

1 **Chemical and petrographic fingerprinting of volcanic ashes as a tool to high-resolution stratigraphy of**
2 **the upper Miocene Pisco Formation (Peru)**

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24
25 **Abstract**

26 Tephra layers are a unique tool for stratigraphy. Their geologically instantaneous deposition together with
27 their dispersion on wide areas make them a powerful instrument for dating and correlating simultaneous
28 events at different localities. In this paper, we present and discuss the application of tephra fingerprinting in
29 the upper Miocene portion of the Pisco Formation.

30 The Pisco Formation is an important marine vertebrate Fossil-Lagerstätte that crops out in the Ica Desert, on
31 the Peruvian Coast. The paleontological relevance of this formation has entailed the necessity of
32 reconstructing a chronostratigraphic framework, using ⁴⁰Ar/³⁹Ar dating and correlations on volcanic ashes.
33 Tephra layers from the volcanic activity of the Peruvian Andes are very frequent in the Pisco Formation and
34 many represent a primary air-fall deposition on the sea floor. Therefore, many samples from tephra layers
35 within measured stratigraphic sections at different sites in the study area were fingerprinted with a combined
36 approach, using petrographic and chemical analyses on phenocrysts and volcanic glasses, as well as glass
37 shard morphology and granulometric analyses, performed on 53 selected samples, collected from different

38 localities. Based on the results obtained, we correlate some tephra layers in ~~two~~ localities at several km
39 distance, where the correlation between the measured sections was previously only hypothetical. Major
40 element chemistry of biotite proved a valuable tool to discriminate different tephra in the upper Miocene
41 portion of the Pisco Formation, due to the presence of peraluminous as well as metaluminous compositions.
42 This work shows that it is possible to apply tephra fingerprinting and tephrostratigraphy in a complex
43 situation such as that represented by the Pisco Formation, where a high number of apparently similar
44 volcanic ash layers were deposited in a shallow marine environment. The application of this correlation
45 method allows us to increase the chronostratigraphic detail in the studied interval of the Pisco Formation,
46 providing an accurate framework in which fossil marine vertebrates are stratigraphically located. The
47 obtained high-resolution chronostratigraphy will greatly clarify the evolutionary history of Cetaceans.

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50 **Highlights**

- 51 • Onshore forearc basins provide an archive of late Miocene Andean distal tephra
- 52 • Major element chemistry of glass and biotite allow fingerprinting tephra of Pisco Formation
- 53 • Biotite chemistry is a powerful tool for upper Miocene Peruvian tephra fingerprinting
- 54 • Tephra give a detailed chronostratigraphic framework for the Pisco marine vertebrate Konservat-
55 Lagerstätte

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58 **Keywords**

59 Tephrostratigraphy; Tephra fingerprinting; Fossil-Lagerstätte; Miocene; Pisco Formation; Central Andes

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62 **1. Introduction**

63 Due to their regional dispersion, geologically instantaneous deposition, and the common presence of
64 minerals suitable for radiometric age determination, the value of volcanic ashes as regional
65 chronostratigraphic markers has long been recognized (Lowe et al., 2017).

66 Detailed chronostratigraphic reconstructions are particularly important for the sedimentary fill of the East
67 Pisco Basin exposed on the southern Peruvian coast (Fig. 1A). The East Pisco Basin, indeed, hosts one of the
68 most important world-class cetacean Fossil-Lagerstätten, with exceptionally well-preserved fossils of marine
69 vertebrates (Bianucci et al., 2016a, 2016b). In particular, along the western side of the Ica River Valley,
70 strata of the Mio-Pliocene Pisco Formation are characterized by fossil remains of cetaceans, both
71 odontocetes and mysticetes, but also of pinnipeds, sea-birds, sea-turtles, crocodiles, sharks, and bony fish
72 (Muizon, 1988; Bianucci et al., 2010, 2015, 2016c; Lambert et al., 2010, 2015, 2017a, 2017b; Parham and
73 Pyenson, 2010; Esperante et al., 2015; Collareta et al., 2015; Gioncada et al., 2016; Stucchi et al., 2016;

74 Marx et al., 2017). The correspondence between the stratigraphy and the vertebrate findings was a long-term
75 neglected issue and each fossil-bearing locality was not correlated with the adjacent ones. In order to better
76 understand qualitatively and quantitatively the evolution of its rich marine vertebrate fauna during a pivotal
77 time frame for the evolutionary history of marine vertebrates, such as the late Miocene, the Pisco Formation
78 needs the reconstruction of an accurate, high-resolution absolute and relative age framework. This age
79 interval is characterized by a significant cetacean turnover outlined by the diversification of several lineages
80 of crown neocetes as the delphinidians and the ziphiids among the odontocets, and the balaenopterids among
81 the mysticetes (Fordyce and Muizon, 2001; Bianucci and Landini, 2017; Marx et al., 2015). Accurate dating
82 of some taxa can also allow a better definition of several calibration points for molecular divergence
83 estimated among crown neocetes (see, e.g. Lambert et al. 2017b).

84 The Pisco Formation is a diatomite-rich marine unit with numerous layers of volcanic ash representing
85 primary air-fall events from the Peruvian Central Andes volcanoes and a very important tool to define its
86 stratigraphic framework (Di Celma et al., 2017; Gariboldi et al., 2017). So far, their use has been limited to
87 field correlations within a single locality and to obtain $^{40}\text{Ar}/^{39}\text{Ar}$ ages. With the aim of fully exploiting the
88 potential of these volcanic ash layers for tephrostratigraphy, in this paper we fingerprint ash layers by a
89 chemical and petrographic characterization and correlate them between different localities.

90 Fingerprinting of distal tephra is recognized as a useful method for stratigraphic reconstructions (D'Antonio
91 et al., 2016) and is largely employed in the Quaternary (e.g. Zanchetta et al., 2011; D'Antonio et al., 2016)
92 and to correlate the deposits of large eruptions of Central Andes (De Silva and Francis, 1989; Lebtí et al.,
93 2006; Bretkreutz et al., 2013).

94 In the Pisco Formation, however, the high number of ash layers interbedded within a monotonous diatom-
95 rich succession, the similarity of their geochemical features and components, and the possibility that sea
96 currents affected both their grain size and composition during deposition, hamper the unequivocal
97 identification of these ashes directly in the field. In this paper, we focus on some of the ash layers from the
98 P2 depositional sequence, which is the youngest unconformity-bounded unit documented so far in the upper
99 Miocene portion of the Pisco Formation (Di Celma et al., 2017) and the most studied one for its high
100 paleontological content. We fingerprint tephra layers of the P2 sequence by using major element chemistry
101 of biotite and glass combined with petrographic and granulometric features, with the aim to correlate
102 stratigraphic sections in different localities and highlight the feasibility of an approach based on major
103 element biotite chemistry. The same approach could be extended to other fossiliferous successions of the
104 Pisco Basin relevant for the reconstruction of marine vertebrate evolution.

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107 **2. Setting**

108 **2.1. Geological and volcanological setting**

109 The Peruvian margin is part of the long-lived convergent margin of South America and is interested by two
110 extended structural ridges, the Outer Shelf High and the Upper Slope Ridge, dissecting the Peruvian coast

111 into a series of Cenozoic forearc basins (Fig. 1A). The East Pisco Basin, the onshore part of one of these
112 basins at 14°30' S of latitude, is confined by the igneous rocks of the Mesozoic Coastal Batholith to the east
113 (Cobbing, 1999) and by Precambrian to Jurassic rocks of the Coastal Cordillera to the west (Romero et al.,
114 2013). As described by previous authors (Dunbar et al., 1990; DeVries, 1998), this basin was interested by a
115 discontinuous sediment deposition between the Eocene and the Pliocene. Starting from late Pliocene, the
116 subduction of the aseismic Nazca Ridge beneath the South American plate has caused the uplift of the East
117 Pisco Basin (Macharé & Ortlieb 1992; Hampel et al. 2002), resulting in the onland exposure of its Eocene to
118 Pliocene sedimentary fill.

