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

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

The same unetched and chemically etched apatite crystals from five rock samples were dated by 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.

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19 Short summary

20 Unetched and etched apatite grains from five samples were dated by U–Pb method using laser 21 ablation inductively-coupled plasma mass spectrometry. Our experiment indicates that etching 22 needed for apatite fission track dating has insignificant effects on obtaining accurate U–Pb ages; thus, the laser ablation-based technique may be used for apatite fission track and U–Pb double
dating.

25

26 1 Introduction

27

28 Apatite, Ca₅(PO₄)₃[F,Cl,OH], is the most common phosphate mineral in the Earth's crust and can 29 be found in practically all igneous and metamorphic rocks, in many ancient and recent sediments 30 as well as in certain mineral deposits (Piccoli and Candela, 2002; Morton and Yaxley, 2007; 31 Webster and Piccoli, 2015). This accessory mineral is often used as a natural thermochronometer 32 for fission track, helium, U-Th and U-Pb dating (e.g., Zeitler et al., 1987; Wolf et al., 1996; 33 Ehlers and Farley, 2003; Hasebe et al., 2004; Donelick et al., 2005; Chew and Donelick, 2012; 34 Chew et al., 2014; Cochrane et al., 2014; Liu et al., 2014; Spikings et al., 2015; Glorie et al., 35 2017). Presently, apatite fission track (AFT) ages can be obtained rapidly by using laser ablation 36 inductively-coupled plasma mass spectrometry (LA-ICP-MS) for direct measurement of "parent 37 nuclides", i.e., ²³⁸U contents (Cox et al., 2000; Svojtka and Košler, 2002; Hasebe et al., 2004, 38 2009; Donelick et al., 2005; Abdullin et al., 2014, 2016, 2018; Vermeesch, 2017). The LA-ICP-MS technique may be used to measure ²³⁸U for AFT dating, together with Pb isotopes needed for 39 40 U-Pb dating (e.g., Chew and Donelick, 2012; Liu et al., 2014; Glorie et al., 2017; Bonilla et al., 41 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/zircon fission track dating does not interfere with U analysis by LA–ICP-MS. After chemical etching of apatite, a smaller volume of ablated material is analyzed by LA–ICP-MS. The influence of etching needed for AFT dating on

46	the precision and accuracy of dating the same crystals by U-Pb using LA-ICP-MS remains to be
47	quantified. To investigate this issue, the same unetched and etched apatite grains extracted from
48	five rock samples were analyzed via LA-ICP-MS for U-Pb dating. The chosen rock samples
49	have either emplacement or metamorphic ages ranging from the Cretaceous to the
50	Neoproterozoic (see Table 1 for further details).
51	Table 1
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53	
54	2 Sample descriptions
55	
56	2.1 OV-0421 (Tres Sabanas Pluton, Guatemala)
57	
58	This sample is a two mica-bearing deformed granite belonging to the Tres Sabanas Pluton, which
59	is located northwest of Guatemala City, Guatemala. For sample OV-0421, an emplacement age
60	of 115 \pm 4 (2 σ) Ma was proposed based on zircon U–Pb data (Torres de León, 2016). A cooling
61	age of 102 ± 1 (2 σ) Ma, obtained with K–Ar (on biotite), was also reported by the same author.
62	
63	2.2. MCH-38 (Chiapas Massif Complex, Mexico)
64	
65	MCH-38 is an orthogneiss from the Permian Chiapas Massif Complex. This rock was sampled to
66	the west of Unión Agrarista, the State of Chiapas, southeastern Mexico. There is no reported age
67	for this sample. Some zircon U-Pb dates obtained for the Chiapas Massif Complex (Weber et al.,

