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

Fanis Abdullin et al.: LA–ICP-MS U–Pb dating of apatites

Fanis Abdullin[1], Luigi A. Solari[2], Jesús Solé[3], Carlos Ortega-Obregón[2]

[1]CONACyT–Centro de Geociencias, Campus Juriquilla, UNAM, Querétaro, 76230, Mexico

[2]Centro de Geociencias, Campus Juriquilla, UNAM, Querétaro, 76230, Mexico

[3]LANGEM, Instituto de Geología, UNAM, Ciudad Universitaria, CDMX, 04510, Mexico

Correspondence: Fanis Abdullin (fanis@geociencias.unam.mx)

Abstract

The same unetched and chemically etched ~~apatites~~apatite grains from five rock samples were dated with U–Pb ~~using~~via laser ablation inductively~~-~~-coupled plasma mass spectrometry~~.~~ (LA–ICP-MS). The objective of this study is to ~~demonstrate~~assert whether ~~or not the~~chemical etching~~,~~ ~~needed~~ required for ~~the~~ apatite fission track analysis~~, impact on~~ impacts the ~~obtaining~~precision and accuracy of ~~apatite~~same-grain U–Pb ages. The results of ~~this~~our experiment ~~indicate~~suggest that ~~the~~ etching has no significant effect on the ~~determination~~accuracy of apatite U–Pb ages obtained by ~~the laser ablation inductively coupled plasma mass spectrometry technique.~~LA–ICP-MS. Thus, ~~laser ablation inductively coupled plasma mass spectrometry may~~LA–ICP-MS can be used safely for ~~simultaneous~~ apatite fission track ~~*in situ*~~ and U–Pb double dating.

Short summary

Unetched and etched ~~apatites of~~apatite grains from five samples were dated ~~by~~with U–Pb ~~with~~using laser ablation inductively~~-~~-coupled plasma mass spectrometry. Our experiment

~~demonstrates~~indicates that ~~the~~ etching~~,~~ needed for ~~the~~ apatite fission track dating~~,~~ has no ~~important~~ effect on the obtaining ~~of~~accurate U–Pb ages; ~~and~~ therefore, the laser ablation-based technique ~~can~~may be used for apatite fission track and U–Pb double dating.

1 Introduction

Apatite, $Ca_5(PO_4)_3$[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, ~~as well as~~ in many ancient and recent sediments ~~and~~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 ~~(i.e.,~~ for fission track, ~~helium~~He, 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; Cochrane et al., 2014; Liu et al., 2014; Spikings et al., 2015; Glorie et al., 2017).

Presently, apatite fission track (AFT) ages ~~may~~can be obtained rapidly by using ~~LA–ICP-MS (~~laser ablation inductively~~–~~-coupled plasma mass spectrometry (LA–ICP-MS) for direct measurement of “parent nuclides”, i.e., ^{238}U ~~levels~~contents (Cox et al., 2000; Svojtka and Košler, 2002; Hasebe et al., 2004~~, 2009;~~,; Donelick et al., 2005; Vermeesch, 2017). ~~In addition, the~~ LA–ICP-MS~~-based~~ technique ~~allows~~may be used to ~~date apatites simultaneously by~~obtain ^{238}U for AFT ~~and~~dating, together with isotope ratios 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). ~~After chemical etching of apatites, a smaller volume of ablated material is analyzed with LA–ICP-MS. Therefore, there is a doubt on the application of such double dating technique. The~~

question is how chemical etching, required for the AFT dating, may influence on the obtaining of apatite U–Pb ages? To respond to this question, the same unetched and etched apatite crystals from five experimental samples were dated by LA–ICP-MS U–Pb. The chosen rock samples have either emplacement or metamorphic ages varying from the Early Cretaceous to the Neoproterozoic (for details, please see Table 1).

Hasebe et al. (2009) previously performed an important experimental study, during which they demonstrated that chemical etching required for fission track dating has no significant effect on the accuracy of U measurement by LA–ICP-MS method. After chemical etching of apatites, a smaller volume of ablated material is analyzed by LA–ICP-MS. The influence of etching needed for AFT dating on the precision and accuracy of same-grain U–Pb dating analyzed via 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 using LA–ICP-MS for U–Pb dating. The chosen rock samples have either emplacement or metamorphic ages ranging from the Cretaceous to the Neoproterozoic (see Table 1 for further details).

--- Table 1 ---

2 Brief description of samples

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 NW of Guatemala City, Guatemala. For sample OV-0421, an emplacement age of 115 ± 4 (2σ) Ma was proposed based on zircon U–Pb data (Torres de León, 2016). A cooling age of 102 ± 1 (2σ) Ma, obtained with K–Ar (on biotite~~ concentrate~~), has also been reported by the same author.

2.2. MCH-38 (Chiapas Massif Complex, Mexico)

MCH-38 is an orthogneiss from the Permian Chiapas Massif Complex. This rock was sampled to the west of Unión Agrarista, the State of Chiapas, southeastern 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. ~~20~~23 million year period (from ~~306 ± 2~~ca. 308 to ~~287 ± 2~~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 the 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 (2σ) Ma 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 ~~"dry"~~ granulite facies metamorphism at ~~990 ± 10~~1000–980 Ma (Solari et al., 2014).

