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

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ABSTRACT

Understanding the anatomy of magma plumbing systems of active volcanoes is essential not only for unraveling magma dynamics and eruptive behaviors, but also to define the geometry, depth and temperature of the heat sources for geothermal exploration. The Pleistocene-Holocene Los Humeros volcanic complex is part of the Eastern Trans-Mexican Volcanic Belt (Central Mexico) and it represents one of the most important exploited geothermal fields in Mexico with *ca*. 90 MW of produced electricity.

A field-based petrologic and thermobarometric study of lavas erupted during the Holocene (post-Caldera stage) has been performed with the aim to decipher the anatomy of the magmatic plumbing system existing beneath the caldera. New petrographical, whole rock major element data and mineral chemistry were integrated within a suite of mineral-liquid thermobarometric models. Compared with previous studies where a single voluminous melt-controlled magma chamber (or "Standard Model") at shallow depths was proposed, our results support a more complex and realistic scenario characterized by a heterogeneous multilayered system comprising a deep (*ca*. 30 km) basaltic reservoir feeding progressively shallower and smaller distinct stagnation layers, pockets and batches up to very shallow conditions (1kbar, *ca*. 3km). Evolution of melts in the feeding system is mainly controlled by differentiation processes through fractional crystallization (plagioclase + clinopyroxene + olivine + spinel assemblage). We demonstrate the inadequacy of conceptual models based on the classical, melt-dominated, single, voluminous, long-lived magma chamber for the magmatic plumbing systems at LHVC. We instead propose a magmatic plumbing system made of multiple, more or less interconnected magma transport and storage layers within the crust, feeding small (ephemeral) magma pockets at shallow-crust conditions. This revised scenario provides a new configuration of the heat source feeding the geothermal reservoir that should be taken into account to drive future exploration and exploitation strategies.

Keywords

Magmatic plumbing system, Thermobarometry, Calderas, Los Humeros, Trans Mexican Volcanic Belt, heat source, geothermal exploration

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 Bergantz, 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 significant. 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 in space and time (e.g., Solano et al., 2014; Di Renzo et al., 2016; Cashman et al., 2017; Jackson et al., 2018).

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 (Ginibre et al., 2002; Feng and Zhu, 2018; Ginibre et al., 2007; Streck, 2008; 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 thermobarometry models (e.g., Putirka, 2008; Masotta et al., 2013) could lead to the comprehension and reconstruction of the magmatic storage/feeding systems of the erupted products (Feng and Zhu, 2018; Giuffrida and Viccaro, 2017; Elardo and Shearer, 2014; Petrone et al., 2016; Zheng et al., 2016; Eskandari et al., 2018; Shane and Coote, 2018; Scott et al., 2012; Stroncik et al., 2009; Barker et al., 2015; Jeffery et al., 2013; Keiding and Sigmarsson, 2012).

In this paper we present a geothermobarometric study of the post-caldera, Pleistocene-Holocene products of Los Humeros volcanic complex (LHVC), located at the eastern termination of the Neogene-Quaternary Trans-Mexican Volcanic Belt (TMVB) (Fig. 1), with the aim to reconstruct the present-day geometry and structure of the magmatic plumbing system. These data are used to build up a conceptual model for the magmatic heat source of the active and currently exploited geothermal system. The magmatic heat source for LHVC has been constrained by the geometry of the caldera, the volume and mass balance calculations of the associated ignimbrites (Ferriz and Mahood, 1984, 1987; Verma, 1984, 1985a, 1985b, Verma et al., 1990; Verma and Andaverde, 1995; Verma et al., 2011; Verma et al. 2013), all related to a single magma body.

Our results allow us to propose of a new and more realistic vision of the magmatic plumbing systems made of multiple interconnected magma stagnation layers within the crust. These new findings must be considered into the new developing conceptual geothermal models to improve strategies for exploration and exploitation of the geothermal system within the LHVC. The results and approach presented in this work have also a general value and could represent an efficient strategy to explore and reconstruct, through petrological investigation, the pre-eruptive geometry and the anatomy of active magmatic feeding systems.

2.GEOLOGICAL SETTING

2.1 Regional Geology

LHVC is the largest and easternmost Quaternary caldera (Fig. 1) of the 1200 km-long active continental arc of the Trans-Mexican Volcanic Belt (TMVB), generated since *ca.* 20 Ma by the subduction of Cocos plate beneath central Mexico (e.g. Demant, 1978, Ferrari et al. 1999, 2012; Gomez-Tuena et al., 2003, 2007a, 2007b, 2018; Norini et al., 2015). LHVC is located in the eastern sector of the TMVB, which is characterized by monogenetic volcanism, scattered basaltic cinder and scoria cones, maar volcanoes of basaltic and rhyolitic composition, large rhyolitic domes and major stratovolcanoes such as Pico de Orizaba (or Citlaltépetl) and Cofre de Perote (e.g., Yáñez and García, 1982; Negendank et al., 1987; Carrasco-Núñez et al., 2010, 2012a;).

The Paleozoic to Mesozoic crystalline basement of eastern TMVB is exposed along the Teziutlán Massif (Viniegra, 1965; Ferriz and Mahood, 1984) made of metamorphic (greenschists K-Ar dated at 207 ± 7 Ma, in Yáñez and García, 1982) and intrusive (granodiorites and granites with whole-rock K-Ar ages of 246 ±7 Ma and 181 ±5 Ma, Yáñez and García, 1982) rocks. The crystalline basement is partially covered by a thick, highly deformed Mesozoic sedimentary succession part of the Sierra Madre Oriental NW-SE thrusts and folds belt

formed by the Late Cretaceous to Paleocene compressional Laramide Orogeny (e.g. Campos-Enriquez and Garduño-Monroy, 1987; Suter, 1987; Fitz-Díaz et al., 2018). Oligocene to Miocene granodiorite and syenite intrusions are randomly exposed within the area (whole-rock K-Ar ages of 31-15 Ma, Yáñez and García, 1982). Miocene volcanism in the area is represented by andesites of the Cerro Grande volcanic complex (Gómez-Tuena and Carrasco-Núñez, 2000), dated at 8.9 to 11 Ma (K/Ar method on whole-rock, Carrasco-Núñez et al. 1997), and the Cuyoaco Andesite dated at 10.5 Ma (K/Ar method, Yáñez and García, 1982) to the west of LHVC, which may correlate with the Alseseca Andesite (Yáñez and García, 1982) exposed to the north. Neogene andesitic volcanism (Ferriz and Mahood, 1984; Yáñez and García, 1982) represented by the Teziutlán Andesite, K-Ar dated (whole-rock) between 3.5 and 5 Ma by Yáñez and García (1982) and at 1.55 Ma by Ferriz and Mahood (1984). This andesitic activity was recently dated by the $^{40}Ar/^{39}Ar$ method at 2.61-1.46 Ma (Carrasco-Núñez et al., 2017a) and correlates with most of the thick andesitic successions of the subsurface geology of LHVC.

2.2 Los Humeros Volcanic Complex

The volcanic evolution of the LHVC consists of three main stages (Carrasco-Núñez et al., 2018): (i) pre-caldera stage; (ii) caldera stage; and (iii) post-caldera stage. The pre-caldera stage is represented by relatively abundant rhyolitic domes, which erupted mainly to the western side of Los Humeros caldera, with an isolated spot to the south, and some buried lavas identified in the geothermal well-logs (Carrasco-Núñez et al., 2017a). This volcanism has been recently dated by both U-Th and $^{40}Ar/^{39}Ar$ methods (Carrasco-Núñez et al., 2018), providing ages spanning from 693.0±1.9 ($^{40}Ar/^{39}Ar$, plagioclase) to 270±17 ka (U/Th, zircon), which overlap with the age range obtained from other domes of the western sector outside the caldera, where K-Ar ages (sanidine) of 360±100 ka and 220±40 ka were obtained (Ferriz and Mahood, 1984). The Caldera stage consists of two major caldera-forming events, separated by a large Plinian eruptive episode. The first and largest caldera-forming eruption produced Los Humeros caldera (18 km in diameter) during the emplacement of the Xaltipan ignimbrite, a rhyolitic, welded to non-welded, ash-rich deposit, radially distributed around the caldera. The dense rock equivalent (DRE) volume of this event was estimated at 115 km^3 by Ferriz and Mahood (1984). The age of the Xaltipan ignimbrite was established by whole-rock K-Ar dating at 460±20 ka (plagioclase) and 460±130 ka (biotite) (Ferriz and Mahood, 1984), however Carrasco-Núñez et al. (2018) based on coupled zircon U-Th dating and $^{40}Ar/^{39}Ar$ method (plagioclase) geochronology provided a younger age of 164.0 ± 4.2 ka.

Following this catastrophic event an eruptive pause occurred, resuming with a sequence of intermittent Plinian episodes at 70±23 ka ($^{40}Ar/^{39}Ar$ method on plagioclase, Carrasco-Núñez et al., 2018), separated by short gaps marked by thin paleosoils. The deposits consist of thick (1-6 m) coarse pumice-rich, well-sorted, massive and diffuse-stratified layers,rhyodacitic in composition, which are grouped as the Faby Tuff (Ferriz and Mahood 1984; Willcox, 2011). The second caldera-forming episode produced the 9-10 km large Los

Potreros caldera, which is associated with the emplacement of the compositionally-zoned andesitic-rhyodacitic-rhyolitic Zaragoza ignimbrite (Carrasco-Núñez et al., 2012b). This is an intraplinian pyroclastic flow deposit, with an estimated volume of ca. 15 km3 DRE (Carrasco-Núñez and Branney, 2005). Previous ages of this unit were reported at 100 ka (K-Ar dating, plagioclase: Ferriz and Mahhod, 1984) and at 140±24 ka ($^{40}Ar/^{39}Ar$ method, plagioclase: Willcox, 2011). However, a new $^{40}Ar/^{39}Ar$ (on plagioclase) younger age of 69±16 ka for the Zaragoza ignimbrite was recently obtained (Carrasco-Núñez et al., 2018), confirmed by the fact the Zaragoza ignimbrite overlies a rhyodacitic lava flow dated at 74.2±4.5 ka (zircon U-Th dating).

According to Carrasco-Núñez et al. (2018) during the post-caldera stage (Fig. 1) two different eruptive phases occurred. The first one was a late Pleistocene resurgent phase characterized by the emplacement of felsic domes in the central area at about 44.8±1.7 ka (zircon U-Th ages; Carrasco-Núñez et al., 2018), which is slightly younger than the previously reported whole-rock K-Ar date (60±20 ka, glass: Ferriz and Mahood, 1984). Outside of the caldera, to the north, a rhyolitic dome erupted at 50.7±4.4 ka ($^{40}Ar/^{39}Ar$, plagioclase; Carrasco-Núñez et al., 2018), which was followed by a sequence of explosive eruptions, producing dacitic pumice fall units (Xoxoctic Tuff, 0.6 km^3) and interbedded breccia and pyroclastic flows deposits of the Llano Tuff (Ferriz and Mahood 1984; Willcox, 2011), with a maximum age of 28.3±1.1 ka (C-14, Cal BP 30630, Rojas-Ortega, 2016). The second eruptive phase of the post-caldera stage is a Holocene ring-fracture and bimodal phase that occurred towards the south, north and central part of Los Humeros caldera (Carrasco- Núñez et al., 2017). It is characterized by alternated episodes of effusive and explosive volcanism with a wide range of compositions, spanning from basaltic-andesitic,basaltic trachytic, trachyandesitic lava flows and dacitic, trachydacitic, andesitic and basaltic pumice and scoria fall deposits erupted by tens of monogenetic eruptive centers located in the LHVC (Ferriz and Mahood, 1984; Dávila-Harris and Carrasco-Núñez, 2014; Norini et al., 2015; Carrasco-Núñez et al., 2017b). Most of the effusive activity was firstly considered within a range of 40-20 ka (whole-rock K-Ar dating, Ferriz and Mahood, 1984), however, recent dating reveals that most of this activity is Holocene (Carrasco et al., 2017b). Trachyandesitic and andesitic basalts lavas erupted to the north of the LHVC at about 8.9±0.03 ka (C-14 age, Carrasco-Núñez et al, 2017b). A rhythmic alternation of contemporaneous bimodal explosive activity produced trachyandesitic and basaltic fall layers grouped as the Cuicuiltic Member erupted at 7.3±0.1 ka (C-14 age,Dávila-Harris and Carrasco-Núñez, 2014). This activity migrated towards the southern caldera rim to forms a well-defined lava field. This ring-fracture episode erupted trachyandesite and olivine-bearing basaltic lava flows, at 3.9±0.13 ka (C-14 age, Carrasco-Núñez et al, 2017b), and the most recent eruptions erupted trachytic lava flows near the SW caldera rim, at 2.8± 0.03 ka (C-14 age, Carrasco-Núñez et al, 2017b).

2.3 Los Humeros geothermal system

The LHVC hosts one of the three most important geothermal fields in Mexico, with an installed 93 MW of electric power produced from 20 geothermal wells (Romo-Jones et al., 2017). The existing conceptual models

for the Los Humeros geothermal field (LHGF) (see Norini et al., 2015 for a review) stem upon the hypothesis of a unique, large and voluminous cooling magma chamber of 1000-1500 Km^3 in volume, at depth of 5 to 10 km from the surface (Verma, 1984, 1985a, 1985b, 2000; Verma et al., 1990; Verma and Andaverde, 1995; Verma et al., 2011; Verma et al. 2013; Carrasco-Núñez et al. 2018), representing the heat source of the geothermal field (Martínez et al., 1983; Verma, 1983, 2000; Campos-Enríquez and Garduño-Monroy, 1987). However, the LHGF is characterized by a low number of productive geothermal wells (ca. 20 out of 50; Norini et al., 2015; Carrasco-Núñez et al., 2017a). The confined distribution of these productive wells along the NNW-SSE trending "Maxtaloya-Los Humeros-Loma Blanca" fault system (MHBfs in Fig. 1) cutting across the Los Potreros caldera (e.g., Norini et al., 2015; Carrasco-Núñez et al., 2017a) also corresponds to the almost unique, narrow and sharp surface thermal anomaly recognized within the caldera (Norini et al., 2015). These observations raise doubts on the existence of a voluminous superficial heat source feeding the LHGF and makes it important, for a better comprehension and exploitation of the geothermal resource, a revised assessment of the structure of the magmatic plumbing system beneath LHVC.

3.MATERIALS AND METHODS

In this work we focus on petrographical investigations, textural and chemical (mineral chemistry and major-elements bulk-rock) characterization of the Los Humeros post-caldera stage (LHPCS) (Carrasco-Núñez et al. 2017b). Following the recently published geological map (Carrasco-Núñez et al. 2017b) and geochronology (Carrasco-Núñez et al. 2018) of the LHVC, more than fifty samples of the LHPCS lavas were collected in the field with the aim to describe all the compositional variability of erupted products during the post-caldera stage activity (Figs. 1, 2a-d). In the description of the volcanic units, abbreviations follow Carrasco et al. (2017b). Petrographic characterization through polarized-light microscopy (PLM) was produced for near all collected samples. The most preserved and representative samples of every major LHPCS volcanic unit were than selected (Fig. 1) for bulk and mineral chemistry investigations.

With respect to the intra-caldera domain (Fig. 2a), we selected lava samples belonging to: (i) LH27-1 from the mafic lavas inside the Xalapasco Crater (Qb1), (ii) LH27-2 from the Maxtaloya trachyandesites (Qta4) constituting the rim-walls of Xalapasco craters, (iii) LH4 from San Antonio-Las Chapas lavas (Qta3) outcropping in the Los Humeros town, (iv) LH5-2 from mafic lavas (Qb1) outcropping west to Los Humeros town, (v) LH5-1 from Chicomiapa-Los Parajes felsic lavas (Qt2) outcropping in the north-western part of Los Potreros caldera, (vi) LH6-1 from El Pajaro unit (Qt1) outcropping in the north-western part of Los Potreros caldera. In addition to these units, we also selected three more samples (LH13, LH26-1 and LH26-2) from lavas and domes of intermediate compositions, outcropping (Fig. 2b-c) in the central part of Los Potreros caldera between Xalapasco crater and Los Humeros town, and not reported on the published geological map.

Concerning the extra-caldera products (Fig. 2d), we selected one sample for each of the four major lava flows: (i) LH15 from El Limón lava flow (Qab), (ii) LH21-2 from Sarabia lava flow (Qta1), (iii) LH17 from Tepeyahualco lava flow (Qtab), and (iv) LH18 from Texcal lava flow (Qb1).

The samples were investigated first by optical microscopy and then through back scattered electron (BSE) imaging for the definition of magmatic fabrics, textures and constituentmineral assemblages. Mineral chemistry was then defined through electron microprobe analyses (EMPA). Whole rocks (major and trace element) composition of selected samples was obtained through ion coupled plasma – optical emission (ICP-OE) and X-ray fluorescence (XRF) analyses. Analytical protocols are described in the Appendix A.

In the following, mineral abbreviations follow Whitney and Evans (2010), whereas types of zoning and textures are after Ginibre et al. (2002), Streck (2008) and Renjith (2014).

4.MAJOR ELEMENT BULK COMPOSITION

Studied samples show a continuous series from mafic to felsic compositions, with SiO_2 ranging 46.5-67.6 wt%, and $Na_2O + K_2O$ ranging 3.4-9.2 wt% (with $K_2O/Na_2O < 1$) (Fig. 3a; Table 1). LHPCS mafic rocks (SiO_2< 50 wt%; 3 samples) show composition with SiO_2 46.5-49.4 wt%, Al_2O_3 16.2-17.1 wt%, CaO 9.8-10.7 wt%, MgO 8.0-8.4 wt% with Mg# (molar $MgO/[MgO+FeO_{tot}]$) = 60-61 and Na_2O+K_2O ranging 3.4-3.5 wt%. 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 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 (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 0.7-1.2 wt% (Mg#: 26-34), CaO 2.1-2.8 wt%, and Na_2O+K_2O 8.2-9.2 wt%.

On the total alkali versus silica (TAS) diagram (Le Maitre et al., 2002) LHPCS lavas span from basalts to trachytes (Fig. 3b). Los Humeros mafic rocks fall in the "Basalt" field and, following the existing literature (e.g., Barberi et al., 1975, Bellieni et al., 1983; Le Maitre et al., 2002; White et al., 2009; Giordano et al., 2012), can be classified as mildly-alkaline (or transitional) basalts and alkali-basalts. The high TiO_2 contents (1.34-1.5 wt%), together with MgO <12 wt% and low Al_2O_3/TiO_2 values (average value 11.5) exclude the LH mafic rocks as high-Mg melts (picrites) or komatiites (e.g., Redman and Keays, 1985; Arndt and Jenner, 1986; Le Maitre et al., 2002; Gao and Zhou, 2013; Azizi et al., 2018a, 2018b).

Intermediate products fall in the "Basaltic trachyandesites" and "Trachyandesites" fields; these rocks will be referred hereafter as "trachyandesites". The Los Humeros felsic (i.e., SiO_2 >63 wt%) lava samples belonging to the post-caldera stage fall in the "Trachyte" field. Selected Harker diagrams for major elements are presented in Figure 3, using SiO_2 wt% as differentiation index. Negative correlations are observed for CaO (Fig. 3c) and Mg# (Fig. 3d), whereas positive correlations are observed for Na_2O (Fig. 3c).

