

Fluid inclusions as an indicator for REE mineralization in the Lizhuang deposit, Sichuan Province, Southwest China

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ABSTRACT

The Lizhuang rare earth element (REE) deposit in Sichuan Province, Southwest China, offers an excellent opportunity to investigate hydrothermally related REE transport and deposition in a carbonatite-related setting. Here, comprehensive fluid inclusion data combined with H–O isotope systematics are presented to provide new constraints on REE mineralization in this deposit. Hydrothermal processes responsible for ore vein formation include at least two stages: (1) Pre-REE stage is marked by the deposition of gangue minerals such as fluorite, quartz, calcite and barite. Four types of fluid inclusions (i.e., aqueous, CO₂-bearing, solid-bearing, and solid-CO₂-bearing inclusions) are distinguished in this stage, which yield homogenization temperatures ranging from 247 to 384 °C and salinities between 4.2 and 45.3 wt% NaCl equiv. Notably, the coexistence of CO₂-bearing inclusions with variable CO₂ volume fractions in this stage suggests that the fluids have experienced intense immiscibility. The immiscible CO₂-bearing inclusions record a pressure range of 950 to 1550 bar, assuming the temperatures varying from 300 to 340 °C. (2) REE stage is represented by the presence of abundant aqueous inclusions and minor CO₂- and solid-bearing inclusions. These aqueous inclusions yield homogenization temperatures ranging from 177 to 298 °C and salinities from 0.7 to 14.4 wt% NaCl equiv. The prevalence of aqueous inclusions in bastnäsite-(Ce), as well as the scarcity of CO₂-bearing inclusions, indicates that REEs were likely precipitated from low- to moderately-saline aqueous fluids containing minor amount of CO₂. The initial mineralizing fluids were rich in CO₂, (SO₄)^{2−}, Cl[−], and F[−] that can potentially mobilize REE. It is clear that the fluids became more dilute and CO₂-poor with decreasing temperature and pressure from pre-REE to REE stage during hydrothermal evolution. All of the available data suggest that fluid cooling and massive influx of meteoric water into the hydrothermal system were responsible for REE mineralization in the Lizhuang deposit. This information is integrated into a predictive model in which the search for potential REE mineralization should target shallower parts of the vein system.

1. Introduction

Rare earth elements (REE) are essential for high-technology industries and crucial defense systems, which can be obtained from primary and secondary deposits (Schönwandt et al., 2016; Smith et al., 2016). Primary REE deposits are generally associated with carbonatite, alkaline, phosphorite, and iron oxide copper-gold deposits (Yang et al., 2009, 2016; Li et al., 2015, 2017; Chen et al., 2013, 2017, 2018; Edahbi et al., 2017, 2018; Li and Zhou, 2018), whereas secondary REE deposits are associated with extensive weathering (Liu et al., 2015c; Xu et al., 2017). Carbonatites are rare mantle-derived rocks that, in some cases,

host industrially viable mineral deposits such as REE, Nb, and Ta (Stoppa et al., 2005; Stoppa and Schiazza, 2013; Xu et al., 2015; Song et al., 2016a, 2016b). > 500 carbonatite localities have been documented worldwide (Bell and Tilton, 2001; Woolley and Kjarsgaard, 2008), but only a few of these host giant REE deposits (Liu and Hou, 2017). Carbonatite-related REE deposit, formed by REE-rich fluids exsolved from carbonatitic melts (Hou et al., 2015), is the most economically significant form of REE mineralization globally (Chakhmouradian and Wall, 2012; Kynický et al., 2012; Weng et al., 2015). The genesis of these deposits involves a sequence of juxtaposed tectonic, magmatic and hydrothermal events that produced a complex

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assemblage of rocks and mineralization styles (Liu and Hou, 2017; Liu et al., 2019a, 2019b; Guo and Liu, 2019; Zhang et al., 2019).

There has been renewed interest in hydrothermally related REE mineralization involving carbonatite-related settings, as many deposits originally thought to be magmatic are now considered to experience both magmatic and hydrothermal processes (Sheard et al., 2012; Pandur et al., 2014). A large body of field, theoretical, and experimental studies support the notion that REE can be concentrated by hydrothermal processes (e.g., Wood, 1990; Williams-Jones et al., 2000; Williams-Jones and Palmer, 2002; Migdisov et al., 2009; Migdisov and Williams-Jones, 2014). In many cases, carbonatites are strongly overprinted by hydrothermal fluids, which results in the transport and deposition of REE in vein-hosted assemblages (Hou et al., 2009). Deposition of REE minerals can be induced by a number of processes, such as changes in temperature (e.g., Trofantenko et al., 2016), mixing of various fluids (e.g., Williams-Jones et al., 2000) or crystallization of gangue minerals (e.g., Gieré, 1996), and these processes can be recorded by zoning of hydrothermal minerals and their hosting fluid inclusions (Fan et al., 2004, 2006; Li and Zhou, 2018). Fluid inclusions are traditionally used to make inferences about pressure-temperature conditions and the concentrations of the dominant ions in hydrothermal fluids (Roedder, 1984, 1997). In turn, they have been used to infer the mechanisms of ore deposition, such as fluid-rock interaction, fluid immiscibility and mixing (Wilkinson, 2001; Heinrich, 2007; Vasyukova and Williams-Jones, 2018). Despite this, fluid inclusion studies on the hydrothermal processes and mineral deposition in carbonatite-related REE deposits are relatively sparse (e.g., Smith and Henderson, 2000; Shu and Liu, 2019; Zheng and Liu, 2019).

Renowned by several discoveries of REE deposit, the Mianning-Dechang (MD) REE belt (Sichuan, China) has become one of the most ideal places in the world to investigate REE mineralization processes (Hou et al., 2015). The Lizhuang REE deposit, which is the subject of this paper, represents an important example of REE mineralization that is associated with a Cenozoic carbonatite-syenite complex. The REE orebodies in this deposit occur mainly as numerous ore veins in which fluorite, barite, calcite, quartz and bastnäsite-(Ce) typically form stable mineral assemblages (Liu and Hou, 2017). Despite its small size, this deposit offers an excellent opportunity to investigate transport and deposition of REE under hydrothermal conditions on account of its weak tectonism and relatively simple, clear, traceable sequence of hydrothermal mineral assemblages. Some studies have examined the formation of the Lizhuang deposit, focusing on geological characteristics (Hou et al., 2009; Liu and Hou, 2017), geochronology (Liu et al., 2015a; Ling et al., 2016), and isotope geochemistry (Hou et al., 2006, 2015; Zhou et al., 2018). The hydrothermal fluids responsible for the formation of Lizhuang ore veins have been discussed with certain flaws (Hou et al., 2009; Xie et al., 2015). The preliminary description of fluid inclusions from the Lizhuang deposit were first reported by Hou et al. (2009), in which fluid inclusion types and their microthermometric properties were roughly constrained. Xie et al. (2015) reconstructed the physicochemical properties of the mineralizing fluids and proposed that fluid immiscibility caused by unmixing of CO₂ and H₂O phases drove bulk REE mineralization. Nevertheless, the significance of volatile components and complexing ligands in the mineralizing fluids that can potentially mobilize REE has been largely ignored. In addition, owing to the absence of inclusion-composition analyses and pressure estimations, little is actually known regarding a P–T–X path for evolution of the mineralizing fluids. Hence, a comprehensive fluid-inclusion study of the Lizhuang REE deposit is required to help understanding the mineral systems.

This paper presents a meticulous study of fluid inclusions that incorporates petrography, microthermometry, laser Raman spectroscopy, and bulk ion analyses in the basis of a detailed description of geology, alteration and mineralization in the Lizhuang REE deposit. Through the newly acquired inclusion data, combined with H–O isotopes, the study aims to (1) give a clear constraint for nature and evolution of the

mineralizing fluids, (2) provide a better insight into understanding of hydrothermally related REE mineralization, and (3) develop an effective exploration guide for REE mineralized system applicable not only to Lizhuang but any carbonatite-related settings.

2. Geological setting

2.1. Regional geology

The Indo-Asia collision that occurred in 65–50 Ma affected the western margin of the Yangtze Craton and formed a collisional orogenic belt (Hou and Cook, 2009). Late-stage collisional metallogenesis in eastern Tibet developed within a transform structure that was dominated by a series of strike-slip faulting, thereby producing one of the most economically significant metallogenic provinces in China (Hou and Cook, 2009). This area hosts porphyry-type Cu–Mo–Au systems controlled by strike-slip faults, orogenic Au systems related to sinistral ductile shearing, and Pb–Zn–Ag–Cu systems controlled by Cenozoic thrusting and subsequent strike-slip faulting (e.g., Deng et al., 2014a, 2014b, 2017; Wang et al., 2014a, 2014b, 2016; Deng and Wang, 2016), as well as REE mineralization systems associated with Cenozoic carbonatite-alkaline complexes (Liu et al., 2015a, 2015b, 2015c, 2019a, 2019b; Liu and Hou, 2017). These carbonatite-alkaline complexes, characterized by the model of some small intrusions forming large deposits, consist of carbonatitic sills or dykes, and alkaline syenite stocks, (Hou et al., 2006, 2009). They mainly intruded a Proterozoic crystalline basement and an overlying Paleozoic–Mesozoic volcano-sedimentary sequence, which constituted a narrow, NS-trending REE-bearing belt (Fig. 1; Hou et al., 2009).

The Mianning-Dechang REE belt, along the western margin of the Yangtze Craton, hosts one giant (Maoniuping), one large (Dalucuo), and two small-medium-sized REE deposits (Muluoizhai and Lizhuang), together with other REE occurrences (Fig. 1; Hou et al., 2009). The carbonatite-syenite complexes in the MD belt were formed by the melting of REE-refertilized, metasomatized sub-continental lithospheric mantle (SCLM) (Hou et al., 2015). This process involved the recycling of marine sediments, which introduced abundant light REE into the SCLM via CO₂-rich fluids during mantle metasomatism (Hou et al., 2015). Sensitive high resolution ion microprobe U–Pb dating results for zircons from syenites of the Dalucuo, Maoniuping, Lizhuang, Muluoizhai deposit have yielded the systematic and precise age determinations for these rocks in the MD belt. The new data give concordant ages of 12.13 ± 0.19 and 11.32 ± 0.23 Ma for the Dalucuo deposit, 22.81 ± 0.31 and 21.3 ± 0.4 Ma for the Maoniuping deposit, 26.77 ± 0.32 Ma for the Muluoizhai deposit, and 27.41 ± 0.35 Ma for the Lizhuang deposit (Liu et al., 2015a). These chronology data suggest that strike-slip shear along the MD belt was initiated at ca. 27 Ma and ended ca. 12 Ma, consistent with movements along the adjacent Ailaoshan–Red River strike-slip fault (Liu et al., 2015a).