119 The numerous volcanic ashes interbedded with the basin-filling sedimentary succession provide a snapshot
120 of the long-lived activity of the Central Andes volcanoes, frequently punctuated by large explosive eruptions.
121 The dispersion of Andean tephra, as demonstrated by historical examples (Adams et al., 2001) as well as by
122 off-shore drilling programs logs (Hart and Miller, 2006), largely affected the margin with off-shore
123 deposition of Plinian and of co-ignimbrite ashes. As reviewed by Mamani et al. (2010), the Central Andean
124 margin has a very complex subduction-related history. The late Paleozoic to middle Cretaceous history was
125 characterized by tectonic stretching, allowing the formation of a marine back-arc basin; a continuous relief,
126 with a continental back-arc environment, formed in the time period from the late Cretaceous to the middle
127 Oligocene, but the major crustal thickening typical of the Andean orogeny was developed only since the
128 middle Oligocene (Mamani et al., 2010). These authors subdivide the continuous magmatic activity into
129 four, partly overlapping, discrete phases: the Tacaza arc, from 30 to 24 Ma, the Huaylillas arc, between 24
130 and 10 Ma, the Lower Barroso arc, from 10 to 3 Ma and the Upper Barroso arc, between 3 and 1 Ma.
131 Voluminous Neogene and Quaternary ignimbrite deposits occur in southern Peru, testifying the main periods
132 of intense and voluminous explosive activity of the arcs (Lebti et al., 2006; Thouret et al., 2007, 2016).
133 According to the samples available to these authors, repeated pulses of ignimbrites occurred every 2-3.8 Ma
134 between 24.5 and 9.0 Ma in the southern Peru and a quasi-continuous volcanism after 5 Ma that produced
135 four smaller ignimbrite sheets and pyroclastic density current deposits. The present-day active volcanic arc,
136 or Western Cordillera, lies about 230 km east of the trench (Fig. 1B). In Southern Peru, the active volcanic
137 arc ends at about 14°S, in correspondence with the Nazca Ridge (Hampel, 2002) and with the change from
138 "normal" to "flat" subduction.

139

140 **2.2. Stratigraphic and geochronological setting**

141 The lithostratigraphic units recognized by Dunbar et al. (1990) and DeVries (1998) are, from the oldest to the
142 youngest, the Eocene Paracas Formation, the upper Eocene-lower Oligocene Otuma Formation, the upper
143 Oligocene to lower Miocene Chilcatay Formation and the upper Miocene to Pliocene Pisco Formation. These
144 formations are separated by regional unconformities marked by pebble- and boulder-grade conglomerates
145 and represent long periods of subaerial exposure.

146 Muizon and Bellon (1980; 1986) and Dunbar et al. (1990) had already noticed the presence of “tuffaceous
147 siltstones” in the Pisco Formation, but no one described the petrology and the chemistry of tephra layers.

148 Some authors have provided ages of the Pisco Formation using K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ radiometric dating on
149 these tephra beds (Muizon and Bellon 1980; 1986; Brand et al., 2011; Esperante et al., 2015), integrating the
150 biostratigraphic framework obtained by diatoms, radiolarians and planktonic foraminifera (Macharè and
151 Fourtanier 1987, Schrader and Ronning 1988, Tsuchi et al. 1988, Dunbar et al. 1990). These radiometric
152 ages, however, are not placed in a stratigraphic context and, therefore, only provide age indications for
153 individual localities without correlations among them.

154 Recently, the stratigraphy of the Pisco Formation has been re-examined in detail (Di Celma et al., 2016a,
155 2016b; 2017). In particular, in order to place its fossil vertebrates in a proper chronostratigraphic framework,
156 new stratigraphically-constrained sediment samples for diatom biostratigraphy and $^{40}\text{Ar}/^{39}\text{Ar}$ isotope ages
157 have been collected and analyzed (Gariboldi et al., 2017). The fossiliferous strata of the Pisco Formation
158 exposed along the western side of the Ica River Valley have been divided into three fining-upward
159 depositional sequences named, from the oldest to the youngest, P0, P1 and P2 and bounded by three
160 regionally extensive erosional surfaces, PE0.0, PE0.1, and PE0.2 (Di Celma et al., 2017). Combined diatom
161 biostratigraphy and tephrochronologic $^{40}\text{Ar}/^{39}\text{Ar}$ results demonstrate that in the study area the P1 sequence
162 was deposited between 9.5 Ma and 8.9 Ma and the P2 sequence is younger than 8.5 Ma and older than $6.71 \pm$
163 0.02 Ma (Di Celma et al., 2017; Gariboldi et al., 2017). With this approach, a detailed chronostratigraphic
164 framework is being reconstructed, previous scattered radiometric data. The stratigraphic framework of the
165 Pisco Formation has been much improved, and a nearly continuous record is now available. For this work, it
166 is important to consider that sediments of the P2 sequence have been dated at the localities of Cerro los
167 Quesos ($14^{\circ}30'59.0''$ S; $75^{\circ}42'59.1''$ W) and Cerro la Bruja ($14^{\circ}31'44.10''$ S; $75^{\circ}40'0.10''$ W), two
168 fossiliferous areas located about 6 km apart (Fig. 1B), where most of the tephra layers studied in this paper
169 were collected. From the oldest to the youngest, the $^{40}\text{Ar}/^{39}\text{Ar}$ ages obtained on biotite phenocrysts from
170 samples collected at Cerro los Quesos are 7.55 ± 0.05 Ma (CLQ-T49 at 128 m from the base of the measured
171 section), 6.93 ± 0.09 Ma (CLQ-T1a at 238 m) and an age older than 6.71 ± 0.02 Ma (CLQ-T9b at the very
172 top of the measured section) (Gariboldi et al., 2017). In order to confirm the field-based correlation between
173 the two stratigraphic sections measured at these localities, an additional $^{40}\text{Ar}/^{39}\text{Ar}$ age of 7.45 ± 0.01 Ma was
174 obtained from biotite phenocrysts of the tephra layer LB-T11 in the Cerro la Bruja section (see the
175 stratigraphic position in Fig. 9), mentioned as preliminary result in Di Celma et al. (2017).

176

177

178 **3. Methods**

179 An area of more than 240 km² in the western side of the Ica River Valley was explored during several field
180 campaigns between 2014 and 2016. In order to reconstruct the stratigraphy of this area, six stratigraphic
181 sections, for a total of about 1200 meters of measured stratigraphy, were logged with a Jacob's Staff (Di
182 Celma et al., 2016a, 2016b, 2017). In the course of measuring stratigraphic sections and prospecting the
183 study area, more than 200 samples were collected from tephra layers; of these, 53 samples from layers
184 interpreted as primary tephra were analyzed for mineral and glass chemistry for this work. The ash samples

185 analyzed for tephrochronological and tephrostratigraphic purposes were collected in the localities of Cerro
186 los Quesos, Cerro la Bruja, Cerro Colorado, Cerro Hueco la Zorra, Cerro Blanco, Cerro Toro Chico, Cerro
187 Cadenas de los Zanjonos and Cerro la Mama y la Hija (Fig. 2).

