

# In Situ U-Th-Pb Dating and Sr-Nd Isotope Analysis of Bastnäsite by LA-(MC)-ICP-MS

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Bastnäsite is the end member of a large group of carbonate–fluoride minerals with the common formula (REE)  $\text{CO}_3\text{F}\cdot\text{CaCO}_3$ . This group is generally widespread and, despite never occurring in large quantities, represents the major economic light rare earth element (LREE) mineral in deposits related to carbonatite and alkaline intrusions. Since bastnäsite is easily altered and commonly contains inclusions of earlier-crystallised minerals, *in situ* analysis is considered the most suitable method to measure its U-Th-Pb and Sr-Nd isotopic compositions. Electron probe microanalysis and laser ablation (multi-collector) inductively coupled plasma-mass spectrometry of forty-six bastnäsite samples from LREE deposits in China, Pakistan, Sweden, Mongolia, USA, Malawi and Madagascar indicate that this mineral typically has high Th and LREE and moderate U and Sr contents. Analysis of an in-house bastnäsite reference material (K-9) demonstrated that precise and accurate U-Th-Pb ages could be obtained after common Pb correction. Moreover, the Th-Pb age with its high precision is preferable to the U-Pb age because most bastnäsites have relatively high Th rather than U contents. These results will have significant implications for understanding the genesis of endogenous ore deposits and formation processes related to metallogenic geochronology research.

Keywords: bastnäsite, U-Th-Pb ages, Sr-Nd isotopes, laser ablation, LREE, carbonatite.

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The ability to accurately date the time of mineralisation is crucial for understanding the genesis of endogenous ore deposits and/or ore-forming processes (Robert 1990). Numerous radio-isotopic methods have been used widely to date mineralisation processes including K (Ar)-Ar, Rb-Sr, Sm-Nd, Lu-Hf, Re-Os and U-Pb techniques. Successful attempts have been reported previously [e.g., Che *et al.* (2015, Re-Os dating of molybdenite, U-Pb dating of columbite–tantalite), Romer and Luders (2006, U-Pb dating of columbite), Gulson and Jones (1992, cassiterite), Anglin

*et al.* (1996, Sm-Nd dating of scheelite) and Nakai *et al.* (1990, Rb-Sr dating of sphalerite)]. Among them, the U-Pb method has been generally considered as the most powerful technique to obtain precise and accurate ages because of the two independent decay schemes and their concordance. Nevertheless, this method cannot be used for metal ore deposits because of the very low U content in most metal ore minerals. This problem is also encountered when dating major economic rare earth element (REE) deposits that are generally related to the occurrence of alkaline and

carbonatite rocks (Sal'Nikova *et al.* 2010). In such cases, it is more suitable to date minerals in gangue veins intruding ore deposits.

Bastnäsite can be used to circumvent the problems mentioned above since it occurs mainly in LREE deposits associated with alkaline or carbonatite rocks. Bastnäsite was first described by the Swedish chemist Wilhelm Hisinger in 1838, who named it after the Bastnäs Mine near Riddarhyttan, Västmanland, Sweden. The occurrences are known from carbonatites, alkali granites and syenites, pegmatites, hydrothermal deposits, skarns, fenites and other metasomatic rocks. Usually, most bastnäsites are bastnäsite-(Ce), and cerium (Ce) is by far the most common of the rare earth elements in this class of minerals. In addition, bastnäsite and monazite are the two largest and most preferred sources of LREE; however, bastnäsite is always the preferable choice over monazite because the high Th content of monazite presents a problem in LREE extraction. Moreover, bastnäsite ranks as first among the major LREE minerals (such as Al clays, xenotime, loparite and parasite) (Anton and Frances 2012). The Bayan Obo, Mianning–Dechang and Weishan deposits in China and Mountain Pass, California, USA are the best-known bastnäsite-bearing LREE deposits in the World (Yang *et al.* 2014a).

As a main ore mineral in LREE deposits, bastnäsite has the potential to record the primary geochemical and isotopic signature of the ore-forming process. Although bastnäsite is unstable in residual fluids, it is normally resistant to weathering processes; hence, it will normally remain unaltered when other minerals will be intensely weathered (Anton and Frances 2012). Additionally, bastnäsite has moderate Sr and low Rb mass fractions which make it suitable to obtain initial Sr isotope ratios that can then be applied to help decipher the petrogenesis and evolution of the LREE ore deposit. Furthermore, since the correction for *in situ* decay is small, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio can be considered as the initial Sr isotopic composition of the ore in which the bastnäsite crystallised (Yang *et al.* 2009a, 2014b). In addition, according to available geochemical data, bastnäsite also contains moderate U, Th and LREE contents (10% *m/m* Nd), as well as moderate Sr ( $> 200 \mu\text{g g}^{-1}$ ), with low Rb ( $< 2 \mu\text{g g}^{-1}$ ) and, hence, extremely low  $^{87}\text{Rb}/^{86}\text{Sr}$  ratio (generally less than 0.001). These characteristics make this mineral a suitable candidate for U-Th-Pb geochronology and Sr-Nd analysis by laser sampling (Yang *et al.* 2009a, Sal'Nikova *et al.* 2010, Yang *et al.* 2014a, b).

Despite the frequent occurrence of bastnäsite in carbonatites and alkaline rocks, and its association with LREE deposits, few publications exist dealing with this mineral

using La-Ba and U-Pb dating by traditional isotope dilution thermal ionisation mass spectrometry (ID-TIMS; Nakai *et al.* 1988, 1989, Sal'Nikova *et al.* 2010). In the present contribution, we report a comprehensive series of laser ablation *in situ* U-Th-Pb and Sr-Nd isotopic measurements in bastnäsite from various and typical LREE ore deposits around the world. Our aim is to identify suitable bastnäsite reference materials by using *in situ* U-Th-Pb and Sr-Nd isotopic measurement that can be used by the geochemical research community working with LREE ore deposits.

## Analytical methods

Forty-seven bastnäsite samples were separated using a Frantz magnetic separator and were concentrated with heavy liquids. They were then selected by hand picking under a binocular microscope. All separated grains were embedded in epoxy, sectioned to expose their interiors, polished and mapped by optical microscopy and back-scattered electron imaging. Samples for solution Sr and Sm-Nd isotope analysis were determined directly by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS), *in situ* trace element and U-Th-Pb age determination by LA-ICP-MS and Sr-Nd isotopic measurement by LA-MC-ICP-MS following the method of Yang *et al.* (2008, 2009b, 2011a, 2014a) and Liu *et al.* (2012), hence only a brief description is given below (Table 1). All analyses were conducted at the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing.

## Bastnäsite reference material

A well-characterised reference material (RM) is critical for *in situ* U-Th-Pb determination using ion or laser probe. There is no bastnäsite reference material for bastnäsite U-Th-Pb geochronology available. For this study, we used the bastnäsite reference material K-9 from the Karasug complex deposit, which is related to the carbonatites of the central Tuva area, Mongolia. The studied minerals were collected from supergene-altered haematite-bearing siderite carbonatites with baritocelastine, and come from the same set of bastnäsite crystals studied by Sal'Nikova *et al.* (2010).

The K-9 bastnäsite crystals are compositionally homogeneous (Figure 1a). Two bastnäsite microsamples consisting of two and three grains 250–500  $\mu\text{m}$  in size were previously dated by Sal'Nikova *et al.* (2010) using the U-Pb method by ID-TIMS. The authors obtained a concordant age of  $118 \pm 1 \text{ Ma}$  (MSWD = 0.05, probability = 0.82) (Figure 2a), which is in good agreement with a Sm-Nd age of  $116 \pm 8 \text{ Ma}$  (bastnäsite) and  $115 \pm 7 \text{ Ma}$  (fluorite) and a

**Table 1.**  
**Typical instrument parameters of U-Th-Pb dating of bastnäsite by LA-ICP-MS and its Sr-Nd isotopic analysis by LA-MC-ICP-MS**

MC-ICP-MS cup configuration							
Faraday cups	L4	L3	L2	L1	Centre	H1 H2 H3 H4	
Nominal mass	83	83.5	84 $^{84}\text{Sr}^+$	85	86 $^{86}\text{Sr}^+$	86.5 87 $^{87}\text{Sr}^+$	88 $^{88}\text{Sr}^+$
$[\text{Kr}^+, \text{Rb}^+, \text{HREE}^{2+}]$	$^{83}\text{Kr}^+, ^{166}\text{Er}^{2+}$	$^{167}\text{Er}^{2+}$	$^{84}\text{Kr}^+, ^{168}\text{Er}^{2+}, ^{168}\text{Yb}^{2+}$	$^{85}\text{Rb}^+, ^{170}\text{Er}^{2+}, ^{170}\text{Yb}^{2+}$	$^{86}\text{Kr}^+, ^{172}\text{Yb}^{2+}$	$^{87}\text{Rb}^+, ^{174}\text{Yb}^{2+}$	$^{176}\text{Yb}^{2+}$
Nominal mass	142	143	144	145	146	147	149
$\text{Nd}^+$	$^{142}\text{Nd}^+$	$^{143}\text{Nd}^+$	$^{144}\text{Nd}^+$	$^{145}\text{Nd}^+$	$^{146}\text{Nd}^+$	$^{148}\text{Nd}^+$	$^{149}\text{Sm}^+$
$[\text{Ce}^+, \text{Sm}^+]$	$^{142}\text{Ce}^+$		$^{147}\text{Sm}^+$			$^{147}\text{Sm}^+$	$^{150}\text{Nd}^+$ $^{150}\text{Sm}^+$
Instrumentations							
Mass spectrometers	Thermo Fisher Neptune MC-ICP-MS						
RF forward power (W)	Agilent 7500a Q-ICP-MS						
Interface cones	~ 1300						
Integration times	Nickel						
Background/baseline	0.262 s for laser Sr and Nd isotope						
Carrier gas ( $\text{l min}^{-1}$ )	4.191 s for solution Sr or Nd isotopes						
Laser ablation systems	30 s on-peak zero (OPZ)						
Laser system	~ 0.75						
Ablation cell and volume	Coherent Geolas Plus						
Fluence	ComPex 102, AF excimer UV 193nm						
Spot diameter	Standard circle low volume cell, volume ca. $4 \text{ cm}^3$						
Ablation duration	~ $4 \text{ J/cm}^2$ for Trace, U-Th-Pb dating, ~ $6 \text{ J cm}^{-2}$ for Sr-Nd isotope						
Sampling mode/repetition rate	40 $\mu\text{m}$ for Trace, U-Th-Pb dating, 16–32 $\mu\text{m}$ for Nd isotope, 44–90 $\mu\text{m}$ for Sr isotope						
Sample preparation	60 s for Trace, U-Th-Pb dating, 60 s for Sr or Nd isotope						
Sample type/mineral	Static spot ablation/~ 4–8 Hz						
Imaging	Conventional mineral separation, 1 inch resin mount						
Data processing	Bastnäsite, monazite and apatite						
Gas blank	Transmissive light, reflected light and BSE imaging						
Calibration strategy	30 s on-peak zero subtracted						
Reference material information	In-house Tuva (K-9) bastnäsite was used as primary RM, LZ (1384) is used as a secondary RM for validation.						
Data processing package used/correction for LIEF	Tuva (K-9) (Saf/Nikova <i>et al.</i> 2010) (ID-TIMS)						
Mass discrimination	Glitter software for U-Th-Pb data processing and in-house spreadsheet for data normalisation of <i>in situ</i> Sr or Nd isotope, uncertainty propagation and age calculation. LIEF correction assumes reference material and samples behave identically.						
Common Pb correction	Tuva (K-9) used for initial mass bias correction with $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{238}\text{U}$ additionally normalised to reference material.						
Uncertainty level and propagation	$^{207}\text{Pb}$ common correction is applied to the $^{206}\text{Pb}/^{238}\text{U}$ and/or $^{209}\text{Pb}/^{232}\text{Th}$ age data by Isoplot software.						
Quality control/validation	Ages are quoted at 2s absolute, propagation is by quadratic addition. Reproducibility and age uncertainty of reference material and common Pb composition uncertainty are propagated where appropriate.						
	$^{206}\text{Pb}/^{238}\text{U}$ age of LZ (1384) = $30 \pm 1 \text{ Ma}$ , $^{143}\text{Nd}/^{144}\text{Nd}$ of ZM (E) = $0.512758 \pm 20 (2s)$ , $^{87}\text{Sr}/^{86}\text{Sr}$ of LZ (1384) = $0.70620 \pm 10 (2s)$ , systematic uncertainty for propagation is 2% (2s).						

Rb-Sr age of  $118 \pm 9$  Ma (muscovite) from carbonatites from the Karasug deposit, central Tuva (Sal'Nikova *et al.* 2010). The K-9 bastnäsite has U, Th and Pb contents of  $\sim 163$ ,  $\sim 1161$  and  $12 \mu\text{g g}^{-1}$ , respectively, and a Th/U ratio of  $\sim 7$  (Yang *et al.* 2014a). In this study, we used the K-9 bastnäsite as the primary U-Th-Pb reference material in the following sample measurements.

### Major element determination

Major element compositions and back-scattered electron (BSE) observations were obtained using a JEOL-JAX8100 electron microprobe at a 15 kV accelerating potential and 12 nA beam current. Counting times were 20 s. Total iron is expressed as  $\text{Fe}_2\text{O}_3$ . The analytical uncertainties are within 2% for  $\text{TiO}_2$  and  $\text{CaO}$ , but  $\sim 10$ –20% for other minor elements due to their low mass fractions.