68	2007, 2008; Ortega-Obregón et al., 2019) suggest that a Lopingian (260-252 Ma) crystallization
69	or metamorphic age may be assumed for sample MCH-38.
70	
71	2.3 TO-AM (Totoltepec Pluton, Mexico)
72	
73	TO-AM is a granitic rock, sampled ca. 5 km west of Totoltepec de Guerrero, the State of Puebla,
74	southern Mexico. There is no reported radiometric data for sample TO-AM. Previous geological
75	studies indicate that the Pennsylvanian-Cisuralian Totoltepec Pluton was emplaced over a ca. 23
76	million year period (from ca. 308 to ca. 285 Ma; e.g., Kirsch et al., 2013).
77	
78	2.4 CH-0403 (Altos Cuchumatanes, Guatemala)
79	
80	CH-0403 was collected 5 km ESE of Barillas, in the Altos Cuchumatanes, Guatemala. It consists
81	of a gray to green granodiorite. Five zircon aliquots of sample CH-0403 were dated using isotope
82	dilution thermal-ionization mass spectrometry, yielding a lower intercept date of 391 \pm 8 (2 σ)
83	Ma that is interpreted as its approximate crystallization age (Solari et al., 2009).
84	
85	2.5 OC-1008 (Oaxacan Complex, Mexico)
86	
87	This sample is a paragneiss from the Grenvillian Oaxacan Complex, southern Mexico. OC-1008
88	was collected in the federal road which connects Nochixtlán to Oaxaca. It was demonstrated that
89	this sample underwent granulite facies metamorphism at 1000–980 Ma (Solari et al., 2014).
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- **3** Analytical procedures
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95 Accessory minerals were concentrated using conventional mineral separation techniques such as 96 rock crushing, sieving, Wilfley table, Frantz magnetic separator, and bromoform. Approximately 97 300 apatite grains were extracted from each rock sample and mounted with their surfaces parallel 98 to the crystallographic *c*-axis in a 2.5 cm diameter epoxy mount. Mounted crystals were polished 99 to expose their internal surfaces (i.e., up to 4π geometry). For this experiment, complete crystals 100 lacking visible inclusions and other defects, such as cracks, were carefully selected for analysis. 101 Sample preparation was performed at Taller de Molienda and Taller de Laminación, Centro de 102 Geociencias (CGEO), Campus Juriquilla, Universidad Nacional Autónoma de Mexico (UNAM). 103 Single spot analyses were performed with a Resonetics RESOlutionTM LPX Pro (193 nm, 104 ArF excimer) laser ablation system, coupled to a Thermo Scientific iCAP[™] Qc quadrupole ICP-105 MS at Laboratorio de Estudios Isotópicos (LEI), CGEO, UNAM. During this experimental work, 106 LA-ICP-MS-based sampling was performed in central parts of the selected apatite grains before 107 and after chemical etching (in 5.5M HNO₃ at 21 °C for 20 s to reveal spontaneous fission tracks), 108 as shown schematically in Fig. 1. The LA–ICP-MS protocol used for apatite analyses, as given in 109 Table 2, was established on the basis of numerous experiments carried out at LEI during the past 110 five years, and can be used for U–Pb and fission track double dating plus multielemental analysis 111 (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 112 and Kamber, 2012). UcomPbine (Chew et al., 2014) was used to model ²⁰⁷Pb/²⁰⁶Pb initial values 113

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

121 apatite U–Pb dating, because the LA–ICP-MS-derived U–Pb results are generally discordant.
122 The lower intercept in the T–W plot is considered as a mean apatite U–Pb age that should have
123 geological significance (crystallization or cooling age, the age of mineralization or metamorphic
124 event). Apatite U–Pb ages were calculated with IsoplotR (Vermeesch, 2017, 2018) and described
125 below. Detailed information on U–Pb experiments is given in Table S1 in the Supplement.

