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1 **Anatomy of the magmatic plumbing system of Los Humeros Caldera (Mexico): implications for**
2 **geothermal systems**

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19 **ABSTRACT**

20 Understanding the anatomy of magma plumbing systems of active volcanoes is essential not only for

21 unraveling magma dynamics and eruptive behaviors, but also to define the geometry, depth and

22 temperature of the heat sources for geothermal exploration. The Pleistocene-Holocene Los Humeros

23 volcanic complex is part of the Eastern Trans-Mexican Volcanic Belt (Central Mexico) and it represents one

24 of the most important exploited geothermal fields in Mexico with *ca*. 90 MW of produced electricity.

25 A field-based petrologic and thermobarometric study of lavas erupted during the Holocene (post-Caldera

26 stage) has been performed with the aim to decipher the anatomy of the magmatic plumbing system

27 existing beneath the caldera. New petrographical, whole rock major element data and mineral chemistry

28 were integrated within a suite of inverse thermobarometric models. Compared with previous studies

29 where a single voluminous melt-controlled magma chamber (or "Standard Model") at shallow depths was

30 proposed, our results support a more complex and realistic scenario characterized by a heterogeneous

31 multilayered system comprising a deep (*ca*. 30 km) basaltic reservoir feeding progressively shallower and

32 smaller distinct stagnation layers, pockets and batches up to very shallow conditions (1kbar, *ca*. 3km).

33 Evolution of melts in the feeding system is mainly controlled by differentiation processes via fractional

34 crystallization, as recorded by polybaric crystallization of clinopyroxenes and orthopyroxenes.

35 Moreover, this study attempts to emphasize the importance to integrate field-petrography, texture

36 observations and mineral chemistry of primary minerals to unravel the pre-eruptive dynamics and

37 therefore the anatomy of the plumbing system beneath an active volcanic complex, which notwithstanding

38 the numerous existing works is still far to be well understood. A better knowledge of the heat source

39 feeding geothermal systems is very important to improve geothermal exploration strategies.

40

41 **Keywords**

42 Magmatic plumbing system, Thermobarometry, Calderas, Los Humeros, Trans Mexican Volcanic Belt, heat

43 source, geothermal exploration

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1.INTRODUCTION

Recent views on the structure of volcanic plumbing systems have deeply changed, moving from the "Standard Model" (*sensu* Gualda and Ghiorso, 2013) of a single, bowl-shaped magma chamber inside which all petrologic processes of differentiation and assimilation occur (e.g. Hildreth, 1979, 1981; Hildreth and Wilson, 2007) to more complex arrays of stratified and variably interconnected of transient magma accumulation zones, set in largely crystallized and vertically extensive mush zones (e.g., Bachman and Berganz, 2004; 2008; Cashman and Giordano, 2014; Cashman et al., 2017). Furthermore, the time required for the assembly of large magma chambers is now believed to be very short, in terms of decades to few thousands of years for tens to hundreds of km^3 of eruptible magma (e.g. Glazner, 2004; Charlier et al., 2007), which are then rapidly evacuated during eruptions of caldera forming ignimbrites (e.g., Begué et al., 2014; Rivera et al., 2014; Wotzlaw et al, 2014; Matthews et al., 2015; Carrasco-Núñez et al., 2018). Key factors in determining the internal architecture of the magmatic systems is the magma intrusion rate that controls whether successive pulses of magma will coalesce to form progressively larger chambers, as well as the formation of ductile shells surrounding the magma chamber that prevent country rock failure, favoring the inflation of the reservoir (Jellinek and de Paolo, 1981; Annen, 2009). Numerical simulations suggest that caldera systems smaller than 100 km^2 are feed by plumbing systems encapsulated by country rocks that remain sufficiently brittle, while larger systems are more ductile favoring increase in size (Gregg et al., 2012).

The implications of such innovative conceptual models on the modeling of the heat source in magmatic-bearing geothermal systems are profound. Nonetheless, common numerical modeling of conductive-convective heat transfer in caldera-related geothermal systems have commonly envisaged the classic magma chamber as a single body, more or less chemically stratified entirely at magmatic temperatures, whose dimensions and depths have been usually constrained by volcanological and petrological data (e.g. Verma, 1985; Wohletz et al., 1999). More complex modeling requires the "unpacking" of the stratigraphy of a volcano by the identification of the various "magma chambers" or magma storage layers that fed the different eruptions over time and space (e.g., Di Renzo et al., 2016).

A key to decipher where magmas are stored and, therefore, the anatomy of a magmatic plumbing system, is the understanding of pre-eruptive processes such as mineral crystallization, migration and stagnation of melts prior to their eruption (Feng and Zhu, 2018, Putirka, 2008; Keiding and Sigmarsson, 2012; Scott et al., 2012, Barker et al., 2015; Jeffery et al., 2013; Cashman and Giordano, 2014; Pamukcu et al., 2015;Lucci et al., 2018). As a matter of fact, early segregated minerals reflect the magmatic environment (i.e., pressure – temperature – magma/fluid composition, oxidation state) and, therefore, with their growth, texture and chemistry provide an important archive of information (Feng and Zhu, 2018; Ginibre et al., 2007; Giuffrida and Viccaro, 2017; Viccaro et al., 2016; Putirka et al., 2008; Lucci et al., 2018). Accordingly, petrographic observations and mineral chemistry of primary minerals, integrated with opportunely selected

80   thermobarometry models (e.g., Putirka, 2008; Masotta et al., 2013) could lead to the comprehension and

81   reconstruction of the magmatic storage/feeding systems of the erupted products (Feng and Zhu, 2018;

82   Giuffrida and Viccaro, 2017; Elardo and Shearer, 2014; Petrone et al., 2016; Zheng et al., 2016; Eskandari et

83   al., 2018; Shane and Coote, 2018; Scott et al., 2012; Stroncik et al., 2009; Barker et al., 2015; Jeffery et al.,

84   2013; Keiding and Sigmarsson, 2012).

85   In this paper we present a geothermobarometric study of the post-caldera, Pleistocene-Holocene products

86   of Los Humeros volcanic complex (LHVC), at the eastern termination of the Neogene-Quaternary Trans-

87   Mexican Volcanic Belt (TMVB) (Fig. 1) in order to reconstruct the present-day geometry and structure of

88   the magmatic plumbing system, necessary to build up a conceptual model for the magmatic heat source of

89   the active and currently exploited geothermal system. The magmatic heat source for LHVC has been

90   constrained by the geometry of the caldera, the volume and mass balance calculations of the associated

91   ignimbrites (Ferriz and Mahood, 1984, 1987; Verma, 1984, 1985a, 1985b, Verma et al., 1990; Verma and

92   Andaverde, 1995; Verma et al., 2011; Verma et al. 2013), all related to a single magma body. Our results

93   indicate that the present configuration of the plumbing system is vertically extensive and extends across

94   the entire crust comprising a deeper residence zone for basalts at ca. 30 km and a complex middle to upper

95   crust zone where smaller batches of magma differentiate to trachyandesites and trachytes at times

96   interconnected with the lower feeding zone. The main outcome for the modeling of the magmatic heat

97   source of the geothermal system is the rejection of conservative conceptual models based on the classical

98   melt-dominated, single, voluminous, long-lived magma chamber, and the proposal of a new and more

99   realistic vision of the magmatic plumbing systems made of multiple interconnected magma stagnation

100   layers within the crust. The results and approach presented in this work have a general value and could

101   represent an efficient strategy to explore and reconstruct, through petrological investigation, the pre-

102   eruptive geometry and the anatomy of magmatic feeding systems. These findings in turn, must be

103   considered into the new conceptual geothermal models to improve strategies for geothermal exploration.

104

105   **2.GEOLOGICAL SETTING**

106   **2.1 Regional Geology**

107   LHVC is the largest and easternmost Quaternary caldera (Fig. 1) of the 1200 km-long active continental arc

108   of the Trans-Mexican Volcanic Belt (TMVB), generated since *ca.* 20 Ma by the subduction of Cocos plate

109   beneath central Mexico (e.g. Demant, 1978, Ferrari et al. 1999, 2012; Gomez-Tuena et al., 2003, 2007a,

110   2007b, 2018; Norini et al., 2015). LHVC is located in the eastern sector of the TMVB, which is characterized

111   by monogenetic volcanism, scattered basaltic cinder and scoria cones, maar volcanoes of basaltic and

112   rhyolitic composition, large rhyolitic domes and major stratovolcanoes such as Pico de Orizaba (or

113   Citlaltépetl) and Cofre de Perote (e.g., Yáñez and García, 1982; Negendank et al., 1987; Carrasco-Núñez et

114   al., 2010, 2012a;).

115   The Paleozoic to Mesozoic crystalline basement of eastern TMVB is exposed along the Teziutlán Massif

116   (Viniegra, 1965; Ferriz and Mahood, 1984) made of metamorphic (greenschists K-Ar dated at 207 ± 7 Ma, in

117   Yáñez and García, 1982) and intrusive (granodiorites and granites with whole-rock K-Ar ages of 246 ±7 Ma

118   and 181 ±5 Ma, Yáñez and García, 1982) rocks. The crystalline basement is partially covered by a thick,

119   highly deformed Mesozoic sedimentary succession part of the Sierra Madre Oriental NW-SE thrusts and

120   folds belt formed by the Late Cretaceous to Paleocene compressional Laramide Orogeny (e.g. Campos-

121   Enriquez and Garduño-Monroy, 1987; Suter, 1987; Fitz-Díaz et al., 2018). Oligocene to Miocene

122   granodiorite and syenite intrusions are randomly exposed within the area (whole-rock K-Ar ages of 31-15

123   Ma, Yáñez and García, 1982). Miocene volcanism in the area is represented by andesites of the Cerro

124   Grande volcanic complex (Gómez-Tuena and Carrasco-Núñez, 2000), dated at 8.9 to 11 Ma (K/Ar method

125   on whole-rock, Carrasco-Núñez et al. 1997), and the Cuyoaco Andesite dated at 10.5 Ma (K/Ar method,

126   Yáñez and García, 1982) to the west of LHVC, which may correlate with the Alseseca Andesite (Yáñez and

127   García, 1982) exposed to the north. Neogene andesitic volcanism (Ferriz and Mahood, 1984; Yáñez and

128   García, 1982) represented by the Teziutlán Andesite, K-Ar dated (whole-rock) between 3.5 and 5 Ma by

129   Yáñez and García (1982) and at 1.55 Ma by Ferriz and Mahood (1984). This andesitic activity was recently

130   dated by the $^{40}Ar/^{39}Ar$ method at 2.61-1.46 Ma (Carrasco-Núñez et al., 2017a) and correlates with most of

131   the thick andesitic successions of the subsurface geology of LHVC.

132

2.2 Los Humeros Volcanic Complex

134   The volcanic evolution of the LHVC consists of three main stages (Carrasco-Núñez et al., 2018): (i) pre-

135   caldera stage; (ii) caldera stage; and (iii) post-caldera stage. The pre-caldera stage is represented by

136   relatively abundant rhyolitic domes, which erupted mainly to the western side of Los Humeros caldera,

137   with an isolated spot to the south, and some buried lavas identified in the geothermal well-logs (Carrasco-

138   Núñez et al., 2017a). This volcanism has been recently dated by both U-Th and $^{40}Ar/^{39}Ar$ methods (Carrasco-

139   Núñez et al., 2018), providing ages spanning from 693.0±1.9 ($^{40}Ar/^{39}Ar$, plagioclase) to 270±17 ka (U/Th,

140   zircon), which overlap with the age range obtained from other domes of the western sector outside the

141   caldera, where K-Ar ages (sanidine) of 360±100 ka and 220±40 ka were obtained (Ferriz and Mahood,

142   1984). The Caldera stage consists of two major caldera-forming events, separated by a large Plinian

143   eruptive episode. The first and largest caldera-forming eruption produced Los Humeros caldera (18 km in

144   diameter) during the emplacement of the Xaltipan ignimbrite, a rhyolitic, welded to non-welded, ash-rich

145   deposit, radially distributed around the caldera. The dense rock equivalent (DRE) volume of this event was

146   estimated at 115 km^3 by Ferriz and Mahood (1984). The age of the Xaltipan ignimbrite was established by

147   whole-rock K-Ar dating at 460±20 ky (plagioclase) and 460±130 ky (biotite) (Ferriz and Mahood, 1984),

148   however Carrasco-Núñez et al. (2018) based on coupled zircon U-Th dating and $^{40}Ar/^{39}Ar$ method

149   (plagioclase) geochronology provided a younger age of 164.0 ± 4.2 ka.

150 Following this catastrophic event an eruptive pause occurred, resuming with a sequence of intermittent

151 Plinian episodes at 70±23 ka (^{40}Ar/^{39}Ar method on plagioclase, Carrasco-Núñez et al., 2018), separated by

152 short gaps marked by thin paleosoils. The deposits consist of thick (1-6 m) coarse pumice-rich, well-sorted,

153 massive and diffuse-stratified layers,rhyodacitic in composition, which are grouped as the Faby Tuff (Ferriz

154 and Mahood 1984; Willcox, 2011). The second caldera-forming episode produced the 9-10 km large Los

155 Potreros caldera, which is associated with the emplacement of the compositionally-zoned andesitic-

156 rhyodacitic-rhyolitic Zaragoza ignimbrite (Carrasco-Núñez et al., 2012b). This is an intraplinian pyroclastic

157 flow deposit, with an estimated volume of ca. 15 km3 DRE (Carrasco-Núñez and Branney, 2005). Previous

158 ages of this unit were reported at 100 ka (K-Ar dating, plagioclase: Ferriz and Mahhod, 1984) and at 140±24

159 ka (^{40}Ar/^{39}Ar method, plagioclase: Willcox, 2011). However, a new ^{40}Ar/^{39}Ar (on plagioclase) younger age of

160 69±16 ka for the Zaragoza ignimbrite was recently obtained (Carrasco-Núñez et al., 2018), confirmed by the

161 fact the Zaragoza ignimbrite overlies a rhyodacitic lava flow dated at 74.2±4.5 ka (zircon U-Th dating).

162 According to Carrasco-Núñez et al. (2018) during the post-caldera stage (Fig. 1) two different eruptive

163 phases occurred. The first one was a late Pleistocene resurgent phase characterized by the emplacement of

164 felsic domes in the central area at about 44.8±1.7 ka (zircon U-Th ages; Carrasco-Núñez et al., 2018), which

165 is slightly younger than the previously reported whole-rock K-Ar date (60±20 ka, glass: Ferriz and Mahood,

166 1984). Outside of the caldera, to the north, a rhyolitic dome erupted at 50.7±4.4 ka (^{40}Ar/^{39}Ar, plagioclase;

167 Carrasco-Núñez et al., 2018), which was followed by a sequence of explosive eruptions, producing dacitic

168 pumice fall units (Xoxoctic Tuff, 0.6 km^3) and interbedded breccia and pyroclastic flows deposits of the

169 Llano Tuff (Ferriz and Mahood 1984; Willcox, 2011), with a maximum age of 28.3±1.1 ka (C-14, Cal BP

170 30630, Rojas-Ortega, 2016). The second eruptive phase of the post-caldera stage is a Holocene ring-

171 fracture and bimodal phase that occurred towards the south, north and central part of Los Humeros

172 caldera (Carrasco- Núñez et al., 2017). It is characterized by alternated episodes of effusive and explosive

173 volcanism with a wide range of compositions, spanning from basaltic-andesitic,basaltic trachytic,

174 trachyandesitic lava flows and dacitic, trachydacitic, andesitic and basaltic pumice and scoria fall deposits

175 erupted by tens of monogenetic eruptive centers located in the LHVC (Ferriz and Mahood, 1984; Dávila-

176 Harris and Carrasco-Núñez, 2014; Norini et al., 2015; Carrasco-Núñez et al., 2017b). Most of the effusive

177 activity was firstly considered within a range of 40-20 ka (whole-rock K-Ar dating, Ferriz and Mahood,

178 1984), however, recent dating reveals that most of this activity is Holocene (Carrasco et al., 2017b).

179 Trachyandesitic and andesitic basalts lavas erupted to the north of the LHVC at about 8.9±0.03 ka (C-14

180 age, Carrasco-Núñez et al, 2017b). A rhythmic alternation of contemporaneous bimodal explosive activity

181 produced trachyandesitic and basaltic fall layers grouped as the Cuicuiltic Member erupted at 7.3±0.1 ka (C-

182 14 age,Dávila-Harris and Carrasco-Núñez, 2014). This activity migrated towards the southern caldera rim to

183 forms a well-defined lava field. This ring-fracture episode erupted trachyandesite and olivine-bearing

184 basaltic lava flows, at 3.9±0.13 ka (C-14 age, Carrasco-Núñez et al, 2017b), and the most recent eruptions

185   erupted trachytic lava flows near the SW caldera rim, at 2.8± 0.03 ka (C-14 age, Carrasco-Núñez et al,

186   2017b).

