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Multi-banded pumice in the Campo de la Piedra Pómez rhyolitic ignimbrite (Southern Puna Plateau): Pre-eruptive physical and chemical interactions between mafic and rhyolitic melts

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Abstract

The rhyolitic Campo de la Piedra Pómez ignimbrite crops out in the Southern Puna of NW Argentina and it is related to the youngest caldera-complex (Cerro Blanco caldera complex) of the Central Andes (73 - 4 kyr). The presence of rhyolitic pumice and mafic enclaves with different compositional and textural features, which variability can be observed within a single juvenile clast (multiple-banded pumice), characterized these deposits. The enclaves are associated with hybrid (trachydacitic) pumice and sporadic remnants of rhyolitic material included in the trachydacite. To unravel the possible role of the mafic recharge as eruption trigger, the occurrence of mixing events and the mechanisms of enclave formation, we studied the enclaves and silicic pumice material (petrography, whole rock analyses, mineral and glass chemistry) to decipher the magmatic interaction between the host rhyolitic melt and the enclave-forming magmas. Results allowed recognizing two main mafic recharge events. During the first episode, the mixing of the rhyolite with the injecting magma generated sporadic dacitic products. Mixing was favored by the relatively high temperature of both the injecting magma and the rhyolitic melt, as revealed by clinopyroxene-liquid, plagioclase-liquid and two-pyroxene geothermometers (≥ 875 °C). The second mafic recharge event involved magma that remained confined at the bottom of the
reservoir and crystallized with differential cooling rates. At the interface with the silicic host, the magma generated sub-millimetric mineral assemblage in which amphibole has normally zoned rims. Differently, within the body of the mafic intrusion, crystallization proceeded with a lower undercooling degree, generating a coarser crystalline assemblage in which amphibole crystals do not display zoning. The convergence of different thermobarometric models (applied to the rhyolite, trachydacite, and enclaves) suggests that these magmas interacted at a crustal depth of ca. 2.7 Kbar, here interpreted as the base of the Campo de la Piedra Pómez rhyolitic reservoir (~ 10 Km b.s.l.). A time lapse occurred between the last mafic recharge and the eruptive events, where the felsic magma cooled down to ~ 800 °C and the amphibole re-equilibration took place.

**Key words:** mafic recharge, magma mixing, quenching textures, amphibole zoning, thermobarometry

### 1 Introduction

Mafic enclaves are typical products of arc-related volcanic rocks of intermediate to rhyolitic compositions (Heiken and Eichelberger, 1980; Bacon, 1986; Murphy et al., 1998; Mortazavi and Sparks, 2004). Their study helps to disclose different aspects of volcanic systems, from the role of mafic recharge as eruption trigger (Pallister et al., 1992; Murphy et al., 1998, 2000; Streck and Grunder, 1999; Scruggs and Putirka, 2018) to the mechanisms of magma interaction (Bacon, 1986; Clynne, 1999; Coombs et al., 2003; Browne et al., 2005; Martin et al., 2006; Morgavi et al., 2013, 2016; Plail et al., 2014, 2018; Hernando et al., 2016). Specifically, the textural characteristics of the enclaves (shape, groundmass texture, crystallinity, vesiculation), provide information about the thermal history of the enclave-forming magma/s, which can be recorded in the morphology of groundmass crystals (from acicular to less elongated habits) and modal content (Bacon, 1986; Coombs et al., 2003; Mortazavi and Sparks, 2004; Browne et al., 2005; Martin et al., 2006; Bacon, 2011; Shea and Hammer, 2013; Plail et al., 2014, 2018). Additionally, the enclave compositional features (major element contents, mineral and glass composition), together with those of the hosting magma, could help to
disclose the occurrence of magma mingling and mixing episodes (crystal transfer, chemical hybridization) during pre- and syn-eruptive phases (Eichelberger, 1980; Bacon, 1986; Couch et al., 2001; Martin et al., 2006; Armosio, 2010; Hernando et al., 2016).

The occurrence of mafic recharge has been suggested for the rhyolitic Campo de la Piedra Pómez Ignimbrite (CPPI) eruption (Báez et al., 2015, 2020a), which is part of the youngest (~73 – 4 myr) calderic system of Argentinian Central Andes, the Cerro Blanco Volcanic Complex (CBVC, Armosio et al., 2005; Montero-López et al., 2010, Báez et al., 2015, 2020a). The presence within the ignimbrite of mafic enclaves, which form multi-banded pumice fragments of different colors, textures, and compositions (alternation of basaltic trachyandesite, trachydacite and rhyolite), provides an interesting opportunity to investigate the consequences of mafic injections into this rhyolitic system of the Argentinian Puna plateau, both in terms of magma mixing occurrence and possible recharge-induced eruption trigger. Thus, we investigated the textural and petrological features (crystal contents and textures, whole-rock analyses, mineral and glass compositions) of both mafic enclaves and rhyolitic pumices from the CPPI. We then applied a suite of thermobarometric models based on (i) amphibole composition (Ridolfi and Renzulli, 2012); (ii) mineral-liquid equilibrium such as olivine-liquid (Putirka et al., 2007; Putirka, 2008), clinopyroxene-liquid (Putirka, 2008), orthopyroxene-liquid (Putirka, 2008) and plagioclase-liquid (Putirka, 2003, 2005, 2008) models; (iii) mineral-mineral equilibrium such as clinopyroxene-orthopyroxene (Putirka, 2008) and plagioclase-alkali feldspar (Putirka, 2008) models; and (iv) zircon-saturation (Watson and Harrison, 1983) model. The purpose of this work is (i) to provide an interpretation for the observed mineral disequilibrium assemblages and textures, (ii) to unravel the occurrence of hybridization (chemical mixing) between the enclave-forming magma/s and the rhyolitic host, (iii) to reconstruct the thermal history of the different magmas, defining the mechanisms of genesis of the enclave types, iv) to constrain the physical conditions of the magmas that interacted in the Campo de la Piedra Pómez magmatic system. Finally, the possible temporal
coincidence between the last injection of mafic magma and the beginning of the Plinian eruption is discussed.

2 Geological background

Central Andes is one of the most important volcanic zones on Earth, where Cenozoic volcanism is generated by the subduction of the Nazca plate beneath South America (James, 1971; de Silva, 1989). The most prominent feature of the Central Volcanic Zone (CVZ; 18-27 °S; Stern, 2004) is the Altiplano-Puna plateau, an extensive zone of 3800 meters a. s. l. which has been interested during Late Miocene - Holocene by huge magmatism and intense volcanic activity (Kay and Coira, 2006; de Silva and Gosnold, 2007; Schnurr et al., 2007; Kay et al., 2010; Guzmán et al., 2014; Lucci et al., 2018). The estimated crustal thickness for this area of the plateau is between 50-80 Km (Bianchi et al., 2013; Heit et al., 2014). The CPPI crops out in the back-arc area of the Southern Puna plateau, close to the boundary between the Central Volcanic Zone and the volcanism-free flat-slab region towards the south at ~27 °S (Barazangi and Isacks, 1976, Jordan et al., 1983; Fig. 1). It is part of the Cerro Blanco Volcanic Complex (CBVC), which represent the youngest volcanic activity related to the Upper Miocene-Quaternary La Hoyada Volcanic Complex (Seggiaro et al., 2000; Montero-López et al., 2010; Báez et al., 2015; 2020b Bustos et al., 2019; Fig. 1). Volcanic activity developed in this area since Late Miocene (~9 Ma) with the emission of predominantly andesitic and dacitic products (Kay et al, 2006; Montero-López et al., 2010; Guzmán et al., 2014; Bustos et al., 2019) and associated minor rhyolites (Siebel et al., 2001; Schnurr et al., 2007). During Pleistocene-Holocene an important bimodal volcanism began, with the generation of numerous mafic centers (e.g. Viramonte et al., 1984; Kay et al., 1994; Risse et al., 2008; Maro et al., 2017a, b, c; Báez et al., 2017b; Filipovich et al., 2019; Hagg et al., 2019), and rhyolitic volcanic episodes represented by the CBVC (comprising the CPPI) and by the eruptive centers of Chascón and Cueros de Purulla (Seggiaro et al., 2000, Montero-Lopez et al., 2010, Báez et al., 2015; 2017a; 2020b; Fig. 1). The CBVC is a nested-caldera system formed by two plinian
events, the oldest CPPI (~73 kyr) and the Holocene Cerro Blanco Ignimbrites (~ 4 kyr) and lava domes. The monogenetic mafic volcanoes in the study area surround the CPPI to the west, east and north, but are not present within the immediate proximity of the ignimbrite outcrops (Risse et al., 2008; Maro et al., 2017a,b,c; Filipovich et al., 2019; Haag et al., 2019; Fig. 1).