5.PETROGRAPHY

5.1 Basalts

LHPCS basalts show vesicle-rich (up to 35 vol%) highly-porphyritic (phenocrysts up to 50 vol%) textures (Fig. 4a-d). Studied basalts do not show presence of fragments from host-rocks or from previous magmatic rocks, therefore can be defined as lithic-free (e.g., Geshi and Oikawa, 2014). The fabric is fluidal as defined by the alignment of plagioclase laths in the groundmass. Based on the presence of clinopyroxene (Cpx) in the mineral assemblage, basalts can be further subdivided into: (i) Cpx-free basalt of extra-caldera Texcal lava flow (LH18); and (ii) Cpx-bearing basalts of intra-caldera lavas at western Los Potreros and at Xalapasco crater (LH5-2 and LH27-1, respectively).

Cpx-free basalt (LH18) contains euhedral to subhedral olivine (ca. 20 vol%) and euhedral to anhedral plagioclase (ca. 25-30 vol%) phenocrysts in a holocrystalline groundmass consisting of plagioclases with swallow-tail morphology, dendritic to spinifex olivines and opaque oxides (Fig. 4a, b). Olivine and plagioclase phenocrysts are generally slightly chemically zoned (see below), showing homogeneous cores with normal concordant monotonous zoning texture at outer rim (Fig. 4a, b). Occasionally, major phenocrysts of olivine (up to 2.5 mm in size) with Cr-spinel inclusions are observed (Fig. 4a). It is worth notice that no pyroxenes are observed in this basalt.

Cpx-bearing intra-caldera basalts (LH5-2, LH27-1) show euhedral to subhedral plagioclase (ca. 25 vol%), euhedral olivine (ca. 10-15 vol%), subhedral to anhedral yellow to colorless clinopyroxene (ca. 10-15 vol%) and rare subhedral anorthoclase (< 2 vol%) phenocrysts (Fig. 4c) in a holocrystalline groundmass (Fig. 4d). The latter is made up of (in order of microlites abundance) elongated platy plagioclase, olivine, colorless to green clinopyroxene, opaque oxides and rare alkali-feldspar. All phenocrysts show core-rim zoning textures (Fig. 4c, d) and in particular: (i) olivine, plagioclase and clinopyroxene with homogeneous cores and normal concordant monotonous zoning at outer rims, (ii) plagioclase and clinopyroxene with homogeneous cores and low-amplitude euhedral oscillatory zoning at rims, (iii) rare plagioclase and clinopyroxene with homogeneous cores and normal concordant step zoning at rims, and (iv) very rare plagioclase with patchy cores and normal convolute monotonous zoning at rims. Large phenocrysts of olivine (up to 1.5 mm in size) and plagioclase (up to 3 mm in length) are commonly observed. Vesicle size is up to 5mm in diameter.

5.2 Trachyandesites

LHPCS intermediate volcanic products are lithic-free and show low- to medium-porphyritic textures (phenocrysts ranging 10-40 vol%), with a general fluidal fabric as indicated by orientation of plagioclase and clinopyroxene laths in the groundmass (Fig. 4e, f). Intermediate products vary from poorly vesiculated (< 10 vol% in LH13) to vesicle-rich (ca. 30 vol% in LH4) lavas. In the highest vesiculated sample (LH4), size of vesicles (3-5 mm in diameter) is comparable to those of intra-caldera basalts (LH5-2, LH27-1). Based on the presence of orthopyroxene (Opx) in the mineral assemblage, rocks of intermediate compositions can be further subdivided into: (i) Opx-free (LH21, LH15); and (ii) Opx-bearing (LH4, LH13, LH17, LH26-1, LH26-2, LH27-2) trachyandesites.

290 Opx-free trachyandesites shows euhedral to subhedral plagioclase (ca. 15-20 vol%), euhedral to subhedral
291 olivine (ca. 10 vol%), euhedral to anhedral yellow-to-colorless clinopyroxene (ca. 10-20 vol%), subhedral
292 alkali-feldspars (ca. 10-15 vol%) phenocrysts, in a holocrystalline microcrystalline groundmass composed of
293 elongated platy plagioclase, colorless clinopyroxene, olvine, alkali-feldspar and opaque oxides, in order of
294 microlites abundance.
295 Opx-bearing trachyandesites are generally characterized by euhedral to subhedral plagioclase (ca. 15-20
296 vol%), euhedral to subhedral clinopyroxene (ca. 10-20 vol%), euhedral colorless orthopyroxene (ca. 10-20
297 vol%), euhedral to subhedral alkali-feldspars (ca. 10-15 vol%) and euhedral to subhedral olivine (< 10 vol%)
298 phenocrysts in a holocrystalline to hypohyaline microcrystalline groundmass made of feldspar (plagioclase
299 and alkali-feldspars) microlites, pyroxene (clinopyroxene and orthopyroxene) microlites, olivine microlites,
300 opaque minerals and glass (Fig. 4f). To note it is the olivine absence in the trachyandesitic sample LH27-2.
301 Most of phenocrysts observed in these intermediate products show zoning textures characterized by
302 homogeneous cores surrounded by (i) monotonous zoning at outer rims, (ii) low-amplitude euhedral
303 oscillatory zoning at rims and (iii) normal concordant step zoning at rim. Homogeneous unzoned
304 clinopyroxene phenocrysts are commonly observed. Major phenocrysts of clinopyroxene (up to 2 mm in size)
305 and plagioclase (up to 2 mm in length) characterized by homogeneous cores and normal concordant
306 monotonous zoning are reported in all studied trachyandesites. It is also reported the presence of (i) rare
307 clinopyroxene phenocrystals with growth mantle textures, (ii) rare plagioclase phenocrysts with patchy
308 rounded zone corners cores, (iii) very rare clinopyroxenes with homogeneous cores and growth mantle
309 texture at rims are observed. Very rare large phenocrysts of olivine (1.5-2.0 mm in size) presenting resorption
310 patterns at rim and characterized by spinel inclusion are reported in the LH26-1 sample.
311
312 **5.3 Trachytes**
313 LHPCS trachytes show lithic-free phyric textures, with low porphyritic index (phenocrysts ranging 10-25 vol%),
314 and fluidal fabrics as shown by iso-orientation of plagioclase, alkali-feldspars and clinopyroxene laths in the
315 groundmass (Fig. 4g, h). They range from vesicle-poor (< 5 vol%) to vesicle-free textures, with size of vesicles
316 never exceeding 0.05 mm in diameter. The two analyzed trachytic samples (LH5-1 and LH6) are both
317 characterized by the presence of orthopyroxene; however, the two mineral assemblages differ substantially.
318 The low-SiO_2 (64.93 wt%) LH5-1 trachyte is characterized by euhedral to subhedral phenocrystals of
319 plagioclase (ca. 10-15 vol%), clinopyroxene (ca. 10 vol%), orthopyroxene (ca. 10 vol%), olivine (ca. 5-10 vol%)
320 and sanidine (< 10 vol%), in a hypohyaline microcrystalline groundmass made of (in order of abundance of
321 microlites and microcrystals) sanidine, orthopyroxene, clinopyroxene, rare plagioclase, rare olivine, rare
322 opaque minerals and very rare glass. All phenocrysts are generally unzoned. Mafic phenocrysts with
323 homogeneous cores surrounded by normal concordant monotonous zoning are also observed. Rare major
324 plagioclase (up to 1.5 mm in length) phenocrysts present patchy cores and normal concordant step zoning

textures at rims. Rare major clinopyroxene (up to 1.0 mm in length) unzoned homogeneous phenocrystals show inclusions of olivine + magnetite.

The high SiO_2 (67.58 wt%) LH6 trachyte is made up of sanidine (ca. 10 vol%), plagioclase (ca. 5-10 vol%) and orthopyroxene (ca. 10 vol%) phenocrystals in a fine grained trachytic mesostasis. Only major plagioclase and orthopyroxene phenocrysts show core-rim zoning textures with homogeneous cores associated either with normal monotonous zoning or normal low-amplitude oscillatory zoning at rims. Dimension of phenocrysts are comparable to those of LH5-1 trachyte.

6.MINERAL CHEMISTRY

Mineral compositions as obtained from electron microprobe analyses and mineral formulae for mineral assemblages of LHPCS lavas are presented in Supplementary Tables 1, 2, 3, 4 and 5 (for feldspar, clinopyroxene, olivine, orthopyroxene and spinel and opaque minerals, respectively).

6.1 Feldspar

In basaltic rocks (Fig. 5a), feldspars are predominantly plagioclase. Plagioclase phenocrysts show anorthitic (XAn = 59-81%, average 67%) cores and normally zoned (XAn = 42-59%, average 53%) rims. Orthoclase component (XOr) is always less than 2%. Plagioclase microlites in the groundmass show andesine (XAn = 19-60%) composition, with XOr ranging 1-7%. Alkali-feldspars occur as both rare anorthoclase phenocrysts ($Ab_{60}Or_{37}$), and microlites in groundmass ($Ab_{62-79}Or_{9-35}An_{0-13}$).

Plagioclase from trachyandesites (Fig. 5b) have anorthite-rich (XAn = 45-87%, average 67%) cores and normally zoned (XAn = 27-69%, average 48%) rims. Cores with XAn in the range 72-87% are observed in all major phenocrysts. Plagioclase core compositions are comparable to those of basalts. The XOr ranges 1-8%. Plagioclase microlites in groundmass show andesine (XAn = 29-63%) composition with XOr always less than 10%. Alkali-feldspars occur as (i) anorthoclase ($Ab_{59-68}Or_{11-30}$) and sanidine ($Ab_{49-50}Or_{43-48}$) phenocrysts, and (ii) anorthoclase ($Ab_{49-70}Or_{15-38}$) and sanidine ($Ab_{38-48}Or_{47-61}$) microlites in groundmass.

Trachytes (Fig. 5c) show generally unzoned plagioclase phenocrysts with oligoclase-andesine (XAn = 26-45%) composition. Rare An-rich (XAn= 52-70%) cores are reported from major plagioclase phenocrysts in the low-silica trachyte LH5-1. The XOr is always less than 8%. Plagioclase microlites in groundmass are rare, with Ab-rich ($An_{21-30}Ab_{66-69}Or_{4-10}$) composition. Alkali-feldspars are represented by anorthoclase as phenocrysts ($Ab_{65-66}Or_{20-21}$) and groundmass microlites ($Ab_{64-66}Or_{21-24}$).

6.2 Clinopyroxene

Apart from the LH18 basalt and LH6 trachyte, clinopyroxene, is the most common mafic mineral recognized in studied samples. It occurs generally as single crystals (Fig. 4e). However rare crystals showing growth mantle textures are locally reported in trachyandesites. Very rare phenocrysts in trachyandesites show

patchy cores. Major clinopyroxene phenocrysts in trachyandesites and trachytes contain inclusions (Fig. 4e, g) of olivine, magnetite and plagioclase.

Polarized light microscopy coupled with BSE images and chemical investigations highlighted the presence of unzoned (Fig. 4g) and zoned (homogeneous cores associated to low-amplitude oscillatory zoning or normal monotonous zoning or normal step zoning textures at rims; e.g., Fig. 4e) clinopyroxene phenocrysts. Very rare phenocrysts showing growth mantle textures at rim are reported. No evidence of resorption/dissolution textures are observed in studied samples.

The Cpx population, based on the integration of textural observations and mineral chemistry, (Fig. 6 a-f) can be classified in five major categories: (i) Cpx1 cluster is represented by homogeneous cores of all zoned phenocrysts in basalts; (ii) Cpx2 subpopulation is represented by homogeneous cores of all zoned phenocrysts from trachyandesites and trachytes; (iii) Cpx3 group represent both the unzoned phenocrysts in all studied samples and the rims (low-amplitude oscillatory, normal monotonous and normal step zoning) of cpx1 and cpx2 phenocrysts from all studied samples; (iv) Cpx4 population is constituted by microlites and microphenocrystals in groundmass from all analyzed samples; and (v) Cpx5 cluster collects together the emerald-green euhedral to subhedral microlites in groundmass of intra-caldera basalts (LH5-2, LH27-1) and rare normal monotonous zoning at outer rims of major clinopyroxene phenocrysts from few trachyandesites (LH15, LH17, LH26-2).

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

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

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 as diopside-rich augite ($Wo_{12-49}En_{14-57}Fs_{8-62}$). The composition of Cpx3 partially overlaps those of Cpx1 and Cpx2 groups, as it would be expected for phenocrysts with homogeneous cores (i.e. Cpx1 and Cpx2) and the respective low-amplitude oscillatory zoning or normal monotonous zoning rims (Cpx3) (e.g., Streck, 2008).

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 diopside-rich augite ($Wo_{12-46}En_{18-60}Fs_{11-38}$). The composition of Cpx4 partly overlaps that of Cpx3, however their textural characteristics are completely different.

The Cpx5 differs from previous pyroxenes, with a large spread in Mg# ranging 5-73, Ca 0.03-0.83 apfu, Q+J 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; 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, XAeg= 0.40-0.88). Cpx5 clinopyroxenes are generally Ti-enriched (TiO_2 up to 2.8 wt%, Ti up to 0.08 apfu) and straddle the Q+J=2 line defining the boundary for "normal" pyroxenes (Morimoto, 1989), thus indicating the presence of a $NaR^{2+}_{0.5}Ti^{4+}_{0.5}Si_2O_6$ component (Morimoto, 1988, 1989; Huraiova et al., 2017) (Fig. 6c).

The compositional variation of clinopyroxenes can be summarized in the Na vs. Ti diagram (Fig. 6e-f). Interestingly, Augite-rich (Cpx1, Cpx2, Cpx3 and Cpx4) clinopyroxenes generally show positive correlation and linear distribution characterized by a progressive Ti- and Na-depletion, from Ti-Augite cores (Cpx1) in basalts to DiHd-rich Augite (Cpx3, Cpx4) specimens in trachytes. The Cpx5, belonging to Aegirine-Augite and Aegirine, moves away from this trend showing a negative correlation characterized by a progressive enrichment of Na content, with respect to a general Ti-depletion. Aegirine enrichment could be diagnostic of ferric iron (Fe3+) content increasing during the magmatic differentiation, whereas the diopside-hedenbergite enrichment testifies increasing of ferrous iron (Fe2+) in magma (e.g. Huraiova et al., 2017).

6.3 Olivine

Olivine is found in all analyzed samples, except for for LH27-2 trachyandesite and LH6 trachyte. It consists of idiomorphic (Fig. 4 a, c) to skeletal (e.g., Donaldson, 1974; Fowler et al., 2002; Faure et al., 2003; Welsch et al., 2013) (Fig. 4b) phenocrysts, and microlites in the groundmass (Fig. 4h). Olivine crystals, both phenocrysts and microcrystals, show homogeneous cores with concordant normal monotonous zoning outer rims. In basalts, olivine shows a continuous compositional range (Fig. 7a) from $Fo_{86}Fa_{14}Mtc_0Tep_0$ (phenocryst in LH5-2 basalt) to $Fo_{05}Fa_{91}Mtc_1Tep_3$ (groundmass microlites in LH27-1 basalt). Maximum MnO (up to 1.7 wt%) values are always found in Fe-rich olivine microlites in basalts. Low monticellite concentration (CaO always < 1.0 wt%) in Los Humeros sample is typical for magmatic olivine (i.e., Melluso et al., 2014). CaO content positively correlates with the fayalite (FeO) compound (Fig. 5a). Together with the Mg#, the CaO content allows to discriminate olivine phenocrysts in three coherent compositional clusters: i) olivine from basalts, with Mg#= 79-87 and CaO= 0.21-0.73 wt%, ii) olivine from trachyandesites, with Mg#= 67-80 and CaO= 0.08-0.43 wt%, and iii) olivine from trachytes with Mg#= 58-63 and CaO= 0.16-0.42 wt%. A minor number of analyzed phenocrysts in basalts show Cr_2O_3 content in the range ca. 0.05-0.07 wt%. It is, instead, below detection limit for almost all analyzed olivine crystals in LHPCS lavas. A minor cluster of peridote Mg-olivine ($Fo_{99}Fa_1$) xenocrysts, characterized by disequilibrium textures (resorption patterns) at rim, have been identified in LH26-1 trachyandesite lava.

6.4 Orthopyroxene

Orthopyroxene occurs in most of the LHPCS trachyandesite (Fig. 4f) and trachyte samples (Fig. 4 g-h). Orthopyroxene phenocrysts are generally unzoned with homogeneous textures. They show intermediate ($En_{41-83}Fs_{14-55}Wo_{2-10}$) compositions (Fig. 7b), with Mg# of 43-86, Al_2O_3 up to 2.12 wt%, TiO_2 0.08-1.33 wt%, and CaO 1.20-4.72 wt%. Similar compositions ($En_{62-79}Fs_{18-33}Wo_{3-7}$) have been obtained for microlites in groundmass (Fig. 7b) with Mg# of 65-81, Al_2O_3 0.48-1.53 wt%, TiO_2 0.21-0.60 wt% and CaO 1.35-3.49 wt%. In trachytes, orthopyroxene phenocrysts present Mg# ranging 59-65, with low Al_2O_3 (0.18-0.73 wt%), low TiO_2 (0.11-0.32 wt%) and CaO (0.81-1.88 wt%), corresponding to Fe-rich composition ($En_{56-63}Fs_{34-39}Wo_{2-4}$) with

a minor Ca-Cpx substitution (Fig. 7b). Orthopyroxene microlites in groundmass (Fig. 7b) show 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 0.19-0.31 wt% and CaO 1.32-3.27 wt%.

The compositional variation of orthopyroxyene is summarized in Al^{Tot} vs. Mg# diagram (Fig. 7c). In general, orthopyroxene from trachyandesites is characterized by higher content of Al (apfu) and higher Mg#, whereas those from trachytes are richer in ferrous iron (lower Mg# values) and in manganese (Mn up to 0.04 apfu).

6.5 Spinel and Opaque Minerals

Basalts show a diversified set of opaque minerals. Phenocrysts are characterized by, in order of abundance, 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-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 wt%). Groundmass is characterized by the only presence of Fe-Ti oxides (ca. 20-30 µm in diameter; Fig. 4f) as ilmenite (MgO 0.27-1.50 wt%) 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 just as inclusions, up to 200 µm in diameter (Fig. 4a), in larger Mg-rich olivine phenocrysts.

Trachyandesites are characterized by phenocrysts of Ti-magnetite (MgO 0.07-3.84 wt%), ilmenite (MgO 1.11-4.79 wt%) and rare rutile (MgO 0.47 wt%). Groundmass crystals (ca. 20-30 µm in diameter) show a comparable composition with Ti-magnetite (MgO 0.33-3.77 wt%), ilmenite (MgO 0.33-4.79 wt%) and rare rutile (MgO < 0.05 wt%). Comparable to basalts, Cr-spinels (TiO_2 6.09-6.47 wt%; Mg# 19-21; Cr# 65-68) are identified only as inclusions (100-200 µm in diameter) in major Mg-rich phenocrysts.

