Technical note: LA–ICP-MS U–Pb dating of unetched and etched apatites

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Received: 1 July 2020 – Discussion started: 24 July 2020
Revised: 5 November 2020 – Accepted: 13 November 2020 – Published: 20 January 2021

Abstract. The same unetched and chemically etched apatite crystals from five rock samples were dated by the U–Pb method via laser ablation inductively coupled plasma mass spectrometry (LA–ICP-MS). The objective of this study is to test whether chemical etching required for apatite fission track analysis impacts the precision and accuracy of apatite U–Pb geochronology. The results of this experiment suggest that etching has insignificant effects on the accuracy of apatite U–Pb ages obtained by LA–ICP-MS. Therefore, LA–ICP-MS is reliable for U–Pb analysis as part of apatite fission track and U–Pb double dating.

1 Introduction

Apatite, $\text{Ca}_5(\text{PO}_4)_3[\text{F,Cl,OH]}$, is the most common phosphate mineral in the Earth’s crust and can be found in practically all igneous and metamorphic rocks, in many ancient and recent sediments as well as in certain mineral deposits (Piccoli and Candela, 2002; Morton and Yaxley, 2007; Webster and Piccoli, 2015). This accessory mineral is often used as a natural thermochronometer for fission track, helium, U–Th, and U–Pb dating (e.g., Zeitler et al., 1987; Wolf et al., 1996; Ehlers and Farley, 2003; Hasebe et al., 2004; Donelick et al., 2005; Chew and Donelick, 2012; Chew et al., 2014; Cochran et al., 2014; Liu et al., 2014; Spikings et al., 2015; Glorie et al., 2017). Presently, apatite fission track (AFT) ages can be obtained rapidly by using laser ablation inductively coupled plasma mass spectrometry (LA–ICP-MS) for direct measurement of “parent nuclides”, i.e., $^{238}\text{U}$ contents (Cox et al., 2000; Svojtka and Košler, 2002; Hasebe et al., 2004, 2009; Donelick et al., 2005; Abdullin et al., 2014, 2016, 2018; Vermeesch, 2017). The LA–ICP-MS technique may be used to measure $^{238}\text{U}$ for AFT dating, together with Pb isotopes needed for U–Pb dating (e.g., Chew and Donelick, 2012; Liu et al., 2014; Glorie et al., 2017; Bonilla et al., 2020; Nieto-Samaniego et al., 2020).

Hasebe et al. (2009) previously performed an important experimental study, during which they demonstrated that chemical etching required for apatite and zircon fission track dating does not interfere with U analysis by LA–ICP-MS. The influence of etching needed for AFT dating on the precision and accuracy of dating the same crystals by U–Pb using LA–ICP-MS remains to be quantified. To investigate this issue, the same unetched and etched apatite grains extracted from five rock samples were analyzed via LA–ICP-MS for U–Pb dating. The chosen samples have either emplacement or metamorphic ages ranging from the Cretaceous to the Neoproterozoic (see Table 1 for further details).

2 Sample descriptions

2.1 OV-0421 (Tres Sabanas Pluton, Guatemala)

This sample is a two-mica-bearing deformed granite belonging to the Tres Sabanas Pluton, which is located northwest of Guatemala City, Guatemala. For sample OV-0421, an emplacement age of $115 \pm 4$ (2$\sigma$) Ma was proposed based on zircon U–Pb data (Torres de León, 2016). A cooling age of $102 \pm 1$ (2$\sigma$) Ma, obtained with K–Ar (on biotite), was also reported by the same author.
2.2 MCH-38 (Chiapas Massif Complex, Mexico)

MCH-38 is an orthogneiss, sampled ca. 5 km west of Totoltepec de Guerrero, the State of Puebla, southern Mexico. There is no reported age for this sample. Some zircon U–Pb dates obtained for the Chiapas Massif Complex (Weber et al., 2007, 2008; Ortega-Obregón et al., 2019) suggest that a Lopingian (260–252 Ma) crystallization or metamorphic age may be assumed for sample MCH-38.

2.3 TO-AM (Totoltepec Pluton, Mexico)

TO-AM is a granitic rock, sampled ca. 5 km west of Totoltepec de Guerrero, the State of Puebla, southern Mexico. There is no reported radiometric data for sample TO-AM. Previous geological studies indicate that the Pennsylvanian–Cisuralian Totoltepec Pluton was emplaced over a ca. 23 million year period (from ca. 308 to ca. 285 Ma; e.g., Kirsch et al., 2013).