126 --- Figure 1 ---127 --- Table 2 ---128 129 130 4 **Results** 131 132 4.1 OV-0421 133 134 For rock sample OV-0421, 41 unetched apatites yielded a lower intercept age of 106 ± 4 (2 σ) Ma 135 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 (2 σ) Ma, was 136

137	obtained after chemical etching of the same apatite grains, yielding a MSWD of 1.13 and a $P(\chi^2)$
138	of 0.27. Both these apatite U–Pb ages lie between the zircon U–Pb date of $115 \pm 4 (2\sigma)$ Ma (i.e.,
139	crystallization age) and the biotite K–Ar age of 102 \pm 1 (2 σ) Ma (i.e., cooling age), which were
140	previously obtained for the same granite sample by Torres de León (2016).
141	
142	4.2. MCH-38
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144	For orthogneiss sample MCH-38, the lower intercept in T–W yielded a U–Pb age of $245 \pm 6 (2\sigma)$
145	Ma (obtained from 41 unetched apatites) with a MSWD of 0.28 and a $P(\chi^2)$ of 1. Etched apatite
146	grains from MCH-38 yielded an age of 240 ± 4 (2 σ) Ma with a MSWD of 0.36 and a $P(\chi^2)$ of 1
147	(Fig. 2). Our U-Pb results are in close agreement with geochronological data reported from the
148	Chiapas Massif Complex in previous studies (Damon et al., 1981; Torres et al., 1999; Schaaf et
149	al., 2002; Ortega-Obregón et al., 2019). For instance, Torres et al. (1999) compiled biotite K-Ar
150	ages, most of which lie within Early-Middle Triassic period. Triassic cooling ages in the Chiapas
151	Massif Complex were also detected by Rb–Sr in mica–whole rock pairs that range from 244 ± 12
152	(2σ) Ma to $214 \pm 11 (2\sigma)$ Ma (Schaaf et al., 2002).
153	
154	4.3 TO-AM

156 Unetched apatites (32 crystals; Fig. 2) from granite TO-AM yielded a lower intercept date of 303 157 $\pm 5 \ (2\sigma)$ Ma with a MSWD of 0.6 and a $P(\chi^2)$ of 0.96. After etching, a slightly younger age of 158 299 $\pm 3 \ (2\sigma)$ 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).
- 161
- 162 4.4 CH-0403
- 163

164 36 unetched apatite grains from sample CH-0403 yielded a lower intercept U–Pb age of 345 ± 10 165 (2σ) Ma with a MSWD of 0.7 and a $P(\chi^2)$ of 0.9, whereas etched grains yielded an age of 334 ± 8 166 (2σ) Ma with a MSWD of 1.37 and a $P(\chi^2)$ of 0.08 (Fig. 2). These cooling dates are considerably 167 younger if compared to the CH-0403 emplacement age of 391 ± 8 (2σ) Ma (Solari et al., 2009).

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169 4.5 OC-1008
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171 41 unetched apatites belonging to sample OC-1008 yielded a U–Pb age of $839 \pm 12 (2\sigma)$ Ma with 172 a MSWD of 0.98 and a $P(\chi^2)$ of 0.50. After etching, the same apatite crystals yielded an age of 173 $830 \pm 10 (2\sigma)$ Ma with a MSWD of 1.24 and a $P(\chi^2)$ of 0.14 (Fig. 2). Both these apatite U–Pb 174 ages are significantly younger than the age of granulite facies metamorphism in the Grenville-175 aged Oaxacan Complex (1 Ga to 980 Ma, Solari et al., 2014), and thus, should be considered as 176 cooling ages.