187

188   **2.3 Los Humeros geothermal system**

189   The LHVC hosts one of the three most important geothermal fields in Mexico, with an installed 93 MW of

190   electric power produced from 20 geothermal wells (Romo-Jones et al., 2017). The existing conceptual

191   models for the Los Humeros geothermal field (LHGF) (see Norini et al., 2015 for a review) stem upon the

192   hypothesis of a unique, large and voluminous cooling magma chamber of 1000-1500 Km^3 in volume, at

193   depth of 5 to 10 km from the surface (Verma, 1984, 1985a, 1985b, 2000; Verma et al., 1990; Verma and

194   Andaverde, 1995; Verma et al., 2011; Verma et al. 2013; Carrasco-Núñez et al. 2018), representing the heat

195   source of the geothermal field (Martínez et al., 1983; Verma, 1983, 2000; Campos-Enríquez and Garduño-

196   Monroy, 1987). However, the LHGF is characterized by a low number of productive geothermal wells (ca.

197   20 out of 50; Norini et al., 2015; Carrasco-Núñez et al., 2017a). The confined distribution of these

198   productive wells along the NNW-SSE trending "Maxtaloya-Los Humeros-Loma Blanca" fault system (MHBfs

199   in Fig. 1) cutting across the Los Potreros caldera (e.g., Norini et al., 2015; Carrasco-Núñez et al., 2017a) also

200   corresponds to the almost unique, narrow and sharp surface thermal anomaly recognized within the

201   caldera (Norini et al., 2015). These observations raise doubts on the existence of a voluminous superficial

202   heat source feeding the LHGF and makes it important, for a better comprehension and exploitation of the

203   geothermal resource, a revised assessment of the structure of the magmatic plumbing system beneath

204   LHVC.

205

206   **3.MATERIALS AND METHODS**

207   In this work we focus on petrographical investigations, textural and chemical (mineral chemistry and major-

208   elements bulk-rock) characterization of the Los Humeros post-caldera stage (LHPCS) (Carrasco-Núñez et al.

209   2017b). Following the recently published geological map (Carrasco-Núñez et al. 2017b) and geochronology

210   (Carrasco-Núñez et al. 2018) of the LHVC, a number of thirteen samples of the LHPCS lavas were collected

211   in the field (Fig. 1), with the aim to describe all the compositional variability of erupted products during the

212   post-caldera stage activity (Figs. 1, 2a-d). In the description of the volcanic units, abbreviations follow

213   Carrasco et al. (2017b). Concerning the extra-caldera products (Fig. 2d), we collected samples from all the

214   four major lava flows: (i) LH15 from El Limón lava flow (Qab), (ii) LH21-2 from Sarabia lava flow (Qta1), (iii)

215   LH17 from Tepeyahualco lava flow (Qtab), and (iv) LH18 from Texcal lava flow (Qb1).

216   With respect to the intra-caldera domain (Fig. 2a), we sampled lavas belonging to: (i) LH27-1 from the mafic

217   lavas inside the Xalapasco Crater (Qb1), (ii) LH27-2 from the Maxtaloya trachyandesites (Qta4) constituting

218   the rim-walls of Xalapasco craters, (iii) LH4 from San Antonio-Las Chapas lavas (Qta3) outcropping in the Los

219   Humeros town, (iv) LH5-2 from mafic lavas (Qb1) outcropping west to Los Humeros town, (v) LH5-1 from

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220   Chicomiapa-Los Parajes felsic lavas (Qt2) outcropping in the north-western part of Los Potreros caldera, (vi)

221   LH6-1 from El Pajaro unit (Qt1) outcropping in the north-western part of Los Potreros caldera. In addition to

222   these units, we also collected three more samples (LH13, LH26-1 and LH26-2) from lavas and domes of

223   intermediate compositions, outcropping (Fig. 2b-c) in the central part of Los Potreros caldera between

224   Xalapasco crater and Los Humeros town, and not reported on the published geological map.

225   The samples were investigated through: i) an integration of polarized-light microscopy (PLM) and electron

226   microprobe analyses (EMPA) for the definition of magmatic fabrics, textures, mineral assemblages and

227   mineral chemistry; and ii) ion coupled plasma – optical emission (ICP-OE) and X-ray fluorescence (XRF)

228   analyses to determine the whole-rock major element compositions.

229   Analytical protocols are described in the Appendix A. In the following, mineral abbreviations are after

230   Whitney and Evans (2010).

231

232

233   **4.MAJOR ELEMENT BULK COMPOSITION**

234   Studied samples (Fig. 3a) show a continuous series from mafic to felsic compositions, with SiO_2 ranging

235   46.5-67.6 wt%, and $Na_2O + K_2O$ ranging 3.4-9.2 wt% (with $K_2O/Na_2O < 1$) (Table 1). LHPCS mafic rocks ($SiO_2<$

236   50 wt%; 3 samples) show composition with SiO_2 46.5-49.4 wt%, Al_2O_3 16.2-17.1 wt%, MgO: 8.0-8.4 wt%,

237   CaO: 9.8-10.7 wt%, with Mg# (molar $MgO/[MgO+FeO_{tot}]$) = 60-61 and Na_2O+K_2O ranging 3.4-3.5 wt%.

238   LHPCS intermediate rocks ($50<SiO_2<63$ wt%; 8 samples) contain 54.4-62.1 wt% SiO_2, with Al_2O_3 15.7-20.7

239   wt%, Na_2O+K_2O 5.3-7.1 wt%, MgO 2.2-3.6 wt% (Mg# 43-51), and low CaO 4.6-8.5 wt%. LHPCS felsic rocks

240   ($SiO_2>63$ wt%; 2 samples) show SiO_2 ranging 64.9-67.6 wt%, associated with Al_2O_3 15.5-15.8 wt%, MgO 0.7-

241   1.2 wt% (Mg#: 26-34), CaO 2.1-2.8 wt%, and Na_2O+K_2O 8.2-9.2 wt%.

242   On the total alkali versus silica (TAS) diagram (Le Maitre et al., 2002) LHPCS lavas span from basalts to

243   basaltic trachyandesites, trachyandesites and trachytes (Fig. 3b). Los Humeros mafic rocks fall in the

244   "Basalt" field and, according to Bellieni et al. (1983), Le Maitre et al. (2002) and Giordano et al. (2012), can

245   be classified as alkali-basalts. The high TiO_2 contents (1.34-1.5 wt%), together with MgO <12 wt% and low

246   Al_2O_3/TiO_2 values (average value 11.5) exclude the LH mafic rocks as high-Mg melts (picrites) or komatiites

247   (e.g., Redman and Keays, 1985; Arndt and Jenner, 1986; Le Maitre et al., 2002; Gao and Zhou, 2013; Azizi et

248   al., 2018a, 2018b).

249   Intermediate products fall in the "Basaltic trachyandesites" and "Trachyandesites" fields; these rocks

250   showing intermediate composition will be referred hereafter as "trachyandesites".

251   The Los Humeros felsic (i.e., SiO_2 >63 wt%) lava samples belonging to the post-caldera stage (i) fall in the

252   "Trachyte" fields, (ii) show potassic signature and (iii) are characterized by Agpaitic Index (molecular ratio

253    $[(Na_2O+K_2O)/Al_2O_3]$) values < 1 (range: 0.7-0.8) thus excluding a peralkaline character of these evolved

254   melts. Selected Harker diagrams for major elements are presented in Figure 3, using SiO_2 wt% as

255 differentiation index. Negative correlations are observed for CaO (Fig. 3c) and Mg# (Fig. 3d), whereas

256 positive correlations are observed for Na$_2$O (Fig. 3c).

257

258 **5.PETROGRAPHY**

259 **5.1 Basalts**

260 LHPCS basalts show vesicle-rich (up to 35 vol%) highly-porphyritic (phenocrysts up to 50 vol%) textures (Fig.

261 4a-d). Studied basalts are invariably free of lithics and a fluidal fabric is defined by the alignment of

262 plagioclase laths in the groundmass. Based on the presence of clinopyroxene (Cpx) in the mineral

263 assemblage, basalts can be further subdivided into: (i) Cpx-free basalt of extra-caldera Texcal lava flow

264 (LH18); and (ii) Cpx-bearing basalts of intra-caldera lavas at western Los Potreros and at Xalapasco crater

265 (LH5-2 and LH27-1, respectively).

266 Cpx-free basalt (LH18) contains euhedral to subhedral olivine (ca. 20 vol%) and plagioclase (ca. 25-30 vol%)

267 phenocrysts in a holocrystalline groundmass consisting of thin platy plagioclase, dendritic to spinifex olivine

268 and opaque oxides (Fig. 4a, b). Olivine and plagioclase phenocrysts are generally slightly chemically zoned

269 (see below) with a typical core-rim texture (Fig. 4a, b). Occasionally, major phenocrysts of olivine (up to 2.5

270 mm in size) with Cr-spinel inclusion are observed (Fig. 4a). It is worth notice that no pyroxenes are observed

271 in this basalt.

272 Cpx-bearing intra-caldera basalts (LH5-2, LH27-1) shows euhedral to subhedral plagioclase (ca. 25 vol%),

273 olivine (ca. 10-15 vol%), yellow to colorless clinopyroxene (ca. 10-15 vol%) and rare anorthoclase (< 2 vol%)

274 phenocrysts (Fig. 4c) in a holocrystalline groundmass (Fig. 4d) made of (in order of microlites abundance)

275 elongated platy plagioclase, olivine, colorless to green clinopyroxene, opaque oxides and rare alkali-

276 feldspar. All phenocrysts show oscillatory growth zoning with distinct core-rim structures (Fig. 4c, d). Large

277 phenocrysts of olivine (up to 1.5 mm in size) and plagioclase (up to 3 mm in length) are commonly

278 observed. Vesicle size is up to 5mm in diameter.

279

280 **5.2 Trachyandesites**

281 LHPCS intermediate volcanic products show low- to medium-porphyritic textures (phenocrysts ranging 10-

282 40 vol%), with a general fluidal fabric as indicated by orientation of plagioclase and clinopyroxene laths in

283 the groundmass (Fig. 4e, f). Intermediate products vary from poorly vesiculated (< 10 vol% in LH13) to

284 vesicle-rich (ca. 30 vol% in LH4) lavas. In the highest vesiculated sample (LH4), size of vesicles (3-5 mm in

285 diameter) is comparable to those of intra-caldera basalts (LH5-2, LH27-1). Based on the presence of

286 orthopyroxene (Opx) in the mineral assemblage, rocks of intermediate compositions can be further

287 subdivided into: (i) Opx-free (LH21, LH15); and (ii) Opx-bearing (LH4, LH13, LH17, LH26-1, LH26-2, LH27-2)

288 trachyandesites.

289 Opx-free trachyandesites shows euhedral to subhedral plagioclase (ca. 15-20 vol%), yellow to colorless

290 clinopyroxene (ca. 10-20 vol%), alkali-feldspars (ca. 10-15 vol%) and olivine (ca. 10 vol%) phenocrysts, in

291 holocrystalline microcrystalline groundmass composed of elongated platy plagioclase, colorless

292 clinopyroxene, olvine, alkali-feldspar and opaque oxides, in order of microlites abundance.

293 Apart from the olivine-free LH27-2 sample, Opx-bearing trachyandesites are generally characterized by

294 euhedral to subhedral plagioclase (ca. 15-20 vol%), clinopyroxene (ca. 10-20 vol%), colorless orthopyroxene

295 (ca. 10-20 vol%), alkali-feldspars (ca. 10-15 vol%) and olivine (< 10 vol%) phenocrysts in a holocrystalline to

296 hypohyaline microcrystalline groundmass made of feldspar (plagioclase and alkali-feldspars) microlites,

297 pyroxene (clinopyroxene and orthopyroxene) microlites, olivine microlites, opaque minerals and glass (Fig.

298 4f).

299 Most of phenocrysts observed in these intermediate rocks present oscillatory growth zoning with core-rim

300 structures (Fig. 4e); however, unzoned Cpx phenocrysts are also observed. Major phenocrysts of Cpx (up to

301 2 mm in size) and Pl (up to 2 mm in length) are commonly observed in all studied trachyandesites.

302 Plagioclase phenocrysts with inherited cores are reported. Rare large phenocrysts of olivine (1.5-2.0 mm in

303 size), presenting disequilibrium textures at rim and characterized by spinel inclusion, are reported in LH26-1

304 sample.

305

306 **5.3 Trachytes**

307 LHPCS trachytes show phyric textures, with low porphyritic index (phenocrysts ranging 10-25 vol%), and

308 fluidal fabrics as shown by iso-orientation of plagioclase, alkali-feldspars and clinopyroxene laths in the

309 groundmass (Fig. 4g, h). They range from vesicle-poor (< 5 vol%) to vesicle-free textures, with size of

310 vesicles never exceeding 0.05 mm in diameter. The two analyzed trachytic samples (LH5-1 and LH6) are

311 both characterized by the presence of orthopyroxene; however, the two mineral assemblages differ

312 substantially.

313 The low-SiO_2 (64.93 wt%) LH5-1 trachyte is characterized by euhedral to subhedral plagioclase (ca. 10-15

314 vol%), clinopyroxene (ca. 10 vol%), orthopyroxene (ca. 10 vol%), olivine (ca. 5-10 vol%) and sanidine (< 10

315 vol%) phenocrysts in a hypohyaline microcrystalline groundmass made of (in order of abundance of

316 microlites) sanidine, rare plagioclase, orthopyroxene, clinopyroxene, olivine, opaque minerals and glass.

317 Phenocrysts are generally unzoned, however rare major plagioclase (up to 1.5 mm in length) and

318 clinopyroxene (up to 1.0 mm in length) phenocrysts are characterized by inherited cores and inclusions of

319 olivine + magnetite, respectively. The high SiO_2 (67.58 wt%) LH6 trachyte is made up of sanidine (ca. 10

320 vol%), plagioclase (ca. 5-10 vol%) and orthopyroxene (ca. 10 vol%) phenocrystals in a fine grained trachytic

321 mesostasis. Only the mafic phenocrysts show core-rim textures. Dimension of phenocrysts are comparable

322 to those of LH5-1 trachyte.

323

324 **6.MINERAL CHEMISTRY**

325 Mineral compositions as obtained from electron microprobe analyses and mineral formulae for mineral

326 assemblages of LHPCS lavas are presented in Supplementary Tables 1, 2, 3, 4 and 5 (for feldspar,

327 clinopyroxene, olivine, orthopyroxene and spinel and opaque minerals, respectively).

328

329 **6.1 Feldspar**

330 In basaltic rocks (Fig. 5a), feldspars are predominantly plagioclase. Phenocrysts show normal core-rim

331 zonation with anorthite-rich (XAn = 43-95%) cores and labradorite (XAn = 42-59%) rims. Orthoclase

332 component (XOr) is always less than 2%. Plagioclase microlites in the groundmass show andesine (XAn = 19-

333 60%) composition, with XOr ranging 1-7%. Alkali-feldspars occur as rare anorthoclase phenocrysts

334 ($Ab_{60}Or_{37}$), and as microlites in groundmass ($Ab_{62-79}Or_{9-35}An_{0-13}$).

335 Plagioclase from trachyandesites (Fig. 5b) have anorthite-rich (XAn = 47-77%) cores and essentially

336 andesine (XAn = 27-69%) rims. Inherited cores with XAn up to 98% are observed in major phenocrysts. The

337 XOr ranges 1-8%. Plagioclase microlites in groundmass show andesine (XAn = 29-63%) composition with

338 XOr always less than 10%. Alkali-feldspars occur as (i) anorthoclase ($Ab_{59-68}Or_{11-30}$) and sanidine ($Ab_{49-50}Or_{43-}$

339 $_{48}$) phenocrysts, and (ii) anorthoclase ($Ab_{49-70}Or_{15-38}$) and sanidine ($Ab_{38-48}Or_{47-61}$) microlites in groundmass.

340 Trachytes (Fig. 5c) show generally unzoned plagioclase phenocrysts with oligoclase-andesine (XAn = 26-

341 45%) composition. Rare labradorite (XAn= 52-70%) inherited cores are reported in the low-silica trachyte

342 LH5-1. The XOr is always less than 8%. Plagioclase microlites in groundmass are rare, with oligoclase (An_{21-}

343 $_{30}Ab_{66-69}Or_{4-10}$) composition. Alkali-feldspars are represented by anorthoclase as phenocrysts ($Ab_{65-66}Or_{20-21}$)

344 and groundmass microlites ($Ab_{64-66}Or_{21-24}$).

345

346 **6.2 Clinopyroxene**

347 Apart from the LH18 basalt and LH6 trachyte, clinopyroxene, is the most common mafic mineral recognized

348 in studied samples. It occurs generally as single crystals (Fig. 4e), however crystals clots are also reported in

349 trachyandesites. Major clinopyroxene phenocrysts in trachyandesites and trachytes contain inclusions (Fig.

350 4e, g) of olivine, magnetite and plagioclase.

351 Polarized light microscopy coupled with BSE images and chemical investigations highlighted the presence of

352 unzoned (Fig. 4g) and zoned (core-rim structure, Fig. 4e) clinopyroxene phenocrysts, with minor or no

353 evidence of resorption/dissolution. The Cpx composition (Fig. 6 a-f) can be grouped in five major

354 categories: (i) cores of zoned phenocrysts in basalts (Cpx1); (ii) cores of zoned phenocrysts in

355 trachyandesites and trachytes (Cpx2); (iii) rims of zoned phenocrysts and unzoned phenocrysts in all

356 studied samples (Cpx3); (iv) microlites in groundmass in all studied samples (Cpx4); and (v) emerald green

357 to greenish euhedral to subhedral microlites in groundmass of intra-caldera basalts (LH5-2, LH27-1) and

358 thin external rims of major clinopyroxene phenocrysts from a restricted number of trachyandesites (LH15,

359 LH17, LH26-2) (Cpx5).

360 The Cpx1 shows Mg# of 45-75, Ca 0.78-0.90 apfu, Q+J 1.84-1.94 and J/(J+Q) 0.03-0.06, and it can be

361 classified as Ti-rich augite ($Wo_{41-48}En_{25-42}Fs_{14-32}$).

