Discrete Zr and REE mineralization of the Baerzhe rare-metal deposit, China

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ABSTRACT

Although REE (lanthanides + Sc + Y) mineralization in alkaline silicate systems is commonly accompanied with Zr mineralization worldwide, our understanding of the relationship between Zr and REE mineralization is still incomplete. The Baerzhe deposit in Northeastern China is a reservoir of REE, Nb, Zr, and Be linked to the formation of an Early Cretaceous, silica-saturated, alkaline intrusive complex. In this study, we use in situ laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) analyses of zircon and monazite crystals to constrain the relationship between Zr and REE mineralization at Baerzhe.

Three groups of zircon are identified and are differentiated based upon textural observations and compositional characteristics. Type Ia zircons display well-developed oscillatory zoning. Type Ib zircons are darker in cathodoluminescence images and have more irregular zoning and resorption features than type Ia zircons. In addition, type Ib zircons can locally occur as overgrowths on type Ia zircons. Type II zircons contain irregular but translucent cores and rims with oscillatory zoning that are murky brown in color and occur in aggregates. Textural features and compositional data suggest that types Ia and Ib zircon crystallized at the magmatic stage, with type Ia being least-altered and type Ib being strongly altered. Type II zircons, on the other hand, precipitated during the magmatic to magmatic-hydrothermal transition. Whereas the magnitude of the Eu anomaly is moderate in the barren alkaline granite, both magmatic and deuteric zircon exhibit pronounced negative anomalies. Such features are difficult to explain exclusively by feldspar fractionation and could indicate the presence of fluid induced modification of the rocks. Monazite crystals occur mostly through replacement of zircon and sodic amphibole; monazite clusters are also present. Textural and compositional evidence suggests that monazite at Baerzhe is hydrothermal.

Types Ia and Ib magmatic zircon yield 207Pb-corrected 206Pb/238U ages of 127.2 ± 1.3 and 125.4 ± 0.7 Ma, respectively. Type II deuteric zircon precipitated at 124.9 ± 0.6 Ma. The chronological data suggest that the magmatic stage of the highly evolved Baerzhe alkaline granite lasted less than two million years. Hydrothermal monazite records a REE mineralization event at 122.8 ± 0.6 Ma, approximately 1 or 2 million years after Zr mineralization. We therefore propose a model in which parental magmas of the Baerzhe pluton underwent extensive magmatic differentiation while residual melts interacted with aqueous hydrothermal fluids. Deuteric zircon precipitated from a hydrosilicate liquid, and subsequent REE mineralization, exemplified by hydrothermal monazite, correlates with hydrothermal metasomatic alteration that postdated the hydrosilicate liquid event. Such interplay between magmatic and hydrothermal processes resulted in the formation of discrete Zr and REE mineralization at Baerzhe.

Keywords: Textural relationship; zircon and monazite; in situ LA-ICP-MS analysis; Baerzhe REE-Nb-Zr-Be deposit
Zirconium and REEs have been widely recognized to be spatially associated with peralkaline and alkaline igneous rocks worldwide, such as the Strange Lake deposit in Canada, the Khalzan Buregte deposit in Mongolia, and the Baerzhe deposit in China. Key aspects of REE mineralization have been well documented, including the nature of the ore-hosting granites (Dumańska-Słowik 2016; Wu et al. 2016), REE solubility and mobility in melts and fluids (e.g., Niu et al. 2008; Gysi and Williams-Jones 2013), geochemical behavior during hydrothermal mobilization (Censi et al. 2017; Dai et al. 2017), and genesis of Zr–Nb–REE mineralization (Yang et al. 2014; Kempe et al. 2015; Gladkocub et al. 2017). Much less understood is the spatio-temporal and genetic relationship between Zr and REE minerals in alkaline systems (e.g., Škoda and Novák 2007; Linnen et al. 2014; Petrella et al. 2014; Möller and Williams-Jones 2016; Wu et al. 2018). A recent mineralogical study on the sodic lujavrite from the Saima alkaline complex in NE China by Wu et al. (2016) suggested that Zr mineralization preceded REE mineralization, but this study lacked robust geochronological constraints.

The Baerzhe REE-Nb-Zr-Be deposit, situated in Inner Mongolia (NE China), has an estimated reserve of 1.0 Mt of total REE oxides at an average grade of 0.57 wt%, 2.8 Mt of ZrO$_2$ at an average grade of 2.73 wt%, 300 Kt of Nb$_2$O$_5$ at an average grade of 0.24 wt%, and 48 470 t of BeO at an average grade of 0.05 wt% (Internal report of the LU’AN mining company 2011). Beryllium is extracted from hingganite [(Y,REE,Ca)$_2$(Fe$^{3+}$)Be$_2$(SiO$_4$)$_2$(OH)$_2$] as an important by-product (Wang and Zhao 1997). The deposit is hosted by the Early Cretaceous Baerzhe alkaline granite (Fig. 1). Previous research on the Baerzhe deposit has defined the petrogenesis of the ore-hosting Baerzhe alkaline granite (Jahn et al. 2001; Yuan et al. 2003), nature and evolution of ore-forming fluids (Sun et al. 2013), timing of the Baerzhe granite emplacement and zirconium mineralization (Zhang and Yuan 1988; Wang and Zhao 1997; Yang 2012; Yang et al. 2014), magmatic-hydrothermal processes controlling the enrichment of REE (Niu et al. 2008; Yang et al. 2011), and ore genesis (Yang et al. 2009; Qiu et al. 2014) by using petro-geochemistry, Sr-Nd-Pb-Hf-O isotopes, zircon U-Pb and whole-rock Rb-Sr geochronology, and microthermometry and Raman laser analysis on crystal-rich fluid and melt inclusions. The previous work provides a platform to build off and to investigate the textural and temporal relationship between Zr and REE mineralization in the Baerzhe alkaline silicate system.

Monazite is a REE-rich orthophosphate mineral that contains a broad array of light rare earth elements (LREEs) and HREEs (including Y) (Zhu et al. 1997; Williams et al. 2007). Because it is present in a wide variety of rock types, and contains significant Th and U, with negligible common Pb relative to radiogenic Pb, monazite has been widely used for Th–U–Pb dating as a robust

**FIGURE 1.** (a) GoogleEarth image showing the location of the Baerzhe REE-Nb-Zr-Be deposit (Inner Mongolia, China). (b) Sketch geological map of the Baerzhe deposit showing the phase relationship of the Baerzhe alkaline igneous complex. (c) Simplified cross section geological profile labeled in b by line A–A’ showing the five lithologic facies and their relationship to Late Jurassic volcanic rocks recognized by mapping from the drilling hole samples (modified after Yuan et al. 1980; Jahn 2004; Niu et al. 2008; Sun et al. 2013).
Zircon and monazite geochronology using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is an important step toward a better understanding of the evolution of magmatic and hydrothermal ore deposits (Zhu and O’Nions 1999; Brown et al. 2002; Vielreicher et al. 2003; Spencer et al. 2016; Deng et al. 2017). Modern research focused on the geochronology of the Baerzhe rare-metal deposit is well established (Table 1); however, few published geochronological data provide convincing age constraints on Zr due to the use of zircon separates and no direct age data on monazite has been reported. The application of in situ compositional and geochronological analyses on the doubly polished thin sections carried out in this study prevent the loss of textural context and potential mixing of polygenetic age populations of zircon and monazite that may occur using methods that require mineral separation and grain mount preparation. However, it should be noted that spot analyses providing lower U abundances and elevated common Pb contents need to be corrected for, along with possible matrix effects.