2.2. Ore deposit geology

2.2.1. General outline

The Lizhuang deposit, located in the north of the MD belt, Sichuan Province, Southwest China, is a small-medium-sized REE deposit with grades of 1.05%–6.69% REO (total rare-earth oxide) (Hou et al., 2009). In the mining area, alkaline granites and a Cenozoic carbonatite-alkaline complex intrude a > 1000 m thick sequence of Silurian–Triassic sedimentary rocks (Fig. 2). The carbonatite-syenite complex is approximately 100–150 m wide, 400 m long, and consists of NNW–SSE-striking carbonatite sills and syenite plutons (Fig. 2). The fresh syenite is a massive structure with a fine-grained texture (Fig. 3c), and mainly consists of albite, aegirine-augite, quartz and minor accessory minerals (Fig. 4a–c). The main REE orebodies within the mining area are elongate parallel to the contact zone between the carbonatite-syenite complex and surrounding wall-rocks (Fig. 2). Recent study used SIMS

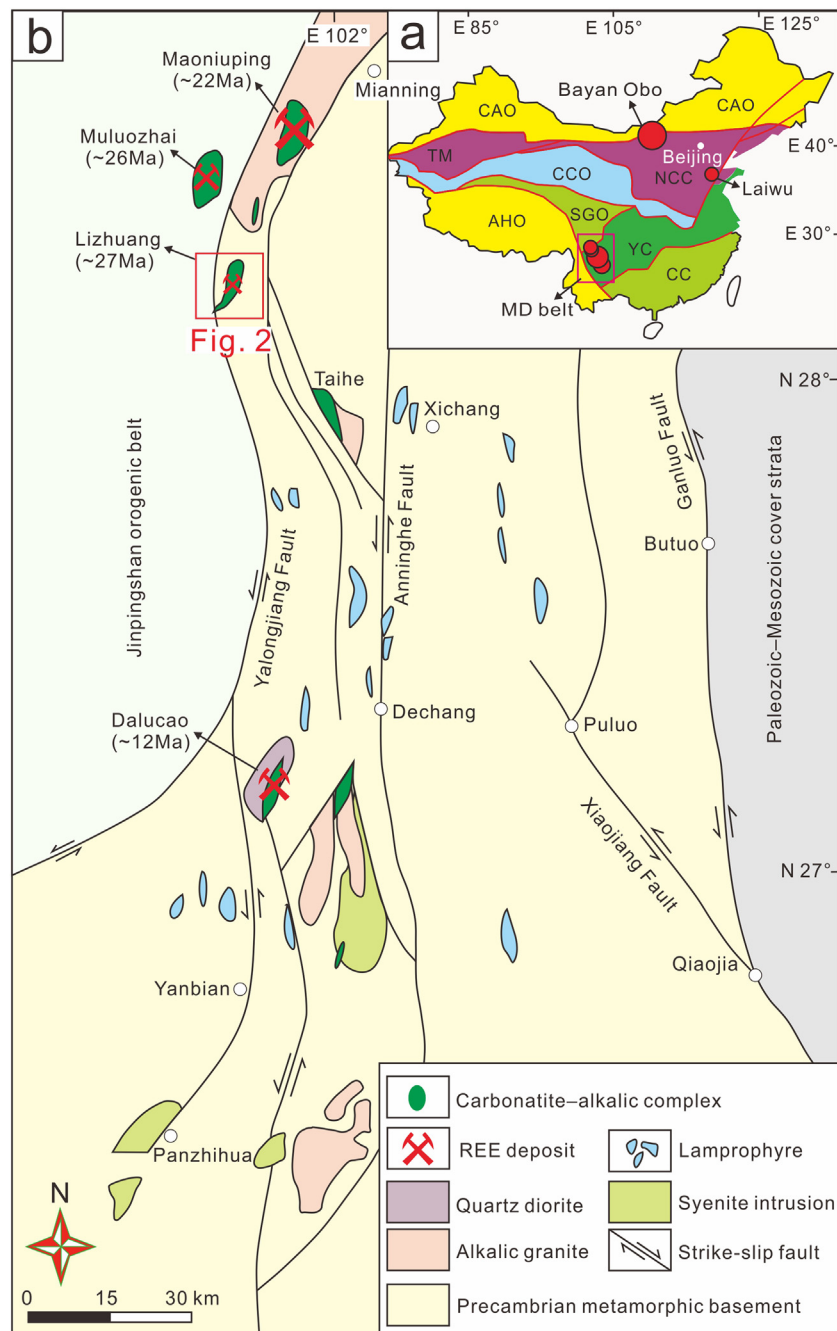


Fig. 1. Location, geology, and tectonics of the Mianning-Dechang REE belt. (a) Tectonic framework showing the spatial distribution of carbonatite-related REE deposits in China (modified after Hou et al., 2015). Abbreviations: AHO = Alps-Himalaya orogeny, CAO = Central Asia orogeny, CC = Cathaysia craton, CCO = Central China orogeny, NCC = North China craton, SGO = Songpan-Ganze orogeny, TM = Tarim block, YC = Yangtze craton. (b) Sketch geological map showing the distribution of Cenozoic carbonatite-alkaline complexes and associated REE deposits in western Sichuan (modified after Yuan et al., 1995).

(secondary ion mass spectrometry) to date bastnäsite-(Ce) (principal REE mineral), yielding an age of 28.4 ± 0.2 Ma (Ling et al., 2016). This timing is in excellent agreement with recently-published zircon U–Pb age of Lizhuang syenite (Liu et al., 2015a), indicating that the development of REE mineralization was essentially coeval with the emplacement of the syenite.

2.2.2. Alteration

Intrusions of both carbonatite and alkaline rocks are typically found in close spatial relationship with aureoles of high temperature metamorphically altered country rock, termed fenites (Le Bas, 2008). Fenitization is generally viewed to result from multiple pulses of fluids

expelled from cooling and crystallizing carbonatitic or alkaline melt (Morogan, 1994), and is widely seen in the Lizhuang deposit (Fig. 3a). Rocks in much of this deposit have been subjected to some degree of fenitization. However, the most intense fenitization occurred around the breccias and produced a fenitization halo. The breccias are typically clast-supported, and the clasts are typically 2–10 cm in diameter and consist largely of angular to rounded fragments of rock (Fig. 3d). The fenitization is manifested by the replacement of K-feldspar by albite and the presence of small grains of biotite (Fig. 4e). The fenite veins containing aegirine-augite, arfvedsonite and biotite (Fig. 4d), in some cases, crosscut adjacent syenite intrusions (Fig. 3e). Field observations show that the Lizhuang fenites are typically cut by later REE-bearing

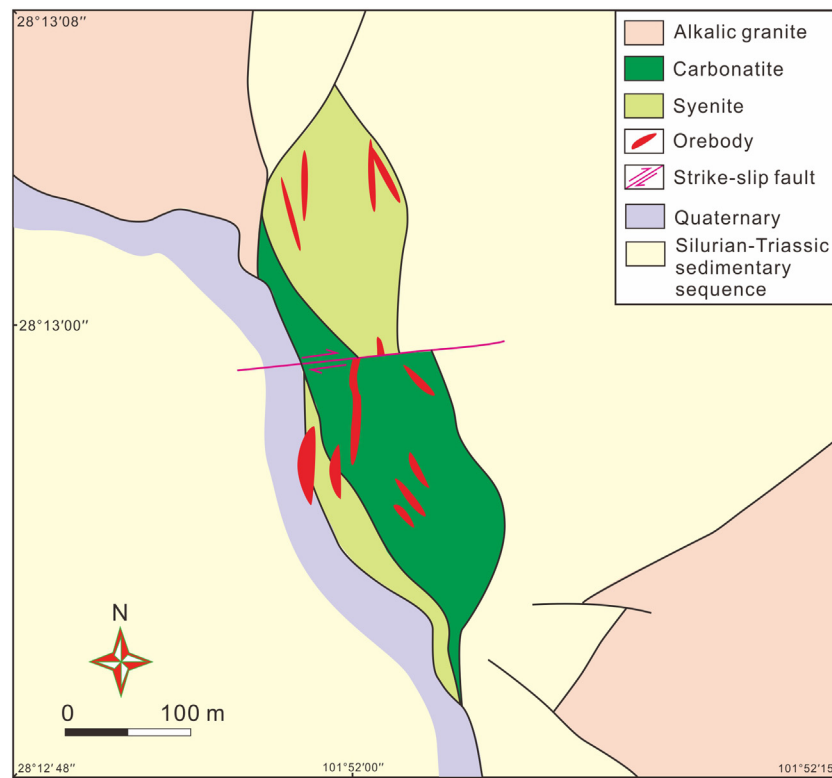


Fig. 2. Schematic geological map showing the carbonatite-syenite complex and associated REE orebodies in the Lizhuang deposit (modified after Hou et al., 2009).

ore vein (Fig. 3a), indicating that REE mineralization formed after fenitization. Unlike the Maoniuping and Muluoizhai deposits, there is a clear alteration of syenite in the Lizhuang deposit, highlighted by a red coloration (Fig. 3d).

2.2.3. Mineralization

The main mineralized zones of the Lizhuang deposit were emplaced along NS-trending fractures within the syenite or carbonatite intrusions (Fig. 2). The ore veins are characterized by regular geometry and vary

from 30 to 100 m length and 2.2 to 11.6 m thick (Hou et al., 2009). Different types of ore may occur together in a single orebody or separately in different orebodies. This deposit is dominated by a disseminated ore that contains calcite, fluorite, quartz, bastnäsite-(Ce), barite, celestite, and pyrite (Fig. 3f). Reddish brecciated ore containing fluorite, barite, calcite, quartz, and bastnäsite-(Ce) is the second most significant type of mineralization (Fig. 3h), which occurs locally within ore lenses or in fractures within the carbonatite-syenite complex. In general, the mineral associations in the Lizhuang deposit are relatively

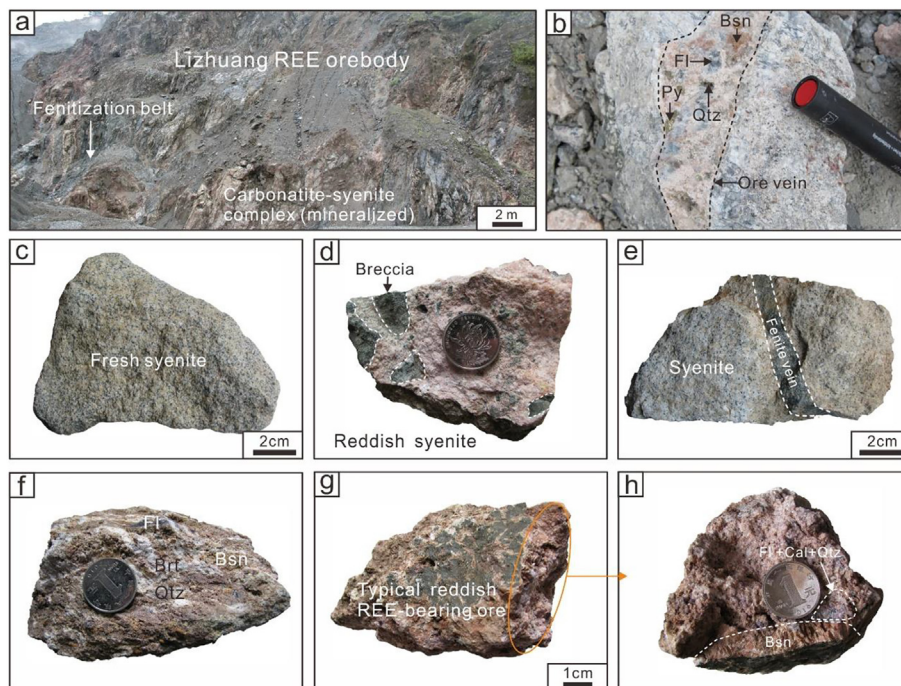


Fig. 3. Characteristic field and mineral relations in the Lizhuang deposit. (a) Panoramic view of the open pit showing carbonatite-syenite complex, fenitization belt and part of vein system. (b) Ore vein comprising fluorite, quartz, bastnäsite-(Ce), and pyrite. (c) Fresh syenite. (d) Reddish syenite that comprises breccias. (e) Fenite vein crosscutting syenite. (f) Disseminated REE-bearing ore that comprises fluorite, quartz, barite and bastnäsite-(Ce). (g-h) Representative reddish REE-bearing ore that comprises fluorite, calcite, quartz and bastnäsite-(Ce). Abbreviations: Fl = fluorite, Qtz = quartz, Cal = calcite, Brt = barite, Bsn = bastnäsite-(Ce), Py = pyrite.

