

1 **Technical note: 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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8

9 **Abstract**

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

17

18

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;

23 thus, the laser ablation-based technique may be used for apatite fission track and U–Pb double
24 dating.

25

26 **1 Introduction**

27

28 Apatite, $\text{Ca}_5(\text{PO}_4)_3[\text{F},\text{Cl},\text{OH}]$, 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; Cochran 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., ^{238}U 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–
39 MS technique may be used to measure ^{238}U for AFT dating, together with Pb isotopes needed for
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).

42 Hasebe et al. (2009) previously performed an important experimental study, during which
43 they demonstrated that chemical etching required for apatite/zircon fission track dating does not
44 interfere with U analysis by LA–ICP–MS. The influence of etching needed for AFT dating on the
45 precision and accuracy of dating the same crystals by U–Pb using LA–ICP–MS remains to be

46 quantified. To investigate this issue, the same unetched and etched apatite grains extracted from
47 five rock samples were analyzed via LA-ICP-MS for U-Pb dating. The chosen samples have
48 either emplacement or metamorphic ages ranging from the Cretaceous to the Neoproterozoic (see
49 Table 1 for further details).

50 --- **Table 1** ---

51

52

53 **2 Sample descriptions**

54

55 2.1 OV-0421 (Tres Sabanas Pluton, Guatemala)

56

57 This sample is a two mica-bearing deformed granite belonging to the Tres Sabanas Pluton, which
58 is located northwest of Guatemala City, Guatemala. For sample OV-0421, an emplacement age
59 of 115 ± 4 (2σ) Ma was proposed based on zircon U-Pb data (Torres de León, 2016). A cooling
60 age of 102 ± 1 (2σ) Ma, obtained with K-Ar (on biotite), was also reported by the same author.

61

62 2.2. MCH-38 (Chiapas Massif Complex, Mexico)

63

64 MCH-38 is an orthogneiss from the Permian Chiapas Massif Complex. This rock was sampled to
65 the west of Unión Agrarista, the State of Chiapas, southeastern Mexico. There is no reported age
66 for this sample. Some zircon U-Pb dates obtained for the Chiapas Massif Complex (Weber et al.,
67 2007, 2008; Ortega-Obregón et al., 2019) suggest that a Lopingian (260–252 Ma) crystallization
68 or metamorphic age may be assumed for sample MCH-38.

69

70 2.3 TO-AM (Totoltepec Pluton, Mexico)

71

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

76

77 2.4 CH-0403 (Altos Cuchumatanes, Guatemala)

78

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

83

84 2.5 OC-1008 (Oaxacan Complex, Mexico)

85

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

89

90

91

92 3 Analytical procedures

93
94 Accessory minerals were concentrated using conventional mineral separation techniques such as
95 rock crushing, sieving, Wilfley table, Frantz magnetic separator, and bromoform. Approximately
96 300 apatite grains were extracted from each rock sample and mounted with their surfaces parallel
97 to the crystallographic *c*-axis in a 2.5 cm diameter epoxy mount. Mounted crystals were polished
98 to expose their internal surfaces (i.e., up to 4π geometry). For this experiment, complete crystals
99 lacking visible inclusions and other defects, such as cracks, were carefully selected for analysis.
100 Sample preparation was performed at Taller de Molienda and Taller de Laminación, Centro de
101 Geociencias (CGEO), Campus Juriquilla, Universidad Nacional Autónoma de Mexico (UNAM).

102 Single spot analyses were performed with a Resonetics RESolution™ LPX Pro (193 nm,
103 ArF excimer) laser ablation system, coupled to a Thermo Scientific iCAP™ Qc quadrupole ICP-
104 MS at Laboratorio de Estudios Isotópicos (LEI), CGEO, UNAM. During this experimental work,
105 LA–ICP-MS-based sampling was performed in central parts of the selected apatite grains before
106 and after chemical etching (in 5.5M HNO₃ at 21 °C for 20 s to reveal spontaneous fission tracks),
107 as shown schematically in Fig. 1. The LA–ICP-MS protocol used for apatite analyses, as given in
108 Table 2, was established on the basis of numerous experiments carried out at LEI during the past
109 five years, and can be used for U–Pb and fission track double dating plus multielemental analysis
110 (Abdullin et al., 2018; Ortega-Obregón et al., 2019). Corrected isotopic ratios and errors were
111 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
114 by apatite standards at the moment of their crystallization (see also Ortega-Obregón et al., 2019).

115 The “First Mine Discovery” apatite from Madagascar, with a mean U–Pb age of ca. 480 Ma
116 (Thomson et al., 2012; Chew et al., 2014), was used as a primary reference material. The results
117 for measured isotopes using NIST-612 (Pearce et al., 1997) were normalized using ^{43}Ca as an
118 internal standard and taking an average CaO content of 55%.

119 Tera–Wasserburg Concordia diagrams (T–W; Tera and Wasserburg, 1972) are used in
120 apatite U–Pb dating, because the LA–ICP–MS-derived U–Pb results are generally discordant.
121 The lower intercept in the T–W plot is considered as a mean apatite U–Pb age that should have
122 geological significance (crystallization or cooling age, the age of mineralization or metamorphic
123 event). Apatite U–Pb ages were calculated with IsoplotR (Vermeesch, 2017, 2018) and described
124 below. Detailed information on U–Pb experiments is given in Table S1 in the Supplement.