### In situ trace element and U-Th-Pb age determination

An Agilent 7500a Q-ICP-MS coupled to a 193 nm ArF excimer laser ablation system was used to determine trace element compositions and U-Pb ages. Helium was used as the carrier gas through the ablation cell and was mixed with argon downstream of the ablation cell (Table 1). Prior to analysis, the pulse/analogue (P/A) factor of the detector was calibrated using a standard tuning solution. The carrier and make-up gas flows were optimised to obtain maximum signal intensity for  $^{238}\text{U}^+$ , while keeping the  $\text{ThO}^+/\text{Th}^+$  ratio below 0.5%. All LA-ICP-MS measurements were carried out using time-resolved analysis in fast, peak jumping mode. The dwell time for each isotope was set at 6 ms for Rb, Sr, Ba, Nb, Ta, Zr, Hf and REE, 10 ms for  $^{232}\text{Th}$ ,  $^{238}\text{U}$ , 15 ms for  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{208}\text{Pb}$  and 30 ms for  $^{207}\text{Pb}$ . A matrix-matched in-house reference material consisting of a crystal of K-9 bastnäsite was used to correct for U-Th-Pb fractionation and instrumental mass discrimination. Two K-9 and LZ1384 or MAD809 analyses were measured after every five unknown bastnäsite spots. The crater mode, rather than the raster mode, was adopted and the total ablated time took about 20 s for blank and 60 s for a single reference material or sample measurement.

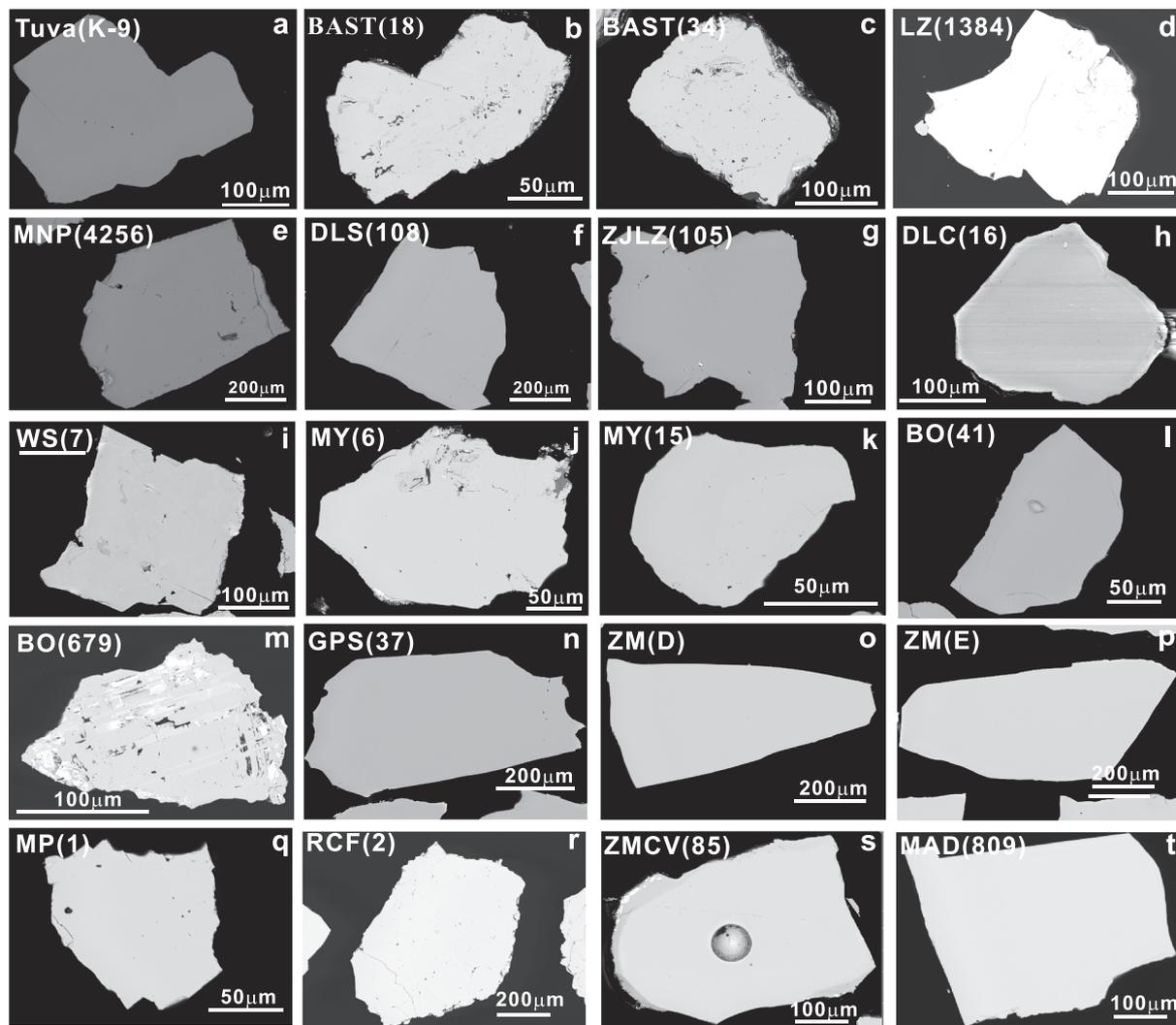
Signals of  $^{204}\text{Pb}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ ,  $^{208}\text{Pb}$ ,  $^{232}\text{Th}$  and  $^{238}\text{U}$  were acquired for U-Th-Pb dating, whereas the  $^{235}\text{U}$  signal was calculated from  $^{238}\text{U}$  on the basis of the ratio  $^{238}\text{U}/^{235}\text{U} = 137.818$ . All measured  $^{207}\text{Pb}/^{206}\text{Pb}$ ,  $^{207}\text{Pb}/^{235}\text{U}$  and  $^{206}\text{Pb}/^{238}\text{U}$  isotopic ratios of the K-9 reference material during sample analyses were regressed and corrected following the method of Sal'Nikova *et al.*

(2010). Reference values of 0.04838 ( $^{207}\text{Pb}/^{206}\text{Pb}$ ), 0.1232 ( $^{207}\text{Pb}/^{235}\text{U}$ ), 0.01847 ( $^{206}\text{Pb}/^{238}\text{U}$ ) and 0.005855 ( $^{208}\text{Pb}/^{232}\text{Th}$ ) for K-9 bastnäsite were used in our work (Sal'Nikova *et al.* 2010), assuming a Th-Pb age equivalent to the U-Pb crystallisation age of 118 Ma. Uncertainties of the calibrated isotope ratios include those from the sample, reference material and deviations from the 'external' reference materials. The uncertainty was measured at *ca.* 2%. The U-Pb or Th-Pb ages, and weighted mean ages were calculated using the Isoplot/EX 3.23 software package (Ludwig 2003). Quantitative results for trace elements were obtained via the calibration of relative element sensitivities using NIST SRM 610 and normalisation of each analysis to  $^{140}\text{Ce}$  as the internal standard element using Glitter software (Griffin *et al.* 2008). The  $\text{Ce}_2\text{O}_3$  content in bastnäsite samples was determined by electron probe microanalysis as detailed in the previous section.

Accurate correction for laser-induced elemental fractionation and instrumental drift is an important consideration in U-Th-Pb dating of accessory minerals by LA-ICP-MS measurements. In this study, we used the matrix-matched in-house K-9 reference material to correct for U-Th-Pb elemental fractionation and variations in sensitivity during a measurement session. Another significant difficulty of U-Th-Pb dating of bastnäsite is the high common Pb content, which is incorporated in the mineral crystallisation phase. As noted by Chew *et al.* (2014), common Pb correction is typically undertaken using either concordia or isochron plots on a suite of co-genetic grains or, alternatively, on individual analyses using an appropriate choice of initial Pb isotopic composition (Williams 1998). In this study, the  $^{207}\text{Pb}$  correction method was applied for common Pb correction assuming a Pb composition equivalent to Stacey and Kramers (1975), intercept age or  $^{206}\text{Pb}/^{238}\text{U}$  weighted ages were calculated using Isoplot 3.23. Moreover, the intercepts of the regression line through the raw data on a Tera-Wasserburg plot provide an estimate of the  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio for the common Pb component (upper intercept) and the inferred crystallisation age (lower intercept) (Yang *et al.* 2009b, 2014a, Wu *et al.* 2010a, b, c). Similarly, considering the lower U content of most bastnäsites, we also conducted  $^{208}\text{Pb}/^{232}\text{Th}$  age calculations after common  $^{207}\text{Pb}$  correction (Ling *et al.* 2016).

### In situ Sr isotopic measurement

A blank Neptune MC-ICP-MS coupled to a 193 nm ArF excimer laser ablation system was used to determine Sr isotopic compositions. A spot size of 44–90  $\mu\text{m}$  was employed with a 6–8 Hz repetition rate and an energy

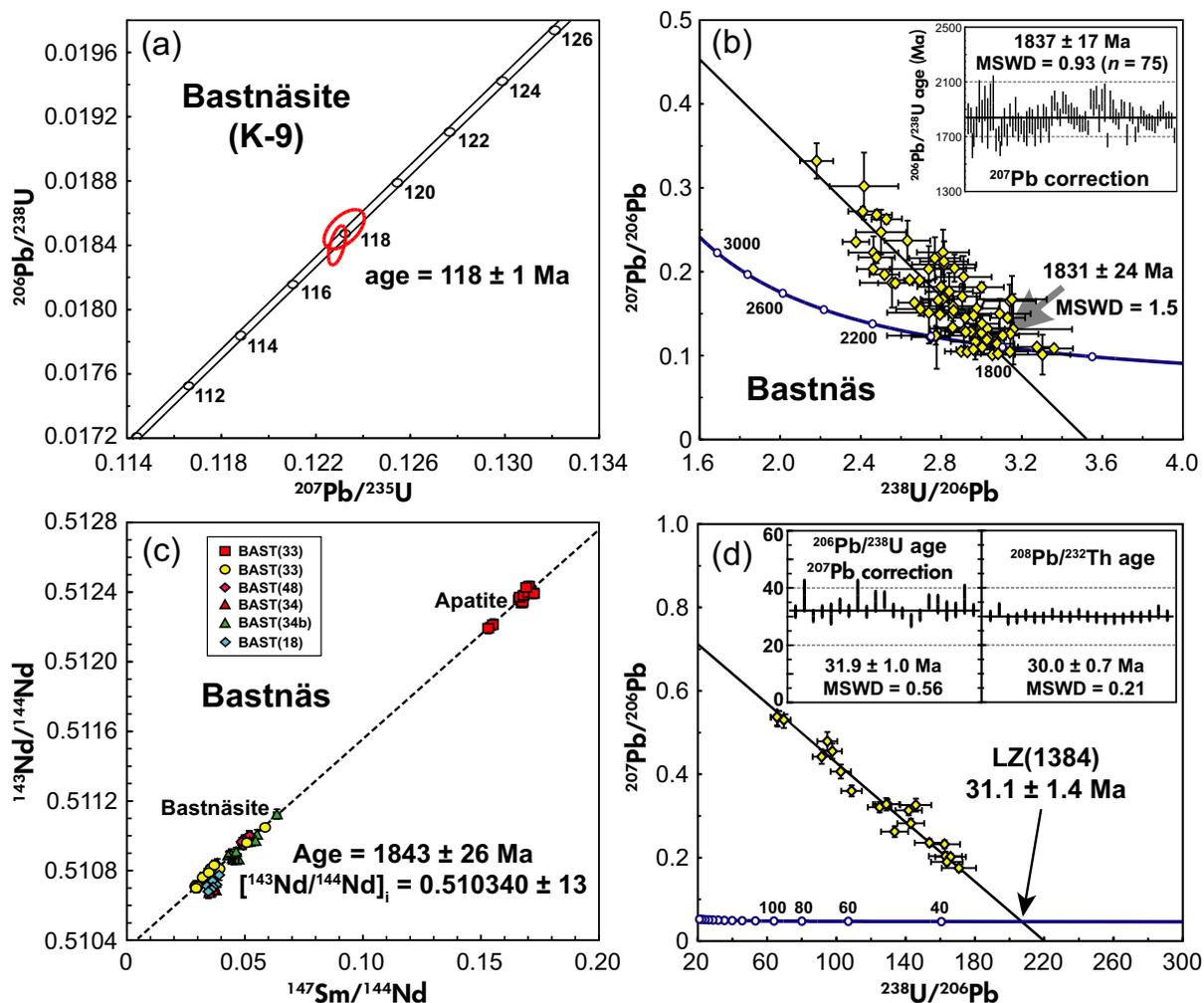


**Figure 1. Back-scattered electron (BSE) images of typical bastnäsite samples investigated in this study. Most bastnäsite samples have clear images with homogenous compositions, indicating a high purity mineral. However, BO679 from Baya Obo shows a complex texture, indicating multi-stage mineralisation during formation.**

density of  $\sim 6 \text{ J cm}^{-2}$ , depending on the Sr mass fraction of the samples (Table 1). The Sr isotopic data were acquired by static multi-collection in low-resolution mode using nine Faraday collectors. Prior to laser analysis, the Neptune MC-ICP-MS was tuned using a standard solution to obtain maximum sensitivity. A typical data acquisition cycle consisted of a 20 s measurement of the Kr gas blank with the laser switched off, followed by 40 s of measurement with the laser ablating. Two LZ1384 or MAD809 in-house secondary bastnäsite reference materials were measured after every ten unknown samples for 'external' calibration (Yang *et al.* 2014b).