Pre-Ordovician and Ordovician metamorphic rocks compose the basement of the area, together with volcanic and volcanoclastic units (Seggiaro, 2000; Lucassen and Becchio, 2003; Suzaño et al., 2014). Pre-Ordovician rocks crop out to the southeast of the study area, while Ordovician basement is present to the west and is composed by metamorphic, sedimentary and volcanic units intruded by basic and ultrabasic rocks (Seggiaro, 2000; Lucassen and Becchio, 2003; Suzaño et al., 2014). At upper stratigraphical levels, basement is composed of turbiditic sequences (Aceñolaza et al., 1976), and of Permian and Eocene continental sedimentary rocks (Fernández Seveso et al., 1991; Turner, 1961).

Báez and coworkers (2015, 2020a) described in detail the architecture of the CPPI and its facies, and defined two eruptive events (CPPI Phase I and Phase II; Fig. 2a), with a total estimated volume of ca. 35 Km$^3$ (DRE). Both phases are composed predominantly by rhyolitic pumice and differ in the composition and abundance of the lithic component. Phase II is characterized by a slightly less evolved rhyolitic pumice population and by greater abundance of mafic material (banded pumice and sparse enclaves) than Phase I deposits, in which mafic material is sporadic (see Section 4.1 for major details).
Figure 1. Schematic map of the CPPI outcrops and its surroundings. Upper-left inset indicates the position of the study area within the Central Volcanic Zone of the Andean chain (black arrow). The inferred CPPI caldera border is from Báez et al. (2020a).

3 Analytical methods
During the fieldwork carried out in December 2017, an extensive sampling of the distinct juvenile clasts from proximal and distal ignimbrite facies of both eruptive Phases I and II (Figs. 1) was developed. Whole-rock analyses (n= 20) were performed on selected preserved samples unaffected by weathering or alteration. They were reduced in a jaw crusher, fine-powdered in a Herzog mill with tungsten carbide bowl and dried at 105 °C for 24 h in an electric oven. Major elements content determinations (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) were carried out at the ALS Minerals Laboratory by inductively coupled plasma mass spectrometry (ICP-MS) following a Lithium metaborate/tetraborate fusion and nitric acid digestion. Additional information about detection limits and methodology are available on www.alsglobal.com. Whole rock analyses were normalized to a 100 % volatile-free basis, and Fe contents are expressed as total FeO. Petrographic study and mineral point counting (about 800 point each thin section) were made on 20 thin polished section at the National University of Salta (UNSa, Argentina), which were then selected (n = 8) for microprobe analyses. These were performed with a Jeol JXA-8230 electron microprobe at the LAMARX (Laboratorio de Microscopía Electrónica y Análisis por Rayos X) at the National University of Córdoba (UNC, Argentina). Measurements include Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, F, Cl. Current and voltage used were 10 nA and 20 kV respectively, with counting times of 20 s for silicates, using natural and synthetic materials as standard and a beam size of 10 - 5 microns for minerals and glass, respectively. F and Na were analyzed first to reduce the loss during measurement. Glass analyses were normalized to 100 % before the interpretation of the data.

4 Results

4.1. CPPI pumice and enclave description

The presence within the CPPI of different juvenile clasts (pumice and enclaves) and their main petrographic features were described by Báez et al. (2015). A white to light grey, poorly crystalline
vesiculated pumice (WP = white pumice) displays rhyolitic composition and represents the main constituent of both CPPI phase I and II (~ 90 %, Fig. 2a, b). Deposits of Phase I contain small amounts of a dark-grey to black microcrystalline sub-rounded enclave (BE = black enclave) which occur with low abundance (< 1 %) as crenulated inclusions within WP and as isolated clasts in the ignimbrite (Fig. 2c). In addition to WP, deposits of eruptive Phase II contain a vesiculated beige pumice (BP = beige pumice) which is associated with texturally different mafic enclaves that alternate forming multiple-banded pumice clasts (up to 60 cm; Fig. 2d, e). Among these bands (i.e., the enclaves), we recognized and described three different mafic types characterized by peculiar colors and textures. The first type is a dark-grey to black enclave equivalent to BE of CPPI phase I (we also refer to these products as BE). It forms partially dismembered layers and pillow-like millimetric blobs in the banded pumice clasts and, to a lesser extent, within WP (Fig. 2f-h). The second and third types constitute centimetric to decimetric brown layers in banded pumice and frequently are in contact with each other (Fig. 2d-g). On the basis of crystal size, we refer to these two enclave types as a coarse brown enclave (CBE) and a fine brown enclave (FBE). CBE is more abundant than FBE (~ 5 Vol % and ~ 1 Vol %, respectively) and contains, sparsely, dark crystal-rich inclusions composed of millimetric biotite + amphibole crystals and vesiculated glass (Fig. 2 h). Some multi-banded pumiceous clasts exhibit the presence of all enclave and pumice types (Fig. 2e, g), which frequently are intensely intermingled (Fig. 2 h). Commonly, beige pumice (BP) contains amygdale-like inclusions of WP blobs (Fig. 2 g).
Figure 2. a) Outcrop of the CPPI facies in which the division between the two volcanic phases (I and II) is indicated (red line). b) Detail of a CPPI phase I outcrop, in which sparse WP clasts (black outline) and lithic fragments from the Miocene Rosada Ignimbrite (Báez et al., 2015; LC; red outline) can be observed. c) WP clasts containing crenulated BE pillow-like blobs (from CPPI Phase I). d) Detail of the proximal CPPI facies of Phase II with banded pumice (CBE + FBE + BP; see text for explanations) and sparse WP clasts. e) Decimetric multiple-banded pumice clast collected in proximal CPPI facies of phase II. f) Multiple-banded pumice clast in which all the juvenile types can be observed. g) Detail of figure 2f in which partially dismembered layers of BE (yellow outline), an amygdale-like WP inclusion and the alternation of FBE, CBE and BP (black outline) can be observed. h) Detail of a crystal-rich inclusion within CBE (red outline); intense intermingling among FBE, CBE, BP and BE can be observed.

4.2. Petrography

We summarize in this section the principal petrographic features of the CPPI pumice and enclave types. Mineral name abbreviations are according to Whitney and Evans (2010), and mineral modal calculations were calculated excluding the glass and vesicles percentages (Table 1).

Table 1

4.2.1. White pumice (WP)

WP is a porphyritic poorly crystalline rhyolite, with a simple phenocrysts assemblage composed of Pl (30-60 %) + Kfs (20-55 %) + Bt (5-20 %) + Qz (~0-10%) + Opq (~5 %) + Cpx (~ 1 %) + accessory Ap + Zrn, immersed in a vesiculated holohyaline glass. Some pumice display a low porphyritic index (P.I. < 5 %) and high crystal fragmentation degree, with micrometric-sized phenocryst fragments of feldspars and quartz plus minor biotite (~0.2-0.4 mm; Fig. 3a). Most WP specimens exhibit larger and unbroken phenocryst populations (1-2 mm) and higher crystal contents (P.I = 15-20%; Fig. 3b). Feldspars are euhedral and occur as isolated grains and as minor glomerophyric aggregates. Some plagioclase phenocrysts exhibit optical low-banded oscillatory zoning, occasionally a slight patchy character, and lack evident resorption surfaces (e.g. Streck, 2008) when observed at back-scattered electron images (BSE; Fig. 3c, d), while other grains are homogeneous. Quartz is present as partially resorbed subehdral grains with millimetric dimensions (up to 1.5 mm; Fig. 3b). Reddish biotite grains are laminar (≤ 1 mm length) and euhedral (Fig. 3b, d, f), as well as clinopyroxene crystals (1-2 mm), which is hosting biotite, oxides and apatite inclusions (Fig. 3e, f). Oxides (magnetite and ilmenite) are present
as rounded subhedral grains (≤ 0.5 mm), and display, when observed with BSE images, slight
development of exsolution lamellae or homogeneous texture (Fig. 3e, f). Accessory apatite (<0.5%)
normally occurs as inclusions in plagioclase and clinopyroxene (~ 150 micron; Fig. 3e). Rare
orthopyroxene and olivine grains occur within WP (<< 1 %), displaying narrow reaction rims formed
by amphibole microcrystals or by an undefined opaque rim.
Figure 3. Petrographic features of rhyolitic WP. a) Microphotograph (cross-polarized lights) of a WP sample with low P.I. and high crystal fragmentation degree; yellow outline indicates vesiculation. b) Microphotograph (cross-polarized lights) of a WP sample with higher Porphyritic Index. c) BSE image of plagioclase phenocryst with oscillatory texture. d) BSE image of oscillatory-textured plagioclase with associated biotite phenocrysts. e) BSE image of euhedral clinopyroxene phenocrysts.
showing opaque minerals and apatite inclusions. f) BSE image of euhedral clinopyroxene phenocrysts with opaque (magnetite + ilmenite) minerals and biotite inclusions.