362 The Cpx2 shows a Mg# of 59-84, Ca 0.20-0.92 apfu, Q+J 1.77-1.95 and J/(J+Q) 0.01-0.06, and it can be

363 classified as diopside-rich augite ($Wo_{11-48}En_{36-64}Fs_{9-32}$).

364 The Cpx3 shows Mg#: 20-86, Ca 0.27-0.97 apfu, Q+J 1.57-1.98 and J/(J+Q) 0.01-0.07, and it can be classified

365 as diopside-rich augite ($Wo_{12-49}En_{14-57}Fs_{8-62}$).

366 The Cpx4 shows Mg# of 31-81, Ca 0.24-0.87 apfu, Q+J 1.87-1.97 and J/(J+Q) 0.01-0.06, corresponding to

367 diopside-rich augite ($Wo_{12-46}En_{18-60}Fs_{11-38}$).

368 The Cpx5 differs from previous pyroxenes, with a large spread in Mg# ranging 5-73, Ca 0.03-0.83 apfu, Q+J

369 1.51-2.07 and J/(J+Q) 0.07-0.89. The Cpx5 can be classified as Aegirine-Augite (Na< 0.3 apfu, XAeg< 0.30;

370 with XAeg= Na apfu if Na < $Fe^{3+\ Tot}$, XAeg= $Fe^{3+\ Tot}$ apfu if Na > Fe^{3+Tot}) to Aegirines (Na= 0.68-0.88 apfu,

371 XAeg= 0.40-0.88). Cpx5 clinopyroxenes are generally Ti-enriched (TiO_2 up to 2.8 wt%, Ti up to 0.08 apfu)

372 and straddle the Q+J=2 line defining the boundary for "normal" pyroxenes (Morimoto, 1989), thus

373 indicating the presence of a $NaR^{2+}_{0.5}Ti^{4+}_{0.5}Si_2O_6$ component (Morimoto, 1988, 1989; Huraiova et al., 2017)

374 (Fig. 6c).

375 The compositional variation of clinopyroxenes can be summarized in the Na vs. Ti diagram (Fig. 6e-f).

376 Interestingly, Augite (Cpx1, Cpx2, Cpx3 and Cpx4) clinopyroxenes generally show positive correlation and

377 linear distribution characterized by a progressive Ti- and Na-depletion, from Ti-Augite in basalts to DiHd-

378 rich Augite in trachytes. The Cpx5, belonging to Aegirine-Augite and Aegirine, moves away from this trend

379 showing a negative correlation characterized by a progressive enrichment of Na content, with respect to a

380 general Ti-depletion. Aegirine enrichment is diagnostic of ferric iron (Fe3+) content increasing during the

381 magmatic differentiation, whereas the diopside-hedenbergite enrichment testifies increasing of ferrous

382 iron (Fe2+) in magma (e.g. Huraiova et al., 2017).

383

384 **6.3 Olivine**

385 Olivine is found in all analyzed samples, except for for LH27-2 trachyandesite and LH6 trachyte. It consists

386 of idiomorphic (Fig. 4 a, c) to skeletal (e.g., Donaldson, 1974; Fowler et al., 2002; Faure et al., 2003; Welsch

387 et al., 2013) (Fig. 4b) phenocrysts, and microlites in the groundmass (Fig. 4h). It shows a continuous

388 compositional range (Fig. 7a) from $Fo_{86}Fa_{14}Mtc_0Tep_0$ (phenocryst in LH5-2 basalt) to $Fo_{05}Fa_{91}Mtc_1Tep_3$

389 (groundmass microlites in LH27-1 basalt). Maximum MnO (up to 1.7 wt%) values are always found in Fe-

390 rich olivine microlites. Low monticellite concentration (CaO always < 1.0 wt%) in Los Humeros sample is

391 typical for magmatic olivine (i.e., Melluso et al., 2014). CaO content positively correlates with the fayalite

392 (FeO) compound (Fig. 5a). Together with the Mg#, the CaO content allows to discriminate olivine

393   phenocrysts in three coherent compositional clusters: i) phenocrysts from basalts, with Mg#= 79-87 and

394   CaO= 0.21-0.73 wt%, ii) phenocrysts from trachyandesites, with Mg#= 67-80 and CaO= 0.08-0.43 wt%, and

395   iii) phenocrysts from trachytes with Mg#= 58-63 and CaO= 0.16-0.42 wt%. A minor cluster of peridotite Mg-

396   olivine ($Fo_{99}Fa_1$) xenocrysts, characterized by disequilibrium textures, have been identified in LH26-1

397   trachyandesite lava.

398

6.4 Orthopyroxene

400   Orthopyroxene occurs in most of the LHPCS trachyandesite (Fig. 4f) and trachyte samples (Fig. 4 g-h).

401   Orthopyroxene phenocrysts show intermediate ($En_{41-83}Fs_{14-55}Wo_{2-10}$) compositions (Fig. 7b), with Mg# of 43-

402   86, Al_2O_3 up to 2.12 wt%, TiO_2 0.08-1.33 wt%, and CaO 1.20-4.72 wt%. Similar compositions ($En_{62-79}Fs_{18-}$

403    $_{33}Wo_{3-7}$) have been obtained for microlites in groundmass (Fig. 7b) with Mg# of 65-81, Al_2O_3 0.48-1.53 wt%,

404   TiO_2 0.21-0.60 wt% and CaO 1.35-3.49 wt%.

405   In trachytes, orthopyroxene phenocrysts present Mg# ranging 59-65, with low Al_2O_3 (0.18-0.73 wt%), low

406   TiO_2 (0.11-0.32 wt%) and CaO (0.81-1.88 wt%), corresponding to Fe-rich composition ($En_{56-63}Fs_{34-39}Wo_{2-4}$)

407   with a minor Ca-Cpx substitution (Fig. 7b). Orthopyroxene microlites in groundmass (Fig. 7b) show

408   comparable hypersthene ($En_{46-60}Fs_{35-45}Wo_{3-7}$) composition with Mg# of 50-63, Al_2O_3 0.25-0.82 wt%, TiO_2

409   0.19-0.31 wt% and CaO 1.32-3.27 wt%.

410   The compositional variation of orthopyroxyene is summarized in Al^{Tot} vs. Mg# diagram (Fig. 7c). In general,

411   orthopyroxene from trachyandesites is characterized by higher content of Al (apfu) and higher Mg#,

412   whereas those from trachytes are richer in ferrous iron (lower Mg# values) and in manganese (Mn up to

413   0.04 apfu).

414

6.5 Spinel and Opaque Minerals

416   Basalts show a diversified set of opaque minerals. Phenocrysts are characterized by, in order of abundance,

417   the presence of: i) Al-spinel (TiO_2 0.58-1.00 wt%; Mg# 58-71; Cr# 21-30) (with [Cr#= 100 Cr/(Cr+Al)]), ii) Ti-

418   magnetite (TiO_2 1.83-21.58 wt%; MgO 0.06-2.19 wt%; MnO 0.44-0.63 wt%) and ilmenite (MgO up to 2.18

419   wt%). Groundmass is characterized by the only presence of Fe-Ti oxides as ilmenite (MgO 0.27-1.50 wt%)

420   and Ti-magnetite (MgO 0.18-1.89 wt%). Cr-spinels (TiO_2 3.37-8.55 wt%; Mg# 14-28; Cr# 62-72) are found

421   just as inclusions in larger Mg-rich olivine phenocrysts.

422   Trachyandesites are characterized by phenocrysts of Ti-magnetite (MgO 0.07-3.84 wt%), ilmenite (MgO

423   1.11-4.79 wt%) and rare rutile (MgO 0.47 wt%). Groundmass shows a comparable composition with Ti-

424   magnetite (MgO 0.33-3.77 wt%), ilmenite (MgO 0.33-4.79 wt%) and rare rutile (MgO < 0.05 wt%).

425   Comparable to basalts, Cr-spinels (TiO_2 6.09-6.47 wt%; Mg# 19-21; Cr# 65-68) are identified only as

426   inclusions in major Mg-rich phenocrysts.

427   In Trachytes, Fe-Ti oxides show euhedral to subhedral habit and, based on chemistry, they are ilmenite

428   (MgO 2.06-3.31 wt%) and titanomagnetite (MgO 1.41-5.47 wt%). Phenocrystals and groundmass show

429   same compositions.

430

431   **7. DISCUSSION**

432   Many different thermobarometry models have been developed since the very early studies of Daubeny

433   (1835), which can be classified as follows: (i) based on mineral-chemistry only (e.g., Lindsley, 1983; Nimis,

434   1995; Schimdt, 1992; Vidal et al., 2005; Putirka, 2008; Mutch et al., 2016); (ii) based on melt-chemistry (or

435   "liquid"-chemistry) only (e.g., Thornber et al., 2003; Putirka, 2008); and (iii) based on equilibria between

436   mineral phase and coexisting melt (or "liquid") pairs (Holland and Blundy, 1994; Anderson et al., 2008;

437   Putirka, 2008 and references therein). As clarified by Putirka (2008), "liquid" could be the composition of

438   the glass, or the whole rock, or either calculated compositions taken to be representative for the melt at

439   equilibrium with a given mineral phase. Furthermore, as a general rule, Putirka (2008) in his review

440   suggests comparing phenocrysts to the whole rock composition as well as microcrystals/microlites to the

441   glass in groundmass.

442   In order to define the thermo-baric environmental conditions of the magmatic feeding system of the

443   LHPCS, we integrated thermobarometry models based on olivine (Beattie, 1993; Putirka et al., 2007;

444   Putirka, 2008), orthopyroxene (Putirka, 2008), plagioclase (Putirka, 2005b; Putirka, 2008), alkali-feldspar

445   (Putirka, 2008) and clinopyroxene (Putirka et al., 1996, 2003; Putirka, 2008; Masotta et al., 2013) chemistry

446   and since the paucity/absence of glasses, we assumed the whole rock composition as representative of the

447   original liquid (or nominal melt) in equilibrium with phenocrysts (Putirka, 1997, 2008; Mordick and Glazner,

448   2006; Aulinas et al., 2010; Dahren et al., 2012; Barker et al., 2015). We are aware that such a procedure put

449   the focus on early steps of the crystallization history, characterized by high melt/crystal ratios. Relatively

450   late melt compositions, related to the solidification of the groundmass, are not present or can simply not

451   be analyzed. Thermobarometric calculations were developed after the application of mineral-melt

452   equilibrium filters and considering pre-eruptive H_2O^{liq} values Plagioclase-liquid thermometry and barometry

453   were calculated using eq. (24a) and eq. (25a), respectively, of Putirka (2008), mainly based on the Ca/Na

454   distribution between melt and Pl. Alkali-feldspar-liquid thermometry was calculated considering the K-Na

455   exchange, applying eq. (24b) in Putirka (2008). Olivine-liquid equilibrium thermometry was calculated

456   integrating the models of Beattie (1993) and Herzberg and O'Hara (2002) with the thermometric eq. (2) in

457   Putirka et al. (2007). Orthopyroxene-liquid thermometry was calculated by Fe-Mg partitioning following

458   the model of Beattie (1993; in the revised form [eq. 28a] in Putirka, 2008). For barometry, based on the Na

459   and Al content in Opx, the model of Wood (1974) in the revised form [eq. 29a] in Putirka (2008) was

460   applied.

461 Clinopyroxene-liquid thermometry and barometry, for diopside-augite pyroxenes in basalts and

462 trachyandesites (groups Cpx1, Cpx2, Cpx3, Cpx4), were calculated by the application of the Jd-DiHd

463 exchange thermometer (Putirka et al, 1996, 2003) using [eq. 33] in Putirka (2008) and the Al-partitioning

464 barometric model [eq. 32c] in Putirka (2008). Clinopyroxene-liquid thermometry and barometry, for

465 diopside-augite pyroxenes in trachytes (groups Cpx3 and Cpx4), were calculated by the application of the

466 Jd-DiHd exchange thermometer (Putirka et al, 1996, 2003; Putirka, 2008) recalibrated for alkaline

467 differentiated magmas using [eqn. Talk33] and [Eqn. Palk 2012], respectively, in Masotta et al. (2013).

468 Clinopyroxene-liquid thermometry and barometry, for augite-aegirine pyroxenes (Cpx5), were calculated

469 integrating [eq. 33] and [eq. 32c] in Putirka (2008) with equations [Eqn. Talk2012] and [Eqn. Palk 2012] in

470 Masotta et al. (2013). Results of mineral-melt equilibrium tests (Figs. 8, 9, 10), hygrometry calculations (Fig.

471 10) and geothermometric estimates are presented contextually in supplementary mineral chemistry tables.

472 Summary of the thermobarometry estimates are reported in a Pressure-Temperature diagram (Fig. 11).

473

474 **7.1 Test for Mineral-Melt Equilibrium**

475 Prerequisite for the application of inverse thermobarometry models based on mineral-melt equilibrium

476 conditions is to test and verify that mineral and the chosen liquid composition represent chemical

477 equilibrium pairs (e.g., Putirka, 2008; Keiding and Sigmarsson, 2012). Petrographic investigations (i.e.,

478 polarized light and BSE imaging) and calculation of mineral-liquid partition coefficients were integrated with

479 the aim to select only mineral populations that are in apparent equilibrium with the melt (e.g., Putirka,

480 2008; Keiding and Sigmarsson, 2012).

481 The predominant euhedral to subhedral habit of crystals is generally considered an evidence of equilibrium

482 with the surrounding melt (e.g., Keiding and Sigmarsson, 2012). Accordingly, in the first step of our analysis

483 we discarded from the analyzed dataset the the minor cluster of crystals presenting morphological

484 evidence of disequilibrium such as patchy chemical zoning (from BSE images) was also discarded.

485 Critical for thermo-barometric studies is the use of strongly oscillatory zoned phenocrysts (e.g., Mordick

486 and Glaznier, 2006; Putirka, 2008; Keiding and Sigmarsson, 2012), because the strongly zoned nature

487 implies that core and rim of a grain formed in evolving liquids with progressively different compositions.

488 Considering the absence of glass in most of the analyzed LHPCS samples, we use whole-rock compositions

489 as representative of pristine liquids in equilibrium with early crystallized phenocrysts and microlites.

490 As second step, mineral-liquid equilibria between liquid and previous selected minerals, were investigated

491 using: (i) the Fe-Mg exchange coefficient, (ii) the An-Ab partitioning coefficient, and (iii) the comparison

492 between observed and predicted normative components of minerals.

493 The partitioning of Fe-Mg between mineral and liquid is known as Fe-Mg exchange coefficient, or $K_D^{min\text{-}liq}$(Fe-Mg)

494 ^{liq}(Fe-Mg) (defined as $K_D^{min\text{-}liq}$(Fe-Mg) = [MgO^{liq}FeO^{min}]/[MgO^{min}FeO^{liq}], where *liq* is the liquid composition,

495 *min* is the mineral composition and MgO and FeO are molar fractions; Roeder and Emslie, 1970; Langmuir

496   and Hanson, 1981; Putirka, 2005a; Putirka, 2008). It is used here to test the equilibrium between mafic

497   minerals (olivine, orthopyroxene and clinopyroxene) and liquid (e.g., Maclennan et al., 2001; Putirka, 2008;

498   Stroncik et al., 2009; Aulinas et al., 2010; Keiding and Sigmarsson, 2012; Melluso et al., 2014; Feng and Zhu,

499   2018). The $K_D^{min-liq}$(Fe-Mg) value in Opx is almost independent of P and T, but decreases slightly with the

500   increasing silica content in melt (Putirka, 2008). For a given liquid, we calculated, the ideal Fe-Mg exchange

501   (hereafter iK_D) value using the equation proposed by Putirka (2008): $iK_D^{min-liq}$(Fe-Mg) = 0.4805-0.3733*Si^{liq},

502   where Si^{liq} is the cation fraction of SiO_2 in the liquid. The criterion [$K_D^{opx-liq}$(Fe-Mg)] − [$iK_D^{opx-liq}$(Fe-Mg)] < 0.10

503   has been here chosen as additional test in evaluating Opx-melt equilibria.