125 --- **Figure 1** ---

126 --- **Table 2** ---

127

128

129 **4 Results**

130

131 4.1 OV-0421

132

133 For rock sample OV-0421, 41 unetched apatites yielded a lower intercept age of 106 ± 4 (2σ) Ma
134 with a mean square weighted deviation (MSWD) of 1.07, passing the chi-squared test with the
135 $P(\chi^2)$ value of 0.35 (see in Fig. 2). Practically the same U–Pb date, 107 ± 5 (2σ) Ma, was
136 obtained after chemical etching of the same apatite grains, yielding a MSWD of 1.13 and a $P(\chi^2)$
137 of 0.27. Both these apatite U–Pb ages lie between the zircon U–Pb date of 115 ± 4 (2σ) Ma (i.e.,

138 crystallization age) and the biotite K–Ar age of 102 ± 1 (2σ) Ma (i.e., cooling age), which were
139 previously obtained for the same granite sample by Torres de León (2016).

140

141 4.2. MCH-38

142

143 For orthogneiss sample MCH-38, the lower intercept in T–W yielded a U–Pb age of 245 ± 6 (2σ)
144 Ma (obtained from 41 unetched apatites) with a MSWD of 0.28 and a $P(\chi^2)$ of 1. Etched apatite
145 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
146 (Fig. 2). Our U–Pb results are in close agreement with geochronological data reported from the
147 Chiapas Massif Complex in previous studies (Damon et al., 1981; Torres et al., 1999; Schaaf et
148 al., 2002; Ortega-Obregón et al., 2019). For instance, Torres et al. (1999) compiled biotite K–Ar
149 ages, most of which lie within Early–Middle Triassic period. Triassic cooling ages in the Chiapas
150 Massif Complex were also detected by Rb–Sr in mica–whole rock pairs that range from 244 ± 12
151 (2σ) Ma to 214 ± 11 (2σ) Ma (Schaaf et al., 2002).

152

153 4.3 TO-AM

154

155 Unetched apatites (32 crystals; Fig. 2) from granite TO-AM yielded a lower intercept date of 303
156 ± 5 (2σ) Ma with a MSWD of 0.6 and a $P(\chi^2)$ of 0.96. After etching, a slightly younger age of
157 299 ± 3 (2σ) Ma was obtained, with a MSWD of 0.89 and a $P(\chi^2)$ of 0.65. These apatite U–Pb
158 ages are in line with the zircon U–Pb ages of 306 ± 2 (2σ) Ma to 287 ± 2 (2σ) Ma reported for
159 the Pennsylvanian–Cisuralian Totoltepec Pluton (e.g., see details in Kirsch et al., 2013).

160

161 4.4 CH-0403

162

163 36 unetched apatite grains from sample CH-0403 yielded a lower intercept U–Pb age of 345 ± 10
164 (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
165 (2σ) Ma with a MSWD of 1.37 and a $P(\chi^2)$ of 0.08 (Fig. 2). These cooling dates are considerably
166 younger if compared to the CH-0403 emplacement age of $391 \pm 8 (2\sigma)$ Ma (Solari et al., 2009).

167

168 4.5 OC-1008

169

170 41 unetched apatites belonging to sample OC-1008 yielded a U–Pb age of $839 \pm 12 (2\sigma)$ Ma with
171 a MSWD of 0.98 and a $P(\chi^2)$ of 0.50. After etching, the same apatite crystals yielded an age of
172 $830 \pm 10 (2\sigma)$ Ma with a MSWD of 1.24 and a $P(\chi^2)$ of 0.14 (Fig. 2). Both these apatite U–Pb
173 ages are significantly younger than the age of granulite facies metamorphism in the Grenville-
174 aged Oaxacan Complex (1 Ga to 980 Ma, Solari et al., 2014), and thus, should be considered as
175 cooling ages.

176

--- Figure 2 ---

177

178

179 **5 Discussion and concluding remarks**

180

181 Most rock samples, except OV-0421, yielded slightly younger apatite U–Pb ages after chemical
182 etching (up to 3.3% in sample CH-0403). However, the lower intercept U–Pb ages obtained from
183 unetched apatite grains are indistinguishable within error from the U–Pb ages obtained on the

184 same etched grains (see diagram in Fig. 3). The results of this experiment demonstrate that
185 chemical etching required for AFT analysis has negligible effects on the accuracy of apatite U–
186 Pb ages determined via LA–ICP-MS. Thus, as a main conclusion of this study, LA–ICP-MS can
187 be used for simultaneous AFT and U–Pb double dating, as it was already done in some previous
188 studies (e.g., Chew and Donelick, 2012; Liu et al., 2014; Glorie et al., 2017; Bonilla et al., 2020;
189 Nieto-Samaniego et al., 2020).

190 --- **Figure 3** ---

191

192 **Supplement**

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

194

195 **Author contributions**

196 Conceptualisation, investigation, and writing of the original draft were done by FA. LS and COO
197 provided technical support. LS and JS acquired funding and resources, supervised the study, and
198 reviewed the manuscript.

199

200 **Competing interests**

201 The authors declare that they have no conflict of interest.

202

203

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213

214

215 **Figure caption**

216

217 **Figure 1**

218 Illustration displaying the LA-ICP-MS-based U-Pb dating of the same apatite crystal before and
219 after chemical etching (i.e., etched in 5.5M nitric acid at 21 °C for 20 s). Spot diameter of 60 µm.

