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1 **Linking magmatic processes and magma chemistry during the post-glacial to recent**  
2 **explosive eruptions of Ubinas volcano (southern Peru)**

3  
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23

24 **Abstract**

25           Understanding the links between the magma differentiation processes, the magma plumbing system and  
26 the magma composition at arc volcanoes is of paramount importance for volcanic hazard assessment. In this work  
27 we focus on the post-glacial, Holocene, historical, and recent eruption products of Ubinas volcano (Peru), which  
28 display an overall decrease in silica content from the older, plinian (VEI 3-5), rhyolitic eruptions (69-71 wt.%  
29 SiO<sub>2</sub>) to the historical and recent (2006-2009, 2013-2017), vulcanian (VEI 1-2) basaltic andesitic eruptions (55-  
30 57 wt.% SiO<sub>2</sub>). Based on a comprehensive study of the major and trace elements and the Sr-Nd-Pb isotopes, we  
31 conclude that this temporal pattern reflects the evolution of the Ubinas magmas in the middle-to-upper crust by a  
32 coupled Assimilation-Fractional Crystallization (AFC) process involving a cumulate composed of plagioclase,  
33 amphibole, clinopyroxene, orthopyroxene and Fe-Ti oxides, with minor amounts of olivine and biotite at the mafic  
34 and felsic end-members, respectively. Upper crustal assimilation is limited to 5-8 vol.%, but the overall radiogenic  
35 Sr-Nd-Pb signature of the Ubinas magmas requires a larger crustal component, which must therefore occur at  
36 middle to lower crustal depths. The petrology of the Ubinas magmas also points to an overall increase in P-T  
37 conditions: the large Holocene dacitic and rhyolitic eruptions record temperatures ranging from 800 to 850°C and  
38 pressures in the range of 200-400 MPa, whereas the historical and recent (2006-2009, 2013-2017) basaltic  
39 andesitic eruptions provide higher temperatures and pressures (1000°C, >300-400 MPa). Overall, the thermo-  
40 barometry, phase equilibrium and geochemical constraints allow us to propose the existence of a middle-to-upper  
41 crust magma column composed of a highly crystalline magma mush containing batches of liquid magma, which  
42 seems to be continually recharged from deeper levels. On the basis of the petrological nature of the historical  
43 basaltic andesitic eruptions (*CE* 1667, 2006-2009, 2013-2017), we postulate that during the last centuries, Ubinas  
44 experienced a recharge-dominated process, with no evidence for a rejuvenation of the silica-rich reservoir that fed  
45 the large Holocene dacitic to rhyolitic eruptions. This study highlights the importance of detailed petrological  
46 studies of Holocene sequences at explosive arc volcanoes in order to constrain the magmatic processes and  
47 conditions that control large explosive eruptions.

48

49 **Keywords:** Ubinas, Peru, arc volcanoes, recharge, thermobarometry, magma plumbing system

50

## 51 **1. Introduction**

52           Understanding the occurrence of explosive eruptions involving intermediate and silica-rich magmas (i.e.  
53 andesites, dacites and rhyolites) in arc volcanoes is of paramount importance for volcanic hazard assessment. It is  
54 widely accepted by the scientific community that primitive arc magmas result from partial melting of a source  
55 located in the mantle wedge which was previously metasomatized by fluids or melts derived from the subducted  
56 slab (Kelemen et al., 2014; Turner et al., 2016; Schmidt and Jagoutz, 2017). These magmas display a large  
57 geochemical heterogeneity related to the nature of their magma sources together with the fluid/melt transport in  
58 the mantle wedge (Grove et al., 2003; Rawson et al., 2016). Primitive arc magmas (mostly magnesium-rich basalts  
59 or basaltic andesites) ascend through the mantle wedge and stagnate at different levels in the arc crust, where they  
60 are modified by various non-exclusive physical and chemical processes. As a result, intermediate and silica-rich  
61 magmas are generated by a complex sequence of petrogenetic processes that include fractional crystallization,  
62 crustal assimilation, and magma mixing (Hildreth and Moorbath, 1988; Annen et al., 2006; Lee and Bachmann,  
63 2014). On one hand, there is a large amount of geochemical and experimental data showing that andesites (and  
64 more differentiated liquids) are by-products of basalt crystallisation (Sisson et al., 2005; Blatter et al., 2013;  
65 Nandedkar et al., 2014; Ulmer et al., 2018). In addition, following the seminal work of Hildreth and Moorbath  
66 (1988), the deep arc crust is considered as a dynamic zone in which the process of melting, assimilation, storage  
67 and homogenisation (the so-called MASH model) are actively at work. This model has been corroborated by  
68 numerical and physical arguments (*cf.* Annen et al., 2006; Jackson et al., 2018). On the other hand, the paucity of  
69 intermediate (andesitic) composition melt inclusions compared to the overwhelming abundance of these  
70 compositions as bulk-rock erupted products suggests that magma mixing between silica-poor (primitive) and  
71 silica-rich (differentiated) magmas is a common process during andesite genesis (Eichelberger et al., 2006; Reubi  
72 and Blundy, 2009; Kent et al., 2010; Schiano et al., 2010). These models are probably end-member situations at  
73 work at different places in the arc crust. Thus, the magmatic plumbing systems that feed active volcanoes are  
74 considered to be vertically-elongated zones consisting of a mixture of solid phases and interstitial melt, in which  
75 ephemeral magma accumulation occurs (Cashman et al., 2016; Bachmann and Huber, 2016; Jackson et al., 2018).  
76 This model of *trans-crustal magmatic systems* rests on theoretical, geophysical, experimental petrology and  
77 geochemical arguments, and challenges the classic view of melt-dominated magma chambers. It accounts for the  
78 different compositional ranges observed in arc volcanoes as well as the overwhelming evidence for a multi-stage,  
79 polybaric sequence of crystallization for most arc magma suites.

80



81 Arc volcanoes show variable compositional trends on a timescale of hundreds to thousands of years. Some  
82 arc volcanoes display homogeneous basaltic andesitic to andesitic magmas [e.g. Sangay (Monzier et al., 1999) and  
83 Reventador (Samaniego et al., 2008) volcanoes in Ecuador, Arenal in Costa Rica (Ryder et al., 2006), Merapi in  
84 Indonesia (Gertisser and Keller, 2003)]; whereas others are broadly dacitic magma systems [e.g. Mount St. Helens  
85 (Blatter et al., 2017), Pinatubo (Newhall and Punongbayan, 1995), Guagua Pichincha (Samaniego et al., 2010),  
86 Huaynaputina (Thouret et al., 1999)]. There are also arc volcanoes that mostly erupt andesitic magmas with scarce  
87 eruptions involving silica-rich magmas during sporadic (albeit larger) events [e.g. Colima in Mexico (Luhr and  
88 Carmichael, 1990; Robin et al., 1991; Macias et al., 2017), Tungurahua in Ecuador (Samaniego et al., 2011;  
89 Andujar et al., 2017; Nauret et al., 2018)]. Lastly, some arc volcanoes display temporal geochemical variations,  
90 for instance Cotopaxi volcano in Ecuador (Hall and Mothes, 2008; Garrison et al., 2011; Martel et al., 2018),  
91 where larger rhyolitic eruptions transitioned to smaller andesitic events. This is also the case for Ubinas volcano  
92 in southern Peru, which is characterized by a temporal geochemical trend showing a progressive decrease in silica  
93 content over the last few thousand years (Thouret et al., 2005; Rivera et al., 2014), from pre-Holocene, large (VEI  
94  $\geq 4$ ) plinian eruptions involving rhyolitic magmas to the historical and recent, small-to-moderate (VEI 1-2)  
95 vulcanian events that involve basaltic andesitic magmas.

96 In this study, we performed a detailed mineralogical and geochemical study that includes whole-rock  
97 major, trace element and Sr-Nd-Pb isotopic analyses, as well as a comprehensive petrogenetical and thermo-  
98 barometric study of a succession of explosive deposits covering the post-glacial, historical and recent eruptive  
99 chronology of Ubinas. These data allow us to identify the main magmatic processes responsible for the diversity  
100 of Ubinas magmas, as well as to petrologically image the magmatic plumbing system during the large eruptions  
101 involving silica-rich magmas and the smaller events involving silica-poor magmas. These findings will contribute  
102 to the hazard assessment at this active volcano of the Andean Central Volcanic Zone (CVZ). More generally, this  
103 case-study provides constraints to discuss the magma processes at work at other arc volcanoes that display large  
104 compositional ranges over relatively short time intervals (several thousands of years).

105

## 106 **2. Eruptive chronology**

107 Ubinas volcano (16° 22'S, 70° 54'W, 5672 meters above sea level – m a.s.l.), located ~75 km east of  
108 Arequipa (Fig. 1), is the most active volcanic centre of the Peruvian arc, and together with Sabancaya and Lascar  
109 are amongst the most active volcanoes in the Andean Central Volcanic Zone (CVZ). This segment of the Andean  
110 arc developed on a thick continental crust (up to 65-75 km thick, Ryan et al., 2016) and results from the subduction

111 of the Nazca plate below the South-American lithosphere. Ubinas has experienced at least 27 low-to-moderately  
112 explosive (VEI 1-3) eruptions in historical and recent times (i.e. from the beginning of the Spanish conquest in  
113 ~1532 CE to the present day) (Siebert et al., 2010; Rivera et al., 2014). The eruptive chronology of Ubinas was  
114 studied in detail by Thouret et al. (2005) and Rivera (2010), who defined two successive edifices (Ubinas I and  
115 Ubinas II). The older, mostly effusive Ubinas I volcano was constructed by the emplacement of andesitic and  
116 dacitic lava flows from around 450 to 370 ka, and suffered a large sector collapse at the end of its growth. The  
117 younger Ubinas II volcano was constructed on top of the older edifice over the last 370 ka and consists of andesitic  
118 and dacitic lava flows and domes and thick successions of block-and-ash-flow deposits that infill the Ubinas valley  
119 to the south. It forms a truncated cone with a summit caldera (1x1.5 km), which testifies to intense explosive  
120 activity in Late Pleistocene times. Based on the stratigraphy, Thouret et al. (2005) suggested that this summit  
121 caldera was formed between 25 and 10 ka by a sequence of large explosive eruptions responsible for a thick  
122 succession of plinian tephra fall deposits. Geochronological data from these deposits are infrequent due to the  
123 scarcity of organic material for radiocarbon dating as a consequence of the extremely arid weather conditions of  
124 the Central Andes. However, rough temporal constraints come from stratigraphic correlations with distal tephra  
125 layers found at Laguna Salinas, 25-30 km west of Ubinas (Juvigné et al., 1997). Based on these data, Thouret et  
126 al. (2005) considered that the basal tephra of the caldera-related succession is older than 14 ka. In any case, these  
127 eruptions occurred after the Late Glacial Maximum (LGM), dated at 17-25 ka in this part of the Andes (Smith et  
128 al., 2008; Bromley et al., 2009; Blard et al., 2014).

129

130 Figure 1

131

132 The post-glacial eruptive succession at Ubinas (Fig. 2a) comprises 10-15 m-thick plinian tephra fallout  
133 deposits that crop out in the southern and south-eastern part of the cone at a distance of up to 15 km from the  
134 summit. Around the hamlet of *Sacuhaya* (8-9 km south of the summit), at least seven pumice-and-lithics tephra  
135 layers were described. The basal layer is a 2-3 m-thick, rhyolitic white pumice deposit (Fig. 2b) that correlates  
136 with the distal Laguna Salinas ash fallout deposit (see above). In this cross-section, we found six additional, 10-  
137 100 cm-thick tephra fallout layers, which correspond to the Holocene plinian activity of Ubinas (Fig. 2c). A  
138 charcoal sample collected from an ash-rich paleosol layer in the lower-middle part of this cross-section, directly  
139 below a 1 m-thick plinian fallout deposit (UBI-10-12 sample, Fig. 2c, 3a), was dated at  $7480 \pm 40$  BP by Thouret  
140 et al. (2005). This date represents the only absolute age for this tephra succession. All these tephra layers

141 correspond to Ubinas post glacial activity, excepting a 10-15 cm-thick, white, fine lapilli, tephra fallout deposit  
142 that blankets the region located to the south of Ubinas (samples UBI-10-15 and UBI-10-08, Fig. 3). Based on  
143 tephra dispersal studies performed by Wright et al. (2017) and the chemical composition of these samples (see  
144 below), we consider the source of this deposit being a different volcano than Ubinas. At *Quebrada Infiernillos*  
145 (5-6 km southeast of the summit), the tephra fallout deposits correlate with the middle-upper part of the Sacuhaya  
146 cross-section. In addition, in this outcrop, we found the deposits of the last two plinian eruptions of Ubinas (VEI  
147 4-5, Thouret et al., 2005; Siebert et al., 2010), which were dated at  $980 \pm 60$  BP (Fig. 2a, d). During the fieldwork  
148 performed for this study, we found at the base of these tephra fallout deposits, a >50 cm, ash-rich layer with  
149 disseminated pumice fragments, containing non-carbonized branches that yielded an age of  $1890 \pm 70$  BP (UBI-  
150 15-03, GrA 65545, Center for Isotope Research, University of Groningen, The Netherlands). Given the  
151 stratigraphic position of this sample (in the underlying ash-rich layer), we consider that this age represents the  
152 oldest age limit for this eruption. Based on the previous and these new data, we consider that the last plinian  
153 eruption at Ubinas occurred at 1-2 ka.

154 Eruptive activity in historical and recent times has been characterized by low-to-moderate (VEI 1-2)  
155 vulcanian eruptions accompanied by long-lasting ash and gas emissions. The large eruption of this period occurred  
156 in CE 1667 (Thouret et al., 2005; Siebert et al., 2010) and was characterized by a moderately explosive (VEI 3)  
157 event that produced low-volume, scoria-rich pyroclastic flow deposits that outcrop on the upper part of the cone,  
158 close to the caldera border (Fig. 2e). During the last two decades, Ubinas has experienced several eruptive periods  
159 in 2006-2009, 2013-2017 and recently in 2019 (Fig. 1b, Fig. 2f). These eruptions show very similar patterns,  
160 starting with a strong phreatic phase followed by intermittent vulcanian events that progressively waned over a  
161 period of a few years (Rivera et al., 2010; 2014).

162

163 Figure 2

164

### 165 **3. Sampling and analytical methods**

166 Based on the comprehensive work of Thouret et al. (2005) and Rivera (2010) we sampled the key cross-  
167 sections of Sacuhaya and Quebrada Infiernillos as well as the historical and recent eruptive products of the CE  
168 1667, 2006-2009 and 2013-2017 eruptions (Fig. 2). Major and trace element concentrations of 33 new whole-rock  
169 samples from the post-glacial eruptive events, including 8 samples from the historical and recent eruptions (CE  
170 1667, 2006-2009, and 2013-2017), were analysed at the Laboratoire Geosciences Océan, Université de Bretagne

171 Occidentale (Brest, France). Agate-grinded powders were dissolved in HNO<sub>3</sub> and HF and then measured by ICP-  
172 AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy), following the procedure of Cotten et al.  
173 (1995). Relative standard deviations are 1% for SiO<sub>2</sub> and ≤ 2% for the other major elements, and ≤ 5% for trace  
174 elements. To these data we added the major and trace element compositions of 24 samples previously published  
175 by Thouret et al. (2005) and Rivera et al. (2014). Sr, Nd and Pb isotopic ratios were measured at Laboratoire  
176 Magmas et Volcans (LMV), Université Clermont Auvergne (Clermont-Ferrand, France) for 15 samples that span  
177 the post-glacial activity of Ubinas. Sr and Nd data were obtained following the techniques described by Pin et al.  
178 (1994) and Pin and Santos Zalduegui (1997), using a TIMS and a MC-ICP-MS respectively. We include 10 Sr-  
179 Nd isotopic ratios published by Thouret et al. (2005), Rivera (2010) and Rivera et al. (2014), which were also  
180 analysed at LMV, following the same analytical procedure. Sr isotopic measurements were corrected for mass-  
181 fractionation using an exponential law and  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$  and normalized to the value of the NIST SRM987  
182 standard ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.710245$ ). Nd isotopic measurements were corrected for mass fractionation using an  
183 exponential law and  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$  and normalized to the value of JNdi-1 standard ( $^{143}\text{Nd}/^{144}\text{Nd} = 0.512100$   
184  $\pm 5$  ( $2\sigma$ ),  $n = 5$ ). External reproducibility was monitored by repeated analyses of JNdi-1 standard  
185 ( $^{143}\text{Nd}/^{144}\text{Nd} = 0.512097 \pm 10$  ( $2\sigma$ ),  $n = 13$ ). This value is equal, within error margins, to the proposed value for  
186 JNdi-1 standard. Pb isotopic ratios were determined following the methods described by Nauret et al. (2018), using  
187 a MC-ICP-MS at LMV. Pb isotope ratios were normalized to values of NIST SRM 981 given by Galer et al.  
188 (1998). Total procedural blanks are lower than 0.15 ng ( $n = 6$ ), which is negligible compared to the amount of Pb  
189 loaded on the columns (200 to 500 ng). We used international standards (AGV2, BHVO2 and BIR-1) in order to  
190 test the reproducibility of our method. Values obtained for AGV-2 are  $^{206}\text{Pb}/^{204}\text{Pb} = 18.870$ ;  $^{207}\text{Pb}/^{204}\text{Pb} = 15.618$ ;  
191  $^{208}\text{Pb}/^{204}\text{Pb} = 38.546$  ( $n = 5$ ), for BHVO-2:  $^{206}\text{Pb}/^{204}\text{Pb} = 18.608$ ;  $^{207}\text{Pb}/^{204}\text{Pb} = 15.536$ ;  $^{208}\text{Pb}/^{204}\text{Pb} = 38.212$  ( $n =$   
192  $2$ ) and for BIR-1:  $^{206}\text{Pb}/^{204}\text{Pb} = 18.848$ ;  $^{207}\text{Pb}/^{204}\text{Pb} = 15.655$ ;  $^{208}\text{Pb}/^{204}\text{Pb} = 38.489$  ( $n = 1$ ). These results are in  
193 agreement with the international reference values. All measured Pb isotope compositions were corrected for mass  
194 fractionation by adding a solution of the NIST SRM 997 Tl standard to the sample before measurement. The new  
195 whole-rock major and trace elements and isotopic ratios are presented in Table 1. Sample locations are given in  
196 the electronic Supplementary material 1.

197 Major element compositions for minerals and matrix glasses of 11 representative samples of Ubinas  
198 eruptive products were analysed at the LMV, using a CAMECA SX-100 microprobe. The operating conditions  
199 for minerals were 15 kV accelerating voltage, 10–12 nA beam current, and 10 s counting time; whereas the matrix  
200 glass measurements were performed using a 15 kV accelerating voltage, 4–8 nA beam current, 5–10  $\mu\text{m}$  beam size,

201 10 s counting time, and using international glass standards. With these operating conditions and given that alkali  
202 elements measurements were performed first, we should avoid significant Na migration under the electron beam  
203 (*cf.* Devine et al., 1995). Selected major elements composition of Ubinas minerals are presented in Tables 2, 3, 4,  
204 5; whereas the entire dataset was included in the Supplementary material 2. In order to measure trace element  
205 concentrations of selected Ubinas minerals, Laser-Ablation-ICP-MS analyses were performed on phenocrysts of  
206 selected Ubinas samples, using a 193 nm Resonetics M-50E excimer laser coupled to an Agilent 7500cs ICP-MS.  
207 The laser energy was about 3 mJ, with a pulse frequency of 2-3 Hz. The spot diameter was set at 60-80  $\mu\text{m}$  and  
208 the analysis time was 100 s after a background measurement ( $\sim 30$  s). The technique uses calcium as an internal  
209 standard and measurements were calibrated relative to the NIST-612 glass. The glass standard BCR was also  
210 measured to check the reliability of the results. Data treatment was performed on Glitter software ([www.glitter-](http://www.glitter-gemoc.com)  
211 [gemoc.com](http://www.glitter-gemoc.com)). The typical analytical error for most trace elements is  $< 10\%$ .