3 Analytical procedures

~~Apatites~~Accessory minerals were concentrated using conventional mineral separation techniques~~. Nearly~~ such as rock crushing, sieving, Wilfley table, Frantz magnetic separator, and bromoform. Approximately 300 apatite grains~~,~~ were extracted from each rock sample~~, were mounted with EpoFix™ in a 2.5 cm diameter ring. Apatites were~~ and mounted with their surfaces parallel to the crystallographic *c*-axis~~.~~ in a 2.5 cm diameter epoxy mount. Mounted ~~grains~~crystals were polished to expose their internal surfaces (i.e., up to 4π geometry). For

~~our~~this experiment, ~~only "sterile" and~~ complete crystals~~, without~~ lacking visible inclusions and other defects, such as cracks, were ~~gently~~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 Mexico (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 ~~exactly~~ in central parts of the selected apatite grains before and after chemical etching (in 5.5M HNO_3 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 five 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 Iolite 3.5 (Paton et al., 2011) and the VizualAge data reduction scheme (Petrus and Kamber, 2012). UcomPbine (Chew et al., 2014) was used to model ^{207}Pb/^{206}Pb initial values and thus force a ^{207}Pb 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 ~~^{206}U–^{238}Pb~~U–Pb age of ca. 480 Ma (Thomson et al., 2012; Chew et al., 2014), was used as a ~~main~~primary reference material. The results for measured isotopes using ~~the~~ NIST-612~~ glass~~ (Pearce et al., 1997) were normalized using ^{43}Ca as an internal standard and taking an average CaO content of 55% (i.e., for F-apatites).

~~--- Figure 1 ---~~

~~--- Table 2 ---~~

~~4 Results~~

Tera and 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 as a “mean” apatite U–Pb age that should have geological significance (crystallization or cooling age, ~~or~~ the ~~ages~~age of mineralization or metamorphic event). Apatite U–Pb ages were calculated with IsoplotR (Vermeesch, 2017, 2018) and described below. Detailed information on our U–Pb experiments is given in Table S1 in the Supplement.

--- Figure 1 ---

--- Table 2 ---

4 Results

4.1 OV-0421

For rock sample OV-0421, 41 unetched apatites ~~analysed~~ yielded a lower intercept age of 106 ± 4 (2σ) Ma with a mean square weighted deviation (MSWD) of 1.07, passing the chi-squared

~~probability~~ test with the $P(\chi^2)$ value of 0.35 (see in Fig. 2). Virtually the same U–Pb ~~age~~date, 107 ± 5 (2σ) Ma, was obtained after chemical etching of the same apatite ~~crystals~~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 ~~age~~date of 115 ± 4 (2σ) Ma (i.e., crystallization age) and the biotite K–Ar ~~date~~age of 102 ± 1 (2σ) Ma (i.e., cooling age), which were 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 ± 6 (2σ) Ma (obtained from 41 unetched ~~grains~~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 ± 4 (2σ) Ma with a MSWD of 0.36 and a $P(\chi^2)$ of 1 (Fig. 2). Our U–Pb ~~ages~~results are in close agreement with geochronological data reported from the ~~Permian~~ 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 ~~the~~ 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 ± 12 (2σ) Ma to 214 ± 11 (2σ) 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 ± 5 (2σ) Ma with a MSWD of 0.6 and a $P(\chi^2)$ of 0.96. After etching, a slightly younger age of 299 ± 3 (2σ) Ma was obtained, with a MSWD of 0.89 and a $P(\chi^2)$ of 0.65. These apatite U–Pb

~~dates~~ages are in line with the zircon U–Pb ages of 306 ± 2 (2σ) Ma to 287 ± 2 (2σ) Ma reported for the Pennsylvanian~~ to ~~–Cisuralian Totoltepec Pluton (e.g., see details in Kirsch et al., 2013).

4.4 CH-0403

36 unetched apatite grains from sample CH-0403 yielded a lower intercept U–Pb age of 345 ± 10 (2σ) Ma with a MSWD of 0.7 and a $P(\chi^2)$ of 0.9, whereas etched grains yielded an age of 334 ± 8 (2σ) 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 ± 8 (2σ) Ma (Solari et al., 2009).

4.5 OC-1008

41 unetched apatites ~~of~~belonging to the sample OC-1008 yielded a U–Pb age of 839 ± 12 (2σ) Ma with a MSWD of 0.98 and a $P(\chi^2)$ of 0.50. After etching, the same ~~apatites~~apatite crystals yielded an age of 830 ± 10 (2σ) 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, ~~can~~should be considered as cooling ages.

--- Figure 2 ---

5 Discussion and concluding remarks

Most rock samples, except OV-0421, yielded slightly younger apatite U–Pb ~~dates~~ages after chemical etching (up to 3.3% in sample CH-0403). ~~The~~However, the lower intercept U–Pb ages obtained from unetched apatite grains are identical within errors to the U–Pb ages obtained on the same ~~apatites~~ etched grains (see diagram in Fig. 3). The results of our experimental study demonstrate that the chemical etching, required for the AFT analysis, has no important effect on the ~~determination~~accuracy of apatite U–Pb ages ~~by~~determined via LA–ICP-MS. Thus, as a main conclusion of this ~~work~~experimental study, LA–ICP-MS can be used safely to obtain simultaneously AFT and U–Pb ages (i.e., double dating), as it was already done in some studies without previous proof (e.g., Chew and Donelick, 2012; Liu et al., 2014; Glorie et al., 2017; Bonilla et al., 2020; Nieto-Samaniego et al., 2020).

--- Figure 3 ---

Supplement

The supplement related to this article is available online at: https://...

Author contributions

Conceptualisation, 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 very grateful to Juan Tomás Vázquez Ramírez and Ofelia Pérez Arvizu for their help with sample preparation for this study. Professor Stuart Thomson (University of Arizona) is acknowledged for sharing the Madagascar apatite. Dr. Michelangelo Martini kindly provided granite sample TO-AM that was very useful for our experimental study. Dr. Ziva Shulaker, Dr. Jakub Sliwinski, and Professor Axel Schmitt are acknowledged for their constructive comments that improved our manuscript.

Financial support

This research has been supported by PAPIIT DGAPA UNAM (grant no. IN101520 to LS).

Figure caption

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 5.5M nitric acid at 21 °C for 20 s). Spot diameter of 60 µm.

Figure 2

Tera–Wasserburg Concordia diagrams for the U–Pb results of unetched and etched apatites from samples OV-0421, MCH-38, TO-AM, CH-0403, and OC-1008. MSWD – mean square weighted deviation, Ngr – number of grains dated. Errors are given in 2σ.