220

221 **Figure 2**

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

225

226 **Figure 3**

227 Plot showing the lower intercept U-Pb ages obtained on unetched and etched apatite grains.

228

229

230 **References**

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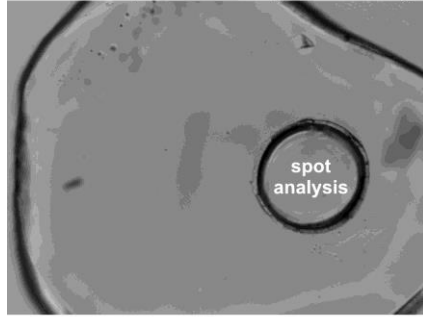
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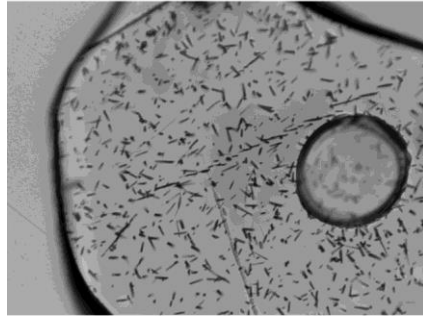
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Figure 1

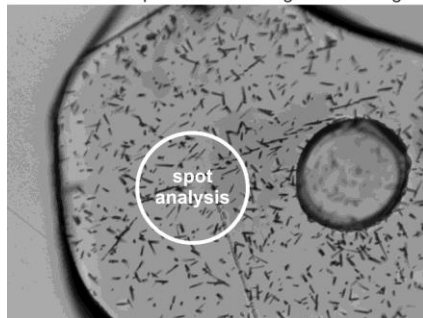
LA-ICP-MS apatite U-Pb dating before etching



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



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



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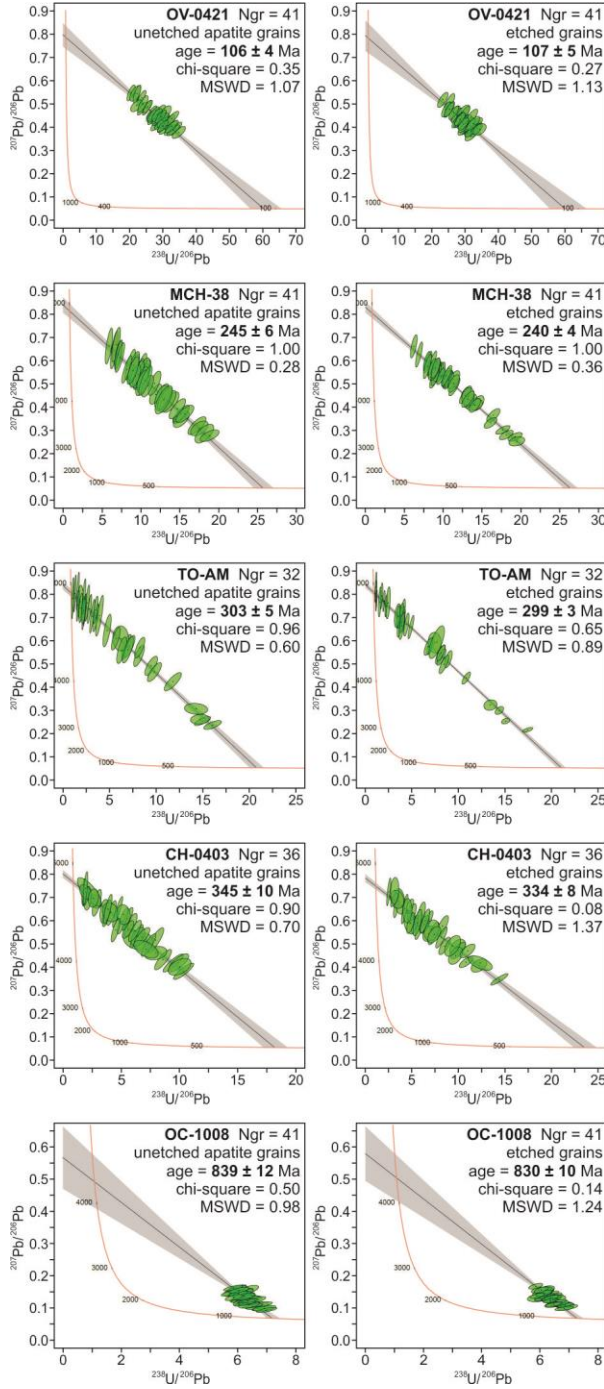
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Figure 2



