwide; but the majority are concentrated in several countries, such as Australia, South Africa, Mozambique, and Indonesia (Tan HC et al., 2015; Shen ZW et al., 2016; Xue FQ et al., 2016; Che D et al., 2016; Yin LW, 2017; Liu HY and Ma Z, 2017; Zhang ZF et al., 2019). China, one of the largest consumers and importers of zirconium resources, accounts for only 0.097% of the zirconium reserves (Joseph G, 2024) due to low domestic production and reserves coupled with high consumption. According to data from the General Administration of Customs of the People's Republic of China (GACPRC, General Administration of Customs of the People's Republic of China, 2017–2023), China's zirconium import increased from 980×10^6 t in 2017 to 1556×10^6 t in 2023 (Fig. 1). During this period, China's external dependence on zirconium resources exceeded 87%, reaching 92% by the end of 2023.

Zirconium deposits in China can be classified into endogenic deposits and exogenic deposits (Zhang ZF et al., 2019). The distribution of these deposits is relatively

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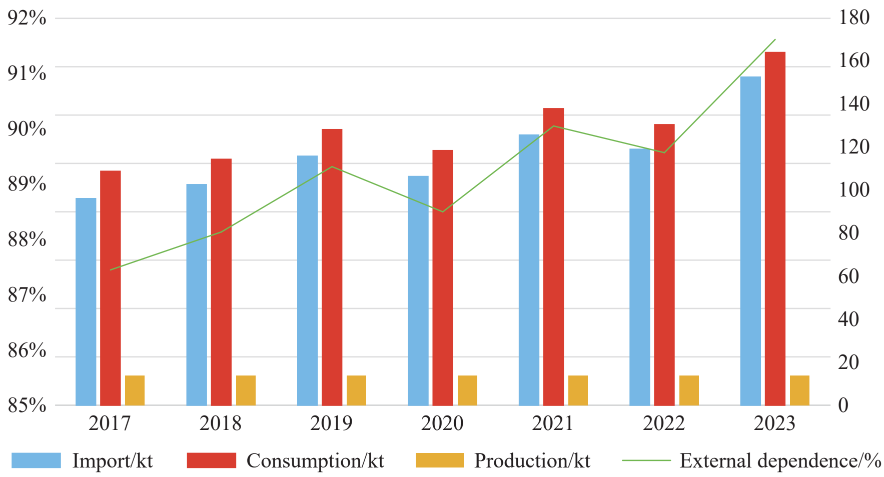

Fig. 1. Demand, import and external dependence of Zircon in China (data of import, consumption, external dependence from GACPRC, General Administration of Customs of the People's Republic of China, 2017–2023; data of production from Joseph G, 2018–2024).

concentrated. Endogenic deposits are predominantly located in Inner Mongolia Autonomous Region (70%), while exogenic deposits are primarily found in Hainan Province (19%) (Sun HW et al., 2019). Additionally, small amounts of exogenic deposits are distributed in coastal areas such as Guangdong, Guangxi, Yunnan, Shandong Peninsula and the Liaodong Peninsula (Chen Z et al., 2006; Wang Q, 2013).

Although the majority of China's zirconium resources are derived from endogenic deposits, their exploitation is still limited. These include low grade, frequent association with REE minerals, high levels of radioactive intensity and consequently high mining costs (Wang ZH and Li QC, 1991; Zhang JW et al., 2019). Moreover, the separation and smelting processes associated with these deposits often result in environmental pollution (Wang ZH and Li QC, 1991; Huang GW et al., 2019). In contrast, exogenic deposits, which are primarily distributed along the coastal belt, are characterized by shallow burial, significant thickness, and good continuity, making them the primary target for current mining activities (Zhang ZF et al., 2019). Therefore, it is crucial to identify potential exogenic deposits and improve the utilization efficiency of existing zirconium resources. This paper systematically integrates previous research on zirconium types, mineralization regularity, and exploration potential in China, providing a scientific foundation for future national investigations of zirconium deposits.

2. Distribution of global zirconium deposits

Zirconium deposits are distributed globally and have been discovered on all five continents. Proven zirconium reserves are primarily concentrated in Australia, South Africa, India, Mozambique, the United States, and China (Zhang ZF et al., 2019). As of 2023, global zirconium resource reserves approximately 74×10^6 t (in ZrO_2), with Australia and South Africa controlling more than 80% of the world's zirconium resources (74% and 8%, respectively) (Joseph G, 2024).

Chinese zirconium resources are characterized by unclear resource potential, limited reserves, and insufficient self-sufficiency. In 2023, China's zirconium reserves are projected to reach only 72×10^6 t, accounting for less than 1% of global reserves (Joseph G, 2024). There are approximately 100 proven zirconium deposits in China, with the majority concentrated in the Inner Mongolia Autonomous Region (70%) and Hainan Province (19%) (Shen ZW et al., 2016; Wang RC et al., 2020). Endogenic deposits are mainly distributed along the northern margin of Tarim and North China cratons, the southern part of the Greater Khingan Mountains metallogenic belt, and the western margin of the Yangtze Craton belt, while exogenic deposits mainly located in the coastal regions of South China (Fig. 2; Table 1). By the culmination of 2015, more than 70 zirconium mineral areas had been identified in Hainan Province, boasting proven reserves of 3.708×10^6 t (Chen HZ, 2018). However, the exploitation and study of zirconium deposits in Hainan remain limited.

3. Types of zirconium deposits

Typical zirconium deposits in China can be classified into two main types: Endogenic deposits and exogenic deposits, which can be further subdivided into different subtypes based on their specific ore-forming geological characteristics. Endogenic deposits can be categorized into alkaline rock-alkaline granite type, and granite pegmatite type zirconium deposits (Wang RC et al., 2020), while exogenic deposits can be divided into clastic sedimentary type, weathering crust type, and fragmentation type zirconium deposits (Tong CL et al., 2018).

In endogenic deposits, zirconium minerals typically occur as secondary mineral within granite rock masses and are frequently associated with niobite, pyrochlore, monazite, fluorite, and bastnaesite (Chen JY et al., 2019; Wang RC et al., 2020; Su HM et al., 2021). Due to their low grade and processing challenges, they have not been extensively exploited on a large scale. In contrast, exogenous zirconium deposits are formed through the epigenetic weathering sedimentation of endogenic deposits. This deposit type is

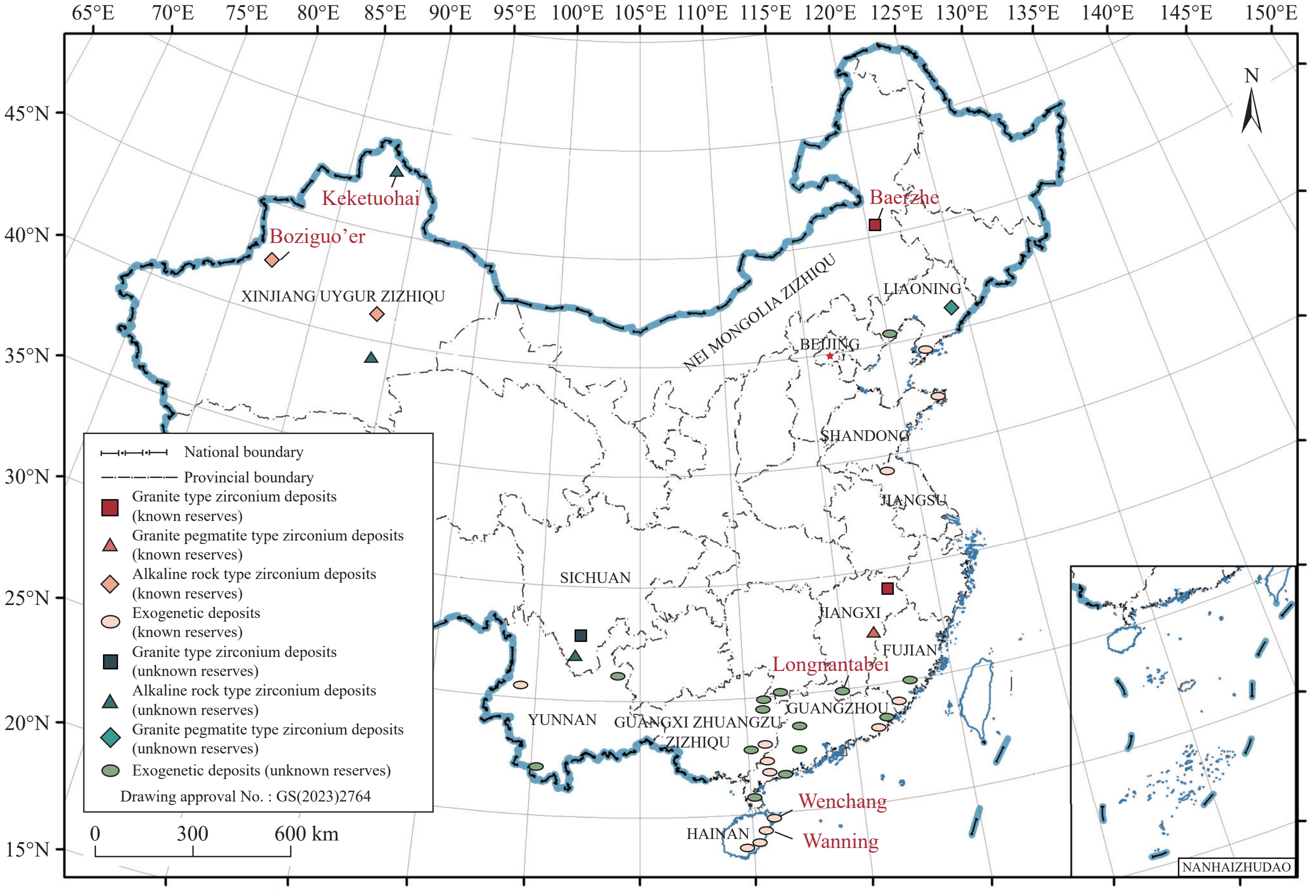

Fig. 2. Distribution map of Zirconium deposits in China (after Wang RC et al., 2020).

presently the primary exploitation target due to its substantial size, adequate continuity, shallow burial depth, and ease of extraction.

3.1. Alkaline rock-alkaline granite type

The alkaline intrusions, which contain feldspathoids, pyroxenes, and amphiboles, are distributed in extensional tectonic environment and coexist with carbonate rocks sometimes (Salvi S et al., 2005; Wang RC et al., 2020). Alkaline rocks can be further classified into alkaline granite according to their alkalinity index and silicon content (Salvi S et al., 2005). The alkaline rock-alkaline granite systems generally enriched in high-field-strength elements (HFSE), such as Zr, Ti, Y, Nb and REE (Wang RC et al.,2020; Fan HR et al., 2020).

Zirconium minerals are primarily disseminated atop the granite, symbioses with microcline, albite, K-feldspar, quartz, aegirine as principal rock-forming minerals (Sun HM et al., 2013; Chen JY et al., 2019). Apart from zircon, zirconium is abundant in complex zirconium silicate minerals such as eudialyte (Salvi S et al., 2000; Sheard ER et al., 2012). Notably, zirconium also occurs in niobium-tantalum minerals [including pyrochlore, columbite (Fe), fluorite, etc.], as well as rare earth minerals such as bastnasite-(Ce) and hingganite-(Y, Ce) (Salvi S and Williams-Jones AE, 2006; Sun Y et al., 2013; Zhu JZ et al., 2013; Chen JY et al., 2019; Wang RC et al., 2020).

In China, the alkaline rock-alkaline granite type zirconium deposits include the Baerzhe deposit in Inner Mongolia, the Boziguo’er in Xinjiang, the Saima deposit in Liaoning Province. Globally, this deposit type is well represented by notable examples such as the Thor Lake and the Strange Lake complex in Canada, the Ilimaussaq complex in Greenland, and the Tamazeght complex in Morocco. This section introduces three typical alkaline rock-alkaline granite type zirconium deposits.