188 In the field, volcanic ash layers were described making observations on their lateral continuity, thickness,
189 vertical grading, color, sedimentary structures and presence of phenocrysts. Samples were collected close to
190 the base of the ash layer, avoiding the upper portion so as to exclude bioturbation, reworking, and mixing
191 with non-volcanic sediments. In order to avoid the weathered particles, the superficial parts of the tephra
192 layers were eliminated before sampling. Samples were examined under a stereomicroscope and prepared as
193 smear slides for petrographic analysis and for a semi-quantitative component analysis, to check the presence
194 of non-volcanic particles and evidence of alteration of volcanic components. Based on the results of this first
195 screening, samples with more than 5% vol. of non-primary particles, which could not be interpreted as
196 representative of the primary deposition on the sea surface of ashes of explosive eruptive events, were
197 discarded (Tada et al., 2015; Griggs et al., 2014). Grain size analyses were performed with the Malvern
198 Mastersizer 2000E™ Laser Granulometer at the University of Milano Bicocca. For each sample, three
199 subsamples were made and each one of them was subject to three measurements. Grain size data were
200 processed with the Grain Size Analysis Program GRADISTAT (Blott and Pye, 2001).

201 Samples were also wet sieved with meshes of 500, 250, 125 and 63 μm . Biotite and glass particles were
202 randomly hand-picked under a stereomicroscope from the 250 μm (for coarser ashes) and 125 μm size
203 fraction, mounted in resin, polished with silicon carbide and alumina and carbon-coated.

204 Glass shard morphology and mineral assemblages of the samples representing tephra of primary deposition
205 of ashes were observed by optical microscopy on smear slides and analyzed by scanning electron microscopy
206 (SEM) back-scattered imaging on the carbon-coated polished mounts, to fingerprint the petrographic and
207 textural features of the juvenile volcanic components.

208 For glass and biotite chemistry, EPMA (Electron Probe Micro Analysis) and EDS (Energy-dispersive X-ray
209 Spectroscopy) analyses were performed on at least 10-15 representative glass shards and 10 biotite
210 phenocrysts (core and rim) per sample, in order to obtain a chemical fingerprinting of the tephra layers and
211 an estimate of the weathering degree of biotite phenocrysts.

212 SEM-EDS analyses were carried out at the University of Pisa with a Philips™ XL30 scanning electron
213 microscope with 20 kV filament voltage, 5 nA beam current and ZAF correction, in raster mode and 10x10
214 or 5x5 microns-size windows. EPMA analyses were performed with a JEOL JXA-8600™ at Consiglio
215 Nazionale delle Ricerche in Florence and with a JEOL 8200 Superprobe™ at the University of Milan.
216 Analytical conditions were 15 kV accelerating voltage, 5nA beam current, 3 μm beam focus for biotite and
217 10 μm for glass shards.

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219

220 **4. Results**

221 **4.1. Field data**

222 Along the measured stratigraphic sections, ash layers were more frequent in the P2 sequence than in the
223 other sequences (about 20 tephra layers thicker than 2 cm every 100 m) and particularly abundant in the
224 diatomitic portion. The thickness, for the majority of the sampled tephra, ranges between 5 and 15 cm.
225 However, while their bases are commonly sharp and easy to recognize, their upper boundaries may be
226 irregular or diffuse and not always clearly detectable, particularly in diatomite-rich sediments (Fig. 3A, B).
227 Some thicker tephra (up to 50 cm), organized in different sublayers, have been found. Except for very fine-
228 grained and crystal-free ashes, the ash beds show an evident normal grading and the base is typically
229 characterized by a concentration of coarser particles and crystals (Fig. 3). Although in most cases they are
230 unconsolidated, in some cases the volcanic ash layers are cemented by secondary minerals such as gypsum
231 and jarosite. At the base, a hard gypsum/anhydrite crust of a few mm thickness is commonly found. The
232 color in the field is usually grey to light grey, with transparent glass and a “pepper and salt” appearance due
233 to biotite (Fig. 3B, C). Thin (2-3 cm) dark grey tephra were found, although less frequently. Internally, a
234 variety of soft-sediment deformation structures, including load casts, small-scale folding, convolutions, and
235 dish and pillars structures, have been observed in some of the thicker layers (CLQ-T1 and CLQT-12). These
236 deformation structures may have developed by rapid deposition of the thick ash layers on waterlogged
237 diatom ooze, which may have started consolidation in the immediately underlying sediments (Pedersen and
238 Surlyk, 1977). Waters escaping from such layers may liquefy or fluidize the lower portion of the ash,
239 resulting in sinking of overlying denser portion into the liquidized lower portion (load casts) and
240 compensatory upward intrusion (diapirs and flames) of the latter into the overlying sediment (Owen, 2003).
241 In one case, this deformation structures are recognizable in the same tephra at 6 km of distance, i.e. CLQ-
242 T12 and LB-T7 ash layers (see Fig. 3).

243

244 **4.2. Petrographic fingerprinting of tephra**

245 **4.2.1. Grain size distribution and components of volcanic ash**

246 The grain sizes of the sampled tephra layers fall in the range of fine-grained sand to silt. Inspections under
247 SEM of bulk samples of some particularly coarse tephra and of the coarser fractions of wet sieved samples
248 indicate that, in some cases, a minor fraction of coarser sand is made of strongly agglomerated particles,
249 cemented by supergene secondary minerals. However, most of the samples consist of loose ash, nearly
250 unaffected by secondary cements. As shown in Fig. 4, the grain-size distribution is unimodal or bimodal and
251 the classification is dominated by fine-grained ashes, very fine-grained ashes or extremely fine-grained ashes
252 (Table S1), mainly moderately to well sorted (White and Houghton, 2006). In case of field evidence of
253 sublayers (e.g. CLQ-T1, CC-T1), each sublayer was sampled, and the lower sublayer is usually coarser than
254 the upper one; only in one case (CLQ-T9), a normally graded coarser layer directly overlies a well sorted
255 fine-grained ash layer, indicating deposition of ashes of two distinct, but relatively close, eruptive events. In
256 several cases, the grain-size distribution is bimodal: rather than fine-grained ash aggregation, we suggest to
257 interpret the coarse-grained and the fine-grained modes as, respectively, the Plinian ash and the co-
258 ignimbrite ash, following observations of Engwell et al. (2014).

259 The component particles are dominated by glass shards (> 85-95% in volume), without visible evidence of
260 alteration, and variable amounts of juvenile phenocrysts (biotite, sanidine and plagioclase, in some cases
261 amphibole, in one case muscovite) and traces of terrigenous and biogenic materials (Table S1). The ash
262 layers containing more than 10% of ~~component~~ particles extraneous to the primary volcanic material, such as
263 diatom frustules, rock fragments, heterogeneous crystal assemblages with olivine, pyroxene, quartz and
264 reddish aggregates probably consisting of Fe-hydroxides and clays, were interpreted as tephra modified by
265 reworking and the samples were not further processed. The 53 ash layers interpreted as primary tephra were
266 studied for textural and chemical characteristics.

267

268 **4.2.2. Texture of ash particles**

269 Glass shard morphology is a promising tool for distinguishing and correlating tephra layers (Lowe, 2011).
270 Optical and scanning electron microscopy allowed the study of the glass morphologies and characteristics.
271 Five main groups of glass shards were identified (Fig. 5): bubble-wall shards, with round and concave sides;
272 vesiculated shards, with variable vesicularity; stretched, vesiculated shards with strongly elongate vesicles
273 due to stretching; platy shards, without any vesicles and not stretched; shards with microlites, mainly
274 plagioclase. Tephra were fingerprinted based on the prevalent shard features in the 125-250-micron size
275 fraction. Samples from tephra layers supposed to be the same level from different localities show similar
276 glass shard morphologies and characteristics (Table S1).

277 BSE imaging of glass shards did not reveal, except in some cases, the formation of hydration cracks or of
278 secondary minerals at the expense of the glass (Fig. 5). Most biotite phenocrysts, inspected by means of BSE
279 imaging, did not show obvious secondary alteration minerals along cleavages. They frequently show
280 accessory minerals apatite and zircon as inclusions, as well as glass inclusions.