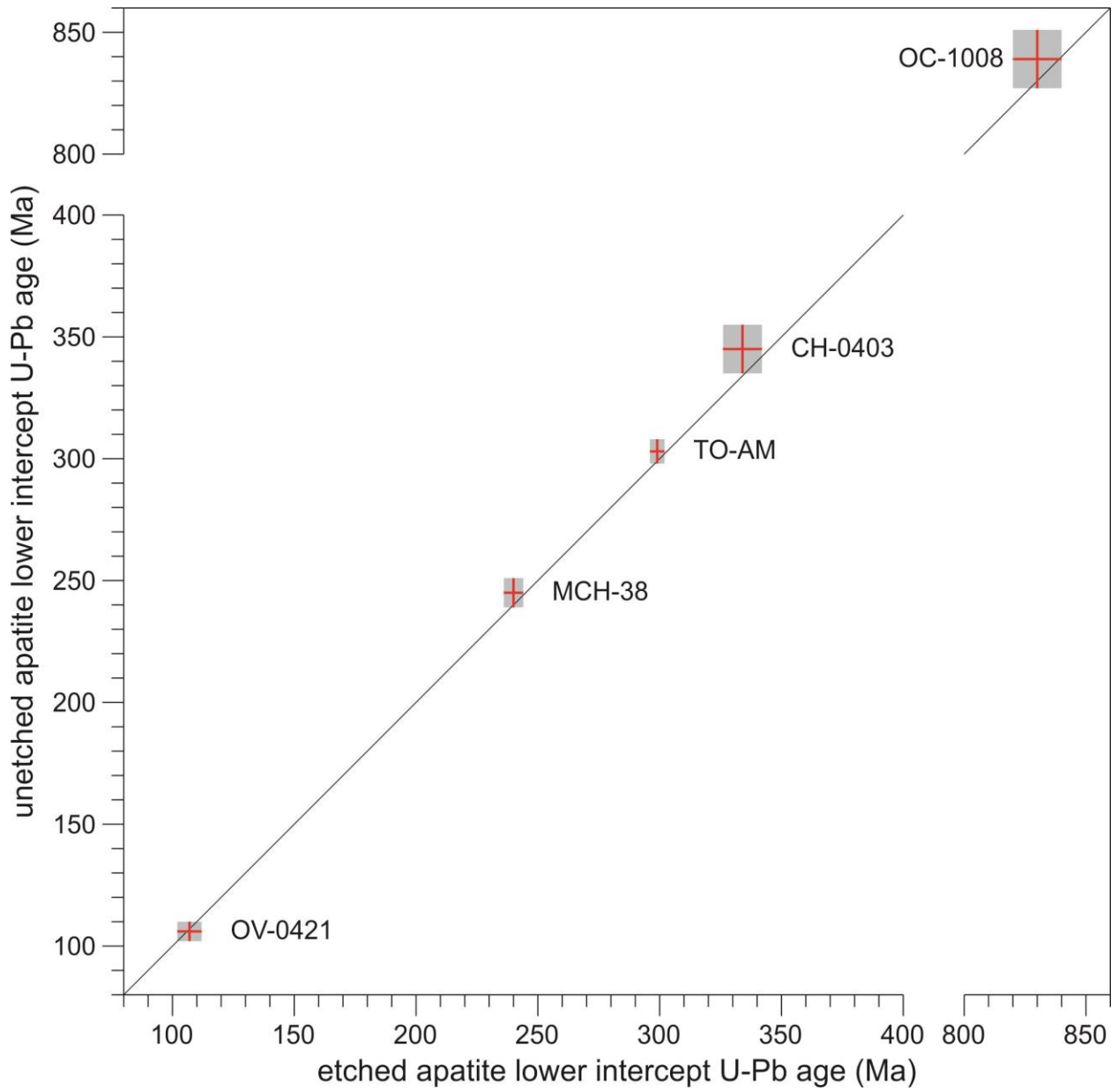
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Figure 3



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427 **Table 1**

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429 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) |

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446 **Table 2**

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

| <i>ICP-MS operating conditions</i> | |
|------------------------------------|---|
| 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 |
| <i>Data acquisition parameters</i> | |
| 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] |
| <i>Laser ablation system</i> | |
| 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 |

450

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

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456 *Letter for Professor Klaus Mezger*

457

458

Santiago de Querétaro, 15 Nov 2020

459

460

461

462

463 **Dear Professor Klaus Mezger,**

464

465

466 We revised our manuscript according to your minor comments.

467 Below, I attached a pdf.file with track changes.

468

469

470

471

472

473 **With Best Wishes,**

474 Fanis

475

476

477

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

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

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485

486 **Abstract**

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

488 the U-Pb method via laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-

489 MS). The objective of this study is to test whether chemical etching required for apatite fission

490 track analysis impacts the precision and accuracy of apatite U-Pb geochronology. The results of

491 this experiment suggest that etching has insignificant effects on the accuracy of apatite U-Pb

492 ages obtained by LA-ICP-MS. Therefore, LA-ICP-MS is reliable for U-Pb analysis as part of

493 apatite fission track and U-Pb double dating.

494

495

496 **Short summary**

497 Unetched and etched apatite grains from five samples were dated by U-Pb method using laser

498 ablation inductively-coupled plasma mass spectrometry. Our experiment indicates that etching

499 needed for apatite fission track dating has insignificant effects on obtaining accurate U-Pb ages;

500 thus, the laser ablation-based technique may be used for apatite fission track and U–Pb double
501 dating.

502

503 **1 Introduction**

504

505 Apatite, $\text{Ca}_5(\text{PO}_4)_3[\text{F},\text{Cl},\text{OH}]$, is the most common phosphate mineral in the Earth’s crust and can
506 be found in practically all igneous and metamorphic rocks, in many ancient and recent sediments
507 as well as in certain mineral deposits (Piccoli and Candela, 2002; Morton and Yaxley, 2007;
508 Webster and Piccoli, 2015). This accessory mineral is often used as a natural thermochronometer
509 for fission track, helium, U–Th and U–Pb dating (e.g., Zeitler et al., 1987; Wolf et al., 1996;
510 Ehlers and Farley, 2003; Hasebe et al., 2004; Donelick et al., 2005; Chew and Donelick, 2012;
511 Chew et al., 2014; Cochran et al., 2014; Liu et al., 2014; Spikings et al., 2015; Glorie et al.,
512 2017). Presently, apatite fission track (AFT) ages can be obtained rapidly by using laser ablation
513 inductively-coupled plasma mass spectrometry (LA–ICP–MS) for direct measurement of “parent
514 nuclides”, i.e., ^{238}U contents (Cox et al., 2000; Svojtka and Košler, 2002; Hasebe et al., 2004,
515 2009; Donelick et al., 2005; Abdullin et al., 2014, 2016, 2018; Vermeesch, 2017). The LA–ICP–
516 MS technique may be used to measure ^{238}U for AFT dating, together with Pb isotopes needed for
517 U–Pb dating (e.g., Chew and Donelick, 2012; Liu et al., 2014; Glorie et al., 2017; Bonilla et al.,
518 2020; Nieto-Samaniego et al., 2020).