3.1.1. Strange Lake REE-Zr-Nb deposit in Canada

The Strange Lake REE-Zr-Nb deposit is a Mesoproterozoic intrusive rock complex (Salvi S and Williams-Jones AE, 2006; Gysi AP et al., 2016) situated on the border between the Canadian provinces of Québec and Newfoundland (Salvi S and Williams-Jones AE, 2006). The deposit contains approximately 278×10^6 t of ore, with an average grade of 1.92% ZrO_2, 0.18% Nb_2O_5 (Gysi AP et al., 2016). The Strange Lake REE-Zr-Nb deposit displays well-defined zonation patterns, featuring hypersolvus granite in the central and southern sections, enveloped by subsolvus granite. Pegmatite veins are present on the top of the subsolvus granite (Salvi S and Williams-Jones AE, 1990, 2006). HFSE minerals are predominantly found at the top of altered subsolvus granite. The primary ore minerals consist of zircon silicate minerals and elpidite, with accessory minerals such hematite,

Table 1. Main zirconium deposits in China.

	Deposit types	Parent rocks	Major mineral species	Instances	Period of mineralization	Reference
Exogenic deposits	Alkaline granite type	Albite granite	REE-Zr-Nb-Be	Baerzhe (Inner Mongolia)	Cretaceous	Qiu KF et al., 2019
		Alkaline granite	Y-Nb-Zr	Cida (Sichuan)	–	Wang RC et al., 2020
		Albite granite	Nb-Ta-Zr-Hf	Huangshan (Jiangxi)	Early Cretaceous	Zhu ZY et al., 2018
		Albite granite	Nb-Ta-Sn-W-Zr	Songshugang (Jiangxi)	Early Cretaceous	Zhu ZY et al., 2018
	Pegmatitic type	Altered granitic pegmatite	Nb-Ta-Zr-W-Sn-Li-Rb	Hailuoling (Jiangxi)	Early Cretaceous	Hu LY et al., 2015
		Albite granite-pegmatite	Nb-Ta-Zr-Hf	Huangshan (Jiangxi)	Early Cretaceous	Zhu ZY et al., 2018
		Alkaline pegmatite	REE-Nb-Ta-Zr	Huililugu-Baicao (Sichuan)	–	Wang RC et al., 2020
		Alkaline pegmatite	Nb-Ta-Zr	Yilanlik (Xinjiang)	–	Wang RC et al., 2020
		Granite pegmatite	Li-Be-Nb-Ta-Zr-Hf	Keketuohai No 3 (Xinjiang)	Jurassic	Liu CQ and Zhang H, 2005
Exogenic deposits	Alkaline type	lujavrite	REE-Zr-U	Saima (Liaoning)	Triassic	Wang RC et al., 2020
		Alkaline syenite	REE-Nb-Ta-Zr	Keketuohai No 3 (Xinjiang)	Triassic	Liu CQ and Zhang H, 2005
		Alkaline syenite	REE-Nb-Ta-Zr	Boziguo’er (Xinjiang)	Permian	Wang RC et al., 2020
		Syenite porphyry	Nb-REE-Zr	Mohe (Heilongjiang)	–	Wang RC et al., 2020
		trachyte	Nb-Ta-Zr-REE	Tudiling (South Qinling)	Silurian	Yan S et al., 2021
	Metamorphic rock type	Metamorphic volcanic-sedimentary rock	Nb-Ta-Zr-REE	Yushishan (Gansu)	Silurian	Jiang SY et al., 2022
Endogenic deposit	Littoral sedimentary type	Placer deposits	Zr-Hf	Rongcheng (Shandong)	Quaternary	Zhao KH, 1997
		Placer deposits	Ti-Fe-Zr-Hf	Wenchang, Qionghai, Wanning, Lingshui (Hainan) Raoping–Haifeng, Zhanjiang–Lufen coastal zircon zone, Huilai (Guangdong)	Quaternary	Tan QX and Sun Y, 1998; Wang Q, 2013
		Ancient placer deposits	Ti-Fe-Zr-Hf	Huashanzi (Jiangsu)	–	Wang RC et al., 2020
	Fluvial alluvial type	Placer deposits	Au-Zr-Hf	Dengshahe (Liaoning)	–	Wang RC et al., 2020
		Placer deposits	REE-Ti-Fe-Zr-Hf	Yangjiang (Guangdong)	Quaternary	Tan QX and Sun Y, 1998
		Placer deposits	Nb-Fe-REE-Ti-Zr-Hf	Xinxing, Dianbai (Guangdong)	Quaternary	Tan QX and Sun Y, 1998
Endogenic deposit	Fluvial alluvial type	Placer deposits	REE-Y-Nb-Zr-Hf	725 deposit, Luchuan Baima (Guangxi),	–	Wang RC et al., 2020
		Placer deposits	Ti-Fe-REE-Zr-Hf	Baoshan, Menghaimeng’a (Yunnan)	–	Wang RC et al., 2020
	Weathering crust and residual slope deposits type	Metamorphic granite weathering crust	REE-Zr-Hf	Beiliu 520 deposit (Guangxi)	–	Wang RC et al., 2020
		Biotite granite weathering crust	Nb-Y-Zr-Hf	Guposhan 729 deposit (Hunan)	–	Wang RC et al., 2020
		Biotite granite weathering crust	REE-Y-Zr-Hf	512, 513 deposits (Guangdong)	Quaternary	Tan QX and Sun Y, 1998
		Granite weathering crust	Ti-Fe-Zr-Hf	Pingding (Guangdong)	Quaternary	Tan QX and Sun Y, 1998
		Granite weathering crust	Ti-Fe-Zr-Hf	Longnan Tabei (Jiangxi)	Early Cretaceous	Xing SJ, 2009
		Alkaline tuff	REE-Zr-Hf-Nb-Ga	Eastern Yunnan, Chongqing, western Guizhou and southern Sichuan	Triassic	Dai SF et al., 2018

Note: “–” indicates no data.

fluorite, thorite, bastnäsite, monazite, pyrochlore, kainosite, allanite, milarite-(Y), and several unidentified HFSE-bearing minerals (Salvi S and Williams-Jones AE, 2006).

The mineralization process of the Strange Lake REE-Zr-Nb deposit can be broadly classified into three stages: The magmatic stage (I), alkali metasomatism stage (II), acidic alteration at high temperature (IIIa) and low temperature (IIIb) (Gysi AP et al., 2016). During the magmatic stage (Fig. 3a), highly saline aqueous fluids were continuously released from the magma chamber. These fluids migrated along structural

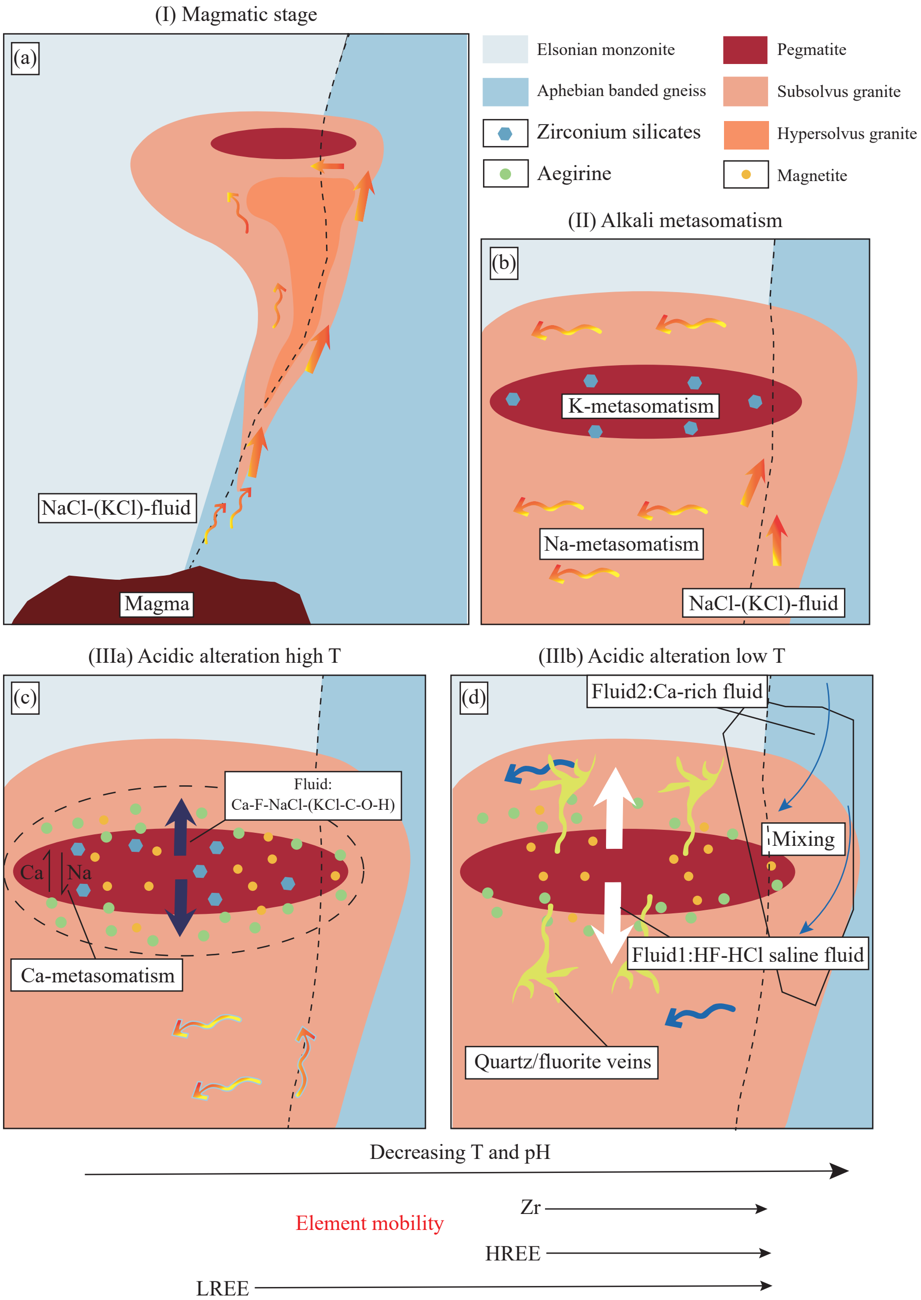

Fig. 3. Mineralization model map of the Strange Lake REE-Zr-Nb deposit (after Gysi AP et al., 2016); a–magmatic stage, highly saline aqueous fluids released from the magma chamber, infiltrating the structural weak zones; b–interaction of fluids with the intrusive rocks; c–high-temperature hydrothermal alteration; d–low-temperature hydrothermal alteration.

weak zones previously occupied by hypersolvus and subsolvus magma, creating a favorable environment for pegmatite formation (Salvi S and Williams-Jones AE, 2006; Gysi AP et al., 2016). The subsequent crystallization of boundary pegmatites triggered the precipitation of zirconium silicates, resulting in significant enrichment of Zr and HREE in this region (Gysi AP et al., 2016).

The interaction of high-salinity aqueous fluids with the intrusive rocks and pegmatites results in Na-metasomatism and K-metasomatism (Fig. 3b) (Salvi S and Williams-Jones AE, 1997, 2006; Gysi AP et al., 2016). Subsequently, as the boundary pegmatite crystallizes but before the core fully solidifies, the magma releases high-temperature, water-rich acidic fluids. This process triggers Ca-metasomatism within the pegmatite and subsolvus granite, which simultaneously transforms arfvedsonite into a combination of aegirine and magnetite (Salvi S and Williams-Jones AE, 1996, 2006; Gysi AP et al., 2016) (Fig. 3c). The previously released acidic fluids become increasingly acidic as the temperature decreases and evolve into HF-HCl-rich fluid 1. This process coincides with quartz/fluorite veins formation within the granite, enhancing the porosity of the pegmatite (Gysi AP et al., 2016). At lower temperatures and pH levels, Zr forms complexes with F^{-} in the HF-HCl-rich fluid, facilitating its migration from the pegmatite to the granite (Salvi S and Williams-Jones AE, 2006; Gysi AP et al., 2016). Concurrent with the leaching of acid fluids, a low-temperature, oxidizing Ca-rich fluid 2, driven by atmospheric water, infiltrates the upper rock mass and mixed with the HF-HCl rich fluid 1, thus precipitating Zr, Y, and REE minerals (Salvi S and Williams-Jones AE, 1990, 2006) (Fig. 3d).

