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In situ U-Pb dating of bastnaesite by LA-ICP-MS

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Abstract Bastnaesite, a common accessory mineral in REE ore deposits, is ideal for U-Pb isotopic
dating because of its relatively high U and Th contents. We report an analytical procedure for U-Pb
dating of this mineral using an 193 nm ArF excimer laser ablation system coupled to an Agilent
7500a (LA-ICP-MS). Laser-induced elemental fractionation and instrumental mass discrimination
were externally corrected using an in-house bastnaesite standard (K-9). The fluence, spot size and
repetition rate of laser was evaluated to assess their effects on age determination in detail. The matrix
effect on zircon and bastnaesite was also investigated and compared in full during laser sampling.
The results indicate that a matrix-matched standard reference material is essential. In order to
validate and demonstrate the effectiveness and robustness of our developed protocol, we dated
several bastnaesite samples from the Himalayan Mianning-Dechang REE belt, South-West China.
The U-Pb ages of ~ 31 to 34 Ma obtained on bastnaesites from the Maoniuping, Diaoloushan,
Zhengjialiangzi and Lizhuang, are in good agreement within error, but differ from the wide range of
age (10 – 40 Ma) obtained using K-Ar and Ar-Ar method on biotite and muscovite and U-Pb in
zircon. These dating applications demonstrate the reliability and feasibility of our established method.
In summary, the LA-ICP-MS dating of bastnaesite can be a complementary dating method to the
more established TIMS and SIMS technique with its advantages of rapidity, moderate spatial
resolution and relatively low cost.

Keywords Bastnaesite; REE deposits; U-Th-Pb isotopic dating; LA-ICP-MS

1. Introduction

The ability to accurately determine the time of mineralization is crucial for understanding the
genesis of endogenous ore deposits and forming processes.\textsuperscript{1} According to the present knowledge, numerous radiometric dating methods have been applied to date mineralization, including K (Ar)-Ar, Rb-Sr, Sm-Nd, Lu-Hf, Re-Os and U-Pb techniques. Among these techniques, U-Pb method has been considered as the most powerful tool to get precise and accurate age of mineralization. However, for most ore deposits, U-Pb method is not applicable due to the lack of suitable minerals. This problem is also encountered in dating rare earth element (REE) deposits which is generally related to the occurrences of alkaline and carbonatite rocks.\textsuperscript{1-3}

Bastnaesite (Bastnäsite, (Ce)CO$_3$F), a carbonate-fluoride mineral, is a common accessory mineral in REE ore deposits and it was firstly described by the Swedish chemist Wilhelm Hisinger in 1838 and named after the Bastnäs mine near Riddarhyttan, Västmanland, Sweden. This mineral can occur as very high quality specimens (Zagi Mountians, Pakistan), but mostly it occurs in alkali granite, syenite and associate pegmatite, and carbonatite. The mineral has a variable composition among La, Ce, Nd, Y and Ba, and forms a group mineral of bastnaesite, parasite, cordylite, Huangheite, cebaite and Zhonghuacerite. Whatever, bastnaesite is one of the most important REE carriers as monazite (Mountain Pass in USA, and Bayan Obo in China). In contrast to monazite, however, bastnaesite is less investigated for its U-(Th)-Pb and other isotopic systems, despite its fairly wide occurrence or distribution in carbonatites, alkaline rocks, and associated REE deposits.\textsuperscript{2-5}