281

282 **4.2.3. Volcanic glass chemistry**

283 The chemical composition of volcanic glass was analyzed avoiding the regions very close to vesicles and
284 cracks, which could be more deeply affected by alteration, and microlites. As regards microlites, these are
285 absent in most samples but are common in a few tephra having dark grey color and an andesitic composition.
286 For each tephra, glass shards were analyzed and the mean and standard deviation recalculated to check for
287 homogeneity. Samples with high standard deviation in glass analysis were discarded, except for a few cases
288 with two distinct homogeneous populations, which could be interpreted as two eruptive events close in time
289 or as the result of magma mixing/mingling processes. Since some hydration affected at variable degree all
290 the analyzed ashes, resulting in microprobe totals of 89 to 95% (Table 1), the analyses were recalculated to
291 100 to allow comparing tephra with different degrees of hydration in the same diagrams.

292 The results are shown in a K₂O vs. SiO₂ diagram in Fig. 6, with fields for arc-related volcanic rocks
293 following Peccerillo and Taylor (1987). The silica content ranges from 57 to 78 wt%. As regards the low-
294 silica glass compositions, these belong to the few dark gray tephra with microlitic shards. Glass chemistry
295 indicates for these ashes an andesitic to dacitic composition when the major elements are recalculated to 100,

296 but the silica content of residual glass can be higher than the magma composition due to the effect of
297 microlite crystallization and to secondary hydration. As regards the silicic tephra samples, the recalculation
298 to 100 and the alkali loss revealed by the negative trends in some samples (see in Fig. 6) results in a higher
299 silica content compared to the original erupted magma. However, considering that the samples suspected of
300 large hydration and/or alkali loss were discarded and that the samples in the diagram have a similar hydration
301 degree, we conclude that the Pisco Formation tephra have a large chemical variation, from andesite to
302 rhyolite. Moreover, for the purpose of fingerprinting, it is worth noting that, even if the composition of glass
303 of most tephra plots in the rhyolite field, it is possible to distinguish different, non-overlapping groups of
304 tephra.

305

306 **4.2.4 Biotite chemistry**

307 Biotite phenocrysts are homogeneous or slightly zoned for what concerns the core-to-rim major elements
308 compositional range (Table 2). The intra-sample compositional variability is moderate in most cases (Fig.
309 7A), and a few samples present some outliers (biotite phenocrysts with very different composition, which
310 can be interpreted as xenocrysts entrained within the ash layer or xenocrysts in the erupted magma). A few
311 samples show bimodal (e.g. CLQ-T9b) or very heterogeneous biotite chemistry (e.g. LB-T2). In terms of
312 mica classification (Rieder et al., 1998), the analyses plot in the biotite field, with a trend to the
313 siderophyllite end-member (Fig. 7B).

314 Interestingly, the significant differences in the major element compositions of biotite, especially the Mg/Fe
315 ratio, expressed as $Mg_v = Mg/(Mg+Fetot+Mn)$, cannot be ascribed entirely to alteration (see Table 2).
316 Alteration of biotite by weathering may result in Fe oxidation, loss of Mg resulting in low Mg_v , loss of
317 interlayer K, while Al and Ti are retained (Gilkes and Suddhiprakarn, 1979), but these chemical
318 transformations correspond to physical and mineralogical features which do not apply to these samples (Fig.
319 5). The large chemical variations in major elements (Mg_v), as well as in minor elements as Ti, Al, Ba and
320 Mn, can be ascribed to the physico-chemical features of the magma from which biotite crystallized and,
321 therefore, can be used for discriminating biotite from different eruptions. Accordingly, a rough correlation
322 exists between biotite Mg_v and the magmatic differentiation degree indicated by the glass composition
323 (Fig..., Table...).

324 In some cases, two biotite populations with different composition have been observed within the same
325 tephra, e.g. samples LB-T19 and CLQ-T23 (Fig. 7A). This feature, which is not correlated to alteration
326 evidence (such as low totals, low K), could be interpreted as coeval eruption of two different volcanoes, two
327 events close in time by the same volcano, or eruption of a mingled magma (Lebti et al., 2006; Shane et al.,
328 2008), and is, thus, an additional characteristic useful for the unequivocal identification of tephra.

329 The strong variation in Al content of biotite accompanied by similarly silicic glasses indicates remarkable
330 differences in magma chemistry of the silicic magmas. In fact, when the chemical composition of biotite is
331 plotted in the ternary discrimination diagram of Abdel-Rahman (1993), as shown in Fig. 7C, two main
332 groups are evident: the calcalkaline orogenic one and the one. The identification of peraluminous tephra, as

333 the pair CLQ-T23 and LB-T19 and the sample MH-T4, by means of biotite is very relevant for correlation.
334 The major element composition of mica grains is more robust than that of glass due to its reactivity to
335 alteration. The removal of mobile cations results in an apparent increase of immobile elements (Al, Ti),
336 simulating peraluminous compositions.

337 Another biotite cluster with a peculiar composition, the pair CLQ-T13b and LB-T10, is shown in Fig. 7C. It
338 is easily recognizable and very different from all other mica samples, and therefore quite useful for tephra
339 fingerprinting.

340

341 **5. Discussion**

342 **5.1 Applying tephra fingerprinting for high-resolution correlation in the Pisco Formation**

343 The mineral chemistry data presented in Gariboldi et al. (2017) indicate that compositionally different
344 sanidine-plagioclase pairs of clusters may be recognized in different rhyolitic samples, suggesting that in the
345 Pisco Formation mineral chemistry could be used to fingerprint ash layers for long-distances correlation
346 purposes. In this work, 53 samples of P2 volcanic ash layers consisting of over 95% volcanic glass and
347 minor amounts of juvenile phenocrysts, considered representing primary air-fall events from the Peruvian
348 Central Andes volcanoes, have been studied for fingerprinting.

349 Data used for fingerprinting the P2 tephra layers include petrographic description of glass and phenocrysts
350 (modal analysis on smear slides, glass shard morphology by Scanning Electron Microscopy), grain size
351 analysis by Laser Granulometry, major element chemistry of biotite and glass by Electron Probe
352 Microanalysis. Using these methods, we were able to establish some correlations between stratigraphic
353 sections. Chemical analyses on biotite phenocrysts show that major (Mg, Fe) and minor (Ti, Al, Ba, Mn)
354 elements can highlight strong differences in the composition, not due to alteration. In general, different
355 samples or group of samples plot in well-defined and non-overlapping clusters, which can be identified in
356 one or more suitable bivariate diagrams. In particular, for the localities of Cerro los Quesos and Cerro la
357 Bruja, we can see that there are some perfectly overlapping tephra pairs (Fig. 8), and different from all
358 others: CLQ-T23 / LB-T19 (the tephra pair containing each two distinct mica populations), CLQ-T21 / LB-
359 T17, CLQ-T16 / LB-T8, CLQ-T15 / LB-T11, CLQ-T13b / LB-T10. The overlapping composition can also
360 be observed in the tephra pair CLQ-T17 / LB-T15, which shows a very dispersed mica composition
361 unrelated to that of glass (Fig. 6), possibly due to (primary or secondary) mixing of ashes from different
362 eruptions. Figure 8 also demonstrates the chemical identity of samples BL-T1 and LZ-T1 from Cerro Blanco
363 and Cerro Hueco la Zorra respectively, two localities at 6 km distance from each other.

364 In Figure 9, we can observe five of the correlated tephra along 60 meters of the measured sections at Cerro
365 los Quesos (between 155 and 220 m) and Cerro la Bruja (between 160 and 220 m). The Ti and Al
366 concentrations and the Mg/Fe ratio (Mg_v) of biotite phenocrysts is typical of each layer and can identify
367 pairs of the same tephra layer in the two stratigraphic sections,. In several cases, grain size validates the
368 correlation, showing a correspondence of the frequency distribution curves; however, the effect of marine
369 currents in redistributing the component particles during the deposition could play a second-order role.