4.2.2. Beige pumice (BP)

Beige pumice shows porphyritic texture and a holohyaline vesiculated glass, displaying a complex mineralogical assemblage composed of Pl (30-45 %) + Bt (~ 20 %) + Kfs (~ 10) + Amp (5-10 %) + Opx (5 %) + Opq (< 5 %) + Cpx (~ 1 %) + Ol (traces). Similarly to WP, BP displays variable P.I. (from ~10 to 20 %; Fig. 4a-d). Plagioclase crystals (0.5-1.5 mm) normally present optical oscillatory zoning or are homogeneous (Fig. 4b, h). Tabular reddish biotite grains (up to 2 mm) resemble texturally those from WP samples (Fig. 4a), as well as K-feldspar crystals (Fig. 4a, b). Clinopyroxene (normally sub-millimetric) occur with subehedral habits with narrow amphibole reaction rims (as well as olivine; Fig. 4e, f), and can form small glomerocrystic aggregates. Pyroxene grains (both Cpx and Opx) were also observed within partially dismembered microlite-rich (Amp + Pl) glassy blobs contained within BP (Fig. 4c, d). Amphibole is euhedral, millimetric in size (1-1.5 mm) and unzoned, and is frequently associated with orthopyroxene (normally present as inclusion within amphibole; Fig. 4g) and with plagioclase (Fig. 4h).
Figure 4. BP petrographic features. a) Microphotograph (parallel-polarized light) showing the association plagioclase + K-feldspar + biotite, all immersed in a holoyaline groundmass. b) Same view of (a) taken with cross-polarized light. c) Microphotograph (parallel-polarized light) of a low P.I. sample with a clinopyroxene grain rimmed by a narrow amphibole reaction rim. d) Same microphotograph of (c) taken with cross-polarized light. e) Microphotograph (parallel-polarized light) of an irregular blob of quenched glass (microlite-rich groundmass + pyroxene crystals). f) Microphotograph of the same view of (e) taken with cross-polarized light. g) BSE image of amphibole + orthopyroxene association. h) BSE image of amphibole + plagioclase association.

4.2.3. Black enclave (BE)

BE is a porphyritic rock (P.I. 15-20%, Fig. 5a) and exhibits a complex mineral assemblage consisting of Pl (30-40 %) + Cpx (~25-30 %) + Opx (10-15 %) + Ol (5 – 10 %) + Opq (< 5 %) + Amp (1 - 5 %) + accessory Kfs, Qz and Bt. The matrix is a micro-vesiculated hialopylitic glass formed by plagioclase laths and tabular to acicular amphibole microlites which, occasionally, can occur in contact with each other (50-150 micron; Fig. 5b, c). The proportion between microlites and glass is about 50-60% crystals and 40-50% glass (vesicle-free), and variation in the dimensions of the matrix minerals towards the enclave edges was not observed. Clinopyroxene and orthopyroxene occur as isolated grains or in crystal aggregates (up to n = 100 crystals; Fig. 5d) and exhibit similar textural features like sub-millimetric to millimetric dimensions (~0.5-1 mm), euhedral to sub-euhedral habits and diffuse amphibole reaction rims (Fig. 5e). Rare orthopyroxene grains reach larger dimensions (up to 3 mm) and show partially resorbed rims surrounded by amphibole microcrystals and orthopyroxene grains that are texturally similar to the phenocrysts (Fig. 5-A1 of Supplementary Material). Olivine consists of rounded crystals (~0.8-1.2 mm) always surrounded by a narrow amphibole reaction rim (Fig. 5f) or by an undefined thin opaque rim. Plagioclase exhibits variable textural and compositional features. Microlites in the matrix form about the 50% of the whole plagioclase population (Fig. 5b, c). Millimetric sub-euhedral to euhedral crystals (up to 1.3 mm; Fig. 5g), partially resorbed sub-millimetric grains (sieve-textured) with fresh overgrowth (~20-30 micron; Fig. 5i) and anhedral crystals compose the remnant 50 % of plagioclase population (Fig. 5h). Amphibole occurs as microlites in the matrix and as reaction rims (100-200 micron) around pyroxene, olivine and opaque crystals (Fig. 5b, c, e, f, l). Large amphibole phenocrysts (up to 3 mm) with inclusions of plagioclase and olivine (Fig. 5k) and rare
biotite and K-feldspar grains (< 1 mm) were sporadically observed (Fig. 5j, k, Fig. 5-A2 of Supplementary Material). Occasionally, sparse blobs of holohyaline glass containing subhedral K-feldspar grains are separated from the typical BE groundmass by a reaction rim of pyroxene microcrystals (Fig. 5j). Opaque minerals exhibit sub-millimetric dimensions (0.5-0.8 mm), subhedral to anhedral habits, and display well-developed exsolution textures when observed at BSE imaging (Fig. 5l).
Figure 5. Petrographic features of BE. a) Microphotograph (cross-polarized light) showing subhedral clinopyroxene + orthopyroxene phenocrysts rimmed by amphibole microlites and immersed in a hialopylitic glass. b) Detail microphotograph (cross-polarized light) of the quenched groundmass (Amp + Pl). c) BSE image of groundmass showing two different amphibole habits (from tabular to acicular) and plagioclase laths, all sparse in a vesiculated glass. d) Microphotograph (cross-polarized light) of a clinopyroxene + orthopyroxene glomerocryst aggregate. e) BSE image of an orthopyroxene grain rimmed by amphibole microlites. f) BSE image of a sub-rounded olivine phenocryst rimmed by amphibole microlites. g) Microphotograph (cross-polarized light) of a slightly resorbed plagioclase crystal. h) BSE image of an anhedral plagioclase grain. i) BSE image of a partially resorbed (sieve-textured) plagioclase grain with fresh overgrowth. j) Microphotograph (cross-polarized light) of K-feldspar + holocline glass with pyroxene reaction rim. k) Microphotograph (cross-polarized lights) of a large amphibole phenocryst. l) BSE image of a magnetite crystal with diffuse exsolution texture and amphibole reaction rims.
4.2.4. Fine brown enclave (FBE)

FBE exhibits an equigranular texture and a micro-vesiculated glass (Fig. 6a, b). Crystal population comprises Pl (40-50 %) + Amp (~40 %) + Bt (~10-15 %) + Opq (~5 %) + Ap (traces), with a P.I. of ~35 % and general sub-millimetric crystal dimensions (0.2-0.8 mm, rarely up to 1 mm; Fig. 6a). Amphibole occurs as subhedral to euhedral prismatic and tabular crystals which display diffuse concentric zoning pattern (BSE images) formed by darker cores and brighter rims (Fig. 6c, d). Amphibole occur mainly as isolated grains in the glass and occasionally associated with plagioclase and biotite (Fig. 6e). Plagioclase displays tabular subhédral to euhedral shapes, showing slight optical oscillatory zoning or homogeneous textures (also in BSE images, Fig. 6e). Biotite occurs as reddish-brown tabular phenocrysts with subhédral to euhedral habits, and is normally associated with the other crystalline phases (Fig. 6a, b). Magnetite are subhédral and sub-millimetric in size, and always display exsolution textures (lamellae) in BSE images (Fig. 6f). Apatite inclusions have been observed within plagioclase, amphibole and biotite phenocrysts.
Figure 6. FBE petrographic features. a) Microphotograph (cross-polarized lights) showing the texture composed of Amp + Pl + Bt + Opq phenocrysts. b) Representative BSE image of FBE texture. c) Highly contrasted BSE image of an amphibole grain. d) Highly contrasted BSE color image of an amphibole crystal. e) BSE image of an amphibole and plagioclase.
association and inclusion of amphibole within plagioclase; zoning in amphibole can be observed also with low-contrast BSE images. f) BSE image of magnetite micro-phenocrysts showing exsolution lamellae texture.

4.2.5. Coarse brown enclave (CBE)

CBE displays seriate texture and a holohyaline vesiculated glass (Fig. 7a, b), with a mineral assemblage constituted by Pl (35-40 %) + Bt (~25 %) + Amp (25 – 30 %) + Opq (5-10 %) + Ap (traces). P.I. is about 20 % and the general crystal grainsize is coarser than FBE (Fig. 7a, b). Plagioclase exhibits subehdral to euhedral tabular habits (0.5-1.5 mm) and displays both optical oscillatory and homogeneous textures. Amphibole generally is present as isolated euhedral grains (~0.3-2 mm) and, to a lesser extent, associated with the other crystalline phases (Fig. 7a-d). Core-rim zoning was not observed at BSE imaging (Fig. 7c, d). Biotite occurs as reddish crystals with millimetric tabular dimension (up to 2.5 mm). Opaque minerals are subehdral and sub-millimetric (~0.5 mm) and always exhibit exsolution texture (Fig. 7e). Apatite occur as inclusion within plagioclase, amphibole and biotite. Crystal rich inclusions (Fig. 2h) display glomero-porphyritic texture and a mineral association composed of Amp + Bt + minor Pl and Opq (P.I. ~40-60%) and a vesiculated glass (Figs. 7f, 7-A1 of Supplementary Material). Commonly, the Amp + Bt aggregates surround cores of resorbed orthopyroxene grains (Fig. 7f).
Figure 7. CBE petrographic features. a) Microphotograph (cross-polarized light) of the general texture. b) BSE image of the texture. c) BSE image of a millimetric amphibole crystal. d) High contrast BSE color image of an amphibole microphenocryst. e) BSE image of a magnetite grain. f) Microphotograph (parallel-polarized light) of a crystal-rich inclusion showing the glomerocrystic association of Amp + Bt surrounding a resorbed Opx grain. Yellow outline highlights the limit between crystal-rich inclusion and CBE.
4.3 Whole-rock, glass and mineral chemical composition

We summarize in this section the main geochemical features of pumice samples and enclaves, together with the composition of glass and mineral assemblages. The opaque mineral analyses will not be described because of the general presence of exolution lamellae textures which invalidate the obtained compositions. We provide the representative analyses in Tables 2 – 7 and the complete dataset in the supplementary material (Tab. 8A).