212 We measured the pre-eruptive water content on selected melt inclusions using a Renishaw InVia confocal  
213 microspectrometer equipped with a 532 nm diode laser (200 mW output power), a Peltier-cooled CCD detector, a  
214 motorized XYZ stage and a Leica DM2500 M optical microscope, at the LMV. The laser power was set to  $\sim 3$   
215 mW. A 2400 grooves/mm grating, a 100 $\times$  objective and 20  $\mu\text{m}$  slit aperture (high confocality setting) were used  
216 for the analyses. These analytical conditions result in lateral spatial resolution of  $\sim 1$   $\mu\text{m}$  and spectral resolution  
217 better than 1  $\text{cm}^{-1}$ . Daily calibration of the spectrometer was performed based on the 520.5  $\text{cm}^{-1}$  peak of Si. The  
218 spectra were recorded in the wavenumber ranges from  $\sim 100$  to 1350  $\text{cm}^{-1}$  (alumino-silicate network domain) and  
219 from  $\sim 3000$  to 3800  $\text{cm}^{-1}$  (water domain), using Wire 4.2 software. Acquisition times were 60-240 s and 120-480  
220 s for the alumino-silicate and water domains, respectively. Spectra treatment was performed using PeakFit 4.0  
221 software. For determination of water content in glasses, we used the external calibration procedure and a set of  
222 hydrous glass standards with rhyolitic, andesitic, and basaltic compositions (see Schiavi et al. (2018) for details  
223 about the method) that were analysed at the same conditions as the samples several times a day. All the analysed  
224 glass inclusions contain “nanolites” of magnetite, as revealed by the presence of its main peak centred at  $\sim 670$   
225  $\text{cm}^{-1}$  (Supplementary material 3). The intensity of the magnetite peak relative to the main glass band near 500  $\text{cm}^{-1}$   
226 varies significantly among the samples (intensity ratio from 0.4 to 1.8). Di Genova et al. (2017) and Schiavi et  
227 al. (2018) observed that the presence of magnetite dispersed in the glass causes underestimation of the water  
228 content of the inclusion. Therefore, the estimated water contents are minimum values. The water contents are  
229 weakly underestimated in inclusions whose spectra show a weak magnetite signal (band intensity ratios 0.4-0.5),  
230 but they are strongly underestimated in inclusions with an intense magnetite peak (Supplementary material 4).

231

## 232 **4. Petrological data**

### 233 **4.1. Whole-rock geochemistry**

234 The post-glacial, historical and recent eruptive products of Ubinas form a continuous high-K magmatic  
235 trend, ranging from basaltic andesites to rhyolites (55-71 wt.% SiO<sub>2</sub>; 2-4 wt.% K<sub>2</sub>O, recalculated as anhydrous,  
236 Fig. 3). The most striking characteristic of this dataset is the overall decrease in silica content through time. At the  
237 base of the tephra succession, we have the older rhyolitic compositions (69-71 wt.% SiO<sub>2</sub>) of the pre-Holocene  
238 eruption deposits, followed by several Holocene dacitic (62-69 wt.% SiO<sub>2</sub>) tephra fall deposits. Above this is the  
239 andesitic (60-62 wt.% SiO<sub>2</sub>) tephra fallout deposits that corresponds to the 1-2 ka plinian eruptions. The Ubinas  
240 stratigraphic succession terminates with the historical and recent eruptive products of basaltic andesitic  
241 compositions (55-57 wt.% SiO<sub>2</sub>), that include those of the *CE* 1667, 2006-2009 and 2013-2017 eruptions (Fig. 3).  
242 A more detailed observation of this dataset reveals that the chemical variation is not uniform, there are two periods  
243 of silica-rich compositions in the middle (samples UBI-10-14, 16; Fig. 3), and in the upper part of the Holocene  
244 volcanic succession (the 1-2 ka eruption). Concomitantly with silica variations, the K<sub>2</sub>O and some incompatible  
245 trace elements (e.g. Rb, Th) show also a decrease through time; whereas MgO concentrations, as well the  
246 compatible elements (e.g. Sr, Ni, Cr) display an overall increase from the older rhyolites to the younger basaltic  
247 andesites, up to a maximum for *CE* 1667 eruption products (Supplementary materials 5 and 6). We should  
248 highlight the presence of two samples that lie off the main trend (UBI-10-15 from Sacuhaya section, and UBI-10-  
249 08 from Quebrada Infiernillos section), which are represented by black dots in Fig. 3 and the other geochemical  
250 plots. Compared to the other tephra layers and for the same silica content, these samples display lower  
251 incompatible elements concentrations (e.g. K<sub>2</sub>O, Rb, Th, La, Fig. 3 and 4; Supplementary materials 5 and 6).

252 Overall, the Ubinas magmatic series displays well-defined negative correlations for silica and most major  
253 elements (Fig. 4, Supplementary materials 5), except for Al<sub>2</sub>O<sub>3</sub>, and Na<sub>2</sub>O that are highly scattered. Sr and the  
254 transition metals (e.g. Sc, V, Co, Cr, Ni) also show negative correlations with silica increase. Conversely, some  
255 trace elements (and K<sub>2</sub>O) show fairly good positive correlations with silica, especially the Large-Ion Lithophile  
256 Elements (LILE; e.g. Rb, Th), while the High Field Strength Elements (HFSE; e.g. Nb and Zr) show a broad  
257 scatter. The Rare Earth Elements (REE) display a notable behaviour: the light REE (LREE; e.g. La, Ce) show no  
258 clear variation with silica increase, spanning over a wide range of values for the same silica content, whereas the  
259 Middle and Heavy REE (MREE and HREE; e.g. Nd, Sm, Yb) display clear negative correlations. As a result, REE  
260 ratios show temporal trends, such as a progressive decrease in La/Sm and increase in Sm/Yb or Dy/Yb ratios from

261 rhyolites to basaltic andesites (Supplementary materials 6). Lastly, the major and trace element variations have a  
262 noticeable break-in-slope at 56-58 wt.% SiO<sub>2</sub>, with the basaltic andesitic group (BA) on one side and a more  
263 widespread andesitic-dacitic-rhyolitic group (ADR) on the other side. We keep this dichotomy for the forthcoming  
264 sections of this manuscript.

265

266 Figure 3

267 Figure 4

268 Table 1

269

270 Sr and Nd isotopic data broadly display homogeneous values at the scale of the CVZ (Fig. 5a). In detail,  
271 <sup>87</sup>Sr/<sup>86</sup>Sr range between 0.70657 and 0.70707 with <sup>143</sup>Nd/<sup>144</sup>Nd between 0.51228 and 0.51235 (Fig. 5b, Table 1).  
272 These isotopic ratios are plotted far from the mantle domain represented by the MORB field and they display a  
273 negative correlation in <sup>87</sup>Sr/<sup>86</sup>Sr vs. <sup>143</sup>Nd/<sup>144</sup>Nd diagram. We should stress that sample UBI-10-15 plots off the  
274 trend with low <sup>143</sup>Nd/<sup>144</sup>Nd and relatively high <sup>208</sup>Pb/<sup>204</sup>Pb values. This characteristic confirms the interpretation  
275 that this deposit does not correspond to Ubinas. Note that although we include these samples on the geochemical  
276 plots, we exclude them from the subsequent analysis. Looking in detail, BA samples display the less radiogenic  
277 values in Sr and the most radiogenic in Nd, although they display a variability that accounts for at least 50% of the  
278 whole Ubinas isotopic variation (Fig. 5b). Surprisingly, the most radiogenic Sr values (and conversely the less  
279 radiogenic Nd values) are displayed by some dacites (rather than rhyolites, Fig. 5b). On the whole, Sr-Nd isotopic  
280 ratios define fairly good correlations with most differentiation indices (e.g. SiO<sub>2</sub>, K<sub>2</sub>O, Rb, Th; Supplementary  
281 materials 7). All samples fall within the isotopic field of the Andean Central Volcanic Zone (Davidson et al., 1991)  
282 and roughly display less radiogenic Sr compositions (Fig. 5a) than those of El Misti volcano (Rivera et al., 2017),  
283 but similar to those of the Andahua monogenetic cones (Delacour et al., 2007). Pb isotopic data also display very  
284 homogeneous values at the scale of the CVZ (Mamani et al., 2010). However, looking at in detail, they display a  
285 quite large range of variation (<sup>206</sup>Pb/<sup>204</sup>Pb: 18.147-18.244; <sup>207</sup>Pb/<sup>204</sup>Pb: 15.610-15.616; <sup>208</sup>Pb/<sup>204</sup>Pb: 38.548-38.649;  
286 Fig. 5c), with no well-defined linear correlations in <sup>206</sup>Pb/<sup>204</sup>Pb vs. <sup>207-208</sup>Pb/<sup>204</sup>Pb diagrams (Fig. 5d). In contrast to  
287 the Sr-Nd isotopic data, the Pb isotopic ratios of Ubinas differ from those of the Andahua monogenetic cones,  
288 plotting at lower <sup>206</sup>Pb/<sup>204</sup>Pb and higher <sup>207</sup>Pb/<sup>204</sup>Pb values (Fig. 5c).

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290 Figure 5

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## 4.2. Petrography and mineral chemistry

Blocks and bombs from the BA group are porphyritic, black to grey, dense to poorly vesiculated rocks bearing 20-25 vol.% phenocrysts of plagioclase, ortho- and clinopyroxene and Fe-Ti oxides, with scarce amphibole and olivine. On the contrary, the ADR samples are mostly phenocryst-poor (< 5 vol.%), highly vesiculated pumices with variable mineral assemblages. Andesitic samples contain plagioclase, amphibole, ortho- and clinopyroxene, Fe-Ti oxides and scarce phenocrysts of biotite, whereas dacites and rhyolites are composed of plagioclase, amphibole, biotite, and Fe-Ti oxides. Thus, the mineral assemblage changed concomitantly with magma chemistry from BA to ADR samples (Fig. 6).

Figure 6

**Plagioclase** is the most abundant phase in Ubinas samples. In BA group, plagioclase (10-20 vol.%) occurs as euhedral and subhedral phenocrysts showing a wide compositional range (An<sub>35-80</sub>, Fig. 7, Table 2), sometimes within a single phenocryst (e.g. An<sub>36-65</sub>, Rivera et al., 2014; and new unpublished data from 2006 and 2015 eruptive products). In spite of this diversity, most (~70%) phenocryst cores and rims display compositions between An<sub>45</sub> and An<sub>65</sub> (Fig. 7). On the basis of textural and chemical characteristics, we identified two different plagioclase populations in BA samples: (1) euhedral, non-altered phenocrysts with normal, oscillatory and reverse zoning patterns; and, (2) sieve-cored and sieve-ringed phenocrysts with frequent dissolution zones and clear overgrowth rims displaying strong reverse zoning (e.g. An<sub>40-64</sub>). In the ADR samples, plagioclase is also the most abundant phase (5-15 vol.%), displaying clear (unaltered), euhedral to subhedral forms with also large compositional variations (e.g. An<sub>33-72</sub>; Fig. 7) and frequent normal zoning patterns (e.g. An<sub>65-40</sub>), while some phenocrysts display no chemical variation. We also found rare reversely zoned phenocrysts (e.g. An<sub>46-51</sub>) as well as some inherited cores (e.g. An<sub>70</sub>). We note that the peak for the An composition shifts from An<sub>50-65</sub> for BA to An<sub>35-50</sub> for ADR (Fig. 7). Although the compositional range observed in ADR is as large as those of for BA plagioclases, the phenocryst's rims display more restricted compositions in the ADR group (An<sub>35-55</sub> for dacites, and An<sub>40-60</sub> for rhyolites). Lastly, the large compositional range of plagioclases from both groups suggest that some of them should be considered as antecrysts (*cf.* Streck, 2008), i.e. the An-poor cores and rims in BA group, and the An-rich cores in ADR group.

Figure 7



321 Table 2

322

323 *Amphibole* phenocrysts are ubiquitous in Ubinas samples. They are an accessory phase (~1 vol.%) in BA  
324 group, displaying anhedral forms with frequent opaque (black) reaction rims (*cf.* De Angelis et al., 2013), whereas  
325 other phenocrysts are completely altered. They display homogeneous magnesium-hastingsite compositions  
326 (according to the classification of Leake et al., 1997). In contrast, amphibole phenocrysts in the ADR samples are  
327 much more abundant (2-5 vol.%), and appear as euhedral phenocrysts without any disequilibrium features. They  
328 display wide compositional variations, spanning the magnesium-hastingsite, tschermakite and magnesium-  
329 hornblende groups. The large compositional variation of Ubinas amphibole phenocrysts is summarized in an Al<sub>2</sub>O<sub>3</sub>  
330 vs. Mg# diagram (Fig. 8a, Table 3). In this figure, amphibole from the BA samples show homogeneous, high-Al  
331 contents (12.5-13.1 wt.% Al<sub>2</sub>O<sub>3</sub>) and relatively high Mg# (65-73) [where Mg# = 100 \* Mg/(Mg + Fe<sup>T</sup>) in mol.%,  
332 and Fe<sup>T</sup> is total iron as Fe<sup>2+</sup>]. Amphiboles in andesites display intermediary and homogeneous Al contents (9.9-  
333 11.0 wt.% Al<sub>2</sub>O<sub>3</sub>) and homogeneous Mg# values (66-68), whereas amphibole phenocrysts in dacites and rhyolites  
334 span a large compositional range (7.0-12.7 wt.% Al<sub>2</sub>O<sub>3</sub>; Mg# 61-71). Such a broad chemical composition of  
335 amphiboles is usually ascribed to changes in chemical and thermodynamic parameters such as melt composition,  
336 pressure, temperature and redox state (Johnson and Rutherford, 1989; Schmidt, 1992; Bachmann and Dungan,  
337 2002; Prouteau and Scaillet, 2003; De Angelis et al., 2013; Krawczynski et al., 2012; Erdmann et al., 2014; Kiss  
338 et al., 2014). In order to constrain the role of the main parameters controlling amphibole chemistry, a substitution  
339 analysis is usually performed (*cf.* Poli and Schmidt, 1992; Bachmann and Dungan, 2002). Fig. 8b and c show the  
340 variation of three key parameters [<sup>IV</sup>Al, <sup>VI</sup>Al and (Na+K)<sup>A</sup>] that suggest a leading role for edenite (*ed*) substitution,  
341 a valuable proxy for temperature variations. However, the variation observed in <sup>VI</sup>Al component also points out  
342 for a role of the tschermakitic (*tk*) substitution, which is considered as a proxy for pressure variations. In addition,  
343 Kiss et al. (2014) propose that the variations in Mg# coupled with the variation in Al content of amphiboles (Fig.  
344 8a) could be used as a proxy for variation in melt composition.

345

346 Figure 8

347 Table 3

348 Table 4

349

350 **Clinopyroxene** phenocrysts in BA samples (~5 vol.%) show diopsidic to augitic compositions (En<sub>38-47-</sub>  
351 Fs<sub>10-21</sub>-Wo<sub>38-46</sub>, Table 4, according to the classification of Morimoto et al., 1988), display euhedral forms, mostly  
352 with reverse zoning patterns, although some phenocrysts show homogeneous compositions. The MgO content of  
353 clinopyroxene, expressed by the Mg#, ranges from 65 to 82. There are also some inherited cores, which are mantled  
354 by thin (10-50 μm), Mg-rich (Mg# 76-80) overgrowth rims. Clinopyroxene is also present as an accessory phase  
355 (<1 vol.%) in andesitic and dacitic samples as phenocrysts or microphenocrysts with very homogeneous  
356 compositions (Mg# 76-77).

357 **Orthopyroxene** phenocrysts appear to some extent (~2 vol.%) in BA group as well as in andesitic and  
358 dacitic samples. They appear as euhedral phenocrysts, frequently associated with clinopyroxene. They have  
359 enstatitic compositions (En<sub>65-71</sub>-Fs<sub>24-34</sub>-Wo<sub>2-4</sub>, Table 4, according to the classification of Morimoto et al., 1988).  
360 Slight differences in Mg# have been observed between orthopyroxenes from BA and andesites (70-76) and dacites  
361 (67-70). We stress that orthopyroxene is absent in rhyolites.

362 **Biotite** phenocrysts are ubiquitous in rhyolites (2-4 vol.%), are much scarcer (1-2 vol.%) in dacites, and  
363 are absent from more mafic rocks. Biotite appears as euhedral (up to 1-2 mm long) phenocrysts without reaction  
364 rims or any other disequilibrium textures. They display homogeneous compositions with Fe<sup>2+</sup>/(Fe<sup>2+</sup>+Mg) ratios of  
365 0.33-0.36 and very restricted Mg# values (64-67, Table 3). These characteristics confirm these micas are classified  
366 as biotites (according to the classification of Deer et al., 2013).

367 **Fe-Ti oxides** appear throughout the Ubina magmatic series as microphenocrysts and microlites in the  
368 matrix (1-2 vol.%) as well as inclusions in other mineral phases. They mostly correspond to titanomagnetite (6-18  
369 wt.% TiO<sub>2</sub>, Table 5), although rare ilmenite (37-38 wt.% TiO<sub>2</sub>) crystals are also observed in some dacites. Rivera  
370 (2010) also reports some rare ilmenite crystals in dacites and rhyolites of Ubina.

371 **Olivine** appears only as an accessory phase (< 1 vol.%) in BA such as those of the 2006-2009 and 2013-  
372 2017 eruptions. They are mostly subhedral or euhedral phenocrysts (up to 300-400 μm) or microlites with  
373 homogeneous compositions (Fo<sub>66-78</sub>, Table 5), and usually normal zoning patterns. Olivine phenocrysts frequently  
374 show reaction rims composed of plagioclase, pyroxene, and Fe-Ti oxides, or more scarce orthopyroxene  
375 overgrowth rims.

376 Lastly, some **apatite** microphenocrysts and microlites are found as inclusions in plagioclase and  
377 amphibole, whereas **zircon** microlites occurs as inclusions in biotites.

378

379 Table 5

380

### 381 **4.3. Trace elements in minerals**

382 Trace element concentrations were measured in plagioclase, ortho- and clinopyroxene, and amphibole  
383 phenocrysts from three Ubinas samples, a basaltic andesite (UBI-10-18B), an andesite (UBI-10-01) and a rhyolite  
384 (UBI-10-10C). Results are plotted in chondrite-normalized REE plots (Fig. 9). Plagioclase patterns are  
385 fractionated, with high LREE and low HREE contents and a conspicuous positive Eu anomaly for the andesite  
386 sample (Fig. 9a), as well as other notable positive anomalies for Ba and Sr (not shown). Orthopyroxene spectra  
387 are homogeneous, displaying low LREE relative to HREE contents, and a small negative Eu anomaly.  
388 Clinopyroxenes from the basaltic andesite sample display slightly flat spectra with maximum values for MREE  
389 and a small negative Eu anomaly (Fig. 9b). Lastly, two distinct populations of amphibole are identified (Fig. 9c):  
390 a REE-poor group that corresponds to amphibole from the basaltic andesite, and a REE-rich group that corresponds  
391 to the andesite and the rhyolite. These two populations are also observed for HFSE (e.g. Nb, Ta, Zr, not shown).  
392 Both groups display concave spectra with higher abundances of Nd (and other MREE) compared with other LREE  
393 and HREE. In addition, the REE-poor group corresponds to high-Al amphibole and display no Eu anomaly;  
394 whereas REE-rich group corresponds to high-Al amphibole and displays a conspicuous negative Eu anomaly. This  
395 feature indicated the contemporaneous crystallization of plagioclase, low-Al amphibole, orthopyroxene and  
396 clinopyroxene in the ADR group.

397

398 Figure 9

399

### 400 **4.4. Chemical composition of interstitial matrix glass and melt inclusions**

401 Interstitial matrix glass from the BA samples distributes into two compositional groups. Glasses from the  
402 CE 1667 eruptive products display homogeneous compositions (62.7-64.1 wt.% SiO<sub>2</sub>; n=5, normalized to  
403 anhydrous values, Table 6), whereas those from the 2006-2009 and 2013-2017 samples show slightly more  
404 differentiated compositions (62.7-67.0 wt.% SiO<sub>2</sub>, n=11). In contrast, interstitial glasses from whole-rock andesite  
405 samples from the 1-2 ka eruptions show dacitic to rhyolitic compositions (68.6-70.3 wt.% SiO<sub>2</sub>; n=13), and glasses  
406 from whole-rock dacites and rhyolites samples display high-silica rhyolitic compositions (73.8-76.1 wt.% SiO<sub>2</sub>;  
407 n=38). We analysed several melt inclusions from an andesitic and a rhyolitic tephra samples. We should stress the  
408 high homogeneity of these analyses that display almost similar compositions for both samples: 66.0 ± 1.4 wt.%  
409 SiO<sub>2</sub> (n=12) for MI in plagioclase crystals from andesitic tephra and 66.2 ± 1.2 wt.% SiO<sub>2</sub> (n=9) for MI in

410 plagioclase crystals from rhyolitic tephra. We should highlight that these compositions are identical to those of the  
411 interstitial matrix glasses from andesitic tephra. When plotted on Harker diagrams (Fig. 10), whole-rock, matrix  
412 glasses and melt inclusions samples define a single magmatic trend, although some scattering is observed for  $\text{Al}_2\text{O}_3$   
413 and  $\text{Na}_2\text{O}$  (not shown). Matrix glasses from the BA group fall outside this trend, especially for  $\text{Al}_2\text{O}_3$  and  $\text{K}_2\text{O}$ . It  
414 is worth noting that the matrix glass from the andesite whole-rock samples displays an almost identical rhyolitic  
415 composition to the whole-rock rhyolites.