370 Chemistry and morphology of volcanic shards give a further characterization useful to fingerprint tephra.
371 Correlated tephra layers based on biotite chemistry also show an overlap of the glass compositions of the
372 following pairs at Cerro los Quesos and Cerro la Bruja: CLQ-T23 / LB-T19, CLQ-T17 /LB-T15, CLQ-T16
373 /LB-T8, CLQ-T15 /LB-T11, CLQ-T13b /LB-T10. The tephra pair BL-T1 /LZ-T1 (Cerro Blanco and Cerro
374 Hueco la Zorra, respectively) also overlap (Fig. 6). The compositional correlation is also supported by the
375 glass morphology and characteristics: pairs of correlated tephra show similarities in the vesicularity,
376 stretching, presence of microlites and glass shape.

377 Tephra fingerprinting and correlation provides a well defined and detailed chronostratigraphy of the P2
378 sequence at the two localities of Cerro los Quesos and Cerro la Bruja. At these two localities, the measured
379 stratigraphic sections were previously correlated on stratigraphic and chronostratigraphic basis (Di Celma et
380 al., 2017). $^{40}\text{Ar}/^{39}\text{Ar}$ ages at Cerro los Quesos, from the oldest to the youngest 7.55 ± 0.05 Ma, 6.93 ± 0.09
381 Ma and an age older than 6.71 ± 0.02 Ma, fit with the $^{40}\text{Ar}/^{39}\text{Ar}$ age obtained from an ash layer at Cerro la
382 Bruja, i.e. 7.45 ± 0.01 Ma, confirming the tephra correlations based on fingerprinting. The improved
383 chronostratigraphy benefits the paleontological reconstruction of the P2 sequence. We also observe that there
384 are many tephra that do not occur in both localities. The reason is probably due to disturbances in the
385 depositional environment, such as marine currents and the shallow water context, which cause a laterally
386 discontinuous sediment deposition.

387 Even in such a complex sedimentary environment, we demonstrate that a petrographic and chemical
388 fingerprinting can be used successfully. The identification of several ash layers with a peculiar biotite
389 chemical composition (e.g. MH-T4, CC-T22 in Table S1), which were recognized in other localities of the
390 Ica Desert thanks by biotite fingerprinting, is an encouraging validation of our approach. Biotite has been
391 already used for Andean tephrostratigraphy, as well as amphibole (De Silva et al. 1989, Lebti et al. 2006).
392 Biotite is ~~really~~ frequent as a phenocryst in Andean explosive eruptions and it can be found enriched in their
393 distal deposits (e.g. Rose and Chesner, 1987), due to the fact that it is transported ~~highly~~ better than other
394 phenocrysts (feldspars, amphibole). The relative ease with which non-stoichiometric mica compositions
395 reveal alteration means that unaltered mica can be confidently recognized as juvenile in primary ash layers.
396 The composition of feldspars can be used as an additional discriminant, if no biotite phenocrysts are found,
397 as shown by Gariboldi et al. (2017) in some P2 tephra.

398

399 **5.3. Implications**

400 The present results clearly show that biotite chemistry is a particularly powerful tool for characterizing
401 tephra. The precise reconstruction of the stratigraphic framework at some fossiliferous localities, such as
402 Cerro los Quesos and Cerro la Bruja, allowed us to reconstruct with great bio- and chrono-stratigraphic detail
403 the fossil record in the continuous P2 sequence between about 8.5 and 6.7 Ma, a very important time interval
404 in the evolutionary history of different groups of marine vertebrates such as cetaceans and pinnipeds.

405

406

407 **6. Conclusion**

408 The regional dispersion and the geologically instantaneous deposition of tephra layers are a great advantage
409 for tephrostratigraphy and tephrochronology. A chemical and petrographic fingerprinting of the ashes
410 enables a bed-by-bed correlation even over relatively long distances. When supplemented by absolute age
411 dating of suitable samples, the reconstruction of an integrated chronostratigraphic framework becomes
412 possible.

413 More than 200 tephra samples were collected in the Ica Desert of Peru, along measured stratigraphic sections
414 in different localities. In this work, which is focused on the youngest depositional sequence of the Pisco
415 Formation, P2, we selected 53 ash layers to show how tephra can be used to correlate different localities.

416 The difficulties found in the Pisco Formation in using tephra as a correlation tool reside in the broadly
417 similar glass or mineral chemistry, the local weathering, the disturbance in deposition due to marine currents
418 and changes in depositional environments among different localities. Despite these issues, the petro-chemical
419 diversity of the volcanic ashes deriving from the Andean volcanoes is high. This encourages using the major
420 element composition of glass and biotite to fingerprint and correlate stratigraphic sections in different
421 localities. The chemical correspondence ~~of the obtained data~~ allowed us to verify stratigraphic correlations
422 that were hypothesized in the field and to trace tephra layers across distant outcrop localities, such as from
423 Cerro los Quesos to Cerro la Bruja. In particular, volcanic biotite chemistry, showing marked variations in
424 Al, Ti, Mn, Mg_v, proved to be a powerful tool for tephra fingerprinting in the Pisco Formation, besides being
425 the main mineral useful for absolute dating.

426 Tephra correlation based on the context of radiometric ages with petrographic and chemical fingerprinting is
427 a promising tool to correlate distant stratigraphic sections and to increase the chronostratigraphic resolution,
428 in the complex sedimentation environment of the Pisco Formation. Extending integrated tephra
429 fingerprinting to proximal fallout deposits near their eruptive sources may improve the volcanological
430 information on Peruvian Andes during the Miocene,

431

432

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438

439

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602

603 Captions

604

605 **Fig. 1 - Map of the major sedimentary basins and volcanism in the Peruvian coast.** A. Sedimentary
606 basins are indicated with names in blue. Major structural high as the Coastal Batholith, Outer Shelf High and
607 Upper Slope Ridge are represented in red-yellow shades. The green square highlighting the East Pisco Basin
608 indicates the study area. B. Volcanism and magmatic arcs during the Cenozoic. From Mamani

609

610 **Fig. 2 – Ica Desert localities.** Main localities in the Ica Desert, where the studies of this paper are focused.

611

612 **Fig. 3 - Tuff layer interbedded in the Pisco basin sedimentary sequence in the field, at different scales.**

613 Tuffs are often revealed by the sharp bottom discontinuity highlighted by gypsum wavy layers protruding

614 from the outcrop (A). Normal grading and crystal concentrations at the base are common features (B), and

615 black biotite concentrations cannot be overlooked even before cleaning the outcrop (C).

616

617 **Fig. 4 - Tephra grain size distribution.** Grain size distribution curves of four representative tephra.

618

619 **Fig. 5 - SEM images.** BSE images of different glass shard morphologies. A) bubble wall; B) vesiculated;

620 C) stretched; D) with microlites.

621

622 **Fig. 6 - Volcanic glass K₂O vs SiO₂ diagram.** Glass composition of P2 sequence tephra layers. Major

623 elements are shown as wt% and recalculated to 100 to compare glasses with variable hydration.

624

625 **Fig. 7A - Biotite Mg/Mg+Fe+Mn vs Al diagram.** Biotite chemical composition of P2 tephra. Al is shown

626 as atoms per formula unit. **B - Chemical ternary diagram of biotite phenocrysts.** Biotite discrimination

627 diagram: fields from Abdel-Rahman, 1994 J. of Petrology. C= calcalkaline orogenic suites; P= peraluminous

628 suites; A= anorogenic alkaline suites.

629

630 **Fig. 8 - Correlations in biotite chemistry.** Ti/Al vs Mg_v diagram of biotite phenocrysts from correlated

631 tephra. Mg_v is the ratio Mg/(Mg+Fe+Mn).

