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Ablation behavior and constraints on the U–Pb and Th–Pb geochronometers in titanite analyzed by quadrupole inductively coupled plasma mass spectrometry coupled to a 193 nm excimer laser

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ABSTRACT

U–Th–Pb geochronology of titanite by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a promising technique to constrain the history of igneous and metamorphic rocks. However, the quality of the resulting ages depends strongly on protocol adopted for the analyses and data reduction. There is no general agreement on the laser ablation settings and methodology that should be applied for titanite LA-ICP-MS geochronology. In particular it is essential to define an analytical procedure that could minimize the elemental fractionation for titanite U–Th–Pb geochronology, and to evaluate if non matrix-matched standards and samples (e.g. zircon and titanite) are suitable to obtain precise and accurate ages. In this study, ablation experiments were carried out in spot mode using an ArF 193 nm excimer laser coupled to a quadrupole ICP-MS, with varying fluence, spot size and repetition rate conditions. The ablation behavior of the Khan titanite reference material was described in details and compared to the Plešovice zircon standard. The ratio-of-the-mean intensity method was used for data reduction. Three sources of fractionation and systematic errors between zircon and titanite are considered together: mass bias coefficients, shape of the time-dependent fractionation, and differences of ablated volumes. Even if the laser-induced elemental fractionation and matrix effects can be minimized between the Plešovice zircon standard and the Khan titanite, a matrix-matched standardization with a titanite standard is required for precise U–Th–Pb titanite ages, as well as at low frequency and fluence conditions.

1. Introduction

Titanite ($CaTiSiO_5$) is a common accessory mineral in many magmatic and metamorphic rocks. It is commonly involved in pressure- and temperature-dependant reactions with other Ca- and Ti-bearing phases, and element substitutions occurring in titanite enhance its stability. The Si site can contain Al, while Ti can be substituted by Al and Fe^{3+} and, to a lesser extent, by Nb and Ta [1]. Titanite is also an important host for REE, occupying the Ca sites. The titanite lattice can incorporate significant amounts of U and Th (up to 100 ppm) and has a closure temperature for the U–Pb and Th–Pb isotope systems of about 650–700 °C, below which diffusion of Pb isotopes can no longer occur [1,2]. For this reason, titanite has become a valuable phase for ID-TIMS and SHRIMP U–Th–Pb geochronology [3–6]. However, titanite often contains significant amounts of common Pb [1,7,8], which must be known and corrected for to obtain precise and accurate U–Th–Pb ages.

The LA-ICP-MS technique has become a widespread and powerful tool for in-situ U–Pb dating of zircon. Precise and accurate absolute ages can be determined, provided that the laser induced time-dependent fractionation of the isotopic ratios is low [e.g. [9–12]]. The LA-ICP-MS technique has recently been applied for titanite geochronology as well [7,8,13–16]. In situ dating of titanite is gaining importance, since its texture and chemistry can be assigned to the different stages of the metamorphic pressure–temperature–time (P–T–t) cycle of its host rock [1,17]. Element fractionation is an important aspect in U–Th–Pb dating by LA-ICP-MS, and can induce significant errors [10–16,18]. This fractionation may result from matrix effects related to laser–sample interactions at the ablation site [19–21], to incomplete aerosol transport from the ablation site to the ICP-MS [22], and to processes occurring in the ICP-MS and subsequent ion extraction and focussing [23]. Various technical approaches have been tested to minimize the laser-induced element fractionation, including shallow ablation craters [24], changing the ablation cell geometry [25,26], rastering [7,18,27–29] or the use of near infrared femtosecond lasers [30,31]. The laser-induced elemental fractionation may vary according to the repetition rate, laser fluence (or on-sample energy density) and crater size [10,12,21,32].