416           The water content of the matrix glasses was estimated using the “by difference” method (Devine et al.,  
417 1995). We stress that these values mostly correspond to degassed magmas and thus these values should be  
418 considered as rough minimum estimates of the pre-eruptive water content. Concerning the ADR samples, we found  
419 large glass shards that allowed us to perform defocused analyses to minimize Na migration. As a result, the water  
420 content of matrix glasses from the ADR samples is  $4.0 \pm 1.2$  wt.% (n=51). In order to better constrain the pre-  
421 eruptive water content for ADR samples, we analysed plagioclase-hosted melt inclusions by Raman spectroscopy.  
422 The inclusions show variable water contents suggesting entrapment at different depths and/or complex degassing  
423 histories. The maximum value (6 wt.%) was measured in an inclusion of the rhyolitic tephra less affected by the  
424 magnetite signal (Supplementary material 3). Overall, minimum water contents of the melt inclusions from the  
425 andesitic samples range from 2.3 to 3 wt.%, whereas those from the rhyolitic samples span a range of 2.3 to 6  
426 wt.%  $\text{H}_2\text{O}$ . Although most of the inclusions seem to be characterised by moderate water contents (2-3 wt.%), the  
427 true water contents are obtained only after correction for the underestimation caused by the presence of magnetite  
428 in the glass. The underestimate is proportional to the intensity of the magnetite peak and is evident in glasses with  
429 low (microprobe + Raman) totals ( $< 97$  wt.%; Supplementary material 4). When this effect is taken into account  
430 and the compositions corrected, the water contents increase to varying degrees between 3 and 6 wt.%. Using the  
431 “by difference” method on MI analyses we obtain an average value of  $5.6 \pm 1.7$  wt.%  $\text{H}_2\text{O}$  (n=21), in agreement  
432 with the results of Raman measurements.

433

434 Figure 10

435 Table 6

436

## 437 **5. Discussion**

### 438 **5.1. Pre-eruptive P-T conditions**

439 **ADR magmas.** Given that amphibole is ubiquitous in this magmatic group, a suitable geothermometer is based on  
440 the amphibole-plagioclase equilibrium, using the edenite-richterite formulation of Holland and Blundy (1994),  
441 which applies to quartz-free assemblages. We applied this geothermometer to euhedral amphibole-plagioclase  
442 pairs in contact or for amphibole inclusions in plagioclase phenocrysts. We stress that this thermometer is weakly  
443 affected by pressure changes (a change of 100 MPa induces a temperature difference of around 5 °C). In Table 7,  
444 the temperature estimates using the amphibole-plagioclase thermometer show a decrease in magmatic  
445 temperatures from andesitic samples that yield very homogeneous values ( $913 \pm 13$  °C, n=15), to dacites ( $881 \pm$   
446  $36$  °C, n=21), and rhyolites that show even lower values ( $846 \pm 30$  °C, n=12).

447 Magnetite-ilmenite pairs are extremely rare in Ubinas magmatic series, however, we analysed 11 pairs  
448 from dacites and rhyolites that follow the equilibrium criteria of Bacon and Hirschmann (1988). Using the Lindsley  
449 and Spencer (1982) thermobarometric procedure, these pairs show very homogeneous T- $fO_2$  results. For dacites,  
450 the magnetite-ilmenite thermometer yields a temperature of  $879 \pm 4$ °C (n=9) and a  $fO_2$  of  $-10.3 \pm 0.1$  (NNO+2);  
451 whereas for rhyolites the temperature is slightly lower,  $849 \pm 3$ °C (n=2) and  $fO_2$  of  $-10.7 \pm 0.1$  (NNO+2). We  
452 should stress the good agreement between these temperature estimates and those obtained from the amphibole-  
453 plagioclase thermometer. However, as mentioned by Rutherford and Devine (1996), the magnetite-ilmenite  
454 thermometer systematically displays higher values (up to 30°C) for highly oxidized magmas ( $fO_2$  between -10 and  
455 -11). If we apply this empirical correction the estimated temperature should be  $\sim 850$ °C for dacites and  $\sim 820$ °C for  
456 rhyolites.

457 Another reliable thermometer for this magmatic group is the plagioclase-melt formulation of Putirka  
458 (2008). We applied this thermometer to mineral rims in equilibrium with the adjacent matrix glasses. We ensured  
459 that equilibrium conditions had been attained by selecting euhedral crystals, and by comparing the plagioclase-  
460 melt exchange coefficients with the putative values from the literature ( $K_d^{Ab-An} = 0.1 \pm 0.05$ ; Putirka, 2008). Given  
461 that the pressure dependency on temperature estimates is negligible, we fixed a crystallisation pressure (see below)  
462 in order to better constrain the magmatic temperature. We stress that a large pressure variation of around 500 MPa  
463 induces a temperature variation within the method's error (Putirka, 2008). In contrast, a critical point with these  
464 models concerns the pre-eruptive water content of magmas, because a change of 1 wt.% H<sub>2</sub>O induces a variation  
465 of  $\sim 20$ °C (i.e. Putirka, 2008; Samaniego et al., 2011; Arpa et al., 2017). In this work, we consider water content of  
466 6 wt.%, which corresponds to the maximum values measured in melt inclusions. In Table 7, we summarize  
467 temperature estimates for the ADR group. As for the previous thermometers, the plagioclase-melt formulation  
468 shows a decrease in magmatic temperatures from andesites ( $881 \pm 5$  °C, n=6) to dacites and rhyolites that show

469 lower but similar values ( $787 \pm 11$  °C, n=5 and  $813 \pm 5$  °C, n=8 respectively). We should stress these estimates are  
470 systematically lower than those obtained by the other methods (Table 7).

471 Amphibole stability in calc-alkaline magmas has been widely used to estimate its crystallization pressure.  
472 The Al-in-hornblende barometer has been experimentally calibrated for different ranges of temperature (Johnson  
473 and Rutherford, 1989; Schmidt, 1992; Mutch et al., 2016). These formulations stipulate that the aluminium content  
474 ( $Al^T$ ) of amphibole is proportional to the crystallization pressure at specific conditions defined by a mineral  
475 assemblage composed of plagioclase, sanidine, amphibole, biotite, quartz, sphene and Fe-Ti oxides. Given that  
476 quartz is absent from the equilibrium assemblages at Ubinas, even from the rhyolitic magmas, this barometer  
477 would yield anomalously high pressures. On the other hand, Ridolfi et al. (2010) and Ridolfi and Renzulli (2012)  
478 looked again into amphibole stability in calc-alkaline magmas and proposed new empirical P-T-fO<sub>2</sub>-XH<sub>2</sub>O  
479 formulations based on amphibole chemistry. However, many authors consider that  $Al^T$  in amphibole is sensitive  
480 to both pressure and temperature variations (Poli and Schmidt, 1992; Anderson and Smith, 1995; Bachmann and  
481 Dungan, 2002; Kiss et al., 2015). This implies that this barometer should be used within the specific temperature  
482 range at which it was calibrated. In order to test the accuracy of these models, Erdmann et al. (2014) compared the  
483 experimentally determined P-T conditions of a set of amphiboles with the values calculated using Ridolfi et al.  
484 (2010) and Ridolfi and Renzulli (2012) formulations. Based on this analysis, Erdmann et al. (2014) concluded that  
485 temperature estimates are acceptable, whereas pressure values are seriously flawed. Temperature estimates  
486 obtained from the Ridolfi et al. (2010) and Ridolfi and Renzulli (2012) methods also show a decrease in magmatic  
487 temperature from andesites to rhyolites groups (Table 7), although the absolute values are 30-60°C higher than  
488 those obtained with the magnetite-ilmenite, amphibole-plagioclase and plagioclase-melt thermometers. It is worth  
489 noting that following Ridolfi and Renzulli (2002) method, for dacitic and rhyolitic magmas we obtain very similar  
490 values for fO<sub>2</sub> that those obtained with the magnetite-ilmenite pairs ( $\Delta NNO = 1.7 \pm 0.3$ , n=45).

491 Pressure estimates are summarized in Table 7. We observe that most barometers show a progressive  
492 decrease in amphibole crystallization pressure through the ADR samples. However, we should stress that the  
493 temperature estimated for ADR group did not match those of the most common experimental calibrations (Johnson  
494 and Rutherford, 1989; Schmidt, 1992; Mutch et al., 2016). For this reason, we focus on other calibrations that take  
495 into account the influence of temperature on  $Al^T$  (Anderson and Smith, 1995) or by applying the formulation that  
496 uses the <sup>VI</sup>Al for barometry (Médard and Le Pennec, 2013; Manrique et al., 2020). If we focus on amphibole  
497 phenocryst of rhyolites and fixing the temperature at 820°C (see above), we obtain  $228 \pm 86$  MPa (n = 16) using  
498 the temperature-corrected barometer of Anderson and Smith (1995). Using the temperature independent barometer

499 of Médard and Le Pennec (2013), we obtain rather higher values of  $316 \pm 51$  MPa, which are indeed in the error  
500 range of the methods. Other concordant results were obtained using the empirical barometers of Ridolfi et al.  
501 (2010) and Ridolfi and Renzulli (2012), which yield similar values ( $237 \pm 81$  MPa and  $252 \pm 91$  MPa,  
502 respectively). In summary, it seems plausible that amphibole in silica-rich magmas (dacites and rhyolites)  
503 crystallized at 200-400 MPa (Fig. 11) and temperatures in the range of 800-850°C.

504

505 **BA magmas.** Given the presence of ortho- and clinopyroxene in BA and andesitic magmas, a suitable  
506 geothermometer is the two-pyroxene thermometer (*cf.* Lindsley, 1983). Rivera et al. (2014) applied this  
507 thermometer for the 2006-2009 magmas and obtained temperatures of 950-1020°C (n=6). A careful observation  
508 of these orthopyroxene-clinopyroxene pairs reveals that most of them do not follow the equilibrium criteria defined  
509 by the comparison of the calculated exchange coefficients with the putative values from the literature ( $K_d^{\text{Fe-Mg}} =$   
510  $1.09 \pm 0.14$ ; Putirka, 2008). This analysis shows that only two orthopyroxene-clinopyroxene pairs from Rivera et  
511 al. (2014), one pair from our dataset and five additional pairs from older samples of older Ubina samples (Rivera,  
512 2010) follow the equilibrium criteria. These pairs yield a temperature of  $993 \pm 24$  (n=8) for BA samples. This  
513 value is very close to the temperatures obtained with the amphibole-based Ridolfi et al. (2010) method ( $994 \pm 9^\circ\text{C}$ ,  
514 n=23).

515         Given that most barometers are not calibrated for basaltic andesitic compositions, that the mineral  
516 assemblage of these magmas do not meet those needed for the method, and that the temperatures obtained for the  
517 BA group are far from the calibration temperatures of most barometers, the pressure estimates for this group are  
518 much more difficult to compute. In addition, we observe that the temperature-controlled edenite substitution is  
519 much more important than the pressure-controlled tschermakite substitution (Fig. 8), which implies that the  
520 differences in amphibole chemistry are mostly related to temperature, with a minor role for pressure and magma  
521 chemistry. The empirical barometers of Ridolfi et al. (2010) and Ridolfi and Renzulli (2012) yield pressures of  
522  $453 \pm 26$  MPa and  $357 \pm 138$  (n = 23) respectively, whereas the temperature-independent barometer of Médard  
523 and Le Pennec (2013) yields values of  $341 \pm 35$  MPa (i.e. no difference between amphiboles from ADR and BA  
524 groups, Fig. 11). Given the uncertainties associated with the application of these models to the BA magmas, we  
525 conclude that these amphiboles probably crystallized at higher pressure (>300-400 MPa) and temperatures (1000-  
526 1050°C).

527

528 Figure 11

529 Table 7

530

531 **5.2. The origin of the magmatic diversity: trans-crustal assimilation and fractional crystallization**

532 **processes**

533 The magmatic differentiation in continental arc settings is a complex process including fractional  
534 crystallization coupled with crustal assimilation at several levels in the crust. In addition, frequent recharge and  
535 the subsequent magma mixing process is ubiquitous of active magmatic systems. We should stress that these  
536 processes are not mutually exclusive, acting at the same time during magma ascent and storage across the crust.  
537 Given that the Andean Central Volcanic Zone developed on a thick (up to 70 km) continental crust, it represents  
538 the archetype for studying the crustal participation on continental arc magmatism. Most studies consider these  
539 magmas stagnate at different levels in the crust and acquire its geochemical signature at the so-called MASH  
540 (Melting-Assimilation-Storage-Homogenization) zones located in the deep and hot lower crust (Hildreth and  
541 Moorbath, 1988; Davidson et al., 1990; Muir et al., 2014). Then, intermediate magmas could stagnate again at  
542 shallow levels, where they differentiate via a coupled assimilation-fractional crystallization process. More  
543 recently, Blum-Oeste and Wörner (2016) identified three different geochemical end-members able to explain the  
544 whole variability of CVZ magmas: (1) a slightly evolved calc-alkaline basaltic andesite; (2) an enriched  
545 shoshonitic basalt; and, (3) a crustal-derived rhyodacite. These authors propose that all CVZ magmas derived from  
546 mixing process at variable proportions of these three end-members.

547 The Ubinas magmatic series, which is composed of basaltic andesites through to rhyolites, has been  
548 interpreted as a result of a coupled assimilation and fractional crystallization process occurring at different depth  
549 in the crust (Thouret et al., 2005; Rivera, 2010). These authors also suggest that the mafic magmas resulted of a  
550 deep crustal differentiation process involving amphibole and/or garnet. Our geochemical data shows a conspicuous  
551 break-in-slope observed at 56-57 wt.% SiO<sub>2</sub> in compatible elements (MgO, Ni, Sr, Fig. 4). This feature indicates  
552 the early crystallization of an olivine-dominated cumulate in BA magmas, followed by the fractionation of  
553 clinopyroxene, amphibole and plagioclase for ADR magmas. In addition, the frequent zoning patterns observed  
554 in plagioclase and pyroxenes; and, the fact that the matrix glass compositions fall on the main Ubinas geochemical  
555 trend (Fig. 10), corroborates the progressive fractionation process.

556 Experimental data on crystallization of primitive arc magmas at mid- to lower-crustal pressures show a  
557 continuous geochemical trend from primitive magnesian basalts up to high-silica rhyolites (Müntener et al., 2001;  
558 Sisson et al., 2005; Pichavant and Macdonald, 2007; Alonso-Perez et al., 2009; Blatter et al., 2013; Nandedkar et



559 al., 2014). These experiments were performed from near-liquidus temperatures (~1150-1200°C) down to  
560 temperatures as low as 700°C; pressures ranging from 900 to 400 MPa; and at oxidizing (NNO+2) and moderately  
561 hydrous (~3-4 wt.% H<sub>2</sub>O) conditions. At high pressure and temperature (900-700 MPa; 1200-950°C), the dominant  
562 crystallizing minerals are clinopyroxene + olivine + Cr-Spinel ± orthopyroxene. At lower pressure and  
563 temperature, plagioclase begins to crystallize, Fe-Ti oxides replaces spinel, olivine dissolves and amphibole  
564 crystallization begins (at temperatures below ~1000°C). At the end of the crystallization sequence, apatite, quartz  
565 and biotite appear as liquidus phases. In Fig. 10 we compare the major element compositions of the whole-rock  
566 and matrix glasses and melt inclusions from Ubinas with fields of selected experimentally-determined liquids  
567 (Sisson et al., 2005; Blatter et al., 2013; Nandedkar et al., 2014). We observe a reasonable correspondence, except  
568 for the mafic compositions (> 5 wt.% MgO), which are lacking in the Ubinas magmatic series, and globally lower  
569 values of K<sub>2</sub>O (not shown), related to the composition of the starting material. These results imply that the  
570 commonly observed mineral assemblage in Ubinas samples records a long crystallization sequence, roughly  
571 spanning from 900 to 200 MPa, and from 1150 to 700°C.

572 Additional constraints on magmatic differentiation come from trace elements systematics. The negative  
573 correlation of Sr with silica increase suggest a significant role of plagioclase, whereas the decrease of the transition  
574 metals (e.g. Ni, Sc, V) suggest the fractionation of clinopyroxene and olivine, namely for BA group. In addition,  
575 trace element systematics supports the leading role of amphibole fractionation for the ADR group. On the basis of  
576 theoretical and experimental studies, amphibole preferentially incorporates MREE over HREE and LREE (*cf.*  
577 Davidson et al., 2007). This observation is corroborated by the Ubinas amphibole trace element patterns (Fig. 9),  
578 which show that fractionation of this mineral leads to an increase in La/Nd and a decrease in Nd/Yb and Dy/Yb  
579 with silica contents in the magma (Fig. 12a, b). In order to test the hypothesis of an amphibole-controlled fractional  
580 crystallization process, we performed a two-steps geochemical modelling procedure. First, major element mass-  
581 balance calculations (Bryan et al., 1969) between mafic and felsic end-members (e.g. UBI-10-18C and UBI-10-  
582 11, respectively) allow us to estimate the modal composition of the cumulate (46–48% Pl + 38–44% Amph + 3–  
583 5% Cpx + 6% Mag + 1% Apt), as well as the degree of fractionation (50-55%) required to evolve from a BA to a  
584 rhyolitic end-members. It is worth noting that the modal composition of the cumulate estimated by mass-balance  
585 is coherent with the observed mineral assemblage of Ubinas samples and confirms the leading role of amphibole  
586 fractionation. Then, these results were used in the trace element modelling of a Rayleigh-type fractional  
587 crystallization (FC), using partition coefficients for intermediate liquids (Rollinson, 1993; Bachmann et al. 2005;  
588 Rivera et al., 2017). We also observe that isotopic ratios are correlated with silica as well as with some trace

589 elements ratios (e.g. Dy/Yb, Fig. 12c, d), and that the higher values for both parameters (i.e. Dy/Yb and  
590  $^{143}\text{Nd}/^{144}\text{Nd}$ ) roughly correspond to the BA samples. Consequently, a pure fractional crystallization processes  
591 cannot explain these variations: the changes in isotopic ratios clearly point at of some degree of crustal  
592 assimilation. Based on this observation, we performed an assimilation-fractional crystallization (AFC, DePaolo,  
593 1981) model, using exactly the same parameters than for the FC model, with different fractionation/assimilation  
594 ratios ( $r = 0.04\text{-}0.10$ ) and using the local upper continental crust represented by the Precambrian Charcani gneiss  
595 (Boily et al., 1990; Rivera et al., 2017) as a potential contaminant. The modelling results for both FC and AFC  
596 models are shown in Fig. 13. These models show a good agreement for most trace elements in the multi-parameter  
597 plot (Fig. 13a), as well as in the binary plots including key trace elements ratios and isotopic rapports (Fig. 13b,  
598 c), although a mismatch is observed for some trace elements as the LREE. These models suggest a proportion of  
599 assimilated crust of 2-6 vol.% (following the procedure of Aitchison and Forrest, 1994).

600         Lastly given that Sr-Nd-Pb ratios plot far beyond the mantle values, with only weak isotopic variations  
601 between the basaltic andesitic and rhyolitic end-members (with a silica variation of more than 15 wt.%), we suggest  
602 that the isotopic signature of BA Ubinas magmas was mostly acquired at a deep stage of magmatic differentiation,  
603 probably in the lower crust MASH zone. Single mass-balance models confirm that 20-30% of a putative lower  
604 crust is needed to shift the mantle-derived magmas to those of the BA Ubinas samples. Given the large  
605 uncertainties concerning the deep fractionation processes as well as the lower crustal compositions, we did not  
606 perform a quantitative analyse of these deep processes. However, this two-steps model has been applied on a  
607 regional Andean scale (Hildreth and Moorbath, 1988; Mamani et al., 2010; Blum-Oeste and Wörner, 2016;  
608 Ancellin et al., 2017) as well as to specific volcanic centres such as the Andahua monogenetic cones (Delacour et  
609 al., 2007), El Misti (Rivera et al., 2017), Ollagüe (Feeley and Davidson, 1994; Matioli et al., 2006), Nevados de  
610 Payachata (Davidson et al., 1990), and Lascar (Sainlot et al., 2020) in the CVZ; and Cotopaxi (Garrison et al.,  
611 2011) and Tungurahua volcanoes (Nauret et al., 2018) in the NVZ.