Mineralogical and geochemical analyses of monazite and zircon and in situ LA-ICP-MS U-Pb isotopic analyses on doubly polished thin sections were conducted in this study. The age differences between monazite (as a proxy for REE mineralization) and zircon (as a proxy for Zr mineralization) provide insight into the magmatic-hydrothermal evolution at the Baerzhe REE-Nb-Zr-Be deposit.

### GEOLOGICAL SETTING AND PREVIOUS GEOCHRONOLOGY

The Baerzhe deposit (Inner Mongolia, China) is covered geochronometric studies (Qiu and Yang 2011; Williams et al. 2011).

Zircon and monazite geochronology using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is a major step toward a better understanding of the mineralogy and hydrothermal ore deposits (Zhu and O’Nions 1999; Brown et al. 2002; Vielreicher et al. 2003; Spencer et al. 2016; Deng et al. 2017). Modern research focused on the geochronology of the Baerzhe rare-metal deposit is well established (Table 1); however, few published geochronological data provide convincing age constraints on Zr due to the use of zircon separates and no direct age data on monazite has been reported. The application of in situ compositional and geochronological analyses on the doubly polished thin sections carried out in this study prevent the loss of textural context and potential mixing of polygenetic age populations of zircon and monazite that may occur using methods that require mineral separation and grain mount preparation. However, it should be noted that spot analyses providing lower U abundances and elevated common Pb contents need to be corrected for, along with possible matrix effects.

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### GEOLOGICAL SETTING AND PREVIOUS GEOCHRONOLOGY

The Baerzhe deposit (Inner Mongolia, China) is covered largely by Mesozoic volcanic basins that developed along a northeast (NE) and north-northeast (NNE) trending deep-seated fault zone on Permian basement (Fig. 1a). The REE-Nb-Zr-Be mineralized Baerzhe granite (125–123 Ma; Wang and Zhao 1997; Qiu et al. 2014; Yang et al. 2014) is exposed over approximately 0.4 km². The granite comprises the west body and the east body and intruded the Late Jurassic Baiyingaolao Formation consisting of andesite lavas and tuffs (Fig. 1b). The east body with abundant miarolitic cavities, and a barren and weakly mineralized, sodic amphibole-rich, hypersolvus granite in the lower part.

The mineralized transsolvus granite in the upper part is commonly coarse-grained with abundant mafic enclaves, and composed of 45–50 vol% subhedral to euhedral quartz that is 0.4 to 1 mm in size, 20–30 vol% subhedral to euhedral quartz that is 0.5 to 1 mm in size, 20–25 vol% albite, 1–5 vol% aegirine, and minor sodic amphibole and zircon. The barren hypersolvus granite in the lower section is usually fine-grained and contains 50–55 vol% of microcline, 15–20 vol% quartz, 10–15 vol% sodic amphibole, 8–12 vol% albite, with minor aegirine and zircon (Fig. 2; Wang and Zhao 1997; Jahn et al. 2001; Yuan et al. 2007; Yang et al. 2013). The REE-Nb-Zr-Be ores of the Baerzhe deposit are hosted by the Baerzhe igneous complex. These alkali granites show a large diversity of medium- to coarse-grained textures (Fig. 2). They are characterized by high silica content (up to 75 wt% SiO₂) and high alkali content (8.6–9.1 wt% K₂O +Na₂O). The pegmatites are rich in volatiles (190–2500 ppm F), poor in sulfur (40–12 wt% Al₂O₃). They contain elevated abundances of incompatible elements, including Rb, Y, Zr, Hf, Ta, Nb, Th, U, REEs (except for Eu), and F, and low concentrations of CaO, MgO, P₂O₅, Ba, and Sr. They are highly fractionated with an average Nb/Th ratio of 27, an average LREE/HREE ratio of 1.3 (normalized from Masuda et al. 1973), and show “v-shaped” REE patterns enriched in Ce, but depleted in Eu (Wang and Zhao 1997; Jahn et al. 2001; Yang 2012).

Previously described mineralogical and geochemical fea-

### TABLE 1. Geochronological data compilation of the Baerzhe deposit

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Age (Ma)</th>
<th>Mineral</th>
<th>Method</th>
<th>Analyses number</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Baerzhe alkaline granite</td>
<td>127.2 ± 3.5</td>
<td>Whole-rock</td>
<td>Rb-Sr isochron</td>
<td>6</td>
<td>Zhang and Yuan 1988</td>
</tr>
<tr>
<td>2</td>
<td>Baerzhe albite granite</td>
<td>125.2 ± 5.2</td>
<td>Whole-rock</td>
<td>Rb-Sr isochron</td>
<td>6</td>
<td>Wang and Zhao 1997</td>
</tr>
<tr>
<td>3</td>
<td>Alkaline granite</td>
<td>127.2</td>
<td>Whole-rock</td>
<td>Rb-Sr isochron</td>
<td>Not available</td>
<td>Yuan et al. 2003</td>
</tr>
<tr>
<td>4</td>
<td>Alkaline granite</td>
<td>121.6 ± 2.3</td>
<td>Whole-rock</td>
<td>Rb-Sr isochron</td>
<td>15</td>
<td>Yang 2012</td>
</tr>
<tr>
<td>5</td>
<td>Alkaline granite</td>
<td>123.1 ± 2.3</td>
<td>Light and dark colored zircon</td>
<td>LA-ICP-MS</td>
<td>14</td>
<td>Yang 2012</td>
</tr>
<tr>
<td>6</td>
<td>Baerzhe alkaline granite</td>
<td>122.7 ± 1.8</td>
<td>Magnetic zircon</td>
<td>SIMS</td>
<td>13</td>
<td>Yang et al. 2013</td>
</tr>
<tr>
<td>7</td>
<td>Alkaline granite</td>
<td>123.9 ± 1.2</td>
<td>Hydrothermal zircon</td>
<td>SIMS</td>
<td>7</td>
<td>Yang et al. 2013</td>
</tr>
<tr>
<td>8</td>
<td>Alkaline granite</td>
<td>123.5 ± 3.2</td>
<td>Least altered magmatic zircon</td>
<td>LA-ICP-MS</td>
<td>13</td>
<td>This study</td>
</tr>
<tr>
<td>9</td>
<td>Alkaline granite</td>
<td>127.2 ± 1.3</td>
<td>Strongly altered magmatic zircon</td>
<td>LA-ICP-MS</td>
<td>28</td>
<td>This study</td>
</tr>
<tr>
<td>10</td>
<td>Alkaline granite</td>
<td>125.40 ± 0.73</td>
<td>Deuterite zircon</td>
<td>LA-ICP-MS</td>
<td>29</td>
<td>This study</td>
</tr>
<tr>
<td>11</td>
<td>Alkaline granite</td>
<td>124.86 ± 0.63</td>
<td>Hydrothermal zircon</td>
<td>LA-ICP-MS</td>
<td>37</td>
<td>This study</td>
</tr>
<tr>
<td>12</td>
<td>Alkaline granite</td>
<td>122.82 ± 0.62</td>
<td>Hydrothermal zircon</td>
<td>LA-ICP-MS</td>
<td>37</td>
<td>This study</td>
</tr>
</tbody>
</table>
tures (Bai et al. 1980; Ding et al. 1985; Sun et al. 2013; Yang et al. 2014) have been interpreted as evidence for a multistage metasomatic alteration that resulted in pronounced compositional and mineralogical heterogeneity in alteration assemblages. The rare-metal mineralization, including Zr, Nb, and REEs, is contained in a series of minerals, including zircon, hingganite, ferrocolumbite, pyrochlore, monazite, and bastnäsite. Zircon is the only ore mineral for Zr, and REEs are predominantly contained in hingganite. The main host of Nb is columbite-(Fe).