To the best of our knowledge, bastnaesite has been dated using La-Ba method by traditional isotopic dilution thermal ionization mass spectrometer (ID-TIMS).\textsuperscript{6} Using this method, an isochron age of 586.8 ± 3.7 Ma was obtained for the bastnaesite from Gakara deposit in Burundi. The pioneering works on the Bayan Obo deposit by Wang et al.\textsuperscript{2} indicated that bastnaesite there contains much less amount of U (mostly less than 0.5 ppm), which makes unavailable to get its U-Pb age,
although a Th-Pb age of 555 to 475 was obtained. Considering that the associated monazite contain extremely low amount of U as well, it is unknown that whether bastnaesite in other area contain the similar level of U concentration. Recently, however, Salnikova et al.\(^4\) conducted a U-Pb isotopic analysis for the bastnaesite from the Karasug carbonatite in central Mongilia, and obtained a concordant age of 118 ± 1 Ma. Therefore, it was demonstrated that bastnaesite could be an important mineral to constrain the age of REE mineralization. It is also interesting to note that the obtained $^{206}\text{Pb}/^{204}\text{Pb}$ ratios for the two analyses are 488 (U of 222 ppm) and 1440 (U of 653 ppm), respectively, which corresponds to 3.8% and 1.3% of $f_{206}$ ratios. Considering that the studied samples were formed in the Mesozoic, most bastnaesite, especially those formed in Precambrian, might have low to negligible common lead, as usually dated minerals of zircon, baddeleyite, monazite and xenotime. However, most REE deposits have a complicated history due to intensive fluid activities. For example, the Bayan Obo, the most important REE deposit in the world, is still in debate for its formation age due to later alteration.\(^2,^3\) In this case, in situ U-Pb analytical technique is desired to decipher the complex history of the REE mineralization. In addition, the crystal structure of bastnaesite can accommodate high concentrations of light rare earth elements (LREE), with Nd content of ~10 wt %, which makes it an ideal candidate for in situ Nd isotopic analyses.\(^5\) This kind of data would definitively provide important information on the origin and genesis of the ore deposits.\(^1\) Therefore, in this study, we developed an \textit{in situ} protocol of U-Pb dating bastnaesite by LA-ICP-MS and explored its application as a dating method. The fluence, spot size and repetition rate of laser was evaluated to check the age of bastnaesite in detail. The matrix effect on zircon and bastnaeiste was also investigated. The reliability and validity of the proposed methodology have been tested by using samples of bastnaesite collected in the Himalayan
Mianning-Dechang REE belt, South-West China. These samples were previously dated by conventional Rb-Sr, Ar-Ar and U-Pb dating methods. Our results indicate that bastnaesite can contain a significant amount of common Pb, therefore indicate a common Pb correction is necessary in order to give a correct U-Pb age, which differs from the previous observation.1

2. Experimental

All bastnaesite samples investigated in this work were analyzed for major, trace element concentration and U-Th-Pb ages by in situ LA-ICP-MS techniques. All analyses were conducted at State Key Laboratory of Lithospheric Evolution at the Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing.

2.1. Sample preparation

All bastnaesite grains were mounted in epoxy in 2.5 cm diameter circular grain mounts and polished until the bastnaesite grains were just revealed. Transmitted, reflected and back-scattered electron microscopic images were used to examine the internal structure, such as inclusions, crack and growth zones which provide a base map for selection of ablation spots. The grain mount was cleaned and left in 2% HNO₃ for several min prior to laser ablation analysis.7

2.2. Bastnaesite reference material

Well-characterized matrix-matched reference material is crucial for in situ analytical technique. Unlike other widely distributed and well characterized mineral standards such as zircon (e.g., 91500, etc.), monazite (e.g., 44069, etc), apatite (e.g., Durango, etc) and titanite (e.g., BLR-1 etc), so far,
there no reported reference material of bastnaesite for in situ laser ablation. The primary bastnaesite
in-house reference standard analyzed in this study was K-9, which has yielded a TIMS concordian
age of $118 \pm 1$ Ma ($\text{MSWD} = 0.05$, probability = 0.82). This standard was collected from the
supergene altered hematite-bearing siderite carbonatite with baritocelestine. Moreover, its ID-TIMS
U-Pb age is in agreement with the Sm-Nd ages obtained on bastnaesite and fluorite from the
carbonatite, and is also consistent with the age of $118 \pm 9$ Ma obtained by the Rb-Sr method on mica
from carbonatites. A detailed description on samples location can be found in SalNikova et al.\textsuperscript{4}

2.3. Instrumentation

Table 1

Experiments were carried out using an Agilent 7500a ICP-MS (Agilent Technologies, Japan) in
combination with an excimer 193 nm laser ablation system (Geolas 2005, Lambda Physik, Gottingen,
Germany). The laser spot size was adjusted to 5, 10, 16, 24, 32, 44, 60, 90, 120 and 160 µm and the
frequency can be adjusted from 1 to 20 Hz.\textsuperscript{8}