Data reduction was conducted offline, and the potential isobaric interferences were accounted for in the following

order: Kr,  $\text{Yb}^{2+}$ ,  $\text{Er}^{2+}$  and Rb. Firstly, the interference of  $^{84}\text{Kr}$  and  $^{86}\text{Kr}$  on  $^{84}\text{Sr}$  and  $^{86}\text{Sr}$ , respectively, was removed using the 30 s Kr gas baseline measurement. The isobaric interference correction of  $^{84}\text{Kr}$  and  $^{86}\text{Kr}$  on  $^{84}\text{Sr}$  and  $^{86}\text{Sr}$  was conducted using the natural Kr isotopic ratios ( $^{83}\text{Kr}/^{84}\text{Kr} = 0.20175$ ,  $^{83}\text{Kr}/^{86}\text{Kr} = 0.66474$ ; Christensen *et al.* 1995, Bizzarro *et al.* 2003). Secondly, the presence of  $^{167}\text{Er}^{2+}$  and  $^{173}\text{Yb}^{2+}$  at masses 83.5 and 86.5 was monitored based on the protocols of Ramos *et al.* (2004). Using the isotopic abundances of Er and Yb (Chartier *et al.* 1999, Horstwood *et al.* 2008, Ling *et al.* 2016), the potential doubly-charged ion isobaric interference of  $^{166}\text{Er}^{2+}$  (at  $m/z$  83),  $^{168}\text{Er}^{2+}$  (at  $m/z$  84) and  $^{170}\text{Er}^{2+}$  (at  $m/z$  85) on  $^{83}\text{Kr}^+$ ,  $^{84}\text{Sr}^+$  and  $^{85}\text{Rb}^+$ , respectively, was evaluated and corrected by monitoring the interference-free  $^{167}\text{Er}^{2+}$  (at  $m/z$  83.5)



**Figure 2.** (a) Wetherill concordia plot showing results of U-Pb isotope measurements for bastnäsite K-9 by ID-TIMS. Ellipses represent 2s. Data are from Sal'Nikova *et al.* (2010). (b, c) Comparison of U-Pb and Sm-Nd ages derived from a Tera-Wasserburg concordia plot after common Pb correction (b) and a Sm-Nd isochron plot (c) of bastnäsite samples from Bastnäs Mines, Sweden. (d) Comparison of U-Pb (Tera-Wasserburg plot),  $^{206}\text{Pb}/^{238}\text{U}$  and  $^{208}\text{Pb}/^{232}\text{Th}$  ages after common Pb correction of LZ1384 bastnäsite from the Lizhuang REE deposit, Sichuan, China. Uncertainty bars for individual analyses are 1SE (in-run uncertainty) for age. MSWD: mean square of weighted deviates. [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

signal intensity. Similarly, the potential doubly-charged ion isobaric interference of  $^{170}\text{Yb}^{2+}$  (at  $m/z$  85),  $^{172}\text{Yb}^{2+}$  (at  $m/z$  86),  $^{174}\text{Yb}^{2+}$  (at  $m/z$  87) and  $^{176}\text{Yb}^{2+}$  (at  $m/z$  88) on  $^{85}\text{Rb}^+$ ,  $^{86}\text{Sr}^+$ ,  $^{87}\text{Sr}^+$  and  $^{88}\text{Sr}^+$ , respectively, was assessed and corrected for by monitoring the interference-free  $^{173}\text{Yb}^{2+}$  (at  $m/z$  86.5) signal intensity (Yang *et al.* 2014b). Thirdly, the natural ratio of  $^{85}\text{Rb}/^{87}\text{Rb}$  (2.5926) was used to correct for isobaric interference of  $^{87}\text{Rb}$  on  $^{87}\text{Sr}$  by the exponential law, assuming that Rb has the same mass discrimination behaviour as Sr (Woodhead *et al.* 2005). It is observed that the obtained  $^{87}\text{Rb}/^{87}\text{Sr}$  ratio is typically less than 0.001 during *in situ* bastnäsite Sr measurement, indicating that the

radiogenic  $^{87}\text{Sr}$  contribution is negligible (Yang *et al.* 2014b). In addition, our previous work demonstrated that Ca argides and dimers had an insignificant influence on Sr isotope analysis using a Neptune MC-ICP-MS (Yang *et al.* 2014b), a conclusion that is also strongly supported by other studies (Vroon *et al.* 2008). Therefore, interferences from Ca argides or dimers are not considered further in this work. Finally, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were calculated and normalised from the interference-corrected  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio using an exponential law. The whole data reduction procedure was performed using an in-house Excel VBA (Visual Basic for Applications) macro program.

### ***In situ* Nd isotopic measurement**

A Neptune MC-ICP-MS coupled to a 193 nm ArF excimer laser ablation system was used to determine Nd isotope ratios. Prior to laser analyses, the Neptune MC-ICP-MS was tuned and optimised for maximum sensitivity using a JNdi-1 standard solution. A laser spot size of 16–32  $\mu\text{m}$  was employed with a 6–8 Hz repetition rate, depending on the Nd mass fraction of the samples. Each spot analysis consisted of approximately 60 s data acquisition with the laser fire on (Yang *et al.* 2008) (Table 1). Two measurements of the K-9 *in-house* reference material were undertaken after every ten unknowns. The LZ1384 or ZM (E) *in-house* secondary bastnäsite reference material was analysed in each measurement session and treated as an unknown sample during the data reduction procedure (Yang *et al.* 2014b, Ling *et al.* 2016).

In order to obtain accurate  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  bastnäsite data by LA-MC-ICP-MS, care must be taken to adequately correct for the contribution of the isobaric interference of  $^{144}\text{Sm}$  on the  $^{144}\text{Nd}$  signal. The Sm interference correction is complicated by the fact that the  $^{146}\text{Nd}/^{144}\text{Nd}$  ratio, which is conventionally used to normalise the other Nd isotope ratios, is also affected by Sm interference. As a result, the mass bias correction of  $^{144}\text{Sm}$  interference on  $^{144}\text{Nd}$  cannot be applied directly from the measured  $^{146}\text{Nd}/^{144}\text{Nd}$  ratio (Foster and Vance 2006, McFarlane and McCulloch 2007, 2008, Yang *et al.* 2008, 2009b, Wu *et al.* 2010a, b, c, Fisher *et al.* 2011, Mitchell *et al.* 2011). In this work, we have adopted the recently revised Sm isotopic abundances ( $^{147}\text{Sm}/^{149}\text{Sm} = 1.08680$  and  $^{144}\text{Sm}/^{149}\text{Sm} = 0.22332$ ) (Dubois *et al.* 1992, Isnard *et al.* 2005). Firstly, we used the measured  $^{147}\text{Sm}/^{149}\text{Sm}$  ratio to calculate the Sm fractionation factor and the measured  $^{147}\text{Sm}$  intensity by employing the natural  $^{147}\text{Sm}/^{144}\text{Sm}$  ratio of 4.866559 (Isnard *et al.* 2005) to estimate the Sm interference on mass 144. Then, the interference-corrected  $^{146}\text{Nd}/^{144}\text{Nd}$  ratio can be used to calculate the Nd fractionation factor. Finally, the  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $^{145}\text{Nd}/^{144}\text{Nd}$  ratios were normalised using the exponential law. The  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio of unknown samples can also be calculated using the exponential law after correcting for isobaric interference of  $^{144}\text{Sm}$  on  $^{144}\text{Nd}$  as described above. The  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio was then 'externally' further calibrated against the  $^{147}\text{Sm}/^{144}\text{Nd}$  ratio of a K-9 reference material during the measurement sessions (Yang *et al.* 2013). The raw data were exported offline, and the whole data reduction procedure was performed using an *in-house* Excel VBA (Visual Basic for Applications) macro program.

### **Strontium and Nd isotopic determination by the solution method**

Chemical separation was undertaken by conventional ion-exchange techniques. Bastnäsite crystals were dissolved with a mixed  $^{149}\text{Sm}$ - $^{150}\text{Nd}$  spike in 2.5 ml concentrated HCl, 0.2 ml  $\text{HNO}_3$  and  $\text{HClO}_4$  using 7 ml round-bottomed Savillex<sup>TM</sup> PTFE screw-top capsules placed in an oven for a week at 190 °C. Following complete dissolution and spike-sample homogenisation, each sample was evaporated to dryness at high temperature (fuming  $\text{HClO}_4$ ) on a hot plate; then the mixture was treated with 6 mol  $\text{l}^{-1}$  HCl, evaporated to dryness and taken up in 3 mol  $\text{l}^{-1}$  HCl before chemical separation. The treatment with 6 mol  $\text{l}^{-1}$  HCl is necessary to completely convert fluorides into chlorides (Yang *et al.* 2011a). The first stage involved standard cation exchange chromatography for Rb and Sr purification. Following this, the Sr fraction was further purified by Sr-specific resin prior to mass spectrometric measurement (Yang *et al.* 2012). The REE eluted with 6 mol  $\text{l}^{-1}$  HCl was further purified using another Eichrom Ln resin (100–150  $\mu\text{m}$ , 2 ml) with 0.25 mol  $\text{l}^{-1}$  HCl for Nd and 0.40 mol  $\text{l}^{-1}$  HCl for Sm (Yang *et al.* 2010b, 2011a).

Strontium and Sm-Nd isotopes were determined using a Neptune MC-ICP-MS. Procedural blanks were less than 100 pg Sr, and 50 pg for Sm and Nd.  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios were normalised to  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$  and  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$  using the exponential law. During the period of data acquisition, analyses yielded results of  $^{87}\text{Sr}/^{86}\text{Sr} = 0.710250 \pm 11$  ( $2s$ ,  $n = 18$ ) for NBS987 and  $^{143}\text{Nd}/^{144}\text{Nd} = 0.512110 \pm 12$  ( $2s$ ,  $n = 12$ ) for Jndi-1. Additionally, USGS reference materials BCR-2 and BHVO-2 were also processed for Sr-Nd isotopes and gave ratios of  $0.704997 \pm 12$  ( $2s_m$ ) and  $0.703474 \pm 11$  ( $2s_m$ ) for  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $0.512635 \pm 10$  ( $2s_m$ ) and  $0.513000 \pm 15$  ( $2s_m$ ) for  $^{143}\text{Nd}/^{144}\text{Nd}$ , respectively, which is identical, within uncertainty, to the recommended values of TIMS (Weis *et al.* 2005, 2006).

### **Method validation of *in situ* U-Th-Pb age and Sr-Nd isotopic analysis**

To validate the reliability of our *in situ* U-Pb data, six bastnäsite samples collected from the Bastnäsite Mine, Sweden, were analysed for *in situ* U-Pb age and Sm-Nd isotopic data. As presented in Figure 2b, all samples yielded an intercept U-Pb age of  $1831 \pm 24$  Ma ( $2s$ ,  $n = 75$ ,  $2s$  means 2SE of one sample by multiple analysis in one measurement session, the same mean in the following sections) without anchoring the upper common  $^{207}\text{Pb}/^{206}\text{Pb}$  composition, in good agreement with the  $1837 \pm 17$  Ma

(2s,  $n = 75$ ) common  $^{207}\text{Pb}$  correction age and also identical to the  $1843 \pm 26$  Ma age of an *in situ* Sm-Nd isochron age within uncertainty (Figure 2c). The consistency between the *in situ* U-Pb and Sm-Nd age for the same samples indicates the robustness of our technique. Moreover, as shown in Figure 2d, the consistency of the U-Th-Pb age of LZ1384 ( $31.9 \pm 1.0$  Ma intercept age;  $31.1 \pm 1.4$  Ma following common  $^{207}\text{Pb}$  correction for  $^{206}\text{Pb}/^{238}\text{U}$  age,  $30.0 \pm 0.7$  Ma following common  $^{207}\text{Pb}$  correction for  $^{208}\text{Pb}/^{232}\text{Th}$  age) is also thought to demonstrate the reliability of our current protocol.

