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1 **Glass shard K-Ar dating of the Chalupas caldera major eruption: main Pleistocene**
2 **stratigraphic marker of the Ecuadorian volcanic arc**

3
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33 trace elements.
34 • All figures should be 2 columns-wide. They will be in color only for the web version, and in
35 black and white for the printed version.

36

37 **Abstract**

38 New K-Ar ages obtained on juvenile pumice glass shards indicate that the Chalupas
39 ignimbrite, one of the main Pleistocene tephra markers of the Ecuadorian arc, was emplaced
40 at 216 ± 5 ka. Morphology and major and trace element contents of the glass shards are
41 similar to those of ash layers from deep-sea cores and allow correlation between continental
42 deposits and marine tephra layers. Based on biostratigraphy and $\delta^{18}\text{O}$ data, the age models of
43 these cores support our K-Ar age. Fine ashes from the Chalupas eruption column have been
44 found about 1000 km away from the source caldera, and the estimated deposit volume of both
45 ignimbrite and co-ignimbrite deposits ranges from 200 to 265 km³. This suggests that the
46 Chalupas event could have been strong enough to reach the stratosphere and inject large
47 amount of SO₂ in both hemispheres, possibly impacting global temperatures. In addition, the
48 age of the Chalupas ignimbrite obtained here could provide a new radiometric constraint for
49 the age of isotope stage 7 recorded in orbitally-tuned $\delta^{18}\text{O}$ deep-sea cores. This study
50 highlights the relevance of K-Ar dating applied to small glass shards from massive ignimbrite
51 deposits, and the potential that it represents to improve risk assessments in volcanic zones
52 where dating crystals is not possible. Finally, detailed tephrochronology of deep-sea cores and
53 correlation between marine ash-layers and continental volcanic deposits constitute a strong
54 tool to investigate the eruptive history of an active volcanic arc whose proximal products have
55 been eroded or deeply buried by younger deposit sequences.

56

57

58 **1. Introduction**

59 Major explosive caldera-forming eruptions are colossal volcanic phenomenon that can
60 eject large volumes of tephra and volatiles into the atmosphere and spread tephra over wide
61 areas. Such events can impact the local population, infrastructures and natural environment,
62 namely the climate system at regional and even global scales (e.g. McCormick et al., 1995;
63 Robock, 2000; Cole-Dai, 2010). Tephrochronology is a powerful tool for dating and
64 correlating deposit sequences scattered over large areas. The method consists in comparing
65 tephra features, such as their age or position in the stratigraphic column, their chemical and
66 mineralogical composition, as well as glass shard morphology, in order to match the deposits
67 associated with a single volcanic event (e.g., Lowe, 2011). Consequently, tephrochronology
68 allows us to investigate magmatic processes, recurrence and impact of past major eruptions,
69 and hence better define the volcanic hazards and its frequency-magnitude relationships. As
70 the time period between tephra emission and deposit is mostly on the order of hours or days
71 (Robock, 2000; Mills, 2000; Rose and Durant, 2009), dating tephra fallouts is a robust way to
72 determine the age of the corresponding eruption. The $^{40}\text{Ar}/^{39}\text{Ar}$ single grain dating method
73 applied on K-rich minerals, such as sanidine, biotite and even plagioclase crystals, is
74 commonly used to date tephra older than ~50 ka, i.e. for which ^{14}C age determination is not
75 possible. For instance, this technique has been used to accurately date the Young Toba Tuff
76 and investigate the relationship between this major eruptive event and global cooling (e.g.,
77 Williams et al, 2009; Storey et al., 2012; Mark et al., 2014), or to date the Yellowstone Tuffs
78 and study the eruptive history of the caldera (e.g., Ellis et al., 2012; Matthews et al., 2015). In
79 offshore Central America this method was used to study characteristics, output rates and
80 recurrence of explosive eruptions (Schindlbeck et al., 2016a; b). Also, applications to North

81 Atlantic marine cores have helped to refine the age of ice-rafted debris recorded in offshore
82 Iceland (Lacasse and van den Bogaard, 2002).

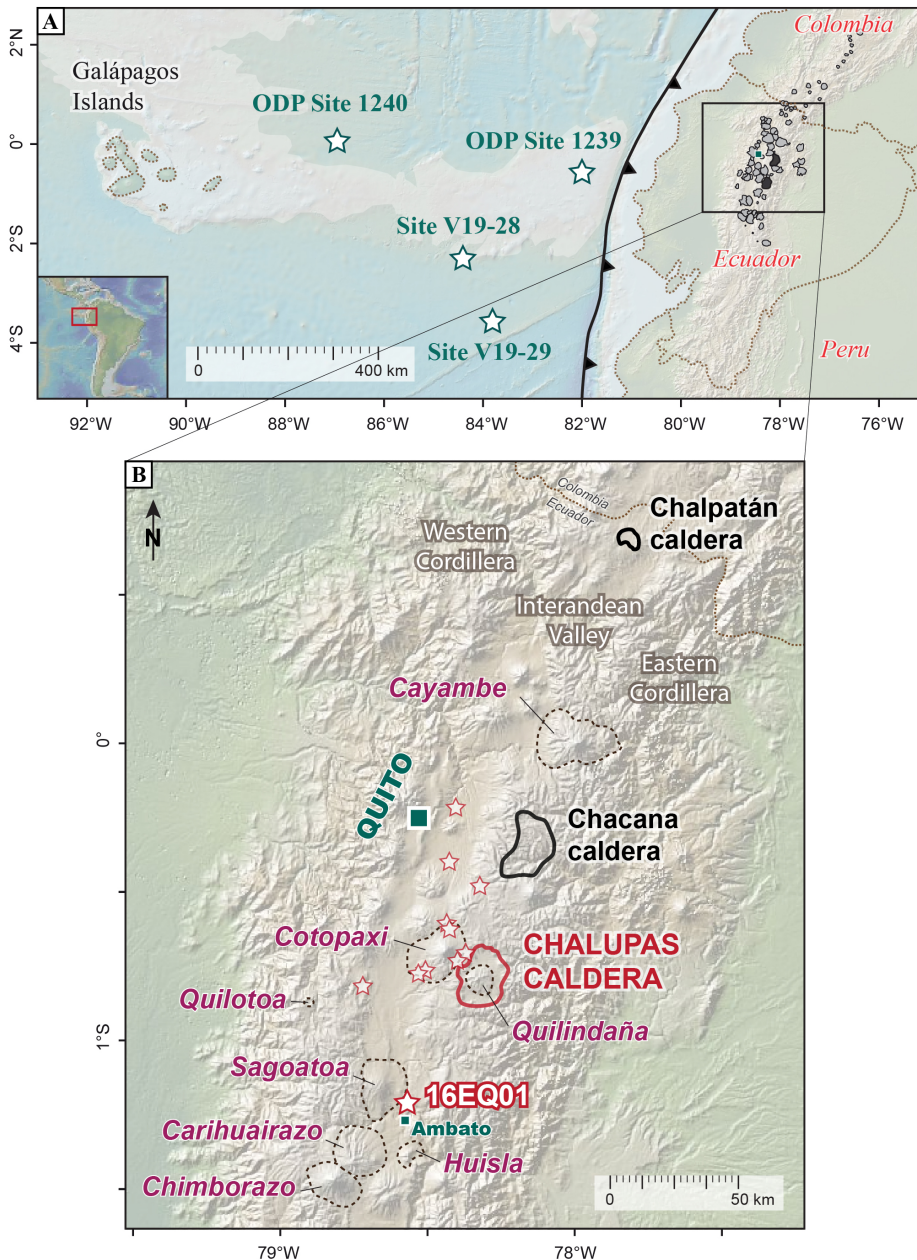
83 As crystals may not be systematically present in pumice samples, glass may be the
84 only juvenile material that can be dated. While the $^{40}\text{Ar}/^{39}\text{Ar}$ technique is not always suitable
85 for glass shard dating because of ^{39}Ar recoil occurring during irradiation for non-crystalline
86 phases and small grains with high surface area to volume ratio (e.g., McDougall and Harrison,
87 1999; Morgan et al., 2009), the potassium-argon (K-Ar) technique may be successfully
88 employed (e.g., Milne, 1973; Pinti et al., 2001). In this paper, we focus on the Chalupas
89 ignimbrite, one of the main Pleistocene stratigraphic markers in Ecuador, and we present new
90 K-Ar ages carried out on pumice glass shards and biotite crystals. We also compare the
91 morphology and geochemistry of glass shards of pumices with those of distal tephra fallouts
92 from Ocean Drilling Project's (ODP) Pacific deep-sea cores in order to provide support for
93 our K-Ar age determination and investigate the volume and magnitude of this major eruption.