3.1.2. Baerzhe Nb-Zr-REE deposit in Inner Mongolia, China

The Baerzhe Nb-Zr-REE deposit is situated in Zhaluteqi Banner, Zhelimumeng League, Inner Mongolia, on the southern margin of Greater Khingan Mountains (Su HM et al., 2021; Wang YX and Zhao ZH, 1997; Chen JY et al., 2019). It contains 2.8 $\times 10^6$ t of zirconium minerals at average grades of 1.84% ZrO_2, 1.00% REE_2O_3, and 0.26% Nb_2O_5. The deposit contains approximately 70% of China's total zirconium reserves, representing the most typical peralkaline granite-hosted zirconium deposit in China. The Baerzhe granite and associated REE-Nb-Zr-Be mineralization are situated in the central of Xingmeng (Xing'an-Mongolia) orogenic belt and occupy a central position (Su HM et al., 2021; Wang YX et al., 1997). The metallogenic age of the deposit between 123–124 Ma (Li MW, 2022; Qiu KF et al., 2019; Su HM et al., 2021). Zircon is the primary zirconium-bearing mineral, while being associated with niobite, monazite, fluorite, pyrochlore, fluocerite and other minerals (Zhu JZ et al., 2013; Chen JY et al., 2019; Su HM et al., 2021). The Baerzhe Nb-Zr-REE deposit exhibits clear vertical zoning characteristics. From bottom to top, the deposit transitions from arfvedsonite-bearing hypersolvus granite, to weakly Na-metasomatized transsolvus granite, moderately Na-metasomatized transsolvus granite, and finally intensely Na-metasomatized subsolvus granite at the top (Yang WB et al., 2014).

The NNE-trending Huanggang-Ganzhuermiao Fault serves as the primary ore-controlling structure within the Xingmeng orogenic belt, which determines the distribution of ore-bearing rock masses and certain dikes (Sun Y et al., 2013). Jahn B et al. (2001b) proposed that the magma in the Baerzhe granite, Inner Mongolia are mainly derived dominantly from juvenile mantle component with subordinate recycled ancient crust. Varuable degrees of partial melting in the juvenile crust generated peralkaline primary magmas that subsequently evolved through fractional crystallization, becoming progressively enriched in volatile components such as water, fluorine, and chlorine. Su HM et al (2021) observed an abundance of spherulitic granites in highly mineralized granites and considered these spherulitic granites formed in evolved magma rich in volatile components, suggesting a close relationship between the mineralization process and volatile-rich fluids in the Baerzhe deposit in Inner Mongolia. The tetrad effect observed in the REE distribution diagram of granite indicates strong differentiation crystallization as well as late-magmatic fluid-melt interaction during the mineralization process (Jahn B et al., 2001b; Yang WB et al., 2014; Su HM et al., 2021). Exsolved magmatic fluids and bubbles may ascend and accumulate to form a segregated fluid phase at the top of the magma chamber (Fig. 4). Meanwhile, these fluids interact with the country rock containing arfvedsonites resulted in the alteration to albite and aegirine, as well as the leaching of Zr, REE, Nb and forming low-melting point complexes with F^- and Cl^-. This process leads to significant zirconium enrichment in the residual melt (Sun Y et al., 2013; Yang WB et al., 2014; Su HM et al., 2021). During the hydrothermal stage, oxidizing conditions promote the replacement of arfvedsonite by Fe-Ti oxides, resulting in the precipitation of HFSE and REE elements (Fig. 5).

3.1.3. Boziguo'er REE-Nb-Ta-Zr deposit in Xinjiang

The Boziguo'er REE-Nb-Ta-Zr deposit, situated in the Southern Tianshan orogenic belt (Huang H et al., 2014; Sun ZH et al., 2013), lies 47 km north of Baicheng County,

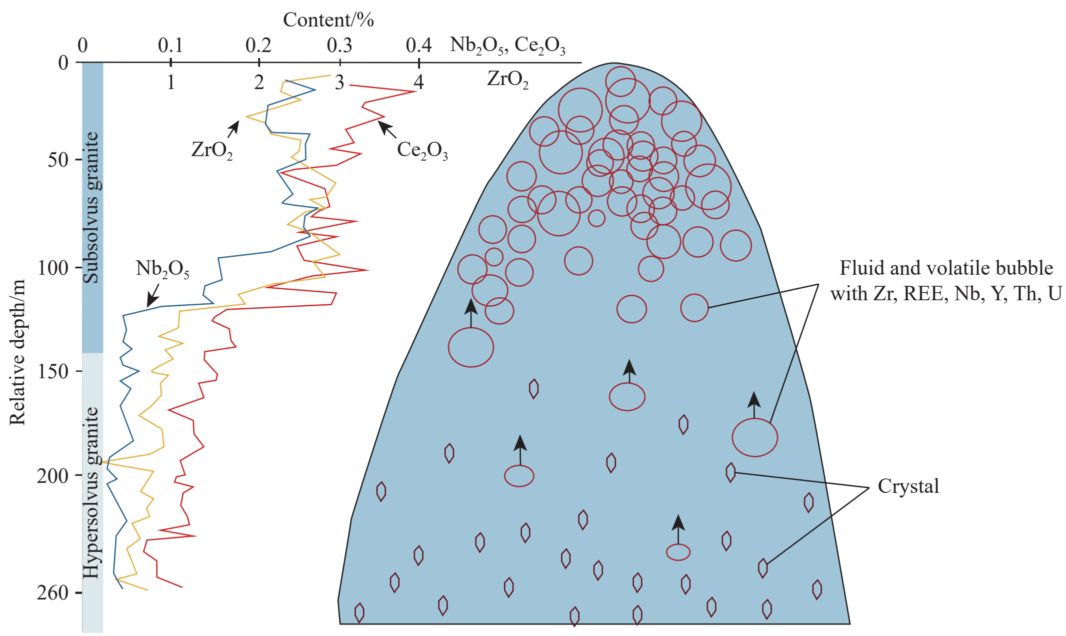

Fig. 4. Model diagram of upward migration of Zr, Nb, REE and other elements (after Yang WB et al., 2014).

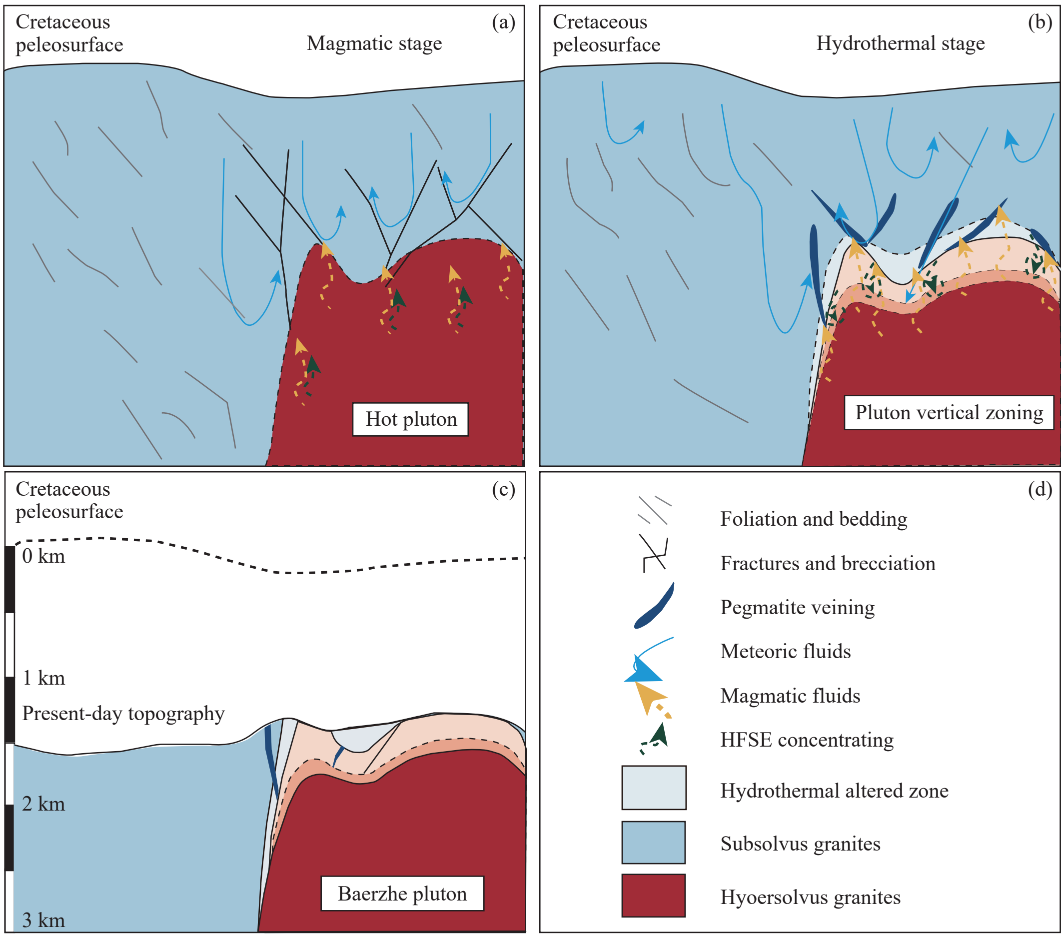

Fig. 5. Mineralization model map of Baerzhe Nb-Zr-REE deposit (after Yang WB et al., 2020). a–During the magmatic stage, granite crystals contain volatile elements such as F and Cl, which form complexes with HFSE to facilitate melting and upward migration; b–hydrothermal fluid rich in HFSE interact with groundmass resulting in alteration and precipitation of zircon. c–present Baerzhe Nb-Zr-REE deposit.

Xinjiang (Liu CH et al., 2012). This super-large deposit (280–291 Ma mineralization age; Sun ZH et al., 2022) hosts zirconium predominantly as interstitial zircon within gangue matrices and late-stage alkaline syenite cumulates. Arfvedsonite serves as a characteristic alkaline mineral in the Boziguo'er deposit. Geochemically, high Na_2O and Fe contents contrasting with depleted Ca, Mg, Ba, Sr, and Ti characterize the rocks of this deposit. The chondrite-normalized REE distribution diagrams display V-shaped patterns with slight LREE enrichment and Eu anomalies (Xu HM et al., 2012; Wu HH et al., 2019; Sun ZH et al., 2021).

The origin of the parental magma for the Boziguo'er deposit remains debated. Huang H et al. (2014; 2018) and Sun ZH et al. (2013) suggested that ore-forming materials are derived from remelting ancient crustal materials, potentially including a small amount of mantle material. Specifically, the upwelling of volatile-rich asthenosphere magma is controlled by tectonic activity (Huang H et al., 2014). A portion of the asthenosphere magma erupted and condensed, forming Xiaotikanlike basalts, while another part intruded the lower crust and triggered partial melting of magmatic rocks. The upwelling asthenosphere released a steam of water, halogen, HFSE, REE and alkali metals from deep asthenosphere to shallow lithosphere, leading to pre-enrichment of F and HFSE in the crust (Huang H et al., 2014).

While Xu HM et al. (2012) assert that ore-forming materials originate from the upper mantle. Alkali- and fluorine-rich fluids played a key role in the mineralization of the Boziguo'er deposit. Fluorine is derived from the breakdown of hydrous minerals in the source region (Aiuppa A et al., 2009). During magma evolution, Fluorine can form stable complexes with Nb, Ta, Zr, and REE to prolong the duration of magmatic differentiation and facilitate complete crystallization of rare metal minerals such as zircon (Mysen BO et al., 2004; Wu HH et al., 2019). The formation of zirconium deposit primarily occurs during the magmatic stage, with significant enrichment of Nb, Ta, Zr, and REE before hydrothermal alteration (Huang H et al., 2014). As magma differentiation progresses, the crystallization differentiation of alkaline feldspar, plagioclase, and other minerals results in further enrichment of Zr and other HFSE. During subsequent magma cooling, zircon reaches saturation, undergoes massive crystallization, and accumulates to form zirconium deposits (Huang H et al., 2018, 2014; Wu HH et al., 2019) (Fig. 6).