Similarly, to assess *in situ* Sr-Nd isotopic protocols, several bastnäsite samples (LZ1384, K-9, ZM (E) and MAD809) were repeatedly measured by solution and laser ablation methods during our method development. As summarised in Table 2, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio obtained by LA-MC-ICP-MS for the LZ1384 and MAD809 bastnäsites was  $0.70623 \pm 13$  (2s,  $n = 22$ ) and  $70844 \pm 7$  (2s,  $n = 12$ ), respectively, agreeing well with those data obtained by the solution method ( $0.70621 \pm 2$  ( $2s_m$ ),  $0.70619 \pm 2$  ( $2s_m$ ) for LZ1384 and  $0.70845 \pm 3$  ( $2s_m$ ) for MAD809, respectively). Moreover, the Sr and Nd isotopic compositions of K-9 by laser sampling were  $0.70570 \pm 25$  (2s,  $n = 12$ ) for  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $0.512780 \pm 13$  (2s,  $n = 45$ ) for  $^{143}\text{Nd}/^{144}\text{Nd}$ , respectively, which are in good agreement with  $0.70556 \pm 2$  ( $2s_m$ ) and  $0.70558 \pm 2$  ( $2s_m$ ) of  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $0.512767 \pm 4$  (2s) and  $0.512763 \pm 4$  (2s) of  $^{143}\text{Nd}/^{144}\text{Nd}$  for bastnäsite of the same location using solution MC-ICP-MS and ID-TIMS (Sal'Nikova *et al.* 2010) (Table 2). Our solution results of 0.0338 and 0.0317 for  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $0.512508 \pm 10$  ( $2s_m$ ) and  $0.512485 \pm 9$  ( $2s_m$ ) for  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios for two individual grains of LZ1384 are identical to 0.0357 and  $0.512512 \pm 12$  (2s,  $n = 15$ ) within uncertainty by laser ablation. In summary, our obtained *in situ* Sr-Nd isotopic data by LA-MC-ICP-MS are also identical to those solution data by multiple analyses, indicating the feasibility of our method for *in situ* Sr-Nd isotopic measurement of bastnäsite (Table 2). Therefore, these bastnäsite samples were used for data monitoring during *in situ* laser ablation measurements of Sr and Nd isotopes.

## Applications

In order to demonstrate the effectiveness and strength of our developed protocol, we measured natural bastnäsite samples from sixteen LREE ore deposits or alkali granite complexes around the world: Mianning-Dechang, Sichuan, Weishan, Shandong, Miaoya, Hubei, Bayan Obo, Inner Mongolia and Guposhan, Guangxi (China), Zagi Mountain (Pakistan), Bastnäs Mine (Sweden), Karasug Teva

(Mongolia), Mountain Pass, California and Red Cloud Fluorite Mine, New Mexico (USA), Zomba-Malosa, Chilwa (Malawi), and Ambatofinandrahana (Madagascar). The results are compared with available published data. A detailed sample description is given in Appendix S1, and information about the different localities is summarised in Table 3.

The samples were investigated in detail, and typical BSE images are presented in Figure 1. Representative major and trace element compositions of bastnäsites from different samples are given in online supporting information Table S1, and the trace element variation diagram patterns are shown in Figure 3. The data obtained in this study by the laser ablation method allow comparisons of the trace element and isotopic composition of bastnäsite from various localities. The *in situ* U-Th-Pb ages and Sr-Nd isotopic data for the analysed bastnäsite, together with monazite or apatite from the samples are summarised in Table 4. As recommended by Horstwood *et al.* (2016) for LA-ICP-MS geochronology, the supporting information data are appended as Table S2 (*in situ* U-Th-Pb laser data), Table S3 (*in situ* Sr laser data) and Table S4 (*in situ* Sm-Nd laser data)).

## China

**Mianning-Dechang (Sichuan):** The Mianning-Dechang (MNDC) REE belt, located in western Sichuan, China, includes one giant (Maoniuping, MNP), one large (Dalucuo, DLC), one intermediate (Muluozhai, MLZ) and several small REE deposits (e.g., Lizhuang, LZ). The carbonatite-alkaline complexes consist of carbonatitic sills or dykes and associated alkaline syenite stocks. A few available radiometric dates define a metallogenic age of 10 to 40 Ma determined by the K-Ar-Ar method for biotite and muscovite, and U-Pb dating of zircon by SHRIMP (Xu *et al.* 2008, Xu *et al.* 2012, Hou *et al.* 2009, Tian *et al.* 2008, Liu *et al.* 2015).

**Maoniuping:** We obtained a  $^{208}\text{Pb}/^{232}\text{Th}$  age of  $26.9 \pm 0.5$  Ma (2s,  $n = 12$ ) for bastnäsite sample MNP4256 (Figures 1e and 4a). These data are in good agreement, within uncertainty, with the  $25.7 \pm 0.2$  Ma age (2s,  $n = 20$ ) obtained by Ling *et al.* (2016) using SIMS. The other three bastnäsite samples (MNP1241, 1242 and 1243) yielded  $^{208}\text{Pb}/^{232}\text{Th}$  ages of  $25.7 \pm 0.8$  Ma (2s,  $n = 10$ ),  $26.0 \pm 0.6$  Ma (2s,  $n = 19$ ) and  $26.3 \pm 0.7$  Ma (2s,  $n = 12$ ), respectively (Figure 4a, b). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios obtained by LA-MC-ICP-MS for these four bastnäsite samples (MNP4256, 1241, 1242 and 1243) are  $0.70651 \pm 6$  (2s,  $n = 13$ ),  $0.70653 \pm 9$  (2s,  $n = 11$ ),  $0.70650 \pm 6$  (2s,  $n = 12$ ) and  $0.70614 \pm 6$  (2s,  $n = 12$ ), respectively. The

**Table 2.**  
Comparison of laser and solution Sr-Nd isotopic data of bastnäsite samples

Sample	Age (Ma)	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$ ( $\pm 2s$ )	$I_{\text{Sr}}$	Sm ( $\mu\text{g g}^{-1}$ )	Nd ( $\mu\text{g g}^{-1}$ )	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$ ( $\pm 2s$ )	$\varepsilon_{\text{Nd}(t)}$ ( $\pm 2s$ )	Method
LZ (1384)	30	0.0018	0.70623 (13)	0.7062			0.0357	0.512512 (12)	-1.85 (0.23)	LA-MC-ICP-MS
			0.70621 (02)	0.7062	4139	73935	0.0338	0.512508 (10)	-1.91 (0.20)	Sol. MC-ICP-MS
			0.70619 (02)	0.7062	4153	79193	0.0317	0.512485 (09)	-2.35 (0.18)	Sol. MC-ICP-MS
ZM (E)	37				17186	171574	0.0652	0.512729 (07)	+2.39 (0.14)	LA-MC-ICP-MS
					18211	206777	0.0606	0.512756 (11)	+2.94 (0.21)	Sol. MC-ICP-MS
							0.0532	0.512760 (12)	+3.06 (0.23)	Sol. MC-ICP-MS
Tuva (K-9)	118	0.0019	0.70570 (25)	0.7057			0.0762	0.512780 (13)	+4.58 (0.25)	LA-MC-ICP-MS
			0.70556 (02)	0.7056	11130 <sup>a</sup>	87650 <sup>a</sup>	0.0768 <sup>a</sup>	0.512767 (04) <sup>a</sup>	+4.32 (0.08) <sup>a</sup>	Sol. MC-ICP-MS
			0.70558 (02)	0.7056	10470 <sup>a</sup>	84300 <sup>a</sup>	0.0751 <sup>a</sup>	0.512763 (04) <sup>a</sup>	+4.27 (0.08) <sup>a</sup>	Sol. MC-ICP-MS
MAD (809)	520	0.0005	0.70844 (07)	0.7084			0.0304	0.511309 (17)	-14.89 (0.34)	LA-MC-ICP-MS
			0.70845 (03)	0.7084						Sol. MC-ICP-MS

<sup>a</sup>Obtained by ID-TIMS (Sal'Nikova *et al.* 2010), others measured by solution or laser MC-ICP-MS in this study.

initial Sr isotope ratios range from 0.7061 to 0.7065 (Table 4), in good agreement with 0.7061–0.7066 for  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios by TIMS for calcite, barite and fluorite from the MNP LREE deposit (Hou *et al.* 2009). *In situ* Sm-Nd measurements in bastnäsite using laser ablation yielded  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of 0.0368 and  $0.512426 \pm 15$  (2s,  $n = 15$ ), 0.0381 and  $0.512495 \pm 12$  (2s,  $n = 15$ ), 0.0363 and  $0.512489 \pm 14$  (2s,  $n = 15$ ) and 0.0349 and  $0.512495 \pm 16$  (2s,  $n = 15$ ), respectively (Table 4), the corresponding  $\varepsilon_{\text{Nd}(t)}$  values for these four samples are  $-3.60 \pm 0.30$  (2s),  $-2.26 \pm 0.24$  (2s),  $-2.37 \pm 0.26$  (2s) and  $-2.26 \pm 0.30$  (2s), respectively, which is almost identical to  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios obtained by TIMS from calcite and fluorite from the MNP LREE deposit (Hou *et al.* 2009). The initial Nd isotope data for these samples are consistent within analytical uncertainty.

**Muluozhai:** The Muluozhai (MLZ) LREE deposit consists of two small deposits: the Diaoloushan (DLS) and the Zhengjialiangzi (ZJLZ). As shown in Figures 4c–e, our nine DLS bastnäsite samples yielded a Th-Pb age of  $\sim 27$  Ma. The different ages are consistent with each other within uncertainty. Recently, Ling *et al.* (2016) reported a SIMS Th-Pb bastnäsite age of  $26.9 \pm 0.2$  Ma (2s,  $n = 20$ ) and  $26.7 \pm 0.2$  Ma (2s,  $n = 20$ ), respectively. Our obtained *in situ* Sr and Sm-Nd data for the DLS LREE deposit samples are also in good agreement with each other (Table 4). The initial Sr isotope data are  $\sim 0.7071$ – $0.7072$ , and the  $\varepsilon_{\text{Nd}(t)}$  value ranges from  $-2.55$  to  $-3.21$ . A 0.7066 value for  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios by TIMS for calcite from this LREE deposit was previously reported by Hou *et al.* (2009). At the same time, the three bastnäsite samples from Zhengjialiangzi (ZJLZ) also yielded a Th-Pb age of  $\sim 28$  Ma (Figure 4f). Moreover,

**Table 3.**  
Summary information for bastnäsite samples investigated in this study

Sample (numbers/names)	Location	Host rock
MNP (4256, 1241, 1242, 1243)	Maoniuping, Sichuan, China	Pegmatitic vein in alkaline syenite
DLS (108, 105, 106a, 106b, 110, 114, 115, 119, 121)	Diaoloushan, Sichuan, China	Pegmatitic vein in alkaline syenite
ZJLZ (103a, 103b, 105)	Zhengjialiangzi, Sichuan, China	Pegmatitic vein in alkaline syenite
LZ (122, 1381, 1382, 1383a, 1383b, 1384)	Lizhuang, Sichuan, China	Pegmatitic vein in alkaline syenite
DLC (16, 43)	Dalucao, Sichuan, China	Pegmatitic vein in alkaline syenite
WS (7, 29, 9)	Weishan, Shandong, China	Pegmatitic vein in alkaline syenite
MY (6, 15)	Miaoya, Hubei, China	Carbonatite
BO (41, 138, 679)	Bayan Obo, Inner Mongolia, China	Carbonatite
GPS (37)	Guposhan, Guangxi, China	Granite
ZM (B, D, E)	Zagi Mountain, Pakistan	Aplite vein in alkaline granite
BAST (18, 34, 34b, 33, 48)	Bastnäs Mine, Sweden	Metavolcanics
Tuva (K-9)	Tuva, Mongolia	Carbonatite
MP (1)	Mountain Pass, California, USA	Carbonatite
RCF (2)	Red Cloud Fluorite Mine, New Mexico, USA	Fluorite-cemented hydrothermal breccias
ZMCV (85)	Zomba-Malosa, Chilwa, Malawi	Pegmatitic vein in alkaline granite
MAD (809)	Madagascar	Alkaline to peralkaline complex

the Sr and Nd isotopic compositions are also identical to those of the nine DLS samples.

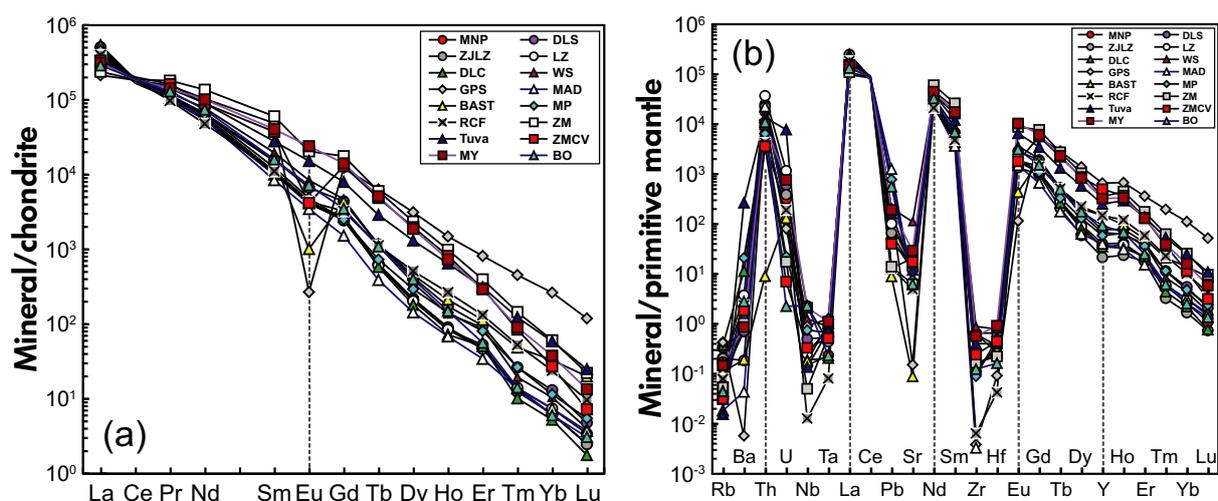
**Lizhuang:** The obtained  $^{208}\text{Pb}/^{232}\text{Th}$  ages for sample LZ122 ( $29.5 \pm 0.6$  Ma;  $2s$ ,  $n = 18$ ) (Figure 4g) are in good agreement, within uncertainty, with the  $28.4 \pm 0.2$  Ma age ( $2s$ ,  $n = 20$ ) obtained by SIMS (Ling *et al.* 2016). The other five bastnäsite samples LZ1381, 1382, 1383a, 1383b and 1384 yielded  $^{208}\text{Pb}/^{232}\text{Th}$  ages of  $28.2 \pm 0.6$  Ma ( $2s$ ,  $n = 19$ ),  $28.9 \pm 0.7$  Ma ( $2s$ ,  $n = 19$ ),  $28.7 \pm 0.7$  Ma ( $2s$ ,  $n = 18$ ),  $30.1 \pm 0.8$  Ma ( $2s$ ,  $n = 18$ ),  $30.0 \pm 0.7$  Ma ( $2s$ ,  $n = 21$ ), respectively (Figure 4g, h). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios obtained by LA-MC-ICP-MS for the six bastnäsite samples are  $0.70628 \pm 4$  ( $2s$ ,  $n = 24$ ),  $0.70642 \pm 10$  ( $2s$ ,  $n = 9$ ),  $0.70637 \pm 8$  ( $2s$ ,  $n = 10$ ),  $0.70650 \pm 12$  ( $2s$ ,  $n = 10$ ),  $0.70641 \pm 9$  ( $2s$ ,  $n = 10$ ) and  $0.70623 \pm 13$  ( $2s$ ,  $n = 22$ ), respectively (Table 4). The initial Sr isotope ratios range from 0.7062 to 0.7064, which is almost identical to 0.7063 and 0.7069 for  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios by TIMS for calcite from the same REE deposit (Hou *et al.* 2009).