Figure 3

~~Binary plot~~Plot showing the lower intercept U–Pb ages obtained on unetched and etched ~~apatites~~apatite grains.

References

Abdullin, F., Solari, L., Ortega-Obregón, C., and Solé, J.: New fission-track results from the northern Chiapas Massif area, SE Mexico: trying to reconstruct its complex thermo-tectonic history, Revista Mexicana de Ciencias Geológicas, 35, 79–92, https://doi.org/10.22201/cgeo.20072902e.2018.1.523, 2018.

Bonilla, A., Franco, J. A., Cramer, T., Poujol, M., Cogné, N., Nachtergaele, S., and De Grave, J.: Apatite LA-ICP-MS U–Pb and fission-track geochronology of the Caño Viejita gabbro in E-Colombia: Evidence for Grenvillian intraplate rifting and Jurassic exhumation in the NW Amazonian Craton, Journal of South American Earth Sciences, 98, 102438, https://doi.org/10.1016/j.jsames.2019.102438, 2020.

Chew, D. M., and Donelick, R. A.: Combined apatite fission track and U-Pb dating by LA-ICP-MS and its application in apatite provenance analysis, Quantitative Mineralogy and Microanalysis of Sediments and Sedimentary Rocks: Mineralogical Association od Canada, Short Course, 42, 219–247, 2012.

Chew, D. M., Petrus, J. A., and Kamber, B. S.: U–Pb LA–ICPMS dating using accessory mineral standards with variable common Pb, Chemical Geology, 363, 185–199, https://doi.org/10.1016/j.chemgeo.2013.11.006, 2014.

Cochrane, R., Spikings, R. A., Chew, D., Wotzlaw, J. F., Chiaradia, M., Tyrrell, S., Schaltegger, U., and Van der Lelij, R.: High temperature (> 350 °C) thermochronology and mechanisms of Pb loss in apatite, Geochimica et Cosmochimica Acta, 127, 39–56, https://doi.org/10.1016/j.gca.2013.11.028, 2014.

Cox, R., Košler, J., Sylvester, P., and Hodych, P.: Apatite fission-track (FT) dating by LAM-ICP-MS analysis, Goldschmidt Conference, Oxford, UK, Journal of Conference Abstracts, 5, p. 322, 2000.

Damon, P. E., Shafiqullah, M., and Clark, K. F.: Age trends of igneous activity in relation to metallogenesis in the southern Cordillera, Tucson, Arizona, Arizona Geological Society Digest, 14, 137–153, 1981.

Donelick, R. A., O'Sullivan, P. B., and Ketcham, R. A.: Apatite fission-track analysis, Reviews in Mineralogy and Geochemistry, 58, 49–94, https://doi.org/10.2138/rmg.2005.58.3, 2005.

Ehlers, T. A., and Farley, K. A.: Apatite (U–Th)/He thermochronometry: methods and applications to problems in tectonic and surface processes, Earth and Planetary Science Letters, 206, 1–14, https://doi.org/10.1016/S0012-821X(02)01069-5, 2003.

Glorie, S., Alexandrov, I., Nixon, A., Jepson, G., Gillespie, J., and Jahn, B. M.: Thermal and exhumation history of Sakhalin Island (Russia) constrained by apatite U-Pb and fission track thermochronology, Journal of Asian Earth Sciences, 143, 326–342, https://doi.org/10.1016/j.jseaes.2017.05.011, 2017.

Hasebe, N., Barbarand, J., Jarvis, K., Carter, A., and Hurford, A. J.: Apatite fission-track chronometry using laser ablation ICP-MS, Chemical Geology, 207, 135–145, https://doi.org/10.1016/j.chemgeo.2004.01.007, 2004.

Hasebe, N., Carter, A., Hurford, A. J., and Arai, S.: The effect of chemical etching on LA–ICP-MS analysis in determining uranium concentration for fission-track chronometry, Geological Society, London, Special Publications, 324, 37–46, https://doi.org/10.1144/SP324.3, 2009.

Kirsch, M., Keppie, J. D., Murphy, J. B., and Lee, J. K.: Arc plutonism in a transtensional regime: the late Palaeozoic Totoltepec pluton, Acatlán Complex, southern Mexico, International Geology Review, 55, 263–286, https://doi.org/10.1080/00206814.2012.693247, 2013.

Liu, W., Zhang, J., Sun, T., Wang, J.: Application of apatite U–Pb and fission-track double dating to determine the preservation potential of magnetite–apatite deposits in the Luzong and Ningwu volcanic basins, eastern China, Journal of Geochemical Exploration, 138, 22–32, https://doi.org/10.1016/j.gexplo.2013.12.006, 2014.

Morton, A., and Yaxley, G.: Detrital apatite geochemistry and its application in provenance studies, Special Papers, Geological Society of America, 420, 319, https://doi.org/10.1130/2006.2420(19), 2007.

Nieto-Samaniego, A. F., Olmos-Moya, M. D. J. P., Levresse, G., Alaniz-Alvarez, S. A., Abdullin, F., del Pilar-Martínez, A., and Xu, S.: Thermochronology and exhumation rates of granitic intrusions at Mesa Central, Mexico, International Geology Review, 62, 311–319, https://doi.org/10.1080/00206814.2019.1602789, 2020.

Ortega-Obregón, C., Abdullin, F., Solari, L., Schaaf, P., and Solís-Pichardo, G.: Apatite U-Pb dating at UNAM laboratories: analytical protocols and examples of its application, Revista Mexicana de Ciencias Geológicas, 36, 27–37, https://doi.org/10.22201/cgeo.20072902e.2019.1.749, 2019.

Paton, C., Hellstrom, J., Paul, B., Woodhead, J., Hergt, J.: Iolite: Freeware for the visualisation and processing of mass spectrometric data, Journal of Analytical Atomic Spectrometry, 26, 2508–2518, https://doi.org/10.1039/C1JA10172B, 2011.