4.3.1. Whole-rock composition

WP is metaluminous to slightly peraluminous rhyolite to trachydacite (Fig. 8a, b). A small decrease in the SiO$_2$ content and alkalis (Na$_2$O + K$_2$O) from the lower part of the deposit (CPPI Phase I) towards the top (CPPI Phase II) has been detected (from an average value of ca. 72 to 70 wt % of SiO$_2$, and from 9 to 8 wt % of Na$_2$O + K$_2$O). WP Al$_2$O$_3$ abundance is comparable with BP and BE, and lower than FBE and CBE (Fig. 8c). Contents of TiO$_2$, FeO, MgO and CaO in WP are lower, and K$_2$O is higher than BP and all enclave types (Fig. 8d-h). WP zirconium contents are in the range of 155 – 214 ppm (Tabs. 2, 8A-1). BP displays metaluminous trachydacitic composition, and shows a slight increment in the sum of alkalis with SiO$_2$ (Fig. 8a, b). In the binary plot of TiO$_2$, FeO, MgO, CaO and K$_2$O versus SiO$_2$ contents, BP composition always plots in intermediate positions respect those of WP and the enclaves (Fig. 8c-h). BE is a basaltic trachyandesite with metaluminous affinity (Fig. 8a, b).

Among the enclaves, it displays the highest MgO and the lowest TiO$_2$ and Al$_2$O$_3$ contents (Fig. 8c-e), while FeO and CaO abundance is similar to FBE and CBE (Fig. 8f, g), which are a basaltic trachyandesites with metaluminous affinity (Fig. 8a, b) and differences in the SiO$_2$ abundance (Fig. 8a-h). In the FeO/MgO ratio versus 1/MgO diagram (whole rock), two different linear relations can be observed among BE, FBE and CBE, and BE, BP and WP facies (Fig. 8i).
4.3.2. Glass

WP glass displays high-silica, slightly peraluminous composition (Fig. 8a,b) with the lowest contents of Al₂O₃, MgO and CaO (Fig. 8c, f, g) and highest K₂O contents of the entire dataset (Fig. 8c, f, g).

The BP-glass major oxide contents display the highest variability among the analyzed samples, showing affinity with both WP and the enclave glass composition (mostly with BE and FBE analyses; Fig. 8c-i).
Glass in the enclaves is peraluminous and rhyolitic. The BE glass displays the most evolved composition (Fig. 8a), while the CBE is the least evolved and the FBE is intermediate (in terms of silica abundance). The three enclave types have similar contents of CaO (Fig. 8g), while relative differences exist in the other oxides. Al₂O₃ and MgO contents are higher in CBE than in FBE and BE (Fig. 8c, f), as well as FeO and TiO₂, for which a partial overlap exists between CBE and FBE and between CBE and BE respectively (Fig. 8d, e).

Tables 2, 3

4.3.3. Feldspars

The general range of the CPPI plagioclase composition spans from oligoclase to bytownite, being andesine and labradorite the most abundant species (Fig. 9). WP homogeneous plagioclase grains vary from oligoclase to andesine (An₂₁-₃₀; Fig. 10a), and the optically-oscillatory zoned crystals (Fig. 9b) reach more anorthitic compositions in the brighter areas (An₃₀-₅₉; Fig. 9a). Plagioclase in BP is similar to WP oscillatory-zoned grains, displaying general andesine composition (An₃₁-₄₄; Fig. 9a). BE plagioclase compositions are the most heterogeneous among the analyzed rocks, spanning from andesine to bytownite (Fig. 9c). Groundmass microlites (Fig. 4a,b) and anhedral grains (Fig. 4e) vary from andesine to bytownite (An₃₈-₈₂ and An₂₇-₈₃ respectively; Fig. 9c; Table 3, 14), the plagioclase phenocrysts (Fig. 5g) have high anorthite cores (An₇₄-₈₃) and lesser calcic rims (An₆₄-₇₇), while sieve-textured grains (Fig. 5i) vary between An₃₀-₅₁ (cores) and An₃₀-₄₇ (rims), similarly to plagioclase composition of WP and BP samples (Fig. 9a, c). FBE and CBE plagioclase are similar (An₃₈-₅₅ and An₄₁-₅₇ respectively; Fig. 9d) with the former showing general less anorthitic composition (average ~An₄₆) than the latter (~An₅₂). Core-rim variations indicate no zoning or slightly normal zoning for FBE plagioclases (average An₄₈ and An₄₇ for core and rim respectively; Fig. 9d), and normal zoning for CBE (average An₅₅ and An₄₆ for core and rim respectively; Fig. 9d).
Analyzed K-feldspar grains display homogeneous composition in all rock in which are contained (WP, BP, and BE). They are sanidine with a structural formula of $\text{Or}_{69-72}\text{Ab}_{26-29}\text{An}_{0-1}$ (Fig. 9a, c).

Figure 9. Classification of CPPI feldspars in An (anorthite) - Ab (Albite) - Or (orthoclase) ternary diagrams. a) WP and BP plagioclase composition. b) BSE image of an oscillatory-zone plagioclase phenocryst of WP; yellow numbers indicate the calculated anorthite contents. c) BE plagioclase composition. d) FBE and CBE plagioclase composition. WP and BP analyses are not divided into core and rim because most point analyses represent the oscillatory-zoned grains (Fig. 3 c-d; see text for details).

Table 4

4.3.4. Biotite
All biotite grains from pumice and enclaves plot in the annite field in the classification diagram of Clarke (1981) and in the calc-alkaline field of the classification of Abdel-Rahman (1994, Fig. 10a, b). WP, BP and BE biotite grains show similar compositions (Fig. 10a-d). They differ from FBE and CBE in terms of $\text{Al}^{\text{IV}}$ (apfu), Fe# (Fe/(Fe + Mg), and wt % of SiO$_2$, FeO and MgO (Fig. 10a-d), while Ti contents are comparable (Fig. 10c). Biotite phenocrysts from FBE and CBE slightly differ in MgO, FeO and $\text{Al}^{\text{IV}}$ contents (Fig. 10 a-d).

Figure 10. a) CPPI biotite classification of Clarke (1981); left inset showing the compositional fields. b) Biotite classification of Abdel Rahman (1994). The right inset indicates the compositional fields: CA = calcalkaline; P = peraluminous; A = alkaline. c) Ti (atom per formula unit) versus Fe# (Fe/Fe + Mg) diagram. d) Binary diagram of MgO versus SiO$_2$. Oxides are expressed as wt %.
4.3.6. Pyroxenes

WP clinopyroxene plots in the limit between augite and diopside fields (classification of Morimoto 1988) showing a more ferric character (Wo\textsubscript{46-47} En\textsubscript{37-38} Fs\textsubscript{18-20}) and lower Mg# (~0.68-0.71; Tab. 5) than clinopyroxene from BE, which display augitic composition (structural formula Wo\textsubscript{41-44} En\textsubscript{41-47} Fs\textsubscript{12-18} with one sample Wo\textsubscript{37} En\textsubscript{49} Fs\textsubscript{16}, Fig. 11a), and higher Mg# (~0.73-0.81). Within BP, clinopyroxene is also augite (n=1 analysis), and display identical structural formula of BE phenocrysts (Wo\textsubscript{43} En\textsubscript{44} Fs\textsubscript{14}) and Mg# (0.77; Tab. 5), which was predictable considering the similar textural features of BE phenocrysts and BP clinopyroxene grains (Fig. 4c-d; Fig. 5a).

All analyzed orthopyroxene grains fall in the enstatite field according to Morimoto (1988) classification (Fig. 11a). Grains within WP display similar structural formula (Wo\textsubscript{1-2} En\textsubscript{76-78} Fs\textsubscript{20-21}) and Mg# (0.78-0.79) to BE phenocrysts (Wo\textsubscript{2-3} En\textsubscript{74-79} Fs\textsubscript{17-22}; Mg# = 0.76-0.81) and large phenocrysts (Wo\textsubscript{2} En\textsubscript{78} Fs\textsubscript{19}; Mg# = 0.80). Differently, BP orthopyroxenes are more ferric in composition (Wo\textsubscript{2-3} En\textsubscript{70-74} Fs\textsubscript{22-30}) and exhibit lower Mg# (0.73-0.77) than crystals from WP and BE (Fig. 11a, b), similarly to orthopyroxene resorbed cores within CBE crystal-rich inclusions (Wo\textsubscript{3} En\textsubscript{66-70} Fs\textsubscript{26-30}; Mg# = 0.68-0.72; Figs. 7g, h; 11).