632

633 **Fig. 9 - Stratigraphic sections correlated.** Correlation of the measured stratigraphic sections of Cerro los

634 Quesos and Cerro la Bruja. Biotite chemistry is shown in the central diagrams: Ti and Al concentration is

635 expressed as atoms per formula unit.

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640 **Table 1 - Representative analyses of glass shards.**

641

642 **Table 2 - Representative analyses of biotite phenocrysts.**

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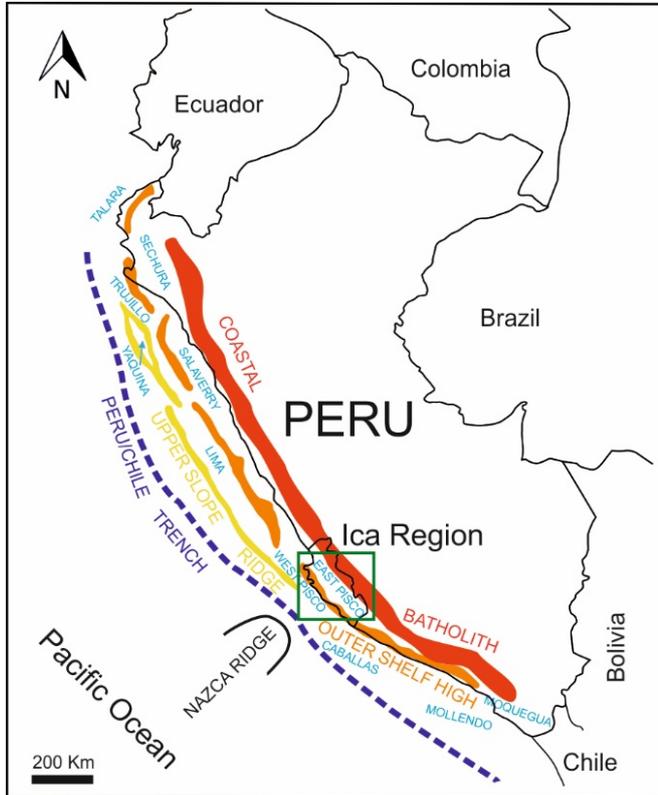
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649 **Figures and tables:**

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652 Fig.1

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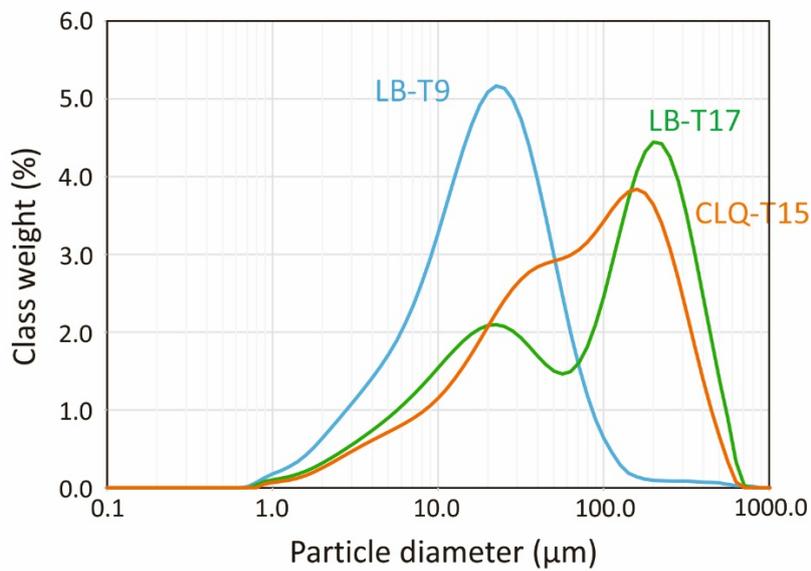
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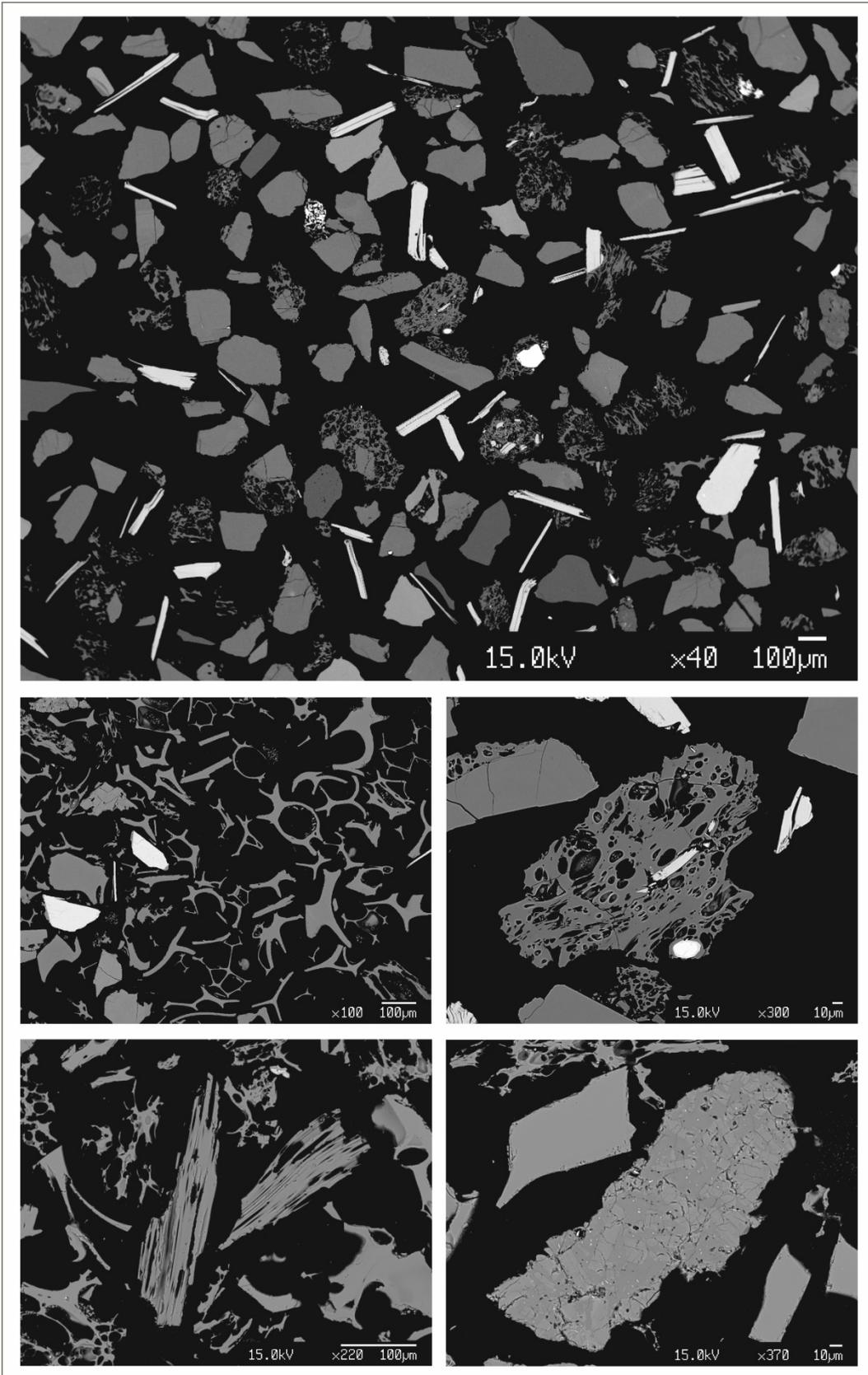


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659 Fig.3
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662 Fig.4 -CLQ-T9a e phi

