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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  $216 \pm 5$  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 km<sup>3</sup>. This suggests that the  
46 Chalupas event could have been strong enough to reach the stratosphere and inject large  
47 amount of SO<sub>2</sub> 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  $^{14}\text{C}$  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).

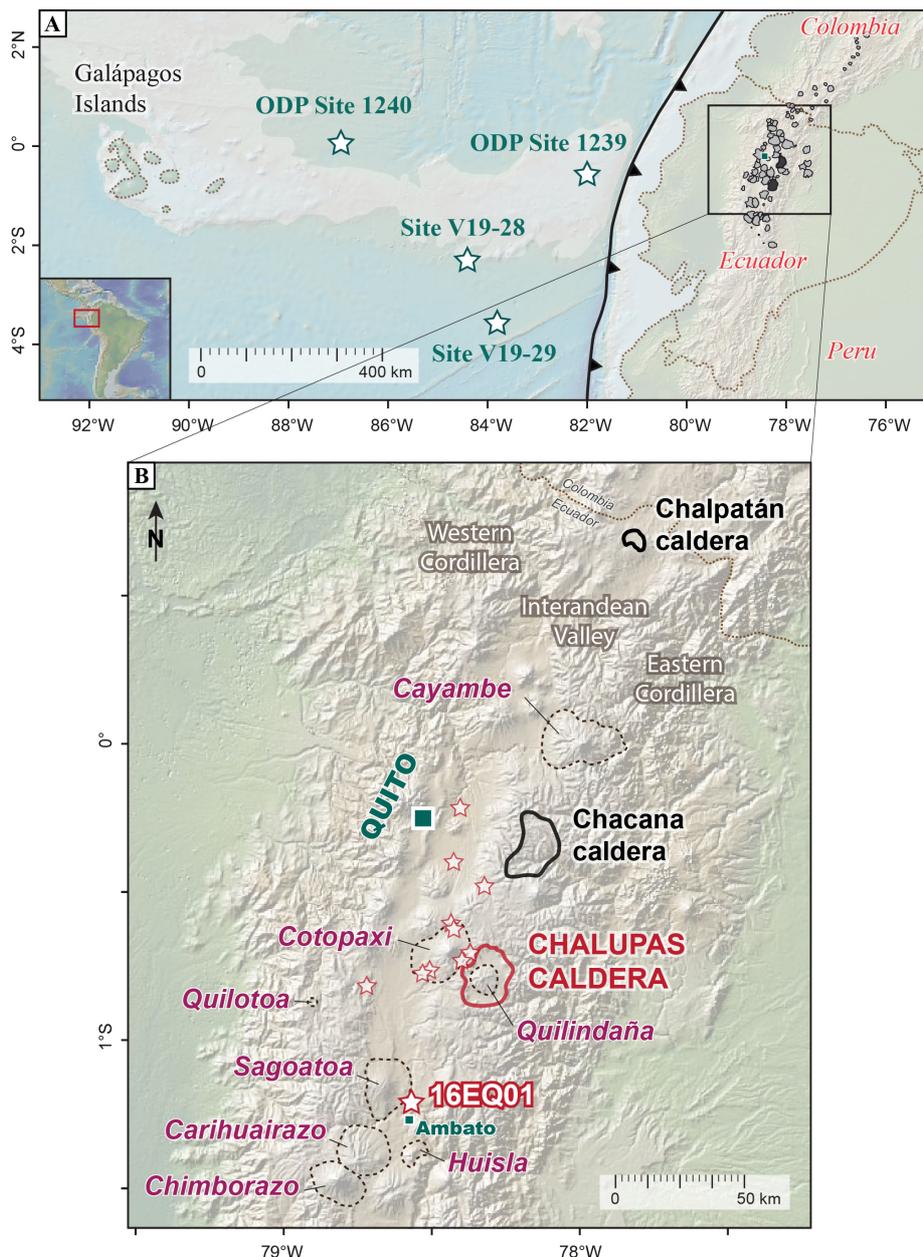
83 As crystals may not be systematically present in pumice samples, glass may be the  
84 only juvenile material that can be dated. While the  $^{40}\text{Ar}/^{39}\text{Ar}$  technique is not always suitable  
85 for glass shard dating because of  $^{39}\text{Ar}$  recoil occurring during irradiation 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  $211 \pm 14$  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