504   Due to the slight temperature dependency of Fe-Mg exchange for Cpx-Liq pairs (Putirka, 2008), we

505   calculated $K_D^{min-liq}$(Fe-Mg) values, based on measured rock and mineral compositions, using (i) equation (17)

506   in Putirka (2008) for Ol and Opx, (ii) temperature-dependent equation (35) in Putirka (2008) for diopsidic-

507   augitic Cpx and iii) Na-dependent equation (35a) in Masotta et al. (2013) is integrated for Cpx-bearing

508   trachytes and Na-aegirine Cpx5. The calculated $K_D^{min-liq}$(Fe-Mg) are plotted in a Rhodes's diagram (Dungan et

509   al., 1978; Rhodes et al., 1979; Putirka, 2005; Putirka, 2008) to graphically test the equilibrium between Ol

510   (Fig. 8a) or Opx (Fig. 8b) and the Liq. Furthermore, the Rhodes's diagram is useful to recognize processes

511   such as: (i) presence of xenocrystals and antecrystals; (ii) late or groundmass crystallization; (iii) crystal

512   removal (decrease of Mg#^{liq} only); and (iv) closed system crystallization (decrease of Mg#^{min} only) by

513   deviations of the measured compositions from the expected ones (Rhodes et al., 1979; Putirka, 2008;

514   Melluso et al., 2014).

515   The calculation of $K_D^{cpx-liq}$(Fe-Mg) does not consider variations of Ca and Al contents in Cpx (Rhodes et al.,

516   1979; Putirka, 1999, 2005b, 2008). Therefore, a further equilibrium test was achieved through the

517   comparison of analysed Cpx compositions (as expressed by the components EnFs, DiHd and Ca-Ts, where

518   Ca-Ts stays for Ca-Tschermak) with component contents predicted from melt composition (e.g., Putirka,

519   2008; Mollo et al., 2010; Jeffery et al., 2013; Barker et al., 2015; Ellis et al., 2017). Normative components

520   of Cpx were calculated following the scheme proposed in Putirka et al., (1996) and Putirka (2008); whereas

521   calculation of Cpx components based on melt composition was performed using equations (eq 3.1a) for

522   DiHd, (eq 3.2) for EnFs and (eq 3.4) for Ca-Ts in Putirka (1999). A graphical presentation (e.g., Jeffery et al.,

523   2013; Barker et al., 2015) of this test is shown in Figure 9.

524   The partitioning of An-Ab between mineral and liquid is known as An-Ab exchange coefficient, or K_D^{pl-liq}(An-

525   Ab) (defined as K_D^{pl-liq}(An-Ab) = [$XAb^{pl}XAlO_{1.5}^{liq}XCaO^{liq}$]/[$XAn^{pl}XNaO_{0.5}^{liq}XSiO_2^{iq}$], where liq is the liquid

526   composition, pl is the plagioclase composition and all components are in molar fractions) (Carmichael et al.,

527   1977; Holland and Powell, 1992; Putirka et al., 2007; Putirka, 2008; Lange et al., 2009; Keiding and

528   Sigmarsson, 2012; Jeffery et al., 2013; Barker et al., 2015; Waters and Lange, 2015). Figure 10 presents a

529   comparison of measured composition of plagioclase with the one calculated from the melt composition

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530   with the thermodynamic model eq (31) in Namur et al. (2012). A similar test can be applied for alkali-

531   feldspars (Putirka, 2008).

532   In summary, we accept: (i) Ol with K_D^{ol-liq}(Fe-Mg)= 0.30 ± 0.06 (Roeder and Emslie, 1970; Putirka, 2005a;

533   Putirka, 2008 and references therein) (Fig. 8a); (ii) Opx with $K_D^{opx-liq}$(Fe-Mg)= 0.29 ± 0.06 (Putirka, 2008 and

534   references therein) (Fig. 8b) or that display differences of ± 0.05 between the observed (K_D) and the ideal

535   (iK_D) values of the Fe-Mg exchange (Putirka, 2008 and references therein); (iii) Cpx with $K_D^{cpx-liq}$(Fe-Mg)=

536   0.28 ± 0.08 (Putirka, 2008) and that verify the one-to-one (± 0.1) relationship between predicted vs.

537   observed normative components (EnFs, DiHd and Ca-Ts) for at least two of the monitored components (Fig.

538   9); (iv) Pl with K_D^{pl-liq}(An-Ab)= 0.27 ± 0.11 for T > 1050°C and K_D^{pl-liq}(An-Ab)= 0.10 ± 0.05 for T < 1050°C

539   (Putirka, 2008) or that fall within ± 0.1 of the one-to-one relationship between predicted vs observed An

540   components (Fig. 10); and (v) Afs with $K_D^{afs-liq}$(An-Ab)= 0.27 ± 0.18 (Putirka, 2008). All mineral-liquid pairs

541   exceeding the accepted exchange coefficient values for Ol, Cpx, Opx and Fsp were discarded for

542   thermobarometric analyses.

543

544   **7.2 Pre-eruptive H_2O^{liq} content estimates**

545   Many thermobarometric models for volcanic system require an initial estimate of the pre-eruptive water

546   concentration (wt%) in melt (H_2O^{liq}), which was determined in this work by using the plagioclase-liquid

547   hygrometer model [eq. 25b] in Putirka (2008). Hygrometry calculations were produced after the application

548   of plagioclase-liquid equilibrium filters. The calculated pre-eruptive H_2O^{liq} wt% values (±1σ standard

549   deviation of the weighted mean) are plotted as isolines in Fig. 10. The hygrometer of Putirka (2008)

550   indicates(Fig. 10): (i) H_2O^{liq} negative values in basalts, from -0.20 to -0.40 wt%, with a weighted mean of -

551   0.37 ± 0.20 wt% (MSWD= 0.0026; n= 95); (ii) trachyandesites pre-eruptive water content in the range H_2O^{liq}:

552   0 – 1.40 wt% (weighted mean of 0.57 ± 0.12 wt%, MSWD= 0.12, n= 246); and (iii) trachytes with the highest

553   water concentration (H_2O^{liq}: 1.40 – 1.90 wt%; weighted mean of 1.46 ± 0.32 wt%, MSWD= 0.059, n= 37).

554   Following the approach of Keiding and Sigmarsson (2012), negative values in basalts are interpreted as

555   anhydrous melt compositions.

556   Application of plagioclase-liquid hygrometer model (Putirka, 2008) define anhydrous environment for

557   pressure-temperature calculations in basalts. Whereas hydrous conditions are required for evolved LHPCS

558   melts and in particular for trachytic lavas, where the impact of 1 wt% H_2O is expected to generate a

559   temperature decrease of ca. -40 °C and a pressure increase of ca. + 1.0 kbar in geothermometers and

560   geobarometers, respectively (Putirka, 2008; Keiding and Sigmarsson, 2012).

561   On contrary, existing studies (e.g., Kushiro, 1969; Sisson and Grove; 1993; Yang et al., 1996; Putirka, 2005a,

562   2005b, 2008; Kelley and Barton, 2008; Keiding and Sigmarsson, 2012) demonstrated a negligible effect of

563   water for basaltic and intermediate melts with H_2O^{liq} 0 – 1 wt%.

564

7.3 Thermobarometry Results

7.3.1 Basalts

When applied to phenocryst cores, the Pl-liq thermobarometry (Fig. 11) show that all basaltic materials have magmatic anhydrous T in the range 1230-1266 °C (weighted mean of 1250 ± 5 °C, ±1σ standard deviation of the weighted mean, MSWD= 0.112, n= 95). Pressure estimates are in the range 6.5-8.7 kbar (weighted mean of 7.9 ± 1.1 kbar, ±1σ standard deviation of the weighted mean, MSWD= 0.024, n= 28) for LH18 Ol-basalts, and 7.2-10.3 kbar (weighted mean of 9.2 ± 0.7 kbar (±1σ), MSWD= 0.064, n= 67) for LH5.2 and LH27.1 Ol-Cpx-basalt. Olivine-melt equilibrium (Fig. 11), for the olivine compositional range of Fo 80-85%, yields T window of 1240-1297 ± 27 °C (±1σ), consistent with the results obtained with Pl-liq thermometry. The Cpx-thermobarometry (Fig. 11), for both Cpx1 (phenocryst cores) and Cpx3 (phenocryst rims and unzoned phenocrysts), provides temperature of 1006-1209 °C (weighted mean of 1124 ± 12 °C (±1σ), MSWD= 3.4, n= 82). , for P in the range 3.1-11.5 kbar (weighted mean of 7.6 ± 0.8 kbar (±1σ), MSWD= 2.7, n= 36) for Cpx1, and 2.5-7.7 kbar (weighted mean of 4.0 ± 0.8 kbar (±1σ), MSWD= 0.63, n= 14) for Cpx3. Thermobaric estimates for Cpx4 (microlites in groundmass) indicate shallow conditions (0.3 – 3.0; weighted mean of 1.6 ± 1.2 kbar (±1σ), MSWD= 0.38, n= 6) for temperatures (1006-1123 °C; weighted mean of 1060 ± 54 °C (±1σ), MSWD= 2.9, n= 6) comparable to those obtained for Cpx1 and Cpx3. Higher temperature estimates (1067-1221 °C; weighted mean of 1157 ± 53 °C (±1σ), MSWD= 2.4, n= 7) at low-pressure (0.4-4.7; weighted mean of 2.9 ± 1.1 kbar (±1σ), MSWD= 0.83, n= 7) are instead obtained for a limited number of Cpx5 (aegirine-rich) compositions.

7.3.2 Trachyandesites

Based on the Opx- presence/absence criterion, two populations of trachyandesites have been discriminated in this study.

Opx-free trachyandesites LH15 and LH21-2 (El Limón and Sarabia lava flows, respectively) are characterized by i) plagioclase phenocryst cores crystallized at T of 1190-1263 °C (weighted mean of 1248 ± 7 °C (±1σ), MSWD= 1.09, n= 39) and P of 4.8-9.4 kbar (weighted mean of 7.7 ± 0.9 kbar (±1σ), MSWD= 0.14, n= 39); ii) comparable temperature (1193-1263 °C; weighted mean of 1227 ± 37 °C (±1σ), MSWD= 2.3, n= 6) and pressure (6.7-9.6 kbar, mean value of 7.8 ± 2.4 kbar (±1σ), MSWD= 0.101, n= 6) obtained for rare phenocryst rims and microlites at equilibrium; iii) olivine-melt equilibrium (with Fo: 75-80%) showing a T window of 1030-1055 ± 27 °C (±1σ); iv) rare Cpx2 (clinopyroxene phenocryst cores) showing equilibrium with melt and yielding T 1061-1239 °C (weighted mean of 1116 ± 29 °C (±1σ), MSWD= 2.3, n= 12) and P ca. 2.9 -8.3 kbar (weighted mean of 5.2 ± 1.2 kbar (±1σ), MSWD= 1.5, n= 12); v) Cpx3 (rims of and unzoned phenocrysts) showing equilibrium with melt and yielding thermobarometric results (T 938-1139 °C, with weighted mean of 1074 ± 15 °C (±1σ), MSWD= 1.9, n= 32; and P 1.0-4.4 kbar with weighted mean of 2.8 ±

599   0.5 kbar (±1σ), MSWD= 0.22, n= 32); vi) Cpx4 (groundmass microcrystals) compositions indicating, with

600   respect to Cpx3, comparable temperatures (1026-1127 °C, with weighted mean of 1059 ± 16 °C (±1σ),

601   MSWD= 0.71, n= 14) at lower pressure conditions (0.3 – 3.6 kbar with weighted mean of 1.4 ± 0.8 kbar

602   (±1σ), MSWD= 0.35, n= 14). The unique Cpx5-liquid pair at equilibrium yielded P-T conditions of 5.6 ± 1.5

603   kbar and 1122 ± 30 °C.

604   Thermobarometric estimates (Fig. 11) for Opx-bearing trachyandesites (LH4, LH13, LH17; LH26-1; LH26-2;

605   LH27-2) show overlapping P-T conditions for plagioclase populations with: i) phenocryst cores crystallizing

606   at T: 1145-1228 °C (weighted mean of 1187 ± 4 °C (±1σ), MSWD= 1.17, n= 166) and P: 4.1-7.7 kbar

607   (weighted mean of 5.8 ± 0.5 kbar (±1σ), MSWD= 0.059, n= 166), and ii) phenocryst rims and microcrysts

608   forming at T: 1140-1224 °C (weighted mean of 1168 ± 8 °C (±1σ), MSWD= 0.90, n= 35) and P: 4.4-8.5 kbar

609   (weighted mean of 6.4 ± 1.0 kbar (±1σ), MSWD= 0.14, n= 35). Lower temperatures (1050-1090 ± 27 °C

610   (±1σ)) are obtained using olivine (Fo 70-80%) – liquid equilibrium model.

611   Thermobarometers applied to pyroxenes indicate: i) Cpx2 (phenocryst cores) crystallizing at T: 979-1204 °C

612   (weighted mean of 1060 ± 8 °C (±1σ), MSWD= 1.7, n= 106) and P: 3.4 -11.65 kbar (weighted mean of 7.0 ±

613   0.3 kbar (±1σ), MSWD= 0.91, n= 106), ii) Cpx3 crystallizing at T: 958-1106 °C (weighted mean of 1026 ± 6 °C

614   (±1σ), MSWD= 1.3, n= 147) and P: 1.2 -6.9 kbar (weighted mean of 4.3 ± 0.2 kbar (±1σ), MSWD= 0.72, n=

615   147), iii) rare Cpx4 showing general equilibrium with melt and forming at P-T conditions of : 920-1123 °C

616   (weighted mean of 1020 ± 21 °C (±1σ), MSWD= 2.7, n= 24) and P: 0.1-3.4 kbar (weighted mean of 1.8 ± 0.6

617   kbar (±1σ), MSWD= 0.56, n= 24), and iv) Opx yielding crystallization conditions, for both phenocrysts and

618   microlites, of T 1048-1123 °C (weighted mean of 1078 ± 5 °C (±1σ), MSWD= 0.24, n= 129) and P: 0 -2.8 kbar

619   (weighted mean of 1.1 ± 0.6 kbar (±1σ), MSWD= 0.057, n= 84). To note the comparable thermometric

620   estimates (Fig. 11) calculated for mafic phases (Ol, Cpx and Opx) whereas only orthopyroxene (Opx) can be

621   considered a tracer of magma stagnations at shallow depth since the invariably lower pressure values

622   obtained by Opx-liquid barometer.

623

624   *7.3.3 Trachytes*

625   Magmatic P-T conditions (Fig. 11) of trachytes (LH5.1 and LH6) melts are defined by: i) plagioclase

626   crystallization at T: 1050-1094 °C (weighted mean of 1069 ± 6 °C (±1σ), MSWD= 0.39, n= 37) and P: 4.7-9.0

627   kbar (weighted mean of 6.5 ± 1.0 kbar (±1σ), MSWD= 0.20, n= 37), ii) olivine (Fo55-65%) – liquid regression

628   indicating olivine crystallization at 900-920 ± 27 °C (±1σ), iii) clinopyroxenes crystallization, both

629   phenocrysts (Cpx3) and groundmass(Cpx4), at temperature of ca. 955 °C (weighted mean of 956 ± 14 °C

630   (±1σ), MSWD= 0.00056, n= 17)   and very shallow-depth conditions (P weighted means of 2.3 ± 0.9 kbar

631   (±1σ), MSWD= 0.047, n= 10 and 1.6 ± 1.1 kbar (±1σ), MSWD= 0.04, n= 7; for Cpx3 and Cpx4, respectively).

632   Shallow-depth conditions are obtained also for orthopyroxene crystallization with temperature in the range

633   960-1006 °C (weighted mean of 990 ± 7 °C (±1σ), MSWD= 0.28, n= 49) and P: 0.2-3.6 kbar (weighted mean

634   of 1.6 ± 0.9 kbar (±1σ), MSWD= 0.101, n= 35). Alkali-feldspar-liquid thermometer produced temperature

635   always < 500°C, here interpreted as a subsolidus equilibration of groundmass after eruption. Interesting to

636   note that P-T conditions of plagioclase crystallization are comparable to those obtained for trachyandesitic

637   rocks.

638

639   **7.4 Magma evolution beneath Los Humeros**

640   The conceptual model of the present-day LHPCS magmatic plumbing system beneath the Los Humeros

641   caldera is presented in Fig. 12. Based on textural observations, mineral chemistry and thermobaric

642   estimates the early HT (1230-1270 °C) stage of LHPCS magma evolution is represented by high-anorthite

643   plagioclase phenocrysts and Mg-rich olivine (XFo= 80-85%) crystallizing in the deep (ca. 8 kbar) basaltic

644   reservoir. Where these magmas erupted directly, they formed Ol-basalt lava flows such as Texcal Lava flow

645   (LH18). This scenario is confirmed by the presence, in LH18 sample, of olivine with spinifex, dendritic and

646   skeletal textures, interpreted as supercooling mineral texture largely resulting from rapid olivine-

647   supersaturate magma rise from deeper level during the eruption (e.g., Donaldson, 1974; Nakagawa et al.,

648   1998; Fowler et al., 2002; Dahren et al., 2012; Welsch et al., 2013). Permanence of Ol-basaltic melts in the

649   deep reservoir, with a decrease in temperature of ca. 100 °C, is indicated by (Ti-rich augites) Cpx1-forming

650   at ca. 7-8 Kbar and 1150 °C (mean values). Where these magmas erupted as intra-caldera ol-basalts (LH5-2,

651   LH27-1), they are characterized by the further crystallization of (i) progressively Fe-rich olivine (up to XFo=

652   17-20%), (ii) Ab-rich plagioclase (XAn= 25-30%), (iii) Cpx3 unzoned phenocrysts and overgrowth on Cpx1-

653   cores, (iv) Cpx5 (Aeg-Aug) Na-clinopyroxenes and (v) Cpx4 microcrystals and microlites. This mineral

654   assemblage describes a near-isothermal magma uprising within a narrow temperature window of ca. 1070-

655   1150 °C. Such crystal-bearing magmas ascend from the deeper reservoir to intermediates and shallower

656   stagnation levels, where different phases would crystallize, before the eruption (e.g., Feng and Zhu, 2018).