However, there is no general agreement on the laser ablation settings and methodology that should be applied for titanite LA-ICP-MS geochronology. Various laser operating conditions and analytical protocols have been chosen, e.g.: laser ablation using a Nd:YAG 213 nm laser in raster mode with a scan speed of 10 μm/s, a 20 Hz repetition

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rate, and a fluence of c. 4 J/cm^2 [7]; laser ablation using an ArF 193 nm excimer laser in spot mode and raster mode (scan speed of 2 μm/s) with a 6 Hz repetition rate and a 10–12 J/cm^2 fluence [16]; laser ablation in spot mode using an ArF 193 nm excimer laser using a 4 Hz retention rate and a 12 J/cm^2 fluence [8]; laser ablation using a Nd:YAG 213 nm laser operating in spot mode at a 4 Hz repetition rate and a 2 J/cm^2 fluence [13,14]. Opinions also differ on matrix-matched standards, various studies using both raster and spot modes showed that high age accuracy can only result from calibration against a matrix-matched standard [13,16]. Storey et al. [7] observed that accurate U–Pb ages in titanite can be obtained by raster ablation using a zircon as external standard.

This study focuses on the ablation behavior of titanite using a 193 nm ArF excimer laser system in spot mode, characterized by a homogeneous energy distribution across ablation craters, allowing for homogeneous, depth-controlled ablation. The high light absorbance and sample irradiance, resulting from the use of lasers emitting at short wavelengths (193 nm), decrease the particle size and the dispersion of the sample aerosol during ablation [33,34]. Large particles are transported in the ICP with less efficiency and are incompletely vaporized and ionized in the plasma [20,33,34]. They constitute major sources of element and isotope fractionation [33,34], as they may vary in chemical composition [20]. Moreover, it is difficult to estimate if the amount of large particles remains constant for various materials ablated under similar ablation conditions [12]. The spot mode used in this study has a better spatial resolution than the raster approach [10] and allows producing less large particles [33], even if down-hole fractionation is likely to occur.

In this study, ablation experiments were carried out on the Khan titanite reference material [35] using different laser operating conditions. The elemental fractionation with varying fluence, ablation rate and beam size is described in details. Experiments aimed at: 1) understanding the laser-induced fractionation of U, Th and Pb with respect to Ti, Ca and Si in Khan titanite; 2) defining an analytical procedure that minimizes the elemental fractionation for titanite U–Th–Pb geochronology; 3) comparing the fractionation of the Pb/U and Pb/Th ratios between the Khan titanite, the Plešovice zircon [36] and the NIST SRM 610 glass reference materials; 4) investigating the matrix effects that may occur between the different matrices; 5) determining if the reduction of the laser-induced elemental fractionation allows substituting a titanite reference material by a reference zircon as external standard to date titanite by LA-ICP-MS.

2. Reference materials

2.1. Khan titanite

Only a few titanite reference materials are currently available for titanite U–Pb geochronology, including: Khan [35], BLR-1 [37], Grenville skarn titanite (GST; [6]) and Fish Canyon Tuff (FCT; [4]). This study employs the titanite from the Khan pegmatite (Namibia). The studied fragments come from the same set of titanite crystals studied by Heaman [35]. The Khan titanite crystals are compositionally homogeneous. The Khan titanite has U, Th and Pb contents of 584 ± 95, 473 ± 73 and 57 ± 8 ppm respectively, and a Th/U ratio of 0.81 ± 0.05. The titanite crystallization age is 522.2 ± 2.2 Ma (2σ) and corresponds to the upper intercept of a model-1 linear regression in a U–Pb concordia diagram using ID-TIMS data [35]. Consequently, values of 0.08438, 0.6724 and 0.05780 were used as ^{206}Pb/^{238}U, ^{207}Pb/^{235}U and ^{207}Pb/^{206}Pb reference ratios, respectively. A value of 0.02617 was adopted for the ^{208}Pb/^{232}Th ratio, assuming a Th–Pb age equivalent to the U–Pb age crystallization age of 522.2 Ma. Khan titanite shows heterogeneities in the ^{207}Pb/^{206}Pb ratio [35]. The common Pb content is low, as indicated by the range of measured ^{206}Pb/^{204}Pb ratio between ca. 780 and 2400, indicating a ^{206}Pb$_c$ content of c. 2.3–6.6% [13,35].

