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Bastnaesite K-9: A Homogenous Natural Reference Material for In-situ U–Pb and Th–Pb Dating

Qiu-Li Li,^{a,b,c,*} Magdalena H. Huyskens,^d Yue-Heng Yang,^{a,b} Xiao-Xiao Ling,^{a,b} Qing-Zhu Yin,^d A. V. Nikiforov,^e and Xian-Hua Li^{a,b,c}

^a State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, P.R. China

^b Innovation Academy for Earth Science, Chinese Academy of Sciences, Beijing 100029, P.R. China

^c College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing 100049, P.R. China

^d Department of Earth and Planetary Sciences, University of California at Davis, One Shields Avenue, Davis, CA 95616, USA

^e Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, Staromonetnyi per. 35, Moscow, 119017 Russia

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ABSTRACT: Bastnaesite, a major economic rare earth element (REE) mineral, has been considered to serve as a U–Th–Pb geochronometer to record REE mineralization time. As previously noted, most bastnaesite contains more Th than U, with Th/U ratios larger than 1000 in some cases, indicating Th–Pb dating is more suitable than U–Pb geochronometry. *In-situ* bastnaesite Th–Pb dating by laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) method and Secondary Ion Mass Spectrometry (SIMS) has been performed. However, there is no independently determined, matrix matched Th–Pb bastnaesite reference material available. In this study, the bastnaesite “K-9” from Karasug siderite carbonatites (Tuva Republic) are evaluated as U–Pb and Th–Pb dating reference material by multiple methods. Major elements, including La, Ce, Pr, Nd, and F are homogenous at < 5 wt% level (1 relative standard deviation, RSD) as verified by electron microprobe analyses (EMPA). SIMS U–Th–Pb dating results prove its homogeneity and concordance of both U–Pb and Th–Pb system at < 2% level (1 RSD). Based on six ID-IRMS (isotope dilution isotope ratio mass spectrometry) analyses, $^{206}\text{Pb}/^{238}\text{U}$ age of 116.80 ± 0.13 Ma and $^{208}\text{Pb}/^{232}\text{Th}$ age of 116.59 ± 0.11 Ma are provided as recommended age data. In summary, K-9 bastnaesite is qualified to serve as an *in-situ* U–Pb and Th–Pb dating reference material and is expected to contribute significantly to the rapidly advancing bastnaesite geochronology in the coming future.

INTRODUCTION

Bastnaesite (or Bastnäsite) with a generic chemical formula of $\text{REE}(\text{CO}_3)\text{F}$, is a major economic rare earth element (REE) mineral in carbonatite or alkaline rocks. It can incorporate high contents of Nd, Sr, and Th(U), which make *in situ* Sr and Nd isotope composition measurement and U–Th–Pb dating feasible.^{1–4} The Pb closure temperature for bastnaesite has been calculated theoretically at around 750–800 °C for a grain size of 100 μm at cooling rates of 10–200 °C Ma^{–1}.² Thus, bastnaesite can effectively trace the evolution of mineralization fluids with timing records. Despite all these advantages, bastnaesite is not yet widely

exploited in geochronology. Firstly, bastnaesite in REE ore deposit are commonly rich in Th, with Th/U ratios > 1000 in some cases. Th–Pb dating method is more suitable than the U–Pb system for these samples.⁴ However, it is relatively difficult to measure Th by Thermal Ionization Mass Spectrometry (TIMS) because Th has poorer thermal ionization efficiency than U. Therefore, the Th–Pb system for mineral dating is rarely measured by TIMS method.⁵ *In-situ* methods, including LA-ICP-MS and ion probe (*i.e.* SIMS), were used as alternative methods for Th–Pb dating. In this case, a suitable, well characterized standard material is essential. Prior to this study a bastnaesite named K-9 with a

TIMS U–Pb determined age of 118 ± 1 Ma was used as a Th–Pb dating standard for LA-ICP-MS and SIMS dating with assumption of consistent U–Pb and Th–Pb ages.^{2,4} In this study, we carried out detailed EMPA for major elements, LA-ICP-MS for REE, SIMS for *in-situ* U–Th–Pb dating and ID-IRMS for U–Th–Pb geochronology on K-9 bastnaesite. We provide detailed information to describe K-9 bastnaesite as a qualified element concentration and U–Th–Pb dating standard reference material.