In Trachytes, Fe-Ti oxides show euhedral to subhedral habit and, based on chemistry, they are ilmenite (MgO 2.06-3.31 wt%) and titanomagnetite (MgO 1.41-5.47 wt%). Phenocrystals (up to 50-100 µm in diameter; Fig. 4g) and groundmass (ca. 15-20 µm in diameter) show same compositions.

7. MINERAL-LIQUID THERMOBAROMETRY

In order to define the thermo-baric (T-P) environmental conditions of the magmatic feeding system of the LHPCS, we integrate thermobarometry models based on olivine (Beattie, 1993; Putirka et al., 2007; Putirka, 2008), orthopyroxene (Putirka, 2008), plagioclase (Putirka, 2005b; Putirka, 2008), alkali-feldspar (Putirka, 2008) and clinopyroxene (Putirka et al., 1996, 2003; Putirka, 2008; Masotta et al., 2013) chemistry. Due to the paucity/absence of glasses, we assume the whole rock composition as representative of the original liquid (or nominal melt) in equilibrium with phenocrysts (Putirka, 1997, 2008; Mordick and Glazner, 2006; Aulinas et al., 2010; Dahren et al., 2012; Barker et al., 2015). We are aware that such a procedure put the focus on early steps of the crystallization history, characterized by high melt/crystal ratios. Relatively late melt compositions, related to the solidification of the groundmass, are not present or can simply not be analyzed. Thermobarometric calculations were developed after the application of mineral-melt equilibrium filters and

considering pre-eruptive H_2O^{liq} values calculated using the plagioclase-liquid hygrometer model (eq. 25b in Putirka, 2008). Plagioclase-liquid thermometry and barometry were calculated using eq. (24a) and eq. (25a), respectively, of Putirka (2008), mainly based on the Ca/Na distribution between melt and Pl. Alkali-feldspar-liquid thermometry was calculated considering the K-Na exchange, applying eq. (24b) in Putirka (2008). Olivine-liquid equilibrium thermometry was calculated integrating the models of Beattie (1993) and Herzberg and O'Hara (2002) with the thermometric eq. (2) in Putirka et al. (2007). Orthopyroxene-liquid thermometry was calculated by Fe-Mg partitioning following the model of Beattie (1993; in the revised form [eq. 28a] in Putirka, 2008). For barometry, based on the Na and Al content in Opx, the model of Wood (1974) in the revised form [eq. 29a] in Putirka (2008) was applied.

Clinopyroxene-liquid thermometry and barometry, for diopside-augite pyroxenes in basalts and trachyandesites (groups Cpx1, Cpx2, Cpx3, Cpx4), were calculated by the application of the Jd-DiHd exchange thermometer (Putirka et al, 1996, 2003) using [eq. 33] in Putirka (2008) and the Al-partitioning barometric model [eq. 32c] in Putirka (2008). Clinopyroxene-liquid thermometry and barometry, for diopside-augite pyroxenes in trachytes (groups Cpx3 and Cpx4), were calculated by the application of the Jd-DiHd exchange thermometer (Putirka et al, 1996, 2003; Putirka, 2008) recalibrated for alkaline differentiated magmas using [eqn. Talk33] and [Eqn. Palk 2012], respectively, in Masotta et al. (2013). Clinopyroxene-liquid thermometry and barometry, for augite-aegirine pyroxenes (Cpx5), were calculated integrating [eq. 33] and [eq. 32c] in Putirka (2008) with equations [Eqn. Talk2012] and [Eqn. Palk 2012] in Masotta et al. (2013). Results of mineral-melt equilibrium tests (Figs. 8, 9, 10), hygrometry calculations (Fig. 10) and geothermometric estimates are presented contextually in supplementary mineral chemistry tables. Summary of the thermobarometry estimates are reported in a Pressure-Temperature diagram (Fig. 11).

7.1 Test for Mineral-Melt Equilibrium

Prerequisite for the application of mineral-liquid thermobarometry models based on mineral-melt equilibrium conditions is to test and verify that mineral and the chosen liquid composition represent chemical equilibrium pairs (e.g., Putirka, 2008; Keiding and Sigmarsson, 2012). Petrographic investigations (i.e., polarized light and BSE imaging) and calculation of mineral-liquid partition coefficients were integrated with the aim to select only mineral specimens showing equilibrium with the hosting melt (e.g., Putirka, 2008; Keiding and Sigmarsson, 2012).

The predominant euhedral to subhedral habit of crystals is generally considered as an evidence of equilibrium with the surrounding melt (e.g., Keiding and Sigmarsson, 2012). However, critical for mineral-liquid thermo-barometric model, it is the use of phenocrysts with strongly zoned textures (patchy-, sector-, reverse-, coarse banding oscillatory-zoning), or with disequilibrium textures (resorption patterns, dissolution surfaces, reaction rims and mineral mantles/clots) (e.g. Ginibre et al., 2002; Streck, 2008). These textures imply that core(s) and rim(s), or different portions of the same grain, crystallized and reacted in an evolving liquid with

progressively different compositions (e.g., Mordick and Glazner, 2006; Putirka, 2008; Keiding and Sigmarsson, 2012). As defined by Streck (2008), when crystals are complexly zoned, it can be difficult to find criteria to be used for evaluation of crystal populations and their equilibrium with respective hosting melt. However, it is not the case of the studied samples, where phenocryst assemblages generally do not show disequilibrium patterns or complexly zoned textures (e.g., Ginibre et al., 2002; Streck, 2008). Moreover, all EMPA related to those rare crystals presenting morphological evidence of disequilibrium texture, such as patchy zoning, were discarded.

As second step, the mineral-liquid equilibria between liquid and previous selected minerals, were investigated using: (i) the Fe-Mg exchange coefficient, (ii) the An-Ab partitioning coefficient, and (iii) the comparison between observed and predicted normative components of minerals.

The partitioning of Fe-Mg between mineral and liquid is known as Fe-Mg exchange coefficient, or $K_D^{min\text{-}liq}$(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, *min* is the mineral composition and MgO and FeO are molar fractions; Roeder and Emslie, 1970; Langmuir and Hanson, 1981; Putirka, 2005a; Putirka, 2008). It is used here to test the equilibrium between mafic minerals (olivine, orthopyroxene and clinopyroxene) and liquid (e.g., Maclennan et al., 2001; Putirka, 2008; Stroncik et al., 2009; Aulinas et al., 2010; Keiding and Sigmarsson, 2012; Melluso et al., 2014; Feng and Zhu, 2018).

We calculated $K_D^{min\text{-}liq}$(Fe-Mg) values using (i) equation (17) in Putirka (2008) for Ol and Opx; (ii) temperature-dependent equation (35) in Putirka (2008) for diopsidic-augitic Cpx in basalts and trachyandesites; and iii) the Na-corrected equation (35a) in Masotta et al. (2013) for Na-rich Cpx5 group and for all Cpx from LH5-1 and LH6-1 trachytes. The calculated $K_D^{min\text{-}liq}$(Fe-Mg) values for olivine and orthopyroxene are plotted in a Rhodes's diagram (Dungan et al., 1978; Rhodes et al., 1979; Putirka, 2005; Putirka, 2008) to graphically test the equilibrium between Ol (Fig. 8a) or Opx (Fig. 8b) and the melt (Liq). Furthermore, the Rhodes's diagram is useful to recognize: (i) presence of xenocrystals and/or antecrystals; (ii) late or groundmass crystallization; (iii) crystal removal (decrease of $Mg\#^{liq}$ only); and (iv) closed system crystallization (decrease of $Mg\#^{min}$ only) by deviations of the measured compositions from the expected ones (Rhodes et al., 1979; Putirka, 2008; Melluso et al., 2014).

The calculation of $K_D^{cpx\text{-}liq}$(Fe-Mg) does not consider variations of Ca and Al contents in Cpx (Rhodes et al., 1979; Putirka, 1999, 2005b, 2008). Therefore, a further equilibrium test was achieved through the comparison of analysed Cpx compositions (as expressed by the components EnFs, DiHd and Ca-Ts, where Ca-Ts stays for Ca-Tschermak) with component contents predicted from melt composition (e.g., Putirka, 2008; Mollo et al., 2010; Jeffery et al., 2013; Barker et al., 2015; Ellis et al., 2017). Normative components of Cpx were calculated following the scheme proposed in Putirka et al., (1996) and Putirka (2008); whereas calculation of Cpx components based on melt composition was performed using equations (eq 3.1a) for DiHd, (eq 3.2) for EnFs and (eq 3.4) for Ca-Ts in Putirka (1999). A graphical presentation (e.g., Jeffery et al., 2013; Barker et al., 2015) of this test is shown in Figure 9.

The partitioning of An-Ab between mineral and liquid is known as An-Ab exchange coefficient, or $K_D^{pl\text{-}liq}$(An-Ab) (defined as $K_D^{pl\text{-}liq}$(An-Ab) = [$XAb^{pl}XAlO_{1.5}^{liq}XCaO^{liq}$]/[$XAn^{pl}XNaO_{0.5}^{liq}XSiO_2^{iq}$], where *liq* is the liquid composition, *pl* is the plagioclase composition and all components are in molar fractions) (Carmichael et al., 1977; Holland and Powell, 1992; Putirka et al., 2007; Putirka, 2008; Lange et al., 2009; Keiding and Sigmarsson, 2012; Jeffery et al., 2013; Barker et al., 2015; Waters and Lange, 2015). Figure 10 presents a comparison of measured composition of plagioclase with the one calculated from the melt composition with the thermodynamic model eq (31) in Namur et al. (2012). A similar test can be applied for alkali-feldspars (Putirka, 2008).

In summary, we accept: (i) Ol with $K_D^{ol\text{-}liq}$(Fe-Mg)= 0.30 ± 0.06 (Roeder and Emslie, 1970; Putirka, 2005a; Putirka, 2008 and references therein) (Fig. 8a); (ii) Opx with $K_D^{opx\text{-}liq}$(Fe-Mg)= 0.29 ± 0.06 (Putirka, 2008 and references therein) (Fig. 8b); (iii) Cpx with $K_D^{cpx\text{-}liq}$(Fe-Mg)= 0.28 ± 0.08 (Putirka, 2008) and that verify the one-to-one (± 0.1) relationship between predicted vs. observed normative components (EnFs, DiHd and Ca-Ts) for at least two of the monitored components (Fig. 9); (iv) Pl with $K_D^{pl\text{-}liq}$(An-Ab)= 0.27 ± 0.11 for T > 1050°C and $K_D^{pl\text{-}liq}$(An-Ab)= 0.10 ± 0.05 for T < 1050°C (Putirka, 2008) or that fall within ± 0.1 of the one-to-one relationship between predicted vs observed An components (Fig. 10); and (v) Afs with $K_D^{afs\text{-}liq}$(An-Ab)= 0.27 ± 0.18 (Putirka, 2008). All mineral-liquid pairs exceeding the accepted exchange coefficient values for Ol, Cpx, Opx and Fsp were discarded for thermobarometric analyses.

7.2 Pre-eruptive H_2O^{liq} content estimates

Thermobarometric models for volcanic system require an initial estimate of the pre-eruptive water concentration (wt%) in melt (H_2O^{liq}), which was determined in this work by using the plagioclase-liquid hygrometer model [eq. 25b] in Putirka (2008). Hygrometry calculations were produced after the application of plagioclase-liquid equilibrium filters. The calculated pre-eruptive H_2O^{liq} wt% values (±1σ standard deviation of the weighted mean) are plotted as isolines in Fig. 10. The hygrometer of Putirka (2008) indicates (Fig. 10): (i) H_2O^{liq} negative values in basalts, from -0.20 to -0.40 wt%, with a weighted mean of -0.37 ± 0.20 wt% (MSWD= 0.0026; n= 95); (ii) trachyandesites pre-eruptive water content in the range H_2O^{liq}: 0 – 1.40 wt% (weighted mean of 0.57 ± 0.12 wt%, MSWD= 0.12, n= 246); and (iii) trachytes with the highest water concentration (H_2O^{liq}: 1.40 – 1.90 wt%; weighted mean of 1.46 ± 0.32 wt%, MSWD= 0.059, n= 37). Following the approach of Keiding and Sigmarsson (2012), negative values in basalts are interpreted as anhydrous melt compositions. Coherently with the existing literature (e.g., Webster et al., 1999), the anhydrous character is then assumed as a H_2O^{liq} < 1wt% content.

Application of plagioclase-liquid hygrometer model (Putirka, 2008) define anhydrous environment for pressure-temperature calculations in basalts. Whereas hydrous conditions are required for evolved LHPCS melts and in particular for trachytic lavas, where the impact of 1 wt% H_2O is expected to generate a

568 temperature decrease of ca. -40 °C and a pressure increase of ca. + 1.0 kbar in geothermometers and
569 geobarometers, respectively (Putirka, 2008; Keiding and Sigmarsson, 2012).
570 On contrary, existing studies (e.g., Kushiro, 1969; Sisson and Grove; 1993; Yang et al., 1996; Putirka, 2005a,
571 2005b, 2008; Kelley and Barton, 2008; Keiding and Sigmarsson, 2012) demonstrated a negligible effect of
572 water for basaltic and intermediate melts with H_2O^{liq} 0 – 1 wt%.
573
574 **7.3 Thermobarometry Results**
575 ***7.3.1 Basalts***
576 When applied to phenocryst cores, the Pl-liq thermobarometry (Fig. 11a-c) show that all basaltic materials
577 have magmatic anhydrous T in the range 1230-1266 °C (weighted mean of 1250 ± 5 °C, ±1σ standard
578 deviation of the weighted mean, MSWD= 0.112, n= 95). Pressure estimates are in the range 6.5-8.7 kbar
579 (weighted mean of 7.9 ± 1.1 kbar, ±1σ standard deviation of the weighted mean, MSWD= 0.024, n= 28) for
580 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
581 and LH27.1 Ol-Cpx-basalt. Olivine-melt equilibrium (Fig. 11a-c), for the olivine compositional range of Fo 80-
582 85%, yields T window of 1240-1297 ± 27 °C (±1σ), consistent with the results obtained with Pl-liq
583 thermometry. The Cpx-thermobarometry (Fig. 11a, c), for both Cpx1 (phenocryst cores) and Cpx3
584 (phenocryst rims and unzoned phenocrysts), provides temperature of 1006-1209 °C (weighted mean of 1124
585 ± 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),
586 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)
587 for Cpx3. Thermobaric estimates for Cpx4 (microlites in groundmass) indicate shallow conditions (0.3 – 3.0;
588 weighted mean of 1.6 ± 1.2 kbar (±1σ), MSWD= 0.38, n= 6) for temperatures (1006-1123 °C; weighted mean
589 of 1060 ± 54 °C (±1σ), MSWD= 2.9, n= 6) comparable to those obtained for Cpx1 and Cpx3. Higher
590 temperature estimates (1067-1221 °C; weighted mean of 1157 ± 53 °C (±1σ), MSWD= 2.4, n= 7) at low-
591 pressure (0.4-4.7; weighted mean of 2.9 ± 1.1 kbar (±1σ), MSWD= 0.83, n= 7) are instead obtained for a
592 limited number of Cpx5 (aegirine-rich) compositions (Fig. 11a, c).
593
594 ***7.3.2 Trachyandesites***
595 Based on the Opx- presence/absence criterion, two populations of trachyandesites have been discriminated
596 in this study.
597 Opx-free trachyandesites LH15 and LH21-2 (El Limón and Sarabia lava flows, respectively) are characterized
598 by i) plagioclase phenocryst cores crystallized at T of 1190-1263 °C (weighted mean of 1248 ± 7 °C (±1σ),
599 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)
600 comparable temperature (1193-1263 °C; weighted mean of 1227 ± 37 °C (±1σ), MSWD= 2.3, n= 6) and
601 pressure (6.7-9.6 kbar, mean value of 7.8 ± 2.4 kbar (±1σ), MSWD= 0.101, n= 6) obtained for rare phenocryst
602 rims and microlites at equilibrium; iii) olivine-melt equilibrium (with Fo: 75-80%) showing a T window of 1030-

603 1055 ± 27 °C (±1σ); iv) rare Cpx2 (clinopyroxene phenocryst cores) showing equilibrium with melt and yielding
604 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
605 mean of 5.2 ± 1.2 kbar (±1σ), MSWD= 1.5, n= 12); v) Cpx3 (rims of and unzoned phenocrysts) showing
606 equilibrium with melt and yielding thermobarometric results (T 938-1139 °C, with weighted mean of 1074 ±
607 15 °C (±1σ), MSWD= 1.9, n= 32; and P 1.0-4.4 kbar with weighted mean of 2.8 ± 0.5 kbar (±1σ), MSWD= 0.22,
608 n= 32); vi) Cpx4 (groundmass microcrystals) compositions indicating, with respect to Cpx3, comparable
609 temperatures (1026-1127 °C, with weighted mean of 1059 ± 16 °C (±1σ), MSWD= 0.71, n= 14) at lower
610 pressure conditions (0.3 – 3.6 kbar with weighted mean of 1.4 ± 0.8 kbar (±1σ), MSWD= 0.35, n= 14). The
611 unique Cpx5-liquid pair at equilibrium yielded P-T conditions of 5.6 ± 1.5 kbar and 1122 ± 30 °C.
612 Thermobarometric estimates (Fig. 11a, d) for Opx-bearing trachyandesites (LH4, LH13, LH17; LH26-1; LH26-
613 2; LH27-2) show overlapping P-T conditions for plagioclase populations with: i) phenocryst cores crystallizing
614 at T: 1145-1228 °C (weighted mean of 1187 ± 4 °C (±1σ), MSWD= 1.17, n= 166) and P: 4.1-7.7 kbar (weighted
615 mean of 5.8 ± 0.5 kbar (±1σ), MSWD= 0.059, n= 166), and ii) phenocryst rims and microcrystals forming at T:
616 1140-1224 °C (weighted mean of 1168 ± 8 °C (±1σ), MSWD= 0.90, n= 35) and P: 4.4-8.5 kbar (weighted mean
617 of 6.4 ± 1.0 kbar (±1σ), MSWD= 0.14, n= 35). Lower temperatures (1050-1090 ± 27 °C (±1σ)) are obtained
618 using olivine (Fo 70-80%) – liquid equilibrium model.
619 Thermobarometers applied to pyroxenes indicate: i) Cpx2 (phenocryst cores) crystallizing at T: 979-1204 °C
620 (weighted mean of 1060 ± 8 °C (±1σ), MSWD= 1.7, n= 106) and P: 3.4 -11.65 kbar (weighted mean of 7.0 ±
621 0.3 kbar (±1σ), MSWD= 0.91, n= 106), ii) Cpx3 crystallizing at T: 958-1106 °C (weighted mean of 1026 ± 6 °C
622 (±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=
623 147), iii) rare Cpx4 showing general equilibrium with melt and forming at P-T conditions of : 920-1123 °C
624 (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
625 kbar (±1σ), MSWD= 0.56, n= 24), and iv) Opx yielding crystallization conditions, for both phenocrysts and
626 microlites, of T 1048-1123 °C (weighted mean of 1078 ± 5 °C (±1σ), MSWD= 0.24, n= 129) and P: 0 -2.8 kbar
627 (weighted mean of 1.1 ± 0.6 kbar (±1σ), MSWD= 0.057, n= 84). In all trachyandesites samples, temperatures
628 obtained through Ol-Liq model and Cpx-Liq model are comparable (Fig. 11a, d), whereas the Pl-Liq model
629 shows higher T values. These can be interpreted as an earlier plagioclase crystallization with respect to the
630 olivine and clinopyroxene. Orthopyroxene (Opx) can be considered a tracer of trachyandesitic magma
631 stagnations at shallow depth since the invariably lower pressure values obtained by Opx-liquid barometer.
632
633 ***7.3.3 Trachytes***
634 Magmatic P-T conditions (Fig. 11a, e) of trachytes (LH5.1 and LH6) melts are defined by: i) plagioclase
635 crystallization at T: 1050-1094 °C (weighted mean of 1069 ± 6 °C (±1σ), MSWD= 0.39, n= 37) and P: 4.7-9.0
636 kbar (weighted mean of 6.5 ± 1.0 kbar (±1σ), MSWD= 0.20, n= 37), ii) olivine (Fo55-65%) – liquid regression