3.2. Pegmatite type

In China, the reserves of pegmatitic zirconium deposits

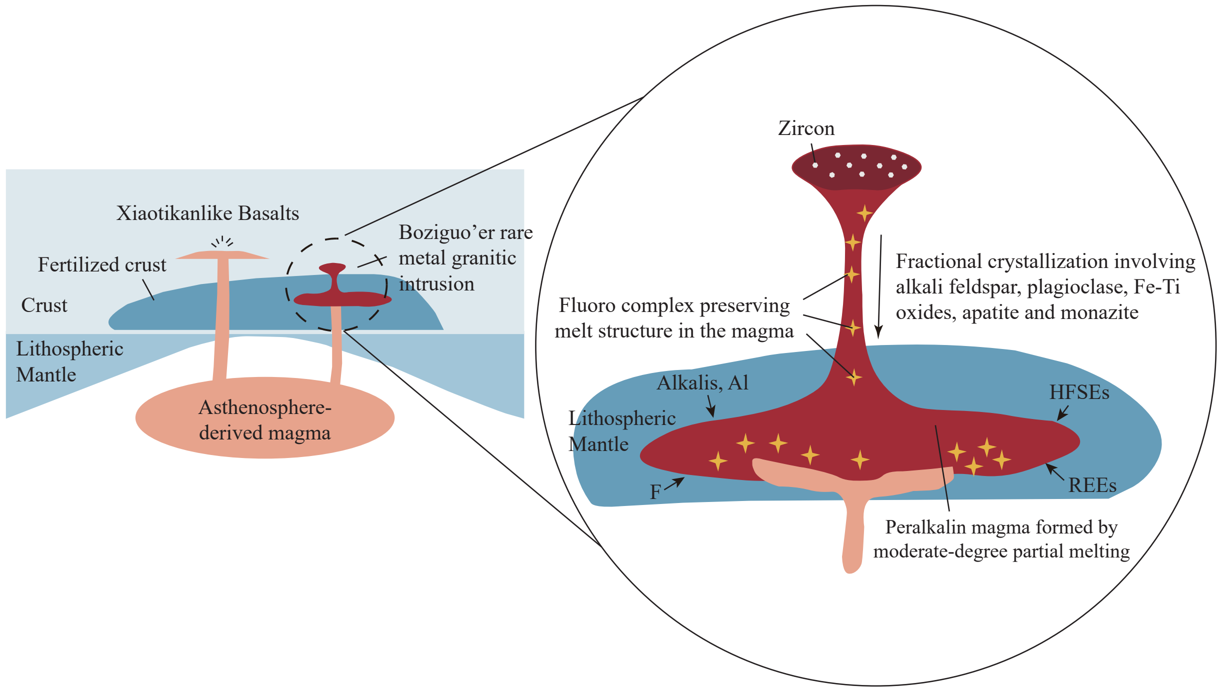

Fig. 6. Metallogenic model map of Boziguo'er deposit (after Huang H et al., 2014).

are rather limited. The Keketuohai Li-Be-Nb-Ta-Cs-Zr-Hf deposit in Xinjiang serves as a quintessential example of such pegmatitic zirconium deposits. (Lv ZH et al., 2018; Wang RC et al., 2020). Pegmatite ore bodies typically occur as irregular veins or lenticular, displaying complex mineral assemblages formed through multiple mineralization events (Zhu JC et al., 2000). These ore bodies are characterized by extremely distinct pronounced internal zonation (Liu CQ and Zhang H, 2005). The principal minerals constituting the pegmatite are quartz, albite, microcline, and muscovite (Zhu JC et al., 2000; Liu CQ and Zhang H, 2005), while rare metal minerals encompass spodumene, lepidolite, beryl, manganotantalite, Pollucite, zircon (Zou TR and Li QC, 2006). The chondrite-normalized REE distribution diagram is characterized by a lanthanide tetrad effect with LREE (Light Rare Earth Elements) being enriched relative to HREE (Heavy Rare Earth Elements). The Keketuohai Li-Be-Nb-Ta-Cs-Zr-Hf deposit situated within the Altay Orogenic Belt. The Altay Orogenic Belt comprises two metallogenic subzones that can be further divided into nine pegmatitic deposits concentration areas, among which the Keketuohai No. 3 pegmatite vein represents the most prominent (Zhang H et al., 2019). The origin of the Keketuohai pegmatite deposit remains controversial. Some scholars posit a close temporal and spatial relationship between the Keketuohai mining area and the Alar granite, suggesting that the formation of rare metal deposits in Keketuohai may be linked to this granite base (Zhu YF et al., 2006; Liu F et al., 2014; Zhang YF et al., 2015). However, Chen JF (2011) and Liu F et al. (2014) contend that Alar granite is not a rare metal granite and therefore unlikely to serve as the parent rock for rare metal pegmatite veins. One plausible formation process for Keketuohai Li-Be-Nb-Ta-Cs-Zr-Hf deposit is proposed as follows. Following the intrusion of rare metal elements (such as Li, Rb, Cs, Be, Ta, Nb and Zr) and volatile (H_2O, Cl and F) enriched (Zou TR et al., 1986; Zhu JC et al., 2000) into metagabbro in Keketohai, the magmasystem became relatively closed (London D, 2018; Fan JJ et al., 2020), facilitating mineral crystallization. Additionally, the shallower emplacement depths of Triassic pegmatites than Permian pegmatites facilitated greater volatile enrichment, thereby promoting more extensive magma differentiation and evolution (Zhang H et al., 2019). During pegmatite separation and crystallization from the pluton margin inward, rare metals form fluoride complexes that progressively enriched in the residual melt (Bai YX et al., 2021). During progressive cooling, Zr- and Hf- beating complexes are sequentially incorporated into zircon, hafnium zircon and hafnium minerals. This process ultimately leads to the formation of the pegmatite type deposit (Zhang H et al., 2019).

3.3. Clastic sedimentary zirconium deposit

Clastic sedimentary zirconium deposits, also referred to as placer, constitute a major source of zircon resources in China. These deposits are primarily classified into alluvial zirconium deposits (AZDs) and littoral sedimentary zircon deposits (LSZDs).

The formation of alluvial deposits involves the progressive fracturing and chemical weathering of parent rocks, fluvial transport and sedimentary sorting based on grain size and density. The Wudaogou monazite-ilmenite placer deposit, exemplifies the typical occurrence of zirconium in alluvial deposits, where it predominantly exists as detrital zircon and monazite (Zhai FR and Liang S, 2023). AZDs are limited and mainly found in coastal regions, such as Guangdong, Guangxi, and Hainan. They are typically distributed in landforms such as alluvial plains and sand spits. Notable examples include the Wanzhoupo deposit in Lingshui, Hainan; the Dianbaicheng alluvial placer deposit in Guangdong; and the Menghai deposit, Baoshan Banqiao deposits in Yunnan (Wang RC et al., 2020).

The littoral sedimentary zirconium deposits (LSZDs) are the concentration of a series of heavy minerals (such as zircon, plagiozircon, monazite, phosphoyttriite and niobium–tantalite) that accumulate in the shoreline and the uppermost coastal environment (Tong CL, 2018; Chen HZ et al., 2018). Wind, wave and tidal processes (Tan QX and Sun Y, 1998) usually control the formation of LSZDs. Notable examples include the Zhanjiang–Xuwen and Raoping–Haifeng costal zircon zone in Guangdong (Wang Q, 2013; Wang SH et al., 2016), Wanning, Linshui and Wenchang littoral placer (Pan YJ et al., 2017; Tong CL et al., 2018). Wind plays an independent role in the zircon concentration along backshore environments, such as Namakawa Sands deposit in South Africa (Rozendaal A, 2017). In China, The ore-bearing rocks of the LSZDs are primarily composed of Indo-Chinese, Yanshanian granite, such as Raoping–Haifeng costal zircon zone in Guangdong (Wang GZ et al., 2023), Wenchang, Qionghai, Wanning littoral placer (Song JW et al., 2021; Pan YJ et al., 2017), and Precambrian metamorphic rocks, such as Wenchang, Qionghai, Wanning littoral placer (Wang RC et al., 2020; Tan QX and Sun Y, 1998). The LSZDs are primarily formed during the Quaternary epoch (Liu HS, 1989; Pan YJ et al., 2017) and mainly distributed in water depths ranging from −10 m to −70 m, as evidenced by the Hainan costal deposits (Pan YJ et al., 2017).

Zirconium is mainly enriched in zircon and commonly associated with rutile and monazite (Tong CL, 2018; Song JW et al., 2021). These detrital minerals typically exhibit good roundness and sorting characteristics, with particle sizes typically ranging from medium- and fine-grain sand to silty sand. Hainan Dao represents a principal concentration area for LSZDs in China, hosting 70 confirmed littoral placers (Chen HZ, 2018). Additionally, LSZDs have also been identified along the continental coastlines of Guangdong, Guangxi, Shandong Peninsula and Liaodong Peninsula (Wang RC, 2020). In Hainan Province, LSZDs can be classified into two types based on their sedimentary environment: Littoral placers and neritic placers (Tong CL, 2018). Littoral placers are located above the present coastal low-tide line and contain a variety of deposits with large reserves, concentrated distribution, which is the primary target for mining activities (Zhang ZY, 1991; Chen Z et al., 2006; Fu QJ and Cen L, 2008; Lin MK et al., 2016). These deposits develop in diverse coastal sedimentary environments, including beaches, barriers, lagoons, and abrasion terraces. Most of the deposits are distributed in a band that is generally aligned with the trend of the coastal zone. Littoral placers are typically found at depths of 0–20 m (Pan YJ et al., 2017) and display well-defined sedimentary rhythm.

Neritic placer deposits are typically distributed in submarine terraces and subaqueous deltas with a large-scale and continuous distribution. These sediments form banded concentrations aligned parallel to the modern coastline. Neritic placers are composed of terrigenous detrital sediments, including gravel, shell and coarse sand, medium sand, silty sand, and clay (Lin MK et al., 2016; Xue YL et al., 2017). Among them, zircons are predominantly round-shaped with particle sizes ranging from medium- and fine-grain sand to silty sand. They mainly occur within the Yandun Formation strata of Quaternary Holocene layers, with their main distribution confined to shallow marine environments at depth of −30 m, with occasional occurrences extending down to −70 m (Tong CL, 2018; Lin MK et al., 2016; Pan YJ et al., 2017).

3.3.1. Wanning East littoral placers, Hainan Province

The Wanning East littoral placer is located in eastern Hainan Dao, north of the South China Sea. The stratigraphic sequence associated with zirconium mineralization in the Wanning coastal zone comprises three Quaternary formations: Yandun Formation (Holocene), Basuo Formation (Upper Pleistocene), and Beihai Formation (Middle Pleistocene) (Han XH et al., 2017). The major sedimentary environment of deposits is characterized by sand spits and abrasion terraces (Fu QJ and Cen L, 2008).

Hainan Dao has abundant beneficial conditions for the mineralization of LSZDs, characterized by massive parent rocks, a suitable geographical location, and tropical monsoon climate conditions. Numerous granites of Triassic, Jurassic, and Cretaceous are widely distributed on Hainan Dao in the form of batholiths and stocks, as well as Neogene volcanic rocks (Mo WR et al., 2015). The massive volcanic rocks provide the average zircon contents in granites of Hainan Dao, notably higher at 374 g/t, compared to other coastal regions in China (Pan YJ et al., 2017). The climate of Hainan Dao falls within the tropical and subtropical zones, characterized by high temperatures, a rainy coastline, and dense river systems (Lin MK et al., 2016; Fu QJ and Cen L, 2008). The island’s geomorphology-characterized by central highlands transitioning to lower peripheral elevations-exhibits a strong spatial correlation with high zirconium concentrations. This topographic configuration enhances erosional processes and facilitates sediment mobilization toward coastal depositional environments (Yang Y et al., 2010; Pan YJ et al., 2017). Hainan littoral placers are mainly distributed in the Yandun Formation (Upper Holocene), the Beihai Formation (Middle Pleistocene) and the Basuo Formation (Upper Pleistocene) (Fig. 7). Among these layers, the Beihai Formation is primarily distributed on the second and third abrasion terraces (Mo WR et al., 2015; Chen ZP, 1997). Their lithology consists predominantly of sandy conglomerate. The Basuo Formation is situated on the second terrace and comprises of silty coarse to medium sand, along with minerals such as ilmenite, chromite, zircon and others. It was formed in a lagoon-coastal depositional environment, with predominant deposition of quartz sand. The Holocene is predominantly distributed on the first terrace, characterized by lithology of silty sand, medium fine sand and silty clay. Littoral placers primarily occur within the Holocene strata, within the Yandun Formation representing the principal host unit, where coastal and lagoon facies constitute the typical sedimentary environment (Chen ZP, 1997; Mo WR et al., 2015; Han XH et al., 2017; Tong CL, 2018;). Additionally, the Qiongdongnan Basin is situated in the shallow and deep sea regions of southeastern Hainan Dao, contains substantial accumulations of heavy minerals such as zircon, tourmaline, magnetite, and rutile (Liu XF, 2015). This area has great potential for zirconium and titanium resources development.