657   However, the high-vesicularity observed in all studied basalts, suggests their rapid ascent and therefore a

658   short time to free-up the volatiles (e.g. Costa et al., 2013; Feng and Zhu, 2018).

659   Crystallization/fractionation of An-rich plagioclase, Fo-rich olivine and Ti-rich augite in the primary basaltic

660   magma produce residual melts of intermediate compositions. These evolved melts can ascend, carrying

661   early-formed phenocrysts (i.e., anorthitic plagioclase antecrysts), to the intermediate reservoir and stall.

662   Within this intermediate vertically-distributed layered storage system in the middle crust, Cpx2

663   clinopyroxene and all the rest of plagioclase phenocrysts start to crystallize producing progressively evolved

664   residual melts able to migrate upward in the feeding system (e.g., Freundt and Schminke, 1995; Patanè et

665   al., 2003; Klugel et al., 2005; Stroncik et al., 2009; Aulinas et al., 2010; Dahren et al., 2012; Keiding and

666   Sigmarsson, 2012; Scott et al., 2012; Jeffery et al., 2013; Coombs and Gardner, 2001; Barker et al., 2015;

667   Feng and Zhu, 2018).

668   The shallowest magma stagnation level (< 3kbar; mean 1.5 kbar) has been here interpreted as a complex

669   magma plexus constituted by a system of small magma volumes, distributed in locally interconnected

670   pockets and batches where (i) mafic and intermediate magmas shortly stall prior to erupt and (ii) evolved

671   melts reside for a relatively prolonged time, enough to crystallize orthopyroxene and to enabling the

672   escape of part of the exsolved volatiles (e.g., Feng and Zhu, 2018; Clarke et al., 2007), as suggested by

673   poor-vesicle textures observed in Opx-trachyte samples (LH5-1, LH6-1).

674   Compositional reverse zoning associated with sieve textures and dissolution (lobate and embayed rims)

675   features in phenocrysts are widely considered indicators of both magma mixing and magma replenishment

676   processes (e.g., Wright and Fiske, 1972; Duda and Schminkcke, 1985; Clague et al., 1995; Yang et al., 1999;

677   Klugel et al., 2000; Zhu and Ogasawara, 2004; Stroncik et al., 2009; Ubide et al., 2014; Viccaro et al., 2015;

678   Gernon et al., 2016; Feng and Zhu, 2018). Almost all investigated samples, from basalts to trachytes,

679   contain mainly normally zoned (Pl+Ol+Cpx) or unzoned (as in case of Cpx3 and Opx) phenocrysts. Rare

680   plagioclase and clinopyroxene with patchy cores (not suitable for thermobarometry) are reported. Since

681   reverse zoning and disequilibrium textures are rarely observed, we suggest that magma mixing and magma

682   replenishment processes occur locally and heterogeneously in the plumbing system (e.g., Cashman et al.,

683   2017 and references therein).

684   This hypothesis is in line with the results obtained from tests for mineral-melt equilibria. Rhodes's diagram

685   (Rhodes et al., 1979; Putirka, 2008) for olivine compositions (Fig. 8a) highlights a progressive decrease in

686   Mg#^{liq} from basalts to trachytes coupled with general absence of xenocrystals/antecrystals cargo. This

687   behavior is compatible with a complete removal from the melt of previously crystallized Mg-olivine (Roeder

688   and Emslie, 1970; Dungan et al., 1978; Rhodes et al., 1979; Putirka, 2008; Melluso et al., 2014). All melts

689   (from basalts to trachytes) show invariably suites of olivines with maximum forsterite (Fo) contents in

690   equilibrium with the respective whole rocks, and vertical trends consistent with closed-system melt

691   differentiation (Roeder and Emslie, 1970; Rhodes et al., 1979; Putirka, 2008; Melluso et al., 2014). Similar

692   behavior is obtained for orthopyroxene (Fig. 8b), where again Rhodes's test highlights absence of

693   antecrystals, and Opx-suites progressively and normally Fe-enriched from trachyandesites to trachytes.

694   Furthermore, the absence of clinopyroxene clots and overgrowth on orthopyroxene do not support the

695   occurrence of magma mixing/refilling (Laumonier et al., 2014; Neave et al., 2014; Zhang et al., 2015; Feng

696   and Zhu, 2018). Such interpretation is supported by field observations, where the interbedded basaltic

697   andesite and trachydacite fall deposits of the ca. 7 ka Cuicuiltic Member show no evidence of magma-

698   mixing (Dávila-Harris and Carrasco-Núñez, 2014).

699   An-Ab partition coefficients (e.g., Putirka, 2008; Jeffery et al., 2013) show a comparable scenario (Fig. 10) in

700   which: (i) basalts are characterized by suites of plagioclases with maximum anorthite (An) contents in

701   equilibrium with the respective whole rocks, and progressive An^{pl} decrease consistent with closed-system

702   differentiation; and (ii) progressive decrease in predicted An^{liq} from basalt to trachyte compatible with

703 evolved melts production via differentiation. Intermediate and evolved products are characterized by

704 antecrystals (or inherited cores) of anorthitic plagioclase, indicating that melt differentiation processes

705 occurred, involving the coexistence of earlier-crystallized An-rich plagioclase in melts. A similar behavior is

706 observed for clinopyroxene and in particular for Cpx1 and Cpx2 (clinopyroxene cores in basalts and in

707 trachyandesites, respectively) populations. Since these mineral cores (Pl, Cpx1 and Cpx2) generally present

708 normall growth rims (i.e., Ab-rich Pl and Cpx3), we suggest that stagnation levels at both intermediate and

709 shallower depths underwent crystallization in a closed system. Otherwise, features such as: i) diffused

710 reverse zoning, ii) high-temperature crystal-clots, mantling and overgrowth, iii) disequilibrium and

711 dissolution textures (e.g., Stroncik et al., 2009; Cashman et al., 2017; Feng and Zhu, 2018 and references

712 therein), should be widely observed, but this is not the case in the LHPCS studied lavas.

713

714 **7.5 The magma plumbing system**

715 The petrological archive constituted by LHPCS lavas, spanning from alkali-basalts to trachytes, describe the

716 Holocene activity of Los Humeros volcanic complex. Major element bulk compositions of LHPCS lavas are

717 characterized, in Harker diagrams (Fig. 3 b-d), by linear trends comparable to those expected for cogenetic

718 melts and progressive magma differentiation via fractional crystallization (e.g., Giordano et al, 2012). Intra-

719 caldera basalts show assemblages containing Aegirine-rich clinopyroxenes (Fig. 4 c, d), widely considered as

720 one of the most reliable indicator of magma transition to peralkaline conditions (i.e., White et al., 2009;

721 Melluso et al., 2014). However, absence of olivine in the most evolved LHPCS trachyte (LH6) excludes, at

722 this stage, a connection with typical basalt-pantellerite suites where tephroitic-fayalite is commonly found

723 in high-silica rocks (i.e., White et al., 2005; Ronga et al., 2010; Macdonald et al., 2012, Melluso et al., 2014

724 and references therein).

725 Results obtained from the application of different and independent thermobarometry models (Fig. 11)

726 confirm the working hypothesis of a complex magmatic plumbing system rather than a single "standard"

727 magma chamber (e.g., Keiding and Sigmarsson, 2012; Cashman and Giordano, 2014; Cashman et al., 2017;

728 Feng and Zhu, 2018) developed beneath the active Los Humeros caldera and feeding the LHPCS volcanism.

729 With the aim to propose an updated and realistic conceptual model of the present-day main storage zones

730 and magma plumbing system within the crust below Los Humeros caldera, we integrate pressure-

731 temperature estimates acquired in this work, with the existing data related to crustal structure and

732 properties of the study area. The resulted model is shown in Figure 12.

733 The density of TMVB crust shows a large range between 1800 Kg/m^3 for unconsolidated sediments to about

734 3000 kg/m^3 for the lower crust and 3300 kg/m^3 for the upper mantle (Dziewonski and Anderson, 1981;

735 Campos-Enríquez and Sánchez-Zamora, 2000; Davies, 2013). A reasonable available up today compilation of

736 crust data for Los Humeros volcanic complex is recovered by the measure N°10 of the Crust 1.0 global

737 model (Dziewonski and Anderson, 1981; Davies, 2013). The measure N°10 (yellow star in Fig. 1) is located

738   within the study area at the southern termination of the Tepeyahualco Lava Flow and describes a crust

739   (Fig. 12) made of five main seismic layers: i) upper sediments (thickness: 1km, density 2110 km/m^3), ii)

740   middle sediments (thickness: 0.5 km, density 2370 km/m^3), iii) upper crust (thickness: 13.58 km, density

741   2740 km/m^3), iv) middle crust (thickness: 15.27 km, density 2830 km/m^3), and v) lower crust (thickness:

742   13.58 km, density 2920 km/m^3). Inferred (seismic) Moho depth is reported at -41.67 km with an upper

743   mantle density of 3310 km/m^3 (Dziewonski and Anderson, 1981; Davies, 2013). Here we use a five-tiered

744   density model, as derived from the Crust 1.0 global model, for the 41.67 Km continental crust beneath Los

745   Humeros caldera, to convert obtained pressure estimates to depths.

746   The thermobarometry models applied to the LHPCS lavas define a broad region of crystallization between 0

747   and ca. 30 km in depth that can be described with a quadrimodal distribution of pressure values (Fig. 12),

748   which allow us to propose a complex polybaric continuous heterogenous multilayered transport and

749   storage magmatic system.

750   A deep-seated anhydrous Ol-basalt reservoir at depths of ca. 28-33 km (7.6-9.2 kbar), at the boundary

751   between lower and middle crust, below the caldera is recorded by (a) An-rich plagioclase cores (XAn = 50-

752   70 %), and (b) Ti-rich augitic clinopyroxene Cpx1 cores (Mg# up to 75, TiO$_2$ up to 4.57 wt%) of Cpx1.

753   Overlapping the calculated anhydrous temperature values from plagioclase-liquid, Cpx1 clinopyroxene-

754   liquid and olivine-liquid pairs provide a total range of ca. 1000 – 1300 °C for this mafic reservoir. Highest

755   anhydrous temperature values are achieved for Cpx-free Ol-basalt Texcal lava flow (LH18) where the

756   convergence of plagioclase-liquid thermobarometry and olivine-liquid thermometry models indicate

757   conditions of ca. 1230-1270°C at ca. 8 kbar. Lower anhydrous temperatures of ca. 1000-1210 °C, are

758   obtained at a comparable average pressure value of 7.6 kbar for Cpx-bearing intra caldera Ol-basalts (LH5-

759   2; LH 27-1). These results are in agreement with existing literature on the near-liquidus melting behavior of

760   high-Al basaltic magmas (Mg# ca. 60-70 and Al$_2$O$_3$: 17-19 wt%) under dry conditions (e.g., Thompson, 1974;

761   Grove et al., 1982; Crawford et al., 1987; Bartels et al., 1991; Grove, 2000). At 1250-1300 °C and ca. 10 kbar

762   (Point *A* in Fig. 11) the basaltic melt is in equilibrium with a mantle peridotite mineral assemblage of olivine

763   + clinopyroxene (Kushiro and Yoder, 1966; Presnall et al., 1978; Grove et al., 1982; Fuji and Scarfe, 1985;

764   Takahashi, 1986; Fallon and Green, 1987; Bartels et al., 1991; Sisson and Layne, 1993; Wagner et al., 1995;

765   Grove et al., 1997; Grove, 2000; Kinzler et al., 2000). Following the models proposed by Thompson (1974),

766   Bartels et al. (1991) and Grove (2000), a temperature decrease would lead primary melts to pass the "dry

767   basaltic liquidus" and start the crystallization of Ol+Pl (higher temperatures) or Ol+Cpx+Pl (lower

768   temperatures) assemblages (see stability fields in Fig. 11). Given the ubiquitous presence in all LHPCS

769   basalts of well-developed euhedral to subhedral olivine crystals (both phenocrysts and microlites) at

770   equilibrium with anorthitic plagioclase, it is possible to exclude that crystallization history started at depth >

771   ca. 10-12 kbar where olivine is not a stable phase and the primary assemblage would be characterized only

772   by Cpx+Pl+Sp in equilibrium with melt (Kushiro and Yoder, 1966; Thompson, 1974; Presnall et al., 1978;

773   Bartels et al., 1991; Grove, 2000).

774   A second magma transport and storage systems can be recognized at depths of 15-30 km (ca. 4.5 − 7.8

775   kbar), in continuity with the deeper basaltic reservoir and distributed along the whole middle crust

776   thickness, as recorded by the wide range of pressure estimates obtained from plagioclase (XAn= 40-70%)

777   and Cpx2 clinopyroxene cores (Mg#: 59-84; TiO_2 mean value 0.99 wt%). Thermometry models based on

778   plagioclase, Cpx2 clinopyroxene and olivine show convergence for hydrous temperature values in the range

779   of 979 − 1263 °C. Thermobarometry models, together with textures and petrographic relations in all

780   analyzed trachyandesite and trachyte samples suggest that all plagioclase, all Cpx2 clinopyroxene

781   phenocrysts, and part of microlites, grew in this second storage system. In particular, it is possible to

782   observe two main crystallization temperature conditions: (a) at ca. 1190°C (weighted mean value, MSWD=

783   2.2, n= 205) plagioclase phenocrysts crystallization in trachyandesite melts is observed, whereas (b) at the

784   lower temperature of ca. 1070 °C (weighted mean value, MSWD= 1.7, n= 155) is reported the crystallization

785   of all olivine, all Cpx2 phenocrysts, and plagioclase phenocryst in trachytes. We interpret the common

786   Pl+Cpx2 phenocryst-forming barometric conditions as evidence of a growth-dominated regime within this

787   second magma storage zone (e.g., Barclay et al., 1998; Humphreys et al., 2006; Scott et al., 2012), whereas

788   the smaller crystals (microcrystals and microlites) represent the nucleation-dominated regime (Scott et al.,

789   2012) that can be associated with ascent-related decompression of melts at shallower levels (e.g.,

790   Cashman, 1992; Cashman and Blundy, 2000; Humphreys et al., 2009).

791   The third melt storage zone occurs at shallower depths of ca. 10-15 km, possibly corresponding to the

792   transition between middle- and upper-crust, as indicated by convergence of barometric estimates

793   (weighted mean value of 3.9± 0.2 kbar (±1σ), MSWD= 0.80, n= 203; P ranging ca. 1-7 kbar) obtained from

794   Cpx3 clinopyroxene (i.e., unzoned phenocrysts and overgrowth/rims around earlier formed Cpx1- and

795   Cpx2-cores) population. Cpx3 clinopyroxene-liquid thermometry model indicates, for this third storage

796   zone a mean temperature of 1040 °C (weighted mean value, MSWD= 2.6, n= 203; T ranging ca. 940-1210

797   °C) comparable to those calculated for Ol+Cpx2 assemblages in the previous described second and deeper

798   stagnation system. The obtained pressure estimates for the second and the third storage systems are

799   compatible with multiple magma storage pockets, in which melts of comparable compositions ascend

800   slowly enough for phenocrysts to form (e.g. Scott et al., 2012), and start cooling before the final ascent to

801   shallower conditions (e.g., Dahren et al., 2012; Chadwick et al., 2013; Gardner et al., 2013; Jeffery et al.,

802   2013; Preece et al., 2013; Troll et al., 2013). Taking into account the textures and the chemistry of Cpx3

803   clinopyroxene phenocrysts, the obtained thermobarometric estimates could be interpreted as the

804   pressure-temperature environment of last major levels of magma stagnation and fractionation (Putirka,

805   1997; Klugel et al., 2005; Galipp et al., 2006; Stroncik et al., 2009).

806   The fourth shallowest storage zone located at depths of ca. 3-7 km (weighted mean value of 1.5± 0.2 kbar

807   (±1σ), MSWD= 0.24, n= 177; P ranging ca. 0.1-4.5 kbar), is required to explain the presence of i) Cpx4

808   clinopyroxene (microcrystals and microlites) in all LHPCS lavas, ii) Aeg-rich Cpx5 clinopyroxene in basalts,

809   and iii) Fe-olivine (Fo = 55-65%) and orthopyroxene in Opx-bearing evolved LHPCS lavas. Magmas in this

810   shallow storage system show a wide range of temperature values calculated for hydrous melts: a) ca. 1060

811   °C (weighted mean value, MSWD= 2.4, n= 7) for Aeg-rich Cpx5 crystallization in basalts, b) ca. 1070 °C

812   (weighted mean value, MSWD= 1.09, n= 168) for Cpx4 and Opx crystallization in trachyandesites, and c) ca.

813   965 °C (weighted mean value, MSWD= 2.2, n= 78) for olivine, Cpx4 and Opx crystallization in trachytes.