519 Hasebe et al. (2009) previously performed an important experimental study, during which
520 they demonstrated that chemical etching required for apatite/zircon fission track dating does not
521 interfere with U analysis by LA–ICP–MS. ~~After chemical etching of apatite, a smaller volume of~~
522 ~~ablated material is analyzed by LA–ICP–MS.~~ The influence of etching needed for AFT dating on

523 the precision and accuracy of dating the same crystals by U–Pb using LA–ICP–MS remains to be
524 quantified. To investigate this issue, the same unetched and etched apatite grains extracted from
525 five rock samples were analyzed via LA–ICP–MS for U–Pb dating. The chosen ~~rock~~ samples
526 have either emplacement or metamorphic ages ranging from the Cretaceous to the
527 Neoproterozoic (see Table 1 for further details).

528 --- **Table 1** ---

529

530

531 **2 Sample descriptions**

532

533 2.1 OV-0421 (Tres Sabanas Pluton, Guatemala)

534

535 This sample is a two mica-bearing deformed granite belonging to the Tres Sabanas Pluton, which
536 is located northwest of Guatemala City, Guatemala. For sample OV-0421, an emplacement age
537 of 115 ± 4 (2σ) Ma was proposed based on zircon U–Pb data (Torres de León, 2016). A cooling
538 age of 102 ± 1 (2σ) Ma, obtained with K–Ar (on biotite), was also reported by the same author.

539

540 2.2. MCH-38 (Chiapas Massif Complex, Mexico)

541

542 MCH-38 is an orthogneiss from the Permian Chiapas Massif Complex. This rock was sampled to
543 the west of Unión Agrarista, the State of Chiapas, southeastern Mexico. There is no reported age
544 for this sample. Some zircon U–Pb dates obtained for the Chiapas Massif Complex (Weber et al.,

545 2007, 2008; Ortega-Obregón et al., 2019) suggest that a Lopingian (260–252 Ma) crystallization
546 or metamorphic age may be assumed for sample MCH-38.

547

548 2.3 TO-AM (Totoltepec Pluton, Mexico)

549

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

554

555 2.4 CH-0403 (Altos Cuchumatanes, Guatemala)

556

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

561

562 2.5 OC-1008 (Oaxacan Complex, Mexico)

563

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

567

568

569

570 **3 Analytical procedures**

571

572 Accessory minerals were concentrated using conventional mineral separation techniques such as
573 rock crushing, sieving, Wilfley table, Frantz magnetic separator, and bromoform. Approximately
574 300 apatite grains were extracted from each rock sample and mounted with their surfaces parallel
575 to the crystallographic *c*-axis in a 2.5 cm diameter epoxy mount. Mounted crystals were polished
576 to expose their internal surfaces (i.e., up to 4π geometry). For this experiment, complete crystals
577 lacking visible inclusions and other defects, such as cracks, were carefully selected for analysis.
578 Sample preparation was performed at Taller de Molienda and Taller de Laminación, Centro de
579 Geociencias (CGEO), Campus Juriquilla, Universidad Nacional Autónoma de Mexico (UNAM).

580 Single spot analyses were performed with a Resonetics RESolution™ LPX Pro (193 nm,
581 ArF excimer) laser ablation system, coupled to a Thermo Scientific iCAP™ Qc quadrupole ICP-
582 MS at Laboratorio de Estudios Isotópicos (LEI), CGEO, UNAM. During this experimental work,
583 LA–ICP-MS-based sampling was performed in central parts of the selected apatite grains before
584 and after chemical etching (in 5.5M HNO₃ at 21 °C for 20 s to reveal spontaneous fission tracks),
585 as shown schematically in Fig. 1. The LA–ICP-MS protocol used for apatite analyses, as given in
586 Table 2, was established on the basis of numerous experiments carried out at LEI during the past
587 five years, and can be used for U–Pb and fission track double dating plus multielemental analysis
588 (Abdullin et al., 2018; Ortega-Obregón et al., 2019). Corrected isotopic ratios and errors were
589 calculated using Iolite 3.5 (Paton et al., 2011) and the VizualAge data reduction scheme (Petrus
590 and Kamber, 2012). UcomPbine (Chew et al., 2014) was used to model ²⁰⁷Pb/²⁰⁶Pb initial values

591 and thus force a ^{207}Pb correction that considers the common Pb (non-radiogenic Pb) incorporated
592 by apatite standards at the moment of their crystallization (see also Ortega-Obregón et al., 2019).
593 The “First Mine Discovery” apatite from Madagascar, with a mean U–Pb age of ca. 480 Ma
594 (Thomson et al., 2012; Chew et al., 2014), was used as a primary reference material. The results
595 for measured isotopes using NIST-612 (Pearce et al., 1997) were normalized using ^{43}Ca as an
596 internal standard and taking an average CaO content of 55%.

597 Tera–Wasserburg Concordia diagrams (T–W; Tera and Wasserburg, 1972) are used in
598 apatite U–Pb dating, because the LA–ICP–MS–derived U–Pb results are generally discordant.
599 The lower intercept in the T–W plot is considered as a mean apatite U–Pb age that should have
600 geological significance (crystallization or cooling age, the age of mineralization or metamorphic
601 event). Apatite U–Pb ages were calculated with IsoplotR (Vermeesch, 2017, 2018) and described
602 below. Detailed information on U–Pb experiments is given in Table S1 in the Supplement.