Under high temperature and massive rainfall, coastal intrusive rocks undergo chemical weathering to form a large area of weathering crust containing zircon and other minerals. In the weathering crust, REE, Zr, and other rare metals appear as free ions due to the acidic conditions prevalent in near-surface soil horizons (Fig. 8b). Following rainfall eluviation, rare metal ions migrate into the lower portion of the weathering crust and adsorb onto clay minerals, forming characteristic a weathering crust type deposits (Xu C et al., 2015; Zhou MF et al., 2020). Meanwhile, some of these free ions combine with F^- in groundwater maintaining mobility

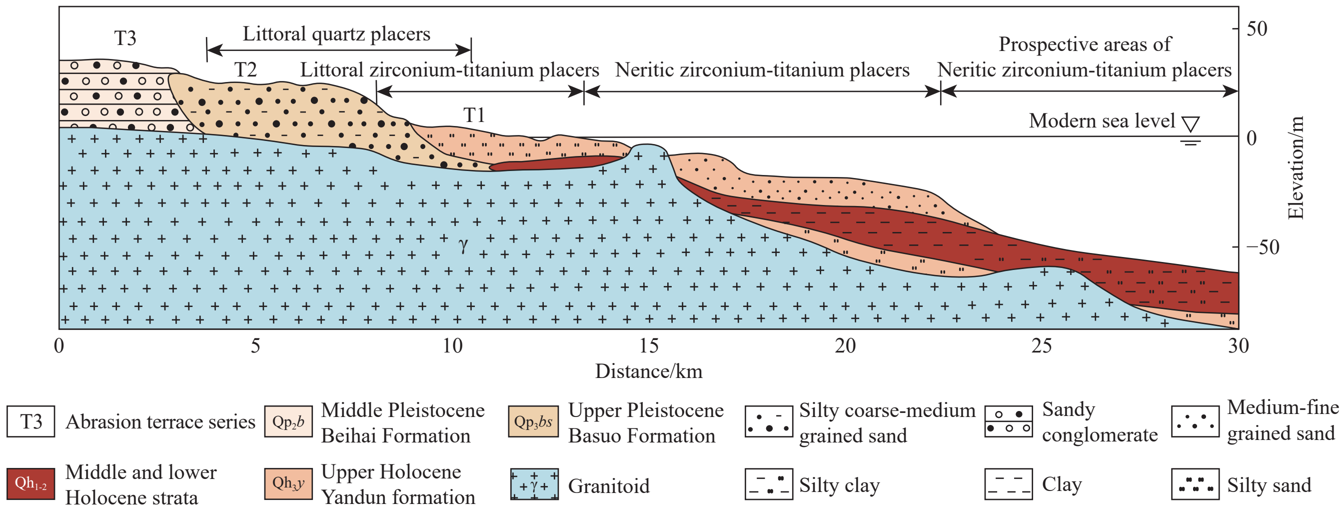

Fig. 7. Comprehensive geological profile of littoral placers in Hainan Dao (modified from Tong CL et al., 2018).

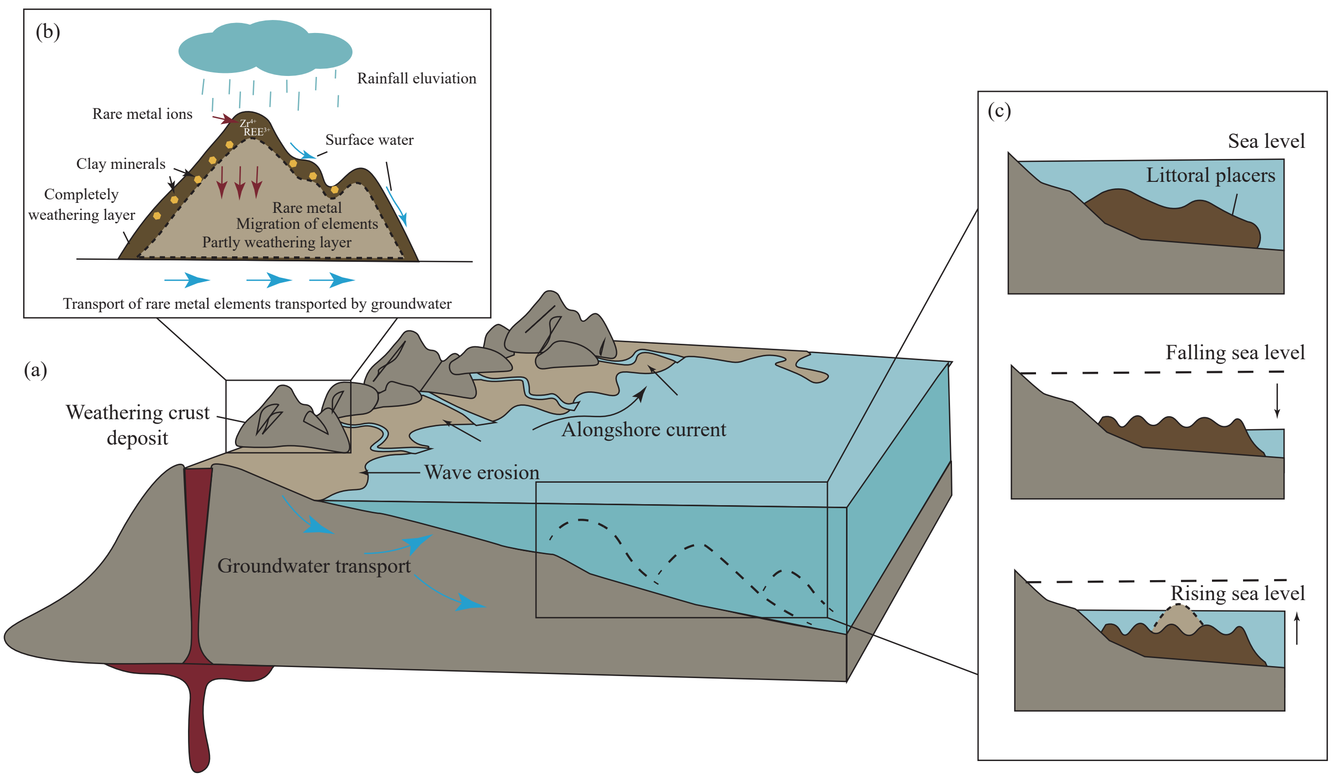

Fig. 8. Schematic diagram of placer metallogenic model on the east coast of Wanning, Hainan (modified from Roy P et al., 1999); a–mineralization pattern of littoral placers; b–composition of weathering crust type deposit and migration mode of rare metal ions; c–change of sea level causes the retrogression or transgression to transform the early deposited coastal placer.

within the hydrological system. The primary water system in eastern Hainan is the Wanquan River, which originates from Wuzhishan. The weathered crust deposits generates detrital materials under the erosion of rivers and are transported by rivers. When rivers flow through estuaries, floodplains and alluvial terraces, some detrital materials will precipitate to form fluvial- alluvial sands deposits. The remaining portion flows into the coastal marine environments providing material sources for littoral placers (Tan QX, 1998; Xu C et al., 2015; Song JW et al., 2021) (Fig. 8a). The alongshore current is the main driving force of large-scale sediment migration. When it encounters barriers and sand spits, the speed of the alongshore current is decreased, causing the deposition of mineral-bearing debris within these geomorphic features (Pan YJ et al., 2017). Moreover, the fluctuations in sea level during the Holocene period have also influenced the formation of littoral placers. The waves pushed earlier deposits ashore and eroded the intrusive rocks along the shoreline, providing detrital material for the littoral placers again. These combined hydrodynamic processes have progressively reshaped initial depositional landforms into characteristic marine geomorphic units, including submarine terraces and subaqueous slopes (Tan QX, 1998; Pan YJ et al., 2017; Tong CL, 2018) (Fig. 8c).

3.3.2. Namakwa sands deposit in South Africa

The Namakawa Sands deposit, located on the west coast of South Africa, is widely regarded as a world-class deposit (Rozendaal A et al., 2010; Philander C and Rozendaal A, 2015a; Rozendaal A et al., 2017). The estimated resource of the Namakawa Sands deposit stands at 1.17×10^9 t, characterized by a composition consisting of 2.98% ilmenite and 0.8% zircon (Philander C and Rozendaal A, 2015a). Moreover, the deposit comprises two adjacent ore bodies, known as the Graauwduinen West body (GD-W) and the Graauwduinen East body (GD-E). These two bodies are distinguished by their respective total heavy mineral content, amounting to 9.7% and 5.7% (Philander C and Rozendaal A, 2015a, 2015b; Rozendaal A et al., 2017). The heavy mineral content of the Namakawa Sands deposit can be classified into two categories: Non-economic minerals such as garnet, pyroxene, magnetite, amphibole, tourmaline, and monazite, as well as valuable minerals including zircon, rutile, and ilmenite (Rozendaal A et al., 2010).

The Graauwduinen West body (GD-W) is the main ore body mined in South Africa, which distributes along the coastline. This body is characterized by a distinct stratigraphic architecture, the late Cenozoic aeolian succession overlaying remnants of paleo-strandline sediments (Rozendaal A and Philander C, 2010; Philander C and Rozendaal A, 2015b). GD-W exhibits distinct vertical zonation, comprising from top to bottom: dune sands, red aeolian sands (mineralized), strandline west deposits, orange feldspathic sands (waste), orange feldspathic sands (mineralized), strandline east deposits, other sands, and bedrock. Within this stratified sequence, the strandline east (33.9% heavy mineral content) and strandline west (29.7%) demonstrate significantly higher economic grades compared to other horizons. (Philander C and Rozendaal A, 2015a). The Cenozoic ore-bearing clastic sequence is superimposed by false strata rich in calcium and magnesium, which serves as a natural cementing medium for the unconsolidated clastic deposits (Philander C and Rozendaal A, 2011).

The mineralization of GD-W is influenced by factors such as continental structure, coastal landform, sea level changes, tide, climate, and provenance composition (Force ER, 1991). The primary provenance for GD-W can be traced back to the medium-to high-grade Namaqualand Metamorphic Complex and younger Cretaceous intrusive suites (Rozendaal A et al., 2010).

During the early Pliocene, tectonic movements uplifted the northern portion of the west coast of South Africa relative to the south (Roberts DL et al., 2009), facilitating the transportation of inland sediments by the Sout River and the Olifants Rivers to the Atlantic Ocean (De W, 1999) (Fig. 9). Strandline east was formed during the early Pliocene when a substantial amount of sediment flowed to Brand-se-baai under the influence of the Sout River, later migrating with the southwest coastal current. The depositional pattern was significantly influenced by a prominent J-bay shaped headland southwest of Brand-se-baai, where wave refraction processes caused either in-situ accumulation or alongshore redistribution of heavy mineral-enriched sediments. (Philander C and Rozendaal A, 2015a; Rozendaal A et al., 2017). Concurrently, the combined effects of tides and wind selectively sort high-density and more resistant detrital particles from sedimentary debris, leading to the development of a well-stratified sequence enriched with valuable mineral-bearing debris (Rozendaal A et al., 2017) (Fig. 10). Strandline west, which formed during the regressive phase after 1 Ma years ago (Cilliers LM, 1995), shares similar mineralization characteristics with strandline east (Rozendaal A et al., 2017).

The Graauwduinen East body (GD-E) is a surficial aeolian place located in the southeast bend of the Olifants River and is covered by a clay-bearing dune sequence (Chase BM and Thomas D, 2007; Philander C and Rozendaal A, 2015a). The provenance of GD-E is consistent with that of GD-W (Philander C and Rozendaal A, 2015a). However, the zircon content in the GD-E deposit higher than GD-W, potentially indicating distinct sediment transport pathways from source terrains to depositional basins (Allen PA, 2008; Prizomwala SP et al., 2014). The formation of the deposit can be attributed to the selective sorting action of inland winds predominantly influenced by the northwest direction (Philander C and Rozendaal A, 2015a; Rozendaal A et al., 2017).