The *in situ* bastnäsite Sm-Nd, using laser ablation, yielded  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of 0.0388 and  $0.512450 \pm 11$  ( $2s$ ,  $n = 22$ ), 0.0360 and  $0.512503 \pm 9$  ( $2s$ ,  $n = 12$ ), 0.0392 and  $0.512500 \pm 9$  ( $2s$ ,  $n = 15$ ), 0.0344 and  $0.512500 \pm 12$  ( $2s$ ,  $n = 15$ ), 0.0339 and  $0.512505 \pm 10$  ( $2s$ ,  $n = 15$ ) and 0.0357 and  $0.512512 \pm 12$  ( $2s$ ,  $n = 15$ ), respectively (Table 4). The corresponding  $\epsilon_{\text{Nd}(t)}$  values for these samples are  $-3.06 \pm 0.20$  ( $2s$ ),  $-2.02 \pm 0.18$  ( $2s$ ),  $-2.10 \pm 0.18$  ( $2s$ ),  $-2.07 \pm 0.23$  ( $2s$ ),  $-1.97 \pm 0.19$  ( $2s$ ) and  $-1.85 \pm 0.23$  ( $2s$ ),

respectively (Table 4). The initial Nd isotope data for the six samples are consistent within analytical uncertainty and also agree well with those data from calcite by TIMS (Hou *et al.* 2009). Therefore, we consider that the age of this deposit is  $\sim 29$  Ma, indicating a narrow range in the mineralisation age by direct determination of bastnäsite.

**Dalucao:** Our obtained  $^{208}\text{Pb}/^{232}\text{Th}$  ages for samples DLC16 and DLC43 are  $13.2 \pm 0.6$  Ma ( $2s$ ,  $n = 8$ ) and  $13.4 \pm 0.6$  Ma ( $2s$ ,  $n = 8$ ) (Figure 4i), which are in good agreement with ages obtained by Ling *et al.* (2016) of  $11.9 \pm 0.2$  ( $2s$ ,  $n = 12$ ) Ma and  $11.8 \pm 0.2$  Ma ( $2s$ ,  $n = 20$ ), within uncertainty, by using the SIMS method. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios obtained by LA-MC-ICP-MS for these two samples are  $0.70809 \pm 9$  ( $2s$ ,  $n = 12$ ) and  $0.70818 \pm 17$  ( $2s$ ,  $n = 12$ ), respectively (Table 4). The initial Sr isotope ratios range from 0.7081 to 0.7082, which is higher than those for the other three REE deposits in MNDC, Sichuan. The *in situ* Sm-Nd data by using laser ablation yielded  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios of 0.0274 and  $0.512387 \pm 13$  ( $2s$ ,  $n = 10$ ), and  $0.512392 \pm 12$  ( $2s$ ,  $n = 10$ ), respectively. The corresponding  $\epsilon_{\text{Nd}(t)}$  values for these two samples are  $-4.62 \pm 0.25$  ( $2s$ ) and  $-4.54 \pm 0.23$  ( $2s$ ), respectively. The initial Nd isotope values for these two samples are consistent with each other within analytical uncertainty.

**Weishan, Shandong:** As shown in Figure 5a, our three bastnäsite samples yielded ages of  $121.2 \pm 1.0$  Ma (WS7,  $2s$ ,  $n = 14$ ),  $123.8 \pm 0.7$  Ma (WS29,  $2s$ ,  $n = 20$ ) and  $121.2 \pm 1.1$  Ma (WS9,  $2s$ ,  $n = 14$ ), respectively, which are



**Figure 3. (a) Chondrite-normalised REE distribution patterns and (b) mantle-normalised patterns of bastnäsite samples analysed in this study. Normalisation values for both primitive mantle and chondrite are from McDonough and Sun (1995). Abbreviations: MNP, Maoniuping; DLS, Diaoloushan; ZJLZ, Zhengjialiangzi; LZ, Lizhuang; DLC, Dalucao; WS, Weishan; MY, Miaoya. [Colour figure can be viewed at wileyonlinelibrary.com]**

in good agreement within uncertainties and are also identical to the  $119.5 \pm 1.7$  Ma ( $2s$ ,  $n = 6$ ) Ma age of a muscovite Rb-Sr isochron and slightly older than a  $\sim 110$  Ma muscovite K-Ar isochron age reported by Tian *et al.* (2002). The K-Ar age reported by Tian *et al.* (2002) for the host rock is  $\sim 140$  Ma. The *in situ* Sr isotopes for the three samples yielded values of  $0.70740 \pm 2$  ( $2s$ ,  $n = 10$ ),  $0.70748 \pm 4$  ( $2s$ ,  $n = 10$ ) and  $0.70727 \pm 11$  ( $2s$ ,  $n = 13$ ) (Table 4), respectively, and the corresponding initial Sr values are 0.7074, 0.7075 and 0.7073, respectively, indicating a similar genetic evolution or rock chemistry. Additionally, the values for *in situ* Sm-Nd isotope are  $0.512092 \pm 11$  ( $2s$ ,  $n = 12$ ),  $0.512074 \pm 12$  ( $2s$ ,  $n = 13$ ) and  $0.512070 \pm 11$  ( $2s$ ,  $n = 30$ ), respectively, and the corresponding  $\epsilon_{Nd(t)}$  values are  $-8.48 \pm 0.20$  ( $2s$ ),  $-8.66 \pm 0.22$  ( $2s$ ) and  $-8.77 \pm 0.21$  ( $2s$ ), respectively. As for the Rb-Sr system, the results of the Sm-Nd isotopic system indicate a relatively narrow age of mineralisation and the same genetic evolution or rock chemistry. The results of *in situ* Sr-Nd isotopic composition of the bastnäsite samples indicate that the source of the REE deposit is the enriched mantle.

**Miaoya, Hubei:** As illustrated in Figure 5b, our two bastnäsite samples yielded Th-Pb ages of  $196.3 \pm 2.8$  Ma (MY6,  $2s$ ,  $n = 22$ ) and  $211.1 \pm 4.1$  Ma (MY15,  $2s$ ,  $n = 12$ ), respectively. Our two monazite samples from the same locality yielded  $229.8 \pm 5.0$  Ma (MY2,  $2s$ ,  $n = 14$ ) and  $232.1 \pm 3.6$  Ma (MY14,  $2s$ ,  $n = 18$ ), respectively, which is similar to the  $233.6 \pm 1.7$  Ma age of monazite from the same location dated by SHRIMP (Xu *et al.* 2014). Additionally, the MY15 bastnäsite for *in situ* Sr isotopes yielded  $0.70358 \pm 4$  ( $2s$ ,  $n = 14$ ) (Table 4). The corresponding initial Sr ratio is 0.7036, which is identical to TIMS values reported by Xu *et al.* (2014) for whole rock and apatite from the same location. As shown in Table 4, the results of *in situ* Sm-Nd isotope data for bastnäsites and monazites are both in good agreement within their respective uncertainties.

**Bayan Obo, Inner Mongolia:** As presented in Figure 5c, the bastnäsite sample BO41 yielded a weighted mean  $^{208}\text{Pb}/^{232}\text{Th}$  age of  $274.2 \pm 3.3$  Ma ( $2s$ ,  $n = 22$ ), which represents the time of REE mineralisation. In addition, the two bastnäsite samples BO138 and BO679 yielded an extremely wide range of  $^{208}\text{Pb}/^{232}\text{Th}$  ages from 320 Ma to 440 Ma (BO138) and from 240 Ma to 1360 Ma (BO679), which indicates a long period of REE mineralisation. The results of *in situ* Sr isotopes range from  $0.71038 \pm 37$  (BO138,  $2s$ ,  $n = 12$ ) to  $0.70974 \pm 15$  (BO679,  $2s$ ,  $n = 15$ ) (Table 4) with initial Sr values of 0.7104 and 0.7097, respectively. Moreover, the *in situ* Sm-Nd isotope values are  $0.511454 \pm 12$  ( $2s$ ,  $n = 11$ ),

$0.511277 \pm 11$  ( $2s$ ,  $n = 10$ ) and  $0.511387 \pm 16$  ( $2s$ ,  $n = 10$ ), which yielded a reference Sm-Nd isochron of ca. 1400 Ma (Table 4).

During the last 20 years, several radiometric dating techniques have been applied to date the mineralisation of the Bayan Obo deposit, resulting in significantly different ages. These include the U-Th-Pb, Sm-Nd, Rb-Sr, K-Ar, Ar-Ar, Re-Os and La-Ba methods (Fan *et al.* 2014, 2016 and references therein). Based on previous La-Ba, Th-Pb and Sm-Nd isotopic data for the main REE ore minerals (monazite and bastnäsite), the oldest age of mineralisation is about 1300–1400 Ma (Nakai *et al.* 1989, Ren *et al.* 1994, Zhang *et al.* 2003, Yang *et al.* 2011b, 2011a) whereas the youngest is about 200–300 Ma, although according to Wang *et al.* (1994) and Chao *et al.* (1997) there are multiple phases of mineralisation.

**Guposhan, Guangxi:** The GPS37 bastnäsite collected from the Guposhan granite, Guangxi Province, southern China, yielded a Th-Pb age of  $161.4 \pm 1.5$  Ma ( $2s$ ,  $n = 13$ ) (Figure 6a), which is in good agreement with a U-Pb age of  $\sim 163$  Ma for three zircons dated by LA-ICP-MS (Gu *et al.* 2006). These results demonstrate that the entire Guposhan granite formed at the same time. As shown in Table 4 and Figure 7, this conclusion is also supported by similar Nd isotopic values for bastnäsite by laser ablation in the present study ( $\epsilon_{Nd(t)} = -2.89 \pm 0.17$ ) ( $2s$ ,  $n = 12$ ) and a whole-rock granite sample by ID-TIMS ( $\epsilon_{Nd(t)} = -4.06 \pm 0.84$  ( $2s$ ,  $n = 8$ )) (Gu *et al.* 2006).

## Pakistan

Our three gem-quality bastnäsite specimens ( $0.5 \times 1.5 \times 2.0$  cm) come from Zagi Mountain (Pechawar), located in the north-western Frontier Province, Pakistan. The ZM B, D and E bastnäsites yielded  $37.8 \pm 1.2$  Ma ( $2s$ ,  $n = 24$ ),  $37.4 \pm 1.1$  Ma ( $2s$ ,  $n = 24$ ) and  $36.2 \pm 1.6$  Ma ( $2s$ ,  $n = 16$ ) (Figure 6b), respectively, which are slightly younger than ages reported for the host granitic rock: 41 Ma (K-Ar, riebeckite),  $40 \pm 5$  Ma (Ar-Ar, riebeckite),  $43.5 \pm 5$  Ma (Ar-Ar, riebeckite) and  $42 \pm 4$  Ma (Ar-Ar, biotite) (Kempe 1973, Maluski and Matte 1984). The results for *in situ* Sm-Nd isotopes are  $0.512737 \pm 10$  ( $2s$ ,  $n = 12$ ),  $0.512725 \pm 9$  ( $2s$ ,  $n = 12$ ) and  $0.512729 \pm 7$  ( $2s$ ,  $n = 12$ ), respectively, and the corresponding  $\epsilon_{Nd(t)}$  mean values are  $+2.50 \pm 0.20$  ( $2s$ ),  $+2.25 \pm 0.18$  ( $2s$ ) and  $+2.39 \pm 0.14$  ( $2s$ ), respectively, indicating a relatively narrow range for the mineralisation age and a similar genetic evolution or rock chemistry (Table 4). Furthermore, the gem-quality bastnäsite is also a potential reference material candidate for *in situ* Nd isotope analysis by laser ablation.