814   Thermobaric estimates obtained for Aeg-rich Cpx5 agree with those calculated for transitional basalts at

815   Pantelleria (White et al., 2009 and references therein), whereas orthopyroxene crystallization conditions

816   overlap with the existing literature for intermediate rocks (e.g., Rutherford et al., 1985; Wallace and

817   Anderson, 2000; Reubi and Nicholls, 2004; Allan et al., 2013; Jeffery et al., 2013). The broad distribution of

818   melt chemistry from basalt to trachyte, together with the obtained thermobaric estimates, define a shallow

819   magma storage environment characterized by progressive accumulation of small locally interconnected

820   magma pockets and batches (e.g., Reubi and Nicholls, 2004; Jeffery et al., 2013) dispersed in the upper

821   crust (<10 km) with a possible magma plexus at a depth of 2-4 km under the caldera (e.g., Armienti et al.,

822   1989; Freundt and Schminke, 1995; Pietruszka and Garcia, 1999; Patanè et al., 2003; Klugel et al., 2005;

823   Stroncik et al., 2009; Dahren et al., 2012; Jeffery et al., 2013; Coombs and Gardner,, 2001, 2004).

824

825   **7.6 Implications for Los Humeros active geothermal systems**

826   Existing conceptual models for Los Humeros volcanic complex are based on the "Standard Model" (*sensu*

827   Gualda and Ghiorso, 2013). These models mainly refer to the Los Humeros activity phase (the "caldera

828   stage" in Carrasco-Núñez et al., 2018 and references therein) that produced voluminous ignimbrites (in

829   particular the Xaltipan ignimbrite) hypothesizing a single, bowl-shaped, long-lived, melt-dominated huge

830   classical magma chamber of 1000-1500 Km³ in volume, at depth of 5 to 10 km from the surface (Verma,

831   1983, 1984, 1985a, 1985b; Verma and Lopez, 1982; Verma et al., 1990; Verma and Andaverde, 1995; Verma

832   et al., 2011; Verma et al. 2013; Carrasco-Núñez et al., 2018).

833   Thermobarometric estimates obtained in this work, combined with petrographic observations and

834   information from the crustal structure beneath Los Humeros caldera, permit us to propose a different

835   conceptual model, made of a complex polybaric magmatic plumbing system of multiple, more or less

836   interconnected magma transport and storage layers, batches and ponds, feeding the Holocene activity of

837   the Los Humeros volcanic complex.

838   Our results indicate that magma transport and storage levels, beneath Los Humeros caldera, are distributed

839   across the whole crust from ca. 30 to 3 km (from the lower- to the very upper-crust) with density contrasts

840   between different crustal layers acting as a controlling parameter for ascending or stalling magmas (e.g.,

841 Dahren et al., 2012). Moreover, it is possible to propose that each of these crust/density boundaries will

842 determine lateral transport and grow of magma stagnation pockets (e.g., Dahren et al., 2012). At depths

843 <5km, magmas (from mafic to felsic) ascending from all the lower storage zones, are stalled once more. The

844 shallowest complex multi-storage system is interpreted as a plexus of scattered, more or less

845 interconnected, ephemeral small-volume batches and pockets of melts, without any defined spatial

846 distribution as ruled out by field-locations of the LHPCS studied lavas eruptive centers.

847 A shallow storage zone presenting magmas with heterogenous compositions (from mafic to felsic) has been

848 already proposed by Dávila-Harris and Carrasco-Núñez (2014) to explain the eruptive history of the intra-

849 caldera Cuicuiltic Member that was produced by the coeval eruption of compositionally contrasting

850 unmixed magmas. However, a shallow ponding system characterized by heterogeneous composition of

851 magmas involved beneath Los Humeros caldera is not an exceptional case. Examples of shallow

852 heterogeneous reservoirs beneath active volcanic complexes are widely reported (e.g., Nairn et al., 1998;

853 Kratzmann et al., 2009; Sigmarsson et al., 2011; Keiding and Sigmarsson, 2012).

854 Our results also agree with the work of Creon et al. (2018) where calculated fluid saturation depths derived

855 for melt inclusions in post-caldera lavas indicate different magma-ponding levels within a range of depths

856 between 5 and 13 km, coupled with a possible deeper reservoir/origin (26-32 km) and a final shallow

857 stagnation level (ca. 1.5-3.0 km).

858 The geothermal activity of a volcanic complex is expected to be the result of stagnation and cooling of

859 magmas in the shallower storage zone (e.g., Gunnarsson and Aradóttir, 2015), where classic conductive

860 models are mainly controlled by age and volume of the magmatic system representing the heat source

861 (Smith and Shaw, 1975; Duffield and Sass, 2003; Gunnarsson and Aradóttir, 2015; Carrasco-Núñez et al.,

862 2018).

863 The present geothermal activity of LHVC is characterized by a limited NNW-SSE non-homogeneous areal

864 distribution within the Los Potreros nested caldera (e.g., Norini et al., 2015). Based on (i) the young (Upper

865 Pleistocene-Holocene) of most of LHPCS volcanic activity, (ii) the relatively small erupted volumes of LHPCS

866 lavas, in particular of those erupted within the Los Potreros caldera, and (iii) a shallow-crust plexus

867 involving heterogeneous unmixed magmas, as derived by results obtained in this work, we therefore

868 discard the hypothesis of a single, large and voluminous shallow magmatic chamber homogenously

869 distributed beneath the caldera, in favor of a more reliable scenario characterized by a shallow magmatic

870 transient batches of different magmas localized beneath Los Humeros nested caldera. In the light of these

871 results, a revision/update of the heat source feeding the Los Humeros geothermal system is needed to

872 produce correct and up-to-date geothermal potential estimates of the geothermal field and to develop

873 efficient geothermal exploration strategies.

874

875 **8.CONCLUSIONS**

876 In this study we propose an integrated field-based petrographic-mineralogical approach to unravel the

877 evolution and configuration of the present-day magmatic plumbing system that is feeding the post-Caldera

878 stage activity of Los Humeros volcanic complex. The main results of this study can be summarized as

879 follows.

880 • A polybaric complex transport and storage system, characterized by multiple magma levels more or

881 less interconnected in time, has been recognized based on application of mineral-melt inverse

882 thermobarometry models.

883 • A deep mafic reservoir (ca. 30km) is identified by Pl+Ol assemblage in basalts. Intermediate magma

884 storage systems (in the whole middle crust) are described by the progressive evolution of

885 clinopyroxene phenocryst-compositions and a shallow magmatic stagnation system (ca. 1.5kbar, 3-

886 5km) has been defined by crystallization of clinopyroxene microlites, aegirine clinopyroxenes in

887 basalt, and in particular by orthopyroxene formation in most evolved melts. All cpx-bearing lavas

888 are produced by progressive differentiation via polybaric fractional crystallization during magmas

889 ascend through the plumbing system.

890 • The compositional behavior of the main phases (olivine, plagioclase, clinopyroxene,

891 orthopyroxene), together with their preserved textures, permits to exclude, at this stage, a

892 magmatic feeding system dominated by magma mixing and magma replenishment, in favor of a

893 plumbing system dominated by levels, pockets and batches of melt underwent single charge.

894 • The thermobarometric results obtained in this work indicate that, unlike previously believed, the

895 present configuration of the plumbing system is vertically extensive across the entire crust with a

896 deeper residence zone for basalts at 8 kbar (ca. 30-33 km) and a complex middle to very upper

897 crust zone (0.5 kbar) where basalts rapidly ascend and stall prior to erupt and where smaller

898 batches of magma differentiate to trachyandesites and trachytes at times interconnected with the

899 lower feeding zone.

900 • The main outcome for the modeling of the magmatic heat source of the geothermal system is the

901 inadequacy of conservative conceptual models based on the classical melt-dominated, single,

902 voluminous, long-lived magma chamber (i.e., "Standard Model"), in favor of an innovative and

903 more realistic vision of magmatic plumbing systems made of multiple, more or less interconnected

904 magma transport and storage layers within the crust, feeding small (ephemeral) magma pockets at

905 shallow-crust conditions.

906 • The proposed model for the magmatic plumbing system at LHVC provides a new configuration of

907 the heat source feeding the present geothermal reservoir, and therefore, must be consider it for

908 geothermal exploration purposes.

909   •   Our study demonstrate that petrology represents a consistent method, with respect to geophysics
910   investigations and seismic surveys, able to unravel the anatomy of complex magmatic plumbing
911   system.

912

913 **APPENDIX A: Analytical details**

914 **A.1 Petrography of volcanic samples**

915 Rock magmatic fabrics, textures and mineral assemblages were studied on polished thin sections, using a

916 Nikon Eclipse 50iPol polarized light microscope (PLM) equipped with Nikon Ds-Fi2 CCD camera (Nikon,

917 Tokyo, Japan) and Nikon Nis-Elements software (Ver4.30.01), at Laboratorio di Microtettonica, Dip. Science,

918 Università Roma Tre (Roma, Italia). Mineral abbreviations follow Whitney and Evans (2010).

919

920 **A.2 Bulk major element geochemistry**

921 After washing in distilled water, samples were grounded in an agate mill, pre-contaminated with an aliquot

922 of sample. Whole-rock major element concentrations (4 samples) were measured at the Activation

923 Laboratories (Ontario, Canada), through ion coupled plasma (ICP)- optical emission (OE).

924 Additional samples (9) were analyzed by X-ray fluorescence (XRF) using a ZSX Primus II (Rigaku Co., Japan)

925 at Nagoya University, Japan. Loss on ignition (LOI) was measured from the sample powder weight in a

926 quartz glass beaker in the oven at 950°C for five hours. XRF-analyses were carried out following the

927 procedure presented in Azizi et al., (2015; 2018a; 2018b).

928 For major elements the uncertainty (1 sigma) is estimated better than 2% for values higher than 5 wt %,

929 and better than 5% in the range 0.1-5 wt %.

930

931 **A.3 Mineral chemistry**

932 Polished thin sections (13 samples) selected for petrography investigations, were then studied for mineral

933 chemistry and ca. 2400 analyses of mineral phases were obtained with a Cameca SX100 electron

934 microprobe (EMP) at the Institut für Anorganische Chemie, Universität Stuttgart. Operating conditions were

935 15 kV and 10 to 15 nA, counting times of 20 s both for peak and background. Compositions were

936 determined relative to natural and synthetic standards. Spot sizes were 1-10 μm depending on the phases

937 analyzed. Back Scattered Electron (BSE) imaging was obtained by using the same electron microprobe with

938 operating conditions of 15 kV, 50 nA. Mineral structural formulae of feldspar, olivine and spinel were

939 calculated through the software CalcMin_32 (Brandelik, 2009). Mineral structural formulae of

940 orthopyroxene were calculated following Putirka et al. (1996) and Putirka (2008). Clinopyroxene formula

941 has been calculated following procedures reported in Putirka et al. (1996), Putirka (2008), Masotta et al.

942 (2013). Clinopyroxenes were then classified integrating the Wo-En-Fs scheme (Morimoto, 1989) and J vs. Q

943 scheme (Morimoto, 1988, 1989) with J= 2Na apfu and Q= (Ca+Mg+Fe^{2+}) apfu. Aegirine (XAeg) component

944 correction, for Na-rich Cpx (Aegirine-Augite series), followed the scheme (XAeg= Na apfu if Na < Fe$^{3+ \text{Tot}}$,

945 XAeg= Fe$^{3+ \text{Tot}}$ apfu if Na > Fe$^{3+\text{Tot}}$) proposed by Putirka et al. (1996), Putirka (2008) and based on Fe^{2+} - Fe^{3+}

946 correction of Lindsley (1983).

947

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1635   **SUPPLEMENTARY MATERIALS**

1636   *Supplementary Tables S1: Feldspar, EMPA complete dataset.*

1637   *Supplementary Table S2: Clinopyroxene, EMPA complete dataset.*

1638   *Supplementary Table S3: Olivine, EMPA complete dataset.*

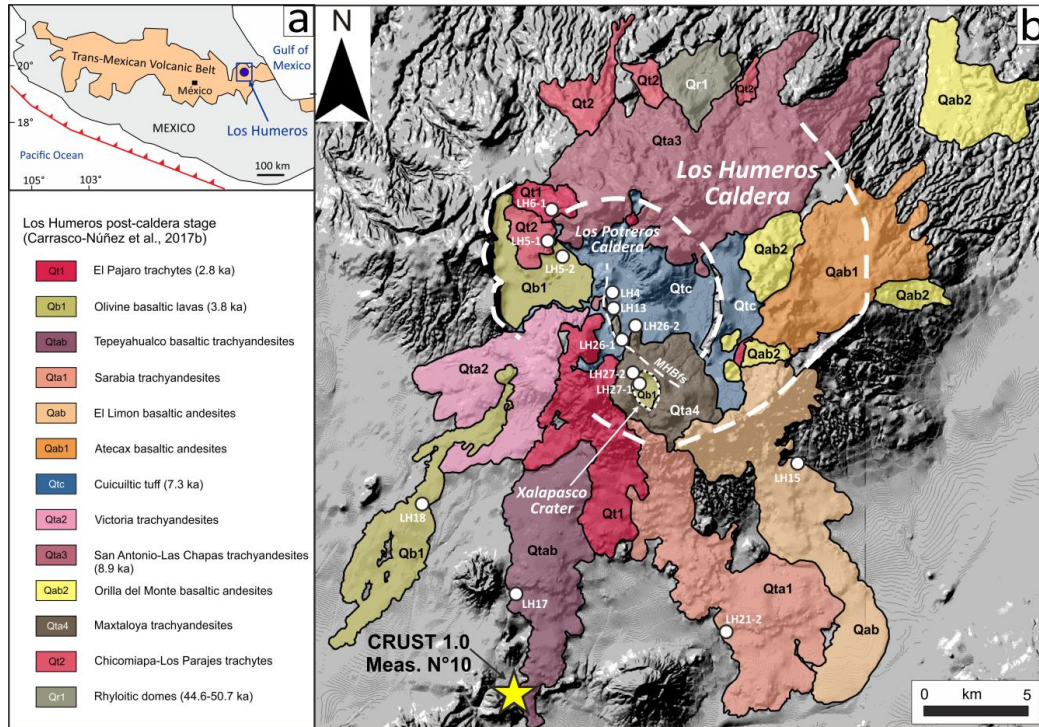1639   *Supplementary Table S4: Orthopyroxene, EMPA complete dataset.*

1640   *Supplementary Table S5: Opaque Minerals and Spinels, EMPA complete dataset.*

1641

1642   **FIGURES**

1643   **Figure 1**

1644

1645   **Figure-1.** Geological Context. (a) The Los Humeros volcanic complex (LHVC, blue dot) with respect to the

1646   Trans-Mexican Volcanic Belt (TMVB). (b) Shaded relief image obtained from 15 m resolution digital

1647   elevation model (DEM) of the LHVC. Volcanic products of the Los Humeros post-caldera stage are redrawn

1648   from Carrasco-Núñez et al. (2017b). The map shows location (white dots) and volcanological significance of

1649   the samples used in this study. The yellow star indicates the locality of the measure N°10 of the Crust 1.0

1650   global model (Dziewonski and Anderson, 1981; Davies, 2013).

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1653   **Figure 2**
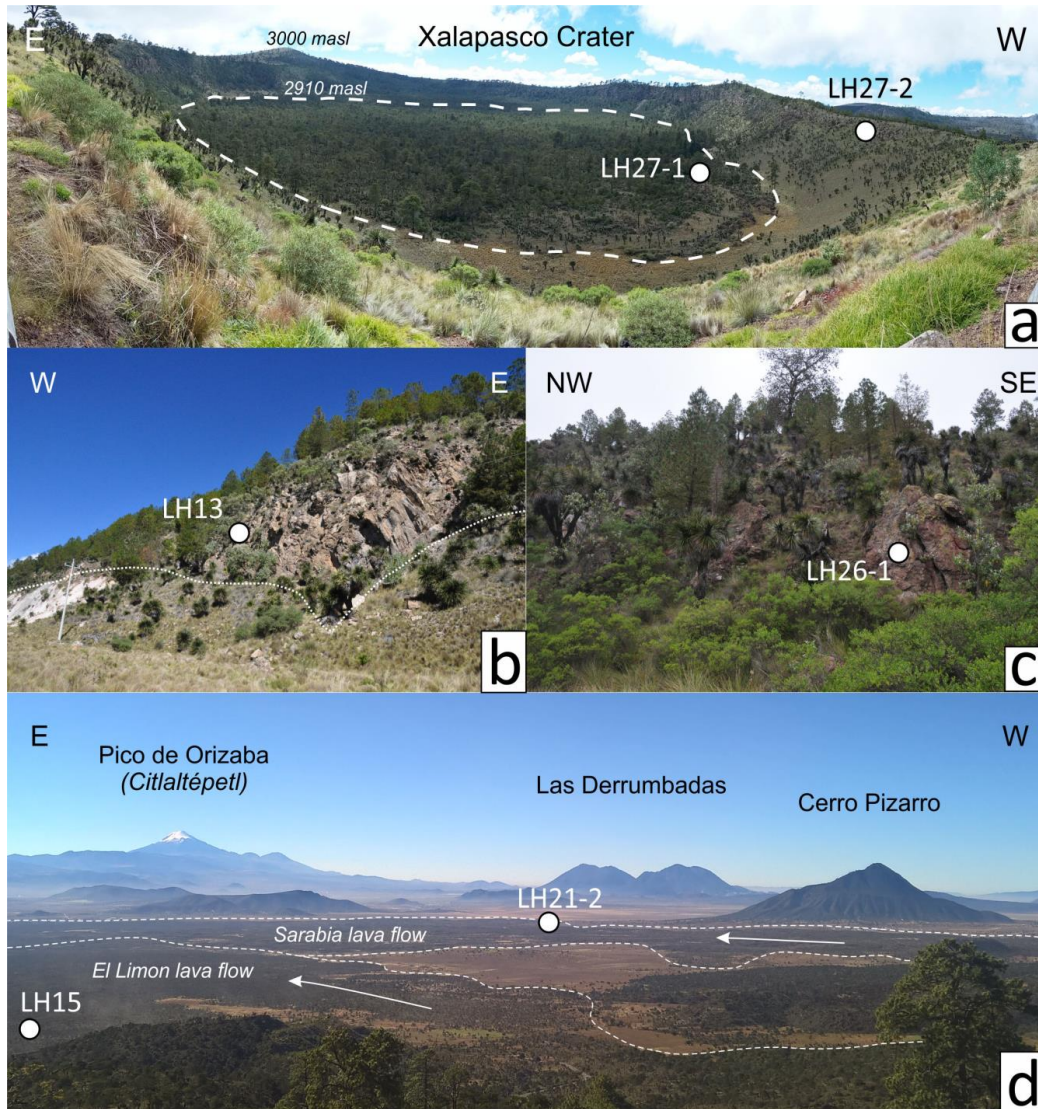
1654

1655   **Figure-2.** Field photographs of LHPCS volcanic products. (a) E-W panoramic view of Xalapasco crater; the

1656   white dashed line indicates the limit of Ol-basalts lavas filling the crater. (b) Trachyandesites lavas

1657   outcropping at Los Potreros, south to Los Humeros town. Joints are indicated with continue white lines. (c)

1658   Trachyandesites lava-dome outcropping inside Los Potreros caldera, north to Xalapasco crater. (d) E-W

1659   panoramic view from the Los Humeros caldera rim. With dashed lines are indicated the two major

1660   trachyandesitic lava flows of "El Limón" and "Sarabia". Pico de Orizaba, Las Derrumbadas and Cerro Pizarro

1661   volcanoes are also indicated. White dots indicate sampling localities.