Table 5

4.3.7. Olivine

Olivine phenocrysts composition in BE (and olivine inclusion within the large amphibole phenocryst; Fig. 5k) varies from Fo\textsubscript{69-78}, and similar compositions were calculated for the olivine grains in WP and BP samples (Fo\textsubscript{75} and Fo\textsubscript{77} respectively; Table 6).
Figure 11. a) Ternary pyroxene classification of the CPPI pyroxenes from Morimoto (1988). Wo = wollastonite; En = enstatite; Fs = ferrosilite. Blu squares indicate BE orthopyroxene large phenocrysts (Fig. 5-A1 of Supplementary Material. b) graphic legend with a clinopyroxene phenocryst of WP (upper left, Fig. 3e), a clinopyroxene-orthopyroxene aggregate within BE (upper right; e.g. Fig. 5a), an orthopyroxene associated to amphibole within BP (lower left, e.g. Fig. 3g), and a resorbed orthopyroxene core surrounded by amphibole and biotite within the CBE crystal-rich inclusions (e.g. Fig. 7f).

Table 5

4.3.8. Amphibole

Amphibole cationic abundances were calculated according to the default method of Ridolfi et al. (2018), and mineral formula was determined with the Locock (2014) and Ridolfi et al. (2018) methods; only one sample (106A-C4-Anf1-ccl) needed minor correction for the formula and cationic abundances calculations. All amphibole grains belong to the W (OH, F, Cl) - dominated group, Ca subgroup (Ridolfi et al., 2018), and classify, according to Locock et al. (2014), as Ti-rich pargasite (n = 46), Ti-rich magnesio-hastingite (n = 17), rootname4 (n = 15) magnesio-hastingite (n = 9) and minor pargasite (n = 3), Ti-rich ferri-sadanagaite (n = 1), and ferri-rootname4 (n = 2). FBE amphiboles display a wider range in the cations Si, Ti, Al[IV] (apfu) and Mg# than CBE (Fig. 12a,b) with cores being more enriched in Ti and depleted in Si than rims. Mg# is rather homogeneous, with average values of 0.70 and 0.67 respectively for core and rim amphibole areas (Fig. 12a, b). CBE grains (core and rim) are more similar to FBE cores in terms of Ti, Si, Al[IV] and also in Mg# (average 0.70) than FBE rims (Fig. 12a, b).

Within BE, groundmass microlites display lower Mg# and comparable (Na+Ca)A than the corona-
forming microcrystals (Fig. 12 c), while the other parameters (Si, Ti, Al$^{IV}$) are comparable (Fig. 12a, b). Amphibole large phenocrysts (Fig. 5k) differ from BE, FBE and CBE amphiboles in having higher Mg# and lower Ti contents (Fig. 12a, b).

Figure 12. a) Binary diagram of cationic Ti (apfu) versus Si (apfu) for all the analyzed amphibole grains. b) Binary diagram showing cationic Al$^{IV}$ (apfu) versus Mg# (Mg/(Mg + Fe$^{2+}$)). c) Binary diagram showing the sum of apfu Na + Ca (A-site) versus Mg#.

Table 7

5. Thermobarometry and hygrometry

In order to define the physical conditions (T, P, H$_2$O$_{liq}$ contents) of the magmas that form the CPPI magmatic system and to disclose the possible depth at which the rhyolitic and enclave-forming magmas interacted, we realized a suite of thermobarometric calculations, following the workflow proposed by
Results from the thermobarometric modelling are then presented and discussed following a statistical approach (e.g. Calzolari et al., 2018; Lucci et al., 2020).

5.1. General considerations

We integrate a suite of mineral-liquid, mineral-mineral and single mineral thermobarometry models such as (i) olivine-liquid (Putirka, 2008), (ii) clinopyroxene-liquid (Putirka, 2008), (iii) orthopyroxene-liquid (Putirka, 2008), (iv) plagioclase-liquid (Putirka, 2005, 2008), (v) plagioclase-alkali feldspar (Putirka, 2008), (vi) clinopyroxene-orthopyroxene (Putirka, 2008), (vii) amphibole chemistry (Ridolfi and Renzulli, 2012) models. For mineral-liquid models we used both glass and bulk rock composition as input, while for the clinopyroxene-orthopyroxene thermobarometric calculations touching pairs (Fig. 8A-6) were used and combined with analyses of sparse crystals. The equilibrium plagioclase-liquid pairs used in the T, P and H2O_{liq} estimations were selected after the application of the filter model proposed by Putirka (2008): (K_D^{pl-liq}(An-Ab) = 0.1 ± 0.05 for T < 1050 °C and = 0.27 ± 0.11 for T > 1050 °C), followed by the test proposed by Namur et al. (2012), which compares the measured anorthite fraction of plagioclase and that calculated for the liquid composition. The pairs that satisfy the test are those with an An_{measured}/An_{calculated} ratio of 1.0 ± 0.1 (Fig. 13). The values of H2O_{liq} (wt % of water in the nominal melt) obtained from the plagioclase-liquid model (equation 25b of Putirka, 2008) were used as input for the clinopyroxene-liquid equations, and compared with the amphibole hygrometer of Ridolfi and Renzulli (2012). The equilibrium clinopyroxene-liquid, orthopyroxene-liquid, olivine-liquid, and two-pyroxene compositional pairs were selected through the equilibrium test proposed by Putirka (2008) for each model (K_D^{cpx-liq}(Fe-Mg) = 0.28 ± 0.7; K_D^{opx-liq}(Fe-Mg) = 0.29 ± 0.6; K_D^{ol-liq}(Fe-Mg) = 0.30 ± 0.3; K_D^{cpx-opx}(Fe-Mg) = 1.09 ± 0.14, respectively). The graphical representation of these equilibrium test (binary diagrams of mineral Mg# versus liquid Mg#; e.g. Risse et al., 2013; Lucci et al., 2020) are provided in the Figure 8-A7 of the Supplementary Material. For the
two-feldspars model we consider the equilibrium test proposed by Elkins and Grove (1990), which considers the relative ratio of the activities of the distinct feldspars components (An, Ab, Or) between plagioclase and K-feldspar crystal pairs (the ratio should be nominally = 0). The input pressure values used for the two-feldspars model were obtained from barometric estimation obtained for clinopyroxene-liquid and plagioclase-liquid for WP. We also calculated the zircon saturation temperatures from the model of Watson and Harrison, (1983), using the Zr content (ppm) of WP samples (Tab. 2). Results (T, P, H₂O wt %) are provided in Figure 14 and Table 9A of the Supplementary Material, except for those from the amphibole composition method that are shown together within the EPMA analysis in Table 6.

5.2. Hygrometric estimates

Fig. 13. Binary plot of the measured plagioclase anorthite fraction versus that calculated from the liquid composition by the method of Namur et al. (2012), applied to the plagioclase-liquid pairs that satisfied the equilibrium test of Putirka (2008; Tab. 8A-3). Equilibrium WP plagioclase-liquid pairs are those obtained combining the high anorthite areas of oscillatory plagioclase with bulk-rock compositions.
The values of $H_2O_{\text{liq}}$ obtained by the plagioclase-liquid and amphibole hygrometer ($\pm 1\sigma$ standard deviation of the weighted mean) are provided as isolines in the P-T diagram of Figure 14. WP calculated $H_2O$ wt % was determined by equilibrium plagioclase + bulk-rock compositions (Fig. 13) and varies between $\sim 0.89$-1.32 wt % (weighted mean of $1.17 \pm 0.49$, MSWD = 0.021; $n = 15$). In BE samples, water contents were determined using the compositions of the plagioclase microlites (Figs. 5b, c; 9c) paired with EPMA glass analyses (Fig. 13). The obtained $H_2O$ range is between $1.2$-1.42 wt % (weighted mean of $1.28 \pm 0.42$ wt %, MSWD = 0.042, $n = 11$). For FBE the plagioclase-liquid model provides water contents of 0.98-1.59 wt % (weighted mean of $1.38 \pm 0.25$ wt %, MSWD = 0.013, $n = 67$), similar to CBE (0.89-1.46 wt %, weighted mean = $1.30 \pm 0.17$ wt %, MSWD = 0.008, $n = 144$). For BP samples the equilibrium test of Putirka (2008) was not satisfied, either using bulk rock and glass composition, and results will not be discussed. The application of the amphibole hygrometer provides, for all the enclave types, higher water contents than the plagioclase-liquid method, with FBE and CBE varying between $\sim 4$-6 wt % and the BE large phenocrysts displaying the highest $H_2O_{\text{liq}}$ range ($\sim 8$ – 10 wt %).

5.3. Thermobarometric estimates

We provide in this section the results obtained for each rock by the equilibrium mineral-liquid and mineral-mineral pairs, together with those from the amphibole composition and zircon saturation methods.