3.4. Weathering crust and fragmentation type

Weathering crust and fragmentation type zirconium deposits are widely distributed in South China’s subtropical monsoon climate, where elevated temperatures and abundant precipitation promote intense chemical weathering of bedrock

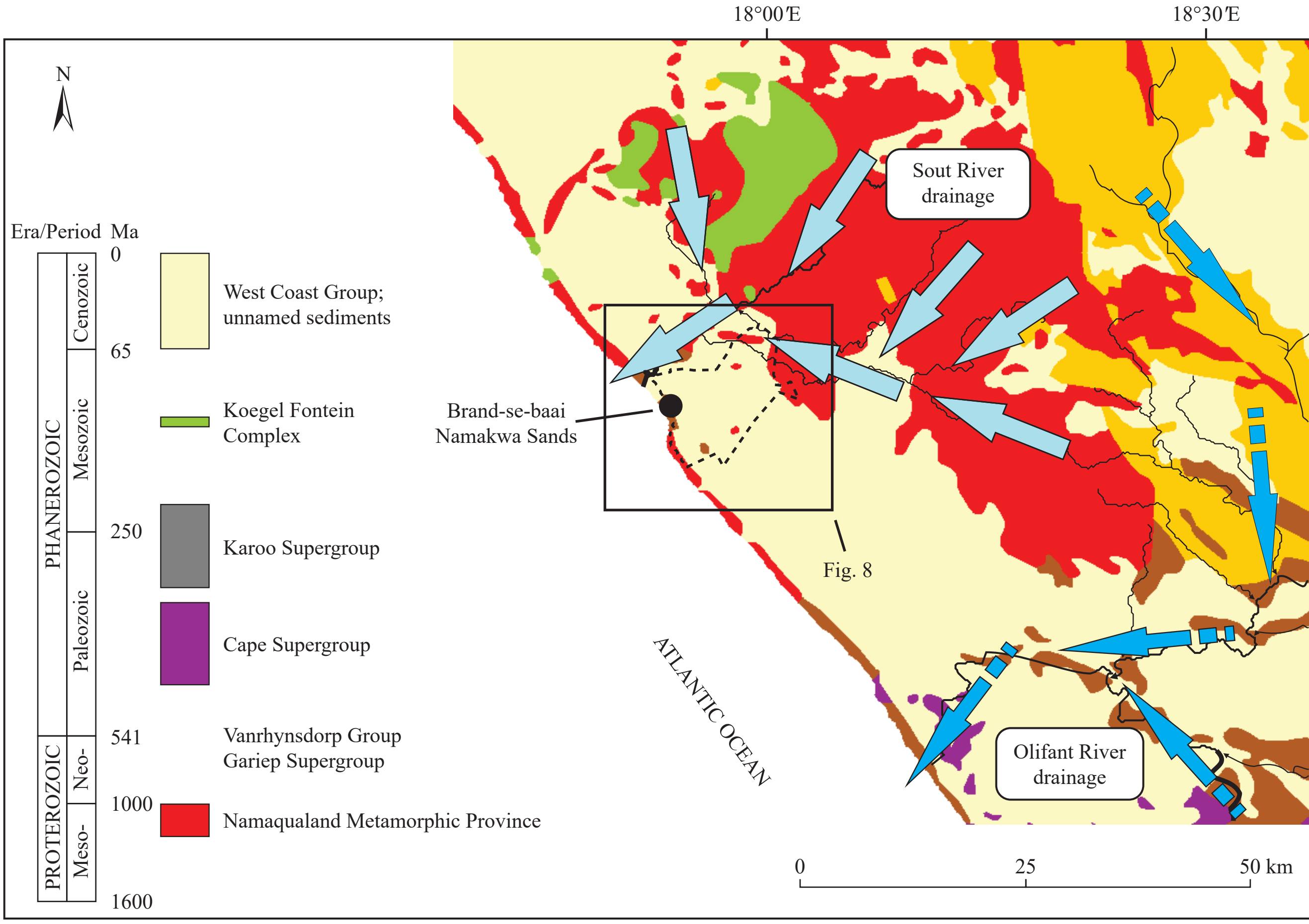

Fig. 9. Most likely provenance areas for the Namakawa Sands deposit. The schematic arrows delineate the sediment transport pathway from the Namakwa Sands provenance through the Sout-Olifants fluvial system to its terminal depocenter in the Atlantic Ocean basin (modified from Philander C and Rozendaal A, 2015a).

(Zhou MF et al., 2020). The thickness of the weathering crusts generally ranges from several meters to tens of meters, with layers including humic layer, completely weathering layer and partly weathering layer (Zhou MF et al., 2020). The deposits mainly exist in the completely weathering layer and are shallow enough for exploration. The ore-bearing parent rocks typically consist of alkaline rocks, such as nepheline syenite, granite, granite porphyry and migmatite. These rocks are abundant in zircon, hingganite (yttroceberysite), fluorite and other accessory minerals (Wang RC et al., 2020).

3.4.1. Longnantabei weathering crust deposit in Jiangxi

The Longnantabei weathering crust deposit in Jiangxi Province is a typical example of weathering crust zirconium deposits. Where the weathering crust ranging from 1.16 m to 2.13 m overlying the primary ore-body. The primary rock of the deposit is predominantly granite-syenite, wherein zirconium exists primarily in the form of zircon and is associated with minerals such as magnetite, ilmenite, niobite, epidote (Xing SJ, 2009). In addition, weathered crust zirconium deposits are also distributed in various locations such as Beiliu 520 deposit in Guangxi, Huazhou Pingding in Guangdong, Jianghua Gupoushan in Hunan, and Wanning Changan and Xinglong in Hainan (Wang RC et al., 2020).

3.4.2. Coal-Nb (Ta)-Zr (Hf)-REE-Ga polymetallic deposit in eastern Yunnan

Coal, as an organic sedimentary rock with reduction and adsorption barrier properties. Under specific geological conditions, it can be rich in zirconium, hafnium, uranium, and rare earth elements (including Lanthanide elements and yttrium), and reached the economically range and scale (Dai SF et al., 2014). A new type of clay-altered coal-Nb (Ta)-Zr (Hf)-REE-Ga polymetallic deposit was discovered by Dai SF et al. (2010) in 2010, within the lowest Lopingian (about 260 Ma) Xuanwei Formation ineastern Yunnan Province (Dai SF et al., 2010). Zhang H and Guo PP. (2022) posit that this particular deposit is classified as a weathering crust polymetallic deposit. The $(Zr,Hf)_2O_5$ grade ranges from 1%–3 % and the deposit thickness varies between 2–5 m, with a maximum of 10 m (Dai SF et al., 2010, 2016a, 2017). Zircon primarily exists in the form of ions adsorption within clay minerals found in alkaline limestone and tuff deposits, as well as partially filling cavities formed by altered primary magmatic minerals (Dai SF et al., 2016b, 2017). Dai SF et al. (2018) research has revealed that these polymetallic deposits are not only limited to Yunnan Province but also occur in western Guizhou, southern Sichuan, Chongqing and other regions. The deposits contain high concentration of critical

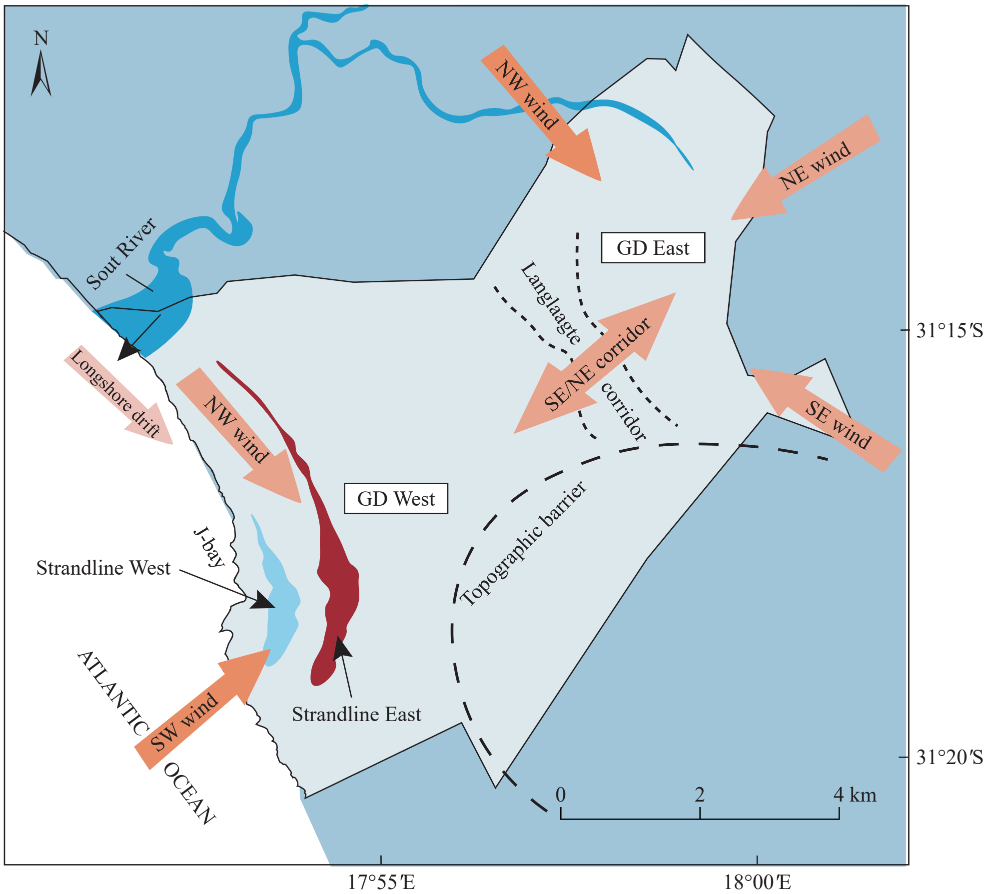

Fig. 10. Mineralization model map of the Namakawa Sands deposit (modified from Philander C and Rozendaal A, 2015a).

metals, including Zr (Hf), REE, and Ga, spanning a minimum area of 12000 km^2, consistent with the extent of the Emeishan large igneous province. This constitutes a world-class giant deposit of key metal minerals with significant resource potential (Zhao LX et al., 2016a, 2016b, 2017).

4. Metallogenic regularity of zirconium deposits in China

4.1. Temporal regularity of zirconium deposit formation

The major metallogenic periods of endogenic and exogenic zirconium deposits in China show different signatures. The mineralization of endogenic zirconium deposits, including alkaline rock- alkaline granite type, granite pegmatitic type, are predominantly formed during Permian to Cretaceous periods (Li MW, 2006; Huang H et al., 2014, 2018; Qiu KF et al., 2019; Lv ZH et al., 2018; Su HM et al., 2021). The Xinjiang Boziguo’er REE-Nb-Ta-Zr deposit formed during the hercynian period (290 Ma) (Huang H et al., 2014,2018), the Baerzhe Nb-Zr-REE deposit in Inner Mongolia in the Yanshanian period (123–124 Ma) (Li MW, 2006; Qiu KF et al., 2019; Su HM et al., 2021).

The exogenic zirconium deposits in China are mainly littoral placers with two main metallogenic stages: Early–Middle Late Pleistocene and Middle–Late Holocene (Ruan T, 1981; Tan QX and Sun Y, 1998; Wang Q, 2013). Current investigations reveal that few littoral placer deposits formed in the Early–Middle Pleistocene have been discovered along the coast of China, with only mineralized anomalies present in the eluvium in localized areas (Liu HS, 1989). Early–Middle Late Pleistocene is a crucial metallogenic stage of coastal placers. The placers formed during this period were primarily in the middle to late Pleistocene (Liu HS, 1989; Tan QX and Sun Y, 1998; Tong CL, 2018), likely due to the proximity of sea level to its present position and the warm, humid climate prevailing at that time. However, due to the considerable time elapsed since their formation, some placers underwent reformation in later periods, resulting in comparatively reduced preservation scales compared to the middle and late Holocene periods (Tan QX and Sun Y, 1998).

The source rocks for these placer deposits exhibit significant age variations, with detrital minerals originating from both submarine material and older endogenic deposits (Tan QX, 1998). These source materials undergo erosion, transportation over prolonged periods before final deposition. Wang SH et al. (2016) concluded that sediments found on the north coast of the South China Sea are primarily derived from Cathaysia blocks, comprised predominantly of Jurassic granites and metamorphosed Proterozoic–Paleozoic rocks. Wang YH et al. (2017) inferred that sediment sources along the coasts of these two seas mainly consist of source sediments from the Yellow River, coastal erosion sediments, as well as mixed sources from ancient subaqueous deltas of both the Yellow River and Yangtze River. Hence, littoral placers show a much younger mineralization age than their primary sources.