94

95 **2. Quaternary stratigraphic markers of the Ecuadorian arc**

96 In Ecuador, at least three large caldera systems originate from past Quaternary
97 volcanic activities. In the northern part of the current Ecuadorian arc, the ~10 km-wide
98 *Chalpatán* caldera is located within the Interandean Valley, near the border between Ecuador
99 and Colombia (Fig. 1B). This poorly documented caldera could have collapsed after a
100 powerful eruption that occurred during the Quaternary (Barberi et al., 1988). Further south,
101 Chalupas and Chacana (Fig. 1B) are the widest caldera systems in Ecuador. The *Chacana*
102 volcanic system is located in the Eastern Cordillera, about 30 km from Quito, the capital city
103 of Ecuador. It experienced two large plinian eruptions at ~160-190 ka (Bigazzi et al., 1992;
104 Hall and Mothes, 1997; Hall and Mothes, 2008c), whose deposits, the Pifo fall layers,
105 constitute one of the main Pleistocene stratigraphic markers of the northern part of the

106 Ecuadorian arc (e.g., Robin et al., 2009; Alvarado et al., 2014; Bablon et al., 2019b). About
 107 50 km south of Chacana, *Chalupas* caldera results from a major Pleistocene ignimbrite
 108 eruption. In this study, we focus on the latter as only an unpublished $^{40}\text{Ar}/^{39}\text{Ar}$ date is
 109 available for the Chalupas ignimbrite (Hammersley, 2003; Beate et al., 2006; Mothes and
 110 Hall, 2008).



111 **Fig. 1.** Location of the samples presented in this study. A) Map of Ecuador and the Galápagos Islands. Grey
 112 circles represent Quaternary volcanoes of Ecuador and Colombia. Stars represent the location of ODP and
 113 Ninkovich and Shackleton (1975) drilling sites presented in the text. B) Zoom on the central part of the volcanic
 114 arc, showing volcanoes and calderas mentioned in the text. The Chalupas caldera is represented in red, and the
 115 location of the Chalupas ignimbrite sample (16EQ01) with a big white and red star. Small white and red stars
 116 indicate the location of Chalupas ignimbrite samples whose major and trace element content are provided in
 117 Appendix A. Dashed lines are basal contours of volcanoes, while continuous lines are used for calderas.
 118

119 Because of its large-scale dispersion, as well as its rather unique rhyolite composition
120 and easily recognizable facies, the Chalupas ignimbrite deposits constitute an important
121 stratigraphic marker of the southern and central parts of the Ecuadorian volcanic arc in the
122 Late Pleistocene record. Thereby, it is important to precisely date this event, in order to
123 provide a geochronological constraint to the construction of Ecuadorian volcanoes, as well as
124 to the Late Pleistocene deformation of the volcanic and volcano-clastic deposits located
125 within the Interandean Valley (e.g., Alvarado et al., 2014). In addition, dating events
126 associated to such major eruptions allow us to investigate their recurrence through time and
127 improve hazard assessment in this populated area of the Andes, and may allow correlation
128 with climatic records to infer any possible global effect of these eruptions.

129

130 **3. The Chalupas ignimbrite**

131 The Chalupas volcanic complex (Lat. 00°47'S; Long. 78°18'W) is located in the
132 Eastern Cordillera of Ecuador, about 50 km from Quito (Fig. 1B), to the west-southwest of
133 Cotopaxi volcano. This volcanic system is characterized by a conspicuous 16 km-wide and
134 18 km-long caldera (Mothes and Hall, 2008; Bernard and Andrade, 2011) that was formed
135 during a large ignimbrite eruption of rhyolitic composition. Andesite to dacite lava flows crop
136 out southwest of the caldera and are the main remnants of the pre-caldera volcanic system
137 (Barberi et al., 1988; Beate et al., 2006). Afterwards, Quilindaña andesitic stratovolcano grew
138 in the center of the caldera (Córdova et al., 2018; Fig. 1B). Channelized by relief and
139 volcanoes already present during the eruption, the Chalupas ignimbrite was deposited in the
140 Interandean Valley south of Quito. Within a radius of about fifty kilometers, the proximal
141 deposits of the Chalupas ignimbrite are a few tens of meters thick (e.g., Beate et al., 2006;
142 Hall and Mothes, 2008a; 2008b; Ordóñez, 2012; this study). They consist of a non-welded
143 juvenile pyroclastic material made up of poorly sorted pumiceous blocks in an ash-rich

144 matrix. Pumices contain rare biotite and plagioclase crystals, as well as accessory apatite and
145 Fe-Ti oxides. Onshore tephra fallout deposits associated to this event spread out to the west
146 and crop out as far as the coast, ~300 km from the caldera (Jackson et al., 2019).

147 Beate et al. (2006) reported an unpublished $^{40}\text{Ar}/^{39}\text{Ar}$ age of 211 ± 14 ka for the
148 Chalupas ignimbrite, obtained on plagioclase crystals (Hammersley, 2003). Although this age
149 is in agreement with stratigraphic relationships that have been described between the
150 Chalupas ignimbrite and deposits from Cotopaxi (Hall and Mothes, 2008a), Huisla (Ordóñez,
151 2012; Espín, 2014), Sagoatoa (Bablon et al., 2019a), Quilotoa (Hall and Mothes, 2008b),
152 Carihuairazo (Ordóñez, 2012), and Chimborazo (Bernard et al., 2008; Samaniego et al., 2012)
153 volcanoes (Fig. 1B), it is not supported by any description of data, the standards used, age
154 spectra, nor the inverse isochron.