**Table 4.**  
Compilation of Sr, Sm-Nd isotopic data and corresponding initial Sr and Nd of bastnäsites investigated in this study

Sample	Age (Ma)	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$ ( $\pm 2s$ )	$I_{\text{Sr}}$	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$ ( $\pm 2s$ )	$\epsilon_{\text{Nd}(t)}$ ( $\pm 2s$ )
MNP 4256	26	0.0013	0.70651 (06)	0.7065	0.0368	0.512426 (15)	-3.60 (0.30)
MNP 1241	26	0.0012	0.70653 (09)	0.7065	0.0381	0.512495 (12)	-2.26 (0.24)
MNP 1242	26	0.0011	0.70650 (06)	0.7065	0.0363	0.512489 (14)	-2.37 (0.26)
MNP 1243	26	0.0007	0.70614 (06)	0.7061	0.0349	0.512495 (16)	-2.26 (0.30)
DLS 108	27	0.0019	0.70710 (07)	0.7071	0.0438	0.512445 (10)	-3.21 (0.20)
DLS 105	27	0.0018	0.70723 (13)	0.7072	0.0386	0.512455 (08)	-3.01 (0.16)
DLS 106a	27	0.0027	0.70714 (07)	0.7071	0.0378	0.512453 (10)	-3.04 (0.19)
DLS 106b	27	0.0045	0.70710 (05)	0.7071	0.0360	0.512457 (11)	-2.95 (0.22)
DLS 110	27	0.0035	0.70724 (08)	0.7072	0.0412	0.512452 (08)	-3.08 (0.15)
DLS 114	27	0.0010	0.70720 (09)	0.7072	0.0451	0.512479 (07)	-2.55 (0.13)
DLS 115	27	0.0019	0.70706 (11)	0.7071	0.0433	0.512472 (05)	-2.69 (0.11)
DLS 119	27	0.0010	0.70720 (11)	0.7072	0.0505	0.512473 (09)	-2.69 (0.18)
DLS 121	27	0.0012	0.70712 (15)	0.7071	0.0403	0.512463 (09)	-2.86 (0.19)
ZJLZ 103a	27	0.0005	0.70708 (10)	0.7071	0.0271	0.512441 (09)	-3.27 (0.18)
ZJLZ 103b	27	0.0016	0.70698 (09)	0.7070	0.0264	0.512440 (17)	-3.28 (0.32)
ZJLZ 105	27	0.0027	0.70717 (07)	0.7072	0.0280	0.512452 (10)	-3.04 (0.19)
LZ 122	30	0.0005	0.70628 (04)	0.7063	0.0388	0.512450 (11)	-3.06 (0.20)
LZ 1381	30	0.0010	0.70642 (10)	0.7064	0.0360	0.512503 (09)	-2.02 (0.18)
LZ 1382	30	0.0011	0.70637 (08)	0.7064	0.0392	0.512500 (09)	-2.10 (0.18)
LZ 1383a	30	0.0013	0.70650 (12)	0.7065	0.0344	0.512500 (12)	-2.07 (0.23)
LZ 1383b	30	0.0009	0.70641 (09)	0.7064	0.0339	0.512505 (10)	-1.97 (0.19)
LZ 1384	30	0.0018	0.70623 (13)	0.7062	0.0357	0.512512 (12)	-1.85 (0.23)
DLC 16	13	0.0038	0.70809 (09)	0.7081	0.0274	0.512387 (13)	-4.62 (0.25)
DLC 43	13	0.0008	0.70818 (17)	0.7082	0.0343	0.512392 (12)	-4.54 (0.23)
WS 7	120	0.0001	0.70740 (02)	0.7074	0.0548	0.512092 (11)	-8.48 (0.20)
WS 29	120	0.0002	0.70748 (04)	0.7075	0.0431	0.512074 (12)	-8.66 (0.22)
WS 9	120	0.0001	0.70727 (11)	0.7073	0.0455	0.512070 (11)	-8.77 (0.21)
MY 2 <sup>a</sup>	230				0.0747	0.512428 (14)	-0.52 (0.28)
MY 6	230				0.0749	0.512427 (17)	-0.54 (0.33)
MY 14 <sup>a</sup>	230				0.0603	0.512410 (11)	-0.45 (0.20)
MY 15	230	0.0004	0.70358 (04)	0.7036	0.0722	0.512429 (12)	-0.42 (0.23)
BO 41	274				0.0531	0.511454 (12)	-18.08 (0.23)
BO 138	370	0.0003	0.71038 (37)	0.7104	0.0353	0.511277 (11)	-18.93 (0.22)
BO 679		0.0014	0.70974 (15)	0.7097	0.0489	0.511387 (16)	
GPS 37	161				0.0878	0.512376 (08)	-2.89 (0.17)
ZM B	37				0.0787	0.512737 (10)	+2.50 (0.20)
ZM D	37				0.0805	0.512725 (09)	+2.25 (0.18)
ZM E	37				0.0652	0.512729 (07)	+2.39 (0.14)
BAST 18	1840				0.0358	0.510718 (15)	+0.53 (0.24)
BAST 34	1840				0.0365	0.510707 (15)	+0.17 (0.25)
BAST 34b	1840				0.0373	0.510813 (21)	+2.06 (0.21)
BAST 33	1840				0.0360	0.510794 (57)	+1.99 (0.18)
BAST 33b	1840				0.1668	0.512359 (40)	+1.63 (0.26)
BAST 48	1840				0.0501	0.510972 (12)	+2.12 (0.14)
Tuva K-9	118	0.0019	0.70570 (25)	0.7057	0.0762	0.512780 (13)	+4.58 (0.25)
MP 1	1400	0.0003	0.70456 (08)	0.7045	0.0349	0.511025 (15)	-2.44 (0.24)
RCF 2	29	0.0016	0.70719 (13)	0.7072	0.0463	0.512475 (13)	-2.61 (0.25)
ZMCV 85	114	0.0010	0.70617 (21)	0.7062	0.0638	0.512656 (16)	+2.29 (0.18)
MAD 809	520	0.0005	0.70844 (07)	0.7084	0.0304	0.511309 (17)	-14.89 (0.34)

<sup>a</sup> Monazite and <sup>b</sup> Apatite, others bastnäsite.

## USA

**Mountain Pass, California:** As illustrated in Figure 6c, twenty-three analyses of bastnäsite sample MP1 yielded a

mean Th-Pb age of  $1422 \pm 20$  Ma ( $2s$ ,  $n = 23$ ). In addition, the  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios are  $0.70456 \pm 8$  ( $2s$ ,  $n = 12$ ) and  $0.511025 \pm 15$  ( $2s$ ,  $n = 12$ ), respectively (Table 4). The corresponding initial Sr

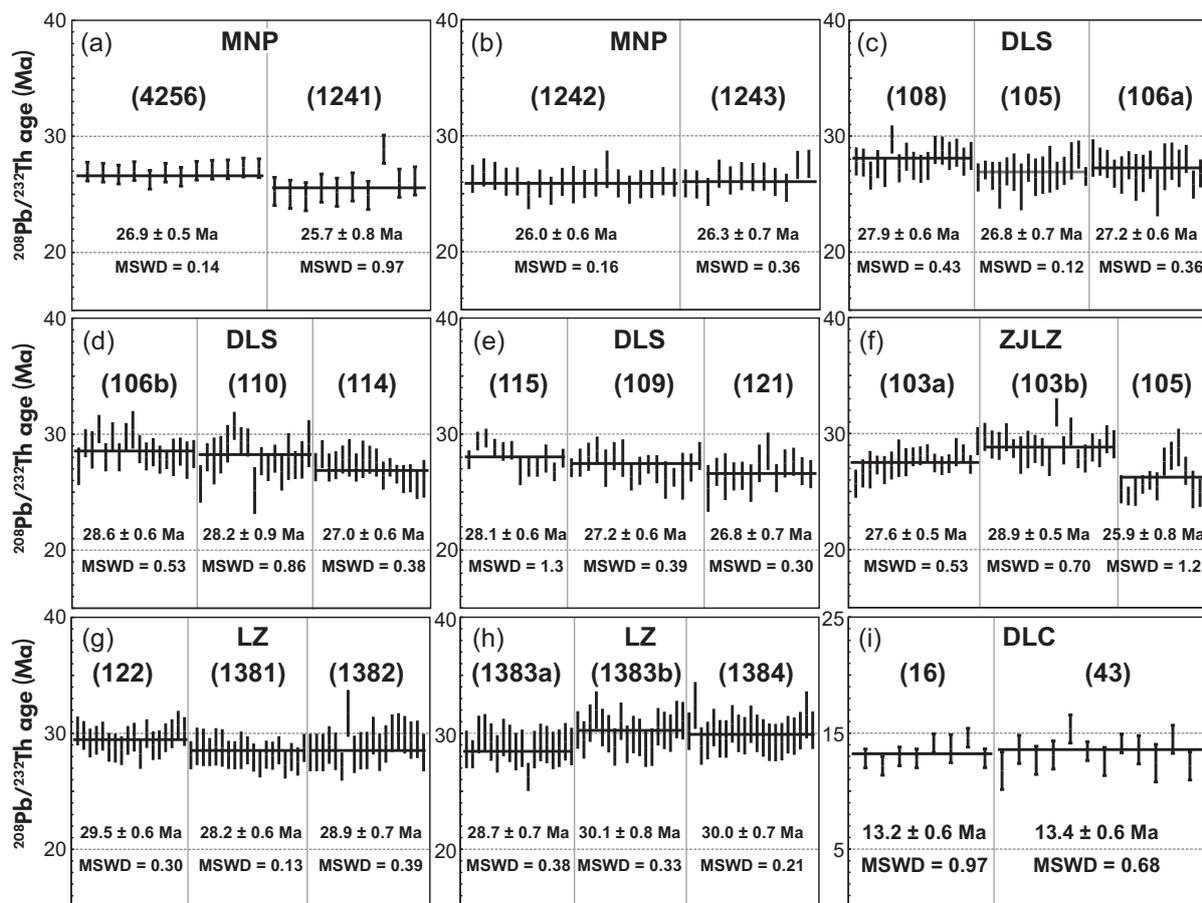
isotope ratio is 0.7045, and the mean  $\epsilon_{Nd(t)}$  is  $-2.44 \pm 0.24$  (2s). Our results support a similar source for the carbonatitic fluids and suggest that the age of bastnäsite mineralisation is associated with the carbonatite intrusion, dated at  $\sim 1400$  Ma (Dewitt *et al.* 1987). Recently, Jacob *et al.* (2016) reported a crystallisation age for titanite and zircon from Mountain Pass ranging from  $1429 \pm 10$  to  $1385 \pm 18$  Ma, increasing the age range of the ultra-potassic rocks in the complex by  $\sim 20$  Ma. Meanwhile, the Th-Pb monazite crystallisation age of carbonatite samples is inferred to be  $\sim 1405$  to  $1395$  Ma and  $\sim 1380$  to  $1370$  Ma (Jacob *et al.* 2016), which is attributed to variable but minor radiogenic Pb loss. The  $\epsilon_{Nd(t)}$  for bastnäsite sample MP-P0913-SQ1 is  $-3.2 \pm 0.3$  (2s,  $n = 25$ ) which is consistent with our result from sample MP1. Therefore, we consider that this famous LREE deposit formed at  $\sim 1400$  Ma.

**Red Cloud Fluorite Mine, New Mexico:** As shown in Figure 6d, our eighteen Th-Pb analyses yielded a mean age of  $29.3 \pm 0.5$  Ma (2s,  $n = 18$ ) that is in good agreement