637 indicating olivine crystallization at 900-920 ± 27 °C (±1σ), iii) clinopyroxenes crystallization, both phenocrysts
638 (Cpx3) and groundmass(Cpx4), at temperature of ca. 955 °C (weighted mean of 956 ± 14 °C (±1σ), MSWD=
639 0.00056, n= 17) and very shallow-depth conditions (P weighted means of 2.3 ± 0.9 kbar (±1σ), MSWD=
640 0.047, n= 10 and 1.6 ± 1.1 kbar (±1σ), MSWD= 0.04, n= 7; for Cpx3 and Cpx4, respectively). Shallow-depth
641 conditions are obtained also for orthopyroxene crystallization with temperature in the range 960-1006 °C
642 (weighted mean of 990 ± 7 °C (±1σ), MSWD= 0.28, n= 49) and P: 0.2-3.6 kbar (weighted mean of 1.6 ± 0.9
643 kbar (±1σ), MSWD= 0.101, n= 35). Alkali-feldspar-liquid thermometer provided temperature estimates
644 always <500°C, here interpreted as feldspar re-equilibration of groundmass after eruption in
645 subsolvus/subsolidus conditions (Nekvasil, 1992; Brown and Parsons, 1994; Plumper and Putnis, 2009;
646 Kontonicas-Charos et al., 2017; Latutrie et al., 2017). Interestingly, temperatures obtained through Pl-Liq
647 model are higher than those obtained with Ol-Liq, Cpx-Liq and Opx-Liq, suggesting an earlier crystallization
648 of plagioclase with respect to mafic minerals. Moreover, the Pl-Liq models indicate thermobaric estimates
649 comparable to those obtained for trachyandesitic rocks.
650
651

8. DISCUSSION

8.1 Major-elements mass balance modeling

Based on the textural evidence documenting: (i) cpx-bearing basalts being mainly characterized by euhedral olivine and plagioclase and subhedral-anhedral clinopyroxene, indicating crystallization of olivine and plagioclase prior to clinopyroxene (e.g., Bindeman and Bailey, 1999); and (ii) all LHPCS volcanic rocks do not show disequilibrium textures (such as fine-sieve textures, resorption surface, crystal clots, disequilibrium growth-mantel, reverse zoning, reaction-rims, breakdown mantle and dissolution; e.g., Streck, 2008) typical of AFC-mixing processes, we suggest that the studied LHPCS volcanic rocks represent cogenetic melts, belonging to the same line of descent, excluding major mass-change due to assimilation and mixing (AFC-mixing) processes. In order to test this hypothesis, we applied fractional crystallization (FC) modelling (e.g., White et al., 2009; Moghadam et al., 2016; Lucci et al., 2016) to test and demonstrate the hypothesis the LHPCS volcanic rocks belong to a unique line of descent. The FC-modeling is focused on these hypotheses: (i) direct cogenetic relationship between all LHPCS basalts, and (ii) common genesis for all LHPCS trachyandesites and trachytes through differentiation via fractional crystallization starting from the same basaltic parental melt.

Major-element mass balance models (e.g., Bryan et al., 1969) can be used to test and define relative proportion of phases involved in Rayleigh fractional crystallization (RFC, Daughter = Parent - fractionating assemblage) and crystal accumulation (Cumulate =Melt + accumulated assemblage) hypotheses (e.g., White et al., 2009; Moghadam et al., 2016; Lucci et al., 2016).

If Parent melt (for RFC) or Cumulate (for crystal accumulation) compositions are assumes as matrix ***b***, and the FC-model is solved for ***b***, then ***b*** = Liquid (Daughter or Melt) + Minerals (fractionating or accumulated assemblage). If compositions of Liquid and Minerals are known (matrix ***A***), it is possible to estimate, by least squares approximation, their proportion (in matrix ***c***). The similarity of ***b'*** (matrix c multiplied with matrix ***A***) to ***b*** (real value) is quantified with the sum of the square of the residuals (Σr^2) as:

$$\sum r^2 = \sum_{i-1}^{n} (b_i' - b_i)^2 \qquad \text{(Eq. 1)}$$

RFC and Cumulate model results are considered acceptable when $\Sigma r^2 < 1.0$. Proportion of Liquid (Daughter or Melt) is expressed with ***F*** in matrix ***c***.

Major-element mass balance models are calculated in the system SiO_2-TiO_2-Al_2O_3-FeO*-MnO-MgO-CaO-Na_2O-K_2O. The LH5-2 cpx-bearing basalt, with the lowest SiO2 and the highest MgO contents, was selected as possible source for all pyroxene-bearing trachyandesites and trachytes. The fractional crystallization hypothesis is then tested for all the LHPCS studied rocks and, considering the magmatic mineralogy made of An-rich plagioclase, Ti-rich clinopyroxene, Mg-rich olivine, Spinel. The same mineral assemblage was used to verify the cogenetic relationship between studied LHPCS basalts through progressive crystal accumulation. All calculations were managed with Microsoft Office Excel2019, results of FC-models are presented in Supplementary Table 6.

687 The RFC model has been applied to all studied trachyandesites and trachytes. It was verified that a
688 fractionation of the Pl+Cpx+Ol+Sp assemblage in the range of: (i) 45-63 wt% (Σr2 0.37-0.92) is necessary to
689 produce Opx-free trachyandesites, (ii) 59-69 wt% (Σr2 0.38-0.92) is capable to produce Opx-bearing
690 trachyandesites, and (iii) 73-74 wt% (Σr2 0.88-0.91) is requested to produce trachytes. The crystal
691 accumulation has been tested to verify the linkage between Cpx-free basalt (LH18-1) and cpx-bearing basalts
692 (LH5-2, LH27-1). It was verified that a crystal accumulation of the Pl+Cpx+Ol+Sp assemblage in the range of
693 16-17 wt% (Σr2 0.05-0.15), with Cpx in the range 5-7 wt%, is able to produce LHPCS cpx-bearing basalts.
694 The results obtained from FC-models indicate that the LHPCS volcanic rocks are genetically linked melts, due
695 to crystal accumulation (basalt) and fractional crystallization (intermediate and felsic rocks) of a
696 Pl+Cpx+Ol+Sp mineral assemblage. Trachyandesites and trachytes represent different degrees of
697 fractionation (RFC values in the range 45-74%) starting from a cpx-bearing basaltic source. Cpx-bearing
698 basalts are interpreted as resulting from crystallization and accumulation of cpx, together with Pl+Ol+Sp, in
699 a pristine cpx-free basaltic melt. Results from FC-models also confirm the possibility to produce hydrous felsic
700 melts starting from a nominal anhydrous (H2O < 1 wt%; e.g., Webster et al., 1999) mafic parental melt.
701 Integrating FC-model and hygrometer (Putirka, 2008) results, LHPCS trachytes show H_2O ca. 1.4-2.0 wt% and
702 represent the ca. 25 wt% fractionated residual melt from a parental basaltic source characterized by H_2O in
703 the range 0.3-0.5 wt%.
704
705 **8.2 Magma evolution beneath Los Humeros**
706 The conceptual model of the present-day LHPCS magmatic plumbing system beneath the Los Humeros
707 caldera is presented in Fig. 12. Based on textural observations, mineral chemistry and thermobaric estimates
708 the early HT (1230-1270 °C) stage of LHPCS magma evolution is represented by high-anorthite plagioclase
709 phenocrysts and Mg-rich olivine (XFo= 80-85%) crystallizing in the deep (ca. 8 kbar) basaltic reservoir. Where
710 these magmas erupted directly, they formed Cpx-free Ol-basalt lava flows such as Texcal Lava flow (LH18).
711 This scenario, for LH18 basalt sample, is confirmed by (i) olivine and plagioclase with homogeneous cores
712 and normal monotonous zoning textures at rims, indicating a fast growth during ascent of magma (e.g.,
713 Streck, 2008); (ii) olivine with spinifex, dendritic and skeletal textures, interpreted as supercooling mineral
714 texture largely resulting from rapid olivine-supersaturated magma rise from deeper level during the eruption
715 (e.g., Donaldson, 1974; Nakagawa et al., 1998; Fowler et al., 2002; Dahren et al., 2012; Welsch et al., 2013),
716 and (iii) plagioclase specimens with swallow-tailed crystal morphology, interpreted as rapid plagioclase
717 growth due to undercooling related to eruption process (e.g., Renjith, 2014).
718 A permanence of these basaltic melts in the deep reservoir together with a temperature decrease of ca.
719 100°C can lead to clinopyroxene appearance/crystallization in the system (e.g., Groove, 2000) and its
720 progressive accumulation in the phenocryst assemblage. This hypothesis is supported by Cpx-Liq
721 thermometry models for Cpx1 (Ti-rich augites in basalts) indicating Cpx appearence at ca. 7-8 Kbar and 1150

°C (mean values), and by FC-models indicating a Pl+Cpx+Ol+Sp crystal accumulation up to 15-17 wt% in the pristine basaltic melt to produce the Cpx-bearing basalts.

Where these magmas erupted as intra-caldera basalts (LH5-2, LH27-1), they are characterized by the further crystallization of (i) progressively Fe-rich olivine (up to XFo= 17-20%), (ii) Ab-rich plagioclase (XAn= 25-30%), (iii) Cpx3 unzoned homogeneous phenocrysts and overgrowth (normal monotonous and normal low-amplitude oscillatory zoning) on Cpx1-cores, (iv) Cpx5 (Aeg-Aug) Na-clinopyroxenes and (v) Cpx4 (Di-rich) microcrystals and microlites. This mineral assemblage (mineral chemistry and textures) together with the thermobarometric results obtained, describes a near-isothermal magma uprising within a narrow temperature window of ca. 1070-1150 °C. Such crystal-bearing magmas ascend from the deeper reservoir to intermediates and shallower stagnation levels, where different phases would crystallize, before the eruption (e.g., Feng and Zhu, 2018). In particular, (i) the homogeneous unzoned cores of phenocrysts represent the early crystallization at equilibrium with the melt, (ii) the normal low-amplitude oscillatory zoning from Pl and Cpx phenocrystals indicates a kinetically driven crystallization (e.g., Ginibre et al., 2002; Streck, 2008; Renjith, 2014), whereas the normal monotonous zoning observed in many Pl, Cpx and Ol phenocrysts indicates a fast growth during ascent of the magma (e.g., Streck, 2008); (iii) microlites formation indicates water exsolution driven crystallization (e.g., Rutherford, 2008; Renjith, 2014) during a relative rapid ascent or eruption processes (e.g. Renjith, 2014); and (iv) the similarity of compositions between Pl and Cpx phenocrysts rims and microlites confirms that there were essentially no major changes in the temperature of any of these basaltic magmas during the ascent (e.g., Rutherford, 2008). The scenario of rapid ascent of LHPCS basaltic magmas is supported also by the observed high-vesicularity textures, interpreted as bubble-growth processes during a relative fast magma rise precluding exsolved volatile to escape (e.g. Sparks, 1978; Sparks et al., 1998; Rutherford and Gardner, 2000; Rutherford, 2008; Costa et al., 2013; Feng and Zhu, 2018).

Fractional crystallization of An-rich plagioclase, Fo-rich olivine, Ti-rich augite and spinel (Pl+Ol+Cpx+Sp in RFC-models) in the primary cpx-bearing basaltic magmas produces residual melts (ca. 30-55 wt%) of trachyandesitic compositions. These evolved buoyant melts will be prone to leave the basaltic reservoir to produce shallower intrusions in a vertically extensive magmatic system (e.g., Jackson et al., 2018), carrying early-formed phenocrysts (i.e., anorthitic plagioclase antecrystals) to the intermediate reservoir and stall. Within this intermediate vertically-distributed layered storage system in the middle crust, Cpx2 clinopyroxene and all the rest of plagioclase phenocrysts start to crystallize producing progressively evolved felsic residual melts able to migrate upward in the feeding system or erupt (e.g., Freundt and Schminke, 1995; Patanè et al., 2003; Klugel et al., 2005; Stroncik et al., 2009; Aulinas et al., 2010; Dahren et al., 2012; Keiding and Sigmarsson, 2012; Scott et al., 2012; Jeffery et al., 2013; Coombs and Gardner, 2001; Barker et al., 2015; Feng and Zhu, 2018). Similarly to LHPCS basalts, the phenocryst morphologies and textures, together with the microlites compositions and the vesicle-rich textures decrived in trachyandesitic melts suggests a nearly

isothermal rapid ascen,t precluding exsolved volatiles to escape and producing water exsolution driven crystallization (e.g., Rutherford, 2008; Renjith, 2014).

The shallowest magma stagnation level (< 3kbar; mean 1.5 kbar) has been here interpreted as a complex magma plexus constituted by a system of small magma volumes, distributed in locally interconnected pockets and batches where (i) mafic and intermediate magmas shortly stall prior to erupt and (ii) more evolved melts reside for a relatively longer time, enough to crystallize orthopyroxene and to enabling the escape of part of the exsolved volatiles (e.g., Sparks et al., 1998; Feng and Zhu, 2018; Clarke et al., 2007), as suggested by phenocryst textures and compositions and by poor-vesicle textures observed in Opx-trachyte samples (LH5-1, LH6-1).

Compositional reverse zoning associated with disequilibrium textures and dissolution/resorption patterns in phenocrysts, are widely considered indicators of both magma-replenishment or assimilation processes (e.g., Wright and Fiske, 1972; Duda and Schminkcke, 1985; Clague et al., 1995; Yang et al., 1999; Klugel et al., 2000; Zhu and Ogasawara, 2004; Stroncik et al., 2009; Ubide et al., 2014; Viccaro et al., 2015; Gernon et al., 2016; Feng and Zhu, 2018). In the case of Los Humeros, almost all investigated LHPCS samples, from basalts to trachytes, contain mainly phenocrysts with homogeneous cores and low-amplitude oscillatory or normal monotonous zoned rims (Pl+Ol+Cpx) or unzoned homogeneous phenocrysts (as in case of Cpx3 and Opx). Rare specimens not suitable for mineral-liquid thermobarometry such as plagioclase and clinopyroxene with patchy cores or olivine xenocrysts are reported. The general absence of disequilibrium textures and patterns in LHPCS studied samples, is therefore interpreted as a lack of evidence of major mixing/recharge and/or assimilation processes acting in the plumbing system (e.g., Cashman et al., 2017 and references therein). This hypothesis is in line with the results obtained from tests for mineral-melt equilibria. Rhodes's diagram (Rhodes et al., 1979; Putirka, 2008) for olivine compositions (Fig. 8a) highlights a progressive decrease in $Mg\#^{liq}$ from basalts to trachytes coupled with general absence of xenocrystals/antecrystals cargo. This behavior is compatible with a complete removal from the melt of previously crystallized Mg-olivine (Roeder and Emslie, 1970; Dungan et al., 1978; Rhodes et al., 1979; Putirka, 2008; Melluso et al., 2014). All melts (from basalts to trachytes) show invariably suites of olivines with maximum forsterite (Fo) contents in equilibrium with the respective whole rocks, and vertical trends consistent with closed-system melt differentiation (Roeder and Emslie, 1970; Rhodes et al., 1979; Putirka, 2008; Melluso et al., 2014). Similar behavior is obtained for orthopyroxene (Fig. 8b), where again Rhodes's test highlights (i) absence of antecrystals, and (ii) Opx-suites progressively and normally Fe-enriched from trachyandesites to trachytes. The absence of clinopyroxene clots and overgrowth mantle textures on orthopyroxene crystals, again excludes the occurrence of magma mixing/recharge processes (Laumonier et al., 2014; Neave et al., 2014; Zhang et al., 2015; Feng and Zhu, 2018). Such interpretation is supported also by field observations, where the interbedded basaltic andesite and trachydacite fall deposits of the ca. 7 ka Cuicuiltic Member show no evidence of magma-mixing (Dávila-Harris and Carrasco-Núñez, 2014).

An-Ab partition coefficients (e.g., Putirka, 2008; Jeffery et al., 2013) show a comparable scenario (Fig. 10) in which: (i) basalts are characterized by suites of plagioclases with maximum anorthite (An) contents in equilibrium with the respective whole rocks, and progressive An^{pl} decrease consistent with closed-system differentiation; and (ii) progressive decrease in predicted An^{liq} from basalt to trachyte compatible with evolved melts differentiation via fractional crystallization. Intermediate and evolved products are characterized by plagioclase phenocrysts characterized by An-rich homogeneous cores (An 70-85%), with compositions comparable to those of basalts. These An-rich cores can be crystallized in two possible scenarios. The first one is related to the H2O content in magma. Increasing the water content in melt strongly favors crystallization of An-richer plagioclase. A water content rise from 0.5 to 2.0 wt% could lead to an increase of the An component up to 6-8 mol% (Bindeman and Bailey, 1999; Sano e Yamashita, 2004; Ushioda et al., 2014). In this view, the An-rich plagioclase in intermediate and felsic rocks can be interpreted as the response to the increasing water-content in the fractionated melt. The second scenario implies that An-rich plagioclase taps a more primitive stage of basalt segregations. Since plagioclase phenocrystals with An in the range 65-81% are commonly found in LHPCS basalts, the An-rich plagioclase cores in trachyndesites and trachytes could represent either antecrysts derived from crystallization of early sills in the magmatic reservoir system (sensu Jackson et al., 2018) or crystallization products in an earlier stage of the trachyandesite and trachyte segregation from the basaltic reservoir (e.g., Bindeman and Bailey, 1999; Kinman and Neal, 2006). We suggest that both scenarios concurred to the genesis of An-rich phenocrysts in trachyandesites and trachytes. Noteworthy, when An-rich plagioclase crystals are found (in mafic and intermediate rocks with Pl+Ol+Cpx assemblages), it implies that no significant clinopyroxene crystallization has occurred prior to the anorthitic plagioclase (Bindman and Bailey, 1999).