Pearce, N. J., Perkins, W. T., Westgate, J. A., Gorton, M. P., Jackson, S. E., Neal, C. R., and Chenery, S. P.: A compilation of new and published major and trace element data for NIST SRM 610 and NIST SRM 612 glass reference materials, Geostandards newsletter, 21, 115–144, https://doi.org/10.1111/j.1751-908X.1997.tb00538.x, 1997.

Petrus, J. A., and Kamber, B. S.: VizualAge: A novel approach to laser ablation ICP-MS U-Pb geochronology data reduction, Geostandards and Geoanalytical Research, 36, 247–270, https://doi.org/10.1111/j.1751-908X.2012.00158.x, 2012.

Piccoli, P. M., and Candela, P. A.: Apatite in igneous systems, Reviews in Mineralogy and Geochemistry, 48, 255–292, https://doi.org/10.2138/rmg.2002.48.6, 2002.

Schaaf, P., Weber, B., Weis, P., Groβ, A., Ortega-Gutiérrez, F., and Kohler, H.: The Chiapas Massif (Mexico) revised: New geologic and isotopic data and basement characteristics, Neues Jahrbuch fur Geologie und Paläontologie, Abhandlungen, 225, 1–23, 2002.

Solari, L. A., Ortega-Gutiérrez, F., Elías-Herrera, M., Schaaf, P., Norman, M., Ortega-Obregón, C., and Chiquín, M.: U-Pb zircon geochronology of Palaeozoic units in western and central Guatemala: Insights into the tectonic evolution of Middle America, Geological Society, London, Special Publications, 328, 295–313, https://doi.org/10.1144/SP328.12, 2009.

Solari, L. A., Ortega-Gutiérrez, F., Elías-Herrera, M., Ortega-Obregón, C., Macías-Romo, C., Reyes-Salas, M.: Detrital provenance of the Grenvillian Oaxacan Complex, southern Mexico: a zircon perspective, International Journal of Earth Sciences, 103, 1301–1315, https://doi.org/10.1007/s00531-013-0938-9, 2014.

Spikings, R., Cochrane, R., Villagomez, D., Van der Lelij, R., Vallejo, C., Winkler, W., and Beate, B.: The geological history of northwestern South America: From Pangaea to the early collision of the Caribbean large igneous province (290–75 Ma), Gondwana Research, 27, 95–139, https://doi.org/10.1016/j.gr.2014.06.004, 2015.

Svojtka, M., and Košler: Fission-track dating of zircon by LA-ICP-MS, Goldschmidt Conference, Davos, Switzerland, Journal of Conference Abstracts, Special Supplement of Geochimica et Cosmochimica Acta, 66, A756, 2002.

Tera, F., and Wasserburg, G. J.: U-Th-Pb systematics in three Apollo 14 basalts and the problem of initial Pb in lunar rocks, Earth and Planetary Science Letters, 14, 281–304, https://doi.org/10.1016/0012-821X(72)90128-8, 1972.

Thomson, S. N., Gehrels, G. E., Ruiz, J., and Buchwaldt, R.: Routine low-damage apatite U-Pb dating using laser ablation–multicollector–ICPMS, Geochemistry, Geophysics, Geosystems, 13(2), https://doi.org/10.1029/2011GC003928, 2012.

Torres, R., Ruiz, J., Patchett, P. J., Grajales, J. M., Bartolini, C., Wilson, J. L., and Lawton, T. F.: Permo-Triassic continental arc in eastern Mexico: Tectonic implications for reconstruction of southern North America, , Geological Society of America, Special Papers, 340, 191–196, https://doi.org/10.1130/0-8137-2340-X.191, 1999.

Torres de León, R,: Caracterización geológica y geocronológica de unidades metamórficas e intrusivas de la región centro–Oeste de la Cuenca del Rio Motagua, Sureste de Guatemala, Centroamerica: implicaciones en las conexiones Sur de México–Bloque Chortís, Universidad Nacional Autónoma de México, Posgrado en Ciencias de la Tierra, Ph.D Thesis, 221 pp., 2016.

Vermeesch, P.: Statistics for LA-ICP-MS based fission track dating, Chemical Geology, 456, 19–27, https://doi.org/10.1016/j.chemgeo.2017.03.002, 2017.

Vermeesch, P.: IsoplotR: A free and open toolbox for geochronology, Geoscience Frontiers, 9, 1479–1493, https://doi.org/10.1016/j.gsf.2018.04.001, 2018.

Weber, B., Iriondo, A., Premo, W. R., Hecht, L., and Schaaf, P.: New insights into the history and origin of the southern Maya block, SE Mexico: U–Pb–SHRIMP zircon geochronology from metamorphic rocks of the Chiapas massif, International Journal of Earth Sciences, 96, 253–269, https://doi.org/10.1007/s00531-006-0093-7, 2007.

Weber, B., Valencia, V. A., Schaaf, P., Pompa-Mera, V., and Ruiz, J.: Significance of provenance ages from the Chiapas Massif Complex (southeastern Mexico): redefining the Paleozoic basement of the Maya Block and its evolution in a peri-Gondwanan realm, The Journal of Geology, 116, 619–639, https://doi.org/10.1086/591994, 2008.

Webster, J. D., and Piccoli, P. M.: Magmatic apatite: A powerful, yet deceptive, mineral, Elements, 11, 177–182, https://doi.org/10.2113/gselements.11.3.177, 2015.

Wolf, R. A., Farley, K. A., and Silver, L. T.: Helium diffusion and low-temperature thermochronometry of apatite, Geochimica et Cosmochimica Acta, 60, 4231–4240, https://doi.org/10.1016/S0016-7037(96)00192-5, 1996.

Zeitler, P. K., Herczeg, A. L., McDougall, I., and Honda, M.: U-Th-He dating of apatite: A potential thermochronometer, Geochimica et Cosmochimica Acta, 51, 2865–2868, https://doi.org/10.1016/0016-7037(87)90164-5, 1987.