2.4. Mass spectrometry

The analytical procedure for bastnaesite U-Th-Pb dating and trace elements compositions
(including REE) is similar to the zircon, monazite and apatite dating by LA-ICP-MS. A summary of
the LA-ICP-MS specifications and typical operating conditions used in this study are presented in
Table 1. Helium was used as the carrier gas through the ablation cell and was merged with argon
(make-up gas) downstream the ablation cell.\textsuperscript{9} Prior to analysis, the Pulse/Analogy (P/A) factor of the
detector was calibrated using standard tuning solution. The carrier and make-up gas flows were
optimized to obtain maximum signal intensity for $^{238}\text{U}^+$, while keeping the ThO$^+/\text{Th}^+$ ratio below 0.5%. All LA-ICP-MS measurements were carried out using time resolved analysis in fast, peak jumping mode. Each spot analysis consists of an approximate 20 s background acquisition and a 65 s sample data acquisition. 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 external bastnaesite standard (K-9) was used to correct for U-Th-Pb fractionation and instrumental mass discrimination. Two K-9 analyses were measured after every five unknown bastnaesite spot. In this work, the cratering model rather than rastering ablated model was adopted and the total ablated time took about 60 second for a single standard or sample measurement.

2.5. Data reduction

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-Pb dating, whereas the $^{235}\text{U}$ signal was calculated from $^{238}\text{U}$ on the basis of the ratio $^{238}\text{U}/^{235}\text{U} = 137.88$. All the 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 standard during the process of sample analyses were regressed and corrected using the reference values. The concordia age of 118 Ma was used as the reference value. Standard deviations of the calibrated isotope ratios include those from sample, external standard, and deviations from the reference values of external standard. The uncertainty was set at 2 %. The U-Pb concordia ages and weighted mean ages were calculated using the ISOPLOT/EX 3.23 software package. Trace concentrations were calibrated against the NIST SRM 610 as external reference material using $^{140}\text{Ce}$ as an internal standard using the Glitter software. Ce was used as an internal standard for calibration purpose.

Accurate correction for laser-induced elemental fractionation and instrumental drift is an
important consideration in U-Pb dating of accessory minerals in LA-ICP-MS measurement. In this study, we used the well characterized matrix-matched in-house K-9 standard protocol to correct for U-Pb elemental fractionation and variations in sensitivity during an analytical session. The procedure is similar to the one used for zircon dating by LA-ICP-MS with GJ-1 or 91500 standard.11,12 Another significant difficulty of U-Pb dating of bastnaesite is the present high common Pb content, which is incorporated from the parental magma in the early phase of mineral crystallization.13 As recently noted by Chew et al.13, 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. In this study, the $^{207}$Pb correction method was applied for common Pb correction using the two-stage model of Stacey and Kramers15 (refer also to Williams16) and the $^{206}$Pb/$^{238}$U weighted ages were calculated using Isoplot 3.23. Moreover, the intercepts of regression line through the raw data on a Tera-Wasserburg plot provide an estimate of the $^{207}$Pb/$^{206}$Pb for the common Pb component (upper intercept) and the inferred crystallization age (lower intercept).17,18

3. Results and discussion

3.1. Matrix effect

The lack of well-characterized matrix-matched reference materials to correct for elemental fractionation is significant obstacle for in situ U-Pb dating of accessory minerals by LA-ICP-MS or SIMS techniques. Therefore, we first evaluated the matrix effect on in situ U-Pb age analysis of bastnaesite (K-9) and zircon (GJ-1) reference materials using zircon standard 91500 as external...
calibrating standard during the same analytical session. When the 91500 zircon was used as external calibration standard, the obtained weighted $^{206}\text{Pb}/^{238}\text{U}$ age for the K-9 standard is 107.86 ± 0.89 Ma (MSWD = 0.83, n = 18, Fig. 1a), which is 10 % younger than the published reference value of 118 ± 1 Ma. However, the weighted $^{206}\text{Pb}/^{238}\text{U}$ age of 611.0 ± 5.7 Ma (MSWD = 0.76, n = 18, Fig. 1b) for GJ-1 agrees well with the published recommended value using ID-TIMS (608.53 ± 0.37 Ma). Similarly, if bastnaesite K-9 was used as external calibration standard, the weighted $^{206}\text{Pb}/^{238}\text{U}$ age of K-9 as a unknown sample is 118.0 ± 1.0 Ma (MSWD = 0.66, n = 18), in good agreement with the classic ID-TIMS data. However, the weighted $^{206}\text{Pb}/^{238}\text{U}$ age (666.9 ± 6.5 Ma, MSWD = 0.94, n = 18) of GJ-1 is 10% older than the reference value. These results means that there are significant matrix effects between bastnaesite and zircon during laser ablation, indicating that a suitable matrix-matched standard is essential and crucial for in situ U-Pb dating of bastnaesite using LA-ICP-MS. Although the exact reason for significant matrix effect is still unknown, the similar situation had been previously observed and reported for titanite, allanite, xenotime, monazite and zircon during in situ U-Pb dating by LA-ICP-MS technique.