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1664   **Figure 3**
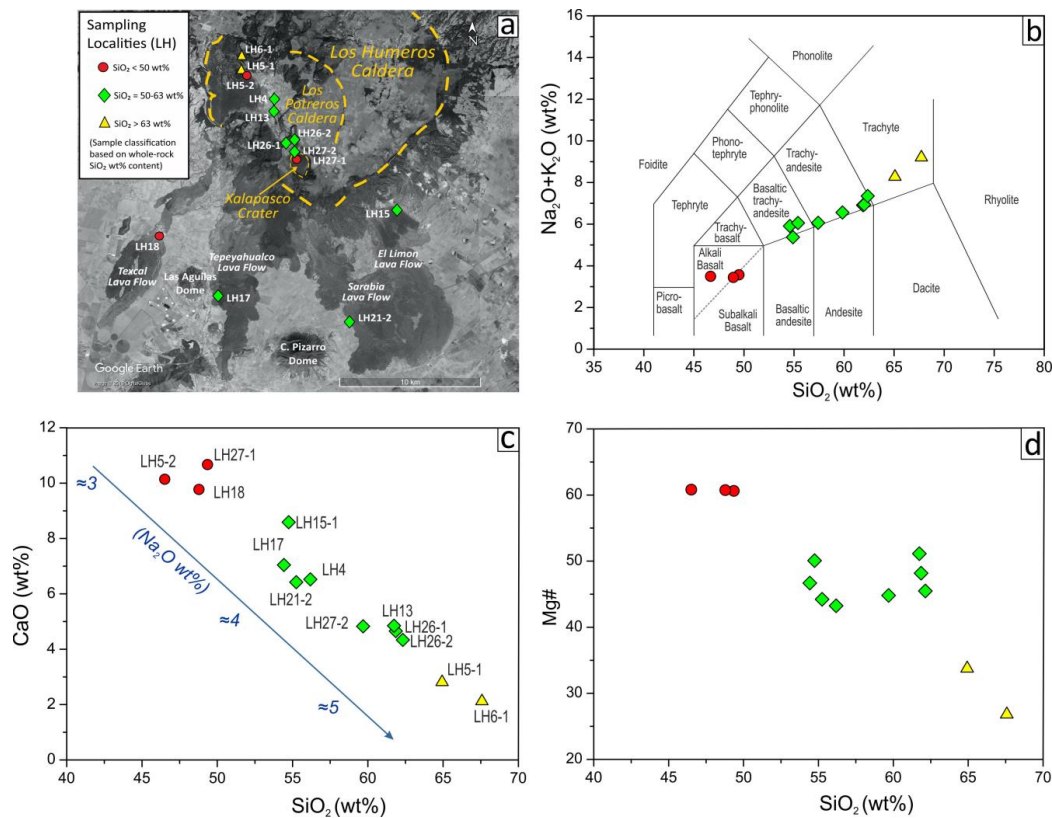
1666   **Figure-3.** (a) Satellite image of the LHVC (Image Landsat from Google Earth Pro, 2018 Digital Globe;

1667   courtesy of Google) with localization of samples selected for this study. (b) Total alkali versus silica (TAS)

1668   diagram (Le Maitre et al., 2002). (c-d) Major elements selected Harker diagrams for LHPCS studied lavas.

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1671 **Figure 4**
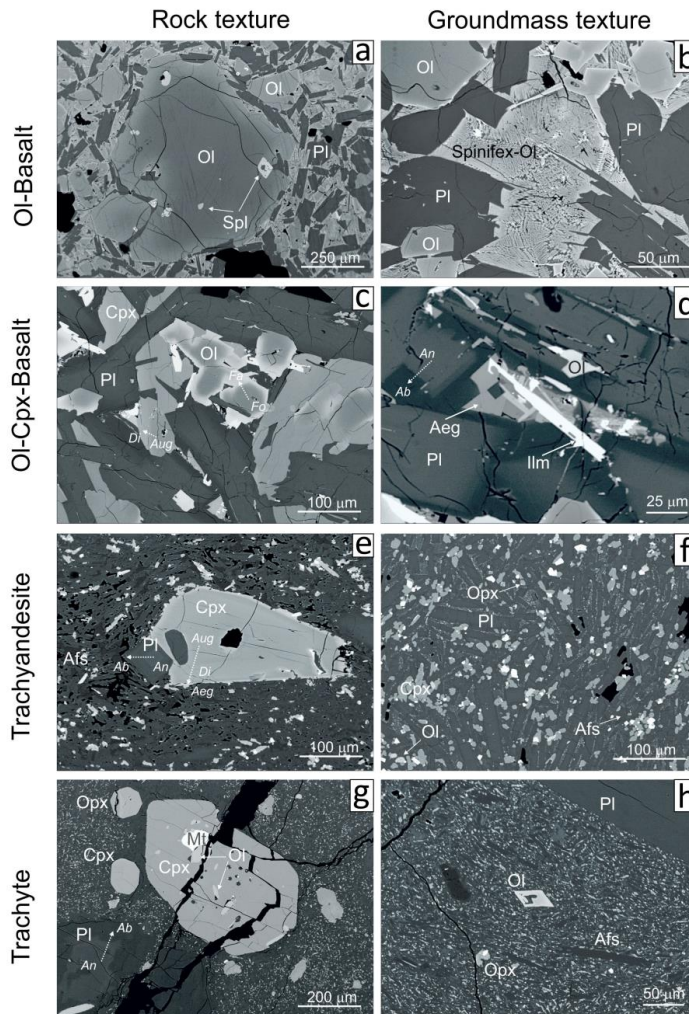
1672

1673 **Figure-4.** Microtextures and fabrics of the LHPCS lavas. (a) Back-scattered electrons (BSE) image of the Ol-

1674 basalt fabric, dominated by euhedral unzoned Pl+Ol, with major olivine phenocryst characterized by Cr-Spl

1675 inclusions. (b) BSE image of Ol-basalt groundmass highlighting the spinifex to skeletal and dendritic

1676 crystallization of olivine. (c) BSE image of Cpx-bearing Ol-basalt. Normal zoning growth is observed for all

1677 the three main mineral phases (Pl+Ol+Cpx). (d) BSE image of Cpx-bearing Ol-basalt groundmass

1678 characterized by albitic plagioclase, aegirine-pyroxene, Fe-rich olivine and ilmenite. (e-f) BSE images of

1679 trachyandesites. It is possible to observe a microcrystalline groundmass where major phenocrysts of Cpx

1680 and Pl are dispersed. (g-h) BSE images of trachytes, characterized by a microcrystalline groundmass and

1681 Pl+Cpx+Opx phenocrysts. Major Cpx phenocrysts present inclusion of Ol+Mt.
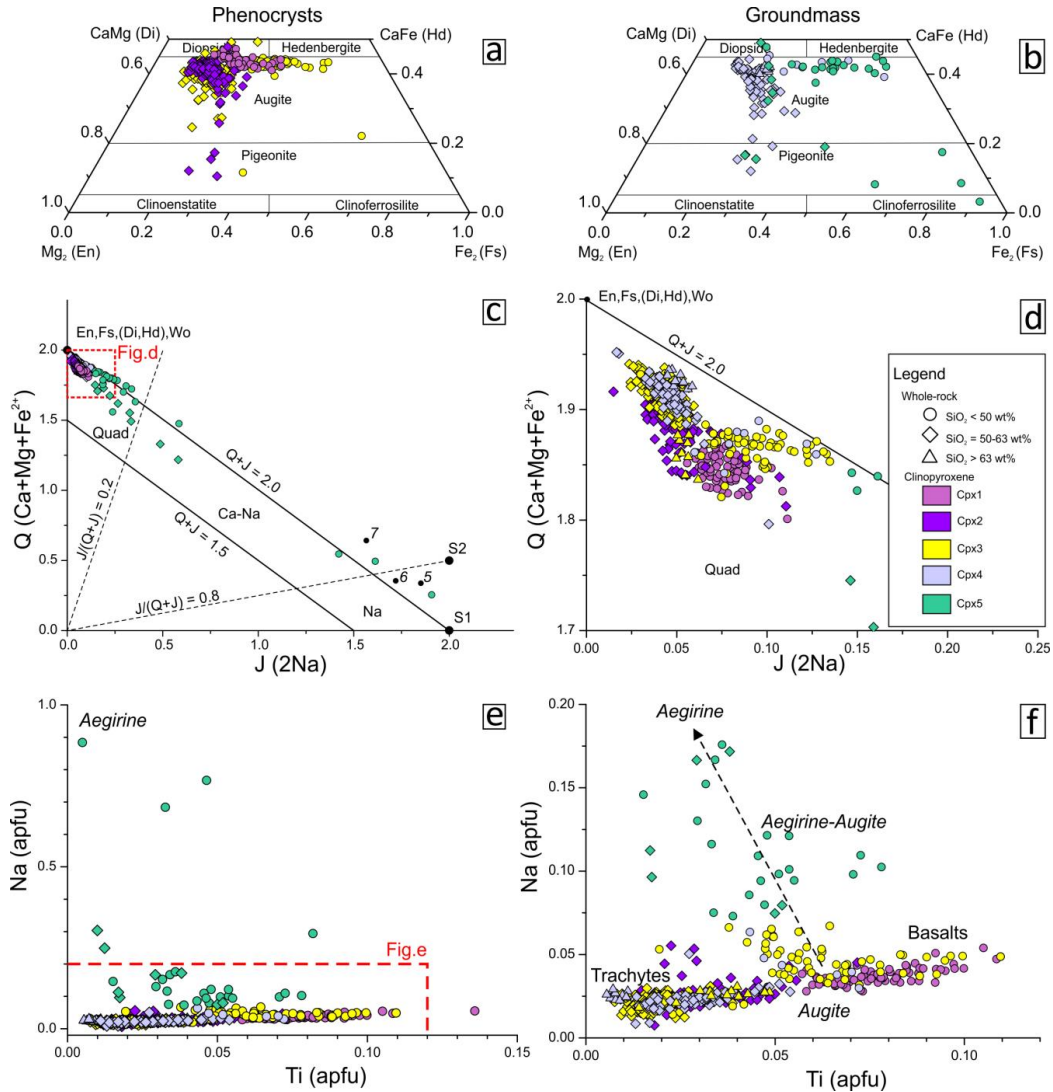
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1683   **Figure 5**
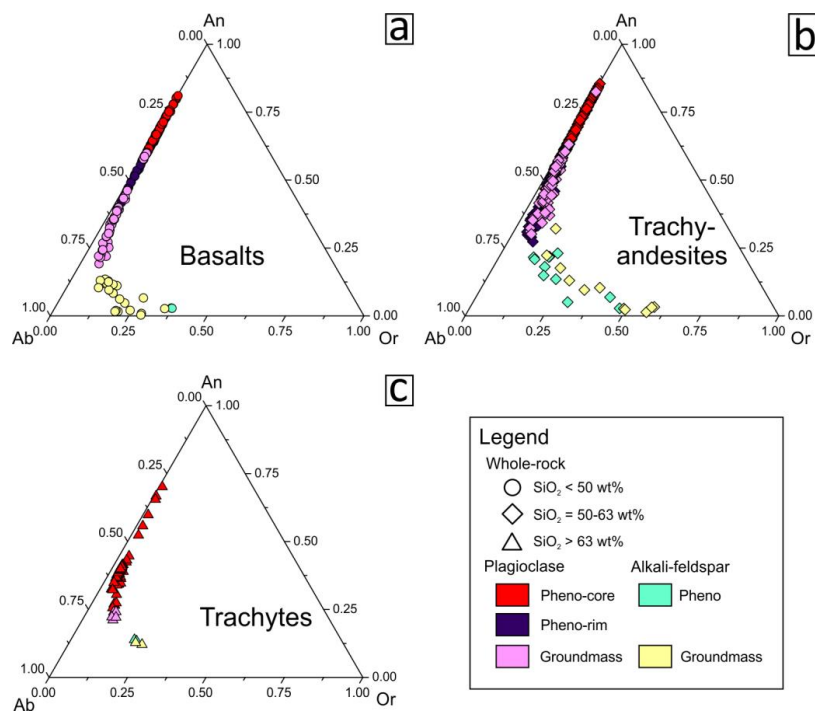
1684

1685   **Figure-5.** An-Ab-Or diagrams showing the composition of feldspar in (a) basalts (circles), (b) trachyandesites

1686   (diamonds) and (c) trachytes (triangles) of LHPCS lavas.

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1688   **Figure 6**

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1690   **Figure-6.** Di-Hd-En-Fs, Q-J and Ti vs. Na diagrams showing the composition of clinopyroxenes in LHPCS

1691   lavas. Basalt, trachyandesites and trachytes are indicated with circles, diamonds and trinagles, respectively.

1692   (a) Di-Hd-En-Fs diagram for clinopyroxene phenocrysts (Cpx1, Cpx2, Cpx3). (b) Di-Hd-En-Fs diagram for

1693   clinopyroxene microlites (Cpx4) and Na-clinopyroxenes (Cpx5). (c) Q-J diagram for pyroxenes with

1694   indication of end-members (Morimoto, 1989). (d) Enlargement of area indicated in (c). (e) Ti vs. Na diagram

1695   illustrating the compositional differences between clinopyroxenes. (f) Enlargement of area indicated in (e),
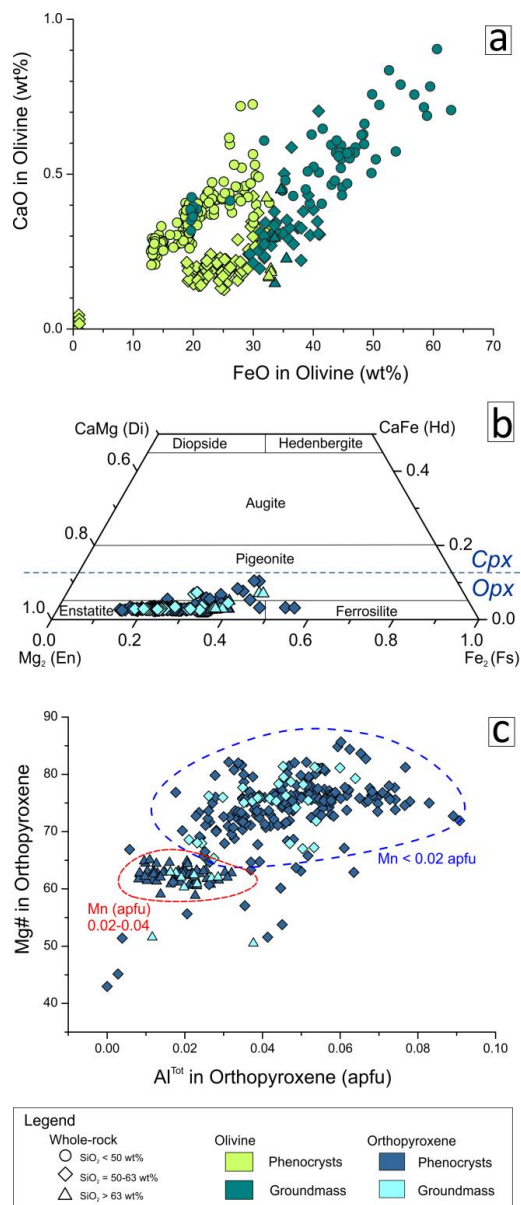
1696   showing the main Augite trend characterizing the evolution from basalts to trachytes and the divergent

1697   presence of Aegirine-Augite and Aegirine series.

