Formation of the Maoniuping giant REE deposit: constraints from mineralogy and in situ bastnäsite U–Pb geochronology

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ABSTRACT

The time and processes of hydrothermal mineralization are long-standing problems in geology. This work addresses these questions with reference to the Maoniuping giant rare earth elements (REE) deposit (SW China), with rare earth oxides (REO) reserves of 3.17 million tons with an average grade of 2.95 wt.%. Bastnäsite is the dominant economic mineral, occurring as four distinct paragenetic types in the Maoniuping syenite–carbonatite complex: (1) Primary euhedral bastnäsite (type-A) in syenite, with isolated melt inclusions; (2) Macro-crystalline tabular euhedral bastnäsite (type-B) in pegmatitic dikes, with diverse variety of fluid inclusions; (3) Fine-grained, anhedral veinlet-disseminated bastnäsite (type-C) in syenite; (4) Coarse-grained anhedral bastnäsite (type-D) in carbonatite dikes,
occurring as veinlets or interstitial to calcite, fluorite and barite. From the paragenetic and compositional variations, it is inferred that type-A bastnäsite is of primary magmatic origin, whereas the other three types have characteristics of hydrothermal origins. In situ LA-ICPMS U–Pb geochronology of the four types of bastnäsite results in lower intercept ages of 28.2 ± 0.5 Ma \((n=95, \text{MSWD}=5.10)\), 27.8 ± 0.4 Ma \((n=43, \text{MSWD}=0.73)\), 26.8 ± 0.7 Ma \((n=50, \text{MSWD}=0.83)\) and 25.8 ± 0.7 Ma \((n=55, \text{MSWD}=1.70)\), respectively, which are consistent with the weighted average \(^{206}\text{Pb}/^{238}\text{U}\) and \(^{208}\text{Pb}/^{232}\text{Th}\) ages by \(^{207}\text{Pb}\)-correction method. Compositional variations of clinopyroxene and apatite from the associated syenite, pegmatitic and carbonatitic dikes indicate a genetic relationship of the Maoniuping alkaline complex. The compositions of clinopyroxene range from \(\text{Ae}_{44-67}\text{Di}_{14-18}\text{Hd}_{17-41}\) in pegmatitic dikes, \(\text{Ae}_{43-66}\text{Di}_{6-20}\text{Hd}_{21-38}\) in carbonatitic dikes to \(\text{Ae}_{88-90}\text{Di}_{0-3}\text{Hd}_{10-30}\) in syenite. Apatites in the pegmatitic and carbonatitic dikes have similar compositions with higher F, total REE and Sr and lower CaO contents than those in the syenite, which suggests a cogenetic origin for the associated pegmatite and carbonatite. Clinopyroxene and apatite compositions suggest that the pegmatitic melt might differentiate directly from the initial carbonatitic melt rather than the syenitic magma. The bastnäsite U–Pb geochronology and minerals data indicate continuous magmatic-hydrothermal evolution for the REE mineralization in the Maoniuping alkaline complex.

**Keywords:** U–Pb geochronology, bastnäsite, Maoniuping giant REE deposit, syenite–carbonatite complex, magmatic–hydrothermal evolution
Rare earth elements (REE) are known as "Critical Metals", which are crucial to the high-technical industry and national security (Chakhmouradian and Wall 2012). More than half of the global REE reserves identified are associated with alkaline igneous rocks, especially diverse carbonatites (Mitchell 2005; Weng et al. 2015). The REE minerals typically occur in hydrothermal systems, such as Bayan Obo (China, Smith et al. 2000), Gallinas Mountains (USA, Williams-Jones et al. 2000), and Kangankunde (Malawi, Broom-Fendley et al. 2017). In contrast, some REE minerals such as bastnäsite and monazite are formed at purely magmatic and/or magmatic-hydrothermal transitional stages, e.g., Mountain Pass (USA, Mariano 1989; Castor 2008), Lovozero-Khibina (Russia, Zaitsev et al. 2014), Palabora (South Africa, Giebel et al. 2017), Ulgii Khiid (Mongolia, Feng et al. 2020), Strange Lake (Canada, Vasyukova and Williams-Jones 2018) and Baerzhe (China, Yang et al. 2014a).

Understanding the genesis of REE minerals is critical to deciphering the processes of REE mineralization in magmatic-hydrothermal deposits.

**Bastnäsite** [(REE)(CO$_3$)F] is a common economic mineral in most hydrothermal REE ore deposits related to alkaline-carbonatite complexes (Gysi and Williams-Jones 2015). Bastnäsite is also considered to be a promising U–Pb geochronological tool, because of its significant U (222–653 ppm) content (Sal’nikova et al. 2010; Yang et al. 2014b; Ling et al. 2016). Sal’nikova et al. (2010) conducted the first U–Pb isotopic analysis by thermal ionization mass spectrometry (TIMS) on bastnäsite (K-9) from the Karasug carbonatite in central Mongolia, which yielded a concordant age of 118 ± 1 Ma. Using this K-9 bastnäsite as reference material, Yang et al. (2014b) carried out bastnäsite U–Pb age determination by *in situ* Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS). With respect to the high Th (1,161–4,165...
ppm) content, Ling et al. (2016) proposed an alternative protocol for in situ bastnäsite Th–Pb analysis and data calibration by secondary ion mass spectrometry (SIMS). Therefore, it is suggested that bastnäsite U (Th)–Pb geochronology would have potential to determine accurately the timing of REE mineralization.