With respect to plagioclase, a similar behavior is observed also for clinopyroxene and in particular for Cpx1 and Cpx2 (clinopyroxene cores in basalts and in trachyandesites+trachytes, respectively) populations. Since these mineral cores (Pl, Cpx1 and Cpx2) generally present normal growth rims (i.e., Ab-rich Pl and Cpx3), we suggest that stagnation levels at both intermediate and shallower depths underwent crystallization in a closed system. Otherwise, features such as: i) diffused reverse zoning, ii) high-temperature crystal-clots, mantling and overgrowth, iii) disequilibrium and dissolution textures (e.g., Stroncik et al., 2009; Cashman et al., 2017; Feng and Zhu, 2018 and references therein), should be widely observed, but this is not the case in the LHPCS studied lavas.

8.3 The magma plumbing system

The petrological archive constituted by LHPCS lavas, spanning from transitional- and alkali-basalts to trachytes, describes the Holocene activity of Los Humeros volcanic complex. Major element bulk compositions of LHPCS lavas are characterized, in selected Harker diagrams (Fig. 3 b-d) by linear trends comparable to those expected for cogenetic melts (e.g., Giordano et al., 2012). Major-element FC-modeling

826 confirms the hypothesis of a common genesis for LHPCS volcanic rocks through crystal
827 fractionation/accumulation processes of the same mineral assemblage (Pl+Cpx+Ol+Sp). Furthermore,
828 textural observations and results from FC-models permit to exclude at this stage mass-change or mass-
829 addition phenomena driven by AFC-Mixing processes.
830 Results obtained from the application of different and independent thermobarometry models (Fig. 11)
831 confirm the working hypothesis of a complex magmatic plumbing system rather than a single "standard"
832 magma chamber (e.g., Keiding and Sigmarsson, 2012; Cashman and Giordano, 2014; Cashman et al., 2017;
833 Feng and Zhu, 2018) developed beneath the active Los Humeros caldera and feeding the LHPCS volcanism.
834 With the aim to propose an updated and realistic conceptual model of the present-day main storage zones
835 and magma plumbing system within the crust below Los Humeros caldera, we integrate pressure-
836 temperature estimates acquired in this work, with the existing data related to crustal structure and
837 properties of the study area. The resulted model is shown in Figure 12.
838 The density of TMVB crust shows a large range between 1800 Kg/m^3 for unconsolidated sediments to about
839 3000 kg/m^3 for the lower crust and 3300 kg/m^3 for the upper mantle (Dziewonski and Anderson, 1981;
840 Campos-Enríquez and Sánchez-Zamora, 2000; Davies, 2013). A reasonable available up today compilation of
841 crust data for Los Humeros volcanic complex is recovered by the measure N°10 of the Crust 1.0 global model
842 (Dziewonski and Anderson, 1981; Davies, 2013). The measure N°10 (yellow star in Fig. 1) is located within the
843 study area at the southern termination of the Tepeyahualco Lava Flow and describes a crust (Fig. 12) made
844 of five main seismic layers: i) upper sediments (thickness: 1km, density 2110 km/m^3), ii) middle sediments
845 (thickness: 0.5 km, density 2370 km/m^3), iii) upper crust (thickness: 13.58 km, density 2740 km/m^3), iv) middle
846 crust (thickness: 15.27 km, density 2830 km/m^3), and v) lower crust (thickness: 13.58 km, density 2920
847 km/m^3). Inferred (seismic) Moho depth is reported at -41.67 km with an upper mantle density of 3310 km/m^3
848 (Dziewonski and Anderson, 1981; Davies, 2013). Here we use a five-tiered density model, as derived from the
849 Crust 1.0 global model, for the 41.67 Km continental crust beneath Los Humeros caldera, to convert obtained
850 pressure estimates to depths.
851 The thermobarometry models applied to the LHPCS lavas define a broad region of crystallization between 0
852 and ca. 30 km in depth that can be described with a quadrimodal distribution of pressure values (Fig. 12),
853 which allow us to propose a complex polybaric continuous heterogenous multilayered transport and storage
854 magmatic system.
855 A deep-seated anhydrous Ol-basalt reservoir at depths of ca. 28-33 km (7.6-9.2 kbar), at the boundary
856 between lower and middle crust, below the caldera is recorded by (a) An-rich plagioclase cores (XAn = 50-70
857 %), and (b) Ti-rich augitic clinopyroxene Cpx1 cores (Mg# up to 75, TiO_2 up to 4.57 wt%) of Cpx1. Overlapping
858 the calculated anhydrous temperature values from plagioclase-liquid, Cpx1 clinopyroxene-liquid and olivine-
859 liquid pairs provide a total range of ca. 1000 – 1300 °C for this mafic reservoir. Highest anhydrous
860 temperature values are achieved for Cpx-free Ol-basalt Texcal lava flow (LH18) where the convergence of

plagioclase-liquid thermobarometry and olivine-liquid thermometry models indicate conditions of ca. 1230-1270°C at ca. 8 kbar. Lower anhydrous temperatures of ca. 1000-1210 °C, are obtained at a comparable average pressure value of 7.6 kbar for Cpx-bearing intra caldera Ol-basalts (LH5-2; LH 27-1). These results are in agreement with existing literature on the near-liquidus melting behavior of high-Al basaltic magmas (Mg# ca. 60-70 and Al_2O_3: 17-19 wt%) under dry conditions (e.g., Thompson, 1974; Grove et al., 1982; Crawford et al., 1987; Bartels et al., 1991; Grove, 2000). At 1250-1300 °C and ca. 10 kbar (Point *A* in Fig. 11) the basaltic melt is in equilibrium with a mantle peridotite mineral assemblage of olivine + clinopyroxene (Kushiro and Yoder, 1966; Presnall et al., 1978; Grove et al., 1982; Fuji and Scarfe, 1985; Takahashi, 1986; Fallon and Green, 1987; Bartels et al., 1991; Sisson and Layne, 1993; Wagner et al., 1995; Grove et al., 1997; Grove, 2000; Kinzler et al., 2000). Following the models proposed by Thompson (1974), Bartels et al. (1991) and Grove (2000), a temperature decrease would lead primary melts to pass the "dry basaltic liquidus" and start the crystallization of Ol+Pl (higher temperatures) or Ol+Cpx+Pl (lower temperatures) assemblages (see stability fields in Fig. 11). Given the ubiquitous presence in all LHPCS basalts of well-developed euhedral to subhedral olivine crystals (both phenocrystals and microlites) at equilibrium with anorthitic plagioclase, it is possible to exclude that crystallization history started at depth > ca. 10-12 kbar where olivine is not a stable phase and the primary assemblage would be characterized only by Cpx+Pl+Sp in equilibrium with melt (Kushiro and Yoder, 1966; Thompson, 1974; Presnall et al., 1978; Bartels et al., 1991; Grove, 2000).

A second magma transport and storage systems can be recognized at depths of 15-30 km (ca. 4.5 – 7.8 kbar), in continuity with the deeper basaltic reservoir and distributed along the whole middle crust thickness, as recorded by the wide range of pressure estimates obtained from plagioclase (XAn= 40-70%) and Cpx2 clinopyroxene cores (Mg#: 59-84; TiO_2 mean value 0.99 wt%). Thermometry models based on plagioclase, Cpx2 clinopyroxene and olivine show convergence for hydrous temperature values in the range of 979 – 1263 °C. Thermobarometry models, together with textures and petrographic relations in all analyzed trachyandesite and trachyte samples suggest that all plagioclase, all Cpx2 clinopyroxene phenocrysts, and part of microlites, grew in this second storage system. In particular, it is possible to observe two main crystallization temperature conditions: (a) at ca. 1190°C (weighted mean value, MSWD= 2.2, n= 205) plagioclase phenocrysts crystallization in trachyandesite melts is observed, whereas (b) at the lower temperature of ca. 1070 °C (weighted mean value, MSWD= 1.7, n= 155) is reported the crystallization of all olivine, all Cpx2 phenocrysts, and plagioclase phenocryst in trachytes. We interpret the common Pl+Cpx2 phenocryst-forming barometric conditions as evidence of a growth-dominated regime within this second magma storage zone (e.g., Barclay et al., 1998; Humphreys et al., 2006; Scott et al., 2012), whereas the smaller crystals (microcrystals and microlites) represent the nucleation-dominated regime (Scott et al., 2012) that can be associated with ascent-related decompression of melts at shallower levels (e.g., Cashman, 1992; Cashman and Blundy, 2000; Humphreys et al., 2009).

The third melt storage zone occurs at shallower depths of ca. 10-15 km, possibly corresponding to the transition between middle- and upper-crust, as indicated by convergence of barometric estimates (weighted mean value of 3.9± 0.2 kbar (±1σ), MSWD= 0.80, n= 203; P ranging ca. 1-7 kbar) obtained from Cpx3 clinopyroxene (i.e., unzoned phenocrysts and overgrowth/rims around earlier formed Cpx1- and Cpx2-cores) population. Cpx3 clinopyroxene-liquid thermometry model indicates, for this third storage zone a mean temperature of 1040 °C (weighted mean value, MSWD= 2.6, n= 203; T ranging ca. 940-1210 °C) comparable to those calculated for Ol+Cpx2 assemblages in the previous described second and deeper stagnation system. The obtained pressure estimates for the second and the third storage systems are compatible with multiple magma storage pockets, in which melts of comparable compositions ascend slowly enough for phenocrysts to form (e.g. Scott et al., 2012), and start cooling before the final ascent to shallower conditions (e.g., Dahren et al., 2012; Chadwick et al., 2013; Gardner et al., 2013; Jeffery et al., 2013; Preece et al., 2013; Troll et al., 2013). Taking into account the textures and the chemistry of Cpx3 clinopyroxene phenocrysts, the obtained thermobarometric estimates could be interpreted as the pressure-temperature environment of last major levels of magma stagnation and fractionation (Putirka, 1997; Klugel et al., 2005; Galipp et al., 2006; Stroncik et al., 2009).

The fourth shallowest storage zone located at depths of ca. 3-7 km (weighted mean value of 1.5± 0.2 kbar (±1σ), MSWD= 0.24, n= 177; P ranging ca. 0.1-4.5 kbar), is required to explain the presence of i) Cpx4 clinopyroxene (microcrystals and microlites) in all LHPCS lavas, ii) Aeg-rich Cpx5 clinopyroxene in basalts, and iii) Fe-olivine (Fo = 55-65%) and orthopyroxene in Opx-bearing evolved LHPCS lavas. Magmas in this shallow storage system show a wide range of temperature values calculated for hydrous melts: a) ca. 1060 °C (weighted mean value, MSWD= 2.4, n= 7) for Aeg-rich Cpx5 crystallization in basalts, b) ca. 1070 °C (weighted mean value, MSWD= 1.09, n= 168) for Cpx4 and Opx crystallization in trachyandesites, and c) ca. 965 °C (weighted mean value, MSWD= 2.2, n= 78) for olivine, Cpx4 and Opx crystallization in trachytes. Thermobaric estimates obtained for Aeg-rich Cpx5 agree with those calculated for transitional basalts at Pantelleria (White et al., 2009 and references therein), whereas orthopyroxene crystallization conditions overlap with the existing literature for intermediate rocks (e.g., Rutherford et al., 1985; Wallace and Anderson, 2000; Reubi and Nicholls, 2004; Allan et al., 2013; Jeffery et al., 2013). The broad distribution of melt chemistry from basalt to trachyte, together with the obtained thermobaric estimates, define a shallow magma storage environment characterized by progressive accumulation of small locally interconnected magma pockets and batches (e.g., Reubi and Nicholls, 2004; Jeffery et al., 2013) dispersed in the upper crust (<10 km) with a possible magma plexus at a depth of 2-4 km under the caldera (e.g., Armienti et al., 1989; Freundt and Schminke, 1995; Pietruszka and Garcia, 1999; Patanè et al., 2003; Klugel et al., 2005; Stroncik et al., 2009; Dahren et al., 2012; Jeffery et al., 2013; Coombs and Gardner,, 2001, 2004).

8.4 “Standard” versus multilayered magmatic plumbing system

930 Existing conceptual models for LHVC are based on the "Standard Model" (*sensu* Gualda and Ghiorso, 2013),
931 hypothesizing a single, bowl-shaped, long-lived, melt-dominated huge classical magma chamber of 1000-
932 1500 Km^3 in volume, at depth of 5 to 10 km from the surface (Verma, 1983, 1984, 1985a, 1985b; Verma and
933 Lopez, 1982; Verma et al., 1990; Verma and Andaverde, 1995; Verma et al., 2011; Verma et al. 2013;
934 Carrasco-Núñez et al., 2018). However, these models mainly refer to the Los Humeros Caldera stage activity
935 (Carrasco-Núñez et al., 2018 and references therein), lasted ca. 130 ky, where the major caldera-forming
936 events (Xaltipan and Zaragoza ignimbrites, 115Km^3 and 15Km^3 DRE, respectively) and the large Plinian
937 eruptive episode (Faby Tuff, 10km^3 DRE) necessitated feeding from a huge, voluminous magma chamber
938 (Carrasco-Núñez and Branney, 2005; Carrasco-Núñez et al., 2018).
939 On the other hand, the Holocene eruptive phase of the LHPCS is a characterised by bimodal volcanism
940 (Carrasco- Núñez et al., 2017a; Carrasco-Núñez et al., 2017b; Carrasco-Núñez et al., 2018), typified by
941 alternating episodes of effusive and explosive volcanism with a wide range of compositions, spanning from
942 basaltic to trachytic lava flows and mafic to felsic pumice and scoria fall deposits, erupted by tens of
943 monogenetic eruptive centers located in the LHVC (e.g., Norini et al., 2015; Carrasco- Núñez et al., 2017a;
944 Carrasco-Núñez et al., 2017b; Carrasco-Núñez et al., 2018). This volcanic activity is characterized by
945 patially distributed, small volumes of erupted material (ca. 6 km3 of mafic lavas, 10 km3 of intermediate and
946 felsic lava, and 1 km3 of mafic and felsic tephra; Carrasco-Núñez and Branney, 2005). Furthermore, elements
947 such as the lithic-free character of the LHPCS volcanic products, their overall textures and chemistry of
948 mineral assemblages, coupled with the results from RFC-models, suggest that LHPCS magmatism is
949 characterized by batches of magma evolving in a nearly closed system, unaffected by magmatic assimilation
950 and mixing/recharge processes. In particular, the almost complete lack of magma mixing/recharge events
951 (e.g., Lee et al., 2014) is confirmed by the absence of the typical expected minerals textures (e.g., Streck,
952 2008; Renjith, 2014) such as: (i) fine-sieve textures and resorption surfaces due to reaction with a more
953 primitive magma; (ii) glomerocryst-forming due to the recrystallization/suturing at rim of resorbed crystals;
954 (iii) reverse zoning due to compositional inversion in open/recharged system; and (iv) reaction rims,
955 breakdown mantle and crystal clots due to the disequilibrium-triggered recrystallization into a new set of
956 minerals instead of dissolution.
957 The existing literature focused on magma recharge (e.g., De Paolo, 1981; Hofmann, 2012; O'Neill and Jenner,
958 2012; Lee et al., 2014) highlights that a high evacuation/eruption efficiency will shorten the residence-time
959 of magma in the storage chamber and will reduce the effect of crystallization in modifying the magma
960 composition (Lee et al., 2014). Moreover, in case of eruption/evacuation rates higher than the recharge rates
961 (e.g., Lee et al., 2014), it is possible to hypothesize a magmatic system dominated by ephemeral closed-
962 system magma batches not affected by major mixing processes prior their evacuation/eruption (e.g., De
963 Paolo, 1981; Hofmann, 2012; O'Neill and Jenner, 2012; Lee et al., 2014). This scenario best approximates the
964 characteristics observed for all the Holocene LHPCS magmatic products. In addition, the absence of liquid-

dominated zone(s) (e.g., Bachmann and Bergantz, 2008) where mixing could occur (e.g., Cashman and Giordano, 2014), moreover suggests that the remnants of the huge magma chamber of the LH caldera stage are now completely solidified and crosscut by the uprising LHPCS mafic and felsic magmas. Once more, this scenario points out the incompatibility of the LHPCS magmatic activity with a feeding system dominated by the single voluminous magma chamber. This scenario is also coherent with the post-caldera eruption behavior observed in other volcanic complexes, such Ischia (e.g., Casalini et al., 2017), and it is consistent with the recent literature proposing complex magma chamber reservoirs made up of multiple discrete melt pockets with no mass-exchange and reactivated shortly before eruption (e.g., Cashman and Giordano, 2014; Cashman et al., 2017; Casalini et al., 2017).

Thermobarometric estimates obtained in this work, combined with the previous observations, with the existing literature and integrated with information from the crustal structure beneath Los Humeros caldera, therefore permit us to discard the "standard model" of the huge voluminous chamber in favor of a more reliable conceptual model characterized by a polybaric magmatic plumbing system of multiple, more or less interconnected magma transport and storage layers, transient batches and ponds of different magmas, localized beneath Los Humeros nested caldera and feeding the Holocene activity of the Los Humeros volcanic complex. Our results indicate that magma transport and storage levels, beneath Los Humeros caldera, are vertically distributed across the whole crust from ca. 30 to 3 km (from the lower- to the very upper-crust) with density contrasts between different crustal layers acting as a controlling parameter for ascending or stalling magmas (e.g., Dahren et al., 2012), reflecting the buoyant magma compositions and the melt fractions (e.g., Cashman et al., 2017; Jackson et al., 2018). Moreover, it is possible to propose that each of these crust/density boundaries will determine lateral transport and grow of magma stagnation pockets (e.g., Dahren et al., 2012; Jackson et al., 2018). At depths <5km, buoyant magmas and fractionated melts (from mafic to felsic) ascending from all the lower storage zones, are stalled once more. The shallowest complex multi-storage system is interpreted as a plexus of scattered, more or less interconnected, ephemeral small-volume batches and pockets of melts, without any defined spatial distribution as ruled out by field-locations of the LHPCS studied lavas eruptive centers.

A shallow storage zone presenting magmas with heterogenous compositions (from mafic to felsic) has been already proposed by Dávila-Harris and Carrasco-Núñez (2014) to explain the eruptive history of the intra-caldera Cuicuiltic Member that was produced by the coeval eruption of compositionally contrasting unmixed magmas. However, a shallow ponding system characterized by heterogeneous composition of magmas involved beneath Los Humeros caldera is not an exceptional case. Examples of shallow heterogeneous reservoirs beneath active volcanic complexes are widely reported (e.g., Nairn et al., 1998; Kratzmann et al., 2009; Sigmarsson et al., 2011; Keiding and Sigmarsson, 2012).

Our results also agree with the work of Creon et al. (2018) where calculated fluid saturation depths derived for melt inclusions in post-caldera lavas indicate different magma-ponding levels within a range of depths

between 5 and 13 km, coupled with a possible deeper reservoir/origin (26-32 km) and a final shallow stagnation level (ca. 1.5-3.0 km).