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- 181

---- Figure 2 ----

5 Discussion and concluding remarks

184	Most rock samples, except OV-0421, yielded slightly younger apatite U-Pb ages after chemical
185	etching (up to 3.3% in sample CH-0403). However, the lower intercept U-Pb ages obtained from
186	unetched apatite grains are indistinguishable within error from the U-Pb ages obtained on the
187	same etched grains (see diagram in Fig. 3). The results of this experiment demonstrate that
188	chemical etching required for AFT analysis has negligible effects on the accuracy of apatite U-
189	Pb ages determined via LA-ICP-MS. Thus, as a main conclusion of this study, LA-ICP-MS can
190	be used for simultaneous AFT and U-Pb ages double dating, as it was already done in some
191	previous studies (e.g., Chew and Donelick, 2012; Liu et al., 2014; Glorie et al., 2017; Bonilla et
192	al., 2020; Nieto-Samaniego et al., 2020).
193	Figure 3
194	
195	Supplement
196	The supplement related to this article is available online at: https://
197	
198	Author contributions
199	Conceptualisation, investigation, and writing of the original draft were done by FA. LS and COO
200	provided technical support. LS and JS acquired funding and resources, supervised the study, and
201	reviewed the manuscript.
202	
203	Competing interests
204	The authors declare that they have no conflict of interest.

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227 deviation, Ngr – number of grains dated. Errors are given in 2σ .

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229	Figure 3
230	Plot showing the lower intercept U–Pb ages obtained on unetched and etched apatite grains.
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LA-ICP-MS apatite U-Pb dating before etching

Figure 1



chemical etching (5.5M nitric acid, 21 °C for 20 s)



LA-ICP-MS apatite U-Pb dating after etching







Figure 2





Figure 3 OC-1008 unetched apatite lower intercept U-Pb age (Ma) CH-0403 TO-AM MCH-38 OV-0421 400 800 etched apatite lower intercept U-Pb age (Ma)

- **Table 1**
- 431 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	$115\pm4\ Ma$	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	$391\pm8\;Ma$	Solari et al. (2009)
	OC-1008	Oaxacan Complex, Mexico	paragneiss	$990\pm10~\text{Ma}$	Solari et al. (2014)
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- 447
- 448 **Table 2**
- 449
- 450 LA-ICP-MS protocol established at LEI to be applied for simultaneous apatite U-Pb and fission-
- 451 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 parame	eters	
Mode of operating	STD (standard mode)	
Sampling scheme	-2NIST-612-2MAD-1DUR-10apt-	
Background scanning	15 s	
Data acquisition time	35 s	
Wash-out time	15 s	
	$^{26}Mg\ ^{31}P\ ^{35}Cl\ ^{43}Ca\ ^{44}Ca\ ^{55}Mn\ ^{88}Sr$	
	89Y 139La 140Ce 141Pr 146Nd 147Sm	
Measured isotopes	$^{153}Eu \ ^{157}Gd \ ^{159}Tb \ ^{163}Dy \ ^{165}Ho \ ^{166}Er$	
	$^{169}Tm \ ^{172}Yb \ ^{175}Lu \ ^{202}Hg \ ^{204}Pb \ ^{206}Pb$	
	207 Pb 208 Pb 232 Th 238 U [total = 29]	
Laser ablation system		
Ablation cell	RESOlution [™] Laurin Technic S-155	

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

452

453 Note: MAD – "First mine Discovery" U–Pb apatite standard from Madagascar; DUR – Durango 454 apatite from Cerro de Mercado mine (Mexico); apt – unknown apatite crystals. (*) Laser pulse 455 energy of 4 J/cm², which was measured directly on target with a CoherentTM laser energy meter.

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458	Santiago de Querétaro, 6 Nov 2020
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465	Dear Professor Axel,
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469	First of all, I would like to thank You for your help with English grammar.
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471	I revised our manuscript according to your minor comments.
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490	With Best Wishes.
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494 Technical note: on LA–ICP-MS U–Pb dating of unetched and etched apatites

- 495 Fanis Abdullin et al.: LA–ICP-MS U–Pb dating of apatites
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- ⁴⁹⁹ ³LANGEM, Instituto de Geología, UNAM, Ciudad Universitaria, CDMX, 04510, Mexico
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- 501

502 Abstract

503 The same unetched and chemically etched apatite grainscrystals from five rock samples were 504 dated withby U–Pb method via laser ablation inductively-coupled plasma mass spectrometry 505 (LA–ICP-MS). The objective of this study is to assertest whether chemical etching required for 506 apatite fission track analysis impacts the precision and accuracy of same grainapatite U-Pb 507 agesgeochronology. The results of our this experiment suggest that etching has no significant 508 effectinsignificant effects on the accuracy of apatite U-Pb ages obtained by LA-ICP-MS. 509 Thus Therefore, LA-ICP-MS can be used safely is reliable for U-Pb analysis as part of apatite 510 fission track and U–Pb double dating.