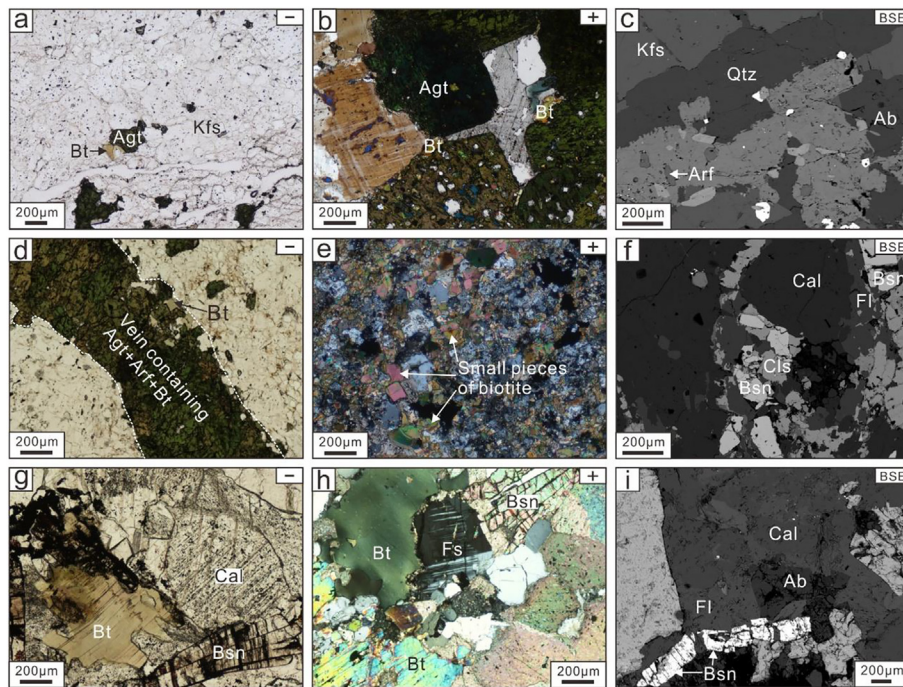


Fig. 4. Photomicrographs and backscattered electron images from the Lizhuang deposit. (a-c) Fresh syenite comprising K-feldspar, albite, biotite, aegirine-augite, arfvedsonite, and quartz. (d) Vein that contains aegirine-augite, arfvedsonite and biotite crosscutting syenite. (e) Typical fenite sample, manifested by the presence of small pieces of biotite. (f-i) Mineral assemblages comprising albite, fluorite, calcite, celestite and bastnäsite-(Ce) in REE-bearing ore. Abbreviations: Agt = aegirine-augite, Arf = Arfvedsonite, Bt = Biotite, Kfs = K-feldspar, Ab = albite, Fs = feldspar, Fl = fluorite, Cal = calcite, Cls = celestite, Bsn = bastnäsite-(Ce). Photomicrograph classifications: (-) = transmitted plane polarized light, (+) = crossed polarized light, BSE = backscattered electron image.

simple and record a paragenetic sequence that is comparable with those of the Maoniuping and Muluozhai deposits (Liu and Hou, 2017).

Fluorite is the most important gangue mineral in the ore veins, which occurs mainly as euhedral or subhedral crystal. Field observations and microscopic analyses both show that only where large amount of fluorite appears can bastnäsite-(Ce) be found (Fig. 3b, f, h). Quartz occurs as fragments of euhedral crystals, which are up to 0.4 cm in length and commonly have distinct overgrowths defined by fluorite and calcite (Fig. 3b, f, h). Barite is present as large anhedral crystal measuring up to 2 cm in diameter, which in many cases suffered intense weathering (Fig. 3g, f). Bastnäsite-(Ce) occurs as fractured or subhedral prisms up to 1.5 cm in length, commonly infilling the spaces between early-formed fluorite, calcite, quartz, and barite or overprinting on these gangue minerals (Figs. 3b, f–h, and 4f–i), indicating that bastnäsite-(Ce) formed later than other hydrothermal minerals.

Magmatic and hydrothermal processes can be distinguished based on textural and paragenetic relationships of various minerals (Fig. 5). Magmatic processes were marked by the formation of the carbonatite-syenite complex when many rock-forming minerals (e.g., K-feldspar and albite) formed. Subsequent hydrothermal processes were represented by fenitization and ore-vein formation, and the latter can be further subdivided into pre-REE and REE stages. The pre-REE stage was associated with the deposition of gangue-mineral aggregates (e.g., fluorite, quartz, calcite, barite, and celestite) in ore veins that occurred in fractures within the carbonatite-syenite complex. The REE stage was characterized by the large-scale crystallization of bastnäsite-(Ce), which typically overprinted early-formed gangue minerals or infilled the spaces between these minerals.

3. Sampling and analytical methods

3.1. Sampling

Representative mineral samples within the ore veins were collected during several field trips to the Lizhuang deposit, with emphasis on pre-REE-stage fluorite, quartz, calcite, together with REE-stage bastnäsite-(Ce). Barite was not collected due to its loose structure caused by serious erosion of weathering. These mineral samples were prepared using conventional methods (crushing, sieving, etc.) at the Langfang Regional

Geological Survey (Hebei, China). > 60 doubly polished thin sections were prepared for optical examination, from which 35 representative ones were chosen for subsequent microthermometric measurements and laser Raman spectroscopic analyses. In order to determine the nature of the initial mineralizing fluids, three samples in a same ore vein were prepared for bulk ion analyses of fluid compositions. In addition, two quartz samples were taken for stable hydrogen and oxygen isotope analyses.

3.2. Fluid inclusions

3.2.1. Microthermometry

Microthermometric measurements were conducted at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Beijing, China. Fluid inclusion microthermometric data were obtained using a Linkam THMSG 600 heating-freezing stage attached to a Leitz microscope. The measurements consisted of ice-melting temperature ($T_{m, ice}$), melting temperature of solid CO_2 (T_{m, CO_2}), final melting temperatures of CO_2 clathrate ($T_{m, cla}$), partial homogenization temperature of CO_2 phase (T_{h, CO_2}), melting temperature of solid phase ($T_{m, s}$) and total homogenization temperature of fluid phases ($T_{h, tot}$). The temperature accuracy of the heating-freezing stage from $-120\text{ }^{\circ}\text{C}$ to $-70\text{ }^{\circ}\text{C}$ is $\pm 0.5\text{ }^{\circ}\text{C}$, from $-70\text{ }^{\circ}\text{C}$ to $100\text{ }^{\circ}\text{C}$ is $\pm 0.2\text{ }^{\circ}\text{C}$, and from $100\text{ }^{\circ}\text{C}$ to $500\text{ }^{\circ}\text{C}$ is $\pm 0.2\text{ }^{\circ}\text{C}$. The heating-freezing rate was generally $0.2\text{--}5.0\text{ }^{\circ}\text{C}/\text{min}$, but was reduced to $0.2\text{ }^{\circ}\text{C}/\text{min}$ close to the phase transition temperature for CO_2 -bearing inclusions and to $0.2\text{--}0.5\text{ }^{\circ}\text{C}/\text{min}$ close to the freezing point and homogenization temperature for aqueous inclusions. Heating cycles of about $5\text{ }^{\circ}\text{C}$ were used to determine the homogenization temperature of bubble and solid phase in solid-bearing fluid inclusions. Heating cycles also constrained the melting temperature of clathrate to within $\pm 0.2\text{ }^{\circ}\text{C}$ in most CO_2 -bearing inclusions. Salinities of aqueous and solid-bearing inclusions were calculated using the methodology of Bodnar and Vityk (1994). Salinities of CO_2 -bearing inclusions were calculated using the melting temperatures of CO_2 clathrate (Collins, 1979). Densities of fluid inclusions were calculated using the Flncon program (Brown, 1989).

3.2.2. Laser Raman spectroscopy

Phases that are present in individual fluid inclusions, including

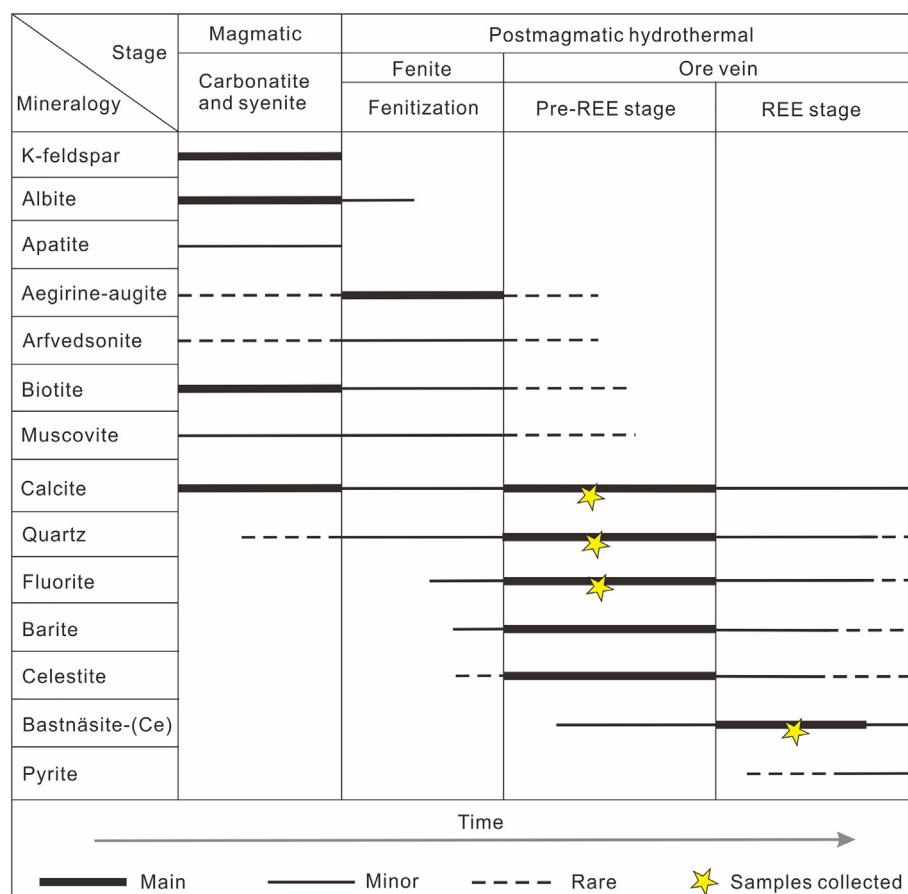


Fig. 5. Paragenetic sequence of REE and gangue minerals in the Lizhuang deposit.

vapor and liquid phases, were identified using a Raman micro-spectrometer (RM2000, Renishaw) at the Institute of Mineral Resources, Chinese Academy of Geological Science, Beijing, China. The excitation wavelength was the 514.53 nm line of an Ar-ion laser operating at 20 mW. The spectrum were recorded with counting time of 30 s and spot size of 1 μm , and ranged from 10 to 4000 cm^{-1} , 1 accumulation, and the spectral resolution was 1–2 cm^{-1} .