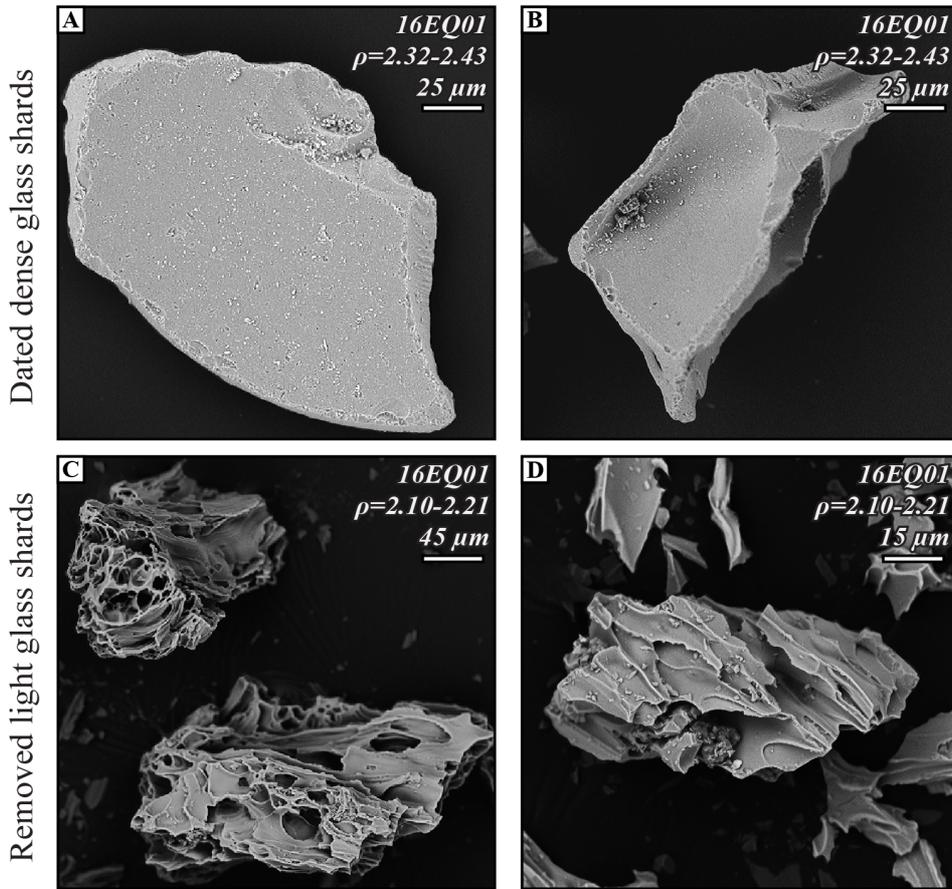
## 156 **4. Materials and methods**

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

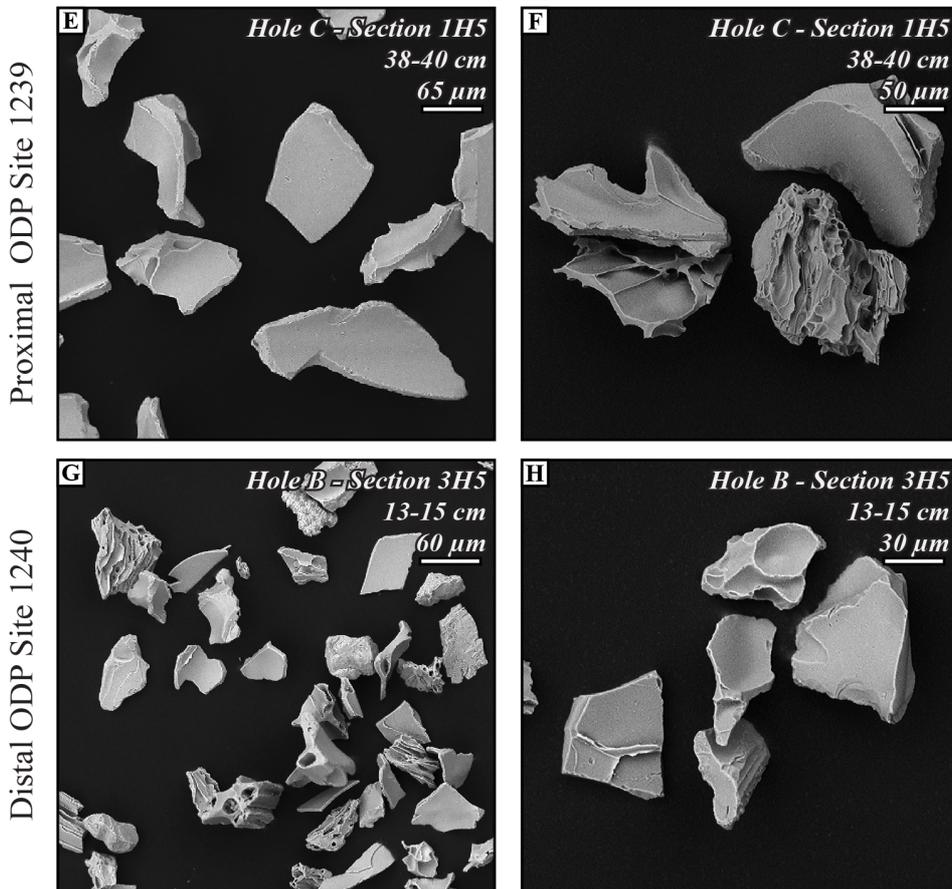
158 The Chalupas ignimbrite deposit was sampled towards the base of a ~30 m-high  
159 quarry outcrop, in the vicinity of Ambato city, 55 km southwest of the caldera (sample  
160 16EQ01; Fig. 1B).

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  $\mu\text{m}$ ;  $\rho=2.32$ -  
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  $^{40}\text{Ar}$  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- $\sigma$

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  $\mu\text{m}$  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  $\text{SiO}_2$ ;  $\sim 1\%$  for  $\text{Al}_2\text{O}_3$ ,  $< 3\%$  for  
231  $\text{CaO}$  and  $\text{MgO}$ ,  $< 4\%$  for  $\text{Na}_2\text{O}$ ,  $< 5\%$  for  $\text{Fe}_2\text{O}_3$ ,  $< 6\%$  for  $\text{K}_2\text{O}$ ,  $10\%$  for  $\text{TiO}_2$  and  $\sim 30\%$  for  
232  $\text{MnO}$ .

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  $3.54 \pm 0.04 \%$ , and reaches  
 243  $6.66 \pm 0.07 \%$  for biotite crystals (Table 1). The content of radiogenic argon, which derives  
 244 from the radioactive decay of  $^{40}\text{K}$ , ranges between 5.1 and  $12.3 \pm 0.10 \%$ . From these values  
 245 combined with the  $^{40}\text{K}$  decay constants (Steiger and Jäger, 1977), we obtain ages of  
 246  $216 \pm 5$  and  $286 \pm 5$  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	$3.54 \pm 0.04$	$5.16 \pm 0.10$	$7.856 \pm 0.155$	$213 \pm 5$	<b><math>216 \pm 5</math></b>
					$5.18 \pm 0.10$	$8.009 \pm 0.158$	$217 \pm 5$	
					$5.09 \pm 0.10$	$8.063 \pm 0.152$	$218 \pm 5$	
			Biotite crystals	$6.66 \pm 0.07$	$12.26 \pm 0.10$	$19.740 \pm 0.161$	$284 \pm 5$	<b><math>286 \pm 5</math></b>
					$7.14 \pm 0.10$	$20.091 \pm 0.282$	$289 \pm 6$	