5.3.1. White pumice

The plagioclase-liquid thermobarometric model (using WP bulk rock composition as liquid input, $n = 15$; Fig. 13) provides a temperature range of 955-971 $^\circ$C (weighted mean of $962 \pm 22$ $^\circ$C, MSWD = 0.014) and a pressure range between 1.3 – 4.0 Kbar (weighted mean of 2.7 $\pm$ 1.3, MSWD = 0.13), using equation 24a and 25a of Putirka (2005), respectively. The unique plagioclase-liquid pairs that
satisfied the equilibrium test of Putirka, (2008) are those obtained using the high-An compositions of
oscillatory plagioclase phenocrysts (Figs. 9a, b; 13). The clinopyroxene-liquid (whole rock) model of
Putirka (2008) yields a temperature range ~ 883-930 °C (weighted mean of 906 ± 9 °C, MSWD =
0.056, n =119), and a pressure of 1.8 – 4.2 Kbar, (weighted mean of 2.6 ± 0.6, MSWD = 0.031). The
two-feldspars thermometer provided a lower and wider temperature range than the clinopyroxene- and
plagioclase-liquid models (810 – 929 °C, weighted mean of 893 ± 13 °C, MSWD = 0.113, n = 43). The
plagioclase – K-feldspar pairs were chosen among those with a calculated An-Ab-Or activity difference
in the feldspars pairs < 0.1 (Table 8A-2). The pairs that resulted in equilibrium are those formed by the
WP low-An phenocrysts and the low-An areas of oscillatory grains (Fig. 9a, b). Finally, the zircon
saturation temperatures are in the range ~ 780-800 °C (weighted mean = 788 ± 15 °C, MSWD = 0.059,
n = 16; Tables. 2, 8A-1).

5.3.2. Beige pumice

Temperature and pressure estimates for BP were determined by the amphibole composition model
(Ridolfi and Renzulli, 2012), which yielded a temperature range of 921-991 °C, (average 946 ± 45 °C,
n = 4) and 966-981 °C (average 969 ± 45 °C, n = 5) for amphibole rim and core, respectively. Pressure
estimates are in the range of 2.4 – 4.4 Kbar, average 3.35 ± 0.48 Kbar and 2.9 – 4.3 Kbar, average 3.5
± 0.48 for rims and cores, respectively.

5.3.3. Black enclave

Temperatures and pressure values for BE were calculated using the olivine-liquid, orthopyroxene-
liquid, the clinopyroxene-liquid (all using BE bulk rock composition), the plagioclase – liquid (using
microlite – glass pairs), the two-pyroxenes and the amphibole composition methods (Fig.14). The
equilibrium olivine-liquid pairs (n = 2) yielded temperatures of 1171-1175 °C (± 52 ° C; eq. 2 of
Putirka et al., 2007; Tab. 9A-5), the orthopyroxene-liquid model provided a temperature range of 1099
– 1131 °C (weighted mean of 1119 ± 18 °C, MSWD = 0.044, n = 19), and a pressure range between 5.7 – 8.5 Kbar (weighted mean = 7.1 ± 1.2, MSWD = 0.112), and the clinopyroxen-liquid equilibrium pairs yielded a temperature range of 1140-1159 °C (weighted mean = 1147 ± 21 °C, MSWD = 0.019) and a pressure range of 5.4-7.8 Kbar (weighted mean = 6.8 ± 1.7, MSWD = 0.055). The two-pyroxenes thermobarometer provided lower temperature and pressure ranges (955 – 1016 °C, weighted mean of 992 ± 5.6 °C, MSWD = 0.13, n = 259), and 1.1 – 6.2 Kbar (weighted mean of 3.0 ± 0.35 Kbar, MSWD = 0.15). The large amphibole phenocrysts (Fig. 5k) yielded a temperature range of 950 – 996 °C (average 973 ± 45 °C, n = 7), and a pressure range of 8.1 – 9.0 Kbar (average 8.51 ± 1.44 Kbar). The Ridolfi and Renzulli (2012) was not applied to BE amphiboles microlithes, which are not suitable for the above-mentioned model (Ridolfi et al., 2010).

5.3.4. Fine brown enclave

Temperature and pressure estimates for FBE were realized using the plagioclase-liquid (with plagioclase-glass pairs; Fig. 13) and the amphibole composition methods. FBE amphiboles are prismatic to tabular and are not microlites (0.25-1.5 mm) in contrast to the BE amphiboles (Fig. 5 b, c). The plagioclase-liquid temperature estimates are in the range ~ 970-980 °C (weighted mean of 975 ± 11 °C, MSWD = 0.0042, n = 67), while pressure is between 1.0 - 5.3 Kbar (weighted mean of 3.42 ± 0.6 Kbar, MSWD = 0.13). FBE amphibole core analyses yielded temperatures between 981 – 1023 °C (weighted mean of 1000 ± 22, MSWD = 0.087, n = 17), and pressure in the range 4.1 – 7.8 Kbar (weighted mean of 5.8 ± 0.64, MSWD = 1.9), and the amphibole rims provided lower temperature (914 – 943 °C, weighted mean of 933 ± 21, MSWD = 0.088, n = 19), and pressure ranges (2.5 – 3.3 Kbar, weighted mean of 2.88 ± 0.17, MSWD = 0.994).

5.3.5. Coarse brown enclave
As well as FBE, CBE temperature and pressure estimates were realized with the plagioclase-glass pairs and with amphibole compositions. The first method yielded temperature in the range 978 – 1000 °C (weighted mean of 989 ± 7 °C, MSWD = 0.073, n = 144), and pressures between 0 – 3.1 Kbar (weighted mean of 1.8 ± 0.4 Kbar, MSWD = 0.047). In contrast to FBE, CBE core and rim analyses do not form two distinct T-P groups (Fig. 14), providing temperatures in the range 968 – 1035 °C (weighted mean of 1000 ± 25, MSWD = 0.993, n = 13) and between 966 – 1029 °C (weighted mean = 1005 ± 25 °C, MSWD = 0.2, n = 13), respectively. Also the estimated pressure is more variable than FBE amphibole (3.1 – 7.0 Kbar, weighted mean = 5.88 ± 0.88 Kbar), and between 3.0 – 7.6 Kbar (weighted mean of 5.4 ± 1.0 Kbar, MSWD = 3.5) for core and rims, respectively.

Fig. 14. Thermobarometric results. Pressure versus Temperature diagram. Symbols indicate the rock types, while colors are associated to the applied thermobarometric models. Shaded light blue, green and orange areas indicate, respectively, the calculated olivine-liquid, two-feldspars and zircon-saturation temperature ranges. Plagioclase-liquid hygrometer H\(_2\)O isolines are provided translated in the central box to uncover them from the symbol cloud.

6. Discussion

6.1. Petrologic and textural evidence of magmatic interaction
The results of our study indicate that the complex petrologic characteristics of the CPPI products reflect variable degrees of interaction (chemical and physical) between the rhyolite and the enclave-forming magmas. The simplified model of Figure 15 resumes our reconstruction of the pre-eruptive stages of the CPPI magmatic system. According to our interpretation, during the mafic recharge phase, mingling between mafic and rhyolitic magmas was very intense, and partial hybridization of the rhyolitic host (i.e. magma mixing) occurred. Mingling is normally associated with magmas with different compositions, temperatures and rheology, which cannot mix completely to form hybrid products (Blake and Fink, 2000). The intense mingling, evidenced by the composition and structure of the multi-banded pumice (Fig. 2h, g), is also reflected in the complex mineralogical assemblages and micro-textures of the enclaves and silicic pumice, suggesting that this interaction acted at different scales (e.g. Perugini and Poli, 2012). Among the enclaves, BE is that displays greater textural and compositional evidence of interaction with WP, occurring as partially dismembered inclusions within WP (Fig. 2c; Fig. 15a-3), and showing the occurrence of crystal transfer to and from WP melt (Figs. 5h-j; 5-A2; 15a-1). This suggests that the BE and WP magma exchanged crystals and melt components (micro-mingling textures), as well as heat and volatiles (e.g. Huppert et al., 1982; Shane et al., 2008; Perugini and Poli, 2012; Scruggs and Putirka, 2018). Moreover, the variability on BE plagioclase composition and textures (Figs. 6g-i; 9c), the silicic sieve-textured plagioclase within BE (Fig. 6h), and the presence of amphibole rims on BE mafic phenocrysts (Fig. 5e, f), are features associated with magma mixing events (Leonard et al., 2002; Coombs et al., 2003; Coombs and Gardner; 2004; de Hoog et al., 2004; Ruprecht and Wörner, 2007; Humphreys et al., 2009; Gogoi and Saikia, 2018). By consequence, it is likely that the generation of hybrid products may have occurred during the initial phase of BE-magma injection (i.e. before quenching), during which mafic magma engulfed some rhyolitic crystal and melts and generated sparse mixed products through chaotic mixing dynamics (e.g. Browne et al., 2005; Perugini and Poli, 2012; Morgavi et al., 2013; Fig. 15a-1). The petrologic characteristic of BP rock
(linear trend between WP, BP and BE in the I/MgO vs FeO/MgO and in the Harker diagrams of both glass and whole-rock compositions), the bimodal BP mineral assemblage (Fig. 4d) and the common presence within BP of BE and WP inclusions (Figs. 2g; 4c), suggest that this pumice type likely represent the product of the mixing between BE-forming magma and the rhyolitic host (Shaw, 2006; Morgavi et al., 2013, 2018; Pritchard et al., 2013; Scruggs and Putirka, 2018). According to the applied geothermometers (Fig. 14), during mafic recharge temperature of the host and injecting magma were both high (respectively > 875 °C and ~ 1000 °C; see discussion Section 5.2; e.g. Ridolfi et al., 2016), and thus, regardless the compositional differences (Fig. 8), the two magmatic endmembers could locally mix and generate hybrid melts (e.g. Perugini and Poli; Plail et al., 2014; Fig. 15a). It is also possible that mixing continued to some extent after quenching of BE magma, by a combination of mechanical processes like disaggregation and dispersion of the enclave crystals and glass (Wiebe, 1996; Clynne, 1999; Streck and Grunder, 1999; Morgavi et al., 2013; 2016; Michel et al., 2017; Gogoi and Saikia, 2018), as suggested by the presence of partially-dismembered BE material (quenched blobs and phenocrysts) within WP and BP samples (Figs. 2c, g; 4c-f).