155

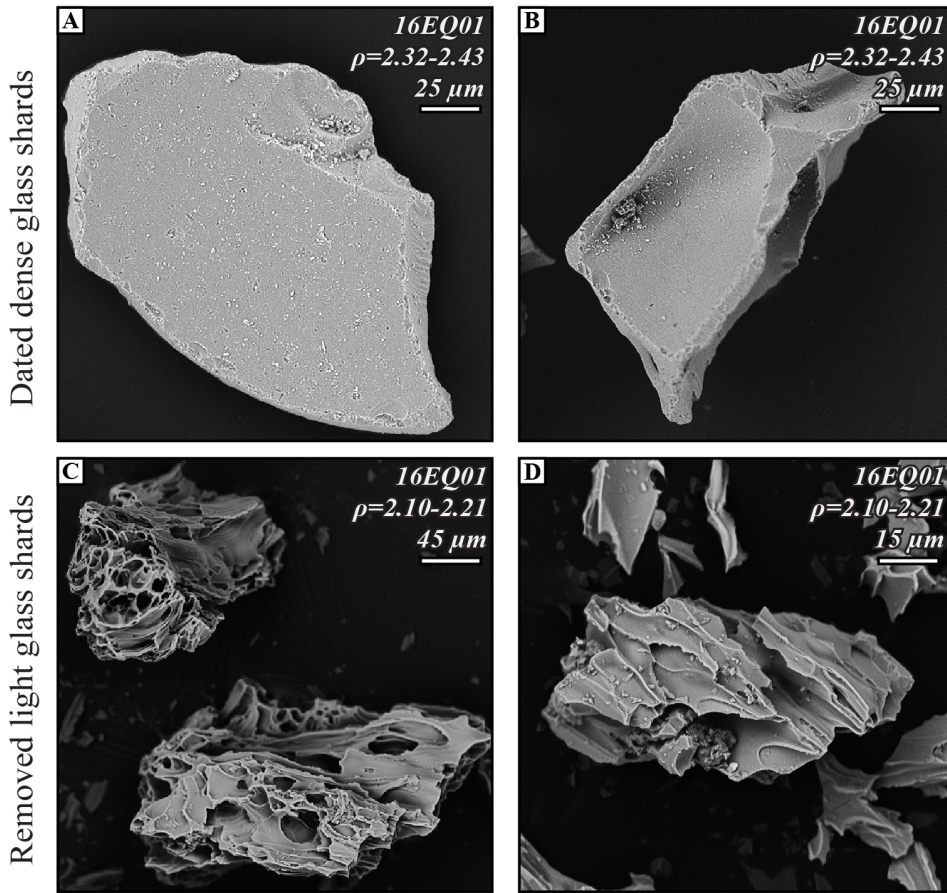
156 **4. Materials and methods**

157 *4.1. Sampling and preparation of samples for K-Ar dating*

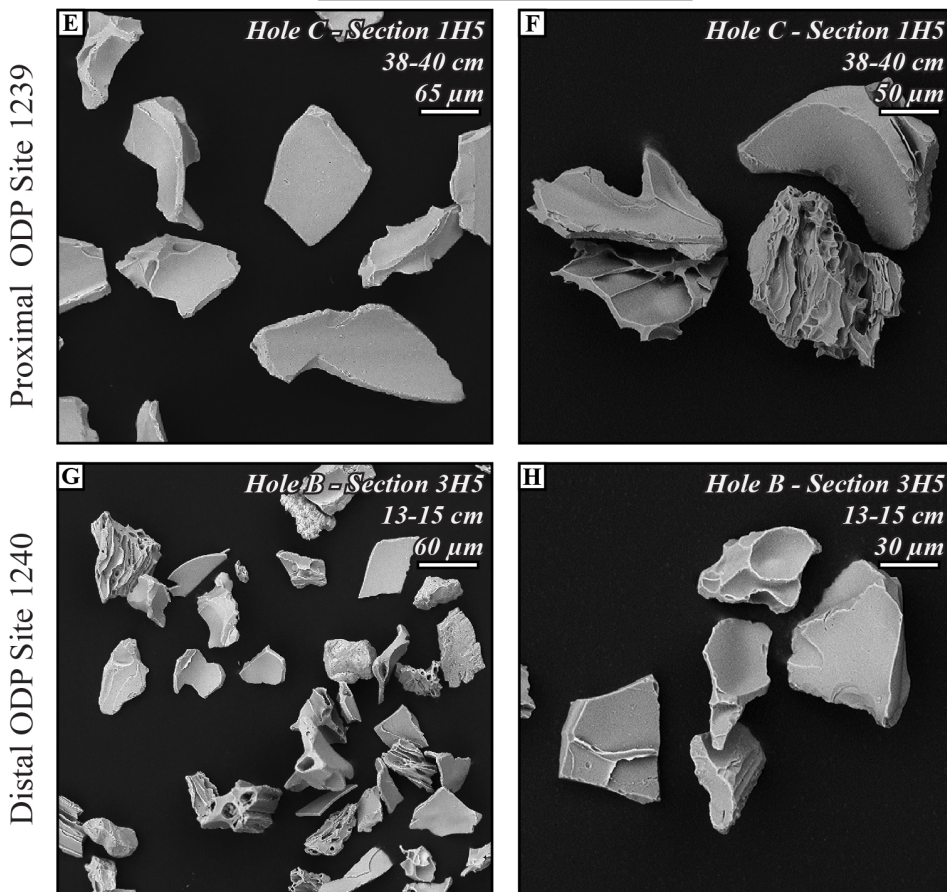
158 The Chalupas ignimbrite deposit was sampled towards the base of a ~30 m-high
159 quarry outcrop, in the vicinity of Ambato city, 55 km southwest of the caldera (sample
160 16EQ01; Fig. 1B).

161 The pumice blocks were crushed manually in an agate mortar, sieved and
162 ultrasonically rinsed with deionized water. A magnetic separator was used to remove the
163 andesite xenoliths, and grains were separated using heavy liquids within a narrow density
164 range (see below). Such procedure allows the preservation of the massive structure of the
165 glass shards and minerals.

Chalupas ignimbrite



~225 ka marine ash layer



167 **Fig. 2.** Scanning Electron Microscopy (SEM) images of glass shards. A-B) Dense, blocky glass shards of the
168 dated fraction of continental Chalupas ignimbrite. C-D) Light glass grain fragments of Chalupas ignimbrite, with
169 a lower density due to a significant increase of vesicle content. E-F) Glass shards from the proximal ODP Site
170 1239, deposited at ~225 ka. G-H) Glass shards from the distal ODP Site 1240, deposited at ~225 ka.

171 The morphology of the glass shards, studied using a Scanning Electron Microscope
172 (SEM), shows a clear difference between the dense glass shards, massive and rather smooth
173 (Figs. 2A and B), and which were used for dating, and the light glass shards, significantly
174 stringier and more vesicular (Figs. 2C and D). Note that glass shards (80-125 μm ; $\rho=2.32$ -
175 2.43) selected from the Chalupas ignimbrite represent less than 5 vol.% of the initial sample.
176 In addition, biotite crystals ($>125 \mu\text{m}$; $\rho=2.85$ -3.28) were also separated for dating.

177 Age measurements were performed using the unspiked K-Ar Cassinot-Gillot
178 technique (Gillot et al., 2006) in the GEOPS laboratory at Orsay (Paris-Sud University,
179 France). This technique is suitable for dating groundmass of young lava flows, as well as K-
180 feldspars from explosive deposits, and has been successfully applied for studying Quaternary
181 subduction volcanic products from many places, such as Ecuador (Bablon et al., 2018;
182 2019a), Argentina or Lesser Antilles (e.g., Samper et al., 2009; Germa et al., 2010; 2011;
183 Ricci et al., 2015). Comparison with the age of the Matuyama-Brunhes paleomagnetic field
184 reversal has shown that it can also be used to date glass shards from volcanic tephra (Pinti et
185 al., 2001). However, this technique requires fresh glass shards, as both the amorphous nature
186 of glass and the large surface to volume ratio of the grains favor a high mobility of K and/or
187 Ar (Cerling et al., 1985). It seems that the K-Ar method is most successful in dating volcanic
188 glass, since a significant recoil effect, induced by the sample irradiation, biases $^{40}\text{Ar}/^{39}\text{Ar}$ ages
189 of glass shards toward erroneous older values (McDougall and Harrison, 1999; Morgan et al.,
190 2009). The full description of analytical procedures, standards and uncertainty calculation is
191 given in Bablon et al. (2018). Ages have been calculated using decay constants of Steiger and
192 Jäger (1977). The ^{40}Ar signal calibration was performed using an age of 24.21 Ma for HD-B1
193 biotite standard (Hess and Lippolt, 1994). Age results are given in Table 1 at the 1- σ

194 confidence level. Each argon measurement has been carried out on ~0.9 and ~0.5 g of glass
195 shards and biotite crystals, respectively.

196

197 4.2. Tephra layers in deep-sea cores

198 For this study, we selected two deep-sea cores from Leg 202 ODP Site 1239, located
199 near the Ecuadorian margin, and ODP Site 1240, located closer to the Galápagos Islands
200 (Fig. 1A; Shipboard Scientific Party, 2003). These cores present many marine ash layers
201 visible to the naked eye throughout the sedimentary sequence, 24 for the proximal ODP Site
202 1239 and 8 for the distal ODP Site 1240, covering the last ~15 and ~2.3 Ma, respectively
203 (Shipboard Scientific Party, 2003). To investigate the correlation between these marine
204 deposits and the proximal deposits of the Chalupas eruption, we focused on ash layers
205 younger than 300 ka. One layer is significantly thicker than the others, and reaches ~16 cm-
206 thick in Site 1239, and ~3 cm-thick in Site 1240. Within cores from Site 1239, the ash layer is
207 located between 6.65 and 6.83 mcd (meters composite depth), between 6.87 and 7.07 mcd,
208 and between 6.72 and 6.88 mcd, for holes A, B and C, respectively. Within cores from Site
209 1240, the ash layer is located between 25.69 and 25.71 mcd, and between 25.69 and
210 25.72 mcd, for holes B and C, respectively (Shipboard Scientific Party, 2003). It is composed
211 of millimetric glass shards with some calcareous nannofossils, foraminifera and diatoms
212 (mainly *Gephyrocapsa spp.*, *Globorotalia menardii* and *Neogloboquadrina dutertrei*;
213 Shipboard Scientific Party, 2003), the proportion of which significantly decreases in the
214 central part of the layer. For each ash layer from both Sites 1239 and 1240, we collected three
215 to six 2 cm-thick samples every 5 cm depth of the core section. Sample preparation for
216 electron microprobe analyses consisted in removing clay by washing and manually sieving
217 each sample at 63 or 40 μm for proximal (Site 1239) and distal (Site 1240) cores,

218 respectively. Then, glass shards were individually selected by hand under a magnifier and
219 mounted on epoxy resin beads before polishing.

220

221 *4.3. Geochemical analyses*

222 Whole-rock major and trace element content of the continental Chalupas ignimbrite
223 sample and trace element content of marine tephra samples were measured by ICP-AES
224 (Inductively Coupled Plasma - Atomic Emission Spectrometry) at the Laboratoire
225 Géosciences Océan of the Université de Bretagne Occidentale (Brest, France), following the
226 procedure detailed in Cotten et al. (1995). Relative uncertainties are $\leq 2\%$ for major elements
227 and $\leq 5\%$ for trace elements.

228 Major element measurements of single glass shards were performed on CAMECA
229 SX-100 and SX-FIVE electron microprobes at the University Pierre and Marie Curie
230 (CAMPARIS, France). Relative uncertainties are $< 0.6\%$ for SiO_2 ; $\sim 1\%$ for Al_2O_3 , $< 3\%$ for
231 CaO and MgO , $< 4\%$ for Na_2O , $< 5\%$ for Fe_2O_3 , $< 6\%$ for K_2O , 10% for TiO_2 and $\sim 30\%$ for
232 MnO .

233

234 **5. Results**

235 *5.1. K-Ar age of Chalupas ignimbrite*

236 K-Ar measurements have been performed on dense glass shards (Figs. 2A and B) and
237 biotite crystals from continental Chalupas ignimbrite. Dated dense glass shards have a fresher
238 aspect and a more massive structure than lighter and vesiculated shards (Figs. 2C and D) that
239 have been removed using heavy liquids. In fact, as vesicles contain gases, they are prone to a
240 high contamination in atmospheric argon, and the content of radiogenic argon is thus more
241 difficult to determine precisely.

242 The potassium content of glass shard samples is 3.54 ± 0.04 %, and reaches
 243 6.66 ± 0.07 % for biotite crystals (Table 1). The content of radiogenic argon, which derives
 244 from the radioactive decay of ^{40}K , ranges between 5.1 and 12.3 ± 0.10 %. From these values
 245 combined with the ^{40}K decay constants (Steiger and Jäger, 1977), we obtain ages of
 246 216 ± 5 and 286 ± 5 ka for the glass shards and biotite crystals from the Chalupas ignimbrite,
 247 respectively (Table 1).