- 511
- 512

513 Short summary

514 Unetched and etched apatite grains from five samples were dated <u>withby</u> U–Pb<u>method</u> using 515 laser ablation inductively-coupled plasma mass spectrometry. Our experiment indicates that 516 etching needed for apatite fission track dating has <u>no effectinsignificant effects</u> on <u>the</u> obtaining accurate U–Pb ages; thereforethus, the laser ablation-based technique may be used for apatite
fission track and U–Pb double dating.

519

520 **1** Introduction

521

522 Apatite, Ca₅(PO₄)₃[F,Cl,OH], is the most common phosphate mineral in the Earth's crust and can 523 be found in practically all igneous and metamorphic rocks, in many ancient and recent sediments 524 as well as in certain mineral deposits (Piccoli and Candela, 2002; Morton and Yaxley, 2007; 525 Webster and Piccoli, 2015). This accessory mineral is often used as a natural thermochronometer 526 for fission track, Hehelium, U–Th and U–Pb dating (e.g., Zeitler et al., 1987; Wolf et al., 1996; 527 Ehlers and Farley, 2003; Hasebe et al., 2004; Donelick et al., 2005; Chew and Donelick, 2012; 528 Chew et al., 2014; Cochrane et al., 2014; Liu et al., 2014; Spikings et al., 2015; Glorie et al., 529 2017). Presently, apatite fission track (AFT) ages can be obtained rapidly by using laser ablation 530 inductively-coupled plasma mass spectrometry (LA-ICP-MS) for direct measurement of "parent nuclides", i.e., ²³⁸U contents (Cox et al., 2000; Svojtka and Košler, 2002; Hasebe et al., 2004;;, 531 532 2009; Donelick et al., 2005; Abdullin et al., 2014, 2016, 2018; Vermeesch, 2017). The LA-ICP-MS technique may be used to obtain measure ²³⁸U for AFT dating, together with isotope ratiosPb 533 534 isotopes needed for U-Pb dating (e.g., Chew and Donelick, 2012; Liu et al., 2014; Glorie et al., 535 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 <u>apatite/zircon</u> fission track dating <u>has no</u> significant effect on the accuracy of<u>does not interfere with</u> U <u>measurementanalysis</u> by LA–ICP-MS-method. After chemical etching of <u>apatitesapatite</u>, a smaller volume of ablated material is

540	analy	zed by LA-ICP-MS. The influence of etching needed for AFT dating on the precision and
541	accur	acy of <u>dating the same-grain crystals by</u> U–Pb dating analyzed viausing LA-ICP-MS
542	remai	ns to be quantified. To investigate this issue, the same unetched and etched apatite grains
543	extrac	cted from five rock samples were analyzed usingvia LA-ICP-MS for U-Pb dating. The
544	chose	n rock samples have either emplacement or metamorphic ages ranging from the Cretaceous
545	to the	Neoproterozoic (see Table 1 for further details).
546		Table 1
547		
548		
549		
550	2	Sample descriptions
551		
552	2.1	OV-0421 (Tres Sabanas Pluton, Guatemala)
553		
554	This s	sample is a two mica-bearing deformed granite belonging to the Tres Sabanas Pluton, which
555	is loc	ated NW northwest of Guatemala City, Guatemala. For sample OV-0421, an emplacement
556	age o	f 115 \pm 4 (2 σ) Ma was proposed based on zircon U–Pb data (Torres de León, 2016). A
557	coolii	ng age of 102 ± 1 (2 σ) Ma, obtained with K–Ar (on biotite), haswas also been reported by
558	the sa	me author.
559		
560	2.2.	MCH-38 (Chiapas Massif Complex, Mexico)
561		