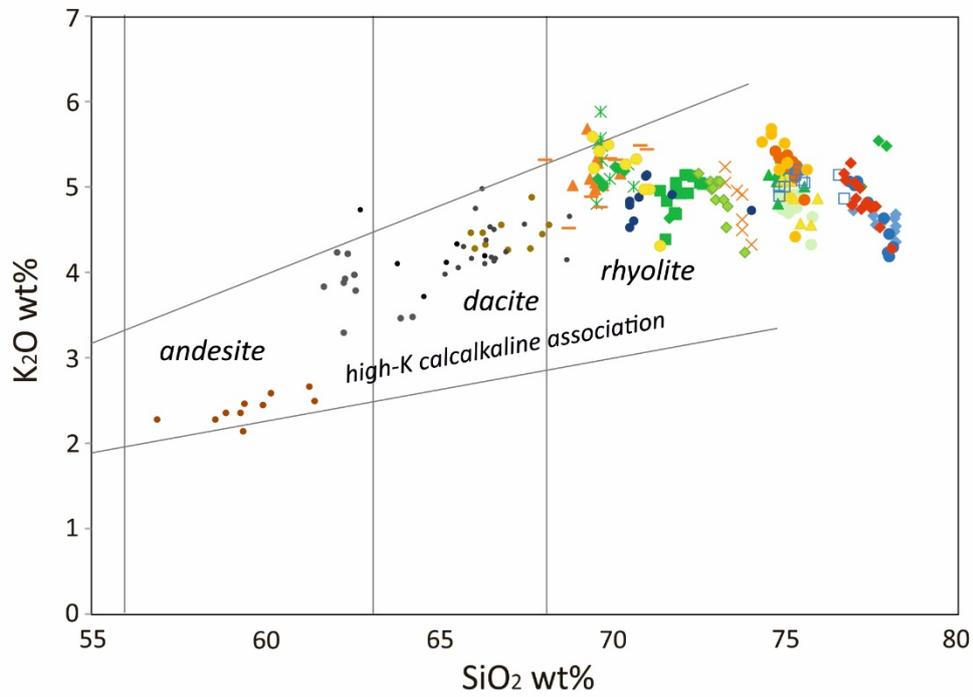
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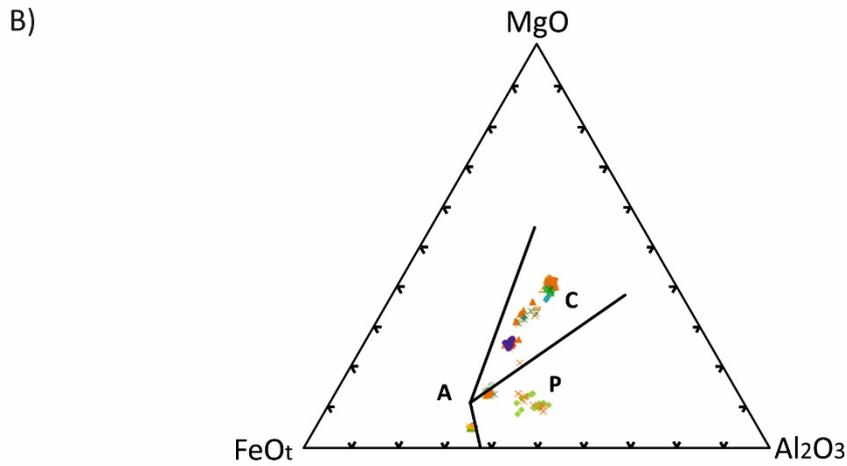
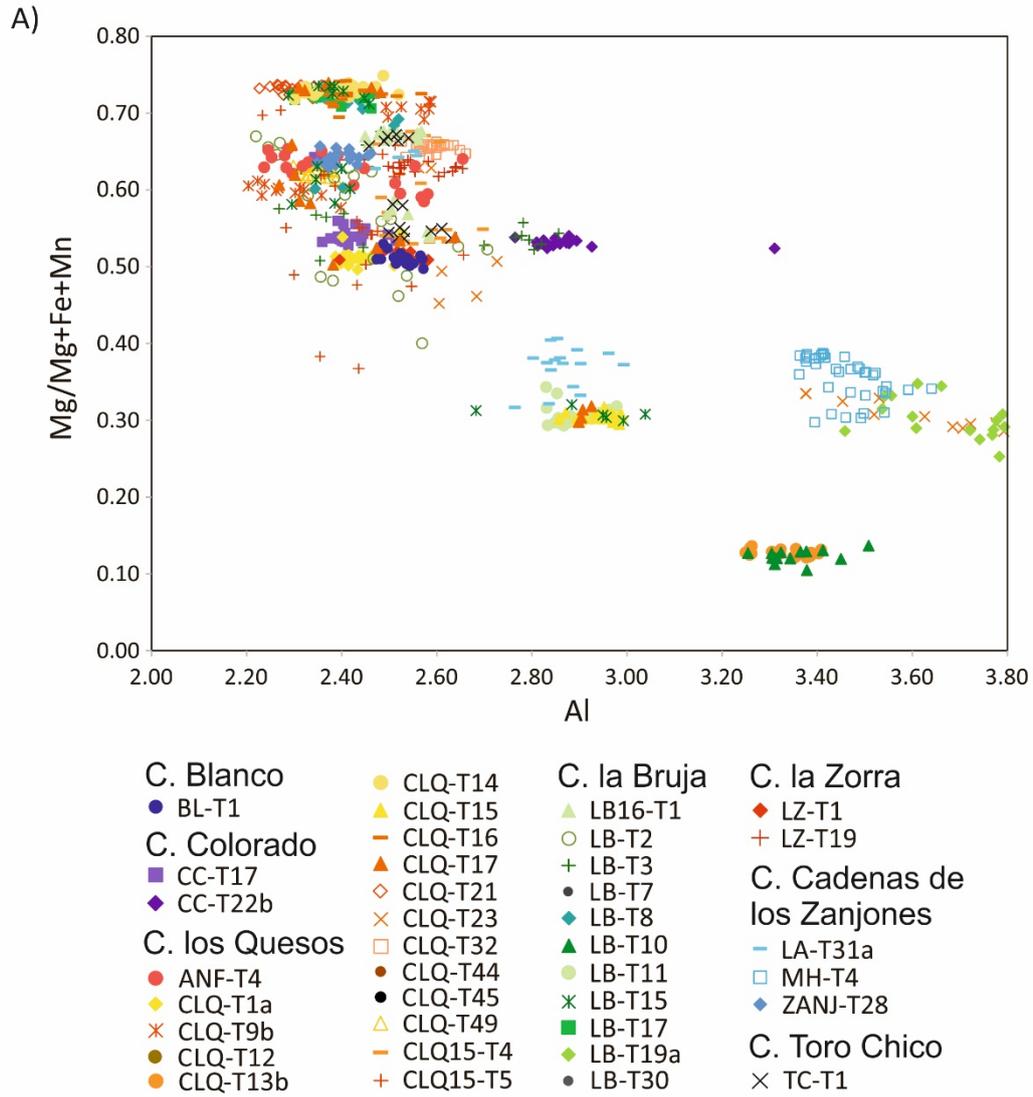
Fig.5 –biotite, vesicles, microlithons