4.2. Spatial regularity of zirconium deposit

Endogenous zirconium deposits exhibit a strong genetic association with alkaline rocks-alkaline granite and pegmatite. Their distribution overlaps spatially with the Nb-Ta metallogenic belt in China. These deposits are preferentially distributed across three principal tectonic domains: (1) The northern margin of Tarim and North China Craton; (2) the southern part of the Greater Khingan Mountains metallogenic belt; (3) the western margin of the Yangtze Craton belt (Wang R et al., 2020). Specifically, the Bozigoer Nb-Ta-Tb-Zr-U-Th-REE deposit, Kuoketage REE-Nb-Ta-Zr deposit and Liaoning Saima U-REE-Zr deposit are located in the northern margin of the Tarim and North cratons in China, and the Inner Mongolia Barzhe Nb-Zr-REE deposit is located in the southern segment of Great Xing'an range. These deposits share a common genetic association with post-collisional tectonic environments, where extensive crust-mantle interactions and magmatic activities facilitate their formation.

The littoral placers are mainly distributed in the South China Sea - East China Sea coastal areas in South China and the Bohai Sea – Yellow Sea coastal areas in North China. These areas are characterized by tropical to subtropical climate, with high temperature, frequent rainfall and high humidity (Fu QJ and Cen L, 2008). Particularly well-developed deposits are found in Hainan, Guangxi and Fujian, with Hainan (Wanning, Wenchang, Lingshui) being most representative (Fu QJ and Cen L, 2008; Pan YJ et al., 2017). Geochemical studies have revealed high zirconium anomalies in coastal regions associated with syenite granite and Precambrian metamorphic basement rocks (Song JW et al., 2021; Wang SH et al., 2016). The spatial linkage between anomalous Zr source rocks and placer deposits indicates that local provenance plays a key role in controlling the distribution of coastal placers.

4.3. Genesis of zirconium deposits

The endogenic and exogenic zirconium deposits in China exhibit distinct temporal and spatial metallogenic regularities, leading to the development of distinct metallogenic models by geological researchers. A comprehensive understanding of these metallogenic models is crucial for zirconium mineral exploration and further geological research in China. In this part, genesis models of endogenous and exogenous zirconium ore in China will be briefly reviewed.

For endogenic deposits, the fluids/melts containing fluoride (F^-) and chloride (Cl^-) ions play a pivotal role in the formation of endogenic zirconium mineralization (Salvi S and Williams-Jones AE, 1990; Salvi S et al., 2000; Su HM et al., 2021). Chlorine and fluorine can form complexes with HFSE in aqueous solutions (Salvi S and Williams-Jones AE, 1996), resulting in Zr enrichment in residual melts. Fluorine can reduce the magma solidus temperatures (Salvi S et al., 2000, 2005), resulting in the precipitation of mineralized elements such as Zr and REE in melt after the magmatic stage (Yang WB et al., 2009, 2011; Su HM et al., 2021). Progressive cooling and pH reduction in these systems ultimately trigger the crystallization and deposition of rare metal-bearing complexes, culminating in economic mineralization.

There is a clear lanthanide tetrad effect in the chondrite-normalized REE distribution diagram of the Baerzhe Nb-Zr-REE deposit, the Boziguo’er REE-Nb-Ta-Zr deposit and the Keketuohai REE-Nb-Ta-Zr deposit (Jahn B et al., 2001b; Liu CQ and Zhang H, 2005; Huang H et al., 2014; Yang WB et al., 2014; Su HM et al., 2021), indicating strong differentiation crystallization as well as late-magmatic fluid-melt interaction during the mineralization process. Alkaline magmas emplace into groundmass along the deep fault which provides metallogenic space for the deposits, and interaction with the surrounding rocks (such as albitization, silicification, amphibolization, fenitization; Wang YX and Zhao ZH, 1997; Kempe U et al., 1999; Zhu JZ et al., 2013; Chen JY et al., 2019). Consequently, a significant amount of rare metal elements including Zr and REE are released from the groundmass, forming stable F^- and Cl^- bearing complexes in the fluids/melts. Rare metal bearing minerals including pyrochlore, monazite, fluorite, niobite, and other niobium-tantalum minerals are abundant in endogenic alkaline and peralkaline granite deposits (Liu CH et al., 2012; Chen JY et al., 2019; Sun ZH et al., 2013). Pegmatitic zirconium deposits are also associated with spodumene and other minerals in addition to niobium-tantalum minerals (Zhu JC et al., 2000).

However, the mineralization process of HFSE has long been contentious (Kogarko LN, 1990; Salvi S and Williams-Jones AE, 2006; Huang H et al. 2014; Yang WB et al. 2014, 2020; Su HM et al. 2021). HFSE enrichment is observed occurring predominantly during magmatic processes in peralkaline rocks (Kogarko LN, 1990; Schmitt AK et al., 2002; Huang H et al. 2014). Yet evidence of hydrothermal alteration has been identified in HFSE-rich alkaline igneous rocks like the Thor Lake and Strange Lake complexes in Canada and the Ilimaussaq complex in Greenland. Notably, HFSE-bearing minerals are present in miarolitic cavities (the Evisa complex, Corsica), and can also be captured within fluid inclusions (the Strange Lake complex, Cannada and the Baerzhe deposit, China) and zircons (the Tamazeght complex, Morocco), indicating a connection between HFSE mineralization and hydrothermal processes (Salvi S and Williams-Jones AE, 2006; Yang WB et al. 2014, 2020; Su HM et al. 2021). Additionally, Sheard ER et al. (2012) proposed the Nechalacho deposit at Thor Lake were formed via the couple of magmatic and hydrothermal processes.

The formation of exogenic type zirconium deposit differs from endogenic zirconium type, as it is closely related to exogenic geological processes, such as weathering processes, erosion processes, and sedimentary processes. Weathering crust type zirconium deposits are commonly found in completely weathering layer and partly weathering layer, the leaching of Zr, REE and other elements is facilitated by the acidic conditions in the surface weathering environment (Zhou MF et al., 2020). The subsequent water-rock interaction gradually increases the pH of infiltrated soil solution, which favors the formation of complexation between rare metal elements and carbonate ions and promote the adsorption of rare metal elements onto clay minerals (Zhou MF et al., 2020; Nechaev VP et al., 2021). Due to its chemical stability, Zr commonly occurs substituted within or adsorbed onto clay minerals in weathering crusts (Xu C et al., 2015).

The area of the littoral placers is widely developed with metamorphic complex and intrusive rocks such as syenite-granite and monzonitic granite that contain abundant zircon, ilmenite, rutile, and monazite (Lin MK et al., 2016; Xue YL et al., 2017; Poon P et al., 2020). Under the influence of high temperature and rainfall, the groundmasses surrounding the placers are prone to be weathered. Zircon accumulates in the weathering crust due to its stable chemical signature and strong resistance to weathering. Subsequently, the weathered crust transforms into both weathering crust deposits and residual slope deposits in certain conditions (Xu C et al., 2015).

The weathered igneous rocks and pre-existing weathering crust are continuously eroded by rivers, forming large amounts of zirconium-rich sediments. These sediments are later transported through river systems into the sea and supply detritus to the littoral placers (Zhang ZY, 1991). Within the coastal zone, the longshore current is the main driving force for large-scale detritus transport (Pan YJ et al., 2017). After the detritus are transported into the sea by the river, the zirconium-bearing mineral detritus are continuously enriched under the sorting action of wave and longshore current. When the longshore current passes through the landform such as the barrier and sand spit, its velocity decreases, and the mineral-bearing detritus are precipitated.

5. Analysis of zirconium deposit prospecting potential

5.1. Prospecting potential of endogenous zirconium deposits

The metallogenic regularity of endogenous zirconium deposits in China is characterized by a concentrated distribution and specific metallogenic age. Tectonically, these deposits are mainly found in the northern margin of Tarim and North China cratons, the southern part of the Greater Khingan Mountains metallogenic belt and the western margin of the Yangtze Craton belt which was formed during an extended period after collision events (Li MW et al., 2006). In terms of metallogenic age, endogenous zirconium deposits are primarily formed during Permian to Cretaceous periods (Li MW et al., 2006; Huang H et al., 2014; Qiu KF et al., 2019; Sun ZH et al., 2021). There exists a close genetic correlation between ore-forming groundmasses and magmatic activities (Salvi S and Williams-Jones AE, 1990; Salvi S et al., 2006; Yang WB et al., 2020; Su HM et al., 2021), wherein fluorine- and chlorine-rich fluids play a vital role in the process of deposits formation (Salvi S et al., 2006). On the basis of previous discussion, the authors recommend prioritizing exploration in these key metallogenic provinces, the Tarim and North China cratons, the Greater Khingan Mountains metallogenic belt and the western margin of the Yangtze Craton belt. These areas should focus on hydrothermally altered complexes, which typically consist of Permian to Cretaceous alkaline granite, alkali feldspar granite, syenite granite, and monzonitic granite formed. Additionally, large geode deposits with fluorite and calcite veins serve as key indicators for locating deposits (Su HM et al., 2021). However, endogenous zirconium deposits are present in the form of associated minerals within ore-bearing groundmasses such as alkaline granite and alkaline complexes, which are restricted by the difficulty of mineral processing and high mining cost during mining.

To enhance the comprehensive use of endogenous zirconium deposits, the authors suggest that further investment in scientific and technological innovation should be increased as well as actively facilitating collaborations between universities and research institutions. These collaborations should prioritize advancing extraction technologies and metallurgical processes specific to endogenous zirconium deposits. In addition, present researched on pegmatitic zirconium deposits are preliminary, many questions urgently need to be solved, for instance the source rock as well as mineralization process remain unclear. Therefore, it is imperative to conduct a systematic study on the mineralization process of pegmatitic zirconium deposits and establish a national database that can serve as a basis for prospecting and exploration.

5.2. Prospecting potential of weathering crust type zirconium deposits

Areas of China with hot and rainy climates are potential zirconium deposits prospects. A notable example is the Coal-Nb (Ta)-Zr (Hf)-REE-Ga polymetallic deposit in eastern Yunnan Province was formed during the Late Permian period (Dai SF et al., 2010) and is located within the lowest Lopingian (about 260 Ma) Xuanwei Formation, where carbonaceous shale and coal deposits are present. Additionally, a significant abundance of rare metal minerals such as zircon and monazite have been discovered within the coal mine (Dai SF et al., 2016b). The mineralization process of this deposit is related to chemical weathering. During the Late Permian, the hot and humid climate in Guizhou, Yunnan, and Sichuan facilitated the activation, migration, enrichment, and mineralization of zirconium and other elements through chemical weathering processes. It is reasonable to infer that under humid climate conditions, weathered crusts containing zirconium deposits may be discovered in other continental regions characterized by alkaline groundmasses undergoing deep weathering. In addition, the natural gamma logging data of the Coal-Nb (Ta)-Zr (Hf)-REE-Ga polymetallic deposit in eastern Yunnan Province exhibits obvious positive anomalies compared to normal sedimentary rocks developed in the provenance area dominated by mafic basalt. These geophysical characteristics provide a reliable exploration criterion for identifying analogous weathering-related polymetallic deposits in the region. However, the research degree of weathered crust zirconium deposits is relatively low, and the tectonic background as well as the evolution process of the deposits remain unclear. Additionally, there is a lack of understanding regarding the enrichment, migration, and mineralization processes of ore-forming elements. Therefore, the authors recommend defining the eastern Yunnan, eastern Jiangxi and southern Jiangxi as areas for prospecting surveys in order to systematically study the metallogenic regularity (Fig. 11). This will enable us to delineate potential prospecting areas and availability of weathering crust deposits.