Figure 1

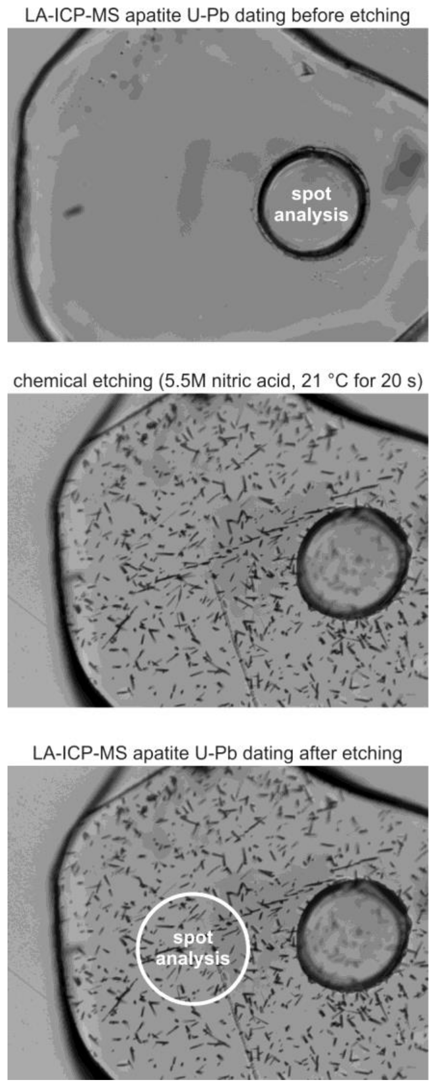
LA-ICP-MS apatite U-Pb dating before etching
spot analysis
chemical etching (5.5M nitric acid, 21 °C for 20 s)
LA-ICP-MS apatite U-Pb dating after etching
spot analysis

Figure 2

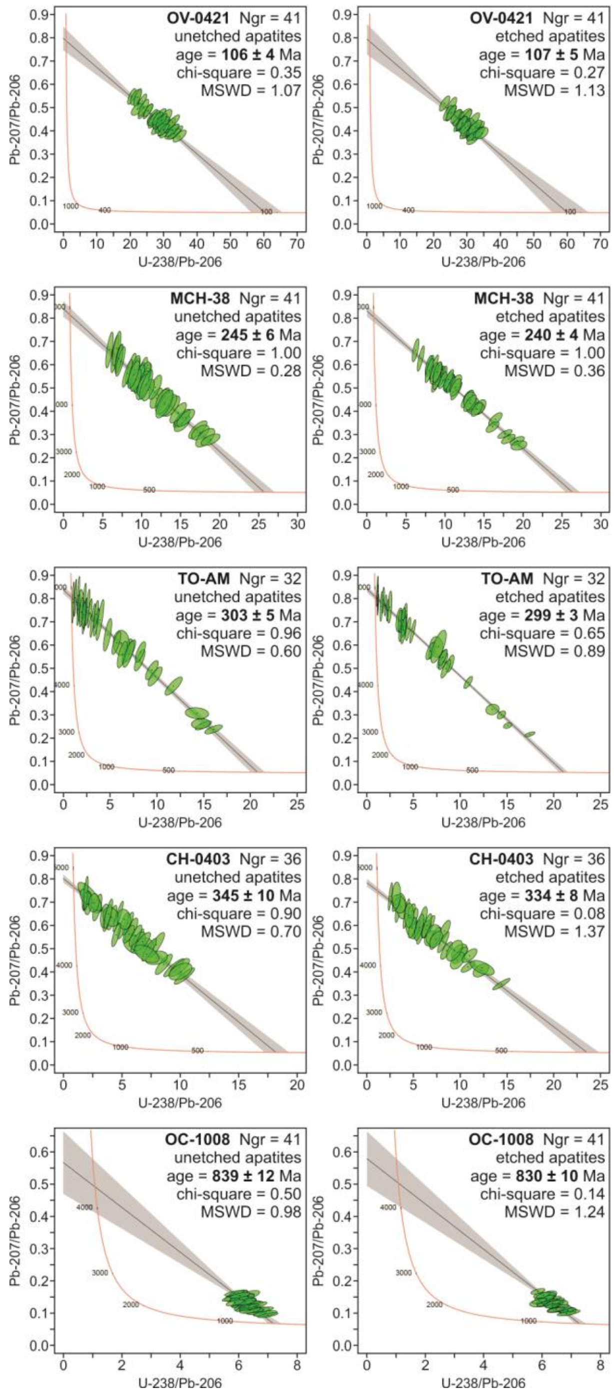
OV-0421 Ngr = 41
unetched apatites
age = 106 ± 4 Ma
chi-square = 0.35
MSWD = 1.07
OV-0421 Ngr = 41
etched apatites
age = 107 ± 5 Ma
chi-square = 0.27
MSWD = 1.13
MCH-38 Ngr = 41
unetched apatites
age = 245 ± 6 Ma
chi-square = 1.00
MSWD = 0.28
MCH-38 Ngr = 41
etched apatites
age = 240 ± 4 Ma
chi-square = 1.00
MSWD = 0.36
TO-AM Ngr = 32
unetched apatites
age = 303 ± 5 Ma
chi-square = 0.96
MSWD = 0.60
TO-AM Ngr = 32
etched apatites
age = 299 ± 3 Ma
chi-square = 0.65
MSWD = 0.89
CH-0403 Ngr = 36
unetched apatites
age = 345 ± 10 Ma
chi-square = 0.90
MSWD = 0.70
CH-0403 Ngr = 36
etched apatites
age = 334 ± 8 Ma
chi-square = 0.08
MSWD = 1.37
OC-1008 Ngr = 41
unetched apatites
age = 839 ± 12 Ma
chi-square = 0.50
MSWD = 0.98
OC-1008 Ngr = 41
etched apatites
age = 830 ± 10 Ma
chi-square = 0.14
MSWD = 1.24
Pb-207/Pb-206
U-238/Pb-206