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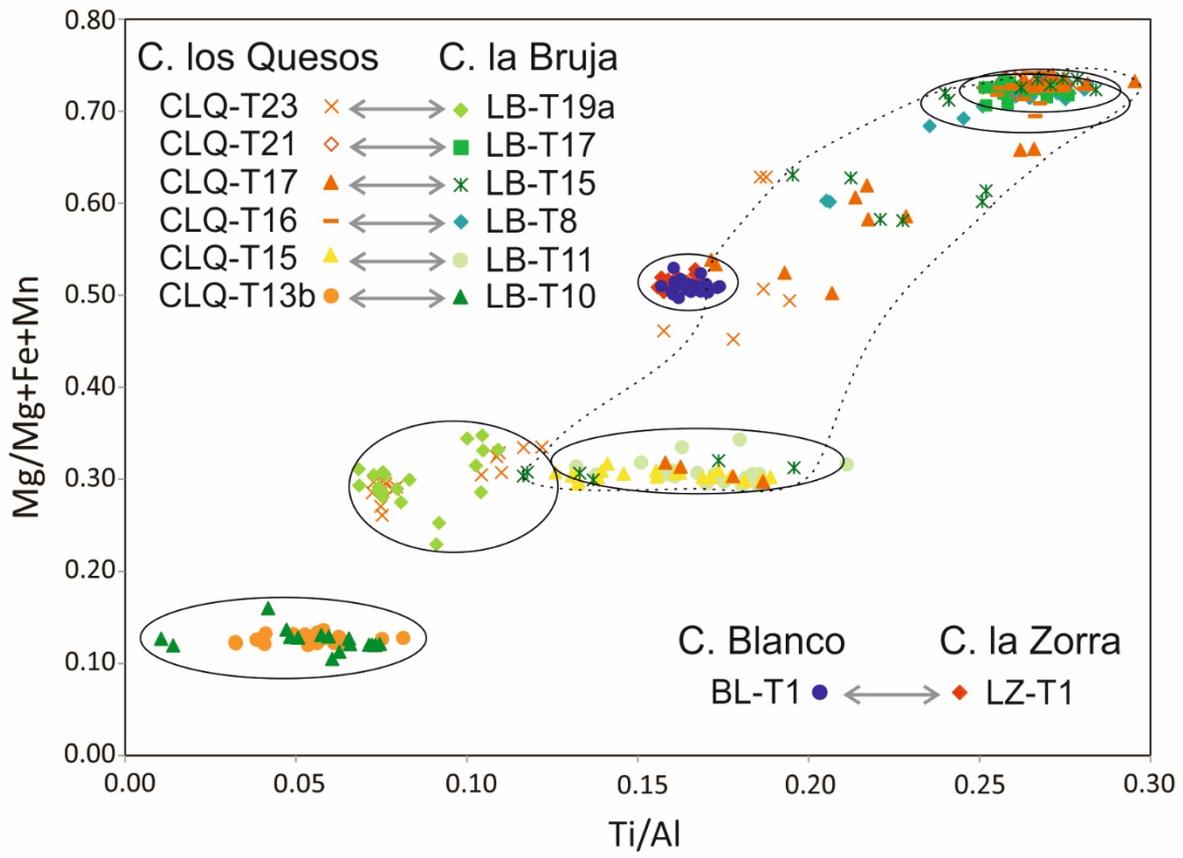
- | | | | |
|----------------------|------------|--------------------|------------------------------------|
| C. Blanco | ● CLQ-T14 | C. la Bruja | C. la Zorra |
| ● BL-T1 | ▲ CLQ-T15 | ▲ LB16-T1 | ◆ LZ-T1 |
| C. Colorado | — CLQ-T16 | ○ LB-T2 | + LZ-T19 |
| ■ CC-T17 | ▲ CLQ-T17 | + LB-T3 | C. Cadenas de los Zanjosnes |
| ◆ CC-T22b | ◇ CLQ-T21 | ● LB-T7 | — LA-T31a |
| C. los Quesos | × CLQ-T23 | ◆ LB-T8 | □ MH-T4 |
| ● ANF-T4 | □ CLQ-T32 | ▲ LB-T10 | ◆ ZANJ-T28 |
| ◆ CLQ-T1a | ● CLQ-T44 | ● LB-T11 | C. Toro Chico |
| × CLQ-T9b | ● CLQ-T45 | × LB-T15 | × TC-T1 |
| ● CLQ-T12 | △ CLQ-T49 | ■ LB-T17 | |
| ● CLQ-T13b | — CLQ15-T4 | ◆ LB-T19a | |
| | + CLQ15-T5 | ● LB-T30 | |

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673 Fig.6
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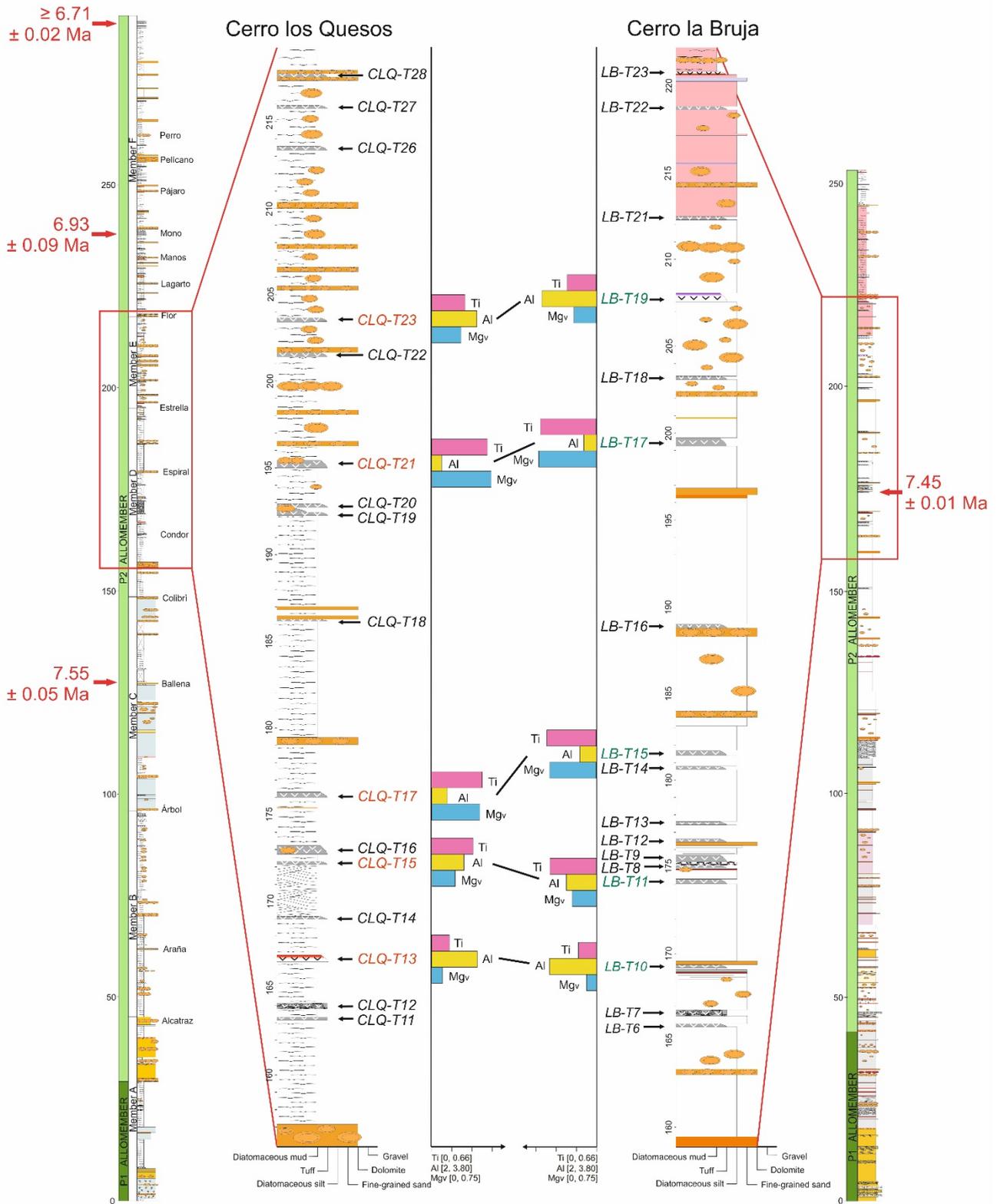


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Fig.7 – Biotite compositions



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 683 Fig.8
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 690 Fig.9
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