2.4 CH-0403 (Altos Cuchumatanes, Guatemala)

CH-0403 was collected 5 km ESE of Barillas, in Altos Cuchumatanes, Guatemala. It consists of a gray to green granodiorite. Five zircon aliquots of sample CH-0403 were dated using isotope dilution thermal-ionization mass spectrometry, yielding a lower intercept date of 391 ± 8 Ma (2σ) that is interpreted as its approximate crystallization age (Solari et al., 2009).

2.5 OC-1008 (Oaxacan Complex, Mexico)

This sample is a paragneiss from the Grenvillian Oaxacan Complex, southern Mexico. OC-1008 was collected in the federal road which connects Nochixtlán to Oaxaca. It was demonstrated that this sample underwent granulite facies metamorphism at 1000–980 Ma (Solari et al., 2014).

3 Analytical procedures

Accessory minerals were concentrated using conventional mineral separation techniques such as rock crushing, sieving, Wilfley table, Frantz magnetic separator, and bromoform. Approximately 300 apatite grains were extracted from each rock sample and mounted with their surfaces parallel to the crystallographic c axis in a 2.5 cm diameter epoxy mount. Mounted crystals were polished to expose their internal surfaces (i.e., up to 4σ geometry). For this experiment, complete crystals lacking visible inclusions and other defects, such as cracks, were carefully selected for analysis. Sample preparation was performed at Taller de Molienda and Taller de Laminación, Centro de Geociencias (CGEO), Campus Juriquilla, Universidad Nacional Autónoma de México (UNAM).

Single spot analyses were performed with a Resonetics RESOlution™ LPX Pro (193 nm, ArF excimer) laser ablation system, coupled to a Thermo Scientific iCAP™ Qc quadrupole ICP-MS at Laboratorio de Estudios Isotópicos (LEI), CGEO, UNAM. During this experimental work, LA–ICP-MS-based sampling was performed in central parts of the selected apatite grains before and after chemical etching (in 5.5 M HNO₃ at 21 °C for 20 s to reveal spontaneous fission tracks), as shown schematically in Fig. 1. The LA–ICP-MS protocol used for apatite analyses, as given in Table 2, was established on the basis of numerous experiments carried out at LEI during the past 5 years and can be used for U–Pb and fission track double dating plus multielemental analysis (Abdullin et al., 2018; Ortega-Obregón et al., 2019). Corrected isotopic ratios and errors were calculated using Ilolite 3.5 (Paton et al., 2011) and the VizualAge data reduction scheme (Petrus and Kamber, 2012). UcomPhine (Chew et al., 2014) was used to model 207Pb / 206Pb initial values and thus force a 207Pb correction that considers the common Pb (non-radiogenic Pb) incorporated by apatite standards at the moment of their crystallization (see also Ortega-Obregón et al., 2019). The “First Mine Discovery” apatite from Madagascar, with a mean U–Pb age of ca. 480 Ma (Thomson et al., 2012; Chew et al., 2014), was used as a primary reference material.

The results for measured isotopes using NIST-612 (Pearce et al., 1997) were normalized using 43Ca as an internal standard and taking an average CaO content of 55 %.

Tera–Wasserburg Concordia diagrams (T–W; Tera and Wasserburg, 1972) are used in apatite U–Pb dating, because the LA–ICP-MS-derived U–Pb results are generally discordant. The lower intercept in the T–W plot is considered a geologically significant (crystallization or cooling age, the age of mineralization or metamorphic event). Apatite U–Pb ages were calculated with IsoplotR (Vermesch, 2017, 2018) and described

| Sample | Unit and locality         | Rock type   | Zircon U–Pb age   | References                      |
|--------|---------------------------|-------------|-------------------|---------------------------------|
| OV-0421| Tres Sabanas Pluton, Guatemala | deformed granite | 115 ± 4 Ma       | Torres de León (2016)          |
| MCH-38 | Chiapas Massif Complex, Mexico | orthogneiss   | ca. 260 to 252 Ma (?) | Weber et al. (2007, 2008)     |
| TO-AM  | Totoltepec Pluton, Mexico  | granite     | ca. 308 to 285 Ma (?) | Kirsch et al. (2013)          |
| CH-0403| Altos Cuchumatanes, Guatemala | granodiorite | 391 ± 8 Ma        | Solari et al. (2009)          |
| OC-1008| Oaxacan Complex, Mexico    | paragneiss  | 990 ± 10 Ma       | Solari et al. (2014)          |
Table 2. LA–ICP-MS protocol established at LEI to be applied for simultaneous apatite U–Pb and fission-track double dating plus multielemental analysis (rare-earth elements, Y, Sr, Mn, Mg, Th, U, and Cl).