Maoniuping is the second largest REE deposit in China, with reserves of 3.17 Mt rare earth oxides (REO) @ 2.95 wt.% (109 Geological Brigade of Sichuan Bureau of Geology and Mineral Resource 2010). Previous studies of the Maoniuping deposit gave zircon U–Pb ages of 21–27 Ma (Liu et al. 2015; Ling et al. 2016), biotite and arfvedsonite K(Ar)/Ar ages of 26–40 Ma (Yuan et al. 1995; Liu and Hou 2017; Liu et al. 2019a), and bastnäsite U–Pb and Th–Pb ages of 31.9±3.9 Ma and 25.7±0.2 Ma, respectively (Yang et al. 2014b; Ling et al. 2016). Such large discrepancies have led to controversy concerning the genesis of the deposit. For example, Pu (1993) proposed that the fluids responsible for the REE mineralization are genetically related to the syenite intrusion. Niu and Lin (1994) suggested that the REE mineralization is possibly induced by immiscibility between sulfate and carbonate salt melts. Xie et al. (2015) and Hou et al. (2015) considered that the REE-enriched fluids mainly originate from the carbonatite rather than the syenite. More recently, Liu et al. (2019b) determined that the ore-forming fluids are essentially derived from the syenite-carbonatite complex. To address these genetic disputes, we directly determine the age of bastnäsite of different parageneses by in situ LA-ICPMS U–Pb method. In combination with the geochronology and mineral compositions as determined by EMPA and LA-ICPMS, a possible genetic model for the formation of the Maoniuping giant REE deposit is proposed.

GEOLOGICAL BACKGROUND
Regional geology

The on-going India–Asia continental collision event began at ca. 65 Ma affected an extensive area beyond the Tibetan plateau (Fig. 1a; Yin and Harrison 2000; Hou et al. 2003; Hou and Cook 2009). This intensive interaction between the India and Asia continents resulted in clusters of collisional orogenic belts in the east of the Tibetan plateau, including the N–S striking Jinpingshan orogeny. The Panxi (Panzhihua-Xichang city) REE metallogenic belt is located in the eastern part of the Jinpingshan orogeny, and related to a series of Cenozoic N–S trending strike-slip faults. Numerous Cenozoic alkaline–peralkaline igneous rocks have been documented in this belt, such as lamprophyre (40–24 Ma, Guo et al. 2005), alkaline syenitic rocks, and syenite-carbonatite complexes (30–11 Ma, Xie et al. 2016). The Panxi REE metallogenic belt, 270 km in length and 15 km in width, runs north from Mianning, through Xichang and Dechang to Panzhihua. Within this belt there are four known economic REE deposits, i.e., Maoniuping, Dulucao, Muluo and Lizhuang, and some REE ore occurrences (Yuan et al. 1995). Most of these are lithology-related to the syenite–carbonatite complexes intruded as stocks or dikes into the Precambrian crystalline basement, Mesozoic alkaline granite and a Paleozoic to Mesozoic volcano–sedimentary sequence (Yuan et al. 1995). The REE deposits are spatially controlled by the N–S trending Anninghe strike-slip fault (Yuan et al., 1995).

Ore deposit geology

The Maoniuping area consists of four main lithological units, including Mesozoic alkaline granite, rhyolite with unknown age, Devonian to Permian sedimentary rocks, and the ore-bearing alkaline complex of syenite stocks and pegmatitic-carbonatitic dikes (Fig. 1b). The syenite–carbonatite complex intruded the rhyolite and Mesozoic alkaline granite (Fig. 1b). The REE mineralization at Maoniuping district occurs as the...
vein systems hosted in syenite, carbonatite, and to a lesser extent, altered granite and rhyolite. The REE minerals in the ore bodies are predominantly bastnäsite. The ores consist of REE-enriched veinlets, stringers, and stock-work zones which surround the carbonatite and the ores occur mainly as disseminations in syenite, pegmatitic dikes, secondary veinlets in syenite and carbonatitic dikes. More than 71 pegmatitic and carbonatitic dikes have been identified with widths ranging from 1 to 30 m and lengths from 10 to 1200 m (Yuan et al. 1995). They show a NNE orientation, with an “S-like” shape (Fig. 1b).

Currently, there are two open pits in operation, Dagudao and Guangtoushan. In the Dagudao open pit, dark-coloured pegmatitic dikes intruded into the syenite stock. These pegmatitic dikes are the main ore type. In contrast, the pink carbonatitic dikes are the main ore type in the Guangtoushan open pit. In this study, rock and mineral samples of unaltered and altered syenite were collected from the Dagudao open pit. Ore samples of pegmatitic and carbonatite dikes are from the Guangtoushan open pits (Fig. 1b).

**PETROGRAPHY**

The grayish-white, medium-grained syenite is the predominant intrusive rock in the Maoniuping alkaline complex. It is composed mainly of euhedral alkali-feldspar (65–75 vol.%) and subhedral- to- anhedral quartz (20–25 vol.%), with minor aegirine, arfvedsonite and biotite (Fig. 2a). The pegmatite is composed of variable volumes of barite (30–50 vol.%), aegirine-augite and arfvedsonite (30–40 vol.%), fluorite (10–20 vol.%) and bastnäsite (10–20 vol.%), with minor calcite, biotite, apatite, feldspar and quartz (Fig. 2b). The veinlets hosted in syenite are composed mainly of aegirine-augite (40–60 vol.%), fluorite (20–30 vol.%), and bastnäsite (10–15 vol.%) (Fig. 2c). The pink coarse-grained carbonatite is composed mostly of euhedral calcite (50–80 vol.%),
barite (10–20 vol.%), fluorite (10–20 vol.%), aegirine-augite and arfvedsonite (5–15 vol.%), bastnäsite (5–10 vol.%), with minor biotite, feldspar and quartz (Fig. 2d).

Bastnäsite is the main economic mineral in the unaltered syenite, the pegmatitic and carbonatite dikes and the secondary veinlets in syenite. Bastnäsite in the unaltered syenite has a hexagonal euhedral habit and occurs within euhedral orthoclase (Fig. 3a). Rounded isolated melt inclusions can be found in this type of bastnäsite (Fig. 3b), referred as “type-A bastnäsite”. In the pegmatites, euhedral- to -subhedral bastnäsite occurs as a tabular mineral (Fig. 3c) with primary fluid inclusions (“type-B bastnäsite”, Fig. 3d). Bastnäsite from the secondary veinlets hosted in syenite is anhedral or euhedral (Fig. 3e), and contains numerous primary fluid inclusions (Fig. 3f), and referred as “type-C bastnäsite”. Bastnäsite (“type-D bastnäsite”), in the carbonatite dikes is commonly euhedral- to- subhedral with fluid inclusions (Figs. 3g and 3h).