248 **Table 1**

249 K-Ar data obtained in this study. Column headings indicate sample name, coordinates (Universal Transverse
 250 Mercator coordinate system, WGS84 spheroid, Zone 17), dated material, potassium concentration in percent,
 251 radiogenic argon content in percent and 10^{11} atoms per gram, ages and weighted mean age in ka ($1-\sigma$
 252 uncertainty).

Sample	Longitude (m)	Latitude (m)	Phase	K (%)	$^{40}\text{Ar}^*$ (%)	$^{40}\text{Ar}^* \times 10^{11}$ (at/g)	Age $\pm 1\sigma$ (ka)	Mean age (ka)
<i>Chalupas ignimbrite</i>								
16EQ01	769765	9867875	Glass shards	3.54 ± 0.04	5.16 ± 0.10	7.856 ± 0.155	213 ± 5	216 ± 5
					5.18 ± 0.10	8.009 ± 0.158	217 ± 5	
					5.09 ± 0.10	8.063 ± 0.152	218 ± 5	
			Biotite crystals	6.66 ± 0.07	12.26 ± 0.10	19.740 ± 0.161	284 ± 5	286 ± 5
					7.14 ± 0.10	20.091 ± 0.282	289 ± 6	

253

254 5.2. Geochemical analyses

255 Results of whole-rock major and trace element contents of continental Chalupas
 256 ignimbrite are provided in Table 2. Analyses show that the chemical composition of the
 257 Chalupas ignimbrite is highly homogeneous at the deposit scale (Table 2; Appendix A).

258

259 **Table 2**
 260 Whole-rock major and trace element composition of our Chalupas ignimbrite sample (16EQ01), with mean and
 261 standard deviation of analyses performed on 20 different outcrops of the Chalupas ignimbrite across Ecuador
 262 (Appendix A; Barberi et al., 1988; Bryant et al., 2003; Ancellin et al., 2017; Córdova, 2018), measured by ICP-
 263 AES. All analyses of major elements were brought down to a total of 100% on a water-free basis.

<i>Whole-rock Chalupas ignimbrite</i>					
Major elements (wt.%)			Trace elements (ppm)		
	16EQ01	<i>Other outcrops</i>		16EQ01	<i>Other outcrops</i>
SiO ₂	74.72	<i>74.64 ± 0.49</i>	Sc	2.06	<i>2.06 ± 0.23</i>
TiO ₂	0.24	<i>0.25 ± 0.02</i>	V	13.46	<i>13.32 ± 3.76</i>
Al ₂ O ₃	13.77	<i>13.89 ± 0.24</i>	Cr	<<	<i>3.65 ± 2.02</i>
Fe ₂ O ₃	1.46	<i>1.42 ± 0.18</i>	Co	0.32	<i>3.00 ± 2.18</i>
CaO	1.22	<i>1.25 ± 0.08</i>	Ni	<<	<i>2.07 ± 1.12</i>
MgO	0.34	<i>0.33 ± 0.03</i>	Rb	191.42	<i>172.76 ± 5.58</i>
MnO	0.05	<i>0.05 ± 0.00</i>	Sr	201.14	<i>207.94 ± 6.50</i>
K ₂ O	4.29	<i>4.38 ± 0.23</i>	Y	12.41	<i>13.22 ± 1.92</i>
Na ₂ O	3.87	<i>3.74 ± 0.29</i>	Zr	153.25	<i>162.35 ± 13.49</i>
P ₂ O ₅	0.04	<i>0.04 ± 0.01</i>	Nb	10.12	<i>11.29 ± 0.36</i>
L.O.I.	3.47		Ba	1099.24	<i>1059.00 ± 49.29</i>
			La	30.9	<i>31.05 ± 1.11</i>
			Ce	55.08	<i>56.49 ± 2.52</i>
			Nd	19.88	<i>19.50 ± 4.32</i>
			Sm	3.37	<i>3.58 ± 0.19</i>
			Eu	0.42	<i>0.60 ± 0.04</i>
			Gd	2.82	<i>2.67 ± 0.29</i>
			Dy	2.07	<i>2.07 ± 0.14</i>
			Er	1.09	<i>1.26 ± 0.07</i>
			Yb	1.24	<i>1.25 ± 0.08</i>
			Th	21.7	<i>21.95 ± 1.33</i>

264
 265
 266 Major element content of the dated continental sample of the Chalupas ignimbrite and
 267 marine tephra layers, determined using electron microprobe on single glass shards, are given
 268 in Table 4.

269
 270 **Table 3**
 271 Major element contents of single glass shards measured by electron microprobe. All analyses were recalculated
 272 to a total of 100%. We report only analysis with oxide sum above 93%. Std: standard deviation.

273

Leg ODP 202 - Site 1239 - Hole C - Section IH5 - 43-45 cm

wt. %																		Mean	Std
SiO ₂	78.96	77.27	77.47	76.27	76.61	75.42	76.50	76.28	76.00	76.66	77.08	76.59	75.44	76.11	77.92	76.31		76.68	0.90
TiO ₂	0.27	0.29	0.09	0.19	0.33	0.38	0.21	0.10	0.12	0.20	0.07	0.12	0.22	0.19	0.18	0.09		0.19	0.09
Al ₂ O ₃	13.49	14.31	14.44	14.08	14.28	13.76	13.26	13.80	14.00	14.22	14.17	13.81	14.20	13.73	13.67	13.88		13.94	0.32
Fe ₂ O ₃	0.81	1.13	1.10	1.06	0.91	0.98	1.10	0.60	0.68	0.63	0.53	0.90	1.08	1.22	1.27	0.71		0.92	0.24
CaO	1.22	1.00	1.14	1.15	1.00	0.91	1.09	0.81	0.82	0.84	0.69	0.86	1.22	1.19	1.15	0.71		0.99	0.19
MgO	0.20	0.22	0.19	0.16	0.26	0.23	0.23	0.10	0.14	0.13	0.14	0.06	0.29	0.25	0.27	0.11		0.19	0.07
MnO	-0.01	0.01	0.10	0.03	0.03	0.08	0.02	0.03	0.04	0.08	0.21	0.13	0.07	-0.01	0.03	-0.03		0.05	0.06
K ₂ O	3.30	3.87	3.70	4.58	3.86	5.09	4.54	4.98	4.88	4.21	3.97	4.28	4.05	3.86	3.69	5.27		4.26	0.57
Na ₂ O	1.77	1.90	1.78	2.48	2.72	3.16	3.06	3.29	3.32	3.03	3.14	3.25	3.42	3.46	1.81	2.95		2.78	0.63

Leg ODP 202 - Site 1240 - Hole C - Section 3H2 - 128-130 cm

wt. %																		Mean	Std
SiO ₂	76.88	76.02	77.75	75.96	75.85	76.71	75.87	75.80	75.00	77.36	76.17	75.53	76.38					76.25	0.76
TiO ₂	0.14	0.23	0.17	0.11	0.25	0.17	0.20	0.22	0.21	0.13	0.11	0.20	0.23					0.18	0.05
Al ₂ O ₃	13.94	13.53	12.77	13.30	14.03	13.83	14.24	14.15	14.48	13.85	14.08	13.67	13.87					13.83	0.44
Fe ₂ O ₃	0.94	1.31	0.96	1.16	1.25	1.00	1.08	1.06	1.25	0.91	1.01	1.07	1.04					1.08	0.13
CaO	0.95	1.05	1.02	0.95	1.15	0.82	1.02	1.13	0.81	1.14	1.00	1.24	0.98					1.02	0.13
MgO	0.19	0.24	0.18	0.19	0.24	0.18	0.23	0.18	0.26	0.26	0.20	0.24	0.17					0.21	0.03
MnO	0.13	0.07	0.02	0.22	-0.05	0.03	0.07	0.03	0.06	-0.03	-0.08	0.03	0.11					0.05	0.08
K ₂ O	3.71	4.63	4.53	4.73	4.12	4.79	4.60	4.20	4.77	3.54	4.20	4.52	4.76					4.39	0.41
Na ₂ O	3.12	2.91	2.59	3.38	3.17	2.49	2.70	3.23	3.16	2.83	3.32	3.51	2.45					2.99	0.35

Chalupas ignimbrite (16EQ01)

wt. %																		Mean	Std
SiO ₂	75.45	75.50	75.90	74.37	75.44	75.21	74.51	75.94	75.29	75.10	76.10	74.37						75.27	0.59
TiO ₂	0.26	0.16	0.21	0.37	0.24	0.23	0.24	0.19	0.35	0.25	0.21	0.25						0.25	0.06
Al ₂ O ₃	14.32	13.72	14.11	13.83	14.65	14.31	14.89	13.93	14.53	13.76	14.36	14.12						14.21	0.37
Fe ₂ O ₃	1.18	0.54	0.75	1.06	0.39	0.99	0.63	0.97	0.94	0.93	0.54	1.41						0.86	0.30
CaO	1.03	1.03	1.04	1.14	0.96	1.03	0.98	1.10	1.06	1.04	1.05	1.15						1.05	0.06
MgO	0.17	0.16	0.22	0.24	0.08	0.22	0.13	0.17	0.22	0.22	0.18	0.22						0.19	0.05
MnO	0.08	0.02	0.05	0.08	0.07	0.12	0.02	0.02	0.10	0.05	0.05	0.05						0.06	0.03
K ₂ O	4.39	4.58	4.19	4.36	4.58	4.51	4.49	4.24	4.43	4.36	4.37	4.51						4.42	0.12
Na ₂ O	3.11	4.30	3.53	4.55	3.59	3.38	4.10	3.44	3.09	4.28	3.13	3.92						3.70	0.51