603 --- **Figure 1** ---

604 --- **Table 2** ---

605

606

607 **4 Results**

608

609 4.1 OV-0421

610

611 For rock sample OV-0421, 41 unetched apatites yielded a lower intercept age of 106 ± 4 (2σ) Ma
612 with a mean square weighted deviation (MSWD) of 1.07, passing the chi-squared test with the
613 $P(\chi^2)$ value of 0.35 (see in Fig. 2). Practically the same U–Pb date, 107 ± 5 (2σ) Ma, was

614 obtained after chemical etching of the same apatite grains, yielding a MSWD of 1.13 and a $P(\chi^2)$
615 of 0.27. Both these apatite U–Pb ages lie between the zircon U–Pb date of 115 ± 4 (2σ) Ma (i.e.,
616 crystallization age) and the biotite K–Ar age of 102 ± 1 (2σ) Ma (i.e., cooling age), which were
617 previously obtained for the same granite sample by Torres de León (2016).

618

619 4.2. MCH-38

620

621 For orthogneiss sample MCH-38, the lower intercept in T–W yielded a U–Pb age of 245 ± 6 (2σ)
622 Ma (obtained from 41 unetched apatites) with a MSWD of 0.28 and a $P(\chi^2)$ of 1. Etched apatite
623 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
624 (Fig. 2). Our U–Pb results are in close agreement with geochronological data reported from the
625 Chiapas Massif Complex in previous studies (Damon et al., 1981; Torres et al., 1999; Schaaf et
626 al., 2002; Ortega-Obregón et al., 2019). For instance, Torres et al. (1999) compiled biotite K–Ar
627 ages, most of which lie within Early–Middle Triassic period. Triassic cooling ages in the Chiapas
628 Massif Complex were also detected by Rb–Sr in mica–whole rock pairs that range from 244 ± 12
629 (2σ) Ma to 214 ± 11 (2σ) Ma (Schaaf et al., 2002).

630

631 4.3 TO-AM

632

633 Unetched apatites (32 crystals; Fig. 2) from granite TO-AM yielded a lower intercept date of 303
634 ± 5 (2σ) Ma with a MSWD of 0.6 and a $P(\chi^2)$ of 0.96. After etching, a slightly younger age of
635 299 ± 3 (2σ) Ma was obtained, with a MSWD of 0.89 and a $P(\chi^2)$ of 0.65. These apatite U–Pb

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

638

639 4.4 CH-0403

640

641 36 unetched apatite grains from sample CH-0403 yielded a lower intercept U–Pb age of 345 ± 10
642 (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
643 (2σ) Ma with a MSWD of 1.37 and a $P(\chi^2)$ of 0.08 (Fig. 2). These cooling dates are considerably
644 younger if compared to the CH-0403 emplacement age of 391 ± 8 (2σ) Ma (Solari et al., 2009).

645

646 4.5 OC-1008

647

648 41 unetched apatites belonging to sample OC-1008 yielded a U–Pb age of 839 ± 12 (2σ) Ma with
649 a MSWD of 0.98 and a $P(\chi^2)$ of 0.50. After etching, the same apatite crystals yielded an age of
650 830 ± 10 (2σ) Ma with a MSWD of 1.24 and a $P(\chi^2)$ of 0.14 (Fig. 2). Both these apatite U–Pb
651 ages are significantly younger than the age of granulite facies metamorphism in the Grenville-
652 aged Oaxacan Complex (1 Ga to 980 Ma, Solari et al., 2014), and thus, should be considered as
653 cooling ages.

654

--- **Figure 2** ---

655

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657

658

659 **5 Discussion and concluding remarks**

660

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

670

--- **Figure 3** ---

671

672 **Supplement**

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

674

675 **Author contributions**

676 Conceptualisation, investigation, and writing of the original draft were done by FA. LS and COO
677 provided technical support. LS and JS acquired funding and resources, supervised the study, and
678 reviewed the manuscript.

679

680 **Competing interests**

681 The authors declare that they have no conflict of interest.

682

683

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686 with sample preparation for this study. Professor Stuart Thomson is acknowledged for sharing
687 Madagascar apatite. Dr. Michelangelo Martini kindly provided sample TO-AM that was useful
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689 are acknowledged for their constructive comments that improved our manuscript significantly.

690

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693

694

695 **Figure caption**

696

697 **Figure 1**

698 Illustration displaying the LA-ICP-MS-based U-Pb dating of the same apatite crystal before and
699 after chemical etching (i.e., etched in 5.5M nitric acid at 21 °C for 20 s). Spot diameter of 60 µm.