SAMPLE BACKGROUND

The studied bastnaesite K-9, as a candidate of U–Pb and Th–Pb dating reference material, is from the Karasug complex deposit (Tuva Republic) related to the carbonatites of the Central Tuva area. The Central Tuva carbonatite region contains several carbonatite occurrences, among which the Karasug carbonatite is the largest one and an ore field bearing REE–Ba–Sr–F–Fe deposit.^{1,6} This carbonatite field is located in the Ordovician and Silurian rocks at the wall of the Devonian Tuva Trough. Carbonatites are represented by ankerite–calcite at the first intrusive phase and ore-bearing siderite at the second phase.⁶ Bastnaesite is a typomorphic mineral in siderite carbonatites and accounts for around 2% in the hematite-bearing varieties. The studied K-9 bastnaesite occurs as evenly scattered transparent and semitransparent tabular light yellow and yellowish-brown grains ranging from 0.04×0.1 to 1×5 mm in size.¹

The K-9 bastnaesite was previously dated by ID-TIMS method and gave a weighted average ^{238}U – ^{206}Pb age of 118 ± 1 Ma, which is interpreted as the intrusion time of the siderite carbonatites.¹ This bastnaesite U–Pb age is consistent with Sm–Nd isochron age of 115 ± 7 Ma defined by bastnaesite and fluorite and Rb–Sr isochron age of 118 ± 9 Ma of mica.^{1,6} K-9 bastnaesite has been used as *in-situ* U–Pb and Th–Pb dating reference material in recent LA-ICP-MS and SIMS studies.^{2,4} Moreover, K-9 bastnaesite was measured for Sr and Nd isotope composition by *in situ* LA-ICP-MS, yielding $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.70570 ± 25 (2σ , $n = 12$) and $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.512780 ± 13 (2σ , $n = 45$), respectively. These values are in good agreement with $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.70556 ± 2 ($2\sigma_m$) and $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.512763 ± 4 ($2\sigma_m$) using solution MC-ICP-MS and ID-TIMS.^{1,3}

ANALYTICAL METHOD

More than 100 K-9 bastnaesite grains chosen randomly were mounted in epoxy. The mounts were polished to expose the crystal interiors. All samples were documented with transmitted and reflected light photomicrographs as well as back scattered electron (BSE) images to reveal their internal structures. EMPA for major elements, LA-ICP-MS for REE, and SIMS measurements to verify the U–Pb and Th–Pb homogeneity were conducted at the Institute of Geology and Geophysics, Chinese Academy of

Sciences (IGGCAS). ID-TIMS(Pb) and MC-ICP-MS (U, Th) analyses were conducted at University of California, Davis.

EMPA Analysis. Major element compositions, including La, Ce, Pr, Nd, F and Ca were measured by A CAMECA SXFiveFE EMPA (France), with an accelerating voltage of 15 kV, a beam current of 20 nA, and a beam size of 5 μm diameter. Natural minerals and synthetic oxides were used as standards. Matrix corrections were performed using the ZAF correction program supplied by the instrument manufacturer.

LA-ICP-MS Analysis. The REE content of K-9 bastnaesite was analysed using an Agilent 7500a ICP-MS (USA) equipped with an excimer 193 nm laser ablation system (USA). A spot size of 32 μm was used. External calibration was performed relative to NIST 612 standard glass (USA) and internal standardization was based on Ce electron microprobe measurements. The BCR-2 standard was monitored during all analytical sessions and treated as unknown during data reduction. Surface inclusion were avoided using a video camera. Subsurface inclusions such as zircons (Zr) and monazite (P), were identified using major element compositions obtained with the laser. The detection limit for LA-ICP-MS is below 0.1 ppm for most elements, and in run precision is better than 10%. Data were collected using time-resolved data acquisition in fast peak-jumping mode and processed using the GLITTER software.⁷ The REE patterns of bastnaesite were normalized to chondrite.⁸