3.2.3. Bulk ion analyses

The bulk ion analyses were performed using a Shimadzu HIC-SP at Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing, China. After cleaning and drying, crushed samples were decrepitated at 500 $^{\circ}\text{C}$ in a vacuum and then leached repeatedly using millipure water in an ultrasonic cleaning bath at room temperature until the electrical conductivity of the leachate was the same as the millipure water. All the collected leachates were volumetrically fixed to 30 ml and then analyzed.

3.3. Hydrogen and oxygen isotope analyses

Hydrogen and oxygen isotope analyses were conducted at Beijing Createch Testing Technology Co., Ltd., Beijing, China. Hydrogen isotope ratios of decrepitated quartz-hosted fluid inclusions were measured by mechanically crushing quartz grains, according to the method described by Gong et al. (2007). Samples were first degassed by heating under a vacuum at 120 $^{\circ}\text{C}$ for 3 h; then, the water was released from fluid inclusions by heating the samples to ~ 1000 $^{\circ}\text{C}$ in an induction furnace. The subsequently released water was trapped, reduced to H_2 by zinc at 410 $^{\circ}\text{C}$ (Friedman, 1953), then analyzed using a MAT-253 mass spectrometer, with a precision for δD of ± 1 ‰. Oxygen was liberated from quartz by reaction with BrF_5 (Clayton and Mayeda, 1963)

and converted to CO_2 on a platinum-coated carbon rod. The $\delta^{18}\text{O}$ determinations were made on a MAT-253 mass spectrometer, with a precision for $\delta^{18}\text{O}$ of ± 0.2 ‰. The isotope data are expressed in the delta (δ) notation as the per mil (‰) deviation relative to the Vienna Standard Mean Ocean Water (V-SMOW).

4. Results

4.1. Fluid inclusions

4.1.1. Petrography and classification

Fluid inclusion types were identified based on phases at room temperature, and phase transitions observed during heating and cooling. Four types of inclusion, designated as aqueous (LV), CO_2 -bearing (LC), solid-bearing (LVS), and solid- CO_2 -bearing (LCS) inclusions, were distinguished. In this classification system, the letters “L”, “V”, “S”, and “C” denote “liquid”, “vapor”, “solid”, and “ CO_2 ” phases, respectively.

Most LV inclusions generally show two visible phases (liquid H_2O + vapor H_2O) at room temperature (Fig. 6a), with vapor/(vapor + liquid) ratios ranging from 10 to 40 vol%. These inclusions are irregular-shaped to rounded and 4–36 μm in size. In bastnäsité-(Ce), most of them are densely scattered or grouped in clusters, and thus, are considered to be primary (Fig. 6h, i). Small numbers of LV inclusions are also present in pre-REE-stage fluorite, quartz, and calcite. The primary LV inclusions are generally small in quartz, whereas some inclusions occur as secondary trails along healed fractures but their abundance is limited.

LC inclusions consist of two (liquid H_2O + liquid CO_2) or three phases (liquid H_2O + liquid CO_2 + vapor CO_2) at room temperature (Fig. 6b), with carbonic phases (liquid CO_2 + vapor CO_2) occupying

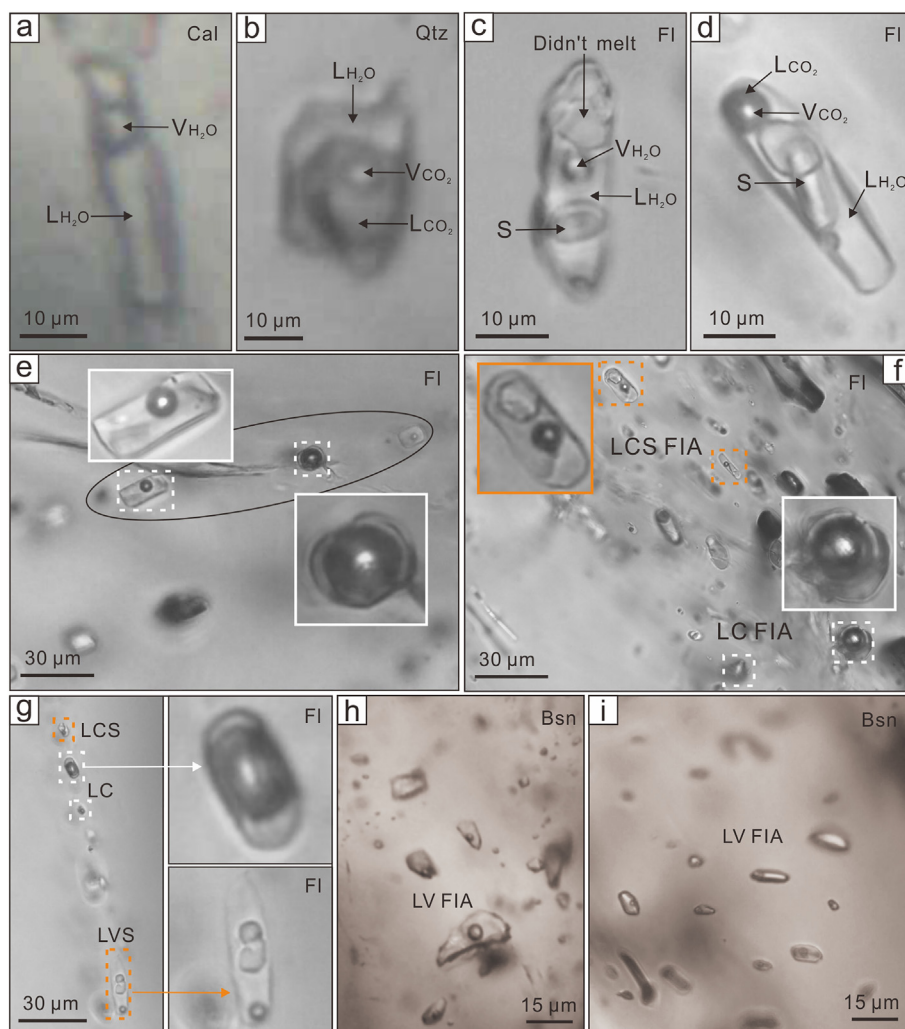


Fig. 6. Photomicrographs of fluid inclusions from the Lizhuang deposit. (a) LV inclusions composed of vapor H₂O and liquid H₂O. (b) LC inclusions composed of liquid H₂O and carbonic content (vapor CO₂ + liquid CO₂). (c) LVS inclusions composed of solid phase, vapor H₂O and liquid H₂O. (d) LCS inclusions composed of solid phase, liquid H₂O and carbonic content (vapor CO₂ + liquid CO₂). (e) Coexistence of LC inclusions with variable CO₂ volume fractions. (f) LC inclusions with high carbonic contents are closely spatially associated with LCS inclusions with low carbonic contents. (g) Coexisting LC, LVS, and LCS inclusion assemblages. (h-i) LV inclusion assemblages with constant bubble volume fractions in bastnäsite-(Ce). Abbreviations: Fl = fluorite, Bsn = bastnäsite-(Ce), Qtz = quartz, Cal = calcite, V = vapor, L = liquid, S = solid, FIA = fluid inclusion assemblage.

20–90% of total volume. They are generally ellipsoidal, elliptic or negative crystal in shape with sizes ranging from 6 to 33 μm. These inclusions widely occur in pre-REE-stage minerals, with minor numbers of them observed in bastnäsite-(Ce). In pre-REE-stage fluorite, LC inclusions with variable CO₂ volume fractions are mainly present in clusters and scattered throughout the sample (Fig. 6e).

LVS inclusions containing one or several solids, liquid H₂O and vapor H₂O show ellipsoid or negative crystal in shape, with the longest dimensions ranging from 7 to 35 μm (Fig. 6c). They are concentrated mainly in pre-REE-stage fluorite, but are also common in quartz cores. Some LVS inclusions contain one solid, whereas others contain several solids occupying over 70 vol% of the inclusion. Note that some solids of this inclusion type did not melt during heating. In some cases, the solid phases may occupy a small proportion of the inclusion volume or appear to extend outside the fluid inclusion.

LCS inclusions consist of one or more solids, carbonic and aqueous phases (Fig. 6d), with bubbles usually accounting for 20–50% in volume. They are ellipsoid, elongated, or negative crystal in shape, and 5–45 μm in size. This type of inclusions observed in pre-REE-stage is closely spatially associated with LC inclusion type, and all of them generally occur in the same cluster (Fig. 6f, g). Some LCS inclusions are present as primary inclusions in fluorite, but hardly exceed 50% of the total inclusion population.

4.1.2. Microthermometry

The microthermometric measurements focused on fluid inclusion assemblages, i.e., closely associated groups of inclusions with visually

identical phase ratios and similar shape (Goldstein and Reynolds, 1994). Based on the criteria of Roedder (1984), only primary inclusions were chosen for the microthermometric analyses. Fluid inclusion microthermometric results are summarized in Table 1 and shown in Figs. 7 and 8.

Pre-REE stage: The measurements for LV inclusions constrain a salinity range of 4.2 to 18.6 wt% NaCl equiv. based on freezing points of −12.0 to −3.2 °C. Total homogenization of this inclusion type was observed at temperatures between 252 and 370 °C, with two modes of homogenization (i.e., to a liquid or vapor phase). LC inclusions display melting of solid CO₂ at temperatures between −61.3 and −58.4 °C, with the majority between −60.3 and −58.7 °C. The temperatures are in part lower than the triple point for pure CO₂ (−56.6 °C), indicating the presence of a subordinate amount of other gases. The melting of CO₂ clathrate in the presence of CO₂ liquid occurred between −0.8 and 6.4 °C, with the calculated salinities ranging from 6.8 to 16.3 wt% NaCl equiv. All of LC inclusions show partial homogenization temperatures ranging from 20.2 to 30.3 °C, with total homogenization temperatures exhibiting a wide range of 247 to 384 °C. The liquid-vapor homogenization of all LVS inclusions was observed at temperatures clustering 275–368 °C, and the solid dissolution occurred at temperatures from 204 to 380 °C, corresponding to calculated salinities of 32.1 to 45.3 wt% NaCl equiv. For LCS inclusions, CO₂ solid dissolved at temperatures between −60.9 and −59.8 °C, with disappear temperatures of CO₂ clathrate varying from 1.2 to 4.8 °C. Liquid-vapor homogenization in these inclusions occurred at temperatures of 282 to 359 °C; and the solid dissolution temperatures range from 280 to 322 °C, with the

Table 1
Microthermometric data of fluid inclusions from the Lizhuang REE deposit.