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 <sub>2</sub>	74.72	<i>74.64 ± 0.49</i>	Sc	2.06	<i>2.06 ± 0.23</i>
TiO <sub>2</sub>	0.24	<i>0.25 ± 0.02</i>	V	13.46	<i>13.32 ± 3.76</i>
Al <sub>2</sub> O <sub>3</sub>	13.77	<i>13.89 ± 0.24</i>	Cr	<<	<i>3.65 ± 2.02</i>
Fe <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O	4.29	<i>4.38 ± 0.23</i>	Y	12.41	<i>13.22 ± 1.92</i>
Na <sub>2</sub> O	3.87	<i>3.74 ± 0.29</i>	Zr	153.25	<i>162.35 ± 13.49</i>
P <sub>2</sub> O <sub>5</sub>	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 1H5 - 43-45 cm

wt. %																		Mean	Std
SiO <sub>2</sub>	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		<b>76.68</b>	0.90
TiO <sub>2</sub>	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		<b>0.19</b>	0.09
Al <sub>2</sub> O <sub>3</sub>	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		<b>13.94</b>	0.32
Fe <sub>2</sub> O <sub>3</sub>	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		<b>0.92</b>	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		<b>0.99</b>	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		<b>0.19</b>	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		<b>0.05</b>	0.06
K <sub>2</sub> 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		<b>4.26</b>	0.57
Na <sub>2</sub> 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		<b>2.78</b>	0.63

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

wt. %																		Mean	Std
SiO <sub>2</sub>	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					<b>76.25</b>	0.76
TiO <sub>2</sub>	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					<b>0.18</b>	0.05
Al <sub>2</sub> O <sub>3</sub>	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					<b>13.83</b>	0.44
Fe <sub>2</sub> O <sub>3</sub>	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					<b>1.08</b>	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					<b>1.02</b>	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					<b>0.21</b>	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					<b>0.05</b>	0.08
K <sub>2</sub> 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					<b>4.39</b>	0.41
Na <sub>2</sub> 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					<b>2.99</b>	0.35

## Chalupas ignimbrite (16EQ01)

wt. %																		Mean	Std
SiO <sub>2</sub>	75.45	75.50	75.90	74.37	75.44	75.21	74.51	75.94	75.29	75.10	76.10	74.37						<b>75.27</b>	0.59
TiO <sub>2</sub>	0.26	0.16	0.21	0.37	0.24	0.23	0.24	0.19	0.35	0.25	0.21	0.25						<b>0.25</b>	0.06
Al <sub>2</sub> O <sub>3</sub>	14.32	13.72	14.11	13.83	14.65	14.31	14.89	13.93	14.53	13.76	14.36	14.12						<b>14.21</b>	0.37
Fe <sub>2</sub> O <sub>3</sub>	1.18	0.54	0.75	1.06	0.39	0.99	0.63	0.97	0.94	0.93	0.54	1.41						<b>0.86</b>	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						<b>1.05</b>	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						<b>0.19</b>	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						<b>0.06</b>	0.03
K <sub>2</sub> 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						<b>4.42</b>	0.12
Na <sub>2</sub> 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						<b>3.70</b>	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.