700

701 **Figure 2**

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

705

706 **Figure 3**

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

708

709

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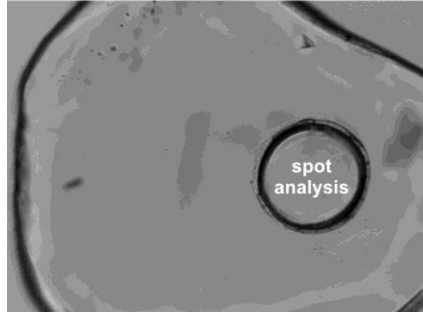
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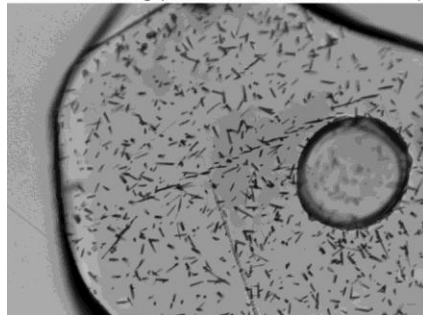
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Figure 1

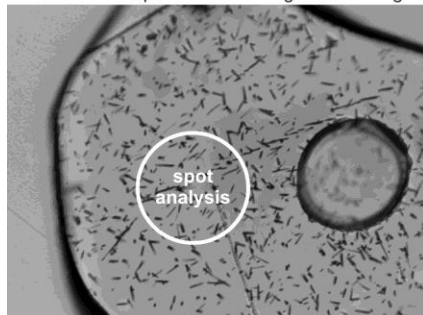
LA-ICP-MS apatite U-Pb dating before etching



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



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



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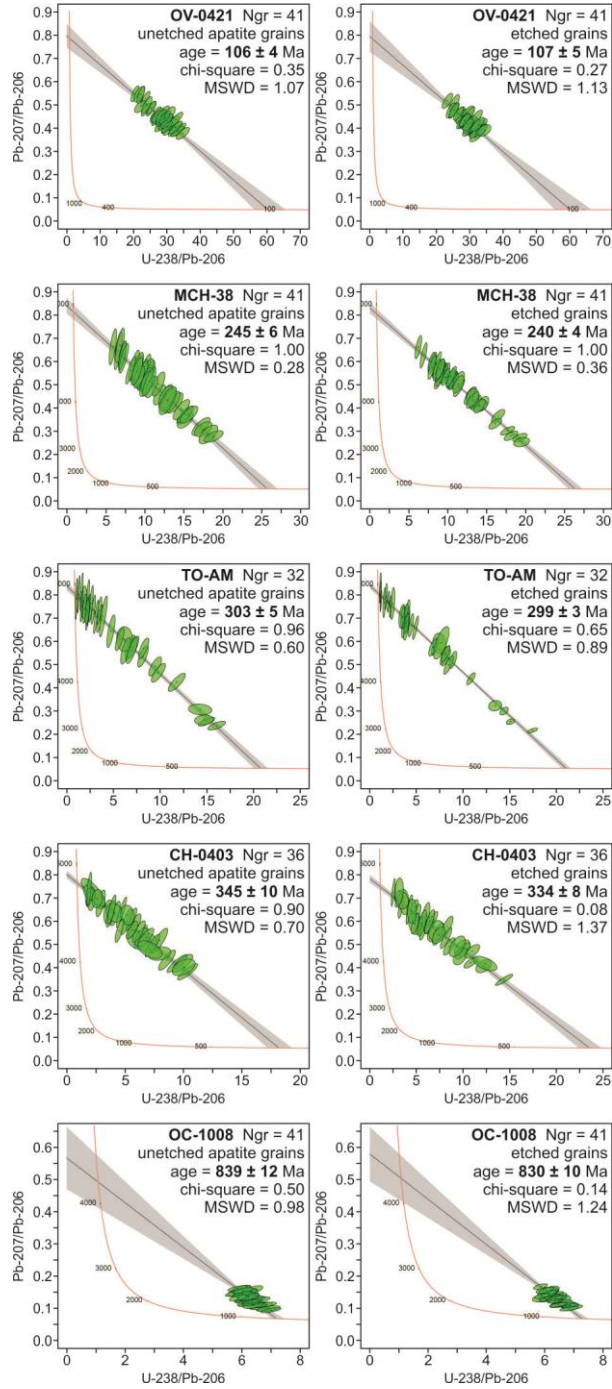
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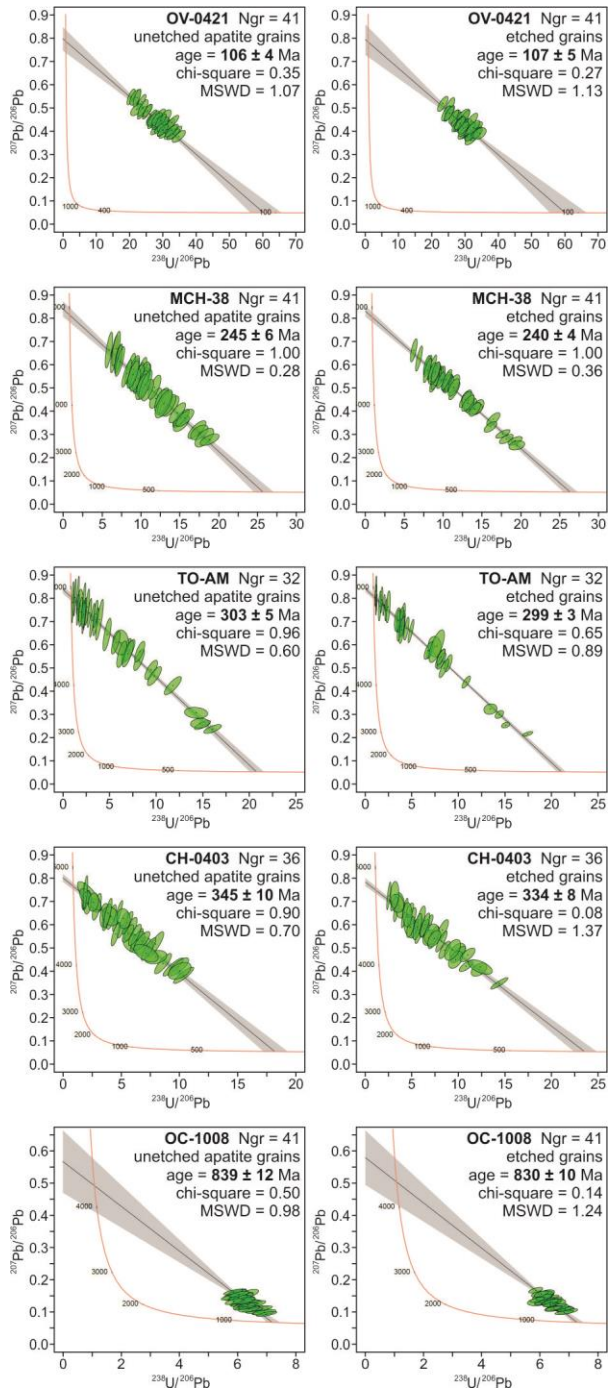
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Figure 2