8.5 Implications for the active geothermal systems

The geothermal activity of a volcanic complex is expected to be the result of stagnation and cooling of magmas in the shallower storage zone (e.g., Gunnarsson and Aradóttir, 2015), where classic conductive models are mainly controlled by age and volume of the magmatic system representing the heat source (Smith and Shaw, 1975; Cathles et al., 1997; Duffield and Sass, 2003; Gunnarsson and Aradóttir, 2015; Carrasco-Núñez et al., 2018).

As widely demonstrated (e.g., Smith and Shaw, 1975; Cathles et al., 1997), a very large intrusion will produce a long-lived hydrothermal/geothermal system. Many numerical models (e.g., Cathles et al., 1997) suggest that, in the most favorable conditions, a voluminous (>2000km^3) intrusion/chamber of mafic melt could be able to sustain a convective geothermal system up to 800 Ky. Opposite, very small mafic sills and dikes intrusions (<10 km^3) produce very localized thermal anomalies and could cool down to the solidus temperature in lesser than 0.1 ky (Nabelek et al., 2012), and definitively cool in ca. 1 ky (e.g. Cathles et al., 1997). Convection due to hydrothermal fluids circulation, increase the cooling rate of a magmatic intrusion (Cathles et al., 1997). Concerning Los Humeros caldera, in the shallower magmatic plexus, every LHPCS magma pocket and cryptodome (see. Urbani et al., submitted to SE) could be interpreted as a scattered and localized short-living (ca. 0.1-1 ky; Cathles et al., 1997) heat source, whereas the cooling and solidified remnants of the huge magma chamber of the caldera stage could still represent a background positive thermal anomaly.

The present geothermal activity of LHVC is characterized by a limited NNW-SSE non-homogeneous areal distribution within the Los Potreros nested caldera (e.g., Norini et al., 2015; Urbani et al., submitted mansucript). Based on (i) the young age (Upper Pleistocene-Holocene) of most of LHPCS volcanic activity, (ii) the relatively small erupted volumes of LHPCS lavas, in particular of those erupted within the Los Potreros caldera, and (iii) a shallow-crust plexus involving heterogeneous unmixed magmas, as derived by results obtained in this work, we therefore discard the hypothesis of a single, large and voluminous shallow magmatic chamber homogenously distributed beneath the caldera, in favor of a more reliable scenario characterized by a superficial plexus made of small single-charge ephemeral pockets of different magmas localized beneath Los Humeros nested caldera, very close or within the Los Humeros exploited geothermal field. In this view, within the Los Humeros caldera every LHPCS magma pocket and cryptodome (see. Urbani et al., submitted mansucript) could be interpreted as a scattered and localized short-living (ca. 0.1-1 ky; Cathles et al., 1997) heat source, whereas the cooling and solidified remnants of the huge magma chamber of the caldera stage could still represent a background positive thermal anomaly affecting the volcanic field.

Our reconstruction of the Los Humeros heat source therefore suggests the possible existence of a wide background positive thermal anomaly associated to the cooling solidified remnants of the voluminous magma chamber of the caldera stage, with juxtaposition of scattered high-frequency heat sources related to the very shallow intrusive complex constituting the superficial plexus of the LHPCS magmatic plumbing system.

In the light of our results, a revision/update of the heat source, feeding the Los Humeros geothermal system is needed to produce correct and up-to-date geothermal potential estimates of the geothermal field and to develop efficient geothermal exploration and exploitation strategies.

9.CONCLUSIONS

In this study we propose an integrated field-based petrographic-mineralogical approach to unravel the evolution and configuration of the present-day magmatic plumbing system that is feeding the post-Caldera stage activity of Los Humeros volcanic complex. The main results of this study can be summarized as follows.

- The Rayleigh fractional crystallization (RFC) models demonstrate that all LHPCS magmas, from basalts to trachytes, belong to the same line of descent and evolve through a progressive fractionation of the Pl+Cpx+Ol+Sp mineral assemblage.
- A polybaric complex transport and storage system, characterized by multiple magma levels more or less interconnected in time, has been recognized based on application of mineral-melt thermobarometry models.
- A deep mafic reservoir (ca. 30km) is identified by Pl+Ol assemblage in basalts. Intermediate magma storage systems (in the whole middle crust) are described by the progressive evolution of clinopyroxene phenocryst-compositions and a shallow magmatic stagnation system (ca. 1.5kbar, 3-5km) has been defined by crystallization of clinopyroxene microlites, aegirine clinopyroxenes in basalt, and in particular by orthopyroxene formation in most evolved melts. All cpx-bearing lavas are produced by progressive differentiation via polybaric fractional crystallization during magmas ascend through the plumbing system.
- The compositional behavior of the main phases (olivine, plagioclase, clinopyroxene, orthopyroxene), together with their preserved textures and results from FC-modelling, permits to exclude, at this stage, a magmatic feeding system dominated by magma mixing and magma replenishment, in favor of a plumbing system dominated by levels, pockets and batches of melt underwent single charge.
- The thermobarometric results obtained in this work indicate that, unlike previously believed, the present configuration of the plumbing system is vertically extensive across the entire crust with a deeper residence zone for basalts at 8 kbar (ca. 30-33 km) and a complex middle to very upper crust zone (0.5 kbar) where basalts rapidly ascend and stall prior to erupt and where smaller batches of

magma differentiate to trachyandesites and trachytes at times interconnected with the lower feeding zone.

- The main outcome for the modeling of the magmatic heat source of the geothermal system is the inadequacy of conservative conceptual models based on the classical melt-dominated, single, voluminous, long-lived magma chamber (i.e., “Standard Model”), in favor of an innovative and more realistic vision of magmatic plumbing systems made of multiple, more or less interconnected magma transport and storage layers within the crust, feeding small (ephemeral) magma pockets at shallow-crust conditions.
- The proposed model for the magmatic plumbing system at LHVC provides a new configuration of the heat source feeding the present geothermal reservoir, and therefore, must be consider it for geothermal exploration and exploitation purposes.
- Our study demonstrate that petrology represents a consistent method able to unravel the anatomy of complex magmatic plumbing system.

APPENDIX A: Analytical details

A.1 Petrography of volcanic samples

Rock magmatic fabrics, textures and mineral assemblages were studied on polished thin sections, using a Nikon Eclipse 50iPol polarized light microscope (PLM) equipped with Nikon Ds-Fi2 CCD camera (Nikon, Tokyo, Japan) and Nikon Nis-Elements software (Ver4.30.01), at Laboratorio di Microtettonica, Dip. Science, Università Roma Tre (Roma, Italia). Mineral abbreviations follow Whitney and Evans (2010).

A.2 Bulk major element geochemistry

After washing in distilled water, samples were grounded in an agate mill, pre-contaminated with an aliquot of sample. Whole-rock major element concentrations (4 samples) were measured at the Activation Laboratories (Ontario, Canada), through ion coupled plasma (ICP)- optical emission (OE). For major elements the uncertainty (1 sigma) is estimated better than 2% for values higher than 5 wt %, and better than 5% in the range 0.1-5 wt %. Additional samples (9) were analyzed by X-ray fluorescence (XRF) using a ZSX Primus II (Rigaku Co., Japan) at Nagoya University, Japan. Loss on ignition (LOI) was measured from the sample powder weight in a quartz glass beaker in the oven at 950°C for five hours. XRF-analyses were carried out following the procedure presented in Azizi et al., (2015; 2018a; 2018b). For major elements the uncertainty (1 sigma) is estimated better than 1% for values higher than 10 wt %, and better than 5% in the range 0.1-10 wt %.

A.3 Mineral chemistry

Polished thin sections (13 samples) selected for petrography investigations, were then studied for mineral chemistry and ca. 2400 analyses of mineral phases were obtained with a Cameca SX100 electron microprobe (EMP) at the Institut für Anorganische Chemie, Universität Stuttgart. Operating conditions were 15 kV and 10 to 15 nA, counting times of 20 s both for peak and background. Compositions were determined relative to natural and synthetic standards. Spot sizes were 1-10 µm depending on the phases analyzed. For major elements the uncertainty (1 sigma) is estimated better than 2% for SiO_2 content, and better than 1% for the other measured elements. Back Scattered Electron (BSE) imaging was obtained by using the same electron microprobe with operating conditions of 15 kV, 50 nA. Mineral structural formulae of feldspar, olivine and spinel were calculated through the software CalcMin_32 (Brandelik, 2009). Mineral structural formulae of orthopyroxene were calculated following Putirka et al. (1996) and Putirka (2008). Clinopyroxene formula has been calculated following procedures reported in Putirka et al. (1996), Putirka (2008), Masotta et al. (2013). Clinopyroxenes were then classified integrating the Wo-En-Fs scheme (Morimoto, 1989) and J vs. Q scheme (Morimoto, 1988, 1989) with J= 2Na apfu and Q= ($Ca+Mg+Fe^{2+}$) apfu. Aegirine (XAeg) component correction, for Na-rich Cpx (Aegirine-Augite series), followed the scheme (XAeg= Na apfu if Na < $Fe^{3+\,Tot}$, XAeg= $Fe^{3+\,Tot}$ apfu if Na > Fe^{3+Tot}) proposed by Putirka et al. (1996), Putirka (2008) and based on Fe^{2+} - Fe^{3+} correction of Lindsley (1983).

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SUPPLEMENTARY MATERIALS

Supplementary Tables S1: Feldspar, EMPA complete dataset.

Supplementary Table S2: Clinopyroxene, EMPA complete dataset.

Supplementary Table S3: Olivine, EMPA complete dataset.

Supplementary Table S4: Orthopyroxene, EMPA complete dataset.

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

Supplementary Table S6: Major-Elements Mass-Balance Models.

FIGURES

Figure 1

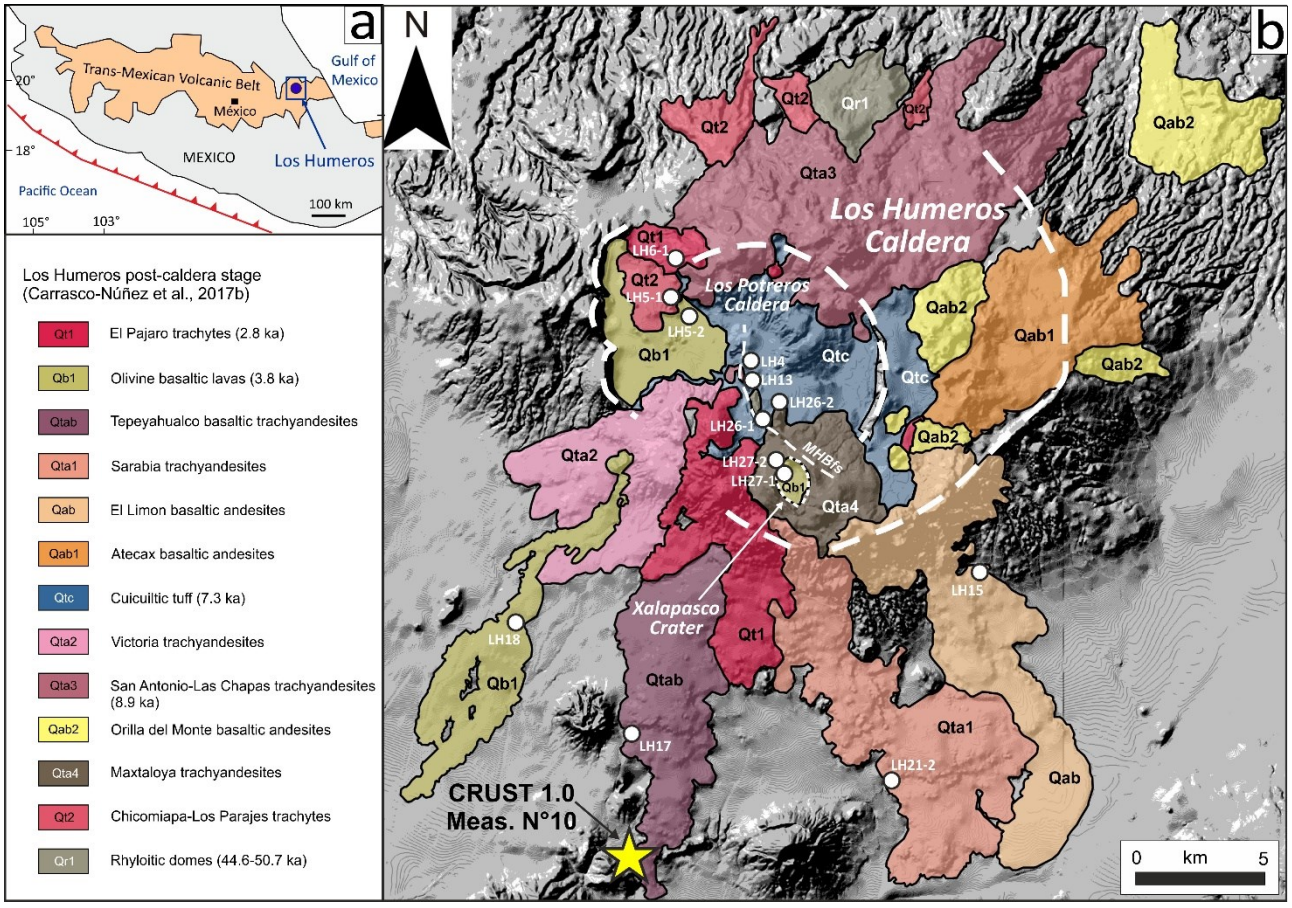


Figure-1. Geological Context. (a) The Los Humeros volcanic complex (LHVC, blue dot) with respect to the Trans-Mexican Volcanic Belt (TMVB). (b) Shaded relief image obtained from 15 m resolution digital elevation model (DEM) of the LHVC. Volcanic products of the Los Humeros post-caldera stage are redrawn from Carrasco-Núñez et al. (2017b). The description of the volcanic units, their names and abbreviations follow Carrasco et al. (2017b). The map shows location (white dots) and volcanological significance of the samples used in this study. The yellow star indicates the locality of the measure N°10 of the Crust 1.0 global model (Dziewonski and Anderson, 1981; Davies, 2013).

Figure 2

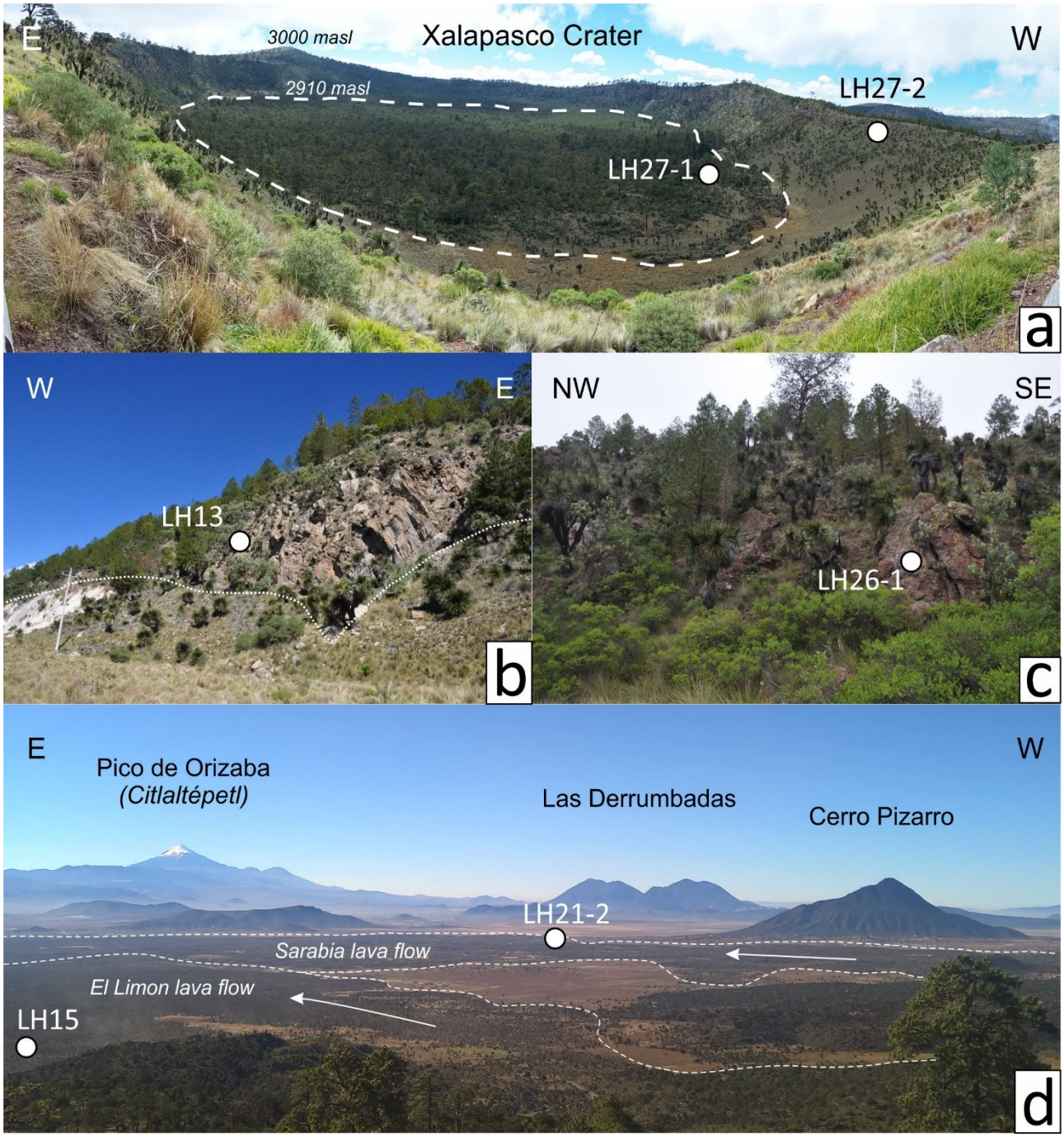


Figure-2. Field photographs of LHPCS volcanic products. (a) E-W panoramic view of Xalapasco crater; the white dashed line indicates the limit of Cpx-bearing Ol-basalts lavas filling the crater. (b) Intra-caldera trachyandesitic lavas outcropping at Los Potreros, south to Los Humeros town. (c) Trachyandesitic lava-dome outcropping inside Los Potreros caldera, north to Xalapasco crater. (d) E-W panoramic view from the SE Los Humeros caldera rim. With dashed lines are indicated the two major trachyandesitic lava flows of "El Limón" and "Sarabia". Pico de Orizaba, Las Derrumbadas and Cerro Pizarro volcanoes are also indicated. White dots indicate sampling localities.