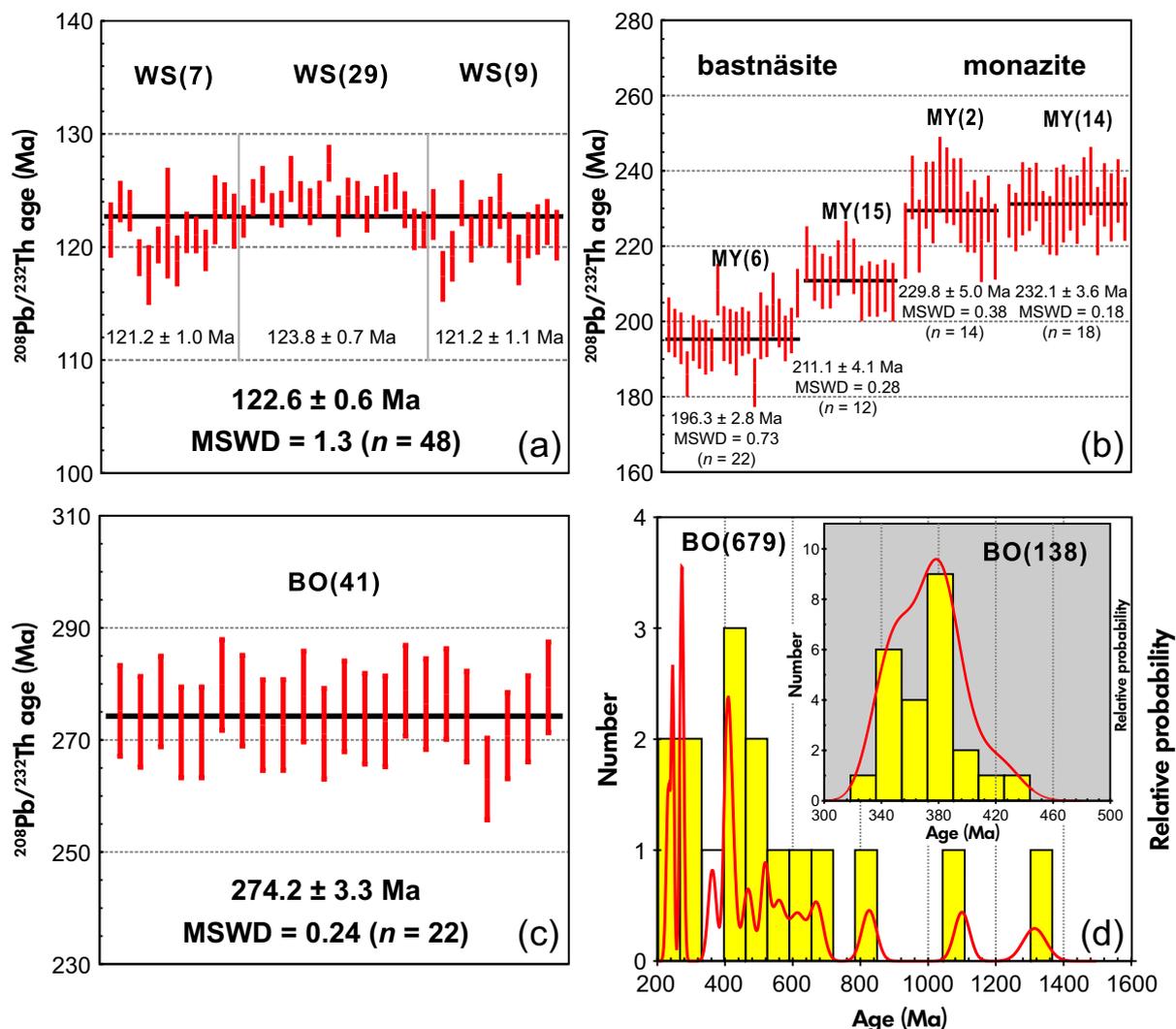
with a K-Ar age of 29.9 Ma reported by Perhac (1970) for an orthoclase from a trachyte/syenite (Gallinas Mountains). The  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios are  $0.70719 \pm 13$  (2s,  $n = 12$ ) and  $0.512475 \pm 13$  (2s,  $n = 12$ ), respectively (Table 4), whereas the corresponding initial Sr ratio is 0.7072 and the mean  $\epsilon_{Nd(t)}$  is  $-2.61 \pm 0.25$  (2s).

### Malawi

As shown in Figure 6e, our twenty-three analyses of sample ZMCV485 yielded a mean Th-Pb age of  $114.5 \pm 2.0$  Ma (2s), whereas the  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios are  $0.70617 \pm 21$  (2s,  $n = 12$ ) and  $0.512656 \pm 16$  (2s,  $n = 12$ ), respectively (Table 4). The corresponding initial Sr ratio is 0.7062, and the mean  $\epsilon_{Nd(t)}$  is  $+2.29 \pm 0.18$  (2s). The age is in good agreement with the  $113 \pm 4$  Ma age of emplacement of the Zomba-Malosa pear-shaped pluton reported by Eby *et al.* (1995). Recently, the emplacement age of pegmatites was well constrained by a single-zircon Pb-Pb evaporation age of  $123 \pm 4$  Ma,



**Figure 4.** Th-Pb ages obtained by LA-ICP-MS for bastnäsites from the MNP, DLS, ZJLZ, LZ and DLC, MNDC LREE deposits, Sichuan province, China. Uncertainty bars for individual analyses are 1SE (in-run uncertainties). Abbreviations as in Figure 3. [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



**Figure 5.** Th-Pb ages of bastnäsites from Weishan, Shandong, Miaoya, Hubei and Bayan Obo, Inner Mongolia, China. [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

a zircon U-Pb SIMS age of  $117 \pm 1$  Ma, a zircon U-Pb LA-ICP-MS age of  $119.3 \pm 2.1$  Ma (zircon I) and  $118.0 \pm 1.2$  Ma (zircon II) (Soman *et al.* 2010). These data indicate the reliability of the present technique.

### Madagascar

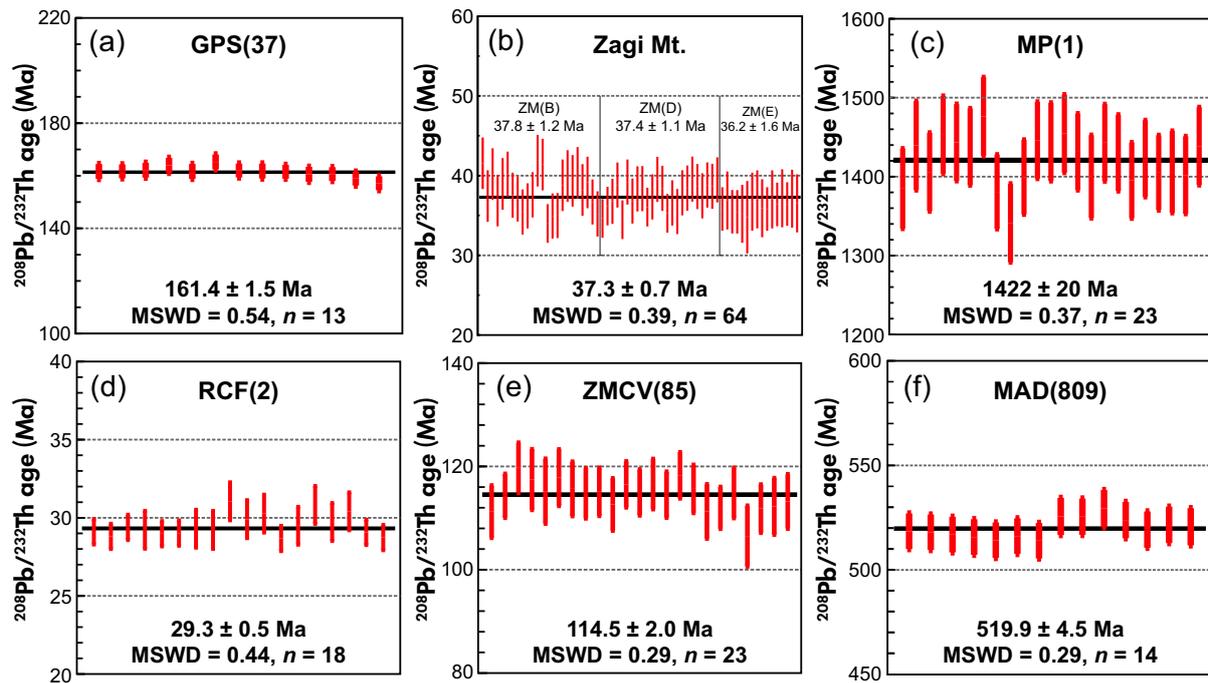
Fourteen analyses of sample MAD809 yielded a mean Th-Pb age of  $519.9 \pm 4.5$  Ma (2s) (Figure 6f). The Sr and Nd isotopic compositions are  $0.70844 \pm 7$  (2s,  $n = 12$ ) for  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $0.511309 \pm 17$  (2s,  $n = 12$ ) for  $^{143}\text{Nd}/^{144}\text{Nd}$ , respectively, the corresponding initial Sr ratio is 0.7084, and the mean  $\epsilon_{\text{Nd}(t)}$  is  $-14.89 \pm 0.34$  (2s) (Table 4). As noted by Rasoamalala *et al.* (2014), the bastnäsite and monazite deposits of the Ambatofinandrahana region of Madagascar are closely associated with an

alkaline to peralkaline complex of Pan-African age (~ 540–570 Ma) (Liu *et al.* 2012).

### Discussion

#### Bastnäsite as a U-Th-Pb geochronometer

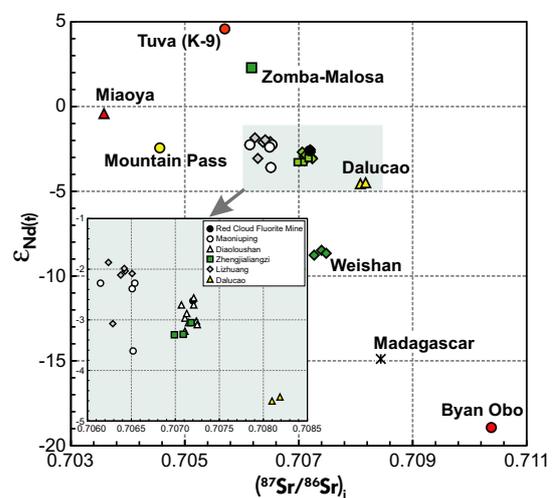
The potential of bastnäsite as a U-Th-Pb geochronometer has not been properly investigated. In the present study, we show that bastnäsite has U and Th mass fractions of 1–200  $\mu\text{g g}^{-1}$  and 300–4000  $\mu\text{g g}^{-1}$  (Table S1), which makes it possible to precisely measure the U-Th-Pb isotopic composition by either traditional TIMS or *in situ* (laser ablation or ion probe) techniques. However, several factors have to be taken into account before using this ore mineral for radiometric dating.



**Figure 6.** Th-Pb ages of bastnäsites from Guposhan (Guangxi, China), Zagi Mountain (Pakistan), Mountain Pass (California, USA), Red Cloud Fluorite Mine (New Mexico, USA), Zomba-Malosa (Chilwa, Malawi) and Ambatofinandrahana (Madagascar). [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

Bastnäsite is easily altered and replaced by secondary zircon, apatite, monazite and other minerals. Some petrographic observations indicate that this mineral is susceptible to alteration during the late stage evolution of agpaitic magmas or thermal fluid activity (Williams-Jones *et al.* 2000). In our study, we observed that some bastnäsite samples display multi-stage alteration (BO679 from Bayan Obo). Consequently, *in situ* measurement techniques are preferable for U-Th-Pb isotopic determination.

Another problem relates to the U-Pb closure temperature of the mineral. To fully understand the U-Pb closure temperature of bastnäsite, a theoretical calculation is illustrated in Figure 8 where The kinetic porosity model of Zhao and Zheng (2007) is applied to the calculation of diffusion coefficients. The diffusion coefficients and closure temperatures of bastnäsite and monazite are thus compared. As shown in Figure 8, it is clear that small bastnäsite grains (radius *ca.* < 100  $\mu\text{m}$ ) have fast Pb diffusion rates and low closure temperatures. However, for larger grains the closure temperatures of monazite and bastnäsite are almost identical (Figure 8b). Therefore, it is readily understandable that the Th-Pb ages of bastnäsite are younger than that of monazite from the Miaoyao Mine (Figures 1j, k and 5b).



**Figure 7.** Initial  $^{87}\text{Sr}/^{86}\text{Sr}$  and Nd isotopic compositions of bastnäsites investigated in this study. [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

The U-Pb decay system, with two independent decay chains ( $^{206}\text{Pb}/^{238}\text{U}$ ,  $^{207}\text{Pb}/^{235}\text{U}$ ), offers an internal check on a closed system. This is the main advantage of the U-Pb system over the Th-Pb system ( $^{208}\text{Pb}/^{232}\text{Th}$ ). However, although the  $^{206}\text{Pb}/^{238}\text{U}$  vs.  $^{208}\text{Pb}/^{232}\text{Th}$  age after  $^{207}\text{Pb}$