The oscillatory zoning of WP plagioclase, in which areas of variable anorthite contents alternate (Fig. 3c, d; Fig. 9a-b), can be associated to heating events affecting the melt in which plagioclase grows (Tsuchiyama and Takahashi, 1983; Andrews et al., 2008; Shcherbakov et al., 2011), and also to variable magmatic H₂O content, oxygen fugacity and pressure conditions (Housh and Luhr, 1991; Coombs et al., 2000; Putirka, 2005). Considering the lack of evident resorption surfaces in WP plagioclase (like those observed in BE plagioclase; Fig. 5i; e.g. Streck, 2008), and that the unique equilibrium plagioclase-liquid pairs are those formed by the high anorthite zones of oscillatory grains (Fig. 13) we interpret that oscillation in WP plagioclase was generated by variable conditions in the magma (i.e. convective environment; e.g. Ginibre et al., 2002; Fig. 15b) likely due to the mafic
recharge event, and that the plagioclase grains that suffered resorption and re-crystallization are mainly those transferred from the silicic host (WP) to BE-forming magma (Figs. 5i; 15b-2).

Leonard et al. (2002) proposed that enclave groundmass textures similar to BE can be generated by undercooling crystallization after mafic magma receives H$_2$O by mixing with the rhyolitic host. Thus, the generation of BE amphibole groundmass microlites (Fig. 6a-c) and corona-forming microlites (Fig. 6e, f) could be a consequence of both the mixing event and quenching. In this case, the variability in Mg# between these amphibole crystals (Fig. 12c) would be due to different crystallization mechanisms (i.e. crystallization from BE melt and from BE mafic phenocrysts, respectively). Moreover, BE groundmass texture is not dyktitaxitic (e.g. Bacon, 1986; Mortazavi and Sparks, 2004; Browne et al., 2005) because amphibole microlites are more tabular than acicular and do not form a continuous crystal touching framework with plagioclase laths (Fig. 6b, c). Experimental works demonstrated that for a dyktitaxitic texture to form, temperature contrast between the injecting and host magmas must be ≥ 150 °C (Logfren, 1980; Coombs et al., 2003; Browne et al., 2005). Taking into account the relatively high temperature calculated for WP and BE (Fig. 14a, b; Table 9A1-3), it is likely that the thermal contrast between these two magmas was not high (lower than 150 °C; see discussion paragraph 6.2), allowing for an initial stage of partial-liquid interaction between BE and WP magmas, which favored magma mixing.

According to our reconstruction, FBE and CBE types represent a later mafic recharge event. Differently from BE, the association of FBE/CBE is only present within the eruptive CPPI Phase II deposits (Fig. 2f), and their reciprocal petrologic affinity (Figs. 8; 9d; 11; 12a, b) suggests that these two enclave types are genetically related to the same parental magma (Fig. 15 b). The textural differences between BE crystalline groundmass and FBE (Figs. 5b, c; 6a, b) indicate that FBE-forming magma crystallized with a lower undercooling degree than BE (Shea and Hammer, 2013), which
corroborate the idea that FBE/CBE melt entered the rhyolitic chamber after BE magmatic injection. The slight differences existing between FBE and CBE glass and mineral compositions (Figs. 8; 11; 12) and mineral modal contents (Table 1) can be related to partial mixing with the silicic host (maybe BP-melt), given the resorbed orthopyroxene cores within CBE crystal-rich inclusions (Figs. 7f) and the similarity in the compositions of FBE and BP glass (Fig. 8c, d, g, h). However, this scenario contrast with the geochemical whole rock (and glass) diagrams in which a linear trend between FBE/CBE and BP sample is not evident (Fig. 8d, i). This suggests that the compositional differences between FBE and CBE (Fig. 8a-h) may due, for example, to compositional heterogeneities in the FBE- and CBE-forming magma, and not by a variable degree of chemical interaction with the host. However, the most evident difference between FBE and CBE regards the crystalline texture (different crystal size and contents; Figs. 6, 7), which indicate variable crystallization conditions (i.e. undercooling) at which this magma crystallized (e.g. Conte et al., 2006; Shea and Hammer, 2013). Thus, it is possible that the external part of the magmatic intrusion (FBE), at the interface with the silicic host where T contrast was higher, crystallized a sub-millimetric (and equigranular) crystal assemblage (Fig. 6a; Fig. 15c-1, c-2), while in the internal part of the intrusion (CBE), where T contrast was lower than the interface, the magma crystallized a coarser mineral association (e.g. Browne et al., 2005; Fig. 15c-3, c4). The presence within CBE of the crystal-rich inclusions (Figs. 2h; 7f) is in accord with the hypothesis that crystallization (and crystal accumulation) did actually occurred (Fig. 15c-5). The amphibole barometric results obtained from FBE and CBE indicate that crystallization may have started in an earlier pre-injection magmatic stage (i.e. polybaric crystallization; Ridolfi et al., 2008). However, care must be taken when interpreting the results of the Ridolfi and Renzulli, (2012) amphibole thermobarometer, considering that the inferred undercooling conditions (i.e. disequilibrium) of crystallization (especially for FBE and BE) are not suitable for this thermobarometric estimation (Ridolfi et al., 2010). More considerations about this point will be discussed in section 6.2. Finally, during the eruption, distinct
parts of the reservoir were evacuated (Fig. 15c), with the first extraction of the upper rhyolitic magma
(higher SiO$_2$ WP) containing low abundance of BE and BP material (CPPI Phase I), and a second
event, which causes the withdraw of the deepest part of the reservoir (CPPI Phase II with WP, BP and
all the enclave types; Fig. 15c).
Figure 15. Simplified model of the pre-eruptive magmatic phases of the CPPI sub-volcanic system. a) Injection of BE partial-liquid magma, with consequent engulfment of WP phenocrysts and glass (a1, Fig. 6j), formation of the hybrid trachy-dacite (a2, Fig. 5d) with remnants of WP melt within the hybrid (a3, Fig 2g), and dispersion of BE blobs within WP and BP (a4, Fig. 2e) b) Crystallization of BE groundmass and formation of amphibole rim on BE phenocrysts (b1, Fig. 6a) and crystallization in the hybrid BP melt (b2, Fig. 6g). c) Injection of FBE/CBE-forming magma at liquid state. d) Differential crystallization of FBE/CBE magma with higher cooling rates at the interface with the host (c1, Fig. 7a; d3, Fig. 7c) and lower cooling rates in the mafic intrusion interior (c2, Fig. 8a-b), with consequent formation of the crystal-rich inclusions (c5, Fig. 2h); c6) banded pumice (Fig. 2c) in which CBE, FBE and the hybrid BP are in contact each other. The relative volume of mafic magmas is exaggerated for clarity.