612

613 Figure 12

614 Figure 13

615

### 616 **5.3. The magmatic plumbing system and the progressive temporal changes in magma chemistry**

617         The geochemical data for the Ubinas magmatic series reveals a large compositional variation that could  
618 be explained by a coupled assimilation-fractional crystallization (AFC) process involving a mineral assemblage

619 composed of plagioclase, amphibole, orthopyroxene, clinopyroxene, Fe-Ti oxides, with minor olivine and biotite  
620 (at the mafic and felsic end-members respectively). A key geochemical characteristic of the Ubina magmatic  
621 series is the overall variation of most geochemical parameters. As discussed above, Ubina magmas become less  
622 differentiated through time (Fig. 3, 4, Supplementary materials 5 and 6), with the recently erupted magmas (the  
623 BA group) displaying the highest  $^{143}\text{Nd}/^{144}\text{Nd}$  and lowest  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopes (Fig. 5, Supplementary materials 6),  
624 indicating that BA magmas are among the most primitive compositions erupted during the last millennium. In  
625 addition, as demonstrated by Rivera et al. (2014) for the 2006-2009 eruptions, and corroborated by 2013-2017  
626 magmas (this work), the BA magmas display frequent disequilibrium textures, such as inversely zoned plagioclase  
627 phenocrysts with sieve textures and overgrowth rims, inversely zoned clinopyroxene phenocrysts, and rare olivine  
628 crystals with reaction and overgrowth rims. These features point to a magma mixing scenario between two magmas  
629 of similar basaltic andesitic compositions but different temperature and volatile contents (Rivera et al., 2014).  
630 Thus, we infer that during the historical and recent eruptions the trans-crustal magmatic reservoir was fed by mafic  
631 magmas at depth. In contrast, it is worth noting that disequilibrium textures and other magma mixing evidences  
632 (e.g. banded samples) are absent in the ADR samples. However, we should stress that mixing of hybrid magmas  
633 of different degrees of differentiation is a ubiquitous process at the trans-crustal magmatic systems.

634 Due to the thick continental crust, primitive basaltic magmas are extremely rare in the Central Andes,  
635 with notable exceptions, for example the Andahua monogenetic cones in Southern Peru (Delacour et al., 2007;  
636 Sørensen and Holm, 2008). On the whole, the primitive Central Andes magmas display variably enriched trace  
637 element patterns as well as variable radiogenic isotopic signatures (Mamani et al., 2010; Blum-Oeste and Wörner,  
638 2016), which must have been acquired at the so-called lower-crustal hot zones (Hildreth and Moorbath, 1988;  
639 Annen et al., 2006). During their ascent from the lower crust, these magmas stall at different levels in the thick  
640 Central Andes crust and then feed the middle-to-upper crustal magma system.

641 On the basis of the petrological data presented in this work, we are able to reconstruct the upper part of  
642 the magma plumbing system over the last millennia. Although most barometers indicate two distinct pressure  
643 populations for ADR and BA magmas, we cannot confirm these differences due to the fact that most magmas  
644 (namely the BA group) do not meet neither the mineralogical assemblage nor the temperature range stipulated for  
645 the models. If we focus on most differentiated magmas of Ubina series (dacites and rhyolites), and taking into  
646 account the intrinsic uncertainties related with the methods, we consider that amphibole from these magmas  
647 crystallized in the range of 200-400 MPa, which is realistic for dacitic and rhyolitic magmas in arc settings  
648 (Rutherford and Hill, 1993; Moore and Carmichael, 1998; Martel et al., 1999; Scaillet and Evans, 1999; Rutherford

649 and Devine, 2003; Andujar et al., 2017; Martel et al., 2018). Considering a bulk density value for upper crustal  
650 rocks of  $2600 \text{ kg/m}^3$ , and the pressure-depth relationship of Blundy and Cashman (2008), the ADR magma storage  
651 region would be located at 8-15 km below the summit. We imagine this magma storage region as a plexus of sill-  
652 like intrusions that conform a mushy magma reservoir (cf. Annen et al., 2006; Wörner et al., 2018). This reservoir  
653 should be frequently fed by primitive BA magmas that certainly formed deeper in the crust as a result of AFC  
654 process from primitive arc magmas, as suggested by phase-equilibrium studies revealing that primitive arc magmas  
655 in arc settings stall and differentiate at even higher pressures (up to 900 MPa, 30-35 km deep; Blatter et al., 2013;  
656 Nandedkar et al., 2014).

657         During Holocene times, the Ubinas magma plumbing system stored a large amount of differentiated  
658 (andesitic to rhyolitic) magmas. As a result, Ubinas experienced notable plinian eruptions, the last one occurred at  
659 1-2 ka. In contrast, over the last few centuries, Ubinas experienced smaller eruptions involving BA magmas.  
660 Although we cannot exclude a bias due to the fact that smaller basaltic andesitic events might not be preserved in  
661 the geological record, it seems clear that the current state of the Ubinas magma plumbing system corresponds to a  
662 phase of recharge, with no evidence for a rejuvenation of the silica-rich reservoir that fed the large Holocene  
663 dacitic to rhyolitic eruptions. This conclusion is corroborated by recent seismological studies showing that  
664 volcano-tectonic events at Ubinas are clustered below the summit caldera and up to 8 km depth (Inza et al., 2014;  
665 Gonzalez et al., 2014; Machacca-Puma et al., 2019). In addition, some regional geophysical studies in this part of  
666 the Andes have not identified low velocity anomalies that could be interpreted as a large magma storage zone,  
667 suggesting a reservoir of relatively modest dimensions that is unable to be imaged by the spatial resolution of the  
668 regional tomographic studies (cf. Ryant et al., 2016).

669

670 Figure 14

671

## 672 **6. Conclusions**

673         During the last millennia (i.e. post-glacial and Holocene times) and recently, the eruptive products of  
674 Ubinas have shown an overall decrease in silica content from the older rhyolites (69-71 wt.%  $\text{SiO}_2$ ) to the historical  
675 and recent basaltic andesites (55-57 wt.%  $\text{SiO}_2$ ).  $\text{K}_2\text{O}$  and certain incompatible trace elements (e.g. Rb, Th) are  
676 positively correlated with silica; whereas MgO concentration, as well the compatible elements (e.g. Sr, Y, Yb, Ni,  
677 Cr) display an overall increase from the older rhyolites to the younger basaltic andesites, peaking in the CE 1667  
678 eruption products. In contrast to these large major and trace element variations, Sr-Nd-Pb isotopic values show

679 generally highly radiogenic values but little variation from basaltic andesites to rhyolites. We note that the isotopic  
680 data indicate that magmas erupted during the recent eruptions of Ubinas rank amongst the most primitive magmas  
681 erupted by this volcano during the last millennia. These temporal patterns indicate that the Ubinas magmatic series  
682 evolved in the middle-to-upper crust by a coupled Assimilation-Fractional Crystallization (AFC) process involving  
683 a cumulate composed of plagioclase, amphibole, clinopyroxene, orthopyroxene and Fe-Ti oxides with minor  
684 amounts of olivine and biotite at the mafic and felsic end-members. The role of upper crustal assimilation is limited  
685 and constrained to maximum a few per cent; however, the highly radiogenic Sr-Nd-Pb signature of Ubinas magmas  
686 requires a higher degree of crustal processing, which must have occurred at lower crustal depths.

687         The detailed petrological study of the Ubinas magmatic series points to an overall variation in P-T  
688 conditions, from the older and colder dacites and rhyolites up to the younger (historical and recent), hotter and  
689 probably deeper basaltic andesites. These data, together with geochemical and phase equilibrium constraints allow  
690 us to propose the existence of an elongated upper crust magma reservoir composed of a highly crystalline mush  
691 with some batches of liquid magma. Our study reveals that the large Holocene andesite-dacite-rhyolite (ADR)  
692 eruptions require the existence of a large shallower reservoir at 200-400 MPa, which seems to be recharged by the  
693 historical and recent (*CE* 1667, 2006-2009, 2013-2017) basaltic andesitic magmas, which were formed at deeper  
694 levels in the crust. This study highlights the importance of detailed petrological studies of Holocene sequences at  
695 explosive arc volcanoes in order to constrain the magmatic processes and conditions that control the occurrence  
696 of large explosive eruptions.

697

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705

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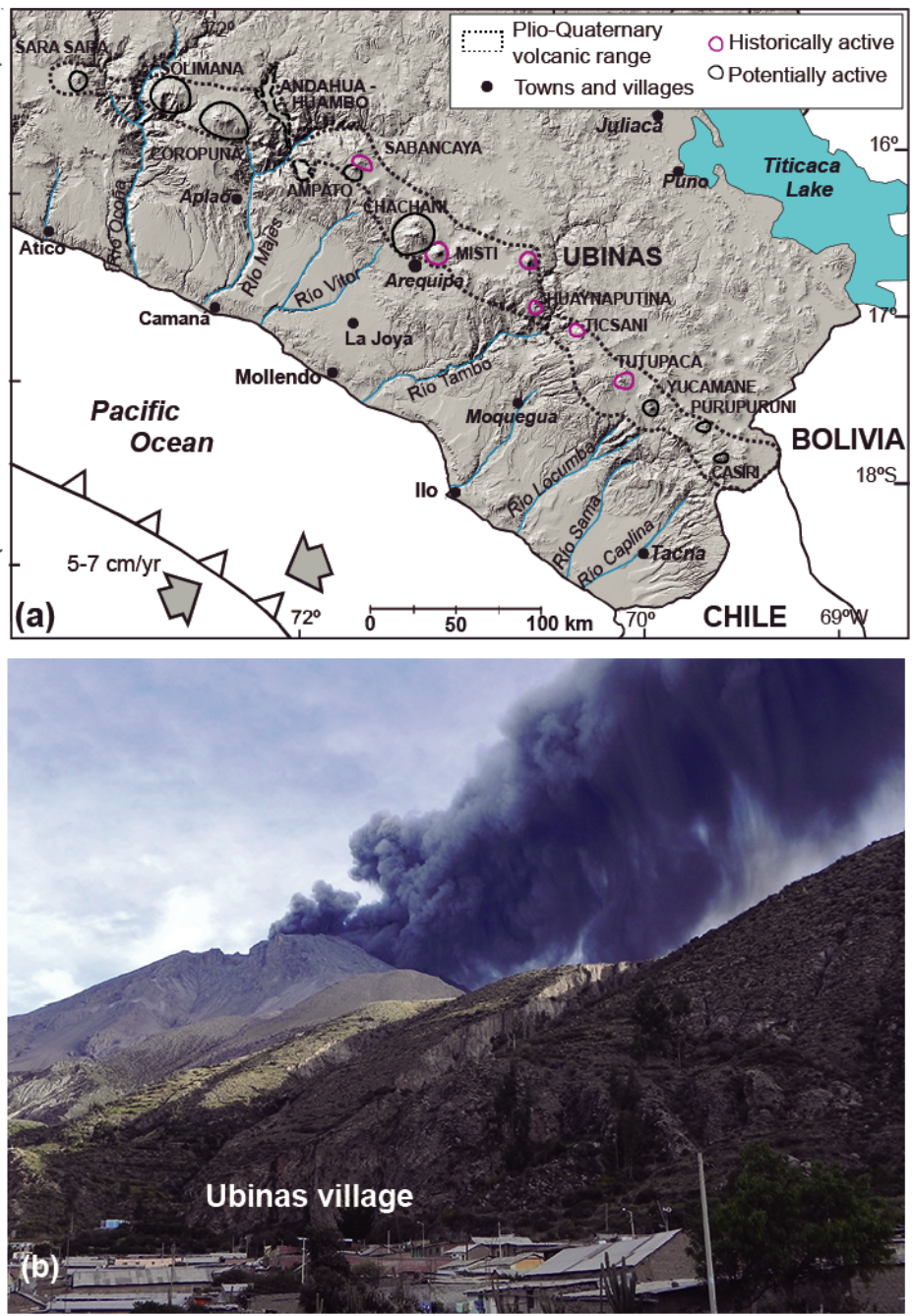
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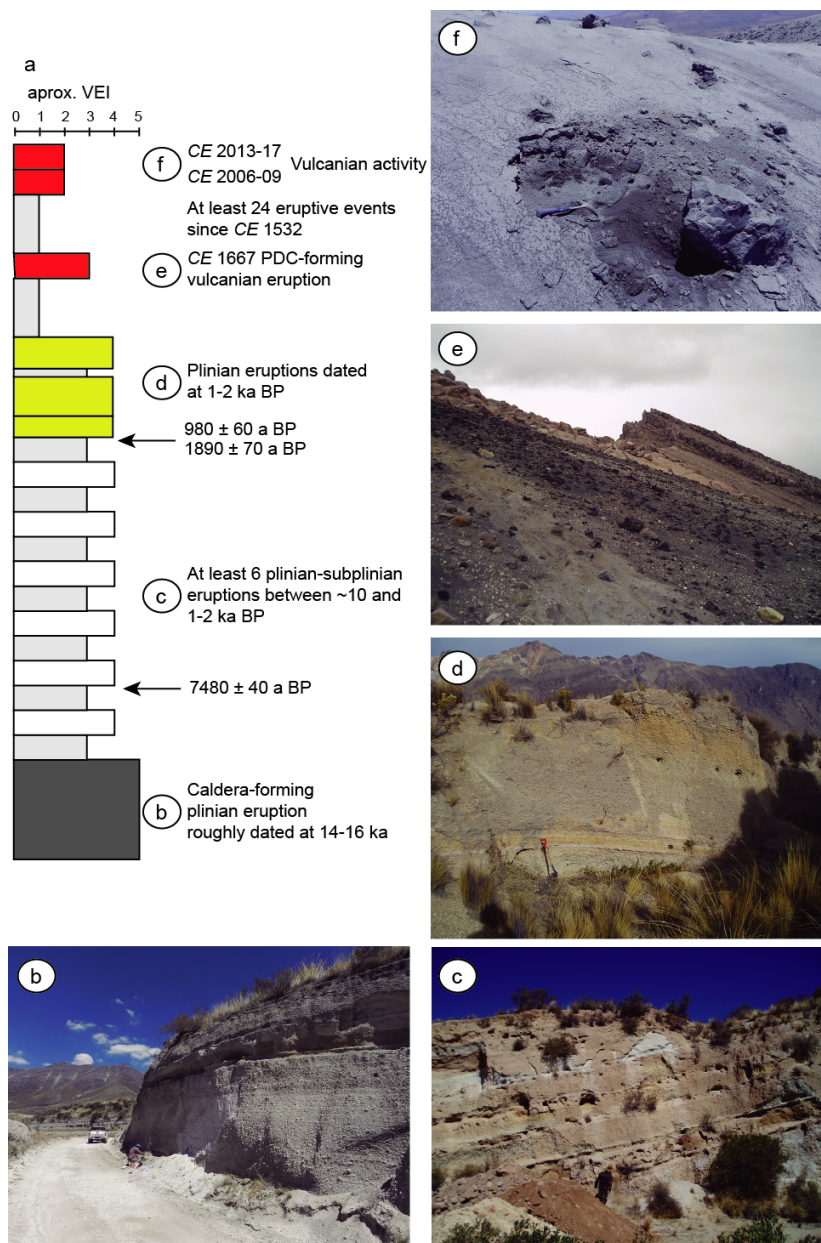
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 937 **Figure 1.** (a) Digital elevation model of southern Peru, showing the location of the active volcanic arc and Ubinas  
 938 volcano. (b) Ubinas volcano seen from the south, showing an ash-rich vulcanian eruption column. This photo was  
 939 taken from Ubinas village on April 26<sup>th</sup>, 2014.

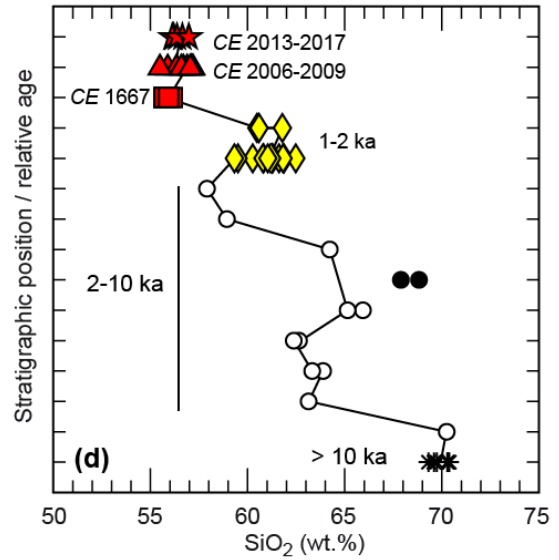
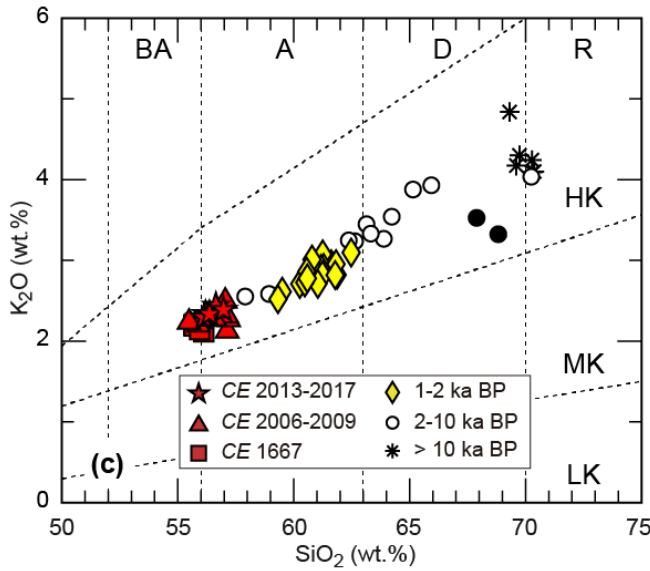
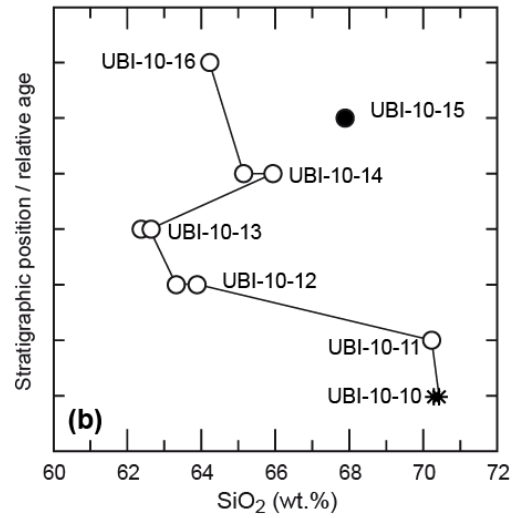
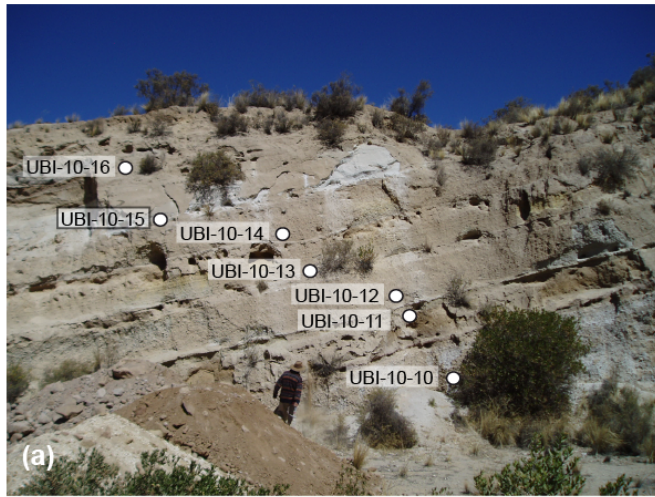
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945 **Figure 2. (a)** Synthetic stratigraphic column showing the main eruptive events of the post-glacial to recent eruptive  
 946 chronology of Ubina volcano (after Thouret et al., 2005 and our own fieldwork). The colour code corresponds to  
 947 the main units defined in the text: grey/black for rhyolites, white for dacites, yellow for andesites and red for  
 948 basaltic andesites. **(b)** Plinian fallout deposit close to Sacuhaya hamlet (UBI-10-10, see Supplementary material 1  
 949 for the UTM location). **(c)** Succession of at least 6 plinian-subplinian fallout deposits interlayered with reworked  
 950 ash horizons outcropping close to Sacuhaya hamlet (UBI-10-11 to UBI-10-16). **(d)** Plinian fallout deposits at  
 951 Quebrada Infiernillos (UBI-10-01 to UBI-10-06) dated at 1-2 ka. **(e)** Scoria-rich pyroclastic density current deposit  
 952 on the western flank of Ubina just below the caldera rim (UBI-10-19). **(f)** Ballistic block near the caldera rim  
 953 associated with the 2015 eruption (UBI-15-14). Note the grey ash layer that covers the caldera rim results from  
 954 the recent eruptions (2006-2009 and 2013-2015).