3.2. Laser spot size, repetition rate and fluence

Ablation experiments on the bastnaesite (K-9) grain were carried out using a spot ablation routine at repetition rates of 4, 6, 8 and 10 Hz and on sample fluences of 4, 6, 8 and 10 J/cm². Spot sizes of 16, 32, 44 and 60 µm were used to obtain enough intensity for the less abundant isotopes, and to avoid potential zonation. As shown in Figure 2 a, b, c & d and Table 2, at a constant repetition rate of 8 Hz and 44 µm crater size, with increasing fluences of 4, 6, 8 and 10 J/cm², the obtained
weighted $^{206}\text{Pb}/^{238}\text{U}$ ages of K-9 for every ten analyses are $125.5 \pm 2.0$ Ma (MSWD = 1.07, 4 J/cm$^2$), $116.9 \pm 1.6$ Ma (MSWD = 0.73, 6 J/cm$^2$), $117.3 \pm 1.5$ Ma (MSWD = 0.50, 8 J/cm$^2$) and $117.4 \pm 1.5$ Ma (MSWD = 0.33, 10 J/cm$^2$), respectively. Similarly, as shown in Figure 2 e, f & g, at a constant repetition rate of 8 Hz and fluence of 8 J/cm$^2$, with increasing crater size 16, 32 and 60 $\mu$m, the above ages are $120.3 \pm 4.8$ Ma (MSWD = 3.6, 16$\mu$m), $119.4 \pm 1.4$ Ma (MSWD = 0.34, 32$\mu$m) and $119.5 \pm 1.2$ Ma (MSWD = 1.18, 60$\mu$m), respectively. Additionally, as shown in Figure 2 h, i & j, at a constant fluence of 8 J/cm$^2$ and 44 $\mu$m crater size, with increasing repetition rate from 4, 6 and 10 Hz, our obtained weighted $^{206}\text{Pb}/^{238}\text{U}$ ages of ten analyses for each are $116.9 \pm 2.1$ Ma (MSWD = 1.9, 4Hz), $117.1 \pm 1.2$ Ma (MSWD = 0.50, 6Hz) and $118.0 \pm 1.2$ Ma (MSWD = 0.92, 10Hz), respectively.

The above experiments indicate that there is no significant age variations with variable spot size, repetition rate and fluence intensity. As shown in Figure 2 and Table 2, the spot size have more significant effect on the age error than repetition rate and fluence because of its less ablated material and less intensity signal (e.g., 16 $\mu$m). Therefore, a spot size of 44 $\mu$m was applied with a repetition rate of 8 Hz, corresponding to an energy density of $\sim$ 10 J/cm$^2$, these condition were applied to the following samples analyses.

4. Application

Figure 3 & 4

In order to demonstrate the effectiveness and robustness of our developed protocol, we dated numerous bastnaesite samples and compared with the results with available published data. The bastnaesite grains were prepared following the procedure described in sample preparation. The chemical compositions of theses samples for REE contents were listed in Appendix and the REE
patterns are shown in Figure 3.

As well-known, the Himalayan Mianning-Dechang (MD) REE belt, western Sichuan, SW China, is approximately 270 km long and 15 km wide, and contains total reserves of more than 3 Mt of LREE, including one giant (Maoniuping), one large (Dalucao) and a number of small-medium REE deposits (Moluozhai and Lizhuang). REE mineralization is associated with Himalayan carbonatite–alkaline complexes, which consist of carbonatitic sills or dykes and associated alkaline syenite stocks. A few available dating data define a Himalayan metallogenic epoch (10 – 40 Ma) by K-Ar or Ar-Ar method on biotite and muscovite or U-Pb dating of zircon by SHRIMP.

The Maoniuping (MNP) is a world-class REE deposit, following only the Bayan Obo REE-Nb-Fe (China) and Mountain Pass (USA) REE deposits in terms of size. Previously, K-Ar dating of hydrothermal minerals (biotite and magnesio-arfvedonite) yielded a age ranging from 27.8 ± 0.5 Ma to 40.3 ± 0.7 Ma, indicating relatively wide REE mineralization age for this deposit. The analysed sample of MNP4256 contains ~ 11 ppm of U and ~ 2467 ppm of Th, with Th/U ratios of ~ 243. Twelve analyses yield a lower intercept age of 31.1 ± 3.9 Ma, which is identical to the 207Pb corrected age of 30.7 ± 3.0 Ma (Fig. 4a). Therefore, we consider that this deposit was formed at ~ 31 Ma.