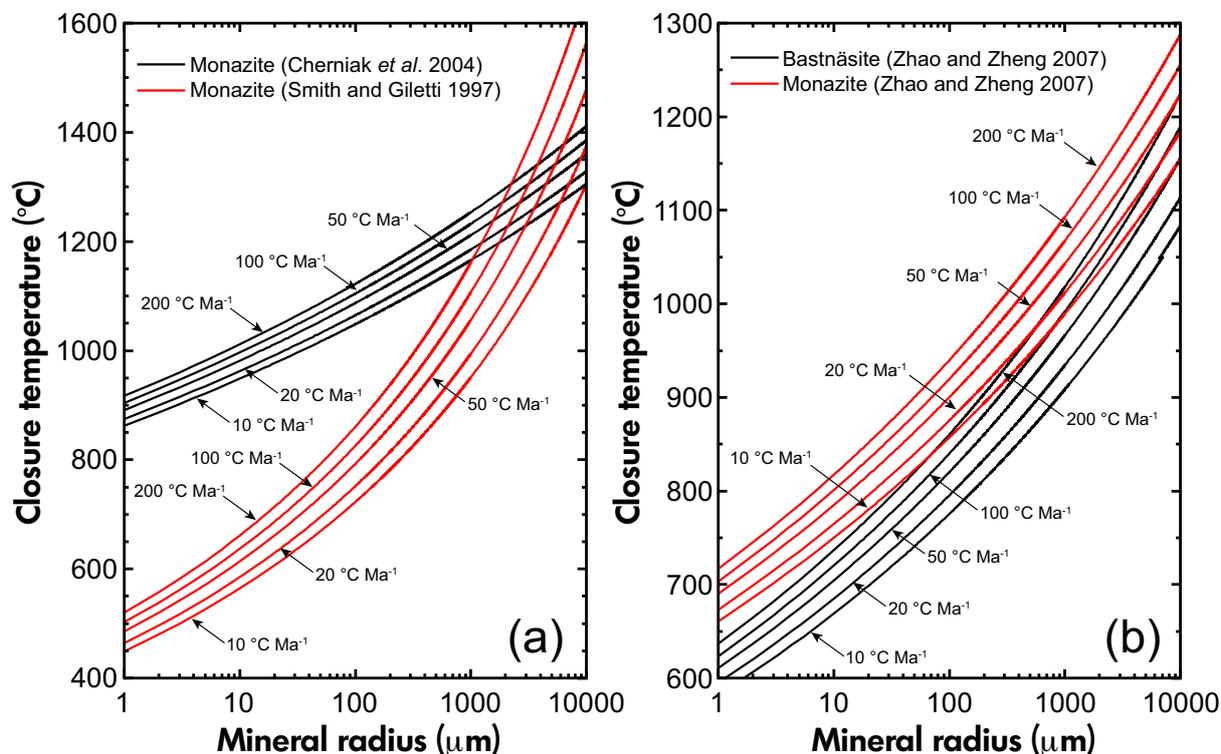
correction for bastnäsite samples from MNDC (e.g., LZ1384) is similar within uncertainties, the Th-Pb age has a better precision than the U-Pb age (Figure 2d). Moreover, other investigations of bastnäsite samples around the world also support this observation. As shown in Figure 9a, except for the Bastnäs and Tuva (K-9) samples, the remaining bastnäsite samples are characterised by much higher Th than U contents with Th/U ratios between 100 and 10000. The U contents of most bastnäsites are less than  $10 \mu\text{g g}^{-1}$  except for samples MNDC and Tuva (K-9). Except for Bastnäs, Red CFM and Tuva (K-9), the  $f_{206}$  (common  $^{206}\text{Pb}$  in proportion to total  $^{206}\text{Pb}$ ) of nearly all samples ranges from 10% to 100% and the  $f_{208}$  (common  $^{208}\text{Pb}$  in proportion to total  $^{208}\text{Pb}$ ) is less than 20%, in which the  $f_{208}$  for most of these is lower than 10% (Figure 9b). Therefore, considerably higher radiogenic  $^{208}\text{Pb}$  and considerably lower  $f_{208}$  give the Th-Pb system an overwhelming advantage over the U-Pb system for most bastnäsites.

Furthermore, the intermediate daughter isotope  $^{230}\text{Th}$  will decay with a half-life of  $\sim 7500$  a in the  $^{238}\text{U}$ - $^{206}\text{Pb}$  decay chain. The younger bastnaesite grains (e.g., LZ1384) with a

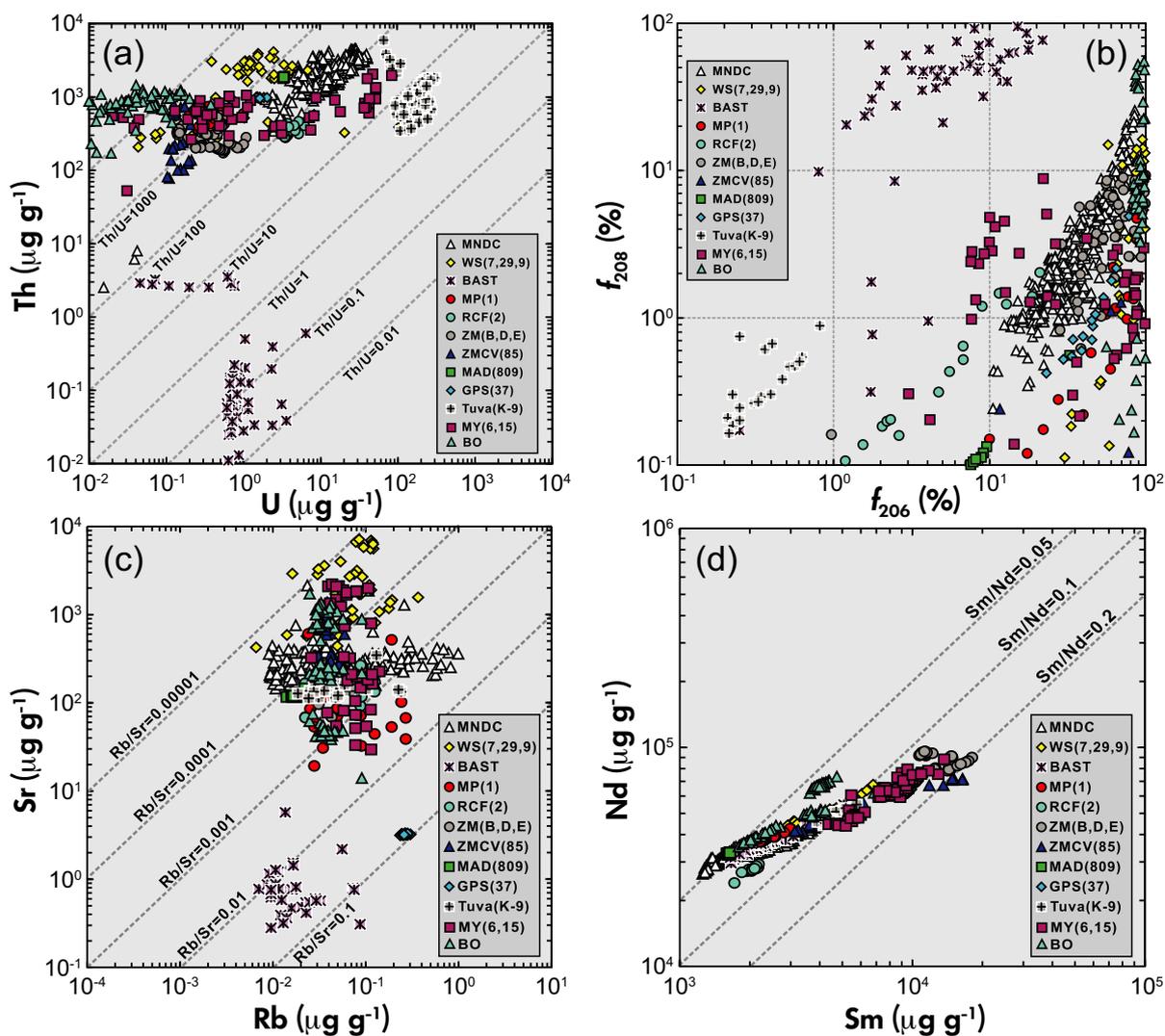
very high Th/U ratio (between 100 and 10000) will incorporate excess  $^{230}\text{Th}$  during crystallisation (Figure 2c). This excess  $^{230}\text{Th}$  will completely decay into  $^{206}\text{Pb}$ , which is not the daughter isotope of  $^{238}\text{U}$  within the mineral (Scharer 1984). This is why the  $^{206}\text{Pb}/^{238}\text{U}$  age after  $^{207}\text{Pb}$  correction can be a bit older than the  $^{208}\text{Pb}/^{232}\text{Th}$  age although they are similar within analytical uncertainty (Figure 2c). Hence, the excess radiogenic  $^{206}\text{Pb}$  makes the U-Pb method more complex for young bastnaesite grains with high Th/U ratios (Ling *et al.* 2016). A similar situation is also observed for many other Th-rich accessory minerals such as monazite, allanite and perovskite. Despite the difficulties due to the excess or deficit of radiogenic  $^{206}\text{Pb}$ , this problem does not exist for the Th-Pb system because each of the intermediate nuclei of the  $^{232}\text{Th}$ - $^{208}\text{Pb}$  decay chain has a very short half-life.

### Potential of bastnäsite for *in situ* Sr-Nd isotopic measurement

Our previous work (Yang *et al.* 2009b, 2014b) demonstrated that a Sr mass fraction of  $\sim 500 \mu\text{g g}^{-1}$  in bastnäsite grains is enough to produce an absolute



**Figure 8.** Theoretical calculation of Pb closure temperature of bastnäsite and monazite based on the methods of Smith and Giletti (1997), Cherniak *et al.* (2004) and Zhao and Zheng (2007). Note that bastnäsite has a Pb closure temperature of  $\sim 750$ – $800$  °C for a grain size of  $100 \mu\text{m}$  at cooling rates of  $10$ – $200$  °C  $\text{Ma}^{-1}$ . The diffusion coefficients of bastnäsite and monazite are from Zhao and Zheng (2007). [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]



**Figure 9.** (a, b) Comparison between U and Th elemental mass fraction and between the  $f_{206}$  and  $f_{208}$  values as well as the percentage of common  $^{206}\text{Pb}$  and  $^{208}\text{Pb}$  in total  $^{206}\text{Pb}$  and  $^{208}\text{Pb}$ , respectively, of bastnäsites analysed in this study. The plot shows that most bastnäsites, except for Bastnäs Mine bastnäsite, have much lower  $f_{208}$  than  $f_{206}$  values. (c, d) Variations of Rb-Sr and Sm-Nd in the bastnäsite samples. [Colour figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

precision of  $\pm 0.0001$  for the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio when using a large laser spot size (100–160  $\mu\text{m}$ ). The extremely low Rb mass fraction (and hence very low Rb/Sr ratios) of bastnäsite mean that isobaric interference of  $^{87}\text{Rb}$  on  $^{87}\text{Sr}$  is usually insignificant and can easily be accounted for (Yang *et al.* 2011c) (Figure 9c). As most bastnäsites yield moderate Sr mass fractions, there is usually sufficient Sr for *in situ* Sr isotopic measurement, except for some from the Bastnäs Mine, Zagi Mountain and Guposhan localities (Table 4).

As shown in Figure 9d, bastnäsite grains with low Sm/Nd ratios (0.05–0.2) are ideal for *in situ* Sm-Nd isotopic measurement by laser sampling. As summarised in Table 2, the results obtained by laser (e.g., Zagi E, LZ1384, K-9,

MAD809) are identical to solution data. This demonstrates the feasibility of our *in situ* Sm-Nd technique. Combined with their age and trace element, we can calculate the corresponding  $\varepsilon_{\text{Nd}}(t)$  values (Table 4). In summary, the data presented in this study demonstrate that reliable Sr and Nd isotopic compositions can be obtained by LA-MC-ICP-MS for the majority of natural bastnäsite samples.

### Bastnäsite RM for *in situ* U-Th-Pb dating and/or Sr-Nd isotopic measurement

Reference materials are essential for *in situ* analysis and are usually a prerequisite for precise analysis (e.g., zircon, apatite, monazite, titanite, etc.) (Wu *et al.* 2006, Liu *et al.* 2012).

An ideal reference material for *in situ* U-Th-Pb dating and/or Sr-Nd isotopic analysis of bastnäsite must meet the following criteria: (a) homogeneity in trace element content both within and between individual grains; (b) low Rb and reasonable Sr and Nd contents; (c) moderate U and Th mass fraction with low common Pb; (d) a well constrained crystallization age (e.g., U-Th-Pb age); (e) be available in sufficient quantity for the scientific community. Up to the present, there have been few available bastnäsite reference materials except for K-9.

As shown in Figures 9a, b, the Th/U ratio of K-9 is usually less than 10, which means excess  $^{206}\text{Pb}$  from  $^{230}\text{Th}$  has an insignificant effect on the  $^{206}\text{Pb}/^{238}\text{U}$  age. Additionally, as shown in the diagram of the  $f_{206}$  vs.  $f_{208}$  (both in the range of 0.2–0.8%), the effect of common  $^{206}\text{Pb}$  and  $^{208}\text{Pb}$  on U-Th-Pb dating for LA-ICP-MS is almost negligible. Based on the results of the present study, we suggest that K-9 bastnäsite is a good candidate as a reference material for U-Th-Pb dating and *in situ* Sr-Nd isotope measurement (Table 2). Although K-9 has a relatively young age, it has a homogenous composition and comes in good gem-quality size. Moreover, samples LZ1384 and ZM E, although with relatively young age, can also be considered as a good secondary reference material for both *in situ* U-Th-Pb dating and/or Sr-Nd measurements. In addition, MAD809 with an age of ~ 520 Ma and negligible common  $^{208}\text{Pb}$  is also a potential candidate as a reference material for Th-Pb age and *in situ* Sr-Nd measurement.

## Conclusions

We demonstrate the capability and applicability of bastnäsite for U-Th-Pb geochronology and Sr-Nd isotopic measurement using *in situ* laser ablation measurement. Laser ablation can yield reasonable U-Th-Pb ages for the bastnäsite group of minerals as they have high Th and moderate U contents. However, a common Pb correction is necessary if reliable results are to be expected. Moreover, our diverse investigation indicates that a Th-Pb age is preferable over the U-Pb age because of the relatively higher Th than U content in most bastnäsites. Bastnäsite usually contains moderate Sr and high Nd content, coupled with low Rb/Sr and Sm/Nd ratios and laser ablation can yield reliable Sr and Nd isotopic data. Therefore, *in situ* analysis is preferable for the determination of age and isotopic composition. As an important ore mineral, the minerals of the bastnäsite group can be considered a promising and significant geochronological tool suitable for research on carbonatites, alkaline rocks and related LREE deposits.

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## Supporting information

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The following supporting information may be found in the online version of this article:

Table S1. Major and trace element compositions of bastnäsite samples.

Table S2. *In situ* U-Th-Pb bastnäsite age data.

Table S3. *In situ* Rb-Sr bastnäsite isotopic data.

Table S4. *In situ* Sm-Nd bastnäsite isotopic data.

Appendix S1. Sample descriptions.

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