SIMS Analysis. *In situ* U–Pb and Th–Pb analyses were performed using a CAMECA IMS 1280HR (France). The O_2^- primary ion beam was accelerated at -13 kV at an intensity of around 10 nA. The aperture illumination mode was used to produce an ellipsoidal spot of $20 \times 30 \mu\text{m}$ in size. Positive secondary ions were extracted with a 10 kV potential. The reference peak of ThO_2^+ is used for centering the secondary ion beam, energy and mass adjustments. A mass resolution of 8000 (defined at 50% peak height, the exit slit #3 for multi collector mode) was used at a dynamic multi ion-counting collector mode. The secondary ion intensities were measured including $^{204}\text{Pb}^+$, $^{206}\text{Pb}^+$, $^{207}\text{Pb}^+$, and $^{208}\text{Pb}^+$ on ion-counting collectors simultaneously and one ion-counting collector for $^{140}\text{Ce}^{16}\text{O}_2^{19}\text{F}_2$, ^{238}U , $^{232}\text{Th}^+$, $^{232}\text{Th}^{16}\text{O}$, $^{238}\text{U}^{16}\text{O}$ and $^{232}\text{Th}^{16}\text{O}_2$ by a peak jumping sequence. $^{238}\text{U}^{16}\text{O}_2^+$ is not suitable for minerals with high Th and F due to the inseparable interference of $^{238}\text{U}^{16}\text{O}^{19}\text{F}^+$ and $^{232}\text{Th}^{19}\text{F}_2^+$. Each measurement consists of 7 cycles, and the total analytical time is approximately 15 min, including 120 s pre-analysis sputtering to erase the gold coating.

The power law relationships between $^{206}\text{Pb}^+ / ^{238}\text{U}^+$ and $^{238}\text{UO}^+ / ^{238}\text{U}^+$, $^{208}\text{Pb}^+ / ^{232}\text{Th}^+$ and $^{232}\text{ThO}_2^+ / ^{232}\text{Th}^+$ were used for calibration of inter-elemental fractionations between Pb and U–Th, respectively.⁴ Th/U was calculated by previously defined linear relationship of $\text{Th}/\text{U} = 1.32 \times \text{ThO}^+/\text{UO}^+$. Th content was determined according to the ThO^+ ion yield of 2.25 cps/ppm/nA.⁴

TIMS and MC-ICP-MS analysis. The bastnaesite fragments were cleaned in distilled acetone in an ultrasonic bath multiple times, followed by cleaning and rinsing MilliQ water. Five single grains and one fraction of two grains (K9-F) were spiked with a ^{205}Pb - ^{229}Th - ^{233}U - ^{236}U tracer^{9,10} and dissolved in 6 M HCl at 100°C on a hotplate. Following evaporation, the samples were re-dissolved in concentrated HNO_3 and traces of concentrated HF. H_2O_2 was added prior to evaporation, and samples were redissolved in 0.5M HBr prior to chemical separation of Pb using anion exchange resin. U and Th were subsequently separated from the matrix elements using UTEVA resin (detailed separation procedures can be found in Iizuka et al. (2014)).¹¹ The Pb fraction was dried down with 0.05 ml of 0.02 M H_3PO_4 .

Pb isotopes were loaded onto zone refined Re filaments using 4 μL of 0.5% silicagel activator from Sigma-Aldrich¹² and measured on a *Triton Plus* thermal ionization mass spectrometer (TIMS) in static mode at University of California at Davis. Measurements were performed with ^{204}Pb in the axial secondary electron multiplier, while all other isotopes were measured on Faraday cups coupled with $10^{13} \Omega$ resistors.

Uranium and Th isotopes were measured on a *Neptune Plus* multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) in static mode on Faraday cups. The isotopes ^{235}U and ^{229}Th were coupled with $10^{12} \Omega$ amplifiers, while all other isotopes (^{232}Th , ^{233}U , ^{236}U , ^{238}U) were paired with a $10^{11} \Omega$ amplifiers. Both, U and Th data was corrected for solution blank and instrumental mass dependent fractionation using an exponential law. The $^{238}\text{U}/^{235}\text{U}$ ratio of the uranium isotopic standard CRM 112a often shows a small discrepancy to the certified ratio of 137.837¹³ and a linear correction was applied for the $^{238}\text{U}/^{236}\text{U}$ ratio.