5.3. Prospecting potential of littoral sedimentary zirconium deposit

The littoral sedimentary zirconium deposit is currently the main source of zirconium in China (Che D et al., 2016; Zhang ZF et al., 2019; Wang RC et al., 2020) However, due to China's import volume of zirconium far exceeds domestic production the exploration for potential littoral zirconium placers in alternative regions holds paramount significance. The littoral zirconium placers are mainly distributed along the coast, with the main enrichment area ranging from the shore to 5–10 km from the coast. These deposits primarily form within medium-fine to silty grained sand layers of the Quaternary system. The parent rocks of littoral zirconium placers mainly consist of granite, pre-Cambrian metamorphic rocks, and Yanshanian intrusive rocks. These rocks are abundant in minerals such as zircon and ilmenite, serving as significant material sources for exogenous zirconium deposits (Table 2). Based on statistical data, medium-acid intrusive rocks in various regions such as Shandong, Fujian, Guangdong, and Hainan demonstrate elevated zircon content, ranging from 35.16 g/t to 153.2 g/t, 30.84 g/t to 41.06 g/t, 35.52 g/t to 96.05 g/t, and 97 g/t to 374 g/t, respectively. Additionally, noteworthy anomalies in zirconium concentrations are observed from a geochemical perspective. (Fig. 11). In addition to Hainan, ZrO_2 concentration in Guangxi, Guangdong, Fujian, Shandong and other regions has a positive anomaly, which has the potential to form deposits. Tectonic conditions play a crucial role in governing the

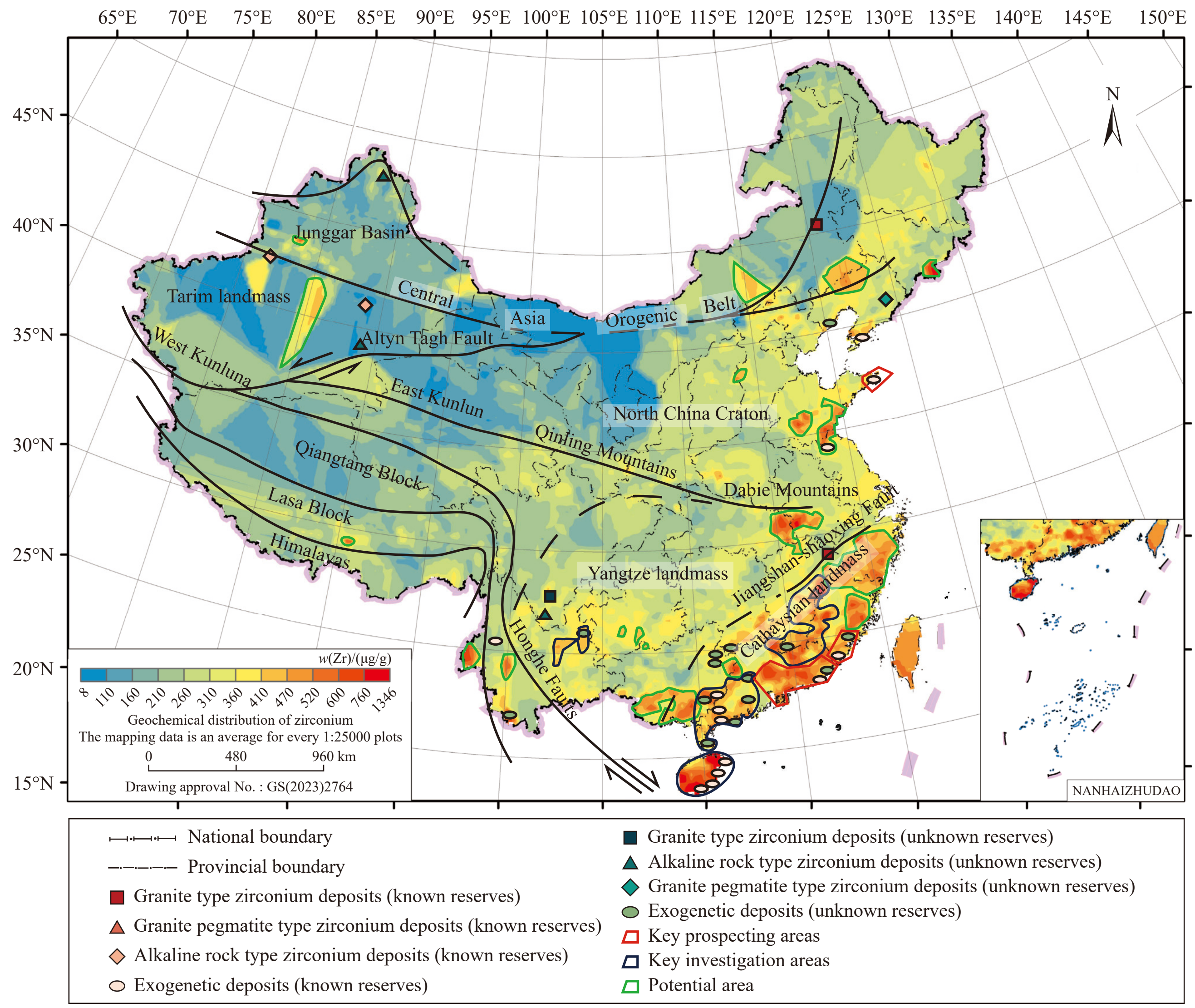

Fig. 11. Prospect area of zirconium deposits in China.

Table 2. Littoral placers resources and parent rock types in various provinces of China.

Provinces	Deposit scale[1]				Parent rock[2]	Primary minerals[3]			Associated minerals[4]
	Large	Medium	Small	Mineral Points		Zircon /(g/t)	Ilmenite /(g/t)	Monazite /(g/t)	
Liaoning	–	–	2	9	Archean-ancient metamorphic rocks	32.1	2.86	Trace	Xenotime, ilmenite, magnetite, rutile, monazite, columbite-tantalite
					Archean-ancient magmatic rocks	59.76	86.29	15.3	
Hebei	–	–	–	4	Yanshannian intrusive rocks	55.79	11.19	0.2	Rutile, cassiterite
Shandong	3	4	9	22	Jiaodong Group metamorphic rocks	148.88	68.76	Trace	Ilmenite, magnetite, rutile, xenotime, columbite-tantalite
					Proterozoic granites	35.16	A small amount	4.33	
					Yanshanian granites	153.2	33.38	–	
Zhejiang	–	–	–	4	Volcanoes-sedimentary rock systems	32.2	1.01	Very Few	Monazite, ilmenite, rutile
Fujian	1	3	7	29	Yanshanian intrusive rocks	30.84	106.48	8.92	Ilmenite, magnetite, rutile, monazite, xenotime
					Volcanic-sedimentary rock systems	41.06	34.65	0.01	
					Dongshan metamorphic rocks	38.26	186.04	48.89	
Guangdong	3	23	54	57	Cambrian Bacun Group metamorphic rocks	96.05	64.66	34.47	Zircon, ilmenite, rutile, magnetite, monazite, cassiterite, columbite-tantalite, xenotime
					Yanshanian acid magmatic rocks	35.52	34.48	17.44	
Guangxi	4	2	5	2	Caledonian granites	–	–	–	Ilmenite, chromite, monazite, rutile, zircon, xenotime
Hainan	10	25	37	57	Basalts	97–133	370–526	Trace	rutile, chromite, monazite, columbite-tantalite, cassiterite, sperrylite, xenotime,
					Diorites and granites	374	436	Trace	

Notes: Data source: 1, 4–Chen Z et al., 2006; 2, 3–Pan YJ et al., 2017. "-" indicates no data.

distribution of placer deposits. Uplift and subsidence during different geological periods exert significant influence on the formation and evolution of continental landforms as well as the spatial distribution of ore-bearing source rocks (Tan QX and Sun Y, 1998). The coastal regions of Guangdong, Fujian, and Shandong are situated in uplift zones that facilitate weathering, denudation, and transportation of ore-bearing debris (Li CX et al., 1988). Among these areas, Guangdong boasts a lengthy coastline with numerous islands and widely distributed first and second abrasion terraces (Fan SY, 2004). According to the regulations, it can be inferred that the coastal areas with the development of syenite-granite, monzonitic granite, Precambrian metamorphic rocks and Yanshanian intrusive rocks are the primary exploration areas. The presence of positive ZrO_2 anomalies in geochemistry indicates that there is a large amount of zircon in this area. Littoral sedimentary zirconium deposits occur primarily in barrier islands, sand spits, abrasion terraces, subaqueous deltas, submarine terraces and other landforms. According to the afore-mentioned prospecting characteristics, the key prospecting areas in the southeast and northeast coastal regions of China are designated as southern Fujian, eastern Guangdong, and Rongcheng of Shandong. Additionally, the key investigation areas are designated as southern Guangdong and Hainan regions (Fig. 11).

Currently, the only zirconium deposits available for mining in China are littoral placers. However, the main mining areas in Hainan Province, which holds the largest reserves of the exogenic deposits, are subject to strict regulations due to the establishment of ecological reserves. Additionally there are challenges in the comprehensive utilization and development of endogenous zirconium deposits. With the increasing demand for zircon in China, it is of great significance to search for potential available zirconium deposits for the development of related industries in China. On one hand, it is imperative to intensify the exploration of zirconium deposits by utilizing techniques such as UAV aeromagnetic measurements, large-scale aerial radioactivity surveys, shallow drilling, and other techniques to conduct targeted exploration of key metallogenic belts (Shandong, Fujian, Guangdong), especially medium-fine to silty grained sand layers within the Quaternary system. To accurately identify potential zirconium deposits, the authors suggest prioritizing areas that exhibit significant enrichment of heavy minerals such as zircon, ilmenite and monazite. On the other hand, for the undeveloped zirconium deposits resources in Inner Mongolia, Xinjiang and other areas, the research and innovation of endogenous zirconium deposits development technology should be intensified to enhance the comprehensive utilization efficiency of endogenous zirconium deposits. Furthermore, the weathered crust zirconium deposits found in Chongqing, western Guizhou, southern Sichuan, and Yunnan exhibit significant resource potential. It is recommended to enhance research efforts to explore the metallogenic background and process of these deposits. This will serve as a foundation for prospecting and exploration activities.

6. Conclusions

(i) China's zirconium deposits exhibit a diverse array of mineralization types, including alkaline rock-alkaline granite-hosted deposits, granite-pegmatite associations, clastic sedimentary-type deposits, weathering crust-type accumulations, and fragmentation-type concentrations. The genesis of endogenic zirconium mineralization is primarily linked to fluorine- (F^-) and chlorine-rich (Cl^-) hydrothermal fluids. These halide ions form stable complexes with highly incompatible elements such as zirconium (Zr) and rare earth elements (REEs), enabling their significant enrichment in fluid-melt systems. Furthermore, these anions play a pivotal role in modulating magmatic cooling processes, thereby facilitating more complete mineral crystallization through their influence on phase equilibria and melt viscosity.

(ii) Exogenic zirconium deposits form through a sequence of surficial processes involving weathering dynamics, sediment transport, and coastal redistribution. The mineralization cycle initiates with chemical weathering of source rocks, generating a mature weathering crust through hydrolytic alteration and mineral decomposition. This weathering regime directly governs the formation of two principal deposit types: residual weathering crust accumulations and slope-alluvial placers. Subsequently, erosion mobilizes rock detritus, with hydrodynamic sorting concentrating heavy minerals in specific depositional environments. Part of the heavy minerals become temporarily sequestered in estuaries and abrasion platforms. The remaining fraction undergoes alongshore redistribution via littoral current systems, ultimately forming extensive strandline placer deposits through wave-energy concentration processes.

(iii) In China, endogenic zirconium deposits constitute 70% of reserves while exogenic types represent 30%. However, endogenic deposits face exploitation challenges due to suboptimal ore grades, complex mineral processing requirements, and elevated extraction costs. Conversely, exogenic deposits dominate current mining operations owing to their large-scale distribution, stratigraphic consistency, near-surface occurrence, simplified open-pit accessibility, and efficient beneficiation-smelting workflows.

(iv) With the advancement of critical emerging industries, urgent requirements emerge to strengthen zirconium exploration targeting medium-fine to silty grained sand deposits in Quaternary strata of strategic metallogenic belts (Shandong, Fujian, Guangdong). These formations contain elevated concentrations of heavy mineral assemblages - zircon, ilmenite, monazite, etc. In regions with untapped zirconium resources like Inner Mongolia and Xinjiang, prioritized research on endogenetic deposits becomes imperative, demanding intensified technoscientific innovation to optimize comprehensive resource utilization efficiency.

Concurrently, prioritized investigation and systematic assessment of weathered zirconium deposits are urgently required. Parallel efforts must focus on strategic overseas market expansion to secure adequate reserves of this critical mineral. This dual-focused strategy establishes robust supply chain resilience while satisfying escalating demands from next-generation industries dependent on zirconium technologies.

CRediT authorship contribution statement

This project was initially conceived by Qiong-Wen Liang, Yong-Shen Li. Qiong-Wen Liang wrote the original draft manuscript, to which Yong-Shen Li, Qiong-Wen Liang, Ying-Cai Sun and De-Gao Zhai provided editing and additional writing. All authors discussed the results and contributed to the final manuscript.

Declaration of competing interest

The authors declare no conflicts of interest.

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