Muluozhai is composed by two small deposits of Diaoloushan (DLS) and Zhengjialiangzi (ZJLZ). The obtained K-Ar ages from potassium feldspar and phlogopite are 31.2 and 35.5 Ma, respectively. The analysed sample of DLS contains ~16 (DLS108), 12 (DLS110) ppm of U and ~2220 (DLS108), ~1603 (DLS110) ppm of Th, with Th/U ratios of ~144 (DLS108), ~136 (DLS110), respectively. The obtained intercept ages are 32.2 ± 2.6 (DLS108) and 34.9 ± 3.1 Ma (DLS110), with 207Pb corrected ages of 31.8 ± 2.1 (DLS108) and 33.0 ± 2.6 Ma (DLS110) (Figure 4b & c).
Zhengjialiangzi deposit, the analysed sample of ZJLZ103 contains ~ 7.8 ppm of U and ~ 1826 ppm of Th, with Th/U ratios of ~ 272. Nineteen analyses for the sample yield intercept and \(^{207}\)Pb corrected ages of 33.3 ± 3.3 and 33.3 ± 2.6 Ma, identical to those obtained from the Maoniuping deposit. Another deposit in the area is Lizhuang (LZ), which gives a K-Ar age ranging between 27.1 and 30.6 Ma. The analysed sample of LZ122 contains ~ 27 ppm of U and ~ 4555 ppm of Th, with Th/U ratios of ~ 167. During this study, sample LZ122 was collected for its U-Pb analysis, the obtained intercept and \(^{207}\)Pb corrected ages are 32.9 ± 3.7 and 33.0 ± 2.1 Ma, respectively (Figure 4e), consistent with those from the Maoniuping and Muluozhai deposits. Dalucao (DLC) is the second largest deposit in the MD REE belt. The obtained K-Ar ages from biotite and muscovite range from 9.8 to 14.5 Ma,\(^{29}\) which is slightly younger than the Rb-Sr isochron age of 15.3 ± 0.5 Ma for REE ores. U-Pb dating of zircons from carbonatite and syenite yielded age of 12.99 ± 0.94 and 14.53 ± 0.31 Ma, respectively.\(^{26}\) Our analysed sample of DLC43 contains ~ 3.0 ppm of U and ~ 475 ppm of Th, with Th/U ratios of ~ 158. Twelve analyses on this sample yield a lower intercept age of 21.9 ± 5.9 Ma, with \(^{207}\)Pb corrected age of 20.8 ± 4.9 Ma (Figure 4f), about 10 Ma younger than those from other deposits presented above. However, it is noted that the obtained ages from this sample show large errors than other samples studied due to its lower U concentration. The age data presented above indicated that all of the deposits in the area were synchrously formed at ~31-34 Ma, consistence with the K-Ar or Ar-Ar ages for most deposits, except of Dalucao. For the latter, our U-Pb age is significant older than the reported K-Ar, Rb-Sr and U-Pb ages. Although this discrepancy needs more analyses to be verified, the consistence of ages among other deposits suggests that our data are reliable. This practical dating example demonstrated the applicability and promising prospect of our developed methodology for commonly
bastnaesite-bearing carbonatite, alkaline rocks and related REE deposits in the near future. Moreover, it is noted from the data that our samples contain significant common lead although exact amounts are not available from laser ablation analyses.

5. Conclusions

In this contribution, we demonstrated the possibility of bastnaesite as a dating mineral for U-Pb geochronology using the LA-ICP-MS. The relatively easy sample preparation and operating system combined with the short running time make it an ideal mineral for dating bastnaesite-bearing rocks. Laser-induced elemental fractionation and instrumental mass discrimination were externally corrected using the reference material K-9. The laser fluence, spot size and repetition rate was evaluated to assess the quality of the obtained age in detail. The matrix effect on zircon and bastnaesite was investigated and compared in detail during laser sampling. Our result indicates that the matrix effects between bastnaesite and zircon maybe significant. In order to validate and demonstrate the efficacy and strength of our developed protocol, we tested the in situ U-Pb dating application on several bastnaesite samples collected in SW China, which show the reliability of our established method. The minerals of the bastnaesite group have a fairly wide distribution and a relatively high U and Th Pb contents making it an ideal mineral for U-Pb isotopic dating LA-ICP-MS can be considered a promising geochronological tool suitable for U-Pb dating of carbonatites, alkaline rocks, and related REE deposits.