U, Th and Pb blank amounts were 0.1, 0.17 and 1.3 pg, respectively. Data reduction for U-Pb was done using algorithms of Schmitz and Schoene (2007)¹⁴ and Th-Pb was calculated using PBDAT¹⁵ using the decay constants of Jaffey et al. (1971)¹⁶ and assuming a Th/U ratio of the magma of 4. Any common Pb in excess of the blank amount is assumed based on the Stacey and Kramers (1975)¹⁷ model at 100 Ma.

RESULTS AND DISCUSSION

EPMA. Based on 76 EMPA analyses, K-9 bastnaesite contains 20.97 ± 0.66 wt% La_2O_3 , 34.67 ± 0.38 wt% Ce_2O_3 , 2.84 ± 0.14 wt% Pr_2O_3 , 10.59 ± 0.40 wt% Nd_2O_3 , 7.23 ± 0.06 wt% F, and 0.09 ± 0.04 wt% CaO (the errors are reported at 1 standard deviation (SD), Table 1). The Ce_2O_3 contents are homogenous at around 1% level (1 RSD), supporting that it can be used as internal standardization for *in-situ* analysis. F content is homogenous at the same level. Other major elements show a little wider range of 2–5% at 1 RSD level.

Table 1 Major and Trace Element Data of K-9 Bastnaesite

Item	Value	Uncertainty 1 SD	Uncertainty 1 RSD %
By EMPA, wt.%, n=76			
F	7.23	0.06	0.8
La_2O_3	20.97	0.66	3.1
Ce_2O_3	34.67	0.38	1.1
Pr_2O_3	2.84	0.14	4.9
Nd_2O_3	10.59	0.40	3.8
CaO	0.09	0.04	44.4
By LA-ICPMS, ppm, n=38			
Sm	8621	897	10
Eu	1746	216	12
Gd	3316	513	15
Tb	228	43	19
Dy	688	157	23
Ho	78	21	27
Er	108	33	31
Tm	6.6	2.5	38
Yb	20	8	42
Lu	1.4	0.6	47

Fig. 1 Chondrite-normalized REE pattern of K-9 bastnaesite determined by LA-ICPMS. The diamonds show the relative standard deviation (shown on right axis) of concentration for each element.

LA-ICP-MS. A total of 38 REE analyses by LA-ICPMS method were conducted, and the contents (Table 1) are normalized to chondrite and shown in Fig. 1. K-9 bastnaesite is largely enriched in light REE and shows an exponential decrease in heavy REE. The standard deviation of each element shows a strong negative correlation with the corresponding concentration (diamonds in Fig. 1). This relationship suggests that the increasing wider range of HREE is not an uneven indication, but a large data uncertainty due to low content.

SIMS. In order to test the homogeneity, a total of 92 analyses of U–Pb and Th–Pb dating were performed on K-9 bastnaesite different grains from four mounts. This dataset shows 75–632 ppm

Fig. 2 SIMS data of K-9 bastnaesite, (a) Th concentration vs. Th/U, (b) the Th–Pb age distribution.

Fig. 3 The Tera-Wasserburg Plot of K-9 bastnaesite SIMS U–Pb data. The insert figure shows the ^{238}U – ^{206}Pb age distribution.

U, 100–6000 ppm Th and Th/U of 1–25 (Fig. 2), where most grains contain <300 ppm U, <2000 ppm Th and <5 Th/U. The ^{207}Pb -based f_{206} (the percentage of common ^{206}Pb in total ^{206}Pb) is around 0.3%, the f_{208} (the percentage of common ^{208}Pb in total ^{208}Pb) is around 0.4%.⁴ Because the U–Pb and Th–Pb ages are self-calibrated according to the ID-IRMS dating results, only the age range is evaluated here. All Th–Pb ages have 1 RSD of 1.7%, while the 1 RSD of U–Pb ages is 1.9% (Fig. 3). These data support that K-9 bastnaesite is an appropriate SIMS U–Pb and Th–Pb dating standard reference material.