Figure 3

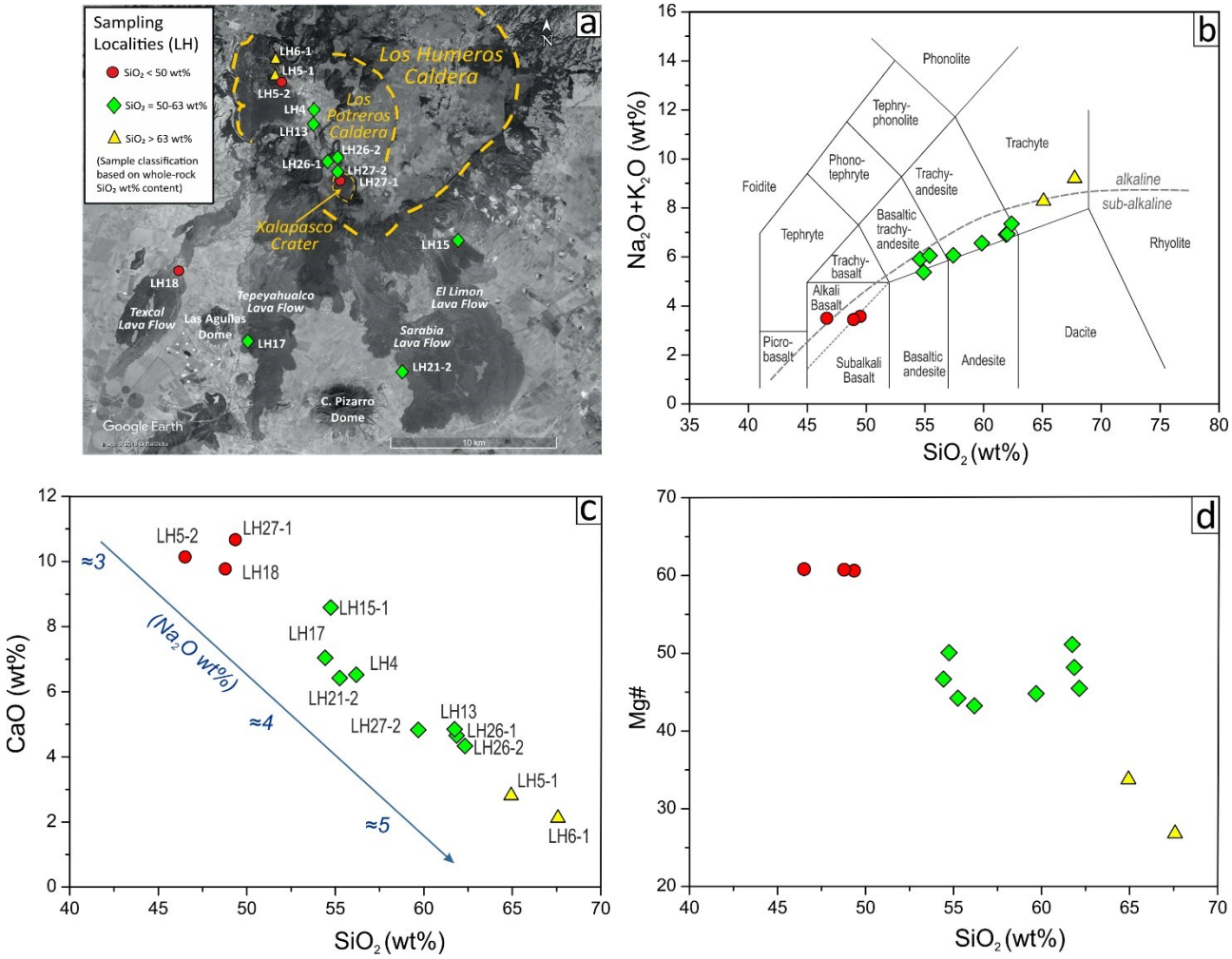


Figure-3. (a) Satellite image of the LHVC (Image Landsat from Google Earth Pro, 2018 Digital Globe; courtesy of Google) with localization of samples selected for the application of Rayleigh Fractional Crystallization model and for thermobarometry models. (b) Total alkali versus silica (TAS) diagram (Le Maitre et al., 2002). (c-d) Major elements selected Harker diagrams for LHPCS studied lavas. The different symbols (circle for basalt, diamond for trachyandesite and triangle for trachyte) represent the graphic code that will be used coherently along the manuscript.

Figure 4

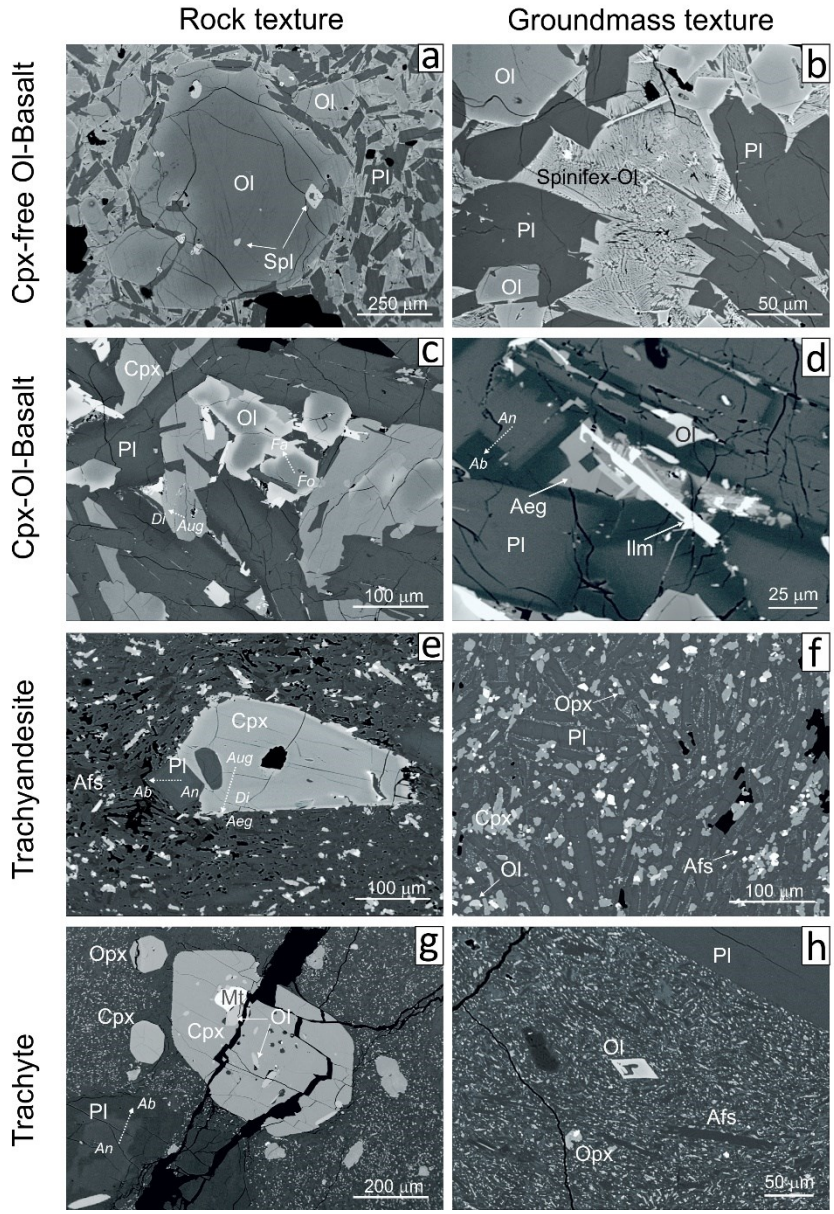


Figure-4. Microtextures and fabrics of the LHPCS lavas. (a) Back-scattered electrons (BSE) image of the Cpx-free Ol-basalt fabric, dominated by euhedral unzoned homogeneous Pl+Ol, with major olivine phenocryst characterized by Cr-Spl inclusions. (b) BSE image of Cpx-free Ol-basalt groundmass highlighting the spinifex to skeletal and dendritic crystallization of olivine, associated to the swallow-tailed morphology of plagioclase. (c) BSE image of Cpx-bearing Ol-basalt. Normal monotonous zoning at rim is observed for all the main mineral phases (Pl+Ol+Cpx). (d) BSE image of Cpx-bearing Ol-basalt groundmass characterized by albitic plagioclase, aegirine-pyroxene, Fe-rich olivine and ilmenite. (e-f) BSE images of trachyandesites. It is possible to observe a microcrystalline groundmass where major phenocrysts of Cpx and Pl are dispersed. (g-h) BSE images of trachytes, characterized by a microcrystalline groundmass and Pl+Cpx+Opx phenocryst. Plagioclase phenocrysts show normal monotonous to normal step zoning. Major Cpx phenocrysts present inclusion of Ol+Mt.

Figure 5

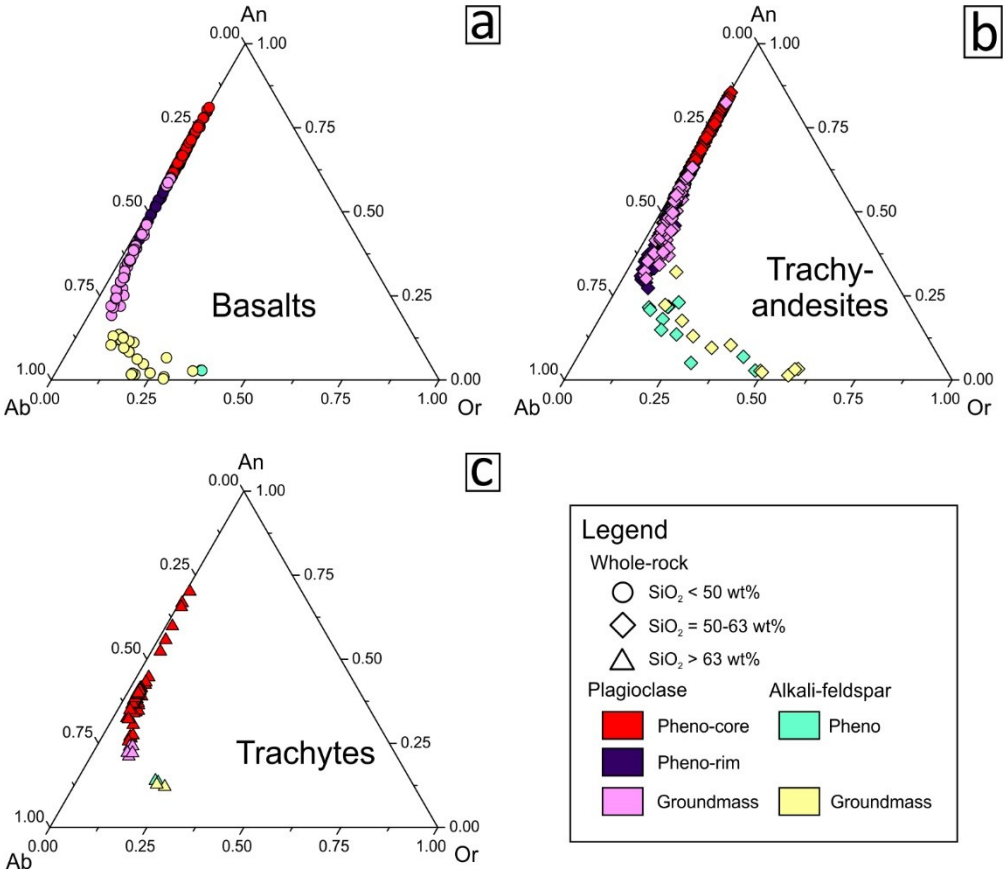


Figure-5. An-Ab-Or diagrams showing the composition of feldspar in (a) basalts (circles), (b) trachyandesites (diamonds) and (c) trachytes (triangles) of LHPCS lavas.

Figure 6

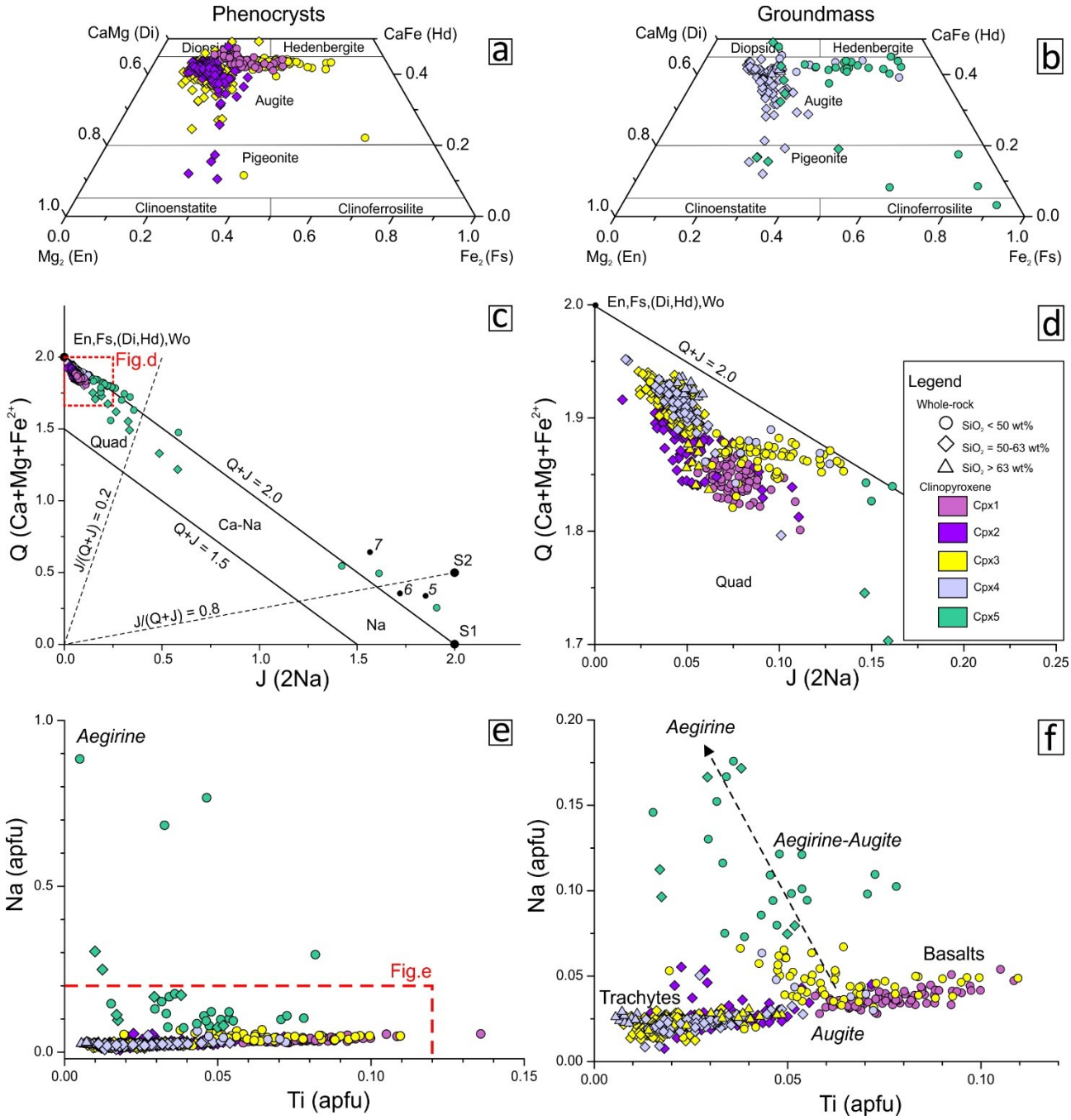


Figure-6. Di-Hd-En-Fs, Q-J and Ti vs. Na diagrams showing the composition of clinopyroxenes in LHPCS lavas. Symbol shapes follow Fig. 3. (a) Di-Hd-En-Fs diagram for clinopyroxene phenocrysts (Cpx1, Cpx2, Cpx3). (b) Di-Hd-En-Fs diagram for clinopyroxene microlites (Cpx4) and Na-clinopyroxenes (Cpx5). (c) Q-J diagram for pyroxenes with indication of endmembers (Morimoto, 1989). (d) Enlargement of area indicated in (c). (e) Ti vs. Na (apfu) diagram illustrating the compositional differences between clinopyroxenes. (f) Enlargement of area indicated in (e), showing the main Augite trend characterizing the evolution from basalts to trachytes and the divergent trend of Aegirine-Augite and Aegirine series.

Figure 7

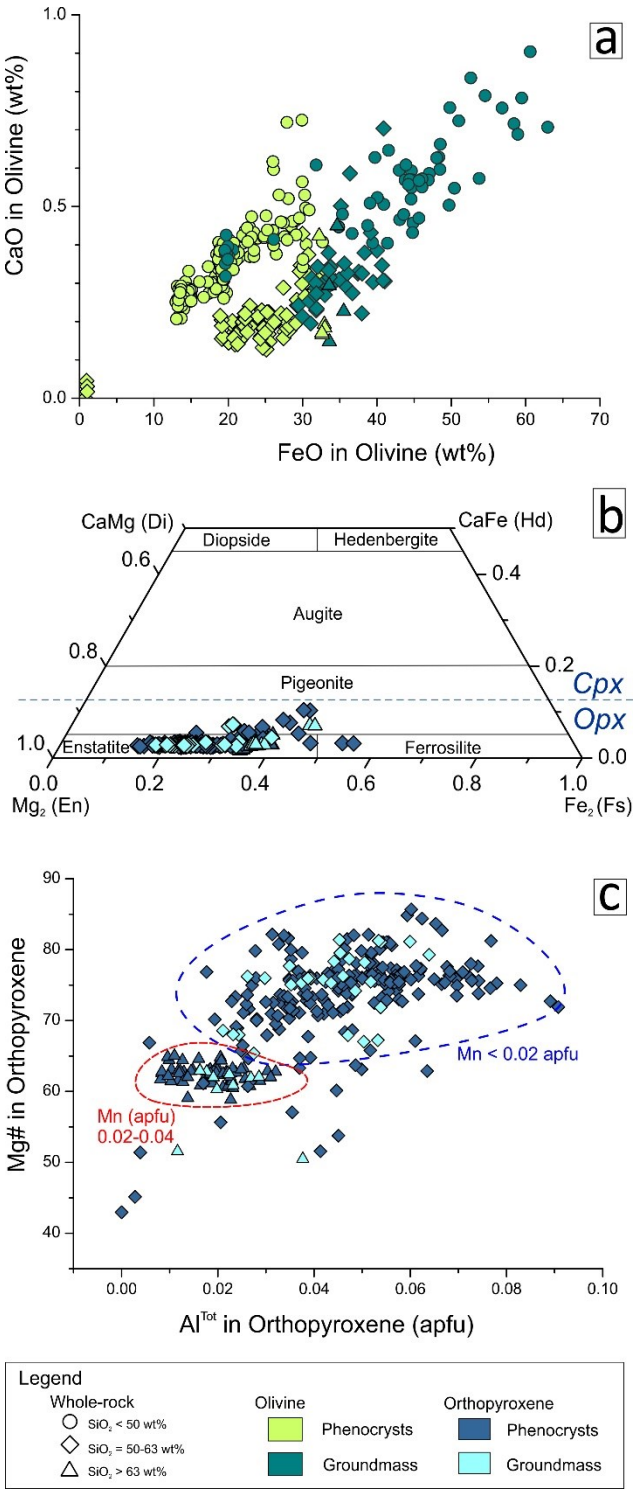


Figure-7. (a) CaO vs. FeO diagram showing the composition of olivine in LHPCS lavas. (b) Di-Hd-En-Fs diagram showing the orthopyroxene chemistry in LHPCS studied lavas. (c) Al vs Mg# diagram showing the main compositional differences between orthopyroxene populations from trachytes and trachyandesites. Mn (apfu) contents are also reported for the two populations.