Figure 3

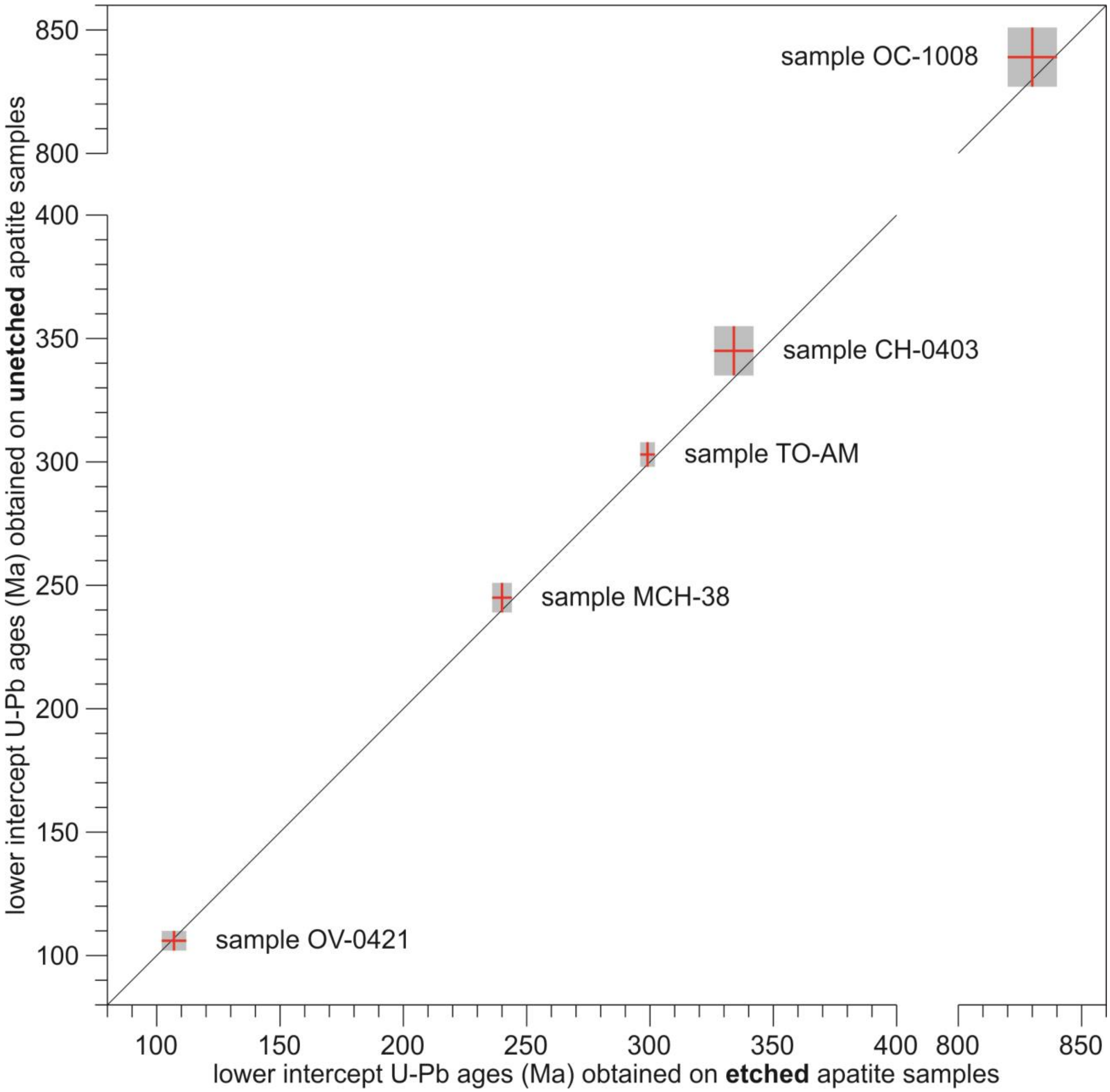
sample OC-1008
sample CH-0403
sample TO-AM
sample MCH-38
sample OV-0421
lower intercept U-Pb ages (Ma) obtained on **unetched** apatite samples
lower intercept U-Pb ages (Ma) obtained on **etched** apatite samples
100
150
200
250
300
350
400
800
850

Table 1

Lithology, locality, and zircon U–Pb data for the selected experimental rock samples.

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 ca. 252 Ma (?)	Weber et al. (2007, 2008)
TO-AM	Totoltepec Pluton, Mexico	granite	ca. 308 to ca. 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 *in-situ* double dating plus multielemental analysis (REEs, Y, Sr, Mn, Mg, Th, U, and Cl).

ICP-MS operating conditions	
Instrument	Thermo Scientific™ iCAP™ Qc
Forward power	1450 W
Carrier gas flow rate	~1 L/min (Ar) and ~0.35 L/min (He)
Auxiliary gas flow rate	~1 L/min
Plasma gas flow rate	~14 L/min
Nitrogen	~3.5 mL/min
Data acquisition parameters	
Mode of operating	STD (standard mode)
Sampling scheme	–2NIST-612–2MAD–1DUR–~~10apts~~10apt–
Background scanning	15 s
Data acquisition time	35 s
Wash-out time	15 s
Measured isotopes	~~^{43}Ca ^{44}Ca~~^{26}Mg ^{31}P ^{35}Cl ~~^{26}Mg~~^{43}Ca ^{44}Ca ^{55}Mn ^{88}Sr ^{89}Y ^{139}La ^{140}Ce ^{141}Pr ^{146}Nd ^{147}Sm ^{153}Eu ^{157}Gd ^{159}Tb ^{163}Dy ^{165}Ho ^{166}Er ^{169}Tm ^{172}Yb ^{175}Lu ~~^{232}Th ^{238}U~~^{202}Hg ^{204}Pb ^{206}Pb ~~^{206}Pb~~ ^{207}Pb ^{208}Pb ~~^{202}Hg~~^{232}Th ^{238}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); ~~apts~~apt – unknown ~~apatites. (*) Constant laser~~apatite crystals. (*) Laser pulse energy of 4 J/cm^2, which was measured directly on target with a Coherent™ laser energy meter.