Much recent research has focused on the geochronology of the intrusive rocks of the Baerzhe rare-metal deposit (Table 1). The Baerzhe alkaline granite host had been previously dated by three different methods, yielding relatively consistent results. Zhang and Yuan (1988) preliminarily reported the alkaline granite was emplaced at 127 Ma (six albite granite samples) using whole-rock Rb-Sr dating. The ~127 Ma age was accepted as the age of mineralization in the Baerzhe deposit until the early 2000s when newer data reported 125 ± 2 Ma (six albite granite samples; Wang and Zhao 1997) and 127.2 Ma (alkaline granite, number of the analyzed samples not clear; Yuan et al. 2003) ages determined by whole-rock Rb-Sr. However, the applicability of the Rb-Sr method for determining the age of mineralization at Baerzhe was recently challenged (Yang 2012). Since the Baerzhe alkaline granite is highly fractionated and contains as much as 1545 ppm Rb and less than 5.387 ppm Sr, this could obscure the original relationship of Rb to common Sr at the time of crystallization and affect calculations of initial Sr (Clark and Černý 1987). Yang (2012) eventually argued that a Rb-Sr isochron age of 121.6 ± 2.3 Ma (15 albite granite samples) represents the age of the highly evolved Baerzhe alkaline granite. Subsequently, high-precision LA-ICP-MS and SIMS U-Pb dating on zircon crystals separated from the mineralized and barren alkaline granite yield ages of the zircon crystals growth at 123.5 ± 3.2 Ma (7 hydrothermal zircons; Yang et al. 2013), and 122.7 ± 1.8 Ma (22 light colored zircons and 12 dark colored zircons; Qiu et al. 2014), and timing of the granite emplacement at 123.9 ± 1.2 Ma (17 magmatic zircons; Yang et al. 2013), and 123.1 ± 2.3 Ma (14 magmatic zircons; Yang 2012).

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**Figure 2.** Hand specimen of the representative samples studied in this work showing the texture and mineral assemblage. Qz = quartz, Ab = albite, Amp = amphibole, Kfs = K-feldspar, Hem = hematite.
SAMPLE PREPARATION AND ANALYTICAL METHODS

Petrography

For the present study, 15 variably altered rock and ore samples were selected from surface exposures and subsurface drill cores. All rock samples were locally affected by late metasomatic alteration and display different degrees of ore mineralization (Fig. 2). Initially, 25 representative doubly polished thin sections (100 μm thick) were prepared for petrographic analysis and examined using a standard petrographic microscope to investigate textures and mineral assemblages, as well as relationships between constituent minerals. Full thin section views were created using a Canon Cool Scan 4000 at the Colorado School of Mines as a tool for mapping and locating the minerals identified during petrographic observations that would be later characterized in situ by geochemical techniques.

Five thin sections were studied using a JEOL JSM-5800LV scanning electron microscope (SEM) at the U.S. Geological Survey (USGS) in Denver, Colorado, to locate and identify the accessory minerals such as zircon and monazite grains as small as a few micrometers in size in direct textural context. The latter was combined with an energy-dispersive spectrometer for mineral identification.

Backscattered electron (BSE) images of mineral grains collected by SEM at the USGS in Denver and the Development and Research Center of the China Geological Survey were used to characterize the distribution and intergrowth relationships of zircon and monazite and their associated minerals at 1–5 μm scales. The cathodoluminescence (CL) images were collected using a JXA-880 electron microprobe and image analysis software under operating conditions of 20 kV and 20 nA at the Tianjin Institute of Geology and Mineral Resources of CGS, to identify the internal structure, texture, and inclusions within zircon grains. Mineral abbreviations throughout the text, including those in the figures, are after Whitney and Evans (2010).

LA-ICP-MS rare earth element analyses of zircon

In situ trace element concentrations and U–Pb ages of 32 analyses spots on 28 zircon grains were determined on a polished thin section of alkaline granite host using the National Institute of Standards and Technology (NIST) 610 (Jochum et al. 2007ab) as an external standard (32.78 wt%). Operating conditions were a 20 kV accelerating voltage, a 10 nA beam current, a beam diameter of 30 μm, an 8 Hz repetition rate, and an energy density of 6.3 J/cm² at a repetition rate of 6 Hz. A 29 μm spot was used for the analyses. Analyzed elements included the following: Si, Ca, Ti, Rh, Sr, Y, Na, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb, Th, and U. Calibration was performed using the National Institute of Standards and Technology (NIST) 610 (Jochum et al. 2007ab) at a repetition rate of 6 Hz. A 29 μm-FX ArF Excimer laser ablation system (ESI Ltd.) was used for both calibration and data reduction. The machine has nine Faraday cups: one fixed central channel and eight motorized Faraday cups. The secondary electron multiplier is bound with the central channel and the four ion counters are bound with the L4 Faraday cup. Detailed operating conditions of the laser ablation system and the ICP-MS instrument and data reduction are provided in Geng et al. (2017). 206Pb/238U, 207Pb/206Pb, 208Pb/206Pb ratios were calculated using measured isotope signal intensities. Mass bias, (mass-induced mass fractionation and instrument drift were corrected using ICPMSDataCal 8.4 (Liu et al. 2010). Concordia diagrams and weighted mean U–Pb ages were processed using Isoplot version 3.75 software (Ludwig 2012). Common-Pb corrections were made using the method of Andersen (2002).

All zircon analyses were conducted with a beam diameter of 30 μm, an 8 Hz repetition rate, and an energy density of 10 J/cm². GI-1 was used as an external standard for U–Pb geochronology analyses (published TIMS ages of 206Pb/238U = 600.7 ± 1.1 Ma, 207Pb/206Pb = 602.0 ± 1.0 Ma, and 208Pb/206Pb = 607.7 ± 4.3 Ma; Jackson et al. 2004). NIST SRM 610 glass was used as an external standard to calculate U, Th, and Pb concentrations of zircon. Five every analyses were followed by two analyses of the standard zircon GI-1.

All monazite analyses were conducted with a beam diameter of 15 μm, a 4 Hz repetition rate, and an energy density of 10 J/cm². The reference standard material 44069 (SIMS U–Pb age: 424.9 ± 0.4 Ma; Aleinikoff et al. 2006) was analyzed after every five unknowns under identical conditions.

RESULTS

Textural features

Zircon grains range in shape from euhedral to anhedral, with sizes up to 300 μm in width. Some euxenite, monazite, and bastnaésite grow in cracks within zircon grains.

Zircon crystals investigated herein are further classified into three types, as indicated below, based on their occurrence mode and relationship with minerals. Type Ia zircons are found as subhedral to euhedral crystals and generally display well-developed oscillatory zoning both in optical and CL images, and they yield condensed growth zones with relatively light rims expressed by CL imaging (Table 2, Fig. 3).