562	MCH-38 is an orthogneiss from the Permian Chiapas Massif Complex. This rock was sampled to
563	the west of Unión Agrarista, the State of Chiapas, southeastern Mexico. There is no reported age
564	for this sample. Some zircon U–Pb dates obtained for the Chiapas Massif Complex (Weber et al.,
565	2007, 2008; Ortega-Obregón et al., 2019) suggest that a Lopingian (260-252 Ma) crystallization
566	or metamorphic age may be assumed for sample MCH-38.
567	
568	2.3 TO-AM (Totoltepec Pluton, Mexico)
569	
570	TO-AM is a granitic rock, sampled ca. 5 km west of Totoltepec de Guerrero, the State of Puebla,
571	southern Mexico. There is no reported radiometric data for sample TO-AM. Previous geological
572	studies indicate that the Pennsylvanian-Cisuralian Totoltepec Pluton was emplaced over a ca. 23
573	million year period (from ca. 308 to ca. 285 Ma; e.g., Kirsch et al., 2013).
574	
575	2.4 CH-0403 (Altos Cuchumatanes, Guatemala)
576	
577	CH-0403 was collected 5 km ESE of Barillas, in the Altos Cuchumatanes, Guatemala. It consists
578	of a gray to green granodiorite. Five zircon aliquots of sample CH-0403 were dated using isotope
579	dilution thermal-ionization mass spectrometry, yielding a lower intercept date of 391 \pm 8 (2 σ)
580	Ma that is interpreted as its approximate crystallization age (Solari et al., 2009).
581	
582	2.5 OC-1008 (Oaxacan Complex, Mexico)
583	

584	This sample is a paragneiss from the Grenvillian Oaxacan Complex, southern Mexico. OC-1008
585	was collected in the federal road which connects Nochixtlán to Oaxaca. It was demonstrated that
586	this sample underwent granulite facies metamorphism at 1000–980 Ma (Solari et al., 2014).
587	
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591	3 Analytical procedures
592	
593	Accessory minerals were concentrated using conventional mineral separation techniques such as
594	rock crushing, sieving, Wilfley table, Frantz magnetic separator, and bromoform. Approximately
595	300 apatite grains were extracted from each rock sample and mounted with their surfaces parallel
596	to the crystallographic c-axis in a 2.5 cm diameter epoxy mount. Mounted crystals were polished
597	to expose their internal surfaces (i.e., up to 4π geometry). For this experiment, complete crystals
598	lacking visible inclusions and other defects, such as cracks, were carefully selected for analysis.
599	Sample preparation was performed at Taller de Molienda and Taller de Laminación, Centro de
600	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 ICPMS 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 5.5M 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

607	Table 2, was established on the basis of numerous experiments carried out at LEI during the past
608	five years, and can be used for U-Pb and fission track double dating plus multielemental analysis
609	(Abdullin et al., 2018; Ortega-Obregón et al., 2019). Corrected isotopic ratios and errors were
610	calculated using Iolite 3.5 (Paton et al., 2011) and the VizualAge data reduction scheme (Petrus
611	and Kamber, 2012). UcomPbine (Chew et al., 2014) was used to model ²⁰⁷ Pb/ ²⁰⁶ Pb initial values
612	and thus force a ²⁰⁷ Pb correction that considers the common Pb (non-radiogenic Pb) incorporated
613	by apatite standards at the moment of their crystallization (see also Ortega-Obregón et al., 2019).
614	The "First Mine Discovery" apatite from Madagascar, with a mean U-Pb age of ca. 480 Ma
615	(Thomson et al., 2012; Chew et al., 2014), was used as a primary reference material. The results
616	for measured isotopes using NIST-612 (Pearce et al., 1997) were normalized using ⁴³ Ca as an
617	internal standard and taking an average CaO content of 55% (i.e., for F-apatites).%.
618	Tera-and_Wasserburg Concordia diagrams (T-W; Tera and Wasserburg, 1972) are used
619	in apatite U-Pb dating, because the LA-ICP-MS-derived U-Pb results are generally discordant.
620	The lower intercept in the T–W plot is considered as a mean apatite U–Pb age that should have
621	geological significance (crystallization or cooling age, the age of mineralization or metamorphic
622	event). Apatite U-Pb ages were calculated with IsoplotR (Vermeesch, 2017, 2018) and described
623	below. Detailed information on-our U-Pb experiments is given in Table S1 in the Supplement.
624	Figure 1
625	Table 2
626	