Fig. 4 ID-IRMS U–Pb and Th–Pb dating results of K-9 bastnaesite. (a) $^{206}\text{Pb}/^{238}\text{U}$ age results, (b) $^{208}\text{Pb}/^{232}\text{Th}$ age results.

Table 2 ID-IRMS U–Pb and Th–Pb Isotopic Compositions and Ages of K-9 Bastnaesite

Sample	Radiogenic Isotope Ratios						Isotopic Ages (Ma)			
	Th U	$\frac{^{206}\text{Pb}}{^{204}\text{Pb}}$	$\frac{^{208}\text{Pb}}{^{232}\text{Th}}$	Err. %	$\frac{^{206}\text{Pb}}{^{238}\text{U}}$	Err. %	$\frac{^{206}\text{Pb}}{^{238}\text{U}}$	±	$\frac{^{208}\text{Pb}}{^{232}\text{Th}}$	±
K9-A	7.0	2569	0.005774	0.24	0.018269	0.19	116.71	0.22	116.36	0.28
K9-B	1.9	1795	0.005791	0.24	0.018292	0.16	116.85	0.18	116.71	0.28
K9-C	2.3	5475	0.005791	0.24	0.018295	0.14	116.87	0.16	116.71	0.28
K9-D	7.4	1250	0.005781	0.24	0.018254	0.28	116.61	0.33	116.52	0.28
K9-E	4.7	6545	0.005782	0.24	0.018261	0.17	116.65	0.19	116.54	0.28
K9-F	4.2	1381	0.005791	0.24	0.018306	0.17	116.94	0.20	116.72	0.28

ID-IRMS. Five single grains and one fraction of two grains were analyzed separately by ID-IRMS, and the results are listed in Table 2. Th/U ratios vary between 1.9 – 7.4. The measured $^{206}\text{Pb}/^{204}\text{Pb}$ ranges from 1800 to 6500, corresponding to f_{206} of 0.29% to 1.35%. The f_{208} is calculated at range of 0.38% to 3.6%. These common Pb proportion values are only a little higher than those during SIMS analyses, indicating tiny impurities with high common Pb in the grains. Six analyses yield consistent age values, with weighted average $^{206}\text{Pb}/^{238}\text{U}$ age of 116.80 ± 0.13 Ma ($n=6$, MSWD = 1.5, Fig. 4a) and $^{208}\text{Pb}/^{232}\text{Th}$ age of 116.59 ± 0.11 Ma ($n=6$, MSWD = 1.1, Fig. 4b). The consistency between U–Pb and Th–Pb age indicates that K-9 bastnaesite has a closed U–Th–Pb system. This new recommended age data is 1% younger than previous used value of 118 ± 1 Ma.¹ The previous *in-situ* dating results with K-9 bastnaesite as standard should be accordingly shift 1% younger, but consistent within uncertainties.^{2–4}

CONCLUSIONS

In this study, the K-9 bastnaesite, separated from Karasug siderite carbonatites (Tuva Republic) are evaluated as U–Pb and Th–Pb dating reference material by multiple methods. Dataset of 76 EMPA analyses demonstrate its homogeneity of major elements at < 5 wt% level (1 RSD). SIMS U–Th–Pb dating results prove its homogeneity of U–Pb and Th–Pb system at <2% level (1 RSD). Six ID-IRMS analyses provide $^{206}\text{Pb}/^{238}\text{U}$ age of 116.80 ± 0.13 Ma and $^{208}\text{Pb}/^{232}\text{Th}$ age of 116.59 ± 0.11 Ma as recommended age data. All the analyses support that K-9 bastnaesite can be used as a qualified *in-situ* U–Pb and Th–Pb dating reference material and has been well characterized. The minerals are available on request sent to the corresponding author.

AUTHOR INFORMATION

Corresponding Author

*Q.-L. Li

Email address: liqiuli@mail.iggcas.ac.cn

Notes

The authors declare no competing financial interest.

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