Type Ia zircons are intergrown with magmatic phases including quartz, K-feldspar, and sodic amphibole (Fig. 4). Such zircons appear darker in CL images, and in some cases form overgrowths on type Ia zircons (Fig. 4e). More irregular zoning and resorption features are identified in type Ib zircons (Table 2, Figs. 4e and 4f).

Type II zircons are the most abundant of the zircon populations at Baerzehe, and exhibit complicated core-mantle texture: irregular cores and well-developed oscillatory zoning at the rim (Table 2, Fig. 5). Rims are commonly murky brown, translucent 20–50 μm thick microcrystals on magmatic cores with chaotic texture. These features are texturally distinct from type Ia and type Ib zircon in the same rock samples. In addition, they have replaced sodic amphibole. The REE-bearing minerals, including euxenite
and bastnäsite, also occur through replacement of type II zircons, suggesting that these REE minerals postdated the type Ia and Ib zircons.

As shown in Figure 6, monazite crystals in this study are subhedral to anhedral (Table 2), and generally are interstitial as discrete grains up to 150 \( \mu \text{m} \) in width in the matrix in contact with margins of quartz and K-feldspar (Fig. 6b) or as small (\(<100 \ \mu \text{m} \) in width) inclusions (Fig. 6a) in primary minerals, mainly in quartz, albite, K-feldspars, and sodic amphibole. Monazite shows mottled zoning in BSE images. In addition, the aggregation textures of monazite grains occurring in clusters within a restricted area and the metasomatic growth texture of monazite that replaces zircon rims testify that the monazite in this study is younger than zircon.

**Table 2.** Comparison between zircon and monazite

<table>
<thead>
<tr>
<th>Features</th>
<th>Type Ia</th>
<th>Type Ib</th>
<th>Type II</th>
<th>Monazite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Light green; transparent</td>
<td>Pale brown; translucent</td>
<td>Murky-brown; translucent</td>
<td>Colorless; transparent</td>
</tr>
<tr>
<td>Occurrence</td>
<td>Individual crystal</td>
<td>Individual crystal or aggregates</td>
<td>Aggregates</td>
<td>Individual crystal or aggregates</td>
</tr>
<tr>
<td>Texture</td>
<td>Euhedral</td>
<td>Euhedral, subhedral</td>
<td>Subhedral, anhedral and core-mantle</td>
<td>Euhedral to anhedral; fluid mediated coupled dissolution-precipitation</td>
</tr>
<tr>
<td>Mineral association</td>
<td>Quartz, perthite, albite, sodic amphibole</td>
<td>Quartz, perthite, albite, sodic amphibole</td>
<td>Euxenite, bastnäsite, hingganite, synchysite</td>
<td></td>
</tr>
<tr>
<td>Growth zone</td>
<td>Well-developed and bright oscillatory growth zoning</td>
<td>Well-developed and dark oscillatory growth zoning</td>
<td>Inner part like weaving guts, and well-developed and dark oscillatory zoning at the rim</td>
<td>No zonation by CL and BSE imaging</td>
</tr>
<tr>
<td>Geochemistry</td>
<td>Flat and low LREE; strongly enriched HREE; distinct negative Eu anomalies</td>
<td>Enriched and negative slope patterns in LREE, moderate enriched and positive slope in HREE pattern</td>
<td>Flat and low REE; distinct negative Eu anomalies</td>
<td>Enriched in LREE; relative depletion in HREE; distinct positive Eu anomalies</td>
</tr>
<tr>
<td>Origin</td>
<td>Magmatic and least-altered by deuteric fluid</td>
<td>Magmatic and strongly altered by deuteric fluid</td>
<td>Late magmatic/deuteric fluid</td>
<td>Hydrothermal</td>
</tr>
<tr>
<td>Age (Ma)</td>
<td>127.2 ± 1.3</td>
<td>125.4 ± 0.7</td>
<td>124.9 ± 0.6</td>
<td>122.8 ± 0.6</td>
</tr>
</tbody>
</table>

_Figure 3._ Photomicrographs showing texture and mode of occurrence of type Ia zircons. (a) Cross-polarized transmitted light. (b and d) CL image. (c) Plane-polarized transmitted light. Qz = quartz, Kfs = K-feldspar, Zr = zircon.

_American Mineralogist, vol. 104, 2019_
Mineral compositions of zircon and monazite

Representative grains of the three textural populations of zircons were analyzed on four doubly polished thin sections (nos. 87b, 106a, 106b, and 108a). Trace element characteristics are given in Supplemental Table S1 and illustrated in Figure 7.

Type Ia zircons have concentrations of REE = 0.90–1.15%, and Th = 346–573 ppm. Their total Pb contents range from 101 to 595 ppm, and (Lu/Yb)\text{CN} = 1.08–2.01. They yield LREE/HREE ratios from 0.01 to 0.03 and have distinct negative Eu anomalies (Eu/Eu* = 0.01–0.03, where Eu* = \sqrt{(Sm)_N \times (Gd)_N}) (Fig. 7a). This type of zircon is characterized by a flat and low LREE pattern, and a strongly enriched HREE pattern (Supplemental Table S1, Fig. 7a).

Type Ib zircons have REE concentrations of 0.03–0.36%, and Th concentrations of 60–1668 ppm. They have total Pb contents of 83 to 196 ppm, and (Lu/Yb)\text{CN} ratios ranging from 0.63 to 0.83. A broad range of LREE concentrations among samples is observed in Figure 7b, which clearly illustrates the overlap in their chondrite-normalized REE trends. A moderate enrichment of LREE relative to HREE (Gd to Er) with LREE/HREE = 0.17–5.03 was determined, as well as a pronounced negative Eu anomaly (Eu/Eu* = 0.01–0.06) in the chondrite-normalized REE patterns. The Ce anomalies (Ce/Ce* ratios, where Ce* = \sqrt{(La)_N \times (Pr)_N}) varying from 0.24 to 2.10 was observed in some cases (Fig. 7b). Most type Ib zircons are enriched and show negative slope patterns in LREE (Supplemental Table S1, Fig. 7b), and commonly show moderately enriched HREE patterns (Supplemental Table S1, Fig. 7b).

Type II zircons have REE concentrations of 0.57–1.76%, and...
Th concentrations of 295–2190 ppm. They have total Pb contents of 51 to 162 ppm, and (Lu/Yb)_CN = 0.46–0.73, and are markedly LREE enriched with LREE/HREE = 0.04–2.96, thus exhibiting flat chondrite-normalized REE patterns (Supplemental Table S1). Type II zircons have notable negative Eu anomalies (Eu/Eu* = 0.02–0.03) and weak negative Ce anomalies (Ce/Ce* = 0.94–1.26) (Fig. 7c).

Twenty-five spots on twenty-two monazite grains were analyzed for trace-element composition (Supplemental Table S2). They have 0.15 to 1.74 wt% SiO₂ and 28.34 to 30.59 wt% P₂O₅, and ThO₂ abundances ranging from 0.26 to 4.25 wt%. Their LREE concentrations range from 53.09 to 59.17 wt% and total REE concentrations from 54.08 to 59.57 wt%. LREE/HREE ratios range from 49.22 to 312.07, and are typified by significant enrichment of chondrite-normalized LREE over HREE with a very steep negative slope. A weak positive Ce anomaly with Ce/Ce* ranges from 1.05 to 1.29. The monazite grains are typified by a distinct positive Eu anomaly display with Eu/Eu* ranging from 1.13 to 22.34 (Fig. 7d).