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We are greatly indebted to Dr. E. B. Sal'Nikova for kindly providing the K-9 bastnaeiste standard. We are particularly thankful to Dr. Yamirka Rojas-Agramonte for correcting the English. We also thank Laura Petley for her patient while handling our manuscript and also grateful for the critical and insightful comments from two anonymous referees who improved the quality of the manuscript.

References


Figure 1 matrix effect on bastnaesite and zircon is investigated in detail during laser sampling U-Pb dating. The results show that there is significant matrix effect on these minerals. Figure a & b show the weighted average $^{206}\text{Pb}/^{238}\text{U}$ ages of bastnaesite (K-9) and zircon (GJ-1) samples using the zircon standard (91500) as external calibration, while Figure c & d show that of bastnaesite (K-9) and zircon (GJ-1) samples using bastnaesite (K-9) as external calibratin standard during the same analytical session, indicating that suitable matrix-matched standard is crucial for in situ U-Pb dating of bastnaesite using LA-ICP-MS. The MSWD shows the mean square of weighted deviates.
Figure 2 Weighted average $^{206}\text{Pb} / ^{238}\text{U}$ ages of K-9 bastnaesite calculated during the same analytical session using 16, 32, 60 µm spot size at repetition rate of 4, 6, 10 Hz and on sample fluence of 4, 6, 10 J/cm$^2$ under the external standard fixed laser parameter using 44 µm spot size at repetition rate of 8 Hz and on sample fluence of 8 J/cm$^2$. The MSWD shows the mean square of weighted deviates.

Figure 3 Chondrite-normalized REE distribution pattern of bastnaesite

Figure 4 Tera-Wasserburg plots for in situ U-Pb data and $^{207}\text{Pb}$ common lead correction for five different localities of bastnasites from the Mianning-Dechang belt REE deposits (Sichuan SW China). Error bar is shown 1σ errors. These results indicate that the narrow mineralization age of Mianning-Dechang REE belt is consistent with a biotite K-Ar or Ar-Ar age within error.
Table 1. The typical operating conditions for *in situ* U-Pb dating of bastnaesite

<table>
<thead>
<tr>
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<td>Auxiliary gas</td>
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<td>Sample gas</td>
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<td>Sensitivity</td>
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<td>Integration time</td>
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<td>6 ms for Rb, Sr, Ba, Nb, Ta, Zr, Hf and REE, 15 ms for $^{204}$Pb, $^{206}$Pb &amp; $^{208}$Pb, 30 ms for $^{207}$Pb, 10 ms for $^{232}$Th &amp; $^{238}$U,</td>
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<td><strong>GeoLas 2005 laser ablation system</strong></td>
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<tr>
<td>Wavelength</td>
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<tr>
<td>Pulse length</td>
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<tr>
<td>Energy density</td>
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<tr>
<td>Spot sizes</td>
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<tr>
<td>Repetition rate</td>
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Table 2: Age comparison with different laser experimental parameters

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<th>8 J/cm²</th>
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<td>1. Fluence (changing)</td>
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<td>206Pb/238U weighted age (Ma)</td>
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<td>116.9 ± 1.6</td>
<td>117.3 ± 1.5</td>
<td>117.4 ± 1.5</td>
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<td>[0.50]</td>
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<td>[0.68]</td>
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<td>[0.97]</td>
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<td>2. Spot size (µm) (changing)</td>
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<td>Fixed 8 J/cm² &amp; 8 Hz</td>
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<tr>
<td>206Pb/238U weighted age (Ma)</td>
<td>120.3 ± 4.8</td>
<td>119.4 ± 1.4</td>
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<td>119.5 ± 1.2</td>
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<tr>
<td>[MSWD]</td>
<td>[3.6]</td>
<td>[0.34]</td>
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<td>[1.18]</td>
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<td>[0]</td>
<td>[0.96]</td>
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<td>[0.30]</td>
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<td>3. Repetition rate (changing)</td>
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<tr>
<td>206Pb/238U weighted age (Ma)</td>
<td>116.9 ± 2.1</td>
<td>117.2 ± 1.2</td>
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<td>118.0 ± 1.2</td>
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<td>[MSWD]</td>
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<td>[Probability]</td>
<td>[0.044]</td>
<td>[0.88]</td>
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Figure 1
Figure 2
Figure 3
Figure 4