6.2. Thermobarometric constraints

The estimations of the intensive parameters obtained by the thermobarometric calculations add physical constraints on the model discussed in section 6.1 (Fig. 15), which is principally based on the petrologic and textural characteristics of the silicic pumice and enclaves. The application of the distinct methods provided a wide range of crystallization conditions, from middle to shallow crustal levels (~9 – 0 Kbar) and between ~1180 – 800 °C (Fig. 14), reflecting the heterogeneity of the mineral assemblages and textures in the CPPI products. We discussed in section 6.1 that mixing between BE- and WP-forming magma was favored by the relatively high temperature of the rhyolitic host, and that the lack of a dyktitaxitic texture on BE groundmass indicates a thermal contrast < 150 °C between the rhyolitic and mafic magmas. Thermometric results confirm this reconstruction, showing that the average value of the two-feldspars geothermometer (T = 890 °C) is within 150 °C respect the two-pyroxenes, amphibole, and plagioclase-liquid calculated temperatures for BE, FBE and CBE (950 – 1000 °C; Fig. 14). Also the plagioclase-liquid and clinopyroxene-liquid methods, which provided a higher temperature range (~900-950) than the former one, are in accord with this assumption (Fig. 14). Considering the average clinopyroxene-liquid temperature calculated for WP (~ 900 °C,) as that of the rhyolitic host at the time of mafic recharge, and the two-pyroxenes temperature of BE (990 ° C) as the temperature of the injecting magma, the thermal contrast between WP- and BE-forming magmas would be lower than 100 °C (ca. 90 °C).
Among the enclave types, BE display the more heterogeneous crystal cargo, carrying a pre-injective mafic crystalline association (Figs. 5a, d, e, l), a post-injection quenched crystal groundmass (Fig. 5b, c), and a minor xenocrystic component derived from the mingling with the rhyolitic host (Figs. 5i, j, k; 15a). This complexity is reflected in the variability of BE T-P results, with the orthopyroxene-liquid, the clinopyroxene-liquid and the olivine-liquid thermobarometric models that yielded the highest temperatures (~1100 - 1175 °C; Fig. 14) and high pressures ranges (~6.0 – 8.8 Kbar; Fig. 14). These conditions may represent the deep stagnation level where BE magma crystallized and cooled (e.g. Ridolfi et al., 2016; Lucci et al., 2020). The presence of clinopyroxene and orthopyroxene crystal aggregates (Figs. 5d; 8A-6) is in accord with this assumption, and the two-pyroxene calculated temperature range (~ 950-1000 °C, average 992 ± 6 °C) indicates that cooling and crystallization of BE magma proceeded up to ca. 1000 °C (Fig. 14). BE amphibole phenocrysts (Fig. 5l) may be related to this lower-T magmatic stage (~ 950 – 990 °C) at deep levels in the crust (P = 7.4 – 9.0 Kbar), prior to the ascent of BE magma toward the surface.

The two direct barometric estimates of WP samples yielded comparable results (Fig. 14), and indicate a shallow crustal depth at about 2.6-2.7 Kbar, similarly to the pressure calculated using the BE clinopyroxene – orthopyroxene pairs (P = 3.0 ± 0.35 Kbar). The plagioclase-liquid pressure estimations for FBE and CBE results are more variable, with average values of 3.4 ± 0.6 Kbar and 1.8 ± 0.4 Kbar, respectively. On the basis of these calculations, we infer that the crustal level at which the silicic and mafic magmas interacted lays at a depth of ca. 10 Km (estimated considering an upper crustal density of 2.74 Kg dm$^{-3}$; e.g. Lucci et al., 2020), a position that can be considered the deepest portion of the CPPI reservoir (e.g. Ridolfi et al., 2008). The FBE and CBE pressure estimates indicate a wide crystallization pressure range (1.0 – 7.8 Kbar; Fig. 14) and the estimation of the depth of this reservoir before the magmatic ascent remains uncertain. We assumed the textural characteristic of FBE and CBE amphiboles (differently from BE amphibole groundmass microlites) as suitable for the Ridolfi and
Renzulli, (2012) model, although the undercooling conditions inferred for FBE and CBE amphiboles (Fig. 15c-1, c2), and the T-P distribution of CBE amphibole core-rim analyses (Fig. 14), suggest the occurrence of disequilibrium crystallization during amphibole growth (Ridolfi et al., 2010; Gorini et al., 2018). By consequence, the amphibole thermobarometer of Ridolfi and Renzulli, (2012) would not be applicable to our rocks, and the pressure results of CBE and FBE amphibole may be overestimated (Ridolfi and Renzulli 2012; Gorini et al., 2018). However, it is interesting to note that the rims of FBE amphiboles, which should have crystallized with higher temperature contrast than those within CBE, provide temperature and pressure ranges (914 – 940 °C, and 2.5 – 3.3 Kbar) comparable with the T-P results obtained from WP phenocrysts (clinopyroxene- and plagioclase-liquid methods; Fig. 14), which likely reflect the physical conditions of the rhyolitic reservoir. This thermobarometric convergence (Fig. 14) and the homogeneous composition of FBE amphibole rims (Fig. 12a, b) suggest that a chemical re-equilibration of these amphibole crystals may have occurred (e.g. Ridolfi et al., 2016; Gorini et al., 2018; Fig. 14). Thus, the amphibole T-P estimates of Ridolfi and Renzulli (2012) may be valid in those cases where amphibole crystallized under disequilibrium and then re-equilibrated with the physical conditions of the host reservoir.

The occurrence of the re-equilibration event implies that an interval of time must have passed between amphibole crystallization and the starting of the Plinian eruption. Chemical zoning on BE and CBE amphibole was not detected, and this contrasts with the hypothesis of re-equilibration, although a slight T-P differentiation is present in BP core-rim phenocrysts (Figs. 14). Possibly, BE amphiboles (groundmass and phenocrysts) were protected from the surrounding magmatic environment by the quenched glassy material, or zoning was not detected during EPMA study. CBE amphiboles, as discussed previously (Fig. 15c), were preserved in the deeper (and hotter) part of the reservoir and did not have the sufficient time (and/or thermal contrast) to re-equilibrate. The occurrence of the proposed temporal gap is also consistent with the thermometric results obtained from the Zr-saturation model (~
790 ± 15 °C), which is indicative of the pre-eruptive magmatic thermal state (e.g. Lucci et al., 2018) and suggest the occurrence of a cooling stage to about 800 °C before the beginning of the eruption (Fig. 14).

These textural and thermometric evidences are in accordance with the existence of a temporal interval between the FBE/CBE magmatic injection/crystallization and the eruption, and contrast with the hypothesis of a strong temporal coincidence between mafic recharge and the volcanic event (e.g. Leonard et al., 2002). According to this reconstruction, the rhyolitic eruption likely occurred during a cooling stage rather than a thermal peak, indicating that other possible factors (like the tectonic control) may have played an important role as an eruption trigger (as already suggested by Báez et al., 2015). The low volume abundance of the mafic products in the CPPI deposits sustains this idea, strengthening the hypothesis that the thermal and chemical consequences of the mafic recharge, although increasing the pressure in the reservoir by volatile exsolution (e.g. Folch and Marti, 1998), were not the main factor in triggering the Campo de la Piedra Pómez eruption.

6. Conclusions

The study of the petrologic characteristics of the CPPI indicates the presence in the ignimbritic deposits of different juvenile clasts (silicic pumice and magmatic enclaves), which record the complex pre-eruptive history of magmatic interactions (physical and chemical), during which magmas developed diffuse macro- and micro-mingling textures. The main conclusions obtained in this work are the following: (i) BE-forming magma is one that most interacted with the rhyolitic host, both physically (diffuse and complex micro-mingling textures) and chemically (hybridization with the rhyolite to form trachydacitic pumice), (ii) mixing between BE and WP started during the initial stage of BE mafic recharge and was favored by the relative high temperature of the rhyolitic host (≥ 875 °C, temperature contrast of ca. 90 °C) calculated with distinct geothermometers, (iii) FBE and CBE reflect a second
maggmatic injection event, and their textural variability is related to different degree of undercooling. FBE crystallized at the interface with the more silicic magma, while CBE reflects crystallization in a deeper and hotter zone of the Campo de la Piedra Pómez reservoir, (iv) the convergence of different barometric methods (using the rhyolite and enclaves compositions) indicates that the interaction among rhyolitic and mafic magmas occurred at a depth of 2.6-2.7 Kbar (~ 10 Km b.s.l.), a level which can be considered as the basal portion of the Campo de la Piedra Pómez magmatic system. Finally, we conclude that a temporal gap existed between the last event of mafic recharge/crystallization and the eruption, during which FBE amphibole had the time to re-equlibrate with the reservoir conditions and the rhyolitic magma cooled down to the temperature of eruption (~ 800 °C).

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## Table 1. Mineral modal compositions of the CPPI rocks

| Rock component | Sample |
|----------------|--------|
|                | WP     | WP     | WP     | WP     | BP     | BP     | BE     | BE     | FBE    | FBE    | CBE    | CBE    |
| Glass/vesicles | 95     | 98     | 92     | 86     | 85     | 90     | 84     | 81     | 67     | 73     | 80     | 85     |
| P.I.           | 5      | 2      | 8      | 14     | 15     | 10     | 16     | 19     | 33     | 27     | 20     | 15     |
| Plagioclase    | 59     | 30     | 45     | 45     | 45     | 40     | 35     | 40     | 42     | 49     | 42     | 39     |
| K-feldspar     | 27     | 54     | 25     | 32     | 10     | 12     | tr.    | /      | /      | /      | /      | /      |
| Quartz         | /      | 5      | 10     | /      | /      | /      | tr.    | /      | /      | /      | /      | /      |
| Biotite        | 10     | 8      | 15     | 16     | 25     | 27     | tr