275

276 Table 4

277 Trace element composition of the bottom and the top parts of marine tephra layers from ODP 1239 and 1240

278 Sites, measured by ICP-AES.

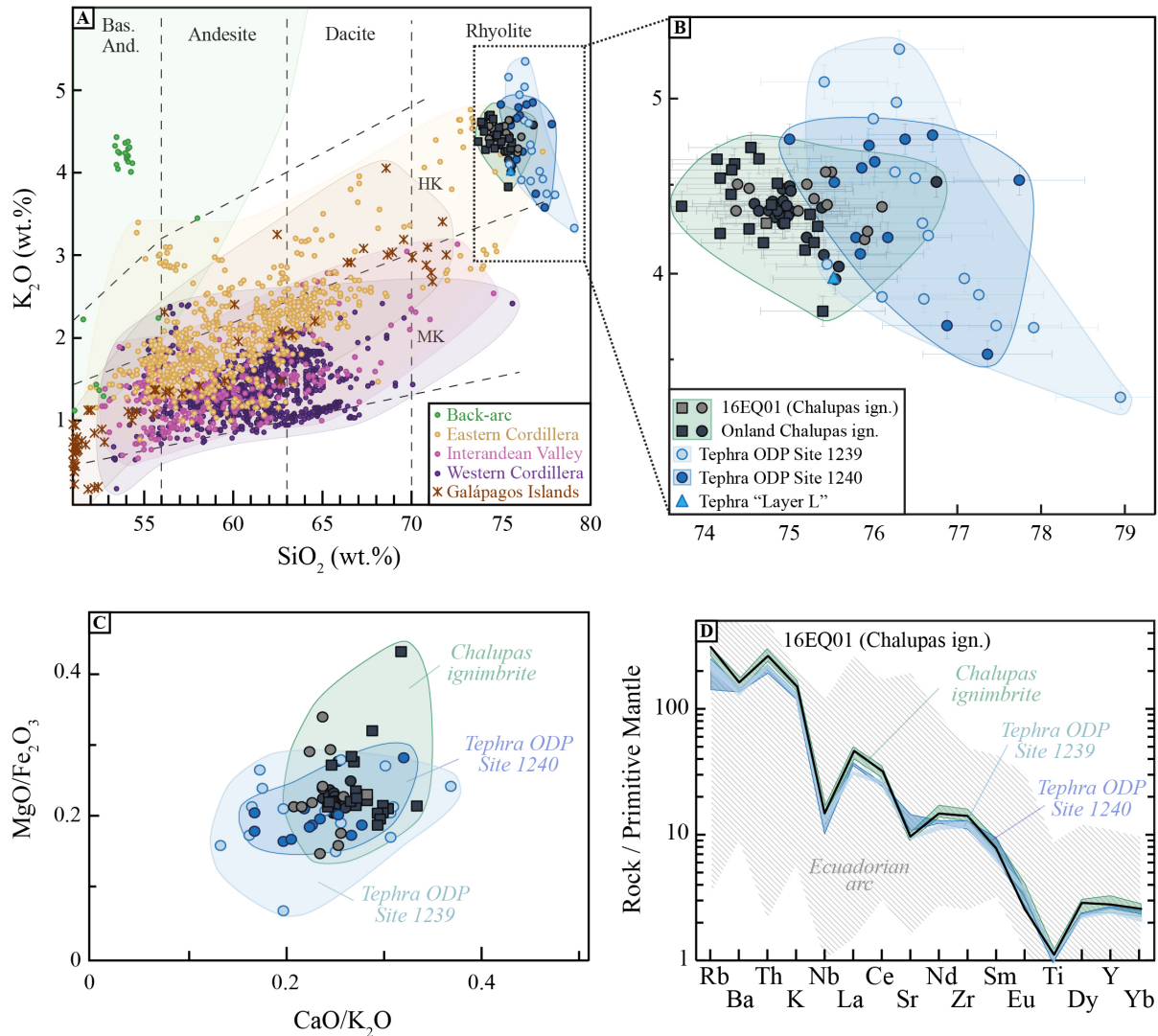
279

<i>ODP tephra layers</i>				
Trace elements (ppm)	Site 1239 - Hole B - Section 1H5		Site 1240 - Hole B - Section 3H5	
	93-95 cm (top of the layer)	98-100 cm (bottom of the layer)	5-7 cm (top of the layer)	13-15 cm (bottom of the layer)
Sc	2.40	2.23	2.47	2.65
V	16.09	16.78	31.21	22.21
Cr	4.95	10.36	13.79	10.04
Co	1.44	2.30	1.61	1.75
Ni	6.01	6.49	17.13	10.42
Rb	146.04	126.99	88.04	152.24
Sr	196.15	192.95	298.73	226.68
Y	11.45	10.86	11.98	11.76
Zr	138.58	127.32	120.63	141.74
Nb	9.95	8.95	7.14	9.30
Ba	989.84	876.87	927.54	993.81
La	21.04	20.63	24.28	24.02
Ce	46.58	43.54	41.78	45.16
Nd	14.71	15.56	16.30	17.01
Sm	3.10	2.71	4.19	2.89
Eu	0.61	0.60	0.46	0.60
Gd	2.06	1.97	2.35	2.43
Dy	1.59	1.67	1.62	1.73
Er	1.28	1.22	1.68	1.09
Yb	1.08	1.01	1.18	1.16
Th	18.08	17.88	15.78	18.31

281

282 Overall, marine tephra from proximal and distal ODP cores (light and dark blue
283 respectively; Figs. 3A and B), and the continental Chalupas ignimbrite (grey circles and
284 squares; Figs. 3A and B), display a rather homogeneous rhyolitic composition, with SiO₂ and
285 K₂O contents higher than 74.3% and 3.3%, respectively. They belong to the high-K calc-
286 alkaline magmatic suite (orange field; Fig. 4A), which characterizes products from the
287 Eastern Cordillera in Ecuador. Whole-rock measurements of minor and trace element contents
288 show that the Chalupas ignimbrite and the proximal and distal marine tephra layers are
289 homogeneous and enriched in most incompatible elements (e.g., Rb, Ba, Th, K) and depleted
290 in Nb, Sr and Ti (Fig. 3D), typical of subduction-related volcanic products.

291



292

293 **Fig. 3.** A) K_2O vs SiO_2 diagram with composition fields of all whole-rock data obtained for the Ecuadorian arc
 294 (purple, pink, yellow and green for the Western Cordillera, Interandean Valley, Eastern Cordillera and back-arc,
 295 respectively) and the Galápagos Islands (brown stars; Georoc database). HK, MK: high-K and medium-K calc-
 296 alkaline series. B) Detail on composition of rhyolite pumices studied in this work. Squares: Whole-rock
 297 measurements (Table 2; Appendix A; Barberi et al., 1988; Bryant et al., 2006; Ancellin et al., 2017; Córdova,
 298 2018). Circles: measurements of single glass shards (Table 3; Jackson et al., 2019). Triangle: ~220 ka “Layer L”
 299 from deep-sea cores (Ninkovich and Shackleton, 1975; see below). Blue field represents compositions that we
 300 associate to a single event of Chalupas ignimbrite. C) MgO/Fe_2O_3 ratio as a function of CaO/K_2O ratio. Legend
 301 as in Fig 3B. Error bars are included in the size of the symbols. D) Incompatible elements normalized to
 302 primitive mantle spider diagram (Sun and McDonough, 1989) of continental sample 16EQ01 (Chalupas
 303 ignimbrite; Table 2) and ODP marine tephra (Table 4). Purple and hatched grey domains represent the range of
 304 all values obtained for the Chalupas ignimbrite (Appendix A) and the Quaternary Ecuadorian arc (Georoc
 305 database).

306

307 6. Discussion

308 *6.1. Use of K-Ar dating method for determining the age of Quaternary pumice*
 309 *deposits*

310 Glass shards from the Chalupas ignimbrite have a significantly younger age than
311 biotite crystals (216 ± 5 and 286 ± 5 ka, respectively; Table 1). Glass shards are fragments of
312 the juvenile fraction that solidified during the eruption, whereas the biotite phenocrysts could
313 crystallize earlier in the magmatic reservoir. The older age of biotite crystals could therefore
314 be explained by the presence of inherited radiogenic argon and/or excess argon trapped in the
315 differentiated magma, where partial pressure of argon prior eruption is high and not
316 equilibrated with atmosphere (e.g., Morgan et al., 2009; Hora et al., 2010). Alternatively, the
317 potassium leaching favored by the lamellar structure of biotite crystals may also result in
318 older ages. However, we note that the K content of Chalupas biotite phenocrysts (6.7%;
319 Table 1) is similar to the mean values of 6.9% obtained for biotite crystals contained in
320 rhyolite products from worldwide arc volcanoes (1562 measurements; Georoc database) and
321 6.8% obtained for dacite and rhyolite Ecuadorian pumices (61 measurements from Monzier et
322 al., 1999; Samaniego et al., 2005; Garrison et al., 2011; Chiaradia et al., 2014; Bernard et al.,
323 2014; Béguelin et al., 2015), which suggests that our biotite crystals are rather fresh. As both
324 phenomena (i.e., inherited and/or excess argon and leaching) may induce older ages for biotite
325 crystals, we propose that the age of the event associated with the eruption of the Chalupas
326 ignimbrite is 216 ± 5 ka, as obtained from glass shards. The very small amount of plagioclase
327 phenocrysts present in the sample prevented us from using this mineral phase for dating.
328 However, our age obtained on glass shards refines and agrees with the unpublished $^{40}\text{Ar}/^{39}\text{Ar}$
329 age of 211 ± 14 ka obtained from plagioclase crystals (Beate et al., 2006).