Response to Referee 1 – Jakub Sliwinski

The authors explore whether chemical etching of apatites for AFT has any influence on subsequent U-Pb dates, concluding that although etched samples tend to be a bit young compared to unetched samples, the results are well within uncertainty. The study is straightforward, and the message is clear, so I have very few comments, apart from noting that the presentation needs to be cleared up in places to avoid ambiguity.

Dear Jakub, thank you for your comments and reviewing our manuscript. Please, find our responses (in red italics) to each of your comments below.

General comments:
1. Perhaps the most substantial comment: While this study demonstrates an important effect, it does not address the fact that a very similar experiment was already undertaken by Hasebe et al., 2009 looking only at U concentrations. While I see this citation in the introduction for the very general concept of AFT, I do not see any other recognition, or any motivation explaining why this present study was undertaken. Furthermore, I see no discussion or comparison with Hasebe's study in the discussion.
OK, done. We compared and mentioned Hasebe's study.

2. Already in the abstract I see a few grammatical mistakes and would therefore strongly recommend a friendly review by a colleague who is a native English speaker. Most of these mistakes are minor (misuse of articles, e.g. "the etching" instead of "etching") but correcting them will improve the quality of the manuscript.
OK, done. Thank You. In our view, the grammar was improved.

3. I find the abstract a little bit disappointing. While I normally enjoy concise writing, I find that a substantial part of the abstract is just "LA-ICP-MS" written out in full, and there is a lack of summary statistics for the analyses that would provide a quick and easy summary of the main results. Furthermore, given how short the abstract is, the "Short Summary" afterwards is completely redundant!
OK. Abstract was improved. Short Summary is required by the Journal.?

4. When reporting the ages and uncertainties (perhaps as early as the abstract), please note clearly if you're using 1s or 2s uncertainties.
OK, done.

5. In Hasebe, 2004 there is a short note on the potential effect of etching on LA-ICP-MS of apatites. While you show no significant difference between etched and unetched grained, the fact that you note a slight young bias makes me curious. I've worked a lot with chemical abrasion of zircons, and while the abrasion process generally removes areas of Pb loss (making the zircons older), the annealing process actually reinforces the matrix and makes the zircon look younger. This is why we always normalize abraded zircons to abraded standards. In iolite, you can actually visualize this with the time-resolved integration and see that the down-hole Pb/U fractionation is more prominent in radiation-damaged, unannealed zircons. I'd be really curious to see a

down-hole fractionation signal for apatites, as this would help to determine if the slight youngling is indicative of some sort of matrix-damaging process, or if it is purely due to statistical chance. This is entirely optional, however (only for my own curiosity), so I leave it to the authors to include it or not.

Thank You for recommendation. You are right, U-Pb ages are slightly younger on etched apatite crystals. This was now discussed.

Detailed comments
(format: page number_line)

2_30: also U-Th dating!

OK, Thank You.

2_39: I find the structure of this paragraph a bit confusing and ambiguous. Please be very clear in saying that LA-ICP-MS can be used to obtain U concentrations for AFT, as well as U-Pb ratios for U-Pb dating. Also, I don't understand the sentence "therefore, there is a doubt. . ." I don't see how the doubt follows what you previously wrote.

OK, done. The sentence was improved.

4_87: perhaps note very quickly which "conventional" techniques you used (e.g. bromoform? Methylene iodide? Frantz?)

OK, done. We used sieving, Frantz, and bromoform.

4_89: combine these two sentences.

OK, done. Thank You.

4_90: what is 4pi geometry?

4pi geometry is generally used for AFT dating. 4pi geometry referees to polishing up to the interior of crystals (e.g., for apatites, removing 15-20 microns, o more).

Table 2: Excellent table with a summary of analytical parameters. I would just note that the masses can be arranged by mass (with 238U at the end).

OK, done.

Figure 1: The third panel is likely unnecessary here. . . it's just the second panel copied and labelled with another spot location.

OK. The third panel was removed.

Figure 2: The aspect ratio of this figure is going to ruin its quality in the final print of the manuscript (i.e. it's too long to fit on a single page). Please consider splitting it into two parts, with a 3x2 grid and a 2x2 grid for two separate pages. Also, what uncertainty is reported? 1s or 2s?

Ok, done.

Figure 3: Just a suggestion, but maybe try plotting in log space in order to minimize the amount of blank space in the figure? Are these error bars 1s or 2s?
I think if we plot in log scale, we cannot see well error bars. 2SE bars.

Response to Referee 2 – Ziva Shulaker

This work investigates whether etching for apatite fission track dating affects the precision and uncertainty of same-grain U-Pb ages obtained via LA-ICP-MS. The authors conclude that U-Pb ages of etched and unetched apatite grains are within error of each other. However, etched grains tend to have slightly younger U-Pb ages compared to unetched grains. The purpose of the study is clear and is presented simply and understandably. However, clarification of some sentences and additional discussion would strengthen the gap in knowledge this study is filling.
Below I present the main points and minor points that require attention for revision. The major points are divided into scientific comments and the paper organization and content. The minor comments are provided in bullet form, line-by-line. I hope the comments below are useful for ensuring that the key findings of the study are highlighted.

Dear Ziva, thank you very much for your comments and reviewing this paper. Please, find our responses (in red italics) to each of your comments below.

Major comments:
- A section summarizing previously published work, on apatite and/or zircon, and the necessity of this study should be presented before the sample description section. This will emphasize what gap in knowledge this study is filling.
OK, done. The section of Introduction was improved, and the importance of our study is now presented in a clearer form.

- Because grains were mounted in a polished epoxy mount, it would be interesting to see if there is evidence for zoning in Cathodoluminescence (CL) or Back-scattered Electron (BSE) imagery. This could be a variable that impacts the collected U-Pb ages.
Unfortunately, we are unable to obtain CL neither BSE images. On the other hand, apatite grains analyzed in this study show no significant variation on elemental composition. We compared REEs and trace elements on same unetched and etched apatite grains and noted that there are no significant differences.