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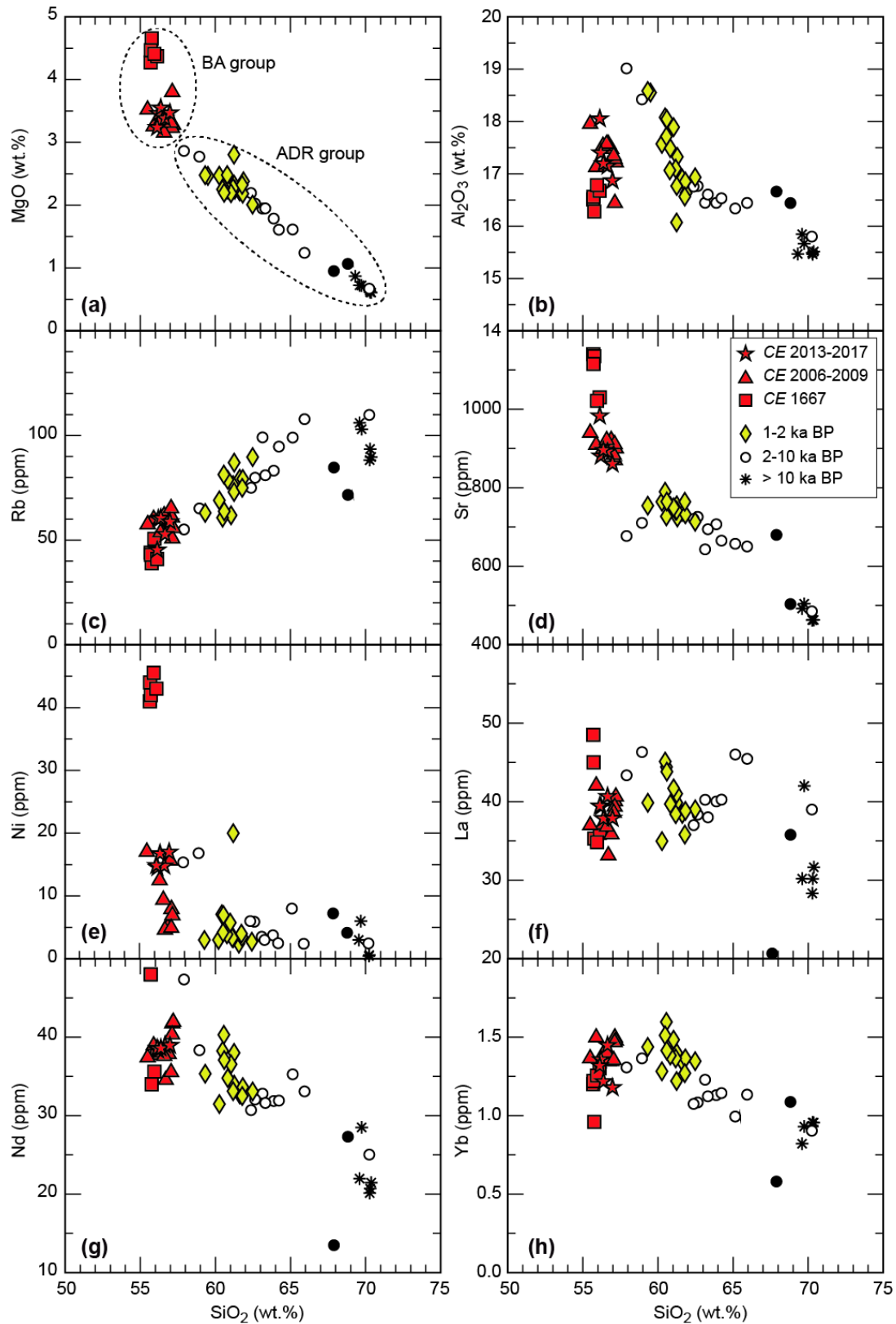
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**Figure 3. (a)** Sample locations on the Sacuhaya cross-section. **(b)** Silica content of samples from the Sacuhaya section. **(c)**  $K_2O$  vs.  $SiO_2$  diagram from the post-glacial, historical, and recent samples of Ubinas volcano. The fields in this diagram are taken from Peccerillo and Taylor (1976). BA, basic andesite; A, andesite; D, dacite; R, rhyolite; LK, low potassium; MK, medium potassium; HK, high potassium. **(d)** Silica contents vs. stratigraphic position for the post-glacial to recent samples. Black dots correspond to samples from a distal tephra fallout (UBI-10-15 and UBI-10-08), whose source is probably other than Ubinas.

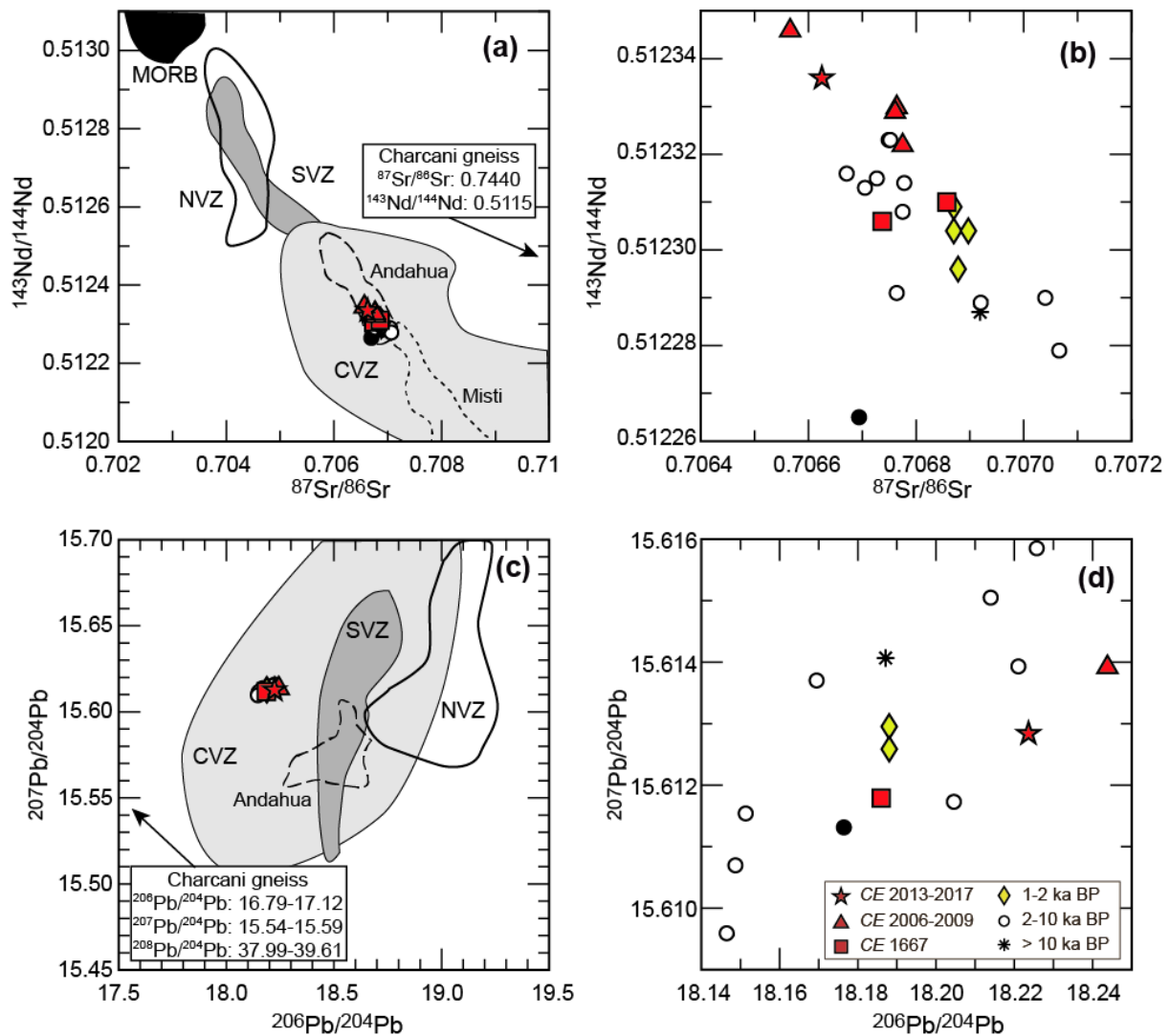




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968 **Figure 4.** Selected major (a, b) and trace (e, f, g, h) elements for Ubina samples. Note the break in slope between  
 969 the basic andesite (BA) group and the andesite, dacite, rhyolite (ADR) group. Symbols are the same as in Fig. 3.

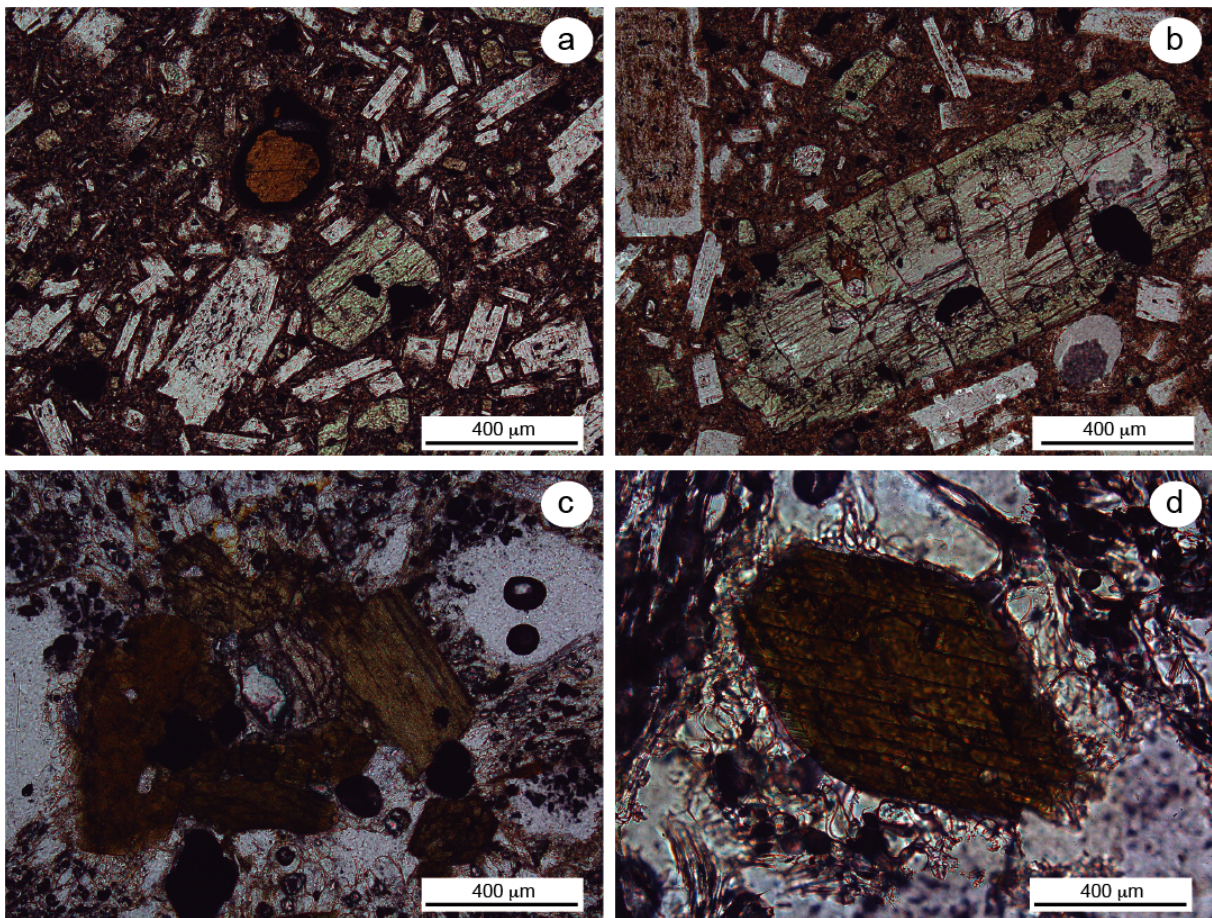
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973 **Figure 5.** (a)  $^{87}\text{Sr}/^{86}\text{Sr}$  vs.  $^{143}\text{Nd}/^{144}\text{Nd}$  diagram for Ubina rocks, compared with published isotopic data for the  
 974 Mid-Ocean Ridge Basalts (MORB, White et al., 1993 and reference therein) and the Andean Northern, Central  
 975 and Southern Volcanic Zones (NVZ, CVZ and SVZ respectively; Davidson et al., 1991; Ancellin et al., 2017). (b)  
 976 Detailed  $^{87}\text{Sr}/^{86}\text{Sr}$  vs.  $^{143}\text{Nd}/^{144}\text{Nd}$  diagram for Ubina samples. (c)  $^{206}\text{Pb}/^{204}\text{Pb}$  vs.  $^{207}\text{Pb}/^{204}\text{Pb}$  diagram for Ubina  
 977 samples. Note the extreme homogeneity of Ubina volcano compared to the very large field displayed for the CVZ.  
 978 (d) Detailed  $^{206}\text{Pb}/^{204}\text{Pb}$  vs.  $^{207}\text{Pb}/^{204}\text{Pb}$  diagram for Ubina samples. The absence of linear correlation suggests that  
 979 a process more complicated than a simple binary mixing process controls Pb isotopes variations. Data from the  
 980 Andahua monogenetic cones (Delacour et al., 2007) and El Misti volcano (Rivera et al., 2017) are also included.  
 981 The isotopic signature of the Precambrian Charcani gneiss comes from Boily et al. (1990), Mamani et al. (2010)  
 982 and Rivera et al. (2017). Symbols are the same as in Fig. 3. Analytical error bars are within the symbol size.

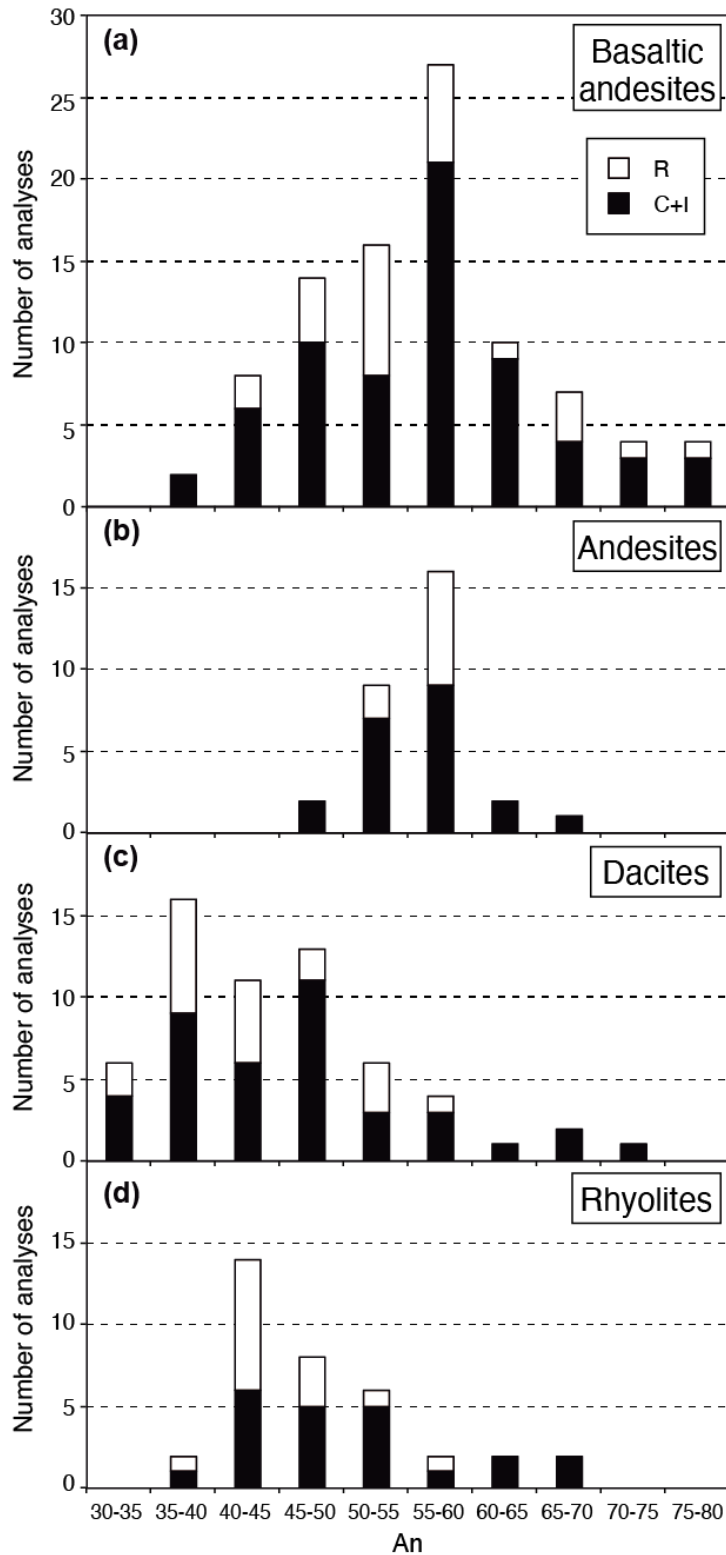
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986 **Figure 6.** Optical microphotographs for Ubina samples. **(a)** Basaltic andesite (UBI-10-18C) showing a mineral  
 987 assemblage composed of plagioclase, ortho- and clinopyroxene, amphibole and Fe-Ti oxides. Note the black  
 988 aureole around the amphibole. **(b)** Disequilibrium textures in the basaltic andesite (UBI-10-18C) showing a  
 989 clinopyroxene phenocryst core mantled with an overgrowth rim and a plagioclase phenocryst (top left) with an  
 990 altered (sieve) core and a fresh overgrowth rim. **(c)** Andesitic tephra (UBI-10-06) showing a mineral clot composed  
 991 of plagioclase, amphibole and orthopyroxene. **(d)** Amphibole phenocryst in a rhyolitic tephra (UBI-10-10B).

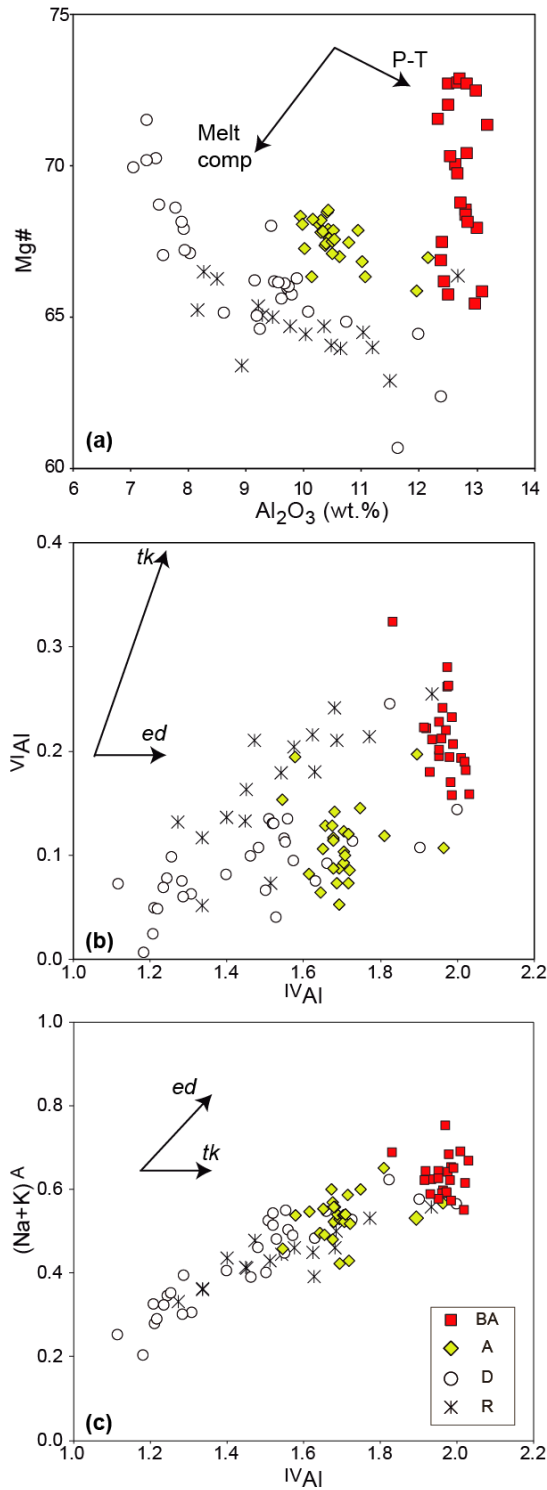
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994 **Figure 7.** Histograms of An contents for plagioclases derived from (a) basaltic andesites, (b) andesites, (c) dacites,  
 995 and (d) rhyolites. Rims (R) are differentiated from core and interior (C+I) compositions. Note the large An  
 996 variations, namely for plagioclase from the BA group, and the fact that most compositions in the BA (and  
 997 andesites) display An<sub>55-65</sub>, whereas the plagioclases in the dacites and rhyolites are generally between An<sub>35-50</sub>.