Mineral	Inclusion type	N	vol. (CO ₂) %	T _{m, CO₂} (°C)	T _{m, cla} (°C)	T _{h, CO₂} (°C)	T _{m, s} (°C)	T _{h, tot} (°C)	T _{m, ice} (°C)	Salinity (wt%)
Pre-REE stage										
Fluorite 1	LV	10						254 to 337 (L, V)	−10.3 to −4.5	7.2 to 14.3
	LC	6	20 to 70	−61.2 to −60.1	0.5 to 5.4	21.1 to 26.3		247 to 343 (L, V)		8.5 to 15.0
Fluorite 2	LV	8						265 to 323 (L)	−9.6 to −5.8	8.9 to 13.6
	LC	4	40 to 50	−60.3 to −58.4	2.0 to 5.3	22.2 to 25.4		275 to 304 (L)		8.6 to 13.3
Fluorite 3	LV	7						279 to 370 (L)	−10.2 to −5.7	8.8 to 14.2
	LC	11	20 to 90	−60.5 to −58.8	1.9 to 4.7	23.9 to 30.3		280 to 384 (L, V)		9.4 to 13.3
	LVS	11					204 to 326	275 to 360 (L, V)		32.1 to 40.3
	LCS	6	20 to 50	−60.9 to −59.8	1.2 to 4.8	24.4 to 30.6	280 to 322	282 to 359 (L)		36.4 to 39.9
Quartz 1	LV	10						275 to 348 (L, V)	−12.5 to −5.2	8.1 to 16.5
	LC	14	20 to 70	−60.7 to −60.1	−0.4 to 4.8	21.3 to 26.9		306 to 371 (L, V)		9.4 to 15.9
Quartz 2	LVS	14					259 to 371	282 to 368 (L, V)		35.3 to 44.4
	LV	11						317 to 364 (L)	−14.8 to −3.2	5.3 to 18.6
Quartz 2	LC	11	20 to 60	−61.3 to −60.6	−0.8 to 5.1	20.2 to 28.9		292 to 362 (L, V)		8.9 to 16.3
	LVS	13					301 to 380	288 to 357 (L, V)		38.2 to 45.3
Calcite 1	LV	9						252 to 321 (L)	−12.0 to −2.5	4.2 to 16.0
	LC	10	30 to 60	−61.2 to −60.5	0.3 to 6.4	23.1 to 26.8		275 to 340 (L)		6.8 to 15.2
REE stage										
Bastnäsite 1	LV	12						190 to 282 (L)	−9.9 to −0.5	0.9 to 13.9
	LVS	4					233 to 262	254 to 315 (L)		33.7 to 35.5
Bastnäsite 2	LV	11						219 to 262 (L)	−8.3 to −1.7	2.9 to 12.1
	LC	3	20 to 30	−59.6 to −57.9	−0.2 to 3.1	20.6 to 24.2		230 to 258 (L)		11.8 to 15.7
	LVS	4					222 to 290	229 to 279 (L)		33.0 to 37.4
Bastnäsite 3	LV	14						177 to 269 (L)	−10.4 to −0.4	0.7 to 14.4
Bastnäsite 4	LV	18						182 to 298 (L)	−8.9 to −1.2	2.1 to 12.7
	LC	3	20 to 30	−58.5 to −58.1	3.8 to 4.7	25.9 to 28.7		233 to 247 (L)		9.4 to 10.7

Notes: N = number of fluid inclusions analyzed, vol. (CO₂) % = volume fraction of CO₂ phase, T_{m, CO₂} = melting temperature of solid CO₂, T_{m, cla} = melting temperature of CO₂ clathrate, T_{h, CO₂} = partial homogenization temperature of CO₂ phase, T_{m, s} = melting temperature of solid phase, T_{h, tot} = temperature of total homogenization and the mode of homogenization (L: to liquid, V: to vapor), T_{m, ice} = melting temperature of final ice. Abbreviations: LV = Aqueous inclusion, LC = CO₂-bearing inclusion, LVS = solid-bearing inclusion, LCS = solid-CO₂-bearing inclusion.

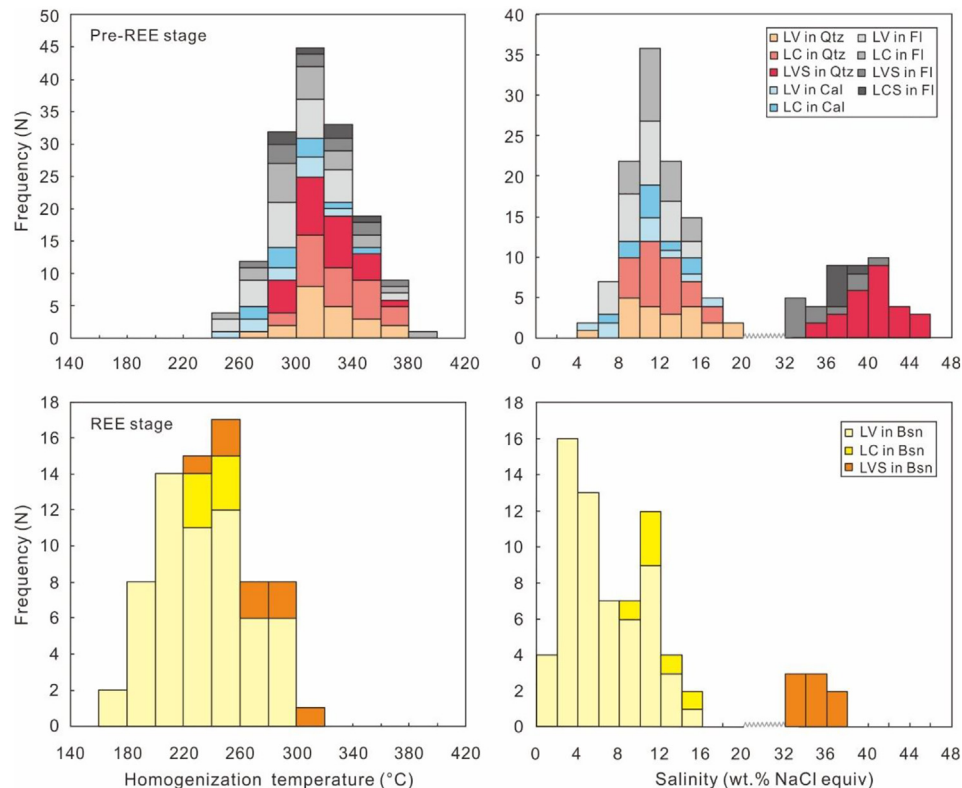


Fig. 7. Histograms of homogenization temperature and salinity for fluid inclusions in different stages. Abbreviations as in Fig. 6.

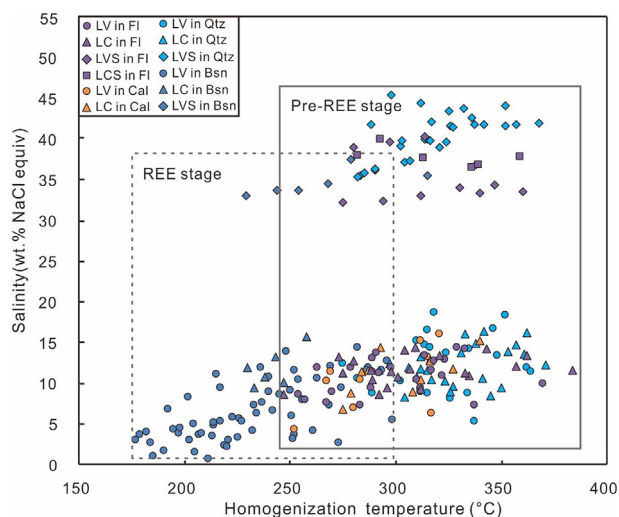


Fig. 8. Homogenization temperature vs. salinity for fluid inclusions in different stages. Abbreviations as in Fig. 6.

calculated salinities of 36.4 to 39.9 wt% NaCl equiv.

REE stage: All measured LV inclusions in bastnäsite-(Ce) show consistent microthermometric mode, i.e., homogenization to a liquid phase, with total homogenization temperatures ranging from 177 to 298 °C. They have salinities varying from 0.7 to 14.4 wt% NaCl equiv. based on ice-melting temperatures of -10.4 to -0.4 °C. LC inclusions are rare, although six inclusions yield homogenization temperatures of 230 to 258 °C. These inclusions give clathrate melting temperatures of -0.2 to 4.7 °C, corresponding to salinities ranging from 9.4 to 15.7 wt% NaCl equiv. Eight LVS inclusions exhibit homogenization behavior of solid dissolution prior to vapor disappearance, and yield the temperatures of liquid-vapor homogenization ranging from 229 to 315 °C. Solid dissolution in these inclusions occurred at temperatures between 222 and 290 °C, corresponding to calculated salinities of 33.0 to 37.4 wt% NaCl equiv.

4.1.3. Laser Raman spectroscopy

Attempts to analyze the carbonic phase of LC inclusions in fluorite were unsuccessful because of the strong fluorescence of fluorite that obscured the CO_2 peaks. Thus, LC inclusions in quartz were select to analyze their compositions. Clearly, the vapor bubbles of LC inclusions are dominated by CO_2 (Fig. 9a). In contrary, CO_2 was absent in the

vapor phase of LV inclusions hosted by bastnäsite-(Ce) (Fig. 9c, d). In addition, the spectrums in Fig. 9a–c show that $(\text{SO}_4)^{2-}$ is the significant anion of the fluids in both quartz and bastnäsite-(Ce).

4.1.4. Bulk ion analyses

The results of bulk ion analyses are listed in Table 2, revealing that ions present in the fluids consisted of $(\text{SO}_4)^{2-}$, Cl^- , F^- , Na^+ , K^+ , as well as minor Mg^{2+} . The molar ratios of Na^+/K^+ and $\text{Cl}^-/(\text{SO}_4)^{2-}$ range from 5.47 to 9.15 and from 0.44 to 1.16, respectively. The ions $(\text{CO}_3)^{2-}$ and $(\text{HCO}_3)^-$ were not analyzed, because a Na_2CO_3 solution was used as the flow phase for anion analysis. Charge imbalance between anions and cations in these data is due to the fact that some cations, in particular REE^{3+} , were not measured. In summary, the fluids have relatively high ratios of Na^+/K^+ and low ratios of $\text{Cl}^-/(\text{SO}_4)^{2-}$.