- There could be additional discussion between etched and not etched apatite U-Pb ages: to further discuss the differences between etched and not etched apatite U-Pb ages, perhaps discuss the average errors on individual U-Pb analyses for each sample. Often in U-Pb geochronology, individual U-Pb analyses can have high errors but the reported weighted mean age and errors can result in an age with a severely underestimated error. This could therefore mask whether U-Pb analyses on etched grains are more imprecise or less accurate compared to unetched grains.

In our view, it is not necessary to compare single-grain U-Pb ages between unetched and etched grains, because apatite U-Pb ages obtained by LA-ICP-MS are generally discordant. You are right, etched grains apparently yielded more precise ages if compared to unetched grains. This now was also discussed.

- Are there noticeable differences between Th, Pb, and/or U concentrations collected via LA-ICP-MS before or after etching apatite grains? Or do these grains have very variable Th, Pb, and/or U concentrations? Does elemental concentration affect ages determined after etching? Homogeneous standards could help assess these points.
- An increasing number of studies couple same-grain multi-analytical techniques to obtain as much information as possible. For instance, performing (U-Th)/He and/or U-Pb and/or trace-element analyses on zircons or apatites. It would be interesting to discuss the effects of apatite fission track etching with U-Pb and trace-elements. I am unsure whether additional trace-elements were collected in this study, as the protocol that was used in this study is stated to have been developed for U-Pb and multi-element analyses (line 101). If this data exists, I think this discussion could enhance the applicability and reach of this manuscript.

We revised carefully Th, U, REE, Sr, Y, Mn, Mg, an Cl contents before and after etching the same crystals. There are no marked differences. Pooled concentrations are identical between unetched and etched apatite groups from each sample.

Minor comments:

- Switch the first and second sentences so that the objective occurs first and then the experiment is discussed.

OK. Done.

- Lines 11-13: incorrect grammar; also clarify the “obtaining” of U-Pb ages; perhaps replace with something similar to as follows: “The objective of this study is to assert whether etching required for apatite fission track analyses impacts the precision and accuracy of same-grain U-Pb ages.”

OK. Done. Thank You.

- Line 14: determination of apatite U-Pb ages is vague; clarify “determination” – such as accuracy, precision?

OK. Done. Thank You.

- Line 16: instead of simultaneously; “double dating” is more accurate. I interpret the goal of this sentence to assert that this paper establishes the viability of double dating apatite via fission track and LA-ICP-MS.

OK. Done.

- Line 19: “of five samples” should be replaced with “from five samples”

OK. Done. Thank You.

- Line 21: clarify – obtaining accurate and precise U-Pb ages?
OK. Done.

- Lines 29-30: “This accessory mineral is often used for fission track, (U-Th)/He, and U-Pb dating”
OK. Done.

- Lines 33-34: acronym should come after the term: eg., “laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)”
OK. Done. Thank You.

- Line 35: clarify 238U levels - concentration?
OK. Done. “concentrations”.

- Line 40: clarify what causes the doubt and what the doubt is.
OK. Done. Thank You.

- Lines 40-43: (my personal preference is to avoid asking questions) could restate questions as: “The influence of chemical etching required for AFT dating of the precision and accuracy of same-grains analyzed for U-Pb dating via LA-ICP-MS remains to be quantified. To investigate this issue, the same unetched and etched apatite grains were analyzed via LA-ICP-MS for U-Pb dating.”
OK. Thank You. The sentence was improved as You suggested.

- Line 47: header can be simpler, such as: Sample descriptions
OK.

- Lines 59-62: validate using the age of a different previously dated sample; where is the other dated sample in relation to the sample in this study? Is it from the same unit?
OK. Sample MCH-38 is from the same unit.

- Lines 87-90: combining sentences for reading ease: “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. The mount was polished...”
OK. Done. Thank You.

- Line 91: “sterile” is unclear; sufficient to state: “For our experiment, complete crystals lacking visible inclusions and other defects, such as cracks, were selected for analysis.”
OK. Done. Thank You.

- Line 97: remove “exactly” unless the center of the polished surface was measured for spot analysis
OK.

- Line 101: were other elements (REEs, Y, Sr, Mn, Mg, Cl) measured in this study? Or the same protocol that was developed to measure those elements was used? If they weren’t measured in this study, I would disregard from Table 2.
Yes, all these mases were measured during this study. I think it is important to demonstrate this protocol, which may be useful for further experiments.

- Line 103: include the Iolite version
OK. Done.

- Line 122: should be moved to the analytical procedures in the paragraph beginning line 94
OK. Done.

- Lines 176-177: this contradicts the first sentence of the paragraph; there is clearly some effect to the U-Pb ages after etching, but it might be within analytical uncertainty and grains analyzed before/after etching have indistinguishable U-Pb ages.
OK. Done. The paragraph was improved and clarified.

- Line 178: word choices of “safely” and “simultaneous;” perhaps restate sentence to describe how this work shows that chemical etching for AFT dating doesn’t significantly affect U and Pb ratios or concentrations, which makes apatite grains analyzed for AFT amenable to same-grain U-Pb dating via LA-ICP-MS.
OK. Done.

- Lines 179-181: this should be in a new section above that discusses previous work. This will emphasize why your study is vital for providing data that validates same-grain AFT and apatite U-Pb dating via LA-ICP-MS.
OK. Done. Thank You.

- Line 217: in the Figure 2 caption, note whether the ages reported are averages, weighted means, etc.; are the uncertainties one or two sigma?
OK. Done.

- Line 223: in figure 3, what are the errors shown on the graph?
OK. Done.

- Line 455: see comment for line 101: if additional elements (REEs, Y, Sr, Mn, Mg, Cl) were not measured, can disregard from table 2 as this wasn’t the set-up for these experiments.
We think it is important to demonstrate this protocol in this manuscript.