- **4 Results**

630 4.1 OV-0421

631

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). <u>VirtuallyPractically</u> 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 previously obtained for the same granite sample by Torres de León (2016).

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640 4.2. MCH-38
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642 For orthogneiss sample MCH-38, the lower intercept in T–W yielded a U–Pb age of 245 ± 6 (2 σ) Ma (obtained from 41 unetched apatites) with a MSWD of 0.28 and a $P(\chi^2)$ of 1. Etched apatite 643 grains from MCH-38 yielded an age of 240 ± 4 (2 σ) Ma with a MSWD of 0.36 and a $P(\chi^2)$ of 1 644 645 (Fig. 2). Our U-Pb results are in close agreement with geochronological data reported from the 646 Chiapas Massif Complex in previous studies (Damon et al., 1981; Torres et al., 1999; Schaaf et 647 al., 2002; Ortega-Obregón et al., 2019). For instance, Torres et al. (1999) compiled biotite K-Ar 648 ages, most of which lie within Early-Middle Triassic period. Triassic cooling ages in the Chiapas 649 Massif Complex were also detected by Rb–Sr in mica–whole rock pairs that range from 244 ± 12 (2σ) Ma to $214 \pm 11 (2\sigma)$ Ma (Schaaf et al., 2002). 650

651

652 4.3 TO-AM

675	Figure 2
674	cooling ages.
673	aged Oaxacan Complex (1 Ga to 980 Ma, Solari et al., 2014), and thus, should be considered as
672	ages are significantly younger than the age of granulite facies metamorphism in the Grenville-
671	of 830 ± 10 (2 σ) Ma with a MSWD of 1.24 and a $P(\chi^2)$ of 0.14 (Fig. 2). Both these apatite U–Pb
670	with a MSWD of 0.98 and a $P(\chi^2)$ of 0.50. After etching, the same apatite crystals yielded an age
669	41 unetched apatites belonging to the sample OC-1008 yielded a U–Pb age of 839 \pm 12 (2 σ) Ma
668	
667	4.5 OC-1008
666	
665	younger if compared to the CH-0403 emplacement age of 391 ± 8 (2 σ) Ma (Solari et al., 2009).
664	(2 σ) Ma with a MSWD of 1.37 and a $P(\chi^2)$ of 0.08 (Fig. 2). These cooling dates are considerably
663	(2 σ) Ma with a MSWD of 0.7 and a $P(\chi^2)$ of 0.9, whereas etched grains yielded an age of 334 ± 8
662	36 unetched apatite grains from sample CH-0403 yielded a lower intercept U–Pb age of 345 ± 10
661	
660	4.4 CH-0403
659	
658	the Pennsylvanian–Cisuralian Totoltepec Pluton (e.g., see details in Kirsch et al., 2013).
657	ages are in line with the zircon U–Pb ages of 306 ± 2 (2 σ) Ma to 287 ± 2 (2 σ) Ma reported for
656	299 ± 3 (2 σ) Ma was obtained, with a MSWD of 0.89 and a $P(\chi^2)$ of 0.65. These apatite U–Pb
655	\pm 5 (2 σ) Ma with a MSWD of 0.6 and a $P(\chi^2)$ of 0.96. After etching, a slightly younger age of
654	Unetched apatites (32 crystals; Fig. 2) from granite TO-AM yielded a lower intercept date of 303