4.1.5. Hydrogen and oxygen isotope systematics

The H and O isotope compositions of selected quartz minerals are given in Table 3 and Fig. 10, including the data reported by previous literatures (Hou et al., 2009; Liu and Hou, 2017). All calculations were based on average temperatures obtained by microthermometry of primary fluid inclusions. The $\delta^{18}\text{O}_{\text{fluid}}$ values were calculated by extrapolation of the fractionation formula: $10^3 \ln \alpha = 3.38 \times 10^6 \times T^{-2} - 3.40$ (Clayton et al., 1972). The calculated $\delta^{18}\text{O}_{\text{fluid}}$ values of five quartz samples from the ore veins range from 0.3‰ to 3.8‰, with $\delta\text{D}_{\text{V-SMOW}}$ values varying from -86.9 ‰ to -62.7 ‰.

5. Discussion

5.1. Nature of the initial fluids

The nature of hydrothermal fluids involved carbonatitic systems has been addressed by a few studies (e.g., Smith and Henderson, 2000; Williams-Jones and Palmer, 2002; Rankin, 2005). Generally, H–O isotopes can well constrain the source of the mineralizing fluids. The Lizhuang quartz samples give available $\delta^{18}\text{O}_{\text{fluid}}$ (0.3‰ to 3.8‰) and $\delta\text{D}_{\text{fluid}}$ (-86.9 ‰ to -62.7 ‰) values, similar to those reported in other carbonatite-related REE deposits in the MD belt (Hou et al., 2009; Liu et al., 2015b). Fig. 10 shows that the H–O isotope values of the mineralizing fluids are plotted in the region between the primary magmatic water box and the meteoric water line, but are still dominated by magmatic water (Taylor, 1974). Considering a possible underestimate of $\delta^{18}\text{O}$ values using fluid inclusion homogenization temperatures, the mixing degree of meteoric water into magmatic fluids is probably less

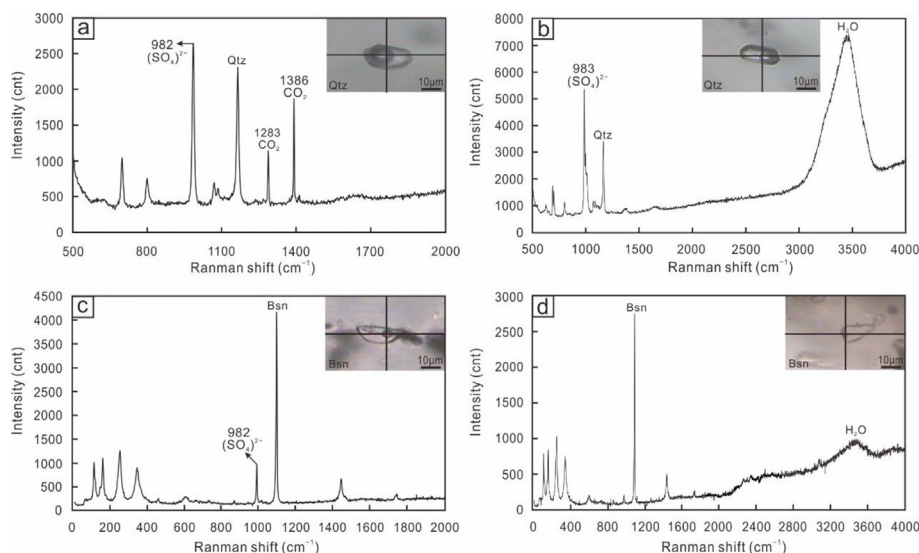


Fig. 9. Laser Raman spectroscopy data for fluid inclusions from the Lizhuang deposit. (a) $(\text{SO}_4)^{2-}$ and CO_2 spectrums in a quartz-hosted CO_2 -bearing inclusion. (b) $(\text{SO}_4)^{2-}$ and H_2O spectrums in a quartz-hosted aqueous inclusion. (c) $(\text{SO}_4)^{2-}$ spectrum in a bastnäsite-hosted aqueous inclusion. (d) H_2O spectrum in a bastnäsite-hosted aqueous inclusion. Abbreviations as in Fig. 6.

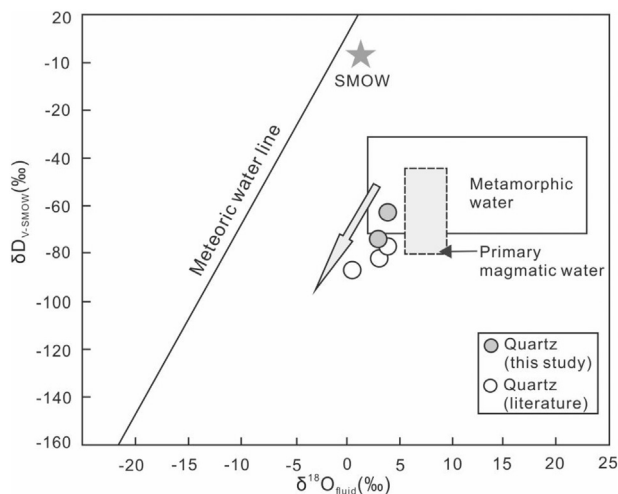
Table 2Ion compositions ($\mu\text{g/g}$) in the bulk analyses of fluid inclusions from the Lizhuang hydrothermal minerals.

¹ Sample no.	Mineral	(SO ₄) ²⁻	Cl ⁻	F ⁻	Na ⁺	K ⁺	Mg ²⁺	² Na ⁺ /K ⁺	Cl ⁻ /(SO ₄) ²⁻
LZ13-3	Calcite	20.7	3.38	1.8	4.87	1.51	0.32	5.47	0.44
LZ130-3	Fluorite	41.4	9.45	³ NO	15.0	2.78	0.15	9.15	0.62
LZ130-4	Fluorite	6.00	2.58	NO	2.46	0.63	NO	6.62	1.16

Notes: Charge imbalance between anions and cations in these data is because some cations, REE³⁺ in particular, were not measured.¹These samples for bulk ion analyses were collected in a same ore vein. ² Molar ratio. ³ The detection result was not obtained.**Table 3**

Hydrogen and oxygen isotope data of selected quartz from the Lizhuang REE deposit.

Sample no.	Mineral	Th (°C)	$\delta^{18}\text{O}_{\text{V-SMOW}}$ (‰)	$\delta^{18}\text{O}_{\text{fluid}}$ (‰)	$\delta\text{D}_{\text{V-SMOW}}$ (‰)	Reference
LZ18-04	Quartz	300	9.8	2.9	-73.9	This study
LZ18-06	Quartz	300	10.7	3.8	-62.7	This study
LZ13-2-2	Quartz	330	6.4	0.3	-86.9	Liu and Hou (2017)
LZ-13	Quartz	300	10.7	3.8	-77.0	Hou et al. (2009)
LZ-14	Quartz	300	9.9	3.0	-82.0	Hou et al. (2009)

Notes: Th is the approximate average homogenization temperature of all inclusions hosted in selected quartz; $\delta^{18}\text{O}_{\text{fluid}}$ values are calculated according to the quartz-water equilibrium temperature formula provided by Clayton et al. (1972).**Fig. 10.** Plot of δD vs. $\delta^{18}\text{O}$ of the fluids from the Lizhuang deposit. Metamorphic water field, magmatic water field, and meteoric water line are from Taylor (1974). SMOW = standard mean ocean water.

than expected. This implies that the initial fluids in the Lizhuang deposit had a dominantly magmatic signature and were gradually diluted by meteoric water during hydrothermal activities.

Carbon dioxide is a common volatile component of mineralizing fluids and plays a significant role in the formation of various types of deposits, such as orogenic Au deposits (Ridley and Diamond, 2000) and porphyry Mo deposits (Ni et al., 2017). The association between REE mineralization and CO₂ activity has been well documented in some REE deposits related to carbonatites, such as Bayan Obo in China (Smith and Henderson, 2000) and Wicheeda in Canada (Trofanenko et al., 2016). In the present study, the presence of abundant CO₂-bearing inclusions occurring in Lizhuang pre-REE-stage minerals (Fig. 6e–f), and their similarities to those described in other carbonatite complexes (e.g., Oka, Samson et al., 1995a, 1995b), indicate that CO₂-bearing fluids are an integral part of the initial mineralizing system. As such, CO₂ probably plays an unnegligible role in hydrothermally related REE transport, as suggested by an experimental petrology evidence that REEs have high partition coefficients in CO₂-bearing fluids (Dasgupta et al., 2009). Given that CO₂ tends to exsolve from magmas during early-stage of emplacement (Giggenbach, 1997; Lowenstern, 2001), it is assumed that CO₂ in the initial fluids was probably derived by the decarbonization of

the host carbonatites. Just as stated by Liu et al. (2015b), decarbonation process (probably involving H₂O) would produce CO₂, leading to the fluid phase becoming a CO₂-bearing solution. Nevertheless, further explanation to this hypothesis has beyond the scope of our current study and additional work is required before a complete understanding can be reached.

In carbonatite-related hydrothermal systems, the presence of cations, such as K⁺, in addition to Na⁺ has been inferred from measured eutectic temperatures (Rankin, 2005). The analyses of saline aqueous inclusions from the Oka carbonatite reported by Samson et al. (1995a, 1995b) have demonstrated that the fluids were rich in Cl⁻ and (SO₄)²⁻, with Na⁺ as the dominant cation, but that K⁺ and Mg²⁺ were also present. Similarly, the intense fenitization that occurred along Lizhuang ore veins implies that the mineralizing fluids were rich in Na⁺ and K⁺ (e.g., Elliott et al., 2018), consistent with the bulk ion data listed in Table 2. Although bulk ion analyses yield mixed compositions including primary and secondary inclusions, the data clearly indicate the presence of (SO₄)²⁻, Cl⁻, F⁻, Na⁺, K⁺, Mg²⁺ in the initial mineralizing fluids. In addition, bastnäsite-(Ce) is the dominant REE mineral, which comprises (CO₃)²⁻ and REE in its chemical formula. Barite is one of the most significant gangue minerals in the ore veins, which indicates the presence of Ba²⁺. Although the presence of fluorite in the ore veins indicates that there was probably some Ca²⁺ in the fluids, the low solubility of fluorite would have buffered the concentration of Ca²⁺ to low values. This is consistent with the lack of detectable Ca²⁺ in the decrepitates from fluorite-host fluid inclusions using bulk ion analyses (Table 2). If the initial fluids had carried both Ca²⁺ and F⁻, fluorite, because of its extremely low solubility, would have started to precipitate immediately on release of the fluids from the magmas (Johnson et al., 1992). This was clearly not the case. The most probable explanation is that Ca²⁺ forming fluorite came from formation water in an external setting. Actually, the formation water is interpreted to have contained Ca²⁺ as a result of interaction with carbonatites, which are known to be common in the stratigraphic succession. A similar scenario has been reported in Gallinas Mountains fluorite-REE deposits (Williams-Jones et al., 2000). Thus, the initial fluids in the Lizhuang deposit contain REE, (SO₄)²⁻, Cl⁻, F⁻, (CO₃)²⁻, Na⁺, K⁺, Ba²⁺, Mg²⁺, in which (SO₄)²⁻, Cl⁻, and F⁻ are the most significant anions. Notably, the high Na⁺/K⁺ and low Cl⁻/(SO₄)²⁻ molar ratios of the fluids in the Lizhuang deposit (Fig. 11) are similar to those documented in previous studies of other carbonatites (e.g., Maoniuping, Zheng and Liu, 2019), but clearly different to those mentioned in other geological settings such as Strange Lake (granite-related REE deposits, Vasyukova