Clinopyroxene and apatite are the pervasive minerals in the Maoniuping syenite-carbonatite complex. Clinopyroxene is augite-aegirine in the alkaline complex and in the syenite is mostly euhedral, prismatic, and closely associated with orthoclase, biotite and quartz (Fig. 4a). In some examples, euhedral clinopyroxene occurs as inclusions hosted by orthoclase. Euhedral clinopyroxenes from the pegmatitic and carbonatite dikes are large- to- megacrystic in size (3-6 mm), and closely associated with barite and calcite (Figs. 4b and 4c). Apatite in the syenite is mainly euhedral, and occurs as prismatic or hexagonal crystals (Fig. 4d). Apatite is rare in the pegmatitic and carbonatite dikes, and can occur as inclusions within clinopyroxene and calcite (Figs. 4e and 4f).

**ANALYTICAL METHODS**

*In situ* bastnäsite U–Pb age determinations from eleven polished thin sections were conducted using an Agilent 7900 quadrupole (Q)-ICP-MS coupled with a Resonetics
RESOlution S155 193 nm laser-ablation system at Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIGCAS). Additional one bastnäsite sample (14MNP-40) was analyzed using an Agilent 7700 coupled with a Coherent 193 nm laser-ablation system at Institute of Geochemistry, Chinese Academy of Sciences. All analyses were undertaken with an energy density of 5 J/cm², beam diameter of 29/32 μm and a repetition rate of 5 Hz. Helium was used as a carrier gas to enhance the transportation efficiency of the ablated material. The U–Pb fractionation and instrumental mass discrimination of bastnäsite were normalized using the matrix-matched external bastnäsite standard K-9 (118 ± 1 Ma; Sal’nikova et al. 2010). Two reference analyses were measured after every five unknown bastnäsite sample spots. Each spot analysis consisted of 20 s background integration followed by 50 s sample data acquisition and then a 20 s delay to wash out the previous sample. Off-line data selection and integration were performed by using Iolite 3.64 software (Paton et al. 2011). Online Isoplot R (http://pieter-vermeesch.es.ucl.ac.uk/shiny/IsoplotRshiny/R/) was used to illustrate the U–Pb Tera-Wasserburg diagrams of bastnäsite (Vermeesch 2018).

The major oxide compositions of minerals were obtained using a JEOL JXA-8230 electron microprobe analyzer (EMPA) at GIGCAS. The analyses were carried out with an accelerating voltage of 15 kV, a beam current of 20 nA with diameter of 5 μm for apatite and 1 μm for clinopyroxene. Natural and synthetic minerals were used as standards. Matrix corrections were applied using a ZAF scheme. For the specific instrument test parameters and analysis protocols refer to Zeng et al. (2017). Trace element analyses were conducted with LA-ICPMS at GIGCAS. The measurements were made on thin sections using a laser beam diameter of 29 μm and an ablation rate of 5 Hz. The acquisition time for the background and sample signal was 20 s and 50 s,
respectively. NIST610 was used as external standard. Data reduction was made using
the CaO content obtained from EMPA as an internal standard. Integration of background
and analytical signals, and time-drift correction and quantitative calibration for trace
elements, were undertaken by using Iolite 3.64 software (Paton et al. 2011).

RESULTS

U (Th)-Pb ages of bastnäsite

The U (Th)-Pb isotopic data for bastnäsite are presented in Supplementary Table
1. Twelve samples and 243 analytical points were used for bastnäsite age
determination (Fig. 5). As the average value of the initial $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of calcite in
Maoniuping deposit is 0.85 (Hou et al. 2015), we choose this as the initial value of
common Pb to anchor the bastnäsite age in Tera-Wasserburg diagrams. Three samples
of type-A bastnäsite (14MNP-40, 14MNP-44 and 14MNP-45) have U and Th
concentrations ranging from 2.98 to 69.3 ppm, and 8,030 to 51,360 ppm, respectively,
with Th/U ratios varying from 296 to 5,739. For type-A bastnäsite, we obtained an
acceptable lower intercept age of $28.2 \pm 0.5$ Ma ($n=95$, MSWD=5.10; Fig. 5a) on the
Tera-Wasserburg diagram. This is consistent with the weighted average $^{206}\text{Pb}/^{238}\text{U}$
age of $28.1 \pm 0.5$ Ma ($n=95$, MSWD=1.6; Fig. 5b) and $^{208}\text{Pb}/^{232}\text{Th}$ age of $28.2 \pm 0.2$
Ma ($n=95$, MSWD=2.8; Fig. 5b) after $^{207}\text{Pb}$ correction by using Pb isotopic
compositions from Stacey and Kramers (1975). Three samples of type-B bastnäsite
(MNPA-2, MNPB-2 and MNPC-1) have U and Th concentrations ranging from 16.9
to 79.1 ppm and 1,658 to 51,110 ppm, respectively, with Th/U ratios varying from
21.3 to 920. Forty three analyses of type-B bastnäsite form a well-fitting regression
line, yielding a lower intercept age of $27.8 \pm 0.4$ Ma ($n=43$, MSWD=0.73; Fig. 5c).
This is consistent (in error) with the weighted average $^{206}\text{Pb}/^{238}\text{U}$ age of $27.5 \pm 0.6$ Ma
($n=43$, MSWD=1.2; Fig. 5d) and $^{208}\text{Pb}/^{232}\text{Th}$ age of $27.5 \pm 0.2$ Ma ($n=43$, MSWD=2.3;
Fig. 5d). Type-C bastnäsite from three samples (17MNP-1, 17MNP-6 and ZK311-12) has U and Th concentrations ranging from 23.8 to 120 ppm and 1,452 to 7,880 ppm, respectively, with Th/U ratios varying from 20.5 to 229. Fifty analyses yield an intercept age of $26.8 \pm 0.7$ Ma ($n=50$, MSWD=0.83; Fig. 5e), with a weighted average $^{206}\text{Pb}/^{238}\text{U}$ age of $26.3 \pm 1.2$ Ma ($n=46$, MSWD=1.2; Fig. 5f) and a weighted average $^{208}\text{Pb}/^{232}\text{Th}$ age of $26.8 \pm 0.2$ Ma ($n=50$, MSWD=2.2; Fig. 5f). Type-D bastnäsite from three samples (18MNP-16-1, ZK341-3-2 and ZK361-23) has U and Th contents ranging from 7.24 to 169 ppm and 2,611 to 45,630 ppm, respectively, with Th/U ratios varying from 59.9 to 1,067. Fifty-five analyses yield a lower intercept age of $25.8 \pm 0.7$ Ma ($n=55$, MSWD=1.7; Fig. 5g) and a weighted average $^{206}\text{Pb}/^{238}\text{U}$ age of $26.4 \pm 2.2$ Ma ($n=42$, MSWD=1.4; Fig. 5h). This is consistent with the weighted average $^{208}\text{Pb}/^{232}\text{Th}$ age of $25.8 \pm 0.2$ Ma ($n=55$, MSWD=1.9; Fig. 5h).