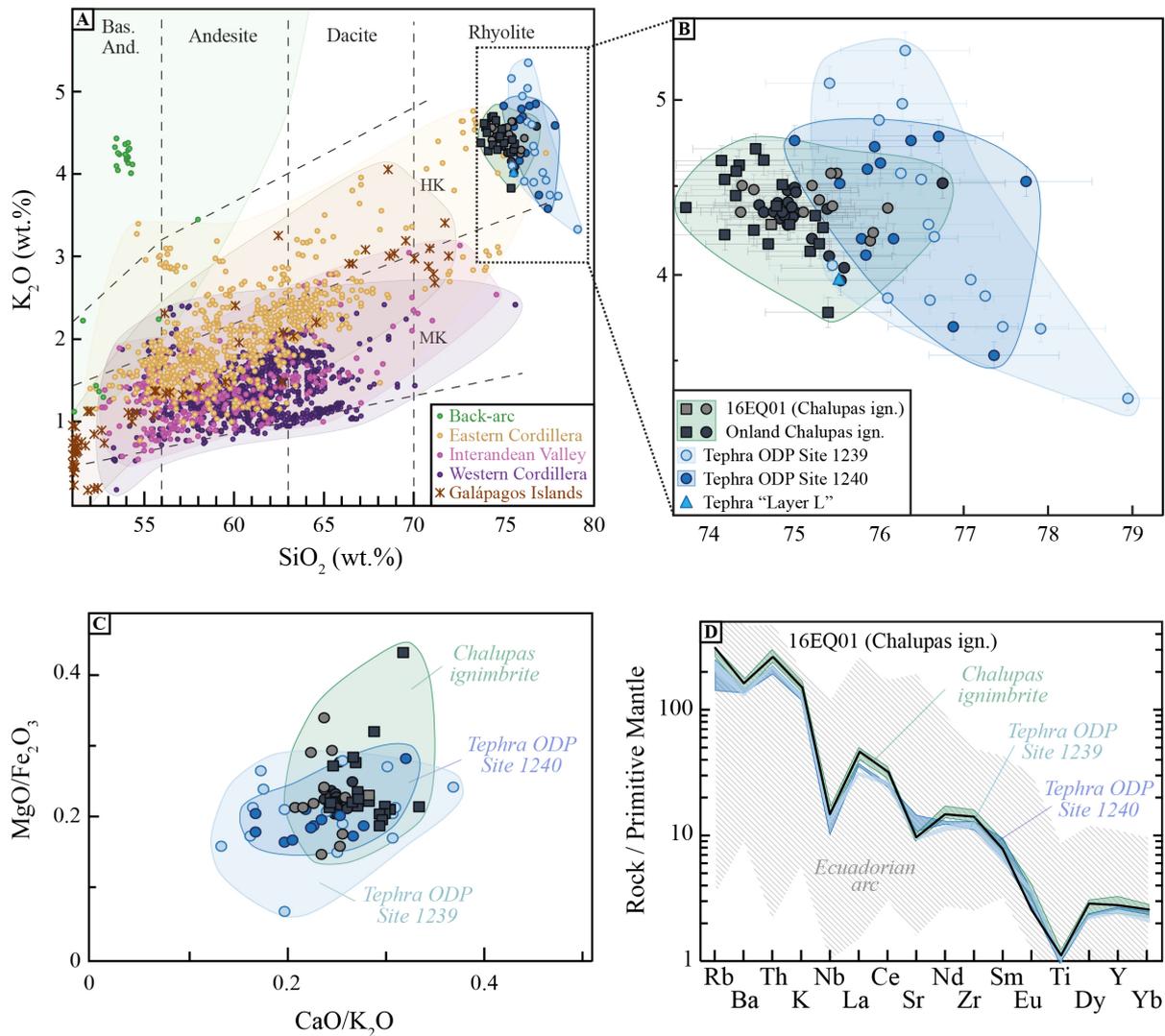
279

<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 SiO<sub>2</sub> and  
285 K<sub>2</sub>O 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 ( $216 \pm 5$  and  $286 \pm 5$  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  $216 \pm 5$  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  $211 \pm 14$  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