**Geochronology of zircon and monazite**

In situ LA-ICP-MS U-Pb data collected on zircon and monazite grains of doubly polished thin sections are summarized in...
Supplemental1 Tables S3 and S4, and subsets of the isotopic ages are illustrated on the Tera–Wasserburg Concordia diagram in Figure 8. The age of the type Ia zircons was determined by 13 analyses from 9 zircon crystals from sample 87b and 106a, and yielded 69–3161 ppm U, 6–734 ppm Th, with Th/U ratios of 0.03 to 1.30. The \(^{207}\)Pb-corrected \(^{206}\)Pb/\(^{238}\)U ages range from 122.8 ± 1.5 to 132.8 ± 1.4 Ma and give a lower intercept age of 127.2 ± 1.3 Ma (MSWD = 1.7, n = 13).

The age of the type Ib zircons was determined by 28 analyses from 15 crystals from sample 108a, and yielded 673–4886 ppm U, 84–2933 ppm Th, with Th/U ratios of 0.06 to 1.46. They have \(^{207}\)Pb-corrected \(^{206}\)Pb/\(^{238}\)U ages ranging from 122.8 ± 1.5 to 132.8 ± 1.4 Ma, with a lower intercept age of 125.4 ± 0.7 Ma (MSWD = 0.72, n = 28).

The age of the type II zircons was determined by 29 analyses of 20 crystals from sample 106b and 108a, and yielded 1124–5137 ppm U, 304–3131 ppm Th, with Th/U ratios of 0.09 to 1.44. All of these data are concordant and have \(^{207}\)Pb-corrected \(^{206}\)Pb/\(^{238}\)U ages ranging from 122.8 ± 1.5 to 132.8 ± 1.4 Ma that produce a lower intercept age of 124.9 ± 0.6 Ma (MSWD = 1.1, n = 29).

The age of monazite was determined by 37 analyses on 22 monazite crystals from sample 106b and 108a. Analyses on monazite crystals have U concentrations of 49–1884, and Th concentrations of 11 900–88 139 ppm with Th/U ratios from 42.46 to 437.79. They yield \(^{207}\)Pb-corrected \(^{206}\)Pb/\(^{238}\)U ages ranging from 122.9 ± 4.8 to 137.3 ± 2.0 Ma, consistent with a lower intercept age at 122.8 ± 0.6 Ma (MSWD = 0.95, n = 37).

**Figure 6.** Photomicrographs showing texture and mode of occurrence of monazite grains. (a) Plane-polarized transmitted light. (b and c) Cross-polarized transmitted light. (d, e, and f) BSE image. Note the numbers 1 and 2 in d and numbers 28 and 29 in e are the number of EPMA spot. Qz = quartz, Amp = amphibole, Kfs = K-feldspar, Ab = albite, Zr = zircon, Mon = monazite.
**DISCUSSION**

**Origins of zircon and monazite**

Distinguishing with certainty between hydrothermal, deuteritic, and magmatic zircon and monazite was greatly aided by studying their texture, occurrence, and the associated mineral assemblages. The REE distribution patterns have also been successfully applied as a sensitive indicator to determine the formation conditions of magmatic and metasomatic rocks (Yang et al. 2014; Taylor et al. 2015). Based on the textural and compositional evidence, acquired during this study, zircons can be divided into three types.

Individual type Ia and Ib zircons are interpreted to be magmatic in origin due to their generally well-developed oscillatory growth zoning (Figs. 3 and 4) and their REE patterns that are typical of magmatic zircon (Figs. 7a and 7b). Compared with primary magmatic zircon, type Ia zircons are slightly enriched in LREE, and type Ib zircons are strongly enriched in LREE and depleted in HREE. Such observations suggest that these magmatic zircons suffered variable degrees of alteration, with type Ia being least-altered and type Ib being strongly altered. The alteration results in altered grains displaying irregular zoning with resorption features cross-cutting the primary zoning and/or metasomatic overgrowths on primary or less-altered zircon crystals (Figs. 3d and 4e). Such irregular zoning and resorption features are similar to textures that were produced in relation to magma mixing processes reported by Tepper and Kuehner (1999).

The textural and geochemical differences found with type II zircons suggest that they are not typical magmatic phases such as types Ia and Ib. They display complicated core-mantle textures and have been identified along the cleavage of sodic amphibole, which is a typical magmatic phase associated with K-feldspar, quartz, and magmatic zircons (Fig. 5). Such paragenetically later textural features indicate that the type II zircon belong to a younger generation than types Ia and Ib.

**FIGURE 7.** The REE distribution patterns of type Ia (a), type Ib (b), and type II (c) zircons analyzed by LA-ICP-MS, and that of monazite grains (d) determined by EPMA. Elemental values below the electron microprobe detection limits are not shown. Bulk-rock REE concentrations of mineralization and barren granites from Yang (2012) are plotted for comparison. The REE concentrations are normalized to the chondrite composition reported by McDonough and Sun (1995).
Type II zircon shows significant enrichment of REE (Supplemental Table S1; Table 2) compared to both the least and strongly altered magmatic zircons and alkaline granite whole-rock samples (at least two orders of magnitude). Non-formula elements U, Hf, Nb, Ta, Ti, and LREE concentrations are enriched relative to magmatic zircon in the same rock, which also suggests that the type II zircons are crystallized from highly fractionated fluids (Supplemental Table S1; Table 2). Metal behavior varies between different media and results in crystals with chemical characteristics dependent upon what they crystallized from. Deuteric crystals, such as type II zircons, can form from a hydrosilicate liquid produced during the magmatic to hydrothermal transition from a media with transitional properties between a melt and a fluid. This is consistent with larger-radii LREE being incompatible in the magmatic zircon structure (Hanchar and Westrenen 2007) and more compatible in magmatic fluids (Bakker and Elburg 2006).

No pristine igneous zircon is observed whose REE pattern may be dominated by the lattice strain model and characterized by a steep positive slope, low La (<0.1 ppm), positive Ce, and negative Eu anomalies (Hoskin 2005), which is the consequence of the exclusion of the large ionic radii LREEs from the crystal structure during crystallization (Hanchar and Westrenen 2007). A majority of zircon grains examined in our study were LREE enriched, thus exhibiting relatively flat patterns on chondrite-normalized diagrams. Comparable variability in chondrite-normalized REE patterns has also been observed in several other studies (e.g., Hoskin 2005; Marsh and Stockli 2015; Skipton et al. 2016; Kelly et al. 2017), and the mechanisms that may form LREE-enriched parent zircon remain enigmatic (Chapman et al. 2016), but could include a LREE-enriched source melt (Hoskin and Ireland 2000), complex substitutions (Hoskin and Schaltegger 2003), and sampling of micro-inclusions during analysis (Hanchar and Westrenen 2007). Any combination of these possibilities may be responsible for the growth of zircon that deviates from the expected REE pattern (cf. Marsh and Stockli 2015).

While the magnitude of the Eu anomaly is moderate in barren alkaline granite whole-rock samples (Eu/Eu* = 0.05–0.65), both magmatic (Eu/Eu* = 0.01–0.06) and deuteric zircons (Eu/Eu* = 0.02–0.03) exhibit more pronounced negative anomalies. Such pronounced Eu anomalies are difficult to explain exclusively by feldspar fractionation and could indicate the importance of the late fluid activity.