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5 Discussion and concluding remarks

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682 Most rock samples, except OV-0421, yielded slightly younger apatite U-Pb ages after chemical 683 etching (up to 3.3% in sample CH-0403). However, the lower intercept U–Pb ages obtained from 684 unetched apatite grains are identical indistinguishable within errors toerror from the U-Pb ages 685 obtained on the same etched grains (see diagram in Fig. 3). The results of our experimental 686 study this experiment demonstrate that the chemical etching, required for the AFT analysis, has 687 no important effectnegligible effects on the accuracy of apatite U–Pb ages determined via LA– 688 ICP-MS. Thus, as a main conclusion of this experimental study, LA-ICP-MS can be used safely 689 to obtain simultaneously for simultaneous AFT and U-Pb ages (i.e., double dating), as it was 690 already done in some studies without previous proofstudies (e.g., Chew and Donelick, 2012; Liu 691 et al., 2014; Glorie et al., 2017; Bonilla et al., 2020; Nieto-Samaniego et al., 2020). 692 --- Figure 3 ----

693

694 Supplement

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

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697 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.
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are acknowledged for their constructive comments that improved our manuscript significantly.
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Figure caption

722	Figure 1
723	Illustration displaying the LA-ICP-MS-based U-Pb dating of the same apatite crystal before and
724	after chemical etching (i.e., etched in 5.5M nitric acid at 21 $^{\circ}$ C for 20 s). Spot diameter of 60 μ m.
725	
726	Figure 2
727	Tera-Wasserburg Concordia diagrams for the U-Pb results of unetched and etched apatites from
728	samples OV-0421, MCH-38, TO-AM, CH-0403, and OC-1008. MSWD – mean square weighted
729	deviation, Ngr – number of grains dated. Errors are given in 2σ .
730	
731	Figure 3
732	Plot showing the lower intercept U–Pb ages obtained on unetched and etched apatite grains.
733	
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735	References
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Figure 1

LA-ICP-MS apatite U-Pb dating before etching



chemical etching (5.5M nitric acid, 21 °C for 20 s)



LA-ICP-MS apatite U-Pb dating after etching















Figure 3





Table 1

954 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	$391\pm8\;Ma$	Solari et al. (2009)
	OC-1008	Oaxacan Complex, Mexico	paragneiss	$990\pm10~\text{Ma}$	Solari et al. (2014)
955					
956					
057					
957					
958					
959					
0.60					
960					
961					
962					
0.62					
903					
964					
965					
066					
900					
967					
968					
0.60					
969					
970					

Table 2

- 973 LA-ICP-MS protocol established at LEI to be applied for simultaneous apatite U-Pb and fission-
- 974 track in-situ double dating plus multielemental analysis (REEs, Y, Sr, Mn, Mg, Th, U, and Cl).

ICP-MS operating cond	litions
Instrument	Thermo Scientific TM iCAP TM 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 param	eters
Mode of operating	STD (standard mode)
Sampling scheme	-2NIST-612-2MAD-1DUR-10apt-
Background scanning	15 s
Data acquisition time	35 s
Wash-out time	15 s
Measured isotopes	²⁶ Mg ³¹ P ³⁵ Cl 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 ²⁰² Hg ²⁰⁴ Pb ²⁰⁶ Pb ²⁰⁷ Pb ²⁰⁸ Pb ²³² Th ²³⁸ U [total = 29]

ESOlution [™] Laurin Technic <i>S</i> -155
esonetics RESOlution [™] LPX Pro
3 nm (Excimer ArF)
Hz
J/cm ²
ot 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/cm², which was measured directly on target with a Coherent[™] laser energy meter.