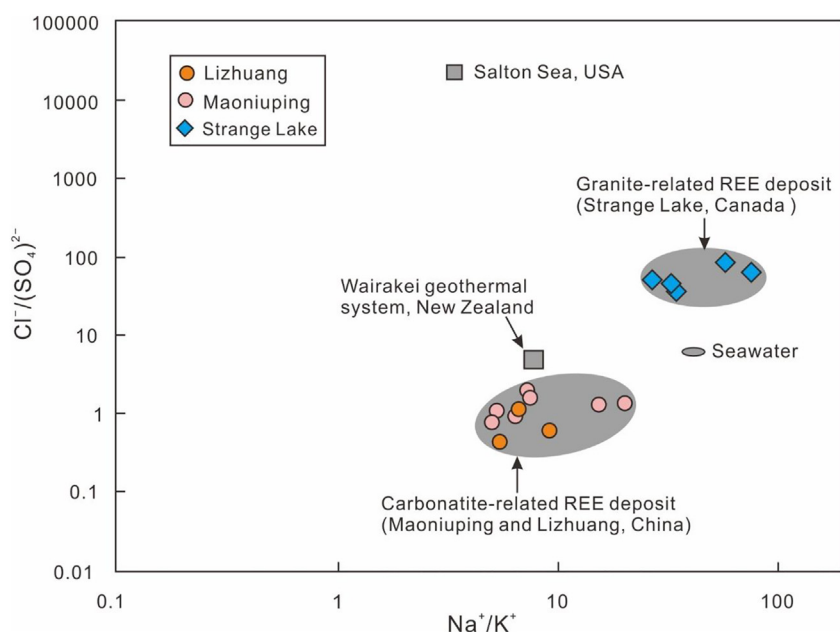


Fig. 11. Na^+/K^+ vs. $\text{Cl}^-/(\text{SO}_4)^{2-}$ (molar ratios) of fluid inclusions from the Lizhuang deposit, compared with other reference fluids: seawater (Frape and Fritz, 1987), Salton Sea, USA (McKibben et al., 1987), Wairakei geothermal system, New Zealand (Hedenquist and Henley, 1985), Strange Lake granite-related REE deposit, Canada (Vasyukova and William-Jones, 2018), and Maoniuping carbonatite-related REE deposit, China (Zheng and Liu, 2019).

and William-Jones, 2018), seawater (Frape and Fritz, 1987), Salton Sea (USA, McKibben et al., 1987), and Wairakei geothermal system (New Zealand, Hedenquist and Henley, 1985).

5.2. Evolution of the mineralizing fluids

The fact that carbonatite and syenite in the Lizhuang deposit are spatially associated with each other suggests that a mixed carbonatite-syenite magmas cannot be ignored (Liu and Hou, 2017). Hou et al. (2015) proposed that the carbonatite-syenite magmas would release highly oxidized, high-flux, and REE-rich fluids during stress relaxation. As discussed earlier, the initial fluids exsolved from the residual magmas were certainly enriched Na^+ , K^+ and, therefore, fenitization occurred in this mining area due to the upwelling fluids interacting with wall-rocks. Further evolution of the hydrothermal system was marked by the formation of ore veins. Fluid inclusion data have identified the fluids with intermediate to high temperatures (247 to 384 °C) and salinities (4.2 to 45.3 wt% NaCl equiv) in pre-REE stage (Table 1). The homogenization temperatures and salinities of fluid inclusions in fluorite, quartz and calcite are remarkably close (Figs. 7 and 8), indicating that these minerals were precipitated simultaneously. This view is consistent with our field observation that fluorite, calcite, and barite commonly occur in the ore veins and show a paragenetic association with coexisting quartz (Fig. 3b, f, h). Fluid immiscibility is addressed firstly before the discussion of P–T–X evolution. Some CO_2 -bearing inclusions with variable CO_2 volume fractions are trapped as primary clusters in pre-REE-stage fluorite, and thus, interpreted as contemporaneous trapping (Fig. 6e). Most of the immiscible CO_2 -bearing inclusions exhibit the similar homogenization temperatures in the range of 300 to 340 °C. In addition, the microscopic observation that some LCS inclusions are closely spatially associated with LC inclusions (Fig. 6f, g) further supports the view. According to Diamond (1994), if fluid inclusions were formed in the immiscible two-phase field, the trapping pressures can be approximated from end-member inclusions trapped nearest the solvus. Thus, these immiscible LC inclusions have been selected to estimate trapping pressures based on their end-member low and high X_{CO_2} values, and isochores have been calculated using the Flincor program (Brown, 1989) and the equations provided by Bowers and Helgeson (1983). Pressure-temperature conditions at which the inclusions formed fall along the path defined by the isochores for the inclusions (Li et al., 2012). Fig. 12a shows

representative isochores for the end members of these immiscible LC inclusions trapped in pre-REE stage, in which the estimated trapping pressure is 950–1550 bar at the temperature range of 300 to 340 °C. The range in pressures recorded by inclusions is probably due in part to repeated reactivation along the structural structure that focused the fluids and hosted the vein system (Baker and Lang, 2003). These discussions mentioned above suggest that fluid evolution from pre-REE stage to bastnäsite-(Ce) deposition may have been via fluid immiscibility, finally resulting in the trapping of high-salinity, dominantly CO_2 -bearing inclusions with variable CO_2 volume fractions.

Abundant LV inclusions with constant bubble fractions occurring in bastnäsite-(Ce) (Fig. 6h, i) suggest that the fluids precipitating bastnäsite-(Ce) are relatively homogeneous. These inclusions provide an insight into fluid chemistry in terms of both temperature (177 to 298 °C) and salinity (0.7 to 14.4 wt% NaCl equiv), indicating a different condition during REE stage compared to the deposition episodes of fluorite, quartz, and calcite. Despite this, it must be emphasized that there are a small number of high-salinity and CO_2 -bearing inclusions observed in bastnäsite-(Ce) (Table 1). These absence of immiscible or boiling inclusion assemblages indicates a plausible explanation for the presence of those inclusions, i.e., they inherited the remnants of pre-REE-stage fluids. Generally, the CO_2 escape resulted from fluid immiscibility will cause a higher salinity in residual liquids. A question that arises from the above interpretation is why, if immiscibility made fluids more saline, is there a large number of low-salinity aqueous inclusions observed in bastnäsite-(Ce). The homogenization temperature vs. salinity plot for fluid inclusions, with a crude linear correlation of salinity and temperature (Fig. 8), shows a trend of dilution. This allows at present a definitive answer in regards to the question, that is, the dilution of the fluids due to mixing with lower salinity fluids of meteoric origin. Therefore, we proposed that with fluid immiscibility ended, most CO_2 was lost, and low-salinity fluids were generated causing by the massive influx of meteoric water. This inference is also supported by new and previously-reported H–O isotopes (Fig. 10). Fig. 12b shows a low pressure distribution of aqueous inclusions (< 200 bar), of which the two-dimensional phase diagram are modified after Driesner and Heinrich (2007) in a simple NaCl– H_2O system.

5.3. Key factors controlling REE mineralization

Investigating how REEs are concentrated to economic levels by

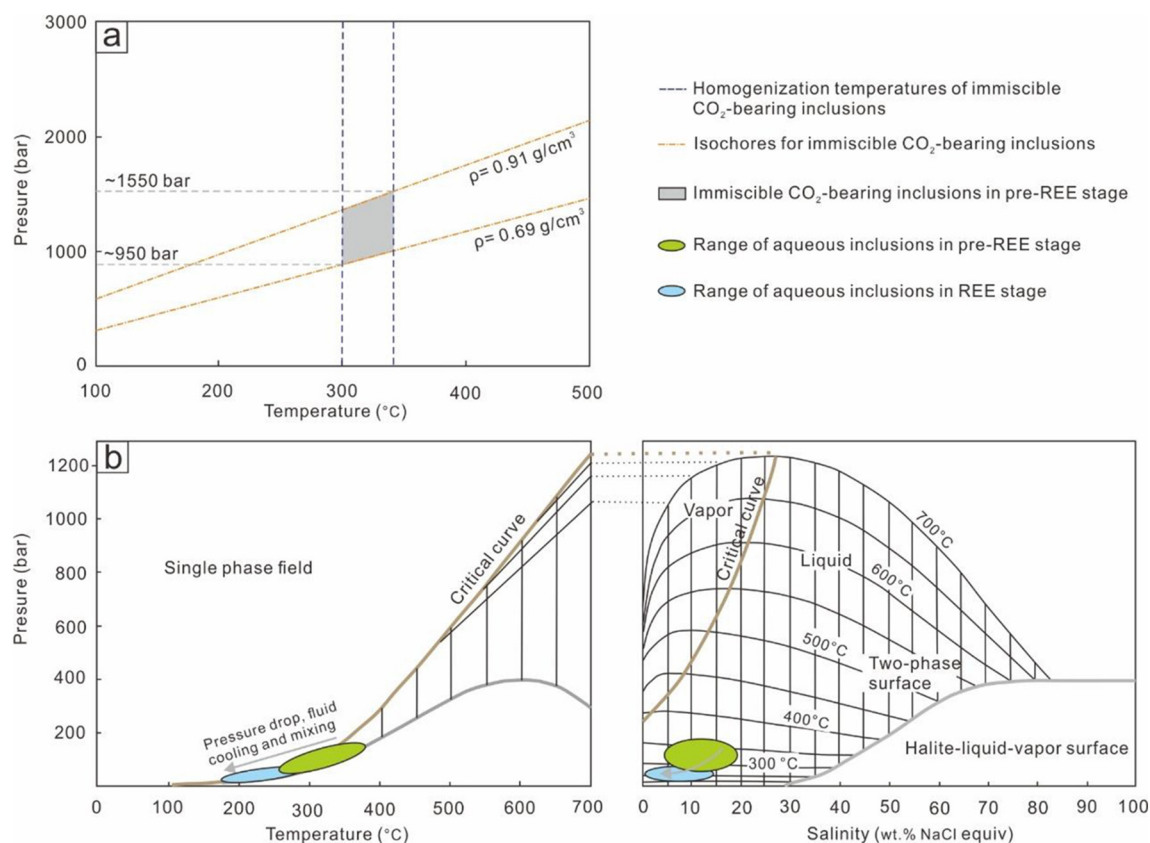


Fig. 12. Pressure estimation for fluid inclusions in different stages. (a) Trapping pressures for fluid immiscibility in pre-REE stage based on intersections (shaded area) between isochores constructed with the minimum and maximum densities of the immiscible CO₂-bearing inclusions, and minimum and maximum homogenization temperatures. The isochores are calculated using the Flincor program (Brown, 1989) and the formula of Bowers and Helgeson (1983). (b) The NaCl–H₂O phase diagram is modified after Driesner and Heinrich (2007). The two-phase surface separates the single-phase field at high pressure from the two-phase fluid stability field at lower pressure and is contoured for composition and temperature with the critical curve on its crest. The halite-liquid-vapor surface is omitted for clarity.