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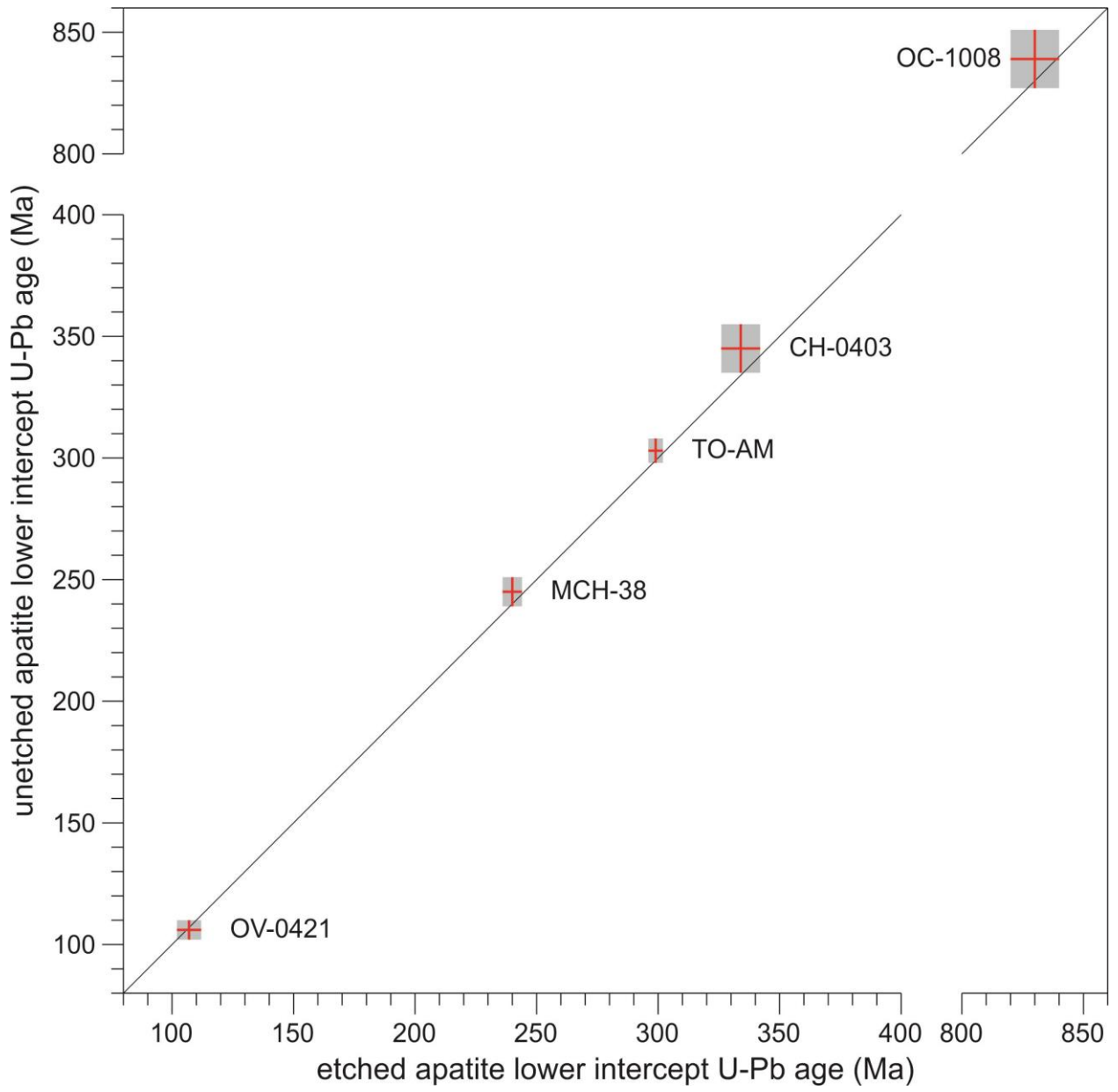
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Figure 3



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908 **Table 1**

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910 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) |

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927 **Table 2**

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

| <i>ICP-MS operating conditions</i> | |
|------------------------------------|---|
| 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 |
| <i>Data acquisition parameters</i> | |
| 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] |
| <i>Laser ablation system</i> | |
| 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 |

931

932 Note: MAD – “First mine Discovery” U–Pb apatite standard from Madagascar; DUR – Durango
933 apatite from Cerro de Mercado mine (Mexico); apt – unknown apatite crystals. (*) Laser pulse
934 energy of 4 J/cm², which was measured directly on target with a Coherent™ laser energy meter.

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