2.2. Plešovice zircon

The Plešovice zircon is a natural crystal from a high-temperature potassic granulite (Bohemian Massif, Czech Republic). The studied crystals are generally uniform and free of inclusions. However, mineral inclusions of K-feldspar, apatite, quartz and garnet can be found [36]. The Plešovice zircon contains high amounts of U (465–1106 ppm), Th (44–181 ppm) and Pb (21–55 ppm) and has a Th/U ratio of c. 0.095 [36]. The weighted mean ^{206}Pb/^{238}U reference age of Plešovice is 337.13 ± 0.37 Ma (2σ) [36]. Values of 0.05393, 0.3954 and 0.05320 were used as ^{206}Pb/^{238}U, ^{207}Pb/^{235}U and ^{207}Pb/^{206}Pb reference ratios, respectively. As no ^{208}Pb/^{232}Th values were published, a ratio of 0.01682 was used as reference in this study, assuming concordance with the ^{206}Pb/^{238}U age.

3. Analytical parameters

3.1. Instrumentation

U–Th–Pb analyses of minerals were carried out by laser ablation inductively coupled plasma mass-spectrometry (LA-ICP-MS) at the Institute of Geological Sciences, University of Bern. The LA-ICP-MS instrument consists of a GeoLas Pro 193 nm ArF excimer laser ablation system (Lambda Physik, Germany) coupled to an ELAN DRC-e quadrupole ICP-MS (Perkin Elmer, Canada). The quadrupole mass analyzer of the instrument operates fast and has a linear dynamic range exceeding eight orders of magnitude, allowing for sequential measurement of heavy trace ions (such as ^{206}Pb, ^{208}Pb, ^{232}Th and ^{238}U) along with the light matrix ions ^{29}Si, ^{42}Ca and ^{49}Ti.

The gas flow rates, torch parameters, ion-lenses and acceleration voltages on the quadrupole were optimized by ablation of the National Institute of Standards and Technology (NIST) standard reference material SRM 610, representing a synthetic glass doped with trace elements. The NIST SRM 610 glass was ablated at a 10 Hz repetition rate, a 6 J/cm^2 fluence and a 44 μm beam size. The operating conditions were set to obtain maximum sensitivity while maintaining equal sensitivity of Th and U to ensure their complete ionization and minimize fractionation effects [23]. ThO$^+$ and UO$^+$ production rates were 0.15 and 0.12%, respectively, and the Ca^{2+}/Ca$^+$ ratio was adjusted to 0.4%. The stability of the operating conditions was then tested by ablation of the Khan titanite using the same operating parameters. The Th/U ratio of the Khan titanite (0.81) approaches the value of the NIST SRM 610 (Th/U in NIST SRM 610: 0.991; http://georem.mpch-mainz.gwdg.de). The limits of detection (LOD) and thus analytical uncertainties associated with low-abundance isotope determinations were reduced by using a mixture of He (1.000 L/min) and H$_2$ (0.008 L/min) as the carrier gas [38]. The nebulizer He–H$_2$ gas was mixed with auxiliary Ar prior to its introduction in the plasma [39].

Typical analytical sequences included the ^{202}Hg, ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{232}Th, ^{235}U, ^{238}U, ^{29}Si, ^{42}Ca and ^{49}Ti isotopes of interest. The ^{202}Hg isotope was used to correct for the isobaric overlap of ^{204}Hg on ^{204}Pb, using mass biased ratios. Dwell times per isotope ranged from 5 to 30 ms (see Table 1 for details). The acquisition times for the background and the ablation interval amounted to 55 and 40 s, respectively. Peak hopping mode was employed, as well as dual (counting and analog) detector mode. Intensities higher than $2 \cdot 10^6$ counts per seconds (^{29}Si, ^{42}Ca and ^{49}Ti) were measured using the analog mode. The dual detector calibration was optimized using solutions in liquid nebulization mode, and monitored before each analytical session using the variation of the ^{29}Si/^{27}Al intensity ratio with time in the NIST SRM 610 glass. Typical acquisition series consisted of an alternation of three measurements of the Khan titanite followed by two measurements of the Plešovice zircon, to minimize the instrumental bias. The analytical parameters are summarized in Table 1.