330

331 *6.2. Age of marine tephra and correlation with the Chalupas eruption*

332 The occurrence of widespread volcanic ash layers in deep-sea sediments is related to
333 the transport in the atmosphere to the ocean of glass shards, which rapidly descend the water

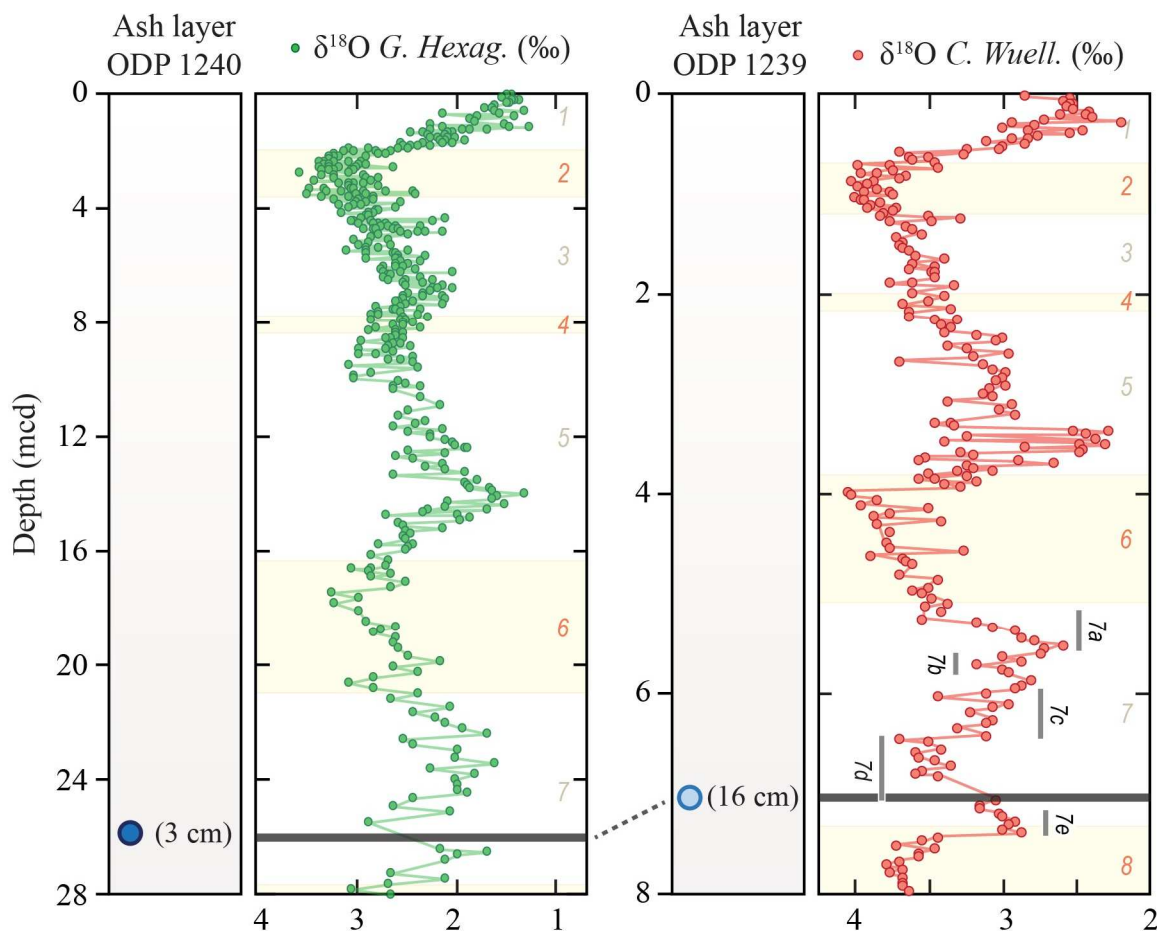
334 column and reach the seafloor in a few days (e.g., Wiesner et al., 1995; Carey, 1997; Manville
335 and Wilson, 2004; Wetzel, 2009), i.e. instantaneously with respect to geological time-scales.

336 The stratigraphic age of the analyzed rhyolitic tephra occurring within both ODP 1239
337 and 1240 Sites can be inferred using the oxygen isotope record ($\delta^{18}\text{O}$) from these deep-sea
338 cores previously published by Rincón-Martínez et al. (2010), Dyez et al. (2016), and Rippert
339 et al. (2017), respectively. The age model of $\delta^{18}\text{O}$ records was based on the global $\delta^{18}\text{O}$ stack
340 of Lisiecki and Raymo (2005), through $\delta^{18}\text{O}$ measurements on the benthic foraminifera
341 *Cibicidoides wuellerstorfi* and on the planktonic foraminifera *Globorotaloides hexagonus* for
342 ODP Sites 1239 and 1240, respectively (Fig. 4; Rincón-Martínez et al., 2010; Rippert et al.,
343 2017).

344 The rhyolitic ash layer lies between 6.72 and 6.88 mcd in ODP Site 1239C. This
345 stratigraphic position corresponds to a cooling event that occurred during the interglacial
346 marine isotope stage 7d (sensu Railsback et al., 2015; Fig. 4), as pointed out by both alkenone
347 temperature estimate and increase of benthic $\delta^{18}\text{O}$ values (Rincón-Martínez et al., 2010; red
348 curve, Fig. 4). Based on the ODP Site 1239 age model (Rincón-Martínez et al., 2010), this
349 tephra is dated at ~ 225 ka. Similarly, in the most distal ODP Site 1240, the rhyolitic ash layer
350 lies between 25.69 to 25.72 mcd. It is in an equivalent stratigraphic position than in ODP Site
351 1239, as indicated by the $\delta^{18}\text{O}$ record performed on planktonic foraminifera (Rippert et al.,
352 2017; Fig. 4), and the isotopic stage 7d cooling event inferred by sea-surface temperature
353 reconstructions (Pena et al., 2008).

354 Bowles et al. (1973), and Ninkovich and Shackleton (1975), identified a similar
355 rhyolitic ash layer, the "Layer L", off the coast of Colombia, Ecuador and northern Peru.
356 Ninkovich and Shackleton (1975) suggested that the volcanic source is located in southern
357 Colombia or Ecuador, based on the thickness of the deposits and the chemical composition of
358 glass shards. The $\delta^{18}\text{O}$ records on the benthic foraminifera *Uvigerina proboscidea* within
359 V19-28 and V19-29 cores (Fig. 1A) show that the volcanic event associated with the

360 "Layer L" occurred during the first cooling episode of the interglacial marine stage 7
 361 (Ninkovich and Shackleton, 1975).



362
 363 **Fig. 4.** $\delta^{18}\text{O}$ (‰) record of the planktonic *Globorotaloides hexagonus* (green curve; modified from Rippert et al.,
 364 2017) and benthic *Cibicidoides wuellerstorfi* (red curve, modified from Rincón-Martínez et al., 2010)
 365 foraminifera as a function of depth, for the ODP Sites 1240 and 1239 (Hole C), respectively. Depth of the ash
 366 layer presented in this study are represented by circles (symbols as in Fig. 3), and its thickness is indicated in
 367 parentheses. White and yellow fields represent marine isotope stages (MIS) defined by Lisiecki and Raymo
 368 (2005). Substages of MIS 7 from Railsback et al. (2015).

369
 370 Marine tephra and the Chalupas ignimbrite present homogeneous contents for all
 371 major elements, with similar $\text{MgO}/\text{Fe}_2\text{O}_3$ and $\text{CaO}/\text{K}_2\text{O}$ ratios (Figs. 3A, B and C). Marine
 372 tephra are slightly more enriched in SiO_2 and present a larger K_2O range than continental
 373 ignimbrite deposits (Fig. 3B). The whole-rock sample of the Chalupas ignimbrite is composed
 374 of a mixture of glass and crystals, whereas single shard measurements of marine tephra were
 375 performed on pristine glass, which concentrates incompatible elements and is slightly more

376 differentiated. Another hypothesis is that marine tephra might originate from a major
377 explosion that occurred in early eruptive phase of the event, while continental ignimbrite
378 deposits might have been emplaced later, when the magma reservoir was emptying, emitting
379 slightly less differentiated and more homogeneous magma. In addition, because the marine
380 tephra layer off the Ecuadorian coast is significantly thicker than in the distal cores
381 (Ninkovich and Shackleton, 1975; Shipboard Scientific Party, 2003), and based on its trace
382 element signature that is typical of arc magmas (light and dark blue fields; Fig. 3D), it cannot
383 originate from the Galápagos Islands (brown stars; Fig. 3A).