The hydrothermal monazite at Baerzhe may be distinguished from igneous monazite by its unique geochemical signature, its occurrence, and its common association with hydrothermal mineral assemblages. Monazite crystals occur in clusters within a restricted area showing distinct petrographic characteristics of hydrothermal monazite (Fig. 6) (Schandl and Gorton 2004). REE-bearing minerals, including euxenite and bastnäsite, also

Figure 8. In situ LA-ICP-MS U-Pb Tera–Wasserburg Concordia diagrams of type Ia (a), type Ib (b), and type II (c) zircon, and monazite grains (d). The 207Pb-corrected 206Pb/238U ages are present and plotted because the analyzed data yield low U abundances and elevated common Pb contents resulting from possible matrix effects and subsequent hydrothermal fluids overprinting.
occur in the cracks of deuteric type II zircons (Figs. 5d–5e), which implies that the REE mineralization postdated the late magmatic processes. Monazite commonly grows along the cleavage of sodic amphibole and metasomatizes zircon, suggesting that they are hydrothermal in origin.

Igneous and hydrothermal monazite grains commonly have similar morphologies making geochemical evidence discriminating between hydrothermal and igneous monazite critical to their identification (Wall and Mariano 1996; Schandl and Gorton 2004; Taylor et al. 2015). First, the monazite at Baerzhe has lower ThO$_2$ abundance (2 wt% on the average), which is distinct from that of magmatic monazite (typically >5 wt%; Schandl and Gorton 2004). Second, hydrothermal monazite patterns show a very steep negative trend, revealing a distinct fractionation between LREE and HREE. Third, hydrothermal monazite is enriched in Eu (Fig. 7d), notably distinguishing it from igneous monazite that crystallizes in equilibrium with plagioclase and therefore has a pronounced negative Eu anomaly (Zhu and O’Nions 1999). This is because unlike magmatic plagioclase that preferentially incorporates Eu, non-magmatic/hydrothermal systems typically evolve in the absence of plagioclase (Kim et al. 2005). The overall REE abundances are broadly similar but can be locally different, because the REE geochemistry of hydrothermal (or metamorphic) monazite can be subtly influenced by the REE contributions of the local country rock or the source from several different geological settings (Zhu et al. 1997; Kositcin et al. 2003).

Geochemically, the REE distribution patterns of hydrothermal monazite grains reveal distinct fractionation between LREE and HREE, and a pronounced positive Eu anomaly. This indicates that the crystallization of monazite is distinct from zircon, which is affected by feldspar in the melt (Fig. 7d). These petrologic, mineralogical, and compositional traits suggest that the monazite at Baerzhe is hydrothermal in origin.

**Timing of Zr and REE formation**

In situ LA-ICP-MS U-Pb analyses of zircon and monazite bracket the magmatic, late magmatic (deuteric) and hydrothermal stages into a geochronological context that is consistent with their textural relationship, unlike age determinations of previous studies. The type Ia and type Ib magmatic zircons yield the $^{207}$Pb-corrected $^{206}$Pb/$^{238}$U ages at 127.2 ± 1.3 and 125.4 ± 0.7 Ma (Figs. 8a and 8b), respectively. The type II deuteric zircons crystallized at 124.9 ± 0.6 Ma (Fig. 8c). Our data suggest that magmatic crystallization and late magmatic processes of the highly evolved Baerzhe alkaline granite lasted less than ~2 million years as shown by the combined Rb-Sr ages at ca. 125.7–125.0 Ma of the Baerzhe alkaline granite whole-rock samples (Zhang and Yuan 1988; Wang and Zhao 1997; Yuan et al. 2003; Yang 2012), and zircon U-Pb ages ranging from 126 to 123 Ma (Yang 2012; Qiu et al. 2014; Yang et al. 2014) reported in the literature. The hydrothermal monazite records a REE mineralization event at 122.8 ± 0.6 Ma, which is possibly 1 or 2 million years later, but coeval within reported errors. This is consistent with the textural relationship that the REE mineralization at Baerzhe is slightly later than the Zr mineralization (Table 2, Fig. 9).

**Implications on Links Between Zr and REE Mineralization at Baerzhe**

Several different mechanisms responsible for the formation of Zr–Nb–REE mineralization have been presented. Gysi and Williams-Jones (2013) proposed that saline HCl–HF-bearing fluids created pathways during acidic alteration from the pegmatite cores outward, leading to the mobilization of REE and Zr due to progressive alteration of primary silicate minerals and increased acidity upon cooling. Kempe et al. (2015) proposed a preliminary multistage metasomatic genetic model assuming that a silica- and carbonate-rich fluid system was responsible for the early alteration that yielded extreme concentrations of Zr, Nb, and LREE and occurred late during or postdating the intrusion/extrusion of the silica-saturated magmas. A “Li-F granite-type” fluid system was active during the late alteration, resulting in enrichment of Y and HREE. The interplay of all these processes led to the formation of complex, economic Zr–Nb–REE mineralization at Khalzan Buregte (Western Mongolia). Wu et al. (2016) recognized that both Zr and REE were strongly incompatible in the sodic melt, but that Zr mineralization preceded REE mineralization in the Triassic Saima alkaline complex (Liaodong Peninsula, NE China). The main Zr–REE mineralization in the Saima lujuvrite resulted from the high peralkalinity, (Na+K)/Al molar ratio (1.2) and HFSE contents (1.4 wt%), low oxygen fugacity (ΔFMQ = −0.5 to −2.0), and the intensive activity of water and volatiles of its evolving magma. Gladkocub et al. (2017) argued a magmatic origin of the Katugin Ta-Nb-Y-Zr (REE) deposit (southern Siberia, Russia) rather than the previously proposed metasomatic fault-related origin, and most of the ore minerals crystallized from the silicate melt during the magmatic stage. Mikhailova et al. (2017) studied the Zr- and REE-bearing Western Keivy peralkaline granite massif (Kola Peninsula, NW Russia), and discovered that the behavior of REE and Zr was controlled by alkalinity of melt/solution, which, in turn, was controlled by crystallization of alkaline pyroxenes and amphiboles at a late magmatic stage. Crystallization of mafic minerals leads to a sharp increase of K$_2$O contents and decrease of SiO$_2$ contents in that in turn cause a decrease of melt viscosity and REE and Zr solubility in the liquid. Therefore, REE and Zr immediately precipitated as zircon and REE-minerals. Dai et al. (2018) studied the Nb–Zr–REE–Ga enrichment in Lopingian altered alkaline volcanic ashes (Yunnan, China), and argued that the ore-forming process represents a combination of alkaline magmatism, hydrothermal alteration, explosive volcanism, and lateritic weathering associated with later influx of meteoric and, in some cases, marine waters under lower-temperature conditions (Deng et al. 2014). These were not separate processes but were contemporaneous, and are specifically related to volcanically active continental regions within humid climates.