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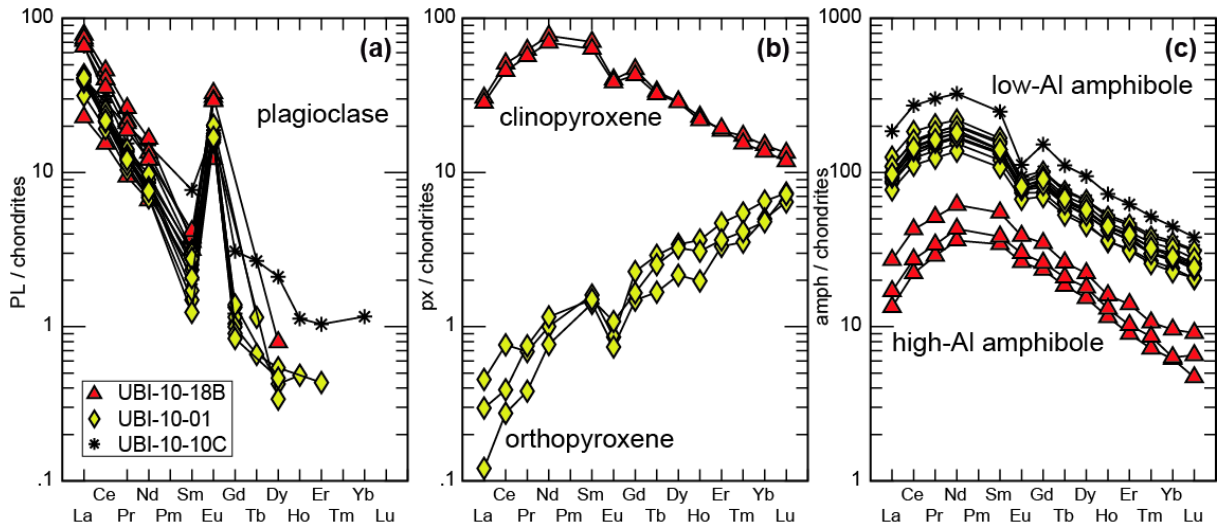
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1000 **Figure 8. (a)** Diagram showing the Al<sub>2</sub>O<sub>3</sub> and Mg# variations for Ubina's amphiboles. The vectors represent in a  
 1001 schematic way the effect of an increase in P-T as well as a variation of mafic to felsic magma chemistry (modified  
 1002 from Kiss et al., 2014). **(b)** <sup>VI</sup>Al vs. <sup>IV</sup>Al, and **(c)** <sup>IV</sup>Al vs. (Na+K)<sup>A</sup> showing the effect of edenite (*ed*) and  
 1003 tshermakite (*tk*) substitutions (after Poli and Schmidt, 1992).

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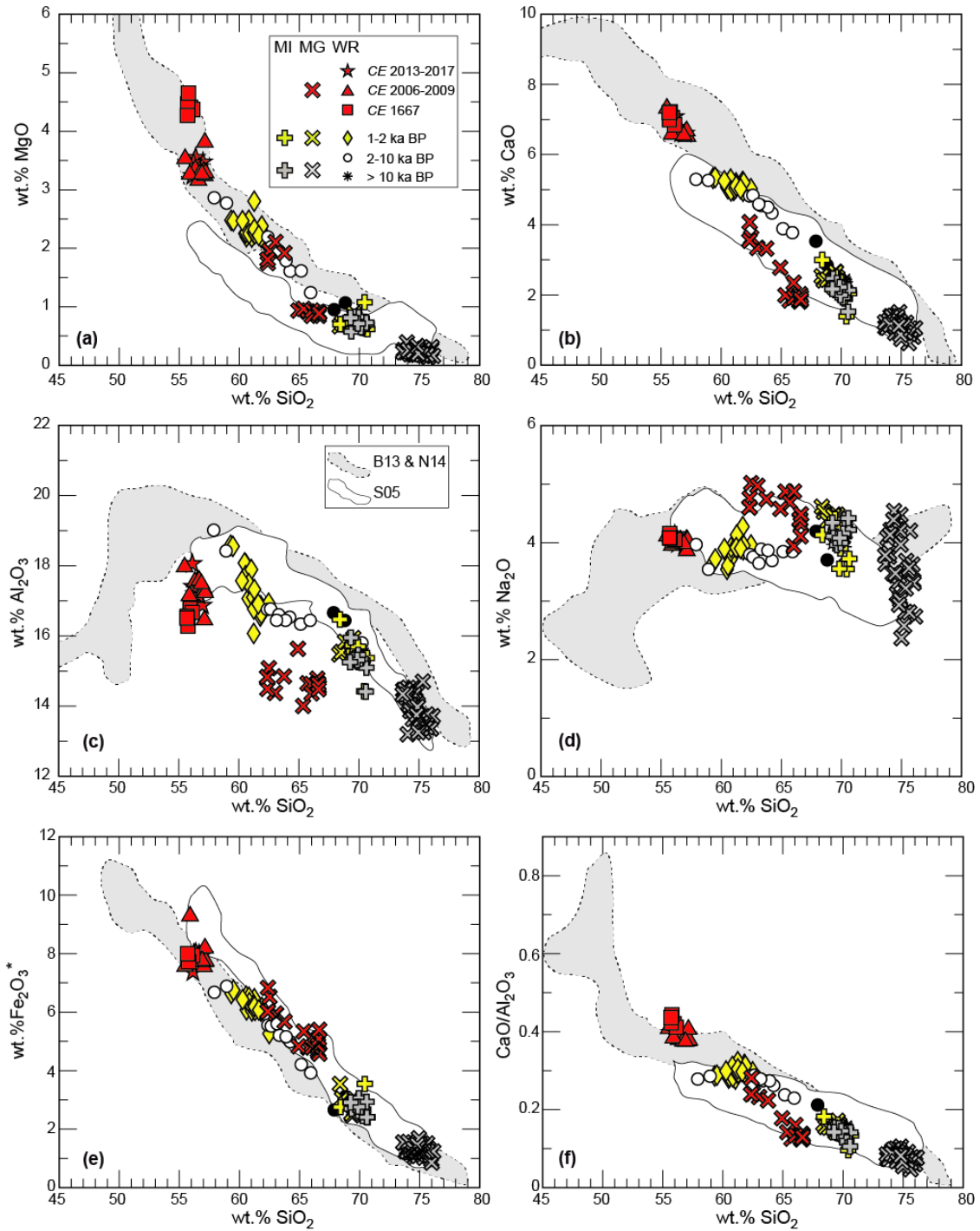




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1007 **Figure 9.** Rare earth element (REE) diagram for selected (a) plagioclase, (b) ortho and clinopyroxene, and (c)  
 1008 amphibole phenocrysts from Ubinas samples. Note that two populations exist for amphibole. Data normalized to  
 1009 chondrite values (Sun and McDonough, 1989). Data correspond to a basaltic andesite (UBI-10-18B), an andesite  
 1010 (UBI-10-01) and a rhyolite (UBI-10-10C).

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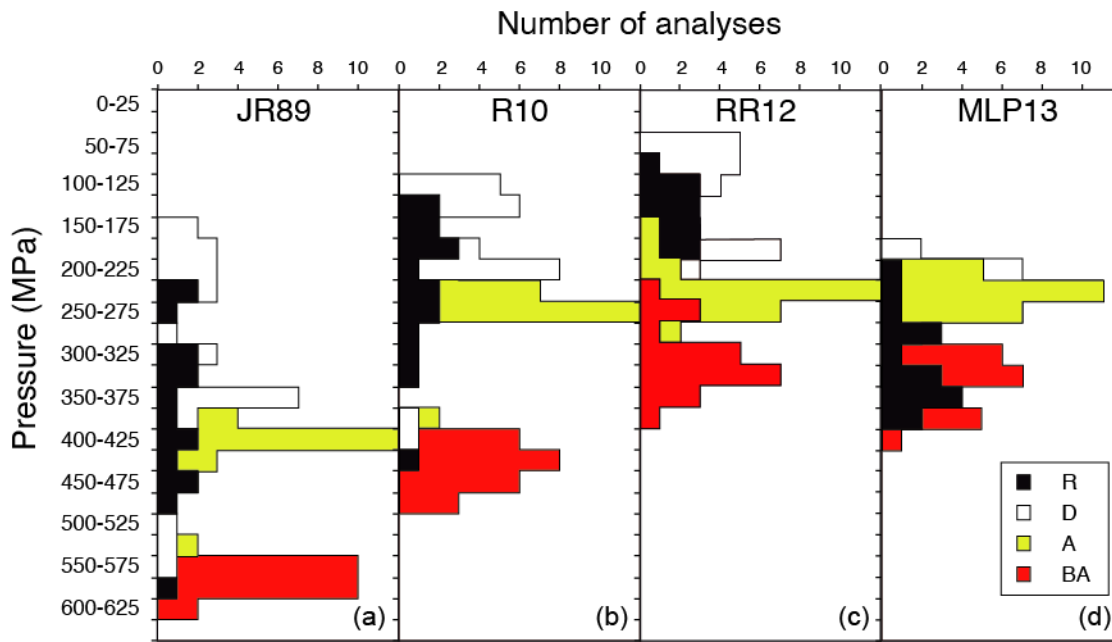
1013 **Figure 10.** MgO (a), CaO (b), Al<sub>2</sub>O<sub>3</sub> (c), Na<sub>2</sub>O (d), Fe<sub>2</sub>O<sub>3</sub>\* (e), CaO/Al<sub>2</sub>O<sub>3</sub> (f) as a function of silica for whole-  
 1014 rocks (WR), matrix glasses (MG) and melt inclusions (MI) of Ubina samples. The fields of experimentally  
 1015 determined liquid-line-of-descent compositions are shown for comparison (S05: Sisson et al., 2005; B13: Blatter  
 1016 et al., 2013; N14: Nandedkar et al., 2014).

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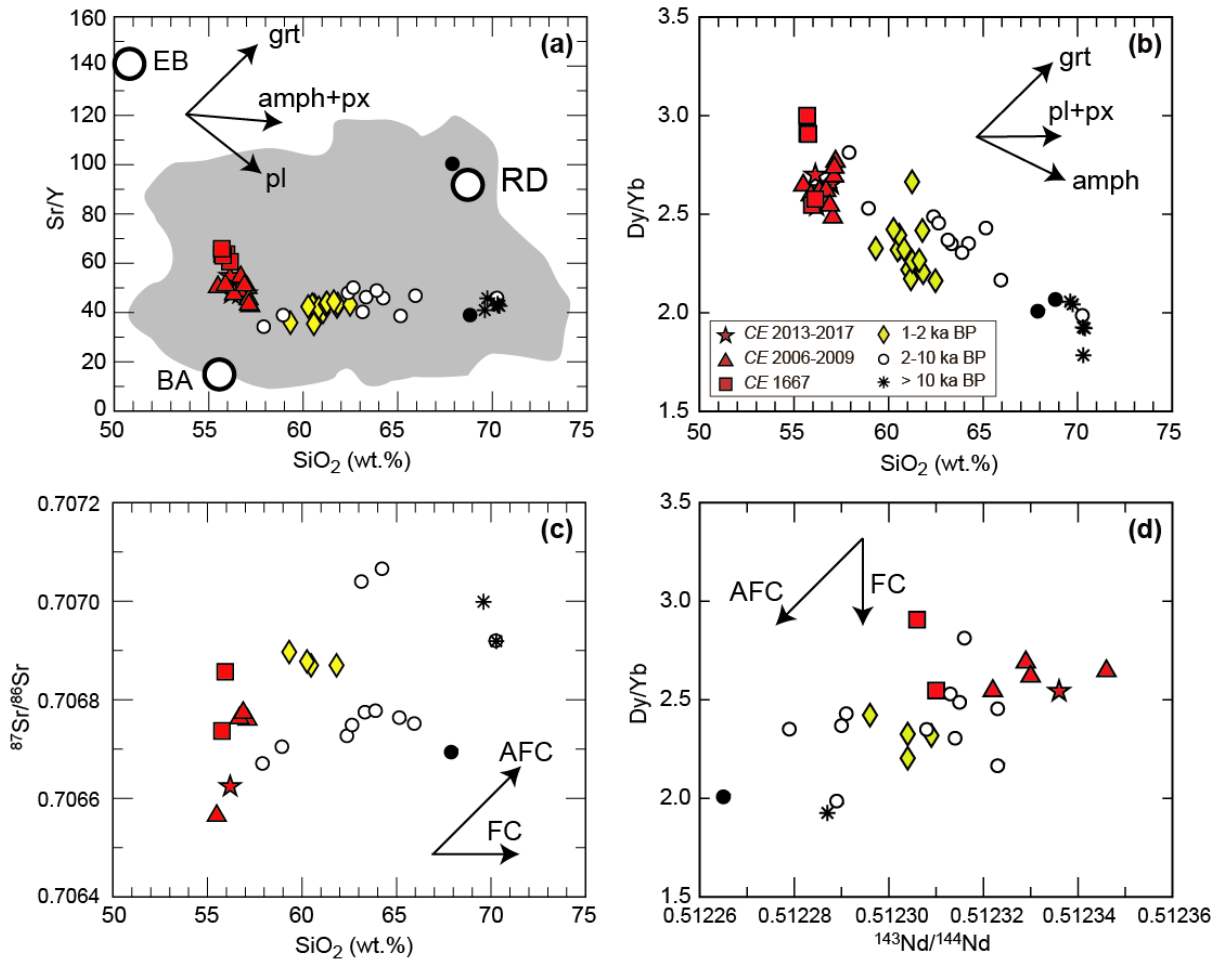
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1023 **Figure 11.** Histograms of amphibole crystallization pressure estimates for Ubina samples (BA: basic andesites;

1024 A: andesites; D: dacites; R: rhyolites). Different models have been tested (JR89: Johnson and Rutherford, 1989;

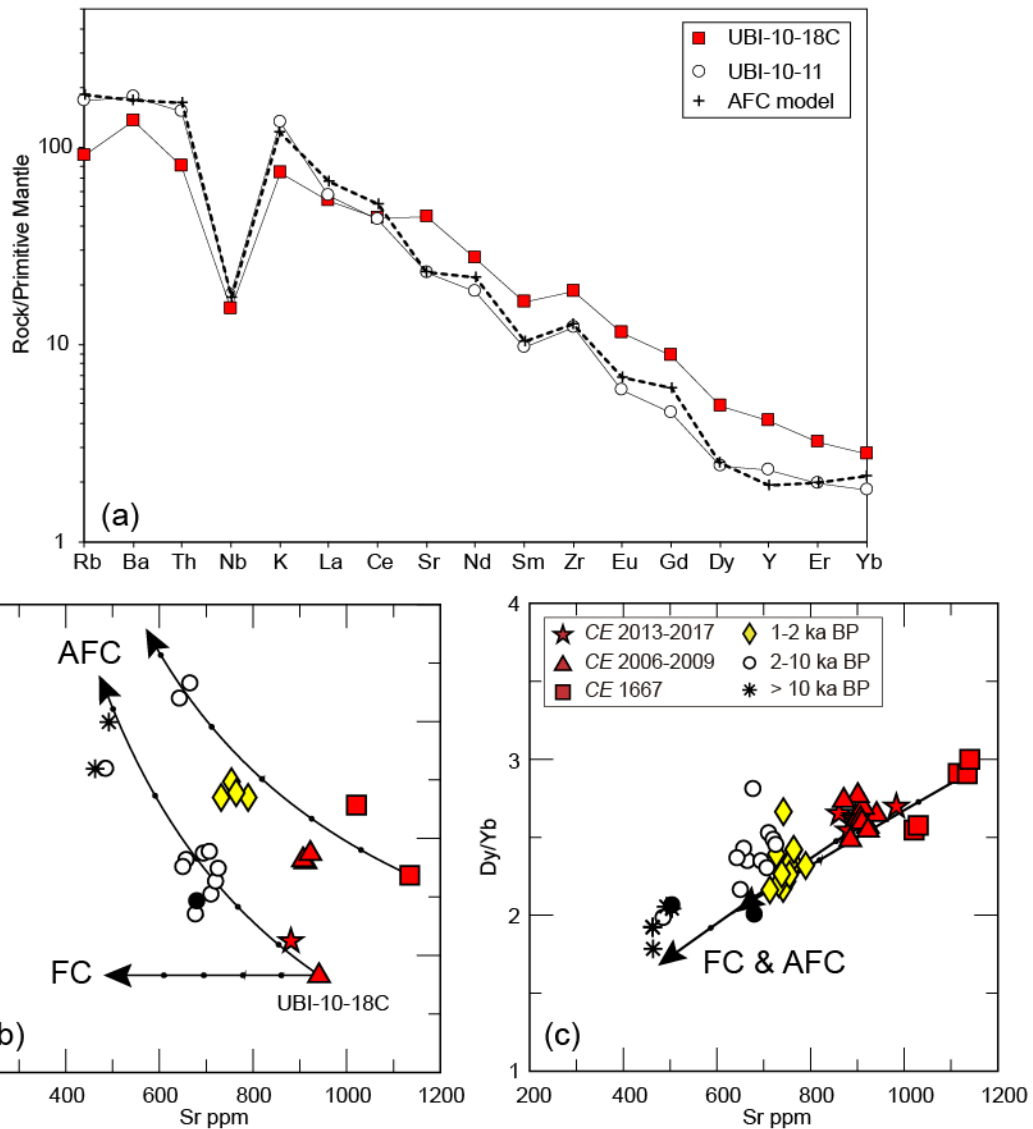
1025 R10: Ridolfi et al., 2010; RR12: Ridolfi and Renzulli, 2012; MLP: Médard and Le Pennec, 2013).