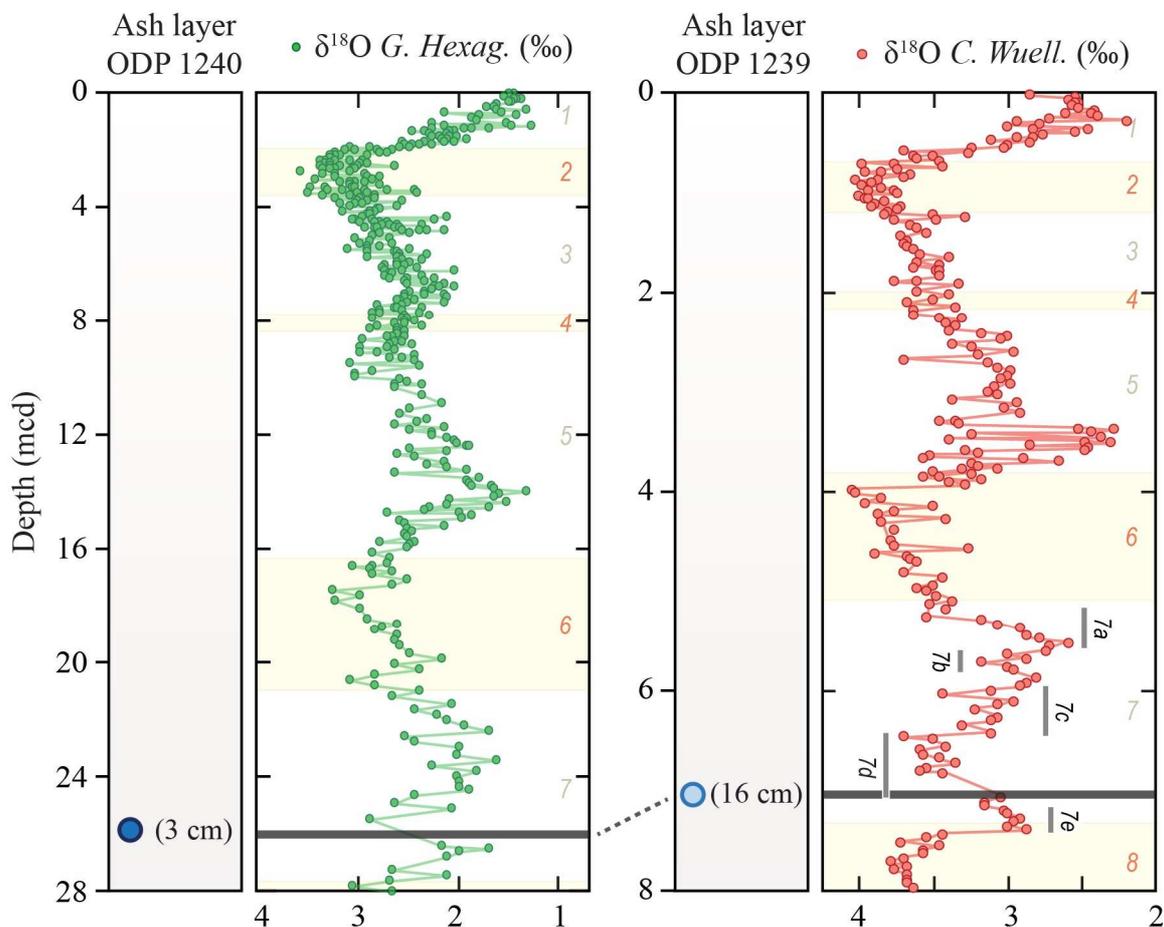
334 column and reach the seafloor in a few days (e.g., Wiesner et al., 1995; Carey, 1997; Manville  
335 and Wilson, 2004; Wetzel, 2009), i.e. instantaneously with respect to geological time-scales.

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  $\text{SiO}_2$  and present a larger  $\text{K}_2\text{O}$  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 ( $216 \pm 5$  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  $^{40}\text{Ar}$  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  $^{40}\text{Ar}$  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*