Figure 8

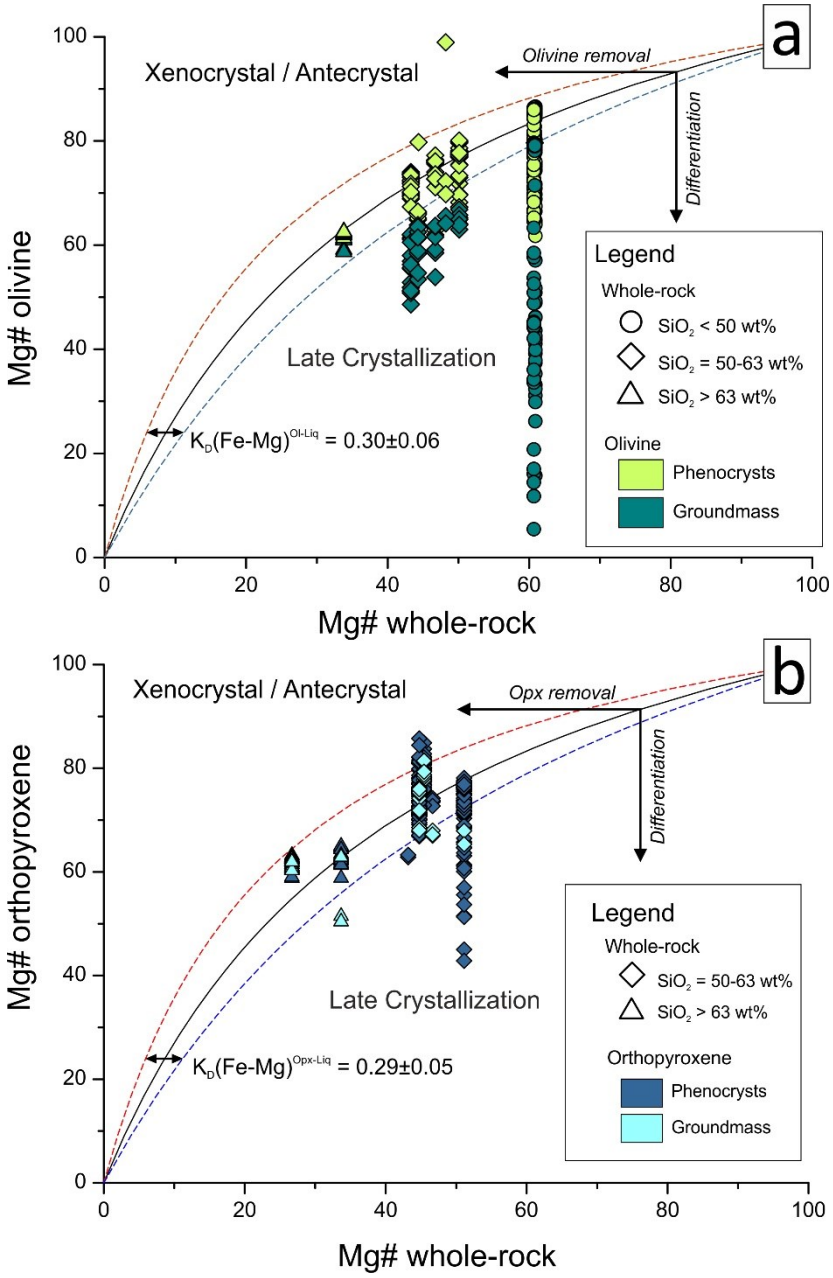
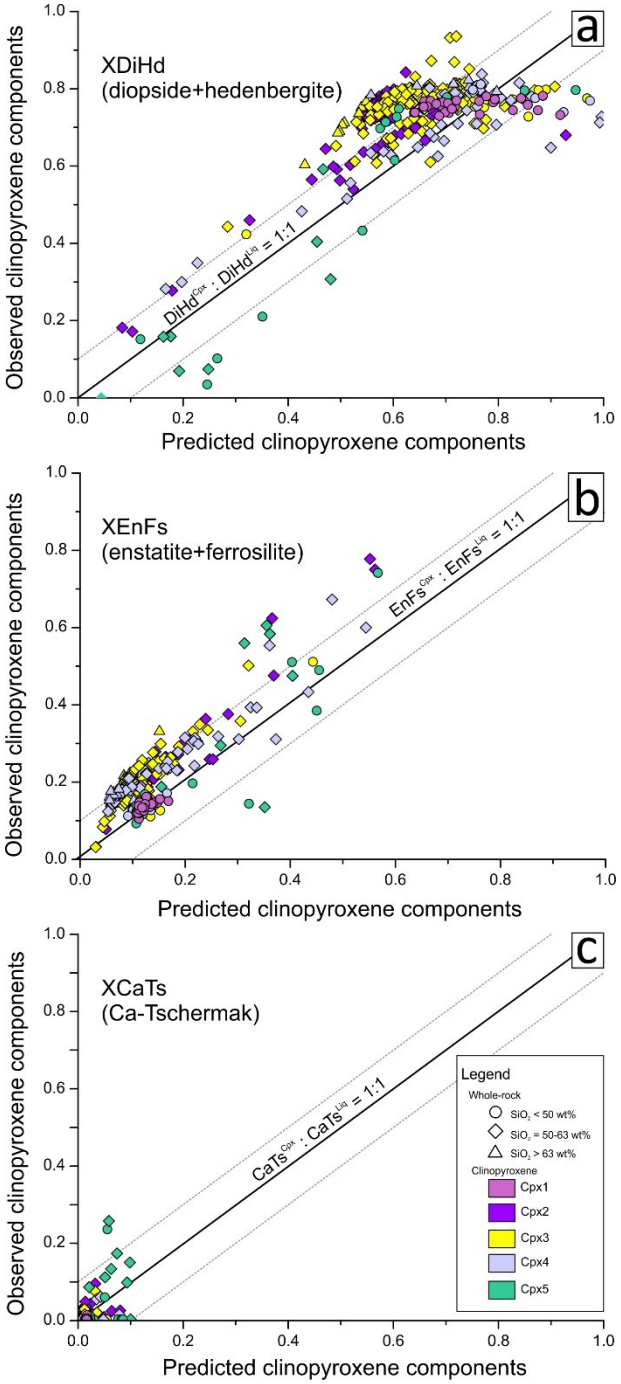


Figure-8. Rhodes diagrams showing the results of test of equilibrium liquid and olivine (a) and orthopyroxene (b). The partitioning of Fe-Mg between mineral and liquid (Fe-Mg exchange coefficient) or $K_D^{min\text{-}liq}$(Fe-Mg) is shown (black lines). The accepted range of equilibrium constant values for both figures (a) and (b) is indicated by dashed lines. $K_D^{min\text{-}liq}$(Fe-Mg) values are from Putirka (2008). Nominal melt compositions are selected from whole-rock analyses. Vectors of olivine and orthopyroxene removal from melt and closed system differentiation are redrawn after Putirka (2008 and references therein). Fields of Xenocrystal/Antecrystals and Late Crystallization are also indicated. Symbols and colors refer to Fig. 7.

Figure 9



Figures-9. Clinopyroxene-melt equilibrium tests: (a) DiHd: diopside-hedenbergite, (b) EnFs: enstatite-ferrosilite, and (c) CaTs: Ca-Tschermak components. Equilibrium associated with observed components in pyroxenes are paired with predicted components in respective hosting-melts. The accepted range of equilibrium is indicated in each figure by dashed lines. Nominal melt compositions for clinopyroxene are selected from whole-rock analyses. Symbols and colors refer to Fig. 6.

Figure 10

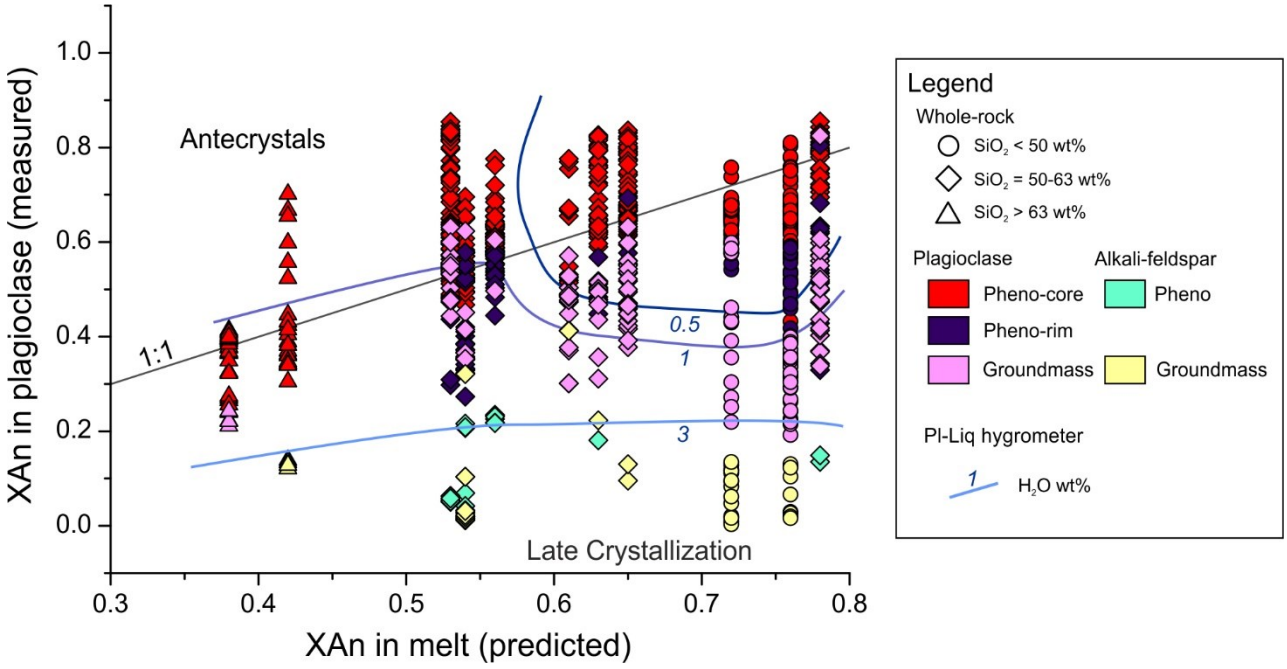


Figure-10. Plagioclase-melt equilibrium test. Equilibrium associated with anorthite (XAn) component in plagioclase are paired with predicted anorthite in melt. Nominal melt compositions for plagioclase are selected from whole-rock analyses. Calculated water concentrations using plagioclase-melt hygrometer (Putirka, 2008) are reported in diagrams with isolines (graded blue lines). Symbols and colors refer to Fig. 5.

Figure 11

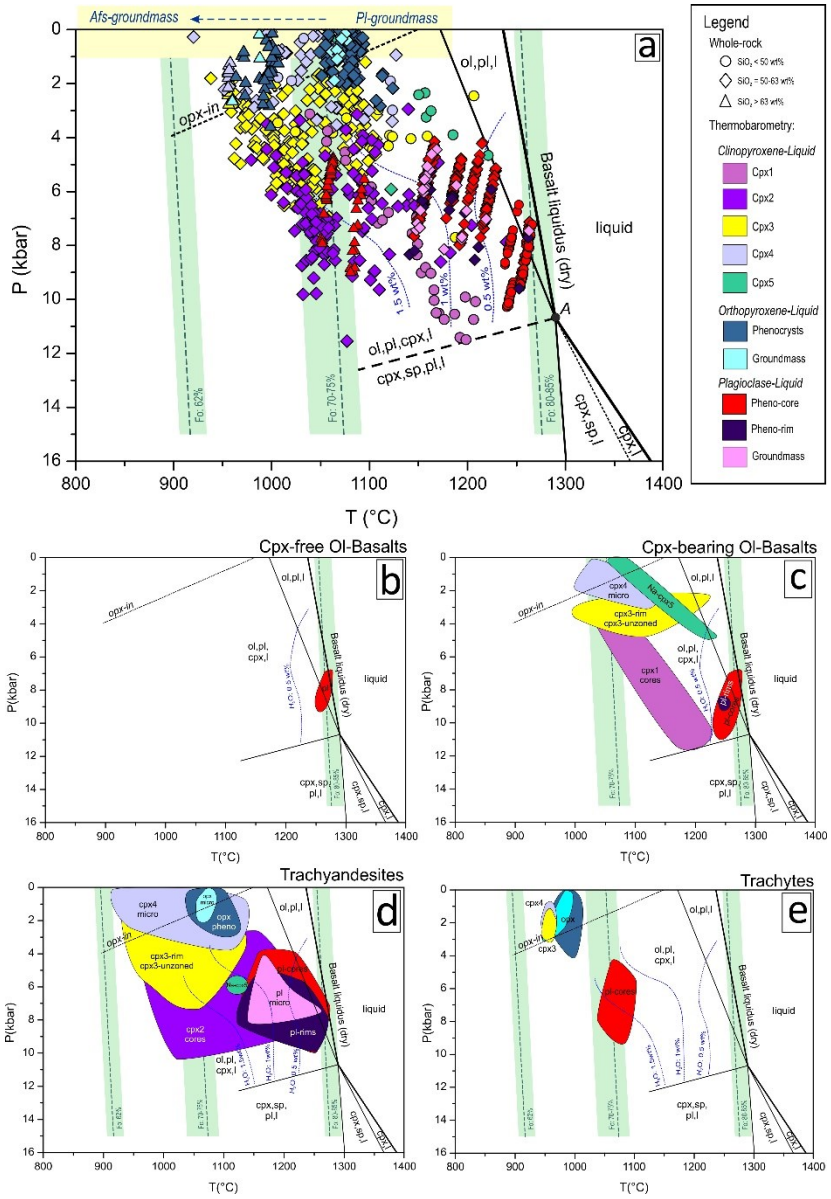


Figure-11. Thermobarometric estimates; a) A summary of the results obtained from thermobarometry models applied to Los Humeros post-caldera stage lavas. Symbols refer to whole-rock chemistry compositions, whereas colors of different phases refer to mineral chemistry diagrams. Green-shaded field shows the results of olivine-liquid thermometry. Blue dashed isolines represent the results of plagioclase-melt hygrometer. Yellow-shaded field indicates pressure-temperature domain of crystallization of feldspars in groundmass. Basalt liquidus curve, ol+cpx+ol+sp+l stability fields and point "A" (basalt liquidus in equilibrium with mantle peridotite mineral assemblage of ol+cpx) are redrawn after Grove (2000). Opx-in stability curve is redrawn after Wallace and Anderson (2000). Schematized results are presented separately for b) cpx-free ol-basalt; c) cpx-bearing ol-basalts; d) trachyandesites; and e) trachytes.

Figure 12

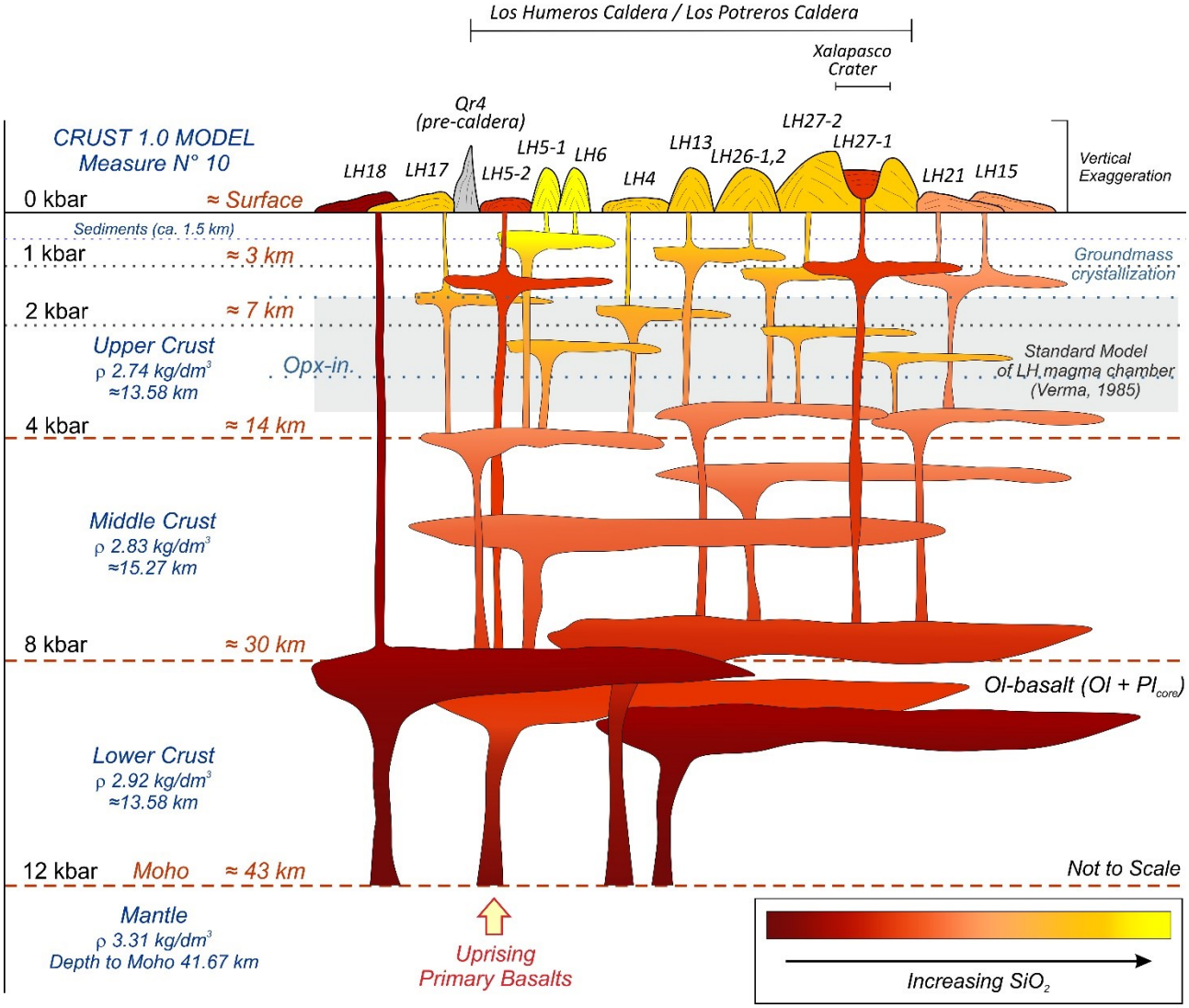


Figure-12. Schematic representation (not to scale) of the magmatic plumbing system feeding LHPCS activity, beneath Los Humeros caldera as derived by pressure-temperature estimates obtained from mineral-liquid thermobarometry models. The conceptual model is integrated with the crustal structure of the study area as derived by the Measure N°10 of the Crust 1.0 global Model (Davies, 2013). Grey shaded field indicates the depth and thickness of the existing conceptual model of a single, huge classical magma chamber proposed by Verma (1985a, 1985b) and mainly related to the Los Humeros caldera-stage activity.

2010 **Table 1**

Table 1 - Major element bulk-rock compositions of LHPCS studied lava samples.

Rock type	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})].

2011

2012