Geochronology, major and trace element geochemistry, and isotope data from previous studies suggest that the Early Cretaceous alkaline granite was derived by melting of a dominantly juvenile mantle component with subordinate recycled ancient crust and is genetically responsible for the Baerzhe REE-Nb-Zr-Be deposit. Niu et al. (2008) conducted Raman spectroscopy and microthermometry on crystal-rich fluid inclusions in quartz of the ore-bearing alkaline granite and recognized that the trapped
minerals in the inclusions are predominantly silicate minerals including feldspar and mica, as well as minor REE minerals. They, therefore, proposed that the genesis of the ore-bearing alkaline granite was directly related to the magmatic-hydrothermal transition process, and the wide distribution of the REE minerals in the crystal-rich fluid inclusions indicates the REE had already been enriched sufficiently in the alkaline granite during the magmatic-hydrothermal stage of magma evolution, and the REE mineralization was constrained by the fluid derived from this stage. Yang et al. (2013) reported that hydrothermal zircon yields extremely negative δ18O values of –18.12‰ to –13.19‰, which are distinguished from magmatic zircon (2.79–5.10‰) with numbers close to mantle values (5.3 ± 0.3‰, Valley et al. 1998). Such a great shift of O isotopes from magmatic to hydrothermal zircon with consistent Hf composition at Baerzhe indicates a physicochemical change of the ore-forming environment.

Textural relations and compositional variation among the characteristic Zr-REE-bearing minerals record that Zr mineralization preceded REE mineralization at Baerzhe. Geochronological results collected by in situ LA-ICP-MS U-Pb dating are consistent with texturally determined paragenetic sequences of Zr-REE-bearing minerals, and demonstrate that the Zr and REE mineralization at Baerzhe is associated with distinct magmatic, transitional, and hydrothermal events. The first two events were responsible for the Zr mineralization that occurred late during or postdating the intrusion/extrusion of the silica-saturated granite. The strongly altered type Ia magmatic zircons are more enriched in LREE than the least-altered magmatic zircons. In addition, the strongly altered type Ib magmatic zircons are more enriched in LREE than the least-altered type Ia magmatic zircons. The age of deuteric zircon is indistinguishable from magmatic zircon, indicating precipitation from a fluid evolved from the magma during the final stages of crystallization. The youngest event resulted in REE mineralization at 122.8 ± 0.6 Ma, less than 2 million years after Zr mineralization. The interplay of all these processes led to the formation of complex REE-Nb-Zr-Be mineralization at Baerzhe.

The magmatic through deuteric origins of Zr mineralization and hydrothermal origin of REE mineralization have been recorded by the geochemical signatures in addition to observations of metasomatic replacement of zircon by monazite. The Baerzhe granites show the characteristic trace element patterns of rare-metal granites, but the magmatic and deuteric zircons yield absolute abundances of REE that differ by as much as two orders of magnitude. One possible explanation of their REE patterns is a late magmatic exsolution of volatiles from the granitic melt. This implies the existence of originally fluid-rich magmas in the alkaline series. The compositions of zircons were significantly altered by these subsequent hydrothermal fluids. Their “enriched-type” REE distribution patterns are similar to those present in some of the Gurvan Uneet and Ulaan Uneet zircon samples (Kempe et al. 2015), which have elevated Zr, Nb, and LREE contents as well as LREE/HREE fractionation that is inferred to be caused by an external fluid.

The magmatic and deuteric zircons, as well as mineralized granite, have pronounced negative Eu anomalies compared to that of barren granite (Fig. 7), which yield REE distribution patterns characteristic of evolved magmatic rocks. Such pronounced Eu anomalies are difficult to explain exclusively by feldspar fractionation and could indicate the importance of fluid activity affecting their compositional characteristics. This assumption is also strengthened by the appearance of positive Eu anomalies documented in hydrothermal monazite.

Two of the zircon populations studied are LREE enriched, and the deuteric zircons are more enriched in LREE than the magmatic zircons.

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The magmatic through deuteric origins of Zr mineralization and hydrothermal origin of REE mineralization have been recorded by the geochemical signatures in addition to observations of metasomatic replacement of zircon by monazite.
This suggests that the effects of the hydrothermal metasomatism during later REE mineralization stage on the REE budget of both magmatic and deuteric zircons are significant. We infer that their distinct features and the deuteric LREE enrichment are an indication of the activity of LREE-rich fluids occurring shortly after plutonic emplacement and crystallization. This corresponds to the fairly heterogeneous Th/U values throughout the zircons (Supplemental Table S3), which have likely been modified by hydrothermal fluids.

Previous studies had difficulty in explaining the origin of type II zircons at Baerzhe. Yang et al. (2013, 2014) proposed that the abundant non-magmatic zircons, which are characterized by tetragonal dipymidal morphology, murky and featureless textures, LREE-enrichment, and high common-lead compositions, are hydrothermal. However, the fact that the type II zircons are generally found interstitial to albite, K-feldspars, quartz, and sodic amphibole and no type II zircon has been observed among the hydrothermal veins most likely suggests that they are not hydrothermal (sensu stricto). In addition, although the solubility of Zr in hydrothermal systems has not been measured directly (Linnen et al. 2014), it could only reach several hundred parts per billion (ppb) in hydrothermal fluids, based on published thermodynamic data (Migdisov et al. 2011). Such low solubility is therefore difficult to transport significant concentrations of Zr in typical hydrothermal aqueous fluids. Hydrosilicate liquids (HSL) can transport high field strength elements in great abundance (Smirnov et al. 2017). At present, the HSL were found not only in experiments but also in “melt/fluid” inclusions entrapped in quartz and other minerals within miorollitic granite pegmatites and rare-metal granites (Thomas and Davidson 2016). The HSL routinely form in the magmatic-hydrothermal transition and have transitional properties between an aqueous fluid and a melt (Smirnov et al. 2012). Experimental investigations showed that the HSL are very effective in extracting, concentrating, and transporting rare metals and should be considered as potentially important media of ore metal transport and mineral formation at the stage of transition from magmatic to hydrothermal crystallization in granitic and pegmatitic systems (Smirnov et al. 2006, 2017). The compositional characteristics and textural observations of type II zircons at Baerzhe are consistent with a deuteric origin likely precipitated from a hydrosilicate liquid.

**IMPLICATIONS**

Direct geochronological constraints on Zr and REE mineralization conducted on the Baerzhe REE-Nb-Zr-Be deposit are reported herein. Using in situ LA-ICP-MS U-Pb dating on zircon and monazite grains eliminates the loss of textural context and potential mixing of polygenetic zircon and monazite age populations, successfully determining discrete Zr and REE crystallization events.

Textural and geochemical characterizations distinguished the least-altered magmatic zircon (type Ia), the strongly altered magmatic zircon (type Ib), and deuteric/late magmatic zircon (type II). The crystallization of magmatic zircon, altered zircon, deuteric zircon, and monazite occurred at 127.2 ± 1.3, 125.4 ± 0.7, 124.9 ± 0.6, and 122.8 ± 0.6 Ma, respectively. Subtle age gaps bracket a ca. 2 million year magmatic-deuteric event of the highly fractionated Baerzhe alkaline granite, and document a magmatic-deuteric process for Zr mineralization, followed by a subsequent hydrothermal REE-precipitating event.

The parental magmas of Baerzhe have undergone extensive magmatic differentiation during which the residual melts interacted with aqueous hydrothermal fluid. The deuteric zircon is interpreted to have precipitated from a hydrosilicate liquid (HSL), based on the chemical and textural characteristics observed in this study. The subsequent REE mineralization is likely related to the metasomatic alteration from external fluid sources. The interplay of these processes resulted in the formation of a complex, economic REE-Nb-Zr-Be deposit at Baerzhe.