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1699   **Figure 7**

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1701   **Figure-7.** (a) CaO vs. FeO diagram showing the composition of olivine in LHPCS lavas. (b) Di-Hd-En-Fs

1702   diagram showing the orthopyroxene chemistry in LHPCS studied lavas. (c) Al vs Mg# diagram showing the

1703   main compositional differences between orthopyroxene populations from trachytes and trachyandesites.
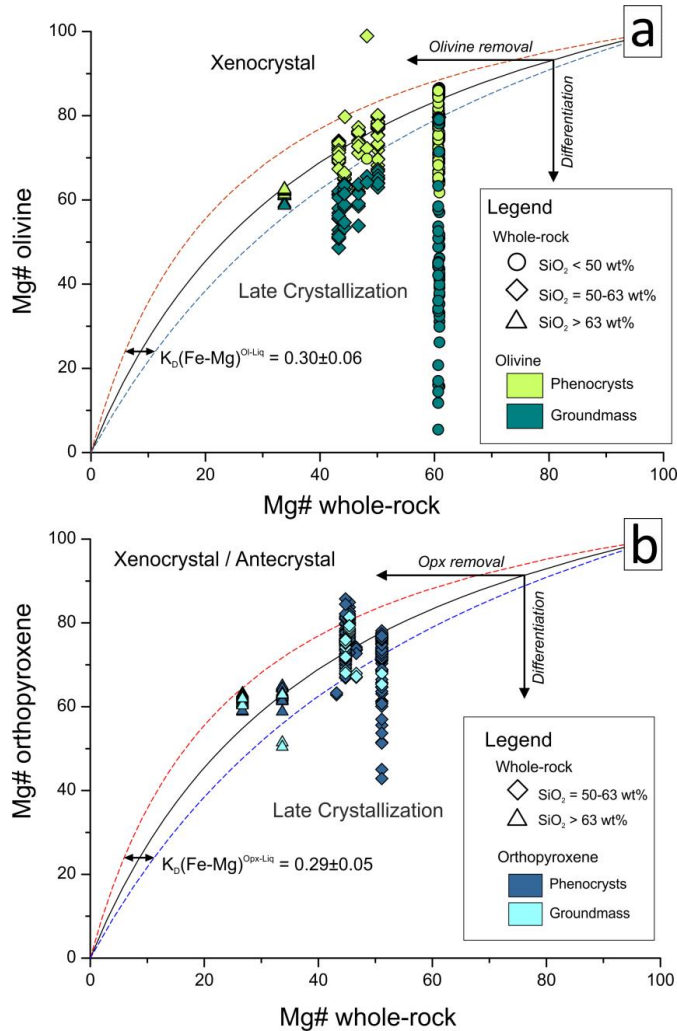
1704   Mn (apfu) contents are also reported.

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1707   **Figure 8**

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1709   **Figure-8.** Rhodes diagrams showing the results of test of equilibrium liquid and olivine (a) and

1710   orthopyroxene (b). The partitioning of Fe-Mg between mineral and liquid (Fe-Mg exchange coefficient) or

1711 $K_D^{min-liq}$(Fe-Mg) is shown (black lines). The accepted range of equilibrium constant values for both figures (a)

1712   and (b) is indicated by dashed lines. $K_D^{min-liq}$(Fe-Mg) values are from Putirka (2008). Nominal melt

1713   compositions for clinopyroxene are selected from whole-rock. Vectors of olivine removal from melt and

1714   closed system differentiation are redrawn after Putirka (2008 and references therein). Fields of

1715   Xenocrystal/Antecrystals and Late Crystallization are also indicated. Symbols and colors refer to Fig. 7.

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1718   **Figure 9**
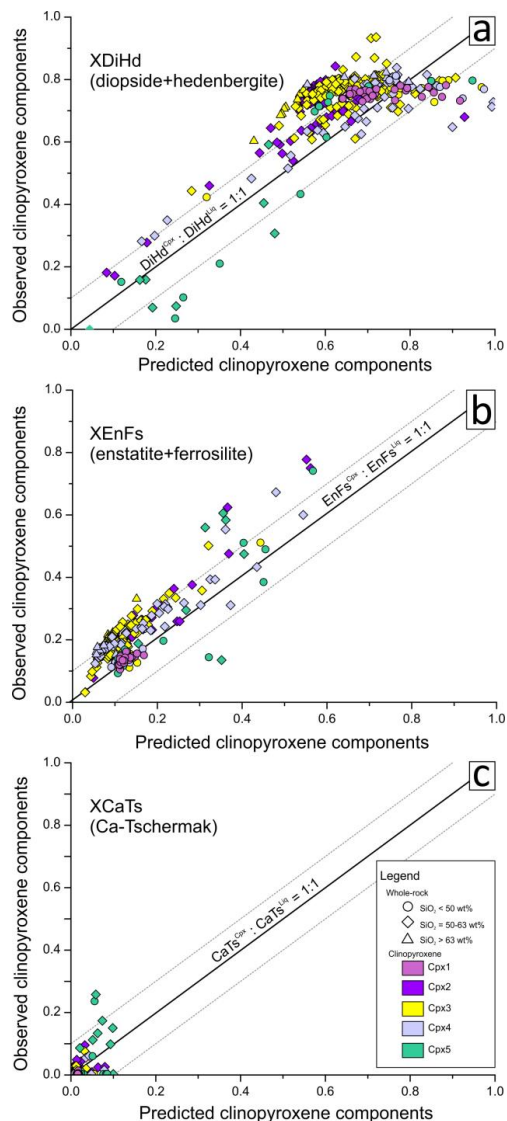
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1721   **Figures-9.** Clinopyroxene-melt equilibrium tests: (a) DiHd: diopside-hedenbergite, (b) EnFs: enstatite-

1722   ferrosilite, and (c) CaTs: Ca-Tschermak components. Equilibrium associated with observed components in

1723   pyroxenes are paired with predicted components in respective hosting-melts. The accepted range of

1724   equilibrium is indicated in each figure by dashed lines. Nominal melt compositions for clinopyroxene are

1725   selected from whole-rock. Symbols and colors refer to Fig. 6.

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1728   **Figure 10**
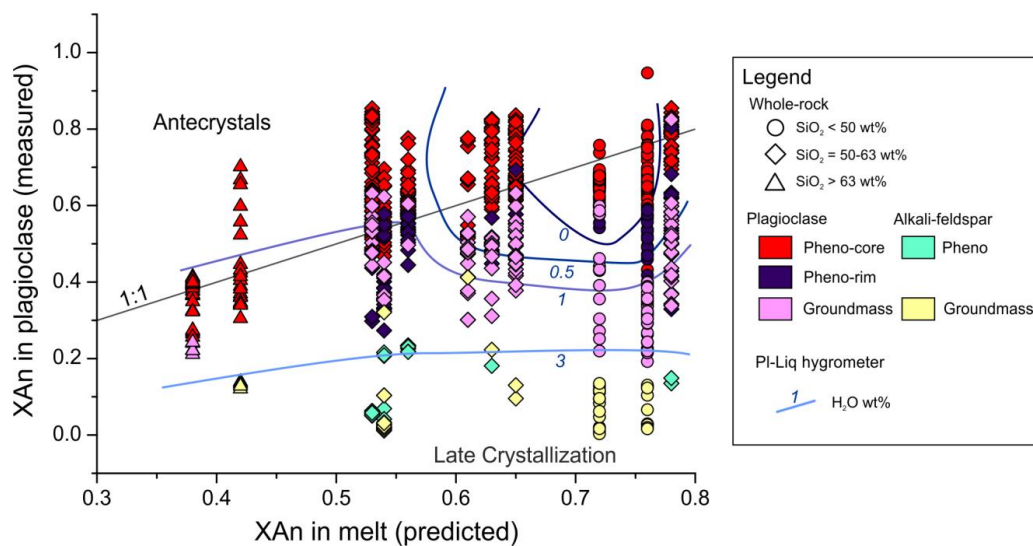
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1731   **Figure-10.** Plagioclase-melt equilibrium test. Equilibrium associated with anorthite (XAn) component in

1732   plagioclase are paired with predicted anorthite in melt. Nominal melt compositions for clinopyroxene are

1733   selected from whole-rock. Calculated water concentrations using plagioclase-melt hygromether (Putirka,

1734   2008) are reported in diagrams with isolines (graded blue lines). Symbols and colors refer to Fig. 5.
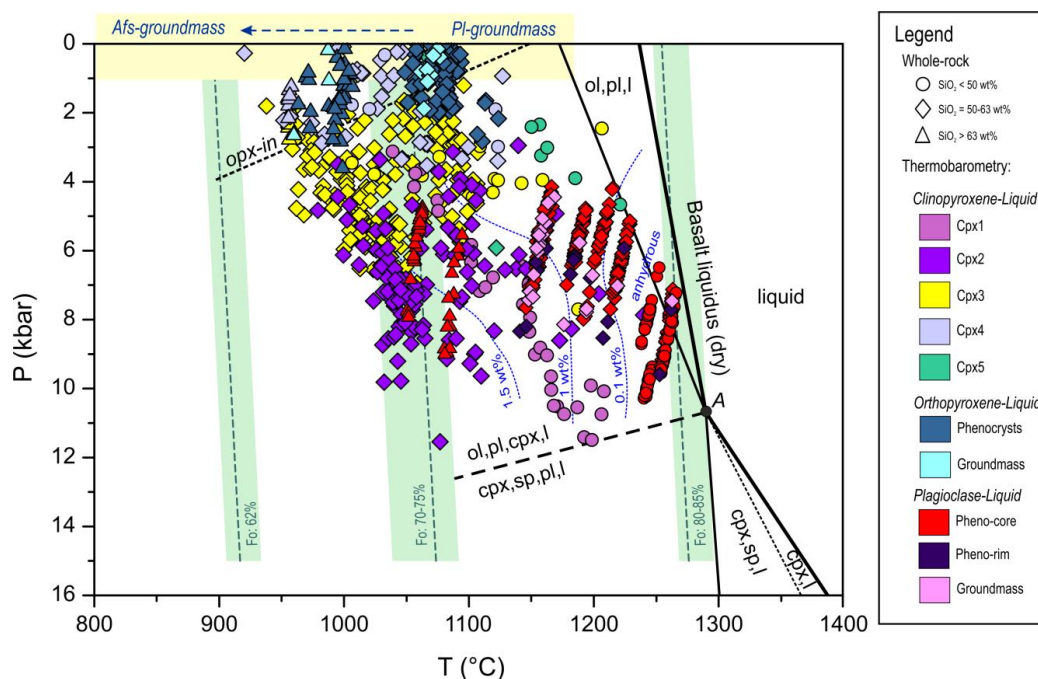
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1739   **Figure 11**

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1742   **Figure-11.** A summary of the results obtained from thermobarometry models applied to Los Humeros post-

1743   caldera stage lavas. Symbols refer to whole-rock chemistry compositions, whereas colors of different

1744   phases refer to mineral chemistry diagrams. Green-shaded field shows the results of olivine-liquid

1745   thermometry. Blue dashed isolines represent the results of plagioclase-melt hygrometer. Yellow-shaded

1746   field indicates pressure-temperature domain of crystallization of feldspars in groundmass. Basalt liquidus

1747   curve, ol+cpx+ol+sp+l stability fields and point "A" (basalt liquidus in equilibrium with mantle peridotite

1748   mineral assemblage of ol+cpx) are redrawn after Grove (2000). Opx-in stability curve is redrawn after

1749   Wallace and Anderson (2000).
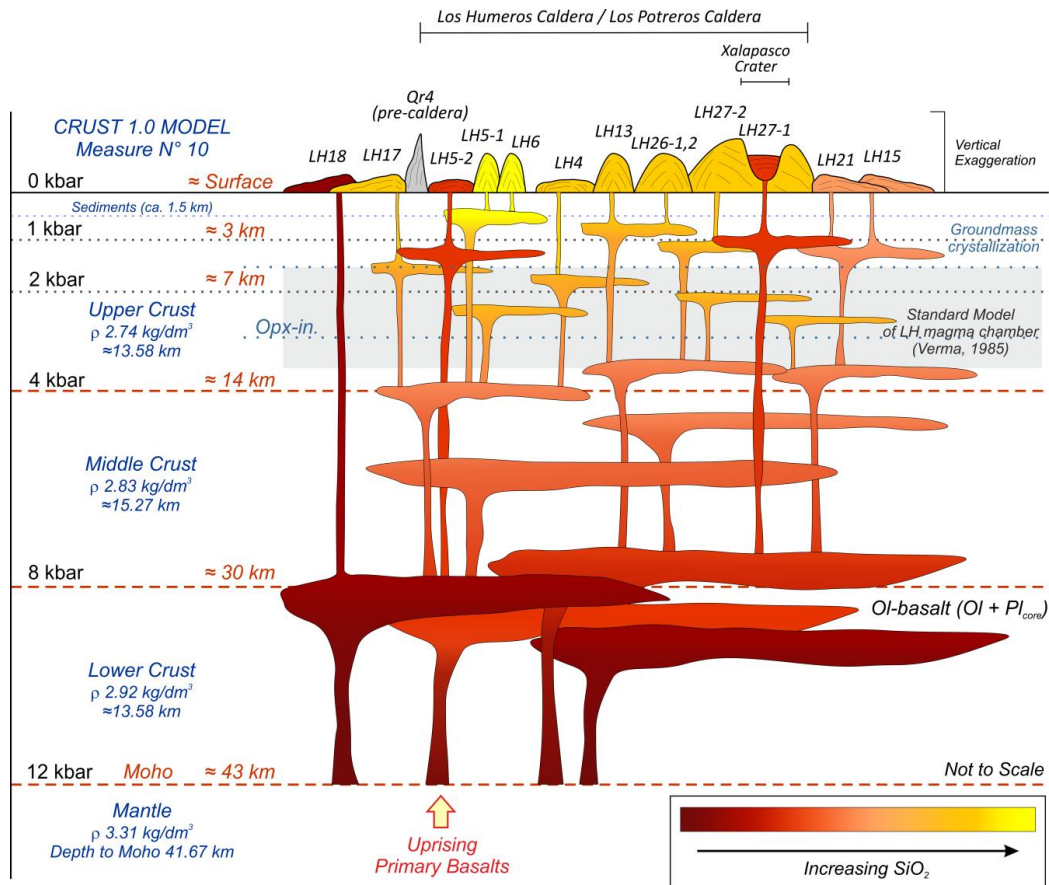
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1754   **Figure 12**

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1757   **Figure-12.** Schematic representation (not to scale) of the magmatic plumbing system feeding LHPCS

1758   activity, beneath Los Humeros caldera as derived by pressure-temperature estimates obtained from

1759   mineral-liquid thermobarometry models. The conceptual model is integrated with the crustal structure of

1760   the study area as derived by the Measure N°10 of the Crust 1.0 global Model (Davies, 2013). Grey shaded

1761   field indicates the depth and thickness of the existing conceptual model of a single, huge classical magma

1762   chamber proposed by Verma (1985a, 1985b).

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1765 **Table 1**

Table 1 - Major element bulk-rock compositions of LHPCS studied lava samples.

Rock type	Alkali-Basalts			Trachyandesites								Trachytes	
Sample	LH5-2	LH18	LH27-1	LH17	LH15-1	LH21-2	LH4	LH27-2	LH13	LH26-1	LH26-2	LH5-1	LH6-1
SiO_2, wt%	46.51	48.78	49.35	54.43	54.74	55.24	56.18	59.69	61.74	61.85	62.14	64.93	67.58
TiO_2	1.471	1.490	1.372	1.394	1.075	1.561	1.375	1.016	0.882	0.889	0.933	0.738	0.605
Al_2O_3	16.23	16.17	17.11	16.33	20.68	15.99	16.57	17.39	15.68	15.70	16.82	15.47	15.83
$Fe_2O_3^{tot}$	10.78	10.62	10.26	8.08	6.49	8.62	7.88	5.76	5.15	5.22	5.32	4.58	3.73
MnO	0.161	0.160	0.155	0.123	0.092	0.133	0.114	0.087	0.085	0.085	0.095	0.077	0.074
MgO	8.44	8.29	7.97	3.57	3.28	3.45	2.90	2.36	2.72	2.45	2.24	1.18	0.69
CaO	10.14	9.77	10.67	7.04	8.59	6.42	6.52	4.83	4.85	4.66	4.52	2.81	2.12
Na_2O	3.11	2.98	3.21	4.10	3.68	4.14	3.96	4.31	4.19	4.31	4.30	4.79	5.26
K_2O	0.33	0.41	0.30	1.76	1.64	1.86	1.99	2.20	2.67	2.58	2.76	3.44	3.89
P_2O_5	0.19	0.21	0.17	0.32	0.26	0.34	0.34	0.27	0.25	0.23	0.22	0.18	0.13
LOI	1.90	0.81	-0.35	0.90	0.49	0.52	1.19	1.55	0.50	0.93	0.70	0.73	0.31
Total (wt%)	99.27	99.68	100.20	98.05	101.01	98.29	99.02	99.47	98.72	98.91	100.10	98.92	100.20
Mg#	61	61	61	47	50	44	43	45	51	48	45	34	27

Note: LOI - loss on ignition; Mg# - molar [Mg*100/(Mg + Fe^{tot})].

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