| Instrument      | Thermo Scientific™ iCAP™ Qc |
|-----------------|-----------------------------|
| ICP-MS operating conditions |                 |
| Forward power   | 1450 W                      |
| Carrier gas flow rate | $\sim 1 \text{ L min}^{-1}$ (Ar) and $\sim 0.35 \text{ L min}^{-1}$ (He) |
| Auxiliary gas flow rate | $\sim 1 \text{ L min}^{-1}$ |
| Plasma gas flow rate | $\sim 14 \text{ L min}^{-1}$ |
| Nitrogen        | $\sim 3.5 \text{ mL min}^{-1}$ |
| Data acquisition parameters |                      |
| Mode of operating | STD (standard mode) |
| Sampling scheme  | –2NIST-612–2MAD–1DUR–1apt– |
| Background scanning | 15 s |
| Data acquisition time | 35 s |
| Wash-out time    | 15 s                        |
| Measured isotopes | $^{26}\text{Mg}$ $^{31}\text{P}$ $^{35}\text{Cl}$ $^{43}\text{Ca}$ $^{44}\text{Ca}$ $^{55}\text{Mn}$ $^{88}\text{Sr}$ $^{89}\text{Y}$ $^{139}\text{La}$ $^{140}\text{Ce}$ $^{141}\text{Pr}$ $^{142}\text{Nd}$ $^{147}\text{Sm}$ $^{153}\text{Eu}$ $^{157}\text{Gd}$ $^{159}\text{Tb}$ $^{163}\text{Dy}$ $^{165}\text{Ho}$ $^{166}\text{Er}$ $^{169}\text{Tm}$ $^{172}\text{Yb}$ $^{175}\text{Lu}$ $^{202}\text{Hg}$ $^{204}\text{Pb}$ $^{206}\text{Pb}$ $^{207}\text{Pb}$ $^{208}\text{Pb}$ $^{232}\text{Th}$ $^{238}\text{U}$ [total = 29] |

Laser ablation system

| Ablation cell | RESOlution™ Laurin Technic S-155 |
| Model of laser | Resonetics RESOlution™ LPX Pro |
| Wavelength | 193 nm (Excimer ArF) |
| Repetition rate | 4 Hz |
| Energy density | 4 J cm$^{-2}$ * |
| Mode of sampling | spot diameter of 60 µm |

Note: MAD – “First Mine Discovery” U–Pb apatite standard from Madagascar; DUR – Durango apatite from Cerro de Mercado mine (Mexico); apt – unknown apatite crystals. * Laser pulse energy of 4 J cm$^{-2}$, which was measured directly on target with a Coherent™ laser energy meter.

below. Detailed information on U–Pb experiments is given in Table S1 in the Supplement.

4 Results

4.1 OV-0421

For rock sample OV-0421, 41 unetched apatites yielded a lower intercept age of 106 ± 4 (2σ) Ma with a mean square weighted deviation (MSWD) of 1.07, passing the chi-squared test with the $P(\chi^2)$ value of 0.35 (see in Fig. 2). Practically the same U–Pb date, 107 ± 5 (2σ) Ma, was obtained after chemical etching of the same apatite grains, yielding a MSWD of 1.13 and a $P(\chi^2)$ of 0.27. Both these apatite U–Pb ages lie between the zircon U–Pb date of 115 ± 4 (2σ) Ma (i.e., crystallization age) and the biotite K–Ar age of 102 ± 1 (2σ) Ma (i.e., cooling age), which were

Figure 1. Illustration displaying the LA–ICP-MS-based U–Pb dating of the same apatite crystal before and after chemical etching (i.e., etched in 5.5 M nitric acid at 21 °C for 20 s). Spot diameter of 60 µm.
previously obtained for the same granite sample by Torres de León (2016).