384 Considering the good match between the major element composition of marine tephra,
385 and continental pumice samples combined to our new age determination, we can consider that
386 the "Layer L" (Ninkovich and Shackleton, 1975), the ~6.8 m-deep ash layer in ODP Site 1239
387 (Fig. 4), the ~25.7 m-deep ash layer in ODP Site 1240, and the continental Chalupas
388 ignimbrite deposit (sample 16EQ01) are related to the same ~216 ka Chalupas eruption.

389 It should be emphasized that the K-Ar age that we obtain for the Chalupas ignimbrite
390 (216 ± 5 ka; Table 1) is slightly younger than that inferred from age models of deep-sea cores
391 (~ 225 ka), although these ages are in agreement within 2-sigma uncertainty. Age models in
392 ODP Sites 1239 and 1340 have been reconstructed using the global orbitally-tuned $\delta^{18}\text{O}$
393 benthic stack of Lisiecki and Raymo (2005), based on 57 worldwide cores, and with an
394 average uncertainty of ~ 4 ka for the last million years (Lisiecki and Raymo, 2005). It is worth
395 mentioning that benthic $\delta^{18}\text{O}$ records are related to sea-level changes, and that the $\delta^{18}\text{O}$ stack
396 of Lisiecki and Raymo (2005) is essentially based on this signal. However, Skinner and
397 Shackleton (2005) state that during the main climatic transitions, local changes in deep-water
398 hydrography could account for a lag deep-eastern Pacific temperatures of ~ 4 ka when
399 compared to the North Atlantic ones. Such further uncertainties should therefore be taken into
400 account for age model reconstructions in this area. Hence, our new K-Ar age combined to
401 $\delta^{18}\text{O}$ records offers a great potential to consider the Chalupas tephra as a new

402 chronostratigraphic marker for the marine isotopic stage 7 in the East Equatorial Pacific
403 Ocean.

404

405 *6.3. K-Ar dating of marine glass shards*

406 In order to compare the age of both Chalupas continental ignimbrite and marine co-
407 ignimbrite, we tentatively performed K-Ar dating on glass shards from the ODP 1239C core
408 (section 1H5, intervals 43-45 and 38-40 cm), following the same sample preparation as for
409 16EQ01 (see Methods). Although the K content of both marine deposits is about 3.5%, in
410 agreement with measurements performed on continental deposits (16EQ01; Table 1), the K-
411 Ar ages we obtained for both marine deposits are meaningless, with values older than 700 ka
412 for both of them. There is therefore probably a high radiogenic ^{40}Ar content in excess. It
413 should be emphasized that deep-sea tephra are distal deposits made of thin particles that
414 cooled rapidly during eruption. On the other hand, pumices within the massive (>50 m)
415 proximal ignimbrite deposit probably cooled much slower, thereby allowing equilibrium with
416 atmosphere. Consequently, any initial excess ^{40}Ar would have been removed from 16EQ01
417 ignimbrite glass, while it was trapped within the glass of distal tephra. Further analyses are
418 required to investigate this important issue regarding the wider applicability of our dating
419 technique.

420

421 *6.4. Spatial distribution and volume of Chalupas eruption*

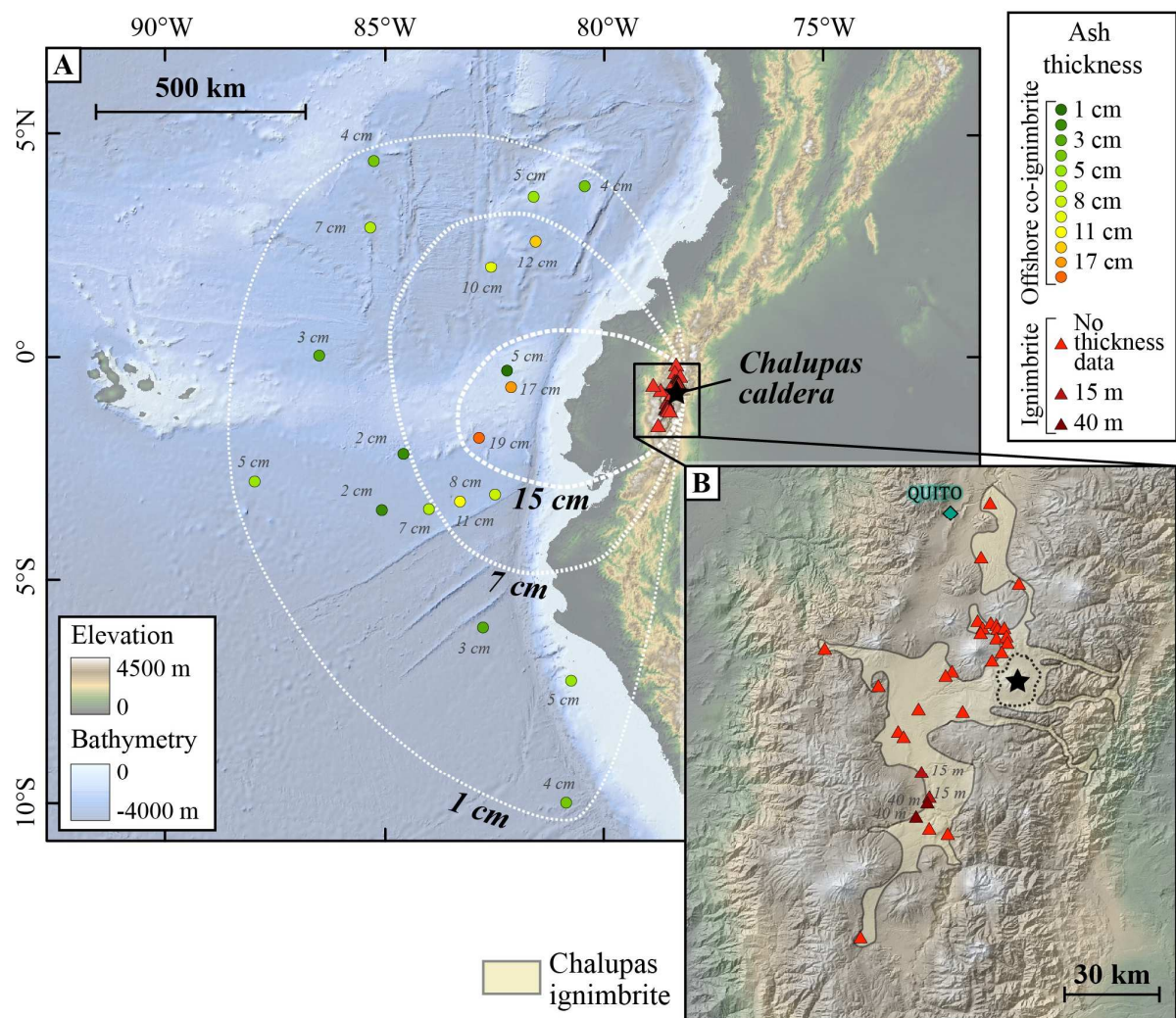
422 There are no clear Plinian fall deposits associated with the 216 ± 5 ka Chalupas
423 ignimbrite, but the offshore ash fall layer preserved in deep-sea cores (Ninkovich and
424 Shackleton, 1975; Shipboard Scientific Party, 2003) and correlated in this study to that
425 eruption (Figs. 3 and 4) seemingly corresponds to a co-ignimbrite ash deposit that shows a
426 consistent thinning pattern from a source in sub-central Ecuador at Chalupas caldera.

427 Although offshore thickness could have been biased by ocean currents, slumping or
428 bioturbation (Manville and Wilson, 2004; Wetzel, 2009; Lowe, 2011), the ash layer thickness
429 data allowed us designing a tentative isopach map with 1, 7 and 15 cm contour lines (areas of
430 $\sim 1.6 \times 10^6$ km², 5.4×10^5 km² and 1.7×10^5 km², respectively; Fig. 5A) in order to derive a plot of
431 ash thickness decay rate (i.e. thickness against square root of isopach area). Because we have
432 only three contour lines, we calculated the minimal ash volume using the single isopach
433 approach of Legros (2000), which yields bulk co-ignimbrite ash volumes in the range of about
434 60 to 140 km³, with an average close to 100 km³. A more realistic approximation that assumes
435 an exponential thickness decay rate from the source and a fit to our data (using two or three
436 isopachs on a single exponential segment, Pyle, 1989) yields volumes in the range of about
437 120 to 155 km³, values that are considered reliable based on our data set.