hydrothermal processes has been a developing focus of REE deposit studies (e.g., Xie et al., 2009, 2015; Li and Zhou, 2018). The observable REE mineralization in the Lizhuang deposit is clearly hydrothermal and is interpreted to be the product of the transport and deposition of REE as complexes. Our bulk analyses of fluid compositions reveal that the mineralizing fluids were enriched in (SO₄)^{2−}, F[−], and Cl[−] ions. Theoretical and experimental studies have shown that these ions have the ability to form stable complexes with REE and could be important for REE transport and deposition (Haas et al., 1995; Migdisov et al., 2009). In this deposit, the temperature of pre-REE stage is still high (peak values > 300 °C, Fig. 7). Such high-temperature fluids had appreciable capacity to transport REE, consequently, no major REE mineralization developed. In contrast, homogenization temperatures of LV inclusions in REE-stage bastnäsite-(Ce) are lower than 300 °C (Fig. 7). There is a clear trend of strongly decreasing temperatures from the early to late stages of ore vein formation (Figs. 7 and 8). One plausible explanation for such a decrease in temperature is a fluid immiscibility event that occurred; an alternative could be a fluid mixing with cooler meteoric water. The solubility of REE minerals decreases strongly with fluid cooling (Migdisov et al., 2009; Gysi and Williams-Jones, 2015), which is also supported by recent geochemical models that the deposition of bastnäsite-(Ce) will occur spontaneously once temperature falls below the limit of their thermal stability (Trofanenko et al., 2016). With this in mind, we proposed that decreasing temperature might be a key control on REE mineralization.

Fluid immiscibility occurred in pre-REE stage but had essentially ceased by the REE stage. If this was the case, fluid immiscibility is unlikely to have caused REE mineralization because the potential

trigger of bastnäsite-(Ce) deposition occurred later. In addition, we cannot exclude the possibility that the inflow of meteoric water favoured or promoted mineralization processes, as the H–O isotope (Fig. 10) and fluid inclusion data (Fig. 8) both support a major fluid mixing event that occurred in REE stage. Inflow of meteoric water should be effective in increasing pH value of the hydrothermal system and further lowering its temperature. All of these processes would severely diminished the stability of REE-bearing complexes and therefore triggered the deposition of bastnäsite-(Ce) (e.g., Williams-Jones et al., 2000; Trofanenko et al., 2016).

We have drew a summary cartoon (Fig. 13) to elegantly explain the continuous magmatic-hydrothermal evolution that occurred in a distinct temporal sequence and at different spatial scales. Hydrothermal activities were initiated by the shallow emplacement of volatile-rich, REE-bearing carbonatite-syenite magmas (Fig. 13a; Hou et al., 2015). With rapid release of the fluids, fenitization occurred as metasomatism on wall-rocks in the Lizhuang deposit, causing the formation of alkali silicates (Fig. 13c). Subsequently, the fluids in pre-REE stage experienced intense immiscibility, as evidenced by the coexistence of CO₂-bearing inclusions with variable CO₂ volume fractions in fluorite. Accompanied by immiscibility and progressively cooling of the fluids, they triggered the deposition of fluorite, calcite and barite that had not yet been “choked” with earlier-crystallized material (Fig. 13d, e). According to Liu et al. (2019a), voluminous deposition of fluorite and calcite, which both have lower (La/Yb)_{cn} values, would further raise the concentration of light lanthanides, while simultaneously stripping the fluids of complexing ligands [e.g., F[−], (SO₄)^{2−}, Cl[−], and (CO₃)^{2−}]. It is assumed that the deposition of bastnäsite-(Ce) did not occur until

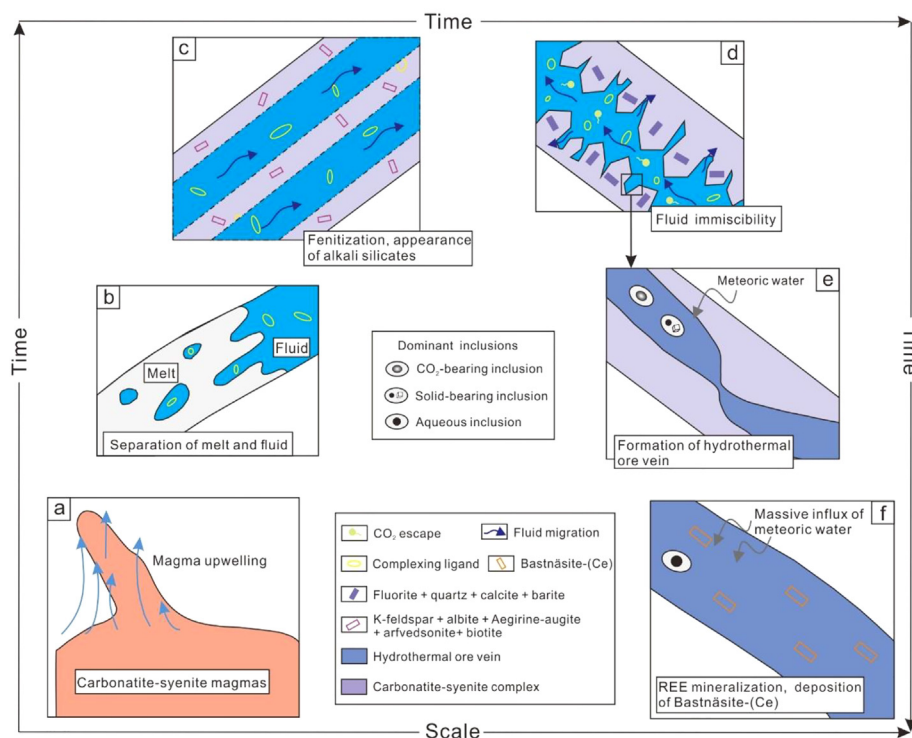


Fig. 13. Summary cartoon showing continuous magmatic-hydrothermal evolution and related REE mineralization process in the Lizhuang deposit. (a) The deep carbonatite-syenite magmas that were derived from the SCLM (Hou et al., 2015) upwelling. (b) The inferred separation of melt and fluid phases occurring. (c) Fenitization occurred as metasomatism on wall-rocks and led to the formation of alkali silicates. (d) The fluids experienced intense immiscibility and, consequently, caused CO_2 -bearing inclusions with variable CO_2 volume fractions to be trapped. (e) Accompanied by the immiscibility, the deposition of fluorite, barite and calcite was triggered in the ore veins. (f) REEs were subsequently precipitated mainly as bastnäsite-(Ce) via fluid cooling and massive influx of meteoric water into the hydrothermal system.

the immiscibility ended, and there were massive influx of external fluids into hydrothermal system. This is based on a hypothesis, which is drawn from the prevalence of aqueous inclusions and the scarcity of CO_2 -bearing inclusions in bastnäsite-(Ce), that REEs were most likely to be precipitated from low- to moderately-saline aqueous fluids with minor amounts of CO_2 . During the late-stage of hydrothermal activities, owing to the massive influx of meteoric water, destabilization and decomposition of REE-bearing complexes caused the deposition of bastnäsite-(Ce) by decreasing temperature and increasing the pH value of this hydrothermal system (Fig. 13f).

5.4. Application of this study in routine exploration

The case study of the Lizhuang deposit offers insight into its use as an exploration guide for potential REE mineralization in a carbonatite-related setting. The first exploration indicator is the presence of a particular alteration of the carbonatite-syenite complex, highlighted by a red coloration. According to Li et al. (2018), the reddish syenites in the Lizhuang deposit have relatively high concentrations of REE. This implies that the red-coloration alteration was closely associated with REE mineralization processes. In addition, other REE deposits (e.g., Gallinas Mountains, Williams-Jones et al., 2000; Maoniuping, Liu et al., 2019a) produce large amount of F-rich minerals, such as fluorite, fluorapatite and other F-bearing minerals, thus resulting in remarkably high fluoride ion contents in the mineralizing fluids. Similarly, we notice that only where large amount of fluorite appears can the bastnäsite-(Ce) be found within Lizhuang ore veins. Hence, the presence of fluorite appears to be a more effective exploration index for REE mineralization in comparison with other gangue minerals.

From the viewpoint of hydrothermal fluids, our fluid inclusion data make it possible to discriminate the fluids associated with carbonatite-related REE mineralization from those forming other deposit types, and to identify potential REE-bearing regions at a strategic distance from the mineralized lithology. Rich in some specific ions that can form strongly associated complexes with REE, such as $(\text{SO}_4)^{2-}$, Cl^- , and F^- , is the most remarkable characteristic of the mineralizing fluids. This is also consistent with the mineralogical signal that fluorite, barite and

bastnäsite-(Ce) typically form stable mineral assemblages in Lizhuang ore veins. In country, recent case study of Miaoya low-grade REE prospect has demonstrated that $(\text{SO}_4)^{2-}$, F^- and other ligands which might have transported and allowed the concentration of REE were absent due to the low amount of fluorite, barite, calcite and celestite in the prospective ores (Zhang et al., 2019). The presence of LC, LVS and LCS inclusions in Lizhuang hydrothermal minerals indicates an introduction of initial high-salinity, CO_2 -bearing fluids into a pre-existing fissure system, which has parallels with the suggestions of others economic REE deposits such as Hoidas Lake in Canada (Pandur et al., 2014). Importantly, our study reveals that REE deposition occurred at low-temperature, low-pressure, low- to moderately-saline aqueous conditions via continuous fluid cooling and mixing. Such a conclusion suggests that the most significant REE mineralization in the ore vein system must have occurred at shallow crustal levels. This view is firmly supported by recently-reported three units of REE mineralized system in the Maoniuping deposit (Liu et al., 2019a), in which the top unit has thick (up to 12 m in width) veins and hosts the bulk of REE mineralization.

6. Conclusions

The following conclusions were drawn from our fluid inclusion study of the Lizhuang REE deposit:

- 1) The initial mineralizing fluids were characteristic by the availability of CO_2 -rich fluids with high $(\text{SO}_4)^{2-}$, Cl^- , and F^- activities, which is strongly favoured to mobilize REE.
- 2) The pre-REE-stage fluids have experienced intense immiscibility, whereas a significant fluid mixing event was identified in REE stage. It is likely that REE mineralization occurred in response to fluid cooling, mixing rather than immiscibility.
- 3) Hydrothermal veins that contain high-salinity, CO_2 -bearing and SO_4 - Cl - F -rich fluid inclusion assemblages are suggested to be an ideal REE-prospecting target. In regions where such veins exist, the search for potential REE mineralization should focus on shallower parts of the vein system.

CRedit authorship contribution statement

Xiaochao Shu:Methodology, Investigation, Writing - original draft, Writing - review & editing.**Yan Liu:**Conceptualization, Supervision.**Deliang Li:**Data curation.

Declaration of competing interest

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

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