These observations provide distinctions between specific events linked to Zr and REE mineralization. Ascertaining whether or not the Zr and REE mineralization share the same source and evaluating their ore-forming conditions are critical for exploration. A better understanding of the genetic model for rare-metal deposits requires more work on hydrothermal fluids and $P-V-T-X$ conditions of melt and fluid inclusions, oxygen isotope compositions of zircon, monazite, feldspar, and quartz.

**ACKNOWLEDGMENTS**

We are indebted to Jun Deng, Jade Star Lackey, Emily Peterman, and Michael Williams for thoughtful discussions concerning zircon and monazite morphology and geochemistry; Heather Lowers and Mike Pribil at the U.S. Geological Survey provided instruction, advice, and assistance during SEM and EPMA data collection. Critical and thorough reviews by Callum Hetherington, Charles Thomman, Graham Lederer, and an anonymous reviewer greatly improved the quality of the manuscript.

**FUNDING**

This research was financially supported by the National Basic Research Program of China (2015CB452606), the National Natural Science Foundation of China (41702069, 41173030), the Fundamental Research Funds for the Central Universities, China (2652018125, 2652018141), Open Research Project from the State Key Laboratory of Geological Processes and Mineral Resources at the China University of Geosciences (GPMR201812), and the 111 Project of the Ministry of Education of China (B07011). K-F Qiu gratefully acknowledges the support of the China Scholarship Council, Society of Economic Geologists, China Postdoctoral Foundation, and K.C. Wong Education Foundation, Hong Kong. Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. government.

**REFERENCES CITED**


Brown, S.M., Fletcher, I.R., Stein, H.J., Snee, L.W., and Grooves, D.I. (2002) Geochemical and mineralogical data (Migdisov et al. 2011). Such low solubility is therefore difficult to transport significant concentrations of Zr in typical hydrothermal aqueous fluids. Hydrosilicate liquids (HSL) can transport high field strength elements in great abundance (Smirnov et al. 2017). At present, the HSL were found not only in experiments but also in “melt/fluid” inclusions entrapped in quartz and other minerals within miorollitic granite pegmatites and rare-metal granites (Thomas and Davidson 2016). The HSL routinely form in the magmatic-hydrothermal transition and have transitional properties between an aqueous fluid and a melt (Smirnov et al. 2012). Experimental investigations showed that the HSL are very effective in extracting, concentrating, and transporting rare metals and should be considered as potentially important media of ore metal transport and mineral formation at the stage of transition from magmatic to hydrothermal crystallization in granitic and pegmatitic systems (Smirnov et al. 2006, 2017). The compositional characteristics and textural observations of type II zircons at Baerzhe are consistent with a deuteric origin likely precipitated from a hydrosilicate liquid.

**REFERENCES CITED**


American Mineralogist, vol. 104, 2019


Valley gold district, Sierra Nevada Foothills province, California. Economic Geology, 110, 1313–1337.


Thomas, R., and Davidson, P. (2016) Revisiting complete miscibility between silicate melts and hydrous fluids, and the extreme enrichment of some elements in the supercritical state—consequences for the formation of pegmatites and ore deposits. Ore Geology Reviews, 72, 1088–1101.

Valley gold district, Sierra Nevada Foothills province, California. Economic Geology, 110, 1313–1337.


Thomas, R., and Davidson, P. (2016) Revisiting complete miscibility between silicate melts and hydrous fluids, and the extreme enrichment of some elements in the supercritical state—consequences for the formation of pegmatites and ore deposits. Ore Geology Reviews, 72, 1088–1101.

Valley gold district, Sierra Nevada Foothills province, California. Economic Geology, 110, 1313–1337.


Thomas, R., and Davidson, P. (2016) Revisiting complete miscibility between silicate melts and hydrous fluids, and the extreme enrichment of some elements in the supercritical state—consequences for the formation of pegmatites and ore deposits. Ore Geology Reviews, 72, 1088–1101.

Valley gold district, Sierra Nevada Foothills province, California. Economic Geology, 110, 1313–1337.


Thomas, R., and Davidson, P. (2016) Revisiting complete miscibility between silicate melts and hydrous fluids, and the extreme enrichment of some elements in the supercritical state—consequences for the formation of pegmatites and ore deposits. Ore Geology Reviews, 72, 1088–1101.

Valley gold district, Sierra Nevada Foothills province, California. Economic Geology, 110, 1313–1337.


Thomas, R., and Davidson, P. (2016) Revisiting complete miscibility between silicate melts and hydrous fluids, and the extreme enrichment of some elements in the supercritical state—consequences for the formation of pegmatites and ore deposits. Ore Geology Reviews, 72, 1088–1101.

Valley gold district, Sierra Nevada Foothills province, California. Economic Geology, 110, 1313–1337.


Thomas, R., and Davidson, P. (2016) Revisiting complete miscibility between silicate melts and hydrous fluids, and the extreme enrichment of some elements in the supercritical state—consequences for the formation of pegmatites and ore deposits. Ore Geology Reviews, 72, 1088–1101.

Valley gold district, Sierra Nevada Foothills province, California. Economic Geology, 110, 1313–1337.


Thomas, R., and Davidson, P. (2016) Revisiting complete miscibility between silicate melts and hydrous fluids, and the extreme enrichment of some elements in the supercritical state—consequences for the formation of pegmatites and ore deposits. Ore Geology Reviews, 72, 1088–1101.

Valley gold district, Sierra Nevada Foothills province, California. Economic Geology, 110, 1313–1337.


Thomas, R., and Davidson, P. (2016) Revisiting complete miscibility between silicate melts and hydrous fluids, and the extreme enrichment of some elements in the supercritical state—consequences for the formation of pegmatites and ore deposits. Ore Geology Reviews, 72, 1088–1101.

Valley gold district, Sierra Nevada Foothills province, California. Economic Geology, 110, 1313–1337.


Thomas, R., and Davidson, P. (2016) Revisiting complete miscibility between silicate melts and hydrous fluids, and the extreme enrichment of some elements in the supercritical state—consequences for the formation of pegmatites and ore deposits. Ore Geology Reviews, 72, 1088–1101.

Valley gold district, Sierra Nevada Foothills province, California. Economic Geology, 110, 1313–1337.


Thomas, R., and Davidson, P. (2016) Revisiting complete miscibility between silicate melts and hydrous fluids, and the extreme enrichment of some elements in the supercritical state—consequences for the formation of pegmatites and ore deposits. Ore Geology Reviews, 72, 1088–1101.

Valley gold district, Sierra Nevada Foothills province, California. Economic Geology, 110, 1313–1337.


Thomas, R., and Davidson, P. (2016) Revisiting complete miscibility between silicate melts and hydrous fluids, and the extreme enrichment of some elements in the supercritical state—consequences for the formation of pegmatites and ore deposits. Ore Geology Reviews, 72, 1088–1101.

Valley gold district, Sierra Nevada Foothills province, California. Economic Geology, 110, 1313–1337.


Thomas, R., and Davidson, P. (2016) Revisiting complete miscibility between silicate melts and hydrous fluids, and the extreme enrichment of some elements in the supercritical state—consequences for the formation of pegmatites and ore deposits. Ore Geology Reviews, 72, 1088–1101.

Valley gold district, Sierra Nevada Foothills province, California. Economic Geology, 110, 1313–1337.


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