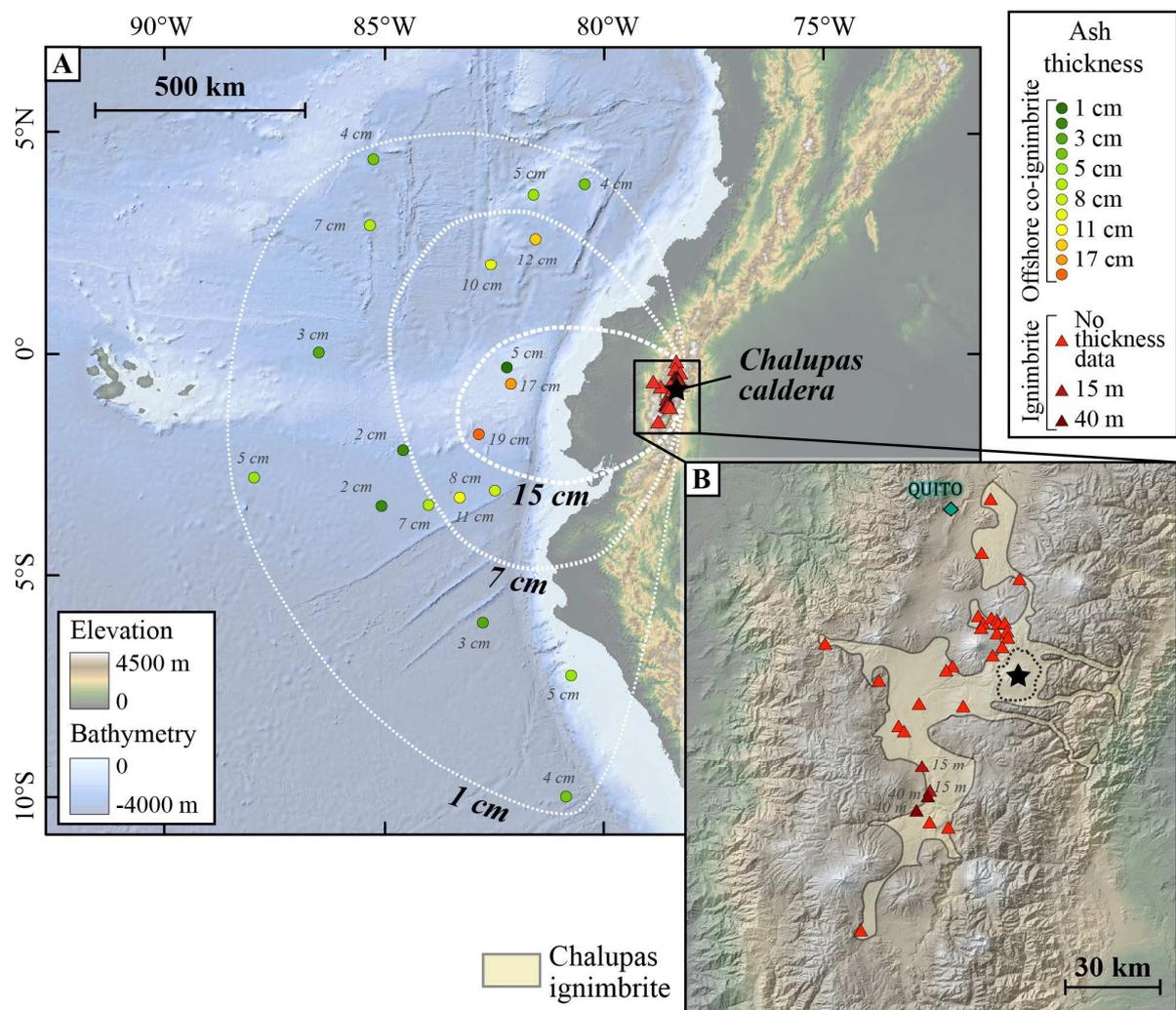
422 There are no clear Plinian fall deposits associated with the  $216 \pm 5$  ka Chalupas  
423 ignimbrite, but the offshore ash fall layer preserved in deep-sea cores (Ninkovich and  
424 Shackleton, 1975; Shipboard Scientific Party, 2003) and correlated in this study to that  
425 eruption (Figs. 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  $\sim 1.6 \times 10^6$  km<sup>2</sup>,  $5.4 \times 10^5$  km<sup>2</sup> and  $1.7 \times 10^5$  km<sup>2</sup>, 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 km<sup>3</sup>, with an average close to 100 km<sup>3</sup>. 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 km<sup>3</sup>, 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  $\sim 3150$  km<sup>2</sup>; 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 km<sup>3</sup> ( $95 \pm 15$  km<sup>3</sup>), slightly above previous literature estimates of 80-200 km<sup>3</sup>  
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 km<sup>3</sup> ( $\sim 230 \pm 30$  km<sup>3</sup>). This result ranks the  $216 \pm 5$  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 **Fig. 5.** A) Tentative isopach map (1, 7 and 15 cm) of the 216 ± 5 ka Chalupas offshore co-ignimbrite ash fall  
 460 deposit. Location of the cores shown as orange, yellow and green circles and thickness data are from Ninkovich  
 461 and Shackleton (1975) and Shipboard Scientific Party (2003). B) Reconstructed distribution of the Chalupas  
 462 ignimbrite (beige field). Location of selected exposure sites shown as red triangles and ignimbrite thickness  
 463 values are from Beate et al. (2006); Bernard et al. (2008); Bustillos (2008); Hall and Mothes (2008a; 2008b);  
 464 Ordóñez (2012); Córdova (2018); Jackson et al. (2019); and this study. The Chalupas caldera is shown with a  
 465 solid star, and its rim is depicted with a dotted line.  
 466

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  $216 \pm 5$  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 km<sup>3</sup> 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.

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488

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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).

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		<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 <sub>2</sub>	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 <sub>2</sub>	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 <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> 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 <sub>2</sub> 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 <sub>2</sub> O <sub>5</sub>	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	

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