438 The bulk volume of the continental ignimbrite around the caldera and in the
439 Interandean Valley (beige field, total area of ~ 3150 km²; Fig. 5B) was estimated on a gross
440 scale through delineating the envelope of known outcrops (red triangles; Beate et al., 2006;
441 Bernard et al., 2008; Bustillos, 2008; Hall and Mothes, 2008a, 2008b; Ordóñez, 2012;
442 Córdova, 2018; Jackson et al., 2019; this study; Fig. 5B), extrapolating the distribution of the
443 ignimbrite in nearby valleys, and assuming from literature data and our field observations an
444 average thickness of about 25-35 m. Results point to a bulk ignimbrite volume in the range of
445 80 to 110 km³ (95 ± 15 km³), slightly above previous literature estimates of 80-200 km³
446 (Beate et al., 2006; Hall and Mothes, 2008a).

447 The total bulk deposit volume of both ignimbrite and co-ignimbrite thus amounts to
448 about 200-265 km³ ($\sim 230 \pm 30$ km³). This result ranks the 216 ± 5 ka Chalupas eruption at
449 VEI 7, consistent with the associated $\sim 16 \times 18$ km caldera size (Lipman, 1999; Geshi et al.,
450 2014). As a comparison, the volume erupted at Chalupas caldera is about two times larger
451 than volumes released by historic eruptions of Tambora, Samalas, Krakatoa and Santorini
452 (e.g., Lipman, 1999; Self et al., 2004; Lavigne et al., 2013; Karátson et al., 2018). Therefore,

453 the Chalupas event may be the largest Quaternary eruption from the Northern Andean
 454 Volcanic Zone and it can be envisioned that such an eruption could have caused a short-term
 455 climate forcing, with a possible global cooling. Measurements of sulphide contents contained
 456 in fluid inclusions of the glass shards are needed to quantify the amount of volatiles injected
 457 into the atmosphere, and to better infer the climatic impact of this super-eruption.
 458



459
 460 **Fig. 5.** A) Tentative isopach map (1, 7 and 15 cm) of the 216 ± 5 ka Chalupas offshore co-ignimbrite ash fall
 461 deposit. Location of the cores shown as orange, yellow and green circles and thickness data are from Ninkovich
 462 and Shackleton (1975) and Shipboard Scientific Party (2003). B) Reconstructed distribution of the Chalupas
 463 ignimbrite (beige field). Location of selected exposure sites shown as red triangles and ignimbrite thickness
 464 values are from Beate et al. (2006); Bernard et al. (2008); Bustillos (2008); Hall and Mothes (2008a; 2008b);
 465 Ordóñez (2012); Córdova (2018); Jackson et al. (2019); and this study. The Chalupas caldera is shown with a
 466 solid star, and its rim is depicted with a dotted line.

467

468 **7. Conclusions**

469 The present study demonstrates the reliability of the K-Ar dating method performed
470 on glass shards from a massive continental ignimbrite deposit. This method is a reliable tool
471 to date Quaternary pyroclastic deposits. The samples require a careful selection of only very
472 fresh material, and removal of all altered and/or vesiculated glass shards. We provide a new
473 K-Ar age of 216 ± 5 ka for the Chalupas ignimbrite.

474 Based on glass shard morphology, whole-rock and glass geochemical data, as well as
475 isopach map of deposits, we have correlated the Chalupas ignimbrite to marine ash-layers
476 from several cores offshore Ecuador. It shows that the Chalupas eruption could have injected
477 between 200 and 265 km³ of pyroclastic material into the atmosphere, and that ashes have
478 reached areas located more than 900 km away from the source caldera.

479 Our K-Ar age obtained for Chalupas ignimbrite also provides reliable independent
480 timing control for the $\delta^{18}\text{O}$ records of isotope stage 7, which is tuned by orbitally derived
481 times-scales.

482 Finally, we hope that our study will reinforce the interest of jointly studying
483 continental volcanic deposits and marine tephra layers to better characterize the major
484 Pleistocene eruptions of the Ecuadorian arc. Such an approach also appears to be the only way
485 to identify catastrophic eruptions that occurred during early stages of the current Ecuadorian
486 arc construction, and could help to better define the recurrence of such major events.

487

488

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502 **XXX**.
503

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744 **Appendix A**

745 Whole-rock major and trace element composition of Chalupas ignimbrite samples (unpublished IRD-IG dataset),
 746 measured by ICP-AES at the Laboratoire Géosciences Océan of the Université de Bretagne Occidentale (Brest,
 747 France; Cotten et al., 1995). All analyses of major elements were brought down to a total of 100% on a water-
 748 free basis. Outcrop coordinates projected using the Universal Transverse Mercator (UTM) coordinate system
 749 (Zone 17) and given within 100 meters (Fig. 1).

750

		<i>Whole-rock Chalupas ignimbrite</i>													
		CHAL 00	CHAL 01 TAMBO	CHAL 01A	CHAL 02A TIS	CHAL 02C TIS	CHAL 02D TIS	CHAL 118	CHAL 750165	CHAL 862348- ING	CHAL 870588	CHAL 893794- AC	CHAL 933243- YPF	COT FD 183 F	CHAL RIO 23
UTM E		798800	789800	778000	778000	754200	754200	754200	787000	775000	786200	787000	789300	793300	793300
UTM S		9949300	9921400	9917500	9917500	9911200	9911200	9911200	9933000	9916500	9934800	9958800	9979400	9924300	9924300
Major elements (wt.%)	SiO ₂	74.32	74.67	74.18	74.54	74.87	74.63	74.19	74.53	74.95	75.3	75.2	75.24	75.34	74.8
	TiO ₂	0.26	0.27	0.26	0.24	0.25	0.24	0.26	0.26	0.24	0.24	0.24	0.24	0.24	0.24
	Al ₂ O ₃	13.78	14.35	14.26	13.71	13.64	13.71	14.11	14.17	13.8	13.75	13.63	13.79	13.73	13.55
	Fe ₂ O ₃	1.61	1.61	1.49	1.45	1.49	1.41	1.48	1.6	1.4	1.47	1.47	1.35	1.4	1.45
	CaO	1.32	1.28	1.2	1.16	1.2	1.14	1.23	1.28	1.29	1.23	1.23	1.18	1.17	1.46
	MgO	0.3	0.34	0.33	0.32	0.33	0.3	0.35	0.33	0.3	0.3	0.29	0.29	0.32	0.31
	MnO	0.04	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.04
	K ₂ O	4.46	4.18	4.23	4.72	4.52	4.66	4.54	4.26	4.29	4.19	4.13	4.34	4.28	4.39
	Na ₂ O	3.86	3.2	3.94	3.78	3.61	3.84	3.74	3.47	3.64	3.44	3.71	3.48	3.44	3.71
	P ₂ O ₅	0.05	0.04	0.04	0.03	0.03	0.03	0.04	0.05	0.04	0.03	0.04	0.03	0.03	0.03
<i>L.O.I.</i>	<i>3.68</i>	<i>5.41</i>	<i>3.16</i>	<i>2.95</i>	<i>2.69</i>	<i>3.4</i>	<i>2.88</i>	<i>5.19</i>	<i>3.38</i>	<i>3.15</i>	<i>4.21</i>	<i>3.96</i>	<i>5.37</i>	<i>3.77</i>	
Trace elements (ppm)	Sc	2.1	2.1	1.8	2	2	2	1.9	2.2	2	2	2	1.9	2	1.8
	V	12	15	12	12	12	11	12.5	15	13	10	13	10	10	11
	Cr	3	5	3	2	2	2	5	4	4	3	2	2	2	3
	Co	1.5	5	1.5	9	5	4.5	1.5	2	1	2	3	2	2	2
	Ni	1.5	4	1	1	2	2	1	4	2	2	1	1.5	4	2
	Rb	174	178	170	170	168	170	177	167	174	181	178	165	167	167
	Sr	215	200	217	209	213	204	222	203	205	210	210	199	202	210
	Y	11.8	13	13.4	12.8	12.6	12.5	14	12.3	12.5	12.2	12.9	12	15	12.5
	Zr	145	155	155	162	162	152	153	149	154	160	170	156	164	160
	Nb	11	11	11.5	11.4	11.5	11.5	11.2	10.5	11.15	10.9	11.4	11	11.1	11.4
	Ba	1060	1010	1100	1080	1120	1080	1095	1005	1080	1000	1050	997	1140	1080
	La	32	31	32	31	31	31	32.5	30.75	32.5	30	31	29.5	31	31
	Ce	56	60	56	57	55	58	57	55	57	57	60	55	58	56
	Nd	21	23	20.5	20.5	21	21.5	21.5	21	21	20	20	20.4	21.5	23
	Sm	3.3		3.85	3.6	3.65	3.6	3.45			3.7	3.5		3.5	3.5
	Eu	0.67	0.55	0.68	0.58	0.58	0.6	0.66	0.58	0.6	0.58	0.56	0.57	0.62	0.56
	Gd	2.8		2.3	2.6	3.35	2.85	2.25			2.7	2.7		2.8	2.6
Dy	1.9	2	2.28	2	2	2	2.2	2.1	2	2	2	1.9	2.3	1.95	
Er	1.2	1.3	1.3	1.2	1.25	1.2	1.4	1.2	1.3	1.2	1.25	1.25	1.4	1.2	
Yb	1.2	1.175	1.4	1.19	1.2	1.2	1.42	1.195	1.245	1.25	1.26	1.19	1.35	1.25	
Th	22.3		22	20	22.4	22.9	23.7			23.5	22.5	21.1	21.8	21	

751