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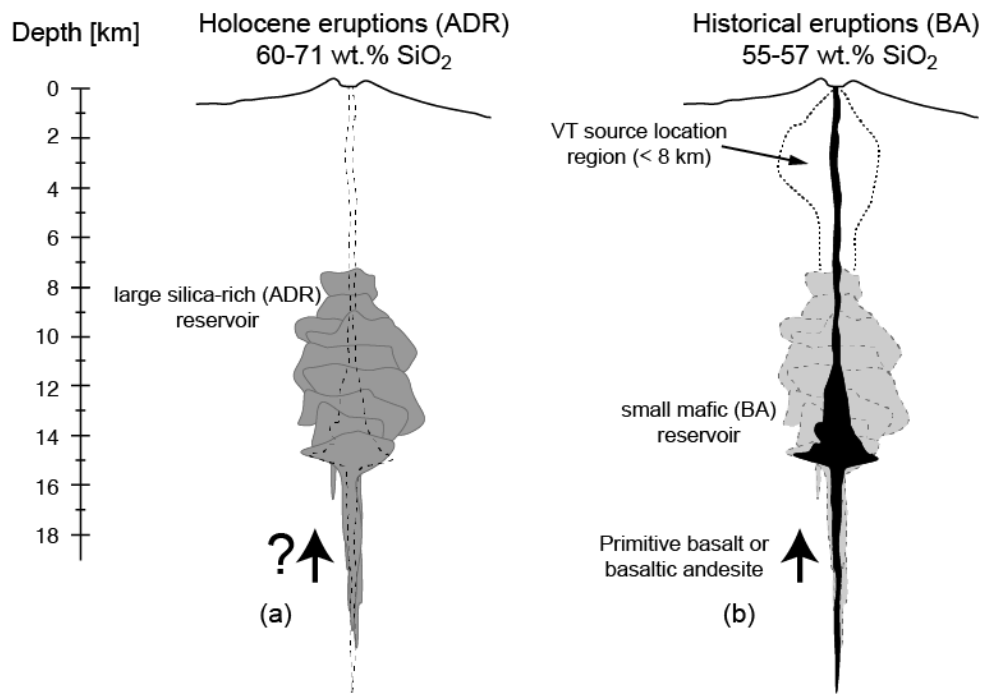
1027 **Figure 12.** (a, b, c) Sr/Y, Dy/Yb, and  $^{87}\text{Sr}/^{86}\text{Sr}$  vs. silica content. (d) Dy/Yb vs.  $^{143}\text{Nd}/^{144}\text{Nd}$ . The white circles  
 1028 labelled as “BA”, “EB” and “RD” correspond to the three end-members identified by Blum-Oeste and Wörner  
 1029 (2016). BA – calc-alkaline basaltic andesite, EB – shoshonitic enriched basalt, RD – crustal-derived rhyodacite.  
 1030 The grey field corresponds to the CVZ geochemical variation. The arrows in (a, b) show the expected effects of  
 1031 garnet, amphibole and plagioclase-pyroxene fractionation. Note that the only mineral able to efficiently fractionate  
 1032 MREE over HREE (i.e. Dy/Yb) is amphibole. The arrows in (c, d) correspond to theoretical trends for FC and  
 1033 AFC process. Symbols are the same as in Fig. 3.



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1035 **Figure 13.** Results of the geochemical modelling. (a) Multi-element diagram normalized to Primitive Mantle (Sun  
 1036 and McDonough, 1989) for the mafic (UBI-10-18C) and silica-rich (UBI-10-11) end-members, as well as an AFC  
 1037 model. (b) Sr vs.  $^{87}\text{Sr}/^{86}\text{Sr}$  diagrams showing the Ubinas samples as well as the AFC and FC models from two  
 1038 mafic end-members (UBI-10-18C and UBI-99-10). (c) Sr vs. Dy/Yb diagram for Ubinas sampled and the two AFC  
 1039 models. The fractionating phases for both models (FC and AFC) are 46% Pl + 44% Amph + 3% Cpx + 6% Mag +  
 1040 1% Apt, and the assimilation/fractional crystallization rate ( $r$ ) = 0.04. Partition coefficients were compiled by  
 1041 Rivera et al. (2017) and correspond to intermediate to acid liquids. Note that in (a) and (c) AFC and FC models  
 1042 display almost the same values due to fact that trace elements are slightly modified by the very low degrees of  
 1043 crustal assimilation, whereas in (b) we clearly show that assimilation is needed for explain the Sr isotopic variation.  
 1044 Symbols are the same as in in Fig. 3.

1045



1046

1047 **Figure 14.** Reconstruction of the magmatic plumbing system beneath Ubinas volcano for (a) the ADR group (post  
 1048 glacial and Holocene), and (b) the BA group (Historical and recent eruptions). The volcano-tectonic (VT) seismic  
 1049 source location comes from Machacca-Puma et al. (2019).

1050

Table 1. Whole-rock major, trace elements and Sr-Nd-Pb isotopes for the Ubinas

Sample No.	UBI-10-10A	UBI-10-10B	UBI-10-10C	UBI-10-11	UBI-10-07	UBI-10-12	UBI-10-13	UBI-10-14	UBI-10-15	UBI-10-08	UBI-10-16	UBI-10-09	UBI-10-05	UBI-10-01A	UBI-10-01B	UBI-10-02
Estimated Age / Volcanic unit	>10 ka	>10 ka	>10 ka	2-10 ka	2-10 ka	2-10 ka	2-10 ka	2-10 ka	2-10 ka	2-10 ka	2-10 ka	2-10 ka	2-10 ka	1-2 ka	1-2 ka	1-2 ka
Stratigraphic position	1	1	1	2	3	4	5	6	7	7	8	9	10	10	11	11
SiO <sub>2</sub> (wt%)	66.80	66.32	66.99	66.78	61.30	61.85	60.19	62.78	65.30	64.88	61.75	55.61	53.24	59.30	59.61	59.59
TiO <sub>2</sub>	0.33	0.33	0.31	0.35	0.75	0.67	0.74	0.53	0.35	0.36	0.64	1.03	1.06	0.84	0.88	0.76
Al <sub>2</sub> O <sub>3</sub>	14.69	14.62	14.77	15.02	15.97	15.52	16.11	15.66	16.03	15.50	15.89	17.38	17.48	16.28	16.32	16.15
Fe <sub>2</sub> O <sub>3</sub>	2.34	2.31	2.28	2.54	5.44	4.99	5.31	3.73	2.56	2.94	4.79	6.50	6.14	5.84	6.03	5.02
MnO	0.07	0.07	0.07	0.07	0.09	0.10	0.10	0.08	0.05	0.09	0.09	0.11	0.08	0.10	0.10	0.09
K <sub>2</sub> O	3.89	4.00	3.90	3.84	3.35	3.16	3.11	3.74	3.39	3.13	3.40	2.44	2.35	2.84	2.99	2.85
CaO	2.33	2.29	2.26	2.26	4.45	4.36	4.65	3.59	3.40	2.68	4.17	4.97	4.87	4.84	4.97	4.79
Na <sub>2</sub> O	3.86	3.71	3.89	3.46	3.54	3.74	3.61	3.66	4.03	3.49	3.55	3.34	3.65	3.75	3.81	3.78
K <sub>2</sub> O	3.89	4.00	3.90	3.84	3.35	3.16	3.11	3.74	3.39	3.13	3.40	2.44	2.35	2.84	2.99	2.85
P <sub>2</sub> O <sub>5</sub>	0.12	0.12	0.11	0.12	0.32	0.29	0.33	0.26	0.16	0.20	0.31	0.37	0.44	0.32	0.35	0.33
LOI**	3.87	3.87	3.75	4.57	2.57	2.54	3.13	3.80	2.97	4.84	2.85	5.39	8.45	3.23	1.94	4.35
Total	98.89	98.24	98.94	99.63	99.66	99.36	99.21	99.02	99.16	99.11	98.99	99.76	100.39	99.48	99.48	99.73
Sc (ppm)	2.88	2.74	2.69	3.17	7.53	6.73	7.37	4.79	4.28	5.63	6.63	10.55	8.93	7.98	8.33	7.88
V	26.42	25.62	25.33	30.37	95.58	81.20	92.35	60.01	50.32	38.74	79.79	125.32	120.61	103.26	108.08	84.78
Cr	1.09	1.20	1.02	3.06	4.36	3.95	9.24	5.65	5.63	7.26	3.28	23.47	18.55	3.54	4.93	4.09
Co	3.64	3.25	3.36	2.18	12.83	10.16	11.50	6.92	6.61	6.10	9.98	17.74	18.45	12.26	13.34	10.60
Ni	0.60	0.45	0.00	2.45	3.51	3.74	5.90	2.99	7.23	4.15	2.48	16.82	15.36	2.42	3.32	2.72
Nb	93.50	88.24	90.71	109.81	99.09	83.17	79.81	107.79	84.68	71.61	94.67	65.13	55.10	79.32	87.03	89.67
Sr	463.36	462.58	462.90	484.95	642.78	706.67	725.53	650.03	679.59	503.43	664.96	710.14	676.78	738.37	755.05	713.07
Y	10.78	10.61	10.83	10.56	15.96	14.44	14.47	13.87	6.77	12.91	14.50	18.22	19.74	16.60	17.17	16.47
Zr	130.28	131.26	130.73	136.74	127.04	99.13	111.85	162.32	49.91	80.58	107.47	223.48	256.67	232.57	232.41	235.46
Nb	11.57	11.81	11.22	12.95	8.28	10.74	11.74	4.82	10.70	11.22	10.95	12.19	13.15	11.01	11.60	10.88
Ba	1186.54	1172.69	1181.56	1263.81	1087.45	1143.87	1150.38	1235.08	971.02	1144.00	1107.36	933.40	968.40	1113.09	1111.79	1113.35
La	30.17	28.32	31.64	38.89	40.23	40.02	38.34	45.45	17.42	35.77	40.25	46.31	43.35	38.42	39.86	39.01
Ce	65.38	62.76	68.09	77.02	80.18	78.20	77.96	84.48	38.45	71.02	80.61	83.45	73.55	75.89	78.45	76.02
Nd	20.71	20.13	21.47	25.04	32.81	31.87	32.06	33.09	13.50	27.31	31.92	38.34	47.35	32.70	33.95	33.08
Sm	4.19	3.99	3.91	4.31	5.93	5.79	5.83	5.70	2.62	4.78	5.93	6.76	8.25	6.04	6.37	6.11
Eu	0.86	0.91	0.90	0.99	1.42	1.42	1.44	1.28	0.78	1.08	1.26	1.70	1.80	1.56	1.64	1.43
Gd	2.53	2.72	2.87	2.67	4.28	3.78	3.98	3.66	1.81	3.17	4.17	4.86	6.06	4.09	4.38	4.40
Dy	1.71	1.80	1.83	1.79	2.91	2.60	2.66	2.45	1.16	2.25	2.69	3.45	3.68	3.04	3.16	2.91
Er	0.84	0.84	0.89	0.95	1.64	1.35	1.32	1.21	0.53	1.08	1.29	1.51	1.30	1.42	1.57	1.52
Yb	0.96	0.93	0.96	0.90	1.23	1.13	1.08	1.13	0.58	1.09	1.14	1.36	1.31	1.34	1.40	1.35
Th	12.35	11.70	12.10	12.88	9.87	9.05	8.95	12.44	6.71	5.84	10.05	10.62	10.65	8.75	8.60	9.20
<sup>87</sup> Sr/ <sup>86</sup> Sr	0.706919		0.706920	0.706920	0.706778	0.706749	0.706752	0.706684		0.707066	0.706705	0.706671		0.706800		
±	0.000006		0.000006	0.000006	0.000009	0.000006	0.000005	0.000007		0.000005	0.000007	0.000005		0.000005		
<sup>143</sup> Nd/ <sup>142</sup> Nd	0.512287		0.512289	0.512290	0.512234	0.512243	0.512233	0.512205		0.512279	0.512213	0.512216		0.512213		
±	0.000005		0.000005	0.000005	0.000004	0.000005	0.000007	0.000004		0.000004	0.000008	0.000005		0.000005		
<sup>206</sup> Pb/ <sup>204</sup> Pb	18.1871		18.1695	18.1487	18.2257	18.2210	18.2139	18.1764		18.1514	18.1465	18.2045		18.2045		
±	0.0007		0.0007	0.0004	0.0009	0.0003	0.0007	0.0006		0.0003	0.0006	0.0004		0.0004		
<sup>207</sup> Pb/ <sup>204</sup> Pb	15.0141		15.0137	15.0107	15.0109	15.0109	15.0109	15.0150		15.0113	15.0096	15.0117		15.0117		
±	0.0007		0.0007	0.0004	0.0008	0.0003	0.0006	0.0006		0.0003	0.0006	0.0003		0.0003		
<sup>208</sup> Pb/ <sup>204</sup> Pb	38.5961		38.6136	38.5601	38.5764	38.5720	38.5660	38.6486		38.5681	38.5708	38.5781		38.5781		
±	0.0019		0.0017	0.0010	0.0022	0.0009	0.0017	0.0017		0.0008	0.0017	0.0008		0.0008		

Table 1. Continued

Sample No.	UBI-10-03	UBI-10-04	UBI-10-05	UBI-14-01A	UBI-10-06	UBI-14-01C	UBI-14-01B	UBI-10-19	UBI-10-20	UBI-10-18A	UBI-10-18B	UBI-10-18C	UBI-14-12	UBI-14-04	UBI-14-03	UBI-15-14	UBI-15-01
Estimated Age / Volcanic unit	1-2 ka	1-2 ka	1-2 ka	1-2 ka	1-2 ka	1-2 ka	1-2 ka	1667 CE	2006-2009 CE	2006-2009 CE	2006-2009 CE	2006-2009 CE	2014-2015 CE	2014-2015 CE	2014-2015 CE	2014-2015 CE	2014-2015 CE
Stratigraphic position	11	11	11	11	12	12	12	13	14	14	14	14	15	15	15	15	15
SiO <sub>2</sub> (wt%)	59.60	58.96	58.64	58.31	57.73	57.66	56.91	55.55	56.19	56.77	56.54	55.40	56.12	55.85	54.70	55.57	55.88
TiO <sub>2</sub>	0.84	0.86	0.87	0.84	0.88	0.87	0.83	1.28	1.18	1.16	1.13	1.23	1.23	1.17	1.12	1.19	1.17
Al <sub>2</sub> O <sub>3</sub>	16.25	16.48	16.86	17.09	16.89	17.24	16.95	16.66	17.59	17.27	17.56	17.93	17.38	16.91	17.60	16.96	16.55
Fe <sub>2</sub> O <sub>3</sub>	5.83	6.01	6.10	5.77	6.24	6.15	5.71	7.74	7.98	7.51	7.92	7.55	7.98	7.87	7.18	7.91	7.81
MnO	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.11	0.12	0.11	0.12	0.11	0.12	0.11	0.11	0.11	0.11
K <sub>2</sub> O	2.11	2.19	2.17	2.09	2.17	2.15	2.06	4.38	3.34	3.30	3.16	3.52	3.46	3.34	3.16	3.50	3.41
CaO	4.78	4.85	4.79	4.76	4.79	4.84	4.87	7.00	6.65	6.50	6.68	7.30	6.72	6.57	6.89	6.62	6.47
Na <sub>2</sub> O	3.74	3.79	3.78	3.63	3.44	3.38	3.54	4.00	4.04	4.00	4.04	4.10	4.00	3.97	4.03	3.92	3.88
K <sub>2</sub> O	2.85	2.79	2.81	2.59	2.73	2.60	2.61	2.13	2.28	2.49	2.28	2.24	2.34	2.41	2.24	2.31	2.34
P <sub>2</sub> O <sub>5</sub>	0.32	0.34	0.30	0.35	0.36	0.36	0.34	0.45	0.47	0.41	0.48	0.44	0.48	0.45	0.45	0.46	0.45
LOI**	3.35	3.52	2.98	4.62	4.51	3.98	4.46	-0.09	-0.15	-0.03	-0.15	-0.25	-0.25	-0.12	-0.23	-0.31	-0.21
Total	99.75	99.89	99.40	100.14	99.84	99.32	98.39	99.21	99.59	99.49	99.76	99.58	99.62	98.48	97.23	98.27	97.87
Sc (ppm)	7.87	8.19	8.22	7.20	8.94	7.18	7.30	15.55	11.39	12.25	10.43	13.33	11.50	10.79	10.52	11.03	10.83
V	101.89	105.89	107.97	98.22	107.29	108.76	99.54	184.74	160.59	164.53	153.42	168.68	159.06	166.34	155.41	161.42	157.42
Cr	3.39	3.73	4.04	6.06	4.33	6.73	6.49	109.94	14.41	21.10	9.86	27.55	14.41	16.06	14.72		



**Table 6.** Matrix glass composition (average  $\pm$  standard deviation) for Ubina samples

Sample	UBI-10-10B	UBI-10-10C	UBI-10-12	UBI-10-14	UBI-10-07	UBI-10-01	UBI-10-19A	UBI-10-18C	UBI-10-18B
Age	>10 ka	>10 ka	2-10 ka	2-10 ka	2-10 ka	1-2 ka	1667 CE	2006 CE	2006 CE
No. Analyses	6	8	6	6	12	13	5	11	3
SiO <sub>2</sub> (wt.%)	71.6 $\pm$ 0.4	71.4 $\pm$ 0.6	73.0 $\pm$ 0.7	70.8 $\pm$ 0.3	71.9 $\pm$ 0.6	66.9 $\pm$ 1.4	62.4 $\pm$ 0.8	65.7 $\pm$ 1.2	69.1 $\pm$ 1.4
TiO <sub>2</sub>	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.3 $\pm$ 0.1	0.5 $\pm$ 0.1	1.8 $\pm$ 0.2	1.6 $\pm$ 0.2	0.7 $\pm$ 0.3
Al <sub>2</sub> O <sub>3</sub>	13.8 $\pm$ 0.2	13.4 $\pm$ 0.3	13.0 $\pm$ 0.2	13.7 $\pm$ 0.2	13.1 $\pm$ 0.3	15.0 $\pm$ 0.4	14.6 $\pm$ 0.3	14.5 $\pm$ 0.5	14.7 $\pm$ 0.3
FeO*	1.1 $\pm$ 0.1	1.1 $\pm$ 0.1	1.0 $\pm$ 0.2	1.2 $\pm$ 0.1	1.2 $\pm$ 0.1	2.4 $\pm$ 0.3	5.5 $\pm$ 0.4	4.4 $\pm$ 0.3	2.4 $\pm$ 0.3
MnO	0.1 $\pm$ 0.1	0.1 $\pm$ 0.1	0.1 $\pm$ 0.05	0.05 $\pm$ 0.05	0.1 $\pm$ 0.05	0.1 $\pm$ 0.1	0.2 $\pm$ 0.1	0.1 $\pm$ 0.1	0.05 $\pm$ 0.05
MgO	0.2 $\pm$ 0.05	0.2 $\pm$ 0.05	0.2 $\pm$ 0.1	0.2 $\pm$ 0.1	0.2 $\pm$ 0.05	0.7 $\pm$ 0.1	1.9 $\pm$ 0.1	0.9 $\pm$ 0.05	0.3 $\pm$ 0.2
CaO	1.3 $\pm$ 0.1	1.2 $\pm$ 0.1	0.9 $\pm$ 0.2	1.1 $\pm$ 0.1	1.0 $\pm$ 0.1	2.9 $\pm$ 0.8	3.6 $\pm$ 0.3	2.0 $\pm$ 0.3	5.4 $\pm$ 1.5
Na <sub>2</sub> O	3.4 $\pm$ 0.6	4.1 $\pm$ 0.1	3.3 $\pm$ 0.3	3.7 $\pm$ 0.2	3.1 $\pm$ 0.5	3.7 $\pm$ 0.9	4.8 $\pm$ 0.2	4.4 $\pm$ 0.3	1.1 $\pm$ 0.8
K <sub>2</sub> O	4.1 $\pm$ 0.3	3.8 $\pm$ 0.1	4.6 $\pm$ 0.3	4.7 $\pm$ 0.2	5.1 $\pm$ 0.3	4.0 $\pm$ 0.4	4.0 $\pm$ 0.4	5.2 $\pm$ 0.3	3.6 $\pm$ 0.7
Total	95,8	95,4	96,2	95,8	96,0	96,3	98,7	98,9	97,2

\* all iron as FeO

1062

**Table 6.** Matrix glass composition (average  $\pm$  standard deviation) for Ubina samples.

	BA	A	D	R	Method
T [°C]	884 $\pm$ 23 (13)	881 $\pm$ 5 (6)	787 $\pm$ 11 (5)	813 $\pm$ 5 (8)	PI-melt, Putirka (2008)
	-	-	879 $\pm$ 4 (9)	849 $\pm$ 3 (2)	Mag-Ilm, Lindsley and Spencer (1982)
	-	913 $\pm$ 13 (15)	881 $\pm$ 36 (21)	846 $\pm$ 30 (12)	Hb-PI, Holland and Blundy (1994)
	994 $\pm$ 9 (23)	933 $\pm$ 16 (26)	880 $\pm$ 35 (29)	894 $\pm$ 37 (16)	Al <sup>T</sup> in amph, Ridolfi et al. (2010)
	993 $\pm$ 24 (8)	-	-	-	Two-pyroxenes, Putirka (2008)
P [MPa]	583 $\pm$ 17 (23)	426 $\pm$ 40 (26)	318 $\pm$ 109 (29)	385 $\pm$ 95 (16)	Al-in-hb, Johnson and Rutherford (1989)
	453 $\pm$ 26 (23)	267 $\pm$ 42 (26)	197 $\pm$ 81 (29)	242 $\pm$ 84 (16)	Al <sup>T</sup> in amph, Ridolfi et al. (2010)
	357 $\pm$ 138 (23)	218 $\pm$ 26 (26)	145 $\pm$ 63 (29)	161 $\pm$ 51 (16)	Al <sup>T</sup> in amph, Ridolfi and Renzulli (2012)
	341 $\pm$ 35 (23)	246 $\pm$ 28 (26)	241 $\pm$ 31 (29)	316 $\pm$ 51 (16)	Al <sup>VI</sup> in amph, Medard and Le Pennec (2019)
H <sub>2</sub> O [wt.%]	5.0 $\pm$ 0.3 (23)	4.3 $\pm$ 0.3 (26)	4.6 $\pm$ 0.3 (29)	5.3 $\pm$ 0.4 (16)	Al <sup>T</sup> in amph, Ridolfi and Renzulli (2012)