4.2 MCH-38

For orthogneiss sample MCH-38, the lower intercept in T–W yielded a U–Pb age of $245 \pm 6$ (2$\sigma$) Ma (obtained from 41 unetched apatites) with a MSWD of 0.28 and a $P(\chi^2)$ of 1. Etched apatite grains from MCH-38 yielded an age of $240 \pm 4$ (2$\sigma$) Ma with a MSWD of 0.36 and a $P(\chi^2)$ of 1 (Fig. 2). Our U–Pb results are in close agreement with geochronological data reported from the Chiapas Massif Complex in previous studies (Damon et al., 1981; Torres et al., 1999; Schaaf et al., 2002; Ortega-Obregón et al., 2019). For instance, Torres et al. (1999) compiled biotite K–Ar ages, most of which lie within Early–Middle Triassic period. Triassic cooling ages in the Chiapas Massif Complex were also detected by Rb–Sr in mica–whole rock pairs that range from $244 \pm 12$ (2$\sigma$) to $214 \pm 11$ (2$\sigma$) Ma (Schaaf et al., 2002).

4.3 TO-AM

Unetched apatites (32 crystals; Fig. 2) from granite TO-AM yielded a lower intercept date of $303 \pm 5$ (2$\sigma$) Ma with a MSWD of 0.6 and a $P(\chi^2)$ of 0.96. After etching, a slightly younger age of $299 \pm 3$ (2$\sigma$) Ma was obtained, with a MSWD of 0.89 and a $P(\chi^2)$ of 0.65. These apatite U–Pb ages are in line with the zircon U–Pb ages of $306 \pm 2$ (2$\sigma$) Ma to $287 \pm 2$ (2$\sigma$) Ma reported for the Pennsylvanian–Cisuralian Totoltepec Pluton (e.g., see details in Kirsch et al., 2013).

4.4 CH-0403

A total of 36 unetched apatite grains from sample CH-0403 yielded a lower intercept U–Pb age of $345 \pm 10$ (2$\sigma$) Ma with a MSWD of 0.7 and a $P(\chi^2)$ of 0.9. After etching, the same apatite crystals yielded an age of $334 \pm 8$ (2$\sigma$) Ma with a MSWD of 1.37 and a $P(\chi^2)$ of 0.08 (Fig. 2). These cooling dates are considerably younger if compared to the CH-0403 emplacement age of $391 \pm 8$ (2$\sigma$) Ma (Solari et al., 2009).

4.5 OC-1008

A total of 41 unetched apatites belonging to sample OC-1008 yielded a U–Pb age of $839 \pm 12$ (2$\sigma$) Ma with a MSWD of 0.98 and a $P(\chi^2)$ of 0.50. After etching, the same apatite crystals yielded an age of $830 \pm 10$ (2$\sigma$) Ma with a MSWD of 1.24 and a $P(\chi^2)$ of 0.14 (Fig. 2). Both these apatite U–Pb ages are significantly younger than the age of granulite facies metamorphism in the Grenville-aged Oaxacan Complex (1 Ga to 980 Ma, Solari et al., 2014) and, thus, should be considered as cooling ages.


Figure 3. Plot showing the lower intercept U–Pb ages obtained on unetched and etched apatite grains.

5 Discussion and concluding remarks

Most rock samples, except OV-0421, yielded slightly younger apatite U–Pb ages after chemical etching (up to 3.3 % in sample CH-0403). However, the lower intercept U–Pb ages obtained from unetched apatite grains are indistinguishable within error from the U–Pb ages obtained on the same etched grains (see diagram in Fig. 3). The results of this experiment demonstrate that chemical etching required for AFT analysis has negligible effects on the accuracy of apatite U–Pb ages determined via LA–ICP-MS. Thus, as a main conclusion of this study, LA–ICP-MS can be used for simultaneous AFT and U–Pb double dating, as it was already done in some previous studies (e.g., Chew and Donelick, 2012; Liu et al., 2014; Glorie et al., 2017; Bonilla et al., 2020; Nieto-Samaniego et al., 2020).

Data availability. The authors declare that all the data supporting the findings of this study are available within the article (see Supplement).

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/gchron-3-59-2021-supplement.

Author contributions. Conceptualization, investigation, and writing of the original draft were done by FA. LS and COO provided technical support. LS and JS acquired funding and resources, supervised the study, and reviewed the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgements. The authors are grateful to Juan Tomás Vázquez Ramírez and Ofelia Pérez Arvizu for their help with sample preparation for this study. Stuart Thomson is acknowledged for sharing the Madagascar apatite. Michelangelo Martini kindly provided the sample TO-AM that was useful for our experimental study. Ziva Shulaker, Jakub Sliwinski, and Axel Schmitt are acknowledged for their constructive comments that improved our manuscript significantly.

Financial support. This research has been supported by the PA-PIIT DGAPA UNAM (grant no. IN101520).

Review statement. This paper was edited by Axel Schmitt and reviewed by Jakub Sliwinski and Ziva Shulaker.

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