**Compositions of bastnäsite, clinopyroxene and apatite**

The compositional data for bastnäsite are listed in Supplementary Table 2 and summarized in Table 1. Compositionally, type-A bastnäsite shows some distinct features from the other three types of bastnäsite. It has relatively lower total REE (532,396–554,745 ppm) contents and $(\text{La/Yb})_n$ (9,878–34,918) ratios than the other three types of bastnäsite (Table 1, Figs. 6a, 6c and 6d). Type-A bastnäsite is characterized by the relatively higher Sr (635–1,236 ppm) contents and $\delta\text{Eu}$ (0.67–0.98) value, as well as Th/U (296–5,739) ratios than other types of bastnäsite (Table 1, Figs. 6b, 6c and 6d).

The compositional data for clinopyroxene are presented in Supplementary Table 3 and summarized in Table 1. Clinopyroxene in the syenite is mostly aegirine ($\text{Ae}_{68-90}\text{Di}_{0-3}\text{Hd}_{10-30}$). In contrast, clinopyroxene in pegmatitic and carbonatite dikes is augite-aegirine with $\text{Ae}_{44-67}\text{Di}_{14-18}\text{Hd}_{17-41}$ and $\text{Ae}_{43-66}\text{Di}_{6-20}\text{Hd}_{21-38}$, respectively. Total
REE and Sr contents of clinopyroxene in syenite (1.01–4.44 ppm and 0.47–53.6 ppm, respectively) are significantly lower than those in the pegmatitic (85.2–133 ppm and 87.9–240 ppm, respectively) and carbonatite dikes (85.7–170 ppm and 146–421 ppm, respectively).

The compositional data for apatite are presented in Supplementary Table 4 and summarized in Table 1. Apatite in syenite has a distinctively lower F (2.78–3.30 wt.%), Sr (2,913–7,331 ppm), and total REE (8,926–35,654 ppm) contents than apatite in pegmatitic dikes (F=3.29–3.75 wt.%, Sr=4,833–10,630 ppm, total REE=12,881–45,146 ppm) and apatite in carbonatite dikes (F=3.19–3.76 wt.%, Sr=5,864–26,597 ppm, total REE=15,766–35,443 ppm) (Table 1, Figs. 8a, 8b and 8c). Furthermore, apatite in syenite is also characterized by relatively higher CaO (51.9–55.4 wt.%) contents, (La/Yb)$_n$ (16.1–194) and Ca/Sr (54.0–134) ratios than apatite in pegmatitic dikes (CaO=51.2–53.5 wt.%, (La/Yb)$_n$=11.0–152, Ca/Sr=35.2–75.9) and apatite in carbonatite dikes (CaO=49.8–53.6 wt.%, (La/Yb)$_n$=11.9–55.0, Ca/Sr=13.7–62.4) (Table 1, Figs. 8b and 8d). Apatites from the syenite, pegmatitic and carbonatite dikes are all fluorapatite, with no detectable Cl contents (Table 1).

DISCUSSION AND CONCLUSION

**Origin and age relationships of bastnäsite**

Bastnäsite is assumed usually to be a typical hydrothermal mineral, as it contains volatile elements such as F and CO$_2$, which are generally enriched in late-stage alkalis-enriched hydrothermal fluids (Bau and Dulski 1995; Agangi et al. 2010; Migdisov and Williams-Jones 2014). In addition, REE, particularly LREE, are strongly incompatible elements that are easily concentrated in such fluids (Michard 1989; Lottermoser 1992; Jaireth et al. 2014). For the Maoniuping deposit, previous micro-thermometric results for the bastnäsite-hosted fluid inclusions have
homogenization temperatures of 137–270 °C (Niu et al. 1996, 1997; Xie et al. 2009, 2015; Liu et al. 2019a; Guo and Liu 2019). As a result of the previous studies, it was suggested that the large-scale precipitation of bastnäsite occurred in the late hydrothermal stage. However, in this investigation we identified a new paragenetic variety of bastnäsite of primary magmatic origin from the unaltered syenite, i.e. “type-A bastnäsite”. This bastnäsite usually occurs as inclusions in orthoclase, indicating that it formed prior to orthoclase and might be synchronous with apatite or zircon (Fig. 3a). Isolated melt inclusions containing solid phase (>95 vol.%) are observed in type-A bastnäsite, indicating that they were formed in the magmatic stage (Fig. 3b). In contrast, other three paragenetic types of bastnäsite are interpreted to be of hydrothermal origin, on the basis of the occurrence of primary fluid inclusions and previous micro-thermometry investigations. The macro-crystalline bastnäsite (type-B) in the pegmatitic dikes is euhedral and tabular, and is host to a large variety of fluid inclusions (Figs. 3c and 3d). The bastnäsite grains in the veinlets of the altered syenite (type-C) and carbonatite dikes (type-D) are mostly anhedral with abundant vapor-liquid fluid inclusions (Figs. 3f and 3h), indicating a hydrothermal origin.

The bastnäsite U–Pb data are highly reliable, even with the variable amounts of common lead (Fig. 5), and indicate a continuous evolution of bastnäsite crystallization from 28.2 Ma to 25.8 Ma. Compared with previous geochronological data, our bastnäsite U–Pb data have a much higher accuracy and a more reliable age for the REE mineralization of the Maoniuping deposit. In earlier investigations mineralization ages of 31–40 Ma were determined using mica and amphibole K-Ar geochronology, which highlighted the presence of excess Ar (Yuan et al. 1995). With the refinement of analytical techniques, recent Ar-Ar methods yield ages of 25–30 Ma (Liu and Hou 2017; Liu et al. 2019a). Zircon from the syenite yields SHRIMP U–Pb...
ages of 21.3–22.8 Ma (Liu et al. 2015) and 26.6 Ma by SIMS (Ling et al. 2016), indicating the possible loss of radiogenic Pb in zircon during late hydrothermal alteration (Liu et al. 2019b). A bastnäsite sample from an unknown location or genesis yielded a LA-ICPMS U–Pb age of 31.9±3.9 Ma (Yang et al. 2014b) and a SIMS Th–Pb age of 25.7±0.2 Ma (Ling et al. 2016).

These data from previous studies required an integrated understanding of the evolution of the alkaline complex. Our new data show that the primary bastnäsite in syenite formed earlier than that in the other three paragenetic types of hydrothermal bastnäsite. Subsequently, crystallization of abundant REE minerals in the pegmatitic dikes, secondary veinlets in the syenite and the carbonatite dikes occurred during a late hydrothermal stage. This evolutionary relationship is similar to that proposed for the Mountain Pass REE deposit (e.g., Poletti et al. 2016). Therefore, the primary and hydrothermal bastnäsite in the Maoniuping deposit indicates continuous REE mineralization during the magmatic and hydrothermal evolution of the syenite-carbonatite complex.

**Genesis and implications of clinopyroxene and apatite**

Clinopyroxene is a ubiquitous mineral in alkaline complexes, and usually displays extensive compositional variation with the potential to incorporate many geochemically-relevant trace elements (e.g., Marks et al. 2004). In the Maoniuping deposit, clinopyroxenes in the pegmatitic and carbonatite dikes show similar REE distribution patterns to those of typical magmatic clinopyroxene from worldwide carbonatites (e.g., Reguir et al. 2012; Fig. 7a). In contrast, clinopyroxene in the syenite has a similar REE distribution pattern to that of the Strange Lake peralkaline granite (Vasyukova and Williams-Jones 2018), with notably lower REE contents (Fig. 7a). Clinopyroxene shows two distinctive evolutionary trends in composition (Figs. 7c
and 7d). Previous studies have determined that the evolutionary trend of clinopyroxene compositions in alkaline complexes is usually from the Ca- and Mg-rich pyroxene (diopside) towards the Na- and Fe-rich end-member (aegirine) as the magmatic evolutions (e.g., Larsen 1976; Mitchell and Platt 1982; Markl et al. 2001; Coulson 2003; Marks et al. 2008). Alternatively, the trend can be from diopside via hedenbergite to aegirine at relatively low oxygen fugacity (e.g., Mitchell and Platt 1978; Markl et al. 2001). At Maoniuping, clinopyroxene in the syenite is mostly aegirine (Ae\textsubscript{68–90}Hd\textsubscript{10–30}Di\textsubscript{0–3}), whereas, clinopyroxene in the pegmatite (Ae\textsubscript{44–67}Hd\textsubscript{17–41}Di\textsubscript{14–17}) and carbonatite (Ae\textsubscript{43–66}Hd\textsubscript{21–38}Di\textsubscript{6–20}) is augite-aegirine (Table 1, Figs. 7c and 7d). These data suggest that the calcic-sodic series of clinopyroxene in the pegmatitic and carbonatite dikes was probably formed from the same magma system, and is genetically different to the sodic series in the syenite. Therefore, the evolution of clinopyroxene suggests that the pegmatitic and carbonatite dikes might result from segregation from a REE- and volatile-rich melt (i.e., initial carbonatitic melt), rather than residual melt/fluid origins from the syenitic magma.

Apatite is predominantly fluorapatite with compositional characteristics of magmatic origin, including enrichment of REE and Sr (e.g., Chakhmouradian et al. 2017). Compared to apatite in the syenite, apatites in the pegmatitic and carbonatite dikes generally have higher F (3.19–3.76 wt.%), Sr (4,833–26,597 ppm), total REE (12,881–45,146 ppm) and lower Ca/Sr and (La/Yb)\textsubscript{n} ratios (Table 1; Fig. 8). These data are consistent with petrological observations that the pegmatitic and carbonatite dikes are enriched in incompatible and volatile components (e.g., REE, Sr, F and CO\textsubscript{2}). The differences in apatite composition between the syenite, pegmatitic and carbonatite dikes give additional support to the hypothesis that the pegmatitic dikes are genetically related to the carbonatite melt/fluid rather than the syenite melt.
Genetic model

On the basis of our bastnäsite U–Pb data and the compositions of clinopyroxene and apatite, four continuous stages of REE mineralization have been recognized in this study. At ca. 28.2 Ma, the syenite first intruded into the rhyolite and Mesozoic alkaline granite, forming the ore-barren syenite plutons with minor primary bastnäsite. Subsequently, the pegmatitic dikes were intruded into the syenite and the nearby Mesozoic alkaline granite at ca. 27.8 Ma. These hydrous melts/fluids were oversaturated with REE and were saline- and sulfate-enriched, resulting in large-scale REE precipitation. Subsequently, intensive fluid interaction occurred within the previously emplaced syenite, forming the widespread veinlets at 26.8 Ma. Finally, the carbonatite was intruded as dikes or stocks at ca. 25.8 Ma. This paragenetic sequence is supported by the four generations of bastnäsite and the U–Pb geochronology. During these generations, the early bastnäsite was recognized as being of magmatic origin, whereas the three later bastnäsite are of hydrothermal origin. The compositions of clinopyroxene and apatite provide additional evidence for the genetic relationship between the pegmatitic and carbonatite dikes. Such magmatic and hydrothermal evolution highlights multi-stage crystallization of REE mineral to form the Maoniuping deposit. Our new bastnäsite U–Pb data suggest that this evolution probably spanned over at least 2.5 Ma.

IMPLICATIONS

This study has concluded that bastnäsite can be used as a potential indicator of magmatic-hydrothermal evolution and associated REE mineralization processes. In the giant Maoniuping deposit, bastnäsite is the dominant economic mineral, occurring as four paragenetic types in the syenite–carbonatite complex. Combined with the paragenetic and compositional variations, we inferred that type-A bastnäsite is of
primary magmatic origin, whereas the other three types have characteristics of hydrothermal origins. *In situ* LA-ICPMS U (Th)–Pb geochronology of the four types of bastnäsite indicates a prolonged multi-stage REE mineralization during the evolution of Maoniuping alkaline complex. Compositional variations of clinopyroxene and apatite favor an explanation of that the pegmatitic melt should be directly separated from the initial carbonatitic melt rather than the syenitic magma. This work shows that bastnäsite geochemistry could be a powerful indicator mineral of magmatic-hydrothermal evolution and REE mineralization of alkaline-carbonatite complexes.

**ACKNOWLEDGEMENTS**

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formation from Strange Lake, Canada. Chemical Geology, 483, 385–396.


FIGURE CAPTIONS

**Figure 1.** Position and geological map of the Maoniuping gaint REE deposit. (a) Simplified tectonic map of the Himalayan–Tibetan orogeny shows that the Maoniuping REE deposit is located in the east of Tibetan plateau and affected by post-collision event of India-Asia continent. (b) Simplified geological map of the Maoniuping REE deposit (modified after Yuan et al. 1995). Dagudao and Guangtoushan are the two open pits currently in production.

**Figure 2.** Representative hand specimens of rock and ore sample in the Maoniuping deposit. (a) Unaltered syenite with primary (type-A) bastnäsite. (b) A representative sample of pegmatite with hydrothermal (Type-B) bastnäsite. (c) A secondary veinlet with hydrothermal (type-C) bastnäsite is hosted in the altered syenite. (d) A representative sample of carbonatite with hydrothermal (Type-D) bastnäsite. Abbreviations: Bast=bastnäsite, Afs=alkali-feldspar, Cal=calcite, Brt=barite, Qz=quartz, Cpx=clinopyroxene, Fl=fluorite.

**Figure 3.** Representative microphotographs of four types of bastnäsite in the Maoniuping deposit. (a) Primary euhedral, nearly hexagonal bastnäsite (type-A) in syenite occurs within euhedral orthoclase (Or) and (b) nearly rounded melt inclusion can be found in this type of bastnäsite. (c) Euhedral to subhedral bastnäsite (type-B) associated with barite in pegmatite occurs as a thick tabular megacrystat and (d) hosts liquid-rich fluid inclusions. (e) Euhedral to anhedral veinlet-disseminated bastnäsite (type-C) hosts in altered syenite and (f) contains variably shaped fluid inclusions. (g) Anhedral to subhedral bastnäsite (type-D) interstitial to calcite in carbonatite and (h) hosts liquid-rich fluid inclusions. V = vapour phase, L =
liquid phase. Mineral abbreviations are shown in Fig. 2.

**Figure 4.** Representative BSE images of clinopyroxene (Cpx) and apatite (Ap) in the Maoniuping deposit. (a) Euhedral clinopyroxene occurs as prismatic crystal in syenite. (b) Euhedral clinopyroxene megacryst in pegmatite is closely associated with barite, fluorite and minor calcite. (c) Euhedral clinopyroxene intergrowth with euhedral calcite in carbonatite. (d) Euhedral apatite occurs as prismatic or hexagonal crystal in syenite. (e) Euhedral and prismatic apatite hosted in clinopyroxene megacrystal from the pegmatitic dikes. (f) Euhedral apatite hosted in calcite megacrystal from the carbonatite dikes. Mineral abbreviations are shown in Fig. 2.

**Figure 5.** Tera–Wasserburg concordia diagrams and weighted average $^{206}\text{Pb}/^{238}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$ ages of four types of bastnäsite from the Maoniuping REE deposit. (a and b) Three samples of type-A bastnäsite yield a lower interpreted age of 28.2±0.5 Ma and the weighted average $^{206}\text{Pb}/^{238}\text{U}$ age of 28.1±0.5 Ma and $^{208}\text{Pb}/^{232}\text{Th}$ age of 28.2±0.2 Ma. (c and d) Three samples of type-B bastnäsite yield a lower interpreted age of 27.8±0.4 Ma and the weighted average $^{206}\text{Pb}/^{238}\text{U}$ age of 27.5±0.6 Ma and $^{208}\text{Pb}/^{232}\text{Th}$ age of 27.5±0.2 Ma. (e and f) Three samples of type-C bastnäsite yield a lower interpreted age of 26.8±0.7 Ma and the weighted average $^{206}\text{Pb}/^{238}\text{U}$ age of 26.3±1.2 Ma and $^{208}\text{Pb}/^{232}\text{Th}$ age of 26.8±0.2 Ma. And (g and h) three samples of type-D bastnäsite yield a lower interpreted age of 25.8±0.7 Ma and the weighted average $^{206}\text{Pb}/^{238}\text{U}$ age of 26.4±2.2 Ma and $^{208}\text{Pb}/^{232}\text{Th}$ age of 25.8±0.2 Ma. In the Tera–Wasserburg concordia diagrams, the lower intercept ages were calculated by anchored the initial common Pb value at $^{207}\text{Pb}/^{206}\text{Pb}$=0.85. The weighted average $^{206}\text{Pb}/^{238}\text{U}$
and $^{208}\text{Pb}/^{232}\text{Th}$ ages were recalibrated by a $^{207}\text{Pb}$-based corrected method.

**Figure 6.** Chemical distribution and variation diagrams of four types of bastnäsite (Bast) from the Maoniuping deposit. (a) Chondrite-normalized REE patterns for four types of bastnäsite. Chondrite values are taken from McDonough and Sun (1995). (b) Th versus U diagram. (c) Sr versus total REE diagram. (d) δEu versus (La/Yb)$_n$ diagram.

**Figure 7.** Chemical distribution and variation diagrams of clinopyroxene (Cpx) from the Maoniuping deposit. (a) Chondrite-normalized REE patterns for clinopyroxene. The shaded region is the REE pattern of typical magmatic clinopyroxene from Alnö, Oka, Eden Lake and Oz.Varaka carbonatite (Reguir et al. 2012) and the gray dotted line is the late aegirine from the Strange Lake deposit in Canada (Vasyukova and Williams-Jones 2018). Chondrite values are taken from McDonough and Sun (1995). (b) Plot of Sr versus total REE. (c) Plot of Q versus J. Quad (quadrilateral) represents Mg-Fe-Ca pyroxene group, Ca-Na represents Ca-Na pyroxene group and Na represents Na pyroxene group. (d) The variation in the Di (diopside, $\text{CaMgSi}_2\text{O}_6$)-Hd (hedenbergite, $\text{CaFe}^{2+}\text{Si}_2\text{O}_6$)-Ae (aegirine, $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$) projection for clinopyroxene from the syenite, pegmatitic and carbonatite dikes. “A” represents an extreme pyroxene evolutionary path of from diopside to aegirine (e.g., Katzenbuckel alkaline complex, SW Germany, Mann et al. 2006), “B” represents an extreme pyroxene evolutionary path from diopside through hedenbergite, then to aegirine (e.g., Ilímaussaq alkaline complex, South Greenland, Markl et al. 2001) and “C” represents an intermediate evolutionary path (e.g., Alnö alkaline complex, Sweden, Vuorinen et al. 2005).
**Figure 8.** Chemical distribution and variation diagrams of apatite (Ap) from the Maoniuping deposit. (a) Chondrite-normalized REE patterns for apatite. Chondrite values are taken from McDonough and Sun (1995). The shaded region is the REE pattern of typical magmatic apatite from Aley alkaline complex (Chakhmouradian et al. 2017). (b) Plots of F versus CaO, (c) total REE versus Sr, and (d) Ca/Sr versus (La/Yb)$_n$ for apatite from the syenite, pegmatitic and carbonatite dikes. The black dotted lines show that the apatite from the pegmatitic and carbonatite dikes is obviously different from the apatite from the syenite, indicating that the pegmatitic and the carbonatite dikes have obvious affinity.

**Figure 9.** Schematic genetic model of the Maoniuping giant REE deposit. The crystallization of primary bastnäsite (type-A) in syenite represents the beginning of REE mineralization (~28.2 Ma). The formation of hydrothermal bastnäsite (type-B) in pegmatitic dikes represents REE mineralization associated with sulfate melt (~27.8 Ma). The formation of hydrothermal bastnäsite veinlets (type-C) in syenite represents REE mineralization associated with syenite (~26.8 Ma). The formation of hydrothermal bastnäsite (type-D) in carbonatite represents REE mineralization associated with carbonate melt (~25.8 Ma). Mineral abbreviations are shown in Fig. 2.
Table 1. Geochemical variations of bastnäsite, clinopyroxene and apatite with different parageneses in the Maoniuping complex.

<table>
<thead>
<tr>
<th>Bastnäsite</th>
<th>In syenite (Type-A, n=13)</th>
<th>In pegmatite (Type-B, n=24)</th>
<th>In veinlet (Type-C, n=15)</th>
<th>In carbonatite (Type-D, n=31)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U (ppm)</td>
<td>2.98–69.3</td>
<td>16.9–79.1</td>
<td>23.8–120</td>
<td>7.24–169</td>
</tr>
<tr>
<td>Th (ppm)</td>
<td>8,030–51,360</td>
<td>1,658–51,110</td>
<td>1,452–7,880</td>
<td>2,611–45,630</td>
</tr>
<tr>
<td>Th/U</td>
<td>296–5,739</td>
<td>21.3–920</td>
<td>20.5–229</td>
<td>59.9–1,067</td>
</tr>
<tr>
<td>Sr (ppm)</td>
<td>635–1,236</td>
<td>312–489</td>
<td>306–644</td>
<td>284–624</td>
</tr>
<tr>
<td>(La/Yb)_n</td>
<td>9,878–34,918</td>
<td>33,763–81,059</td>
<td>45,729–249,521</td>
<td>29,272–132,867</td>
</tr>
<tr>
<td>δEu</td>
<td>0.67–0.98</td>
<td>0.56–0.62</td>
<td>0.52–0.66</td>
<td>0.42–0.62</td>
</tr>
<tr>
<td>Age (Ma)</td>
<td>28.2 ± 0.5 (n=95)</td>
<td>27.8 ± 0.4 (n=43)</td>
<td>26.8 ± 0.7 (n=50)</td>
<td>25.8 ± 0.7 (n=55)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Clinopyroxene</th>
<th>In syenite (n=18)</th>
<th>In pegmatite (n=19)</th>
<th>In carbonatite (n=11)</th>
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</thead>
<tbody>
<tr>
<td>Ae (%)</td>
<td>67.6–89.7</td>
<td>44.1–66.5</td>
<td>43.3–65.7</td>
</tr>
<tr>
<td>Di (%)</td>
<td>0.01–2.61</td>
<td>14.4–17.5</td>
<td>6.38–19.9</td>
</tr>
<tr>
<td>Hd (%)</td>
<td>9.60–29.8</td>
<td>16.9–41.0</td>
<td>20.8–37.7</td>
</tr>
<tr>
<td>REE (ppm)</td>
<td>1.01–4.44</td>
<td>85.2–133</td>
<td>85.7–170</td>
</tr>
<tr>
<td>Sr (ppm)</td>
<td>0.47–53.6</td>
<td>87.9–240</td>
<td>146–421</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Apatite</th>
<th>In syenite (n=17)</th>
<th>In pegmatite (n=15)</th>
<th>In carbonatite (n=15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO (wt.%)</td>
<td>51.9–55.4</td>
<td>51.2–53.5</td>
<td>49.8–53.6</td>
</tr>
<tr>
<td>F (wt.%)</td>
<td>2.78–3.30</td>
<td>3.29–3.75</td>
<td>3.19–3.76</td>
</tr>
<tr>
<td>Cl (wt.%)</td>
<td>bdl</td>
<td>bdl</td>
<td>bdl</td>
</tr>
<tr>
<td>Sr (ppm)</td>
<td>2,913–7,331</td>
<td>4,833–10,630</td>
<td>5,864–26,597</td>
</tr>
<tr>
<td>REE (ppm)</td>
<td>8,926–35,654</td>
<td>12,881–45,146</td>
<td>15,766–35,443</td>
</tr>
<tr>
<td>(La/Yb)_n</td>
<td>16.1–194</td>
<td>11.0–152</td>
<td>11.9–55.0</td>
</tr>
<tr>
<td>Ca/Sr</td>
<td>54.0–134</td>
<td>35.2–75.9</td>
<td>13.7–62.4</td>
</tr>
</tbody>
</table>

Notes: “bdl” means below detection limit; “/” means no data available
Figure 1
Figure 2

(a) Syenite
- Qz
- Afs
- Cpx
- Bast (type-A)

(b) Pegmatite
- Cpx
- Brt
- Fl

(c) Veinlet
- Fl
- Cpx
- Bast (type-C)

(d) Carbonatite
- Cpx
- Cal
- Fl
Figure 3

(a) Type-A Bast Syenite

(b) Melt inclusion

(c) Brt Type-B Bast Pegmatite

(d) Fluid inclusion

(e) Type-C Bast Veinlet Syenite

(f) Fluid inclusion

(g) Type-D Bast Carbonatite

(h) Fluid inclusion

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Figure 4
Figure 5

(a) Intercept at 27.2 ± 0.5 Ma Anchored at $^{207}\text{Pb}/^{206}\text{Pb}$ = 0.85 MSWD=5.10, n=95
Type-A bastnäsite
14MNP-40
14MNP-44

(b) $^{207}\text{Pb}$ correction
$^{238}\text{U}^{206}\text{Pb}$ age
$^{232}\text{Th}^{208}\text{Pb}$ age
28.2 ± 0.2 Ma MSWD=2.8, n=95
28.1 ± 0.5 Ma MSWD=1.6, n=95

(c) Intercept at 27.8 ± 0.4 Ma Anchored at $^{207}\text{Pb}/^{206}\text{Pb}$ = 0.85 MSWD=0.73, n=43
Type-B bastnäsite
MNPA-2
MNPB-2
MNPC-1

(d) $^{207}\text{Pb}$ correction
$^{238}\text{U}^{206}\text{Pb}$ age
$^{232}\text{Th}^{208}\text{Pb}$ age
27.5 ± 0.6 Ma MSWD=2.3, n=43

(e) Intercept at 26.8 ± 0.7 Ma Anchored at $^{207}\text{Pb}/^{206}\text{Pb}$ = 0.85 MSWD=0.83, n=50
Type-C bastnäsite
17MNP-1
17MNP-6
ZK311-12

(f) $^{207}\text{Pb}$ correction
$^{238}\text{U}^{206}\text{Pb}$ age
$^{232}\text{Th}^{208}\text{Pb}$ age
26.8 ± 0.2 Ma MSWD=2.2, n=50
26.3 ± 1.2 Ma MSWD=1.2, n=46

(g) Intercept at 25.8 ± 0.7 Ma Anchored at $^{207}\text{Pb}/^{206}\text{Pb}$ = 0.85 MSWD=1.70, n=55
Type-D bastnäsite
18MNP-16-1
18MNP-6-1
ZK341-3-2
ZK361-23

(h) $^{207}\text{Pb}$ correction
$^{238}\text{U}^{206}\text{Pb}$ age
$^{232}\text{Th}^{208}\text{Pb}$ age
25.8 ± 0.2 Ma MSWD=1.9, n=55
26.4 ± 2.2 Ma MSWD=1.4, n=42
Figure 6
Figure 7

(a) Cpx in syenite
(b) Cpx in pegmatite
(c) Cpx in carbonatite

Magmatic Cpx

Magmatic Cpx

Magmatic Cpx

Magmatic Cpx

Magmatic Cpx

Magmatic Cpx

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Figure 8

(a) 

(b) 

(c) 

(d) 

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Figure 9

![Diagram showing the age (Ma) of different types of basalt and the minerals present in each type. The types are labeled as follows: Type-A Bast, Type-B Bast, Type-C Bast, and Type-D Bast. The ages for each type are: Type-A Bast 28.2 ± 0.5 Ma, Type-B Bast 27.8 ± 0.4 Ma, Type-C Bast 26.8 ± 0.7 Ma, Type-D Bast 25.8 ± 0.7 Ma. The minerals present in each type include: Or, Qz, Ab, Brt, Fl, Cal, Cpx, and Bast. The diagram also shows the relationship between the types of basalt and the alkali magma chamber, syenite, pegmatite, and carbonatite.]