1064

**Table 7.** T-P-H<sub>2</sub>O conditions for Ubina magmas.**Supplementary material 1.** Samples location for Ubina volcano

Sample No.	Estimated Age	Stratigraphic position	UTM North*	UTM East*	Altitude**	Locality	Observations
UBI-10-10A	< 10 ka	1	8184760	300284	3646	Sacuhaya	Pumice on tephra fallout deposit
UBI-10-10B	< 10 ka	1	8184760	300284	3646	Sacuhaya	Pumice on tephra fallout deposit
UBI-10-10C	< 10 ka	1	8184760	300284	3646	Sacuhaya	Pumice on tephra fallout deposit
UBI-10-11	2-10 ka	2	8184760	300284	3646	Sacuhaya	Pumice on tephra fallout deposit
UBI-10-07	2-10 ka	3	8187865	302316	3552	Qda. Infiernillos	Pumice on tephra fallout deposit
UBI-10-12	2-10 ka	4	8184760	300284	3646	Sacuhaya	Pumice on tephra fallout deposit
UBI-10-13	2-10 ka	5	8184760	300284	3646	Sacuhaya	Pumice on tephra fallout deposit
UBI-10-14	2-10 ka	6	8184760	300284	3646	Sacuhaya	Pumice on tephra fallout deposit
UBI-10-15	2-10 ka	7	8184760	300284	3646	Sacuhaya	Pumice on tephra fallout deposit
UBI-10-08	2-10 ka	7	8187865	302316	3552	Qda. Infiernillos	Pumice on tephra fallout deposit
UBI-10-16	2-10 ka	8	8184760	300284	3646	Sacuhaya	Pumice on tephra fallout deposit
UBI-10-09	2-10 ka	9	8187865	302316	3552	Corohuayo	Pumice on tephra fallout deposit
UBI-13-05	2-10 ka	10				Qda. Infiernillos	Pumice on tephra fallout deposit
UBI-10-01A	1-2 ka	11	8188321	301606	3498	Qda. Infiernillos	Pumice on tephra fallout deposit
UBI-10-01B	1-2 ka	11	8188321	301606	3498	Qda. Infiernillos	Pumice on tephra fallout deposit
UBI-10-02	1-2 ka	11	8188321	301606	3498	Qda. Infiernillos	Pumice on tephra fallout deposit
UBI-10-03	1-2 ka	11	8188321	301606	3498	Qda. Infiernillos	Pumice on tephra fallout deposit
UBI-10-04	1-2 ka	11	8188321	301606	3498	Qda. Infiernillos	Pumice on tephra fallout deposit
UBI-10-05	1-2 ka	11	8188321	301606	3498	Qda. Infiernillos	Pumice on tephra fallout deposit
UBI-14-01A	1-2 ka	11	8191605	301958	4065	Ubina-Para road	Pumice on tephra fallout deposit
UBI-10-06	1-2 ka	12	8188321	301606	3498	Qda. Infiernillos	Pumice on tephra fallout deposit
UBI-14-01C	1-2 ka	12	8191605	301958	4065	Ubina-Para road	Pumice on tephra fallout deposit
UBI-14-01B	1-2 ka	12	8191605	301958	4065	Ubina-Para road	Pumice on tephra fallout deposit
UBI-10-19	1667 CE	13	8192554	296907	5432	Upper flank	lava block on PDC
UBI-10-20	2006-2009 CE	14				Upper flank	Ballistic block
UBI-10-18A	2006-2009 CE	14	8192025	296976	5407	Caldera inside	Ballistic block
UBI-10-18B	2006-2009 CE	14	8192025	296976	5407	Caldera inside	Ballistic block
UBI-10-18C	2006-2009 CE	14	8192025	296976	5407	Caldera inside	Ballistic block
UBI-14-12	2014-2015 CE	15				Upper flank	Ballistic block
UBI-14-04	2014-2015 CE	15				Upper flank	Ballistic block
UBI-14-03	2014-2015 CE	15				Upper flank	Ballistic block
UBI-15-14	2014-2015 CE	15				Upper flank	Ballistic block
UBI-15-02	2014-2015 CE	15				Upper flank	Ballistic block

\* WGS84

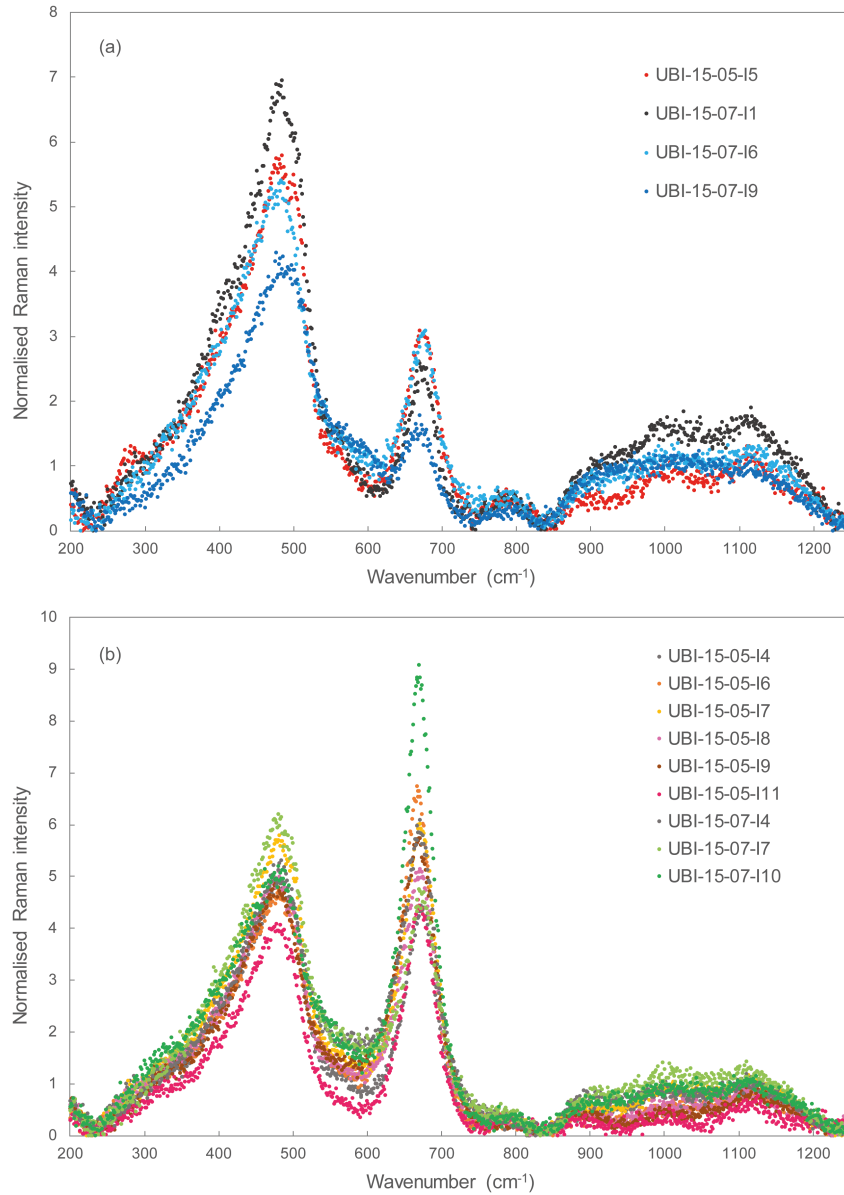
\*\* meters above sea level

1066

1067 **Supplementary material 1.** Samples location for Ubinas volcano.

1068

1069 **Supplementary material 2.** Mineral composition for Ubinas samples.



1070

1071 **Supplementary material 3.** Raman spectra showing the glass bands in the aluminosilicate network domain. The

1072 intense peak at  $\sim 670 \text{ cm}^{-1}$  indicates the presence of magnetite nanolites dispersed in the glass. **(a)** Spectra of

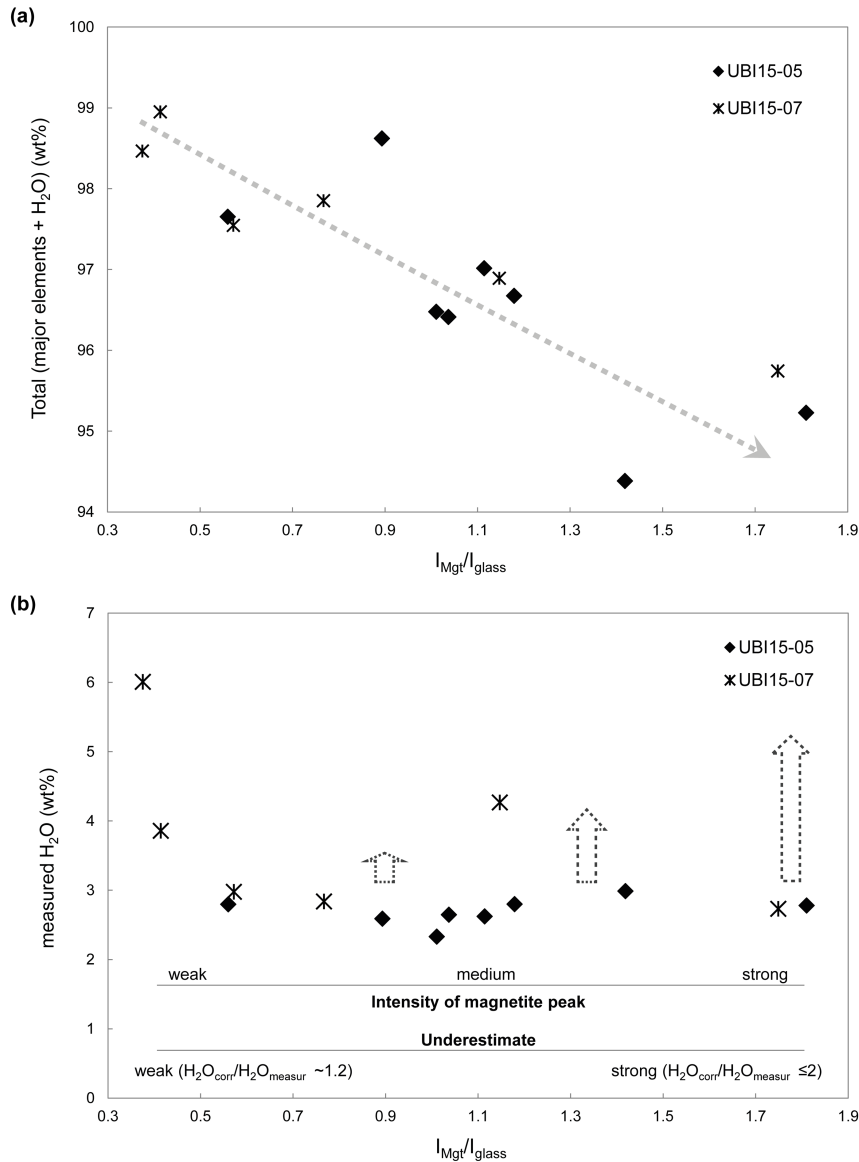
1073 selected inclusions only slightly affected by the presence of magnetite (intensity ratios of magnetite peak to glass

1074 band ranging from 0.4 to 0.6). **(b)** Spectra of glass inclusions strongly affected by the presence of magnetite

1075 (intensity ratios from 0.6 to 1.8). Signal intensity is normalized to acquisition time and laser power.

1076

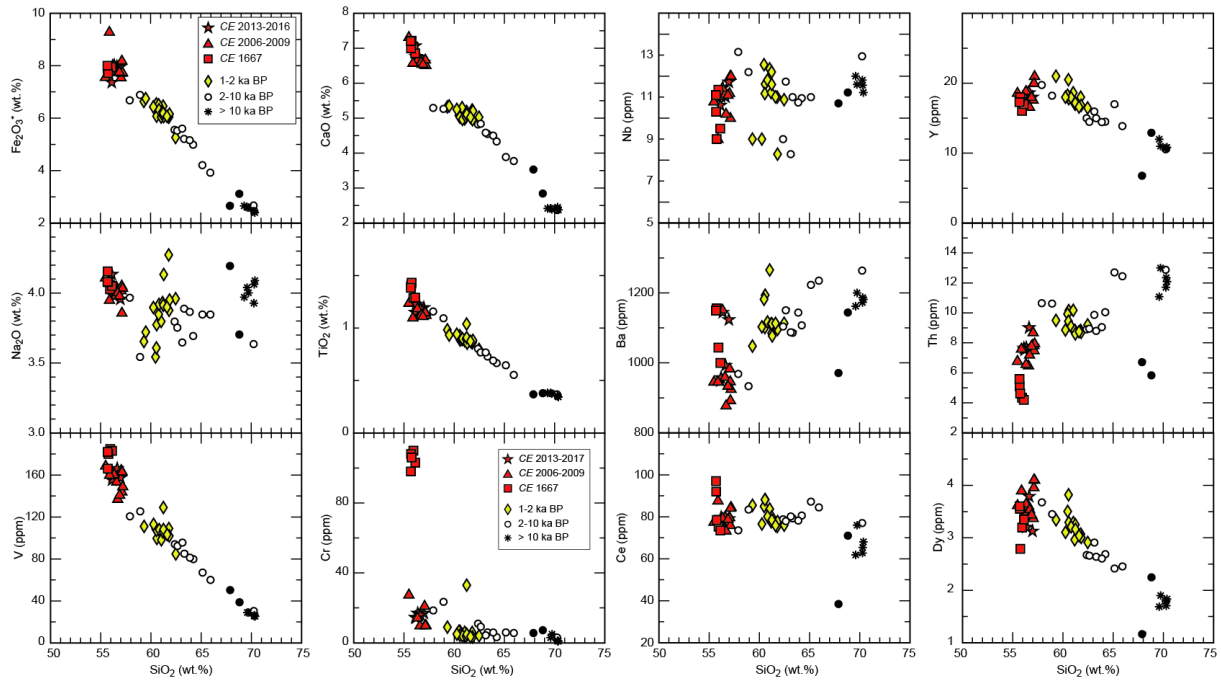
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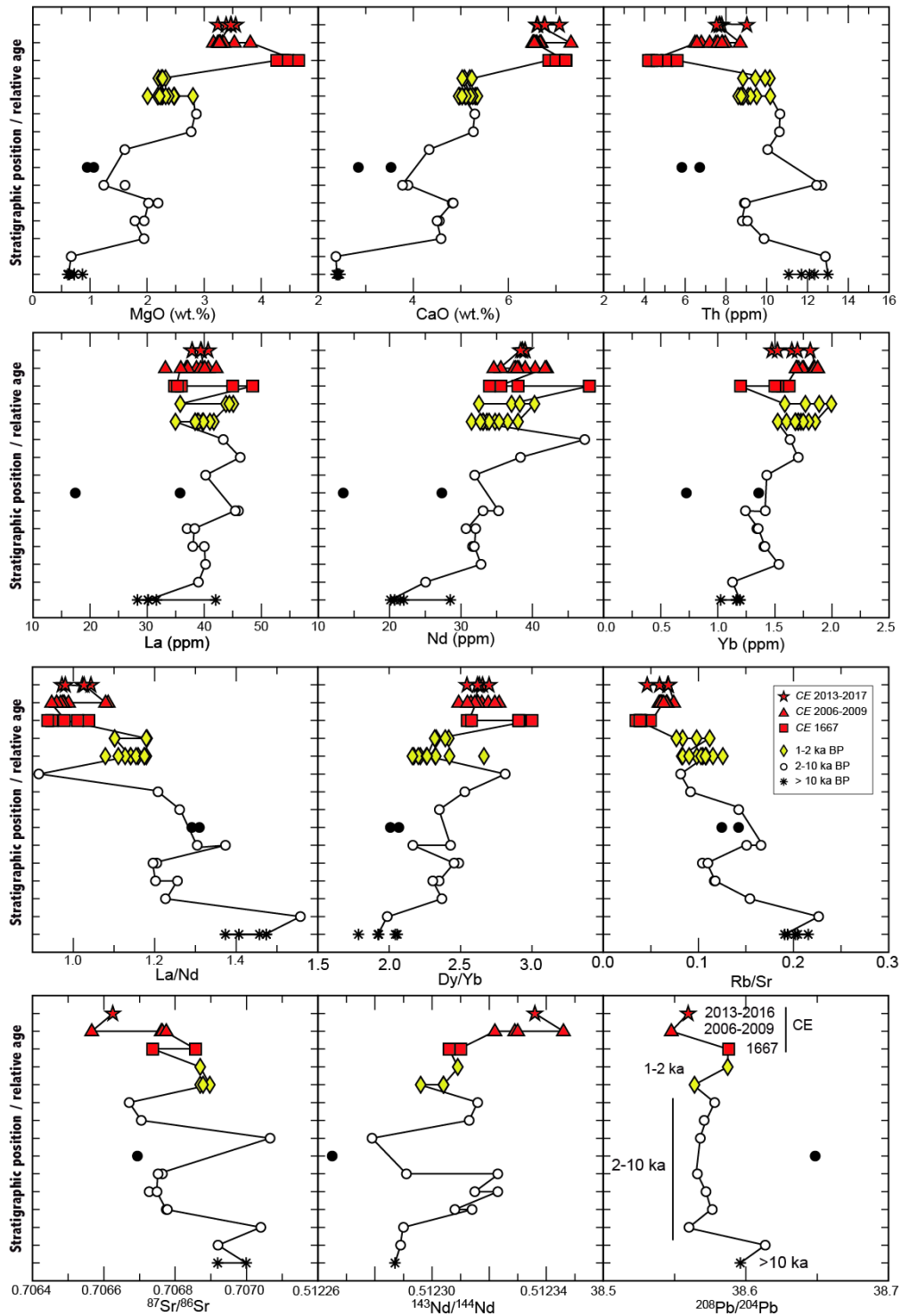
1079 **Supplementary material 4.** Effect of the presence of magnetite nanolites on the quantification of water in glass  
 1080 inclusions by Raman spectroscopy.  $I_{Mgt}/I_{glass}$  is the ratio of the intensity of the main Raman peak of magnetite to  
 1081 the intensity of the principal Raman band of the glass. **(a)** Plot of  $I_{Mgt}/I_{glass}$  versus the totals calculated as the sum  
 1082 of all major elements measured by electron microprobe and H<sub>2</sub>O values measured by Raman spectroscopy. A  
 1083 negative correlation is observed, indicating that the measured water content is more accurate for inclusions weakly  
 1084 affected by the presence of magnetite (low  $I_{Mgt}/I_{glass}$ ) and that low totals are due to underestimate of the water  
 1085 contents for high  $I_{Mgt}/I_{glass}$ . **(b)** Plot of  $I_{Mgt}/I_{glass}$  versus the measured water contents. For low  $I_{Mgt}/I_{glass}$ , the measured  
 1086 water contents are not or weakly underestimated, whereas they deviate progressively from the correct contents as  
 1087 the  $I_{Mgt}/I_{glass}$  ratio increases. The three dashed arrows indicate the approximate extent of the correction needed to  
 1088 obtain the true water contents.





1089

1090 **Supplementary material 5.** Binary diagrams of the Ubina magmatic series, showing major ( $\text{Fe}_2\text{O}_3^*$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  
 1091  $\text{TiO}_2$ ) and trace elements ( $\text{V}$ ,  $\text{Cr}$ ,  $\text{Nb}$ ,  $\text{Y}$ ,  $\text{Ba}$ ,  $\text{Th}$ ,  $\text{Ce}$ ,  $\text{Dy}$ ) plotted against silica as a differentiation index.



1092

1093 **Supplementary material 6.** Temporal variation of the Ubina magmatic series, showing some key major (MgO  
 1094 and CaO), trace elements concentrations (Th, La, Nd, Yb) and ratios (La/Nd, Dy/Yb, Rb/Sr), as well as some  
 1095 isotopic ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$ ,  $^{208}\text{Pb}/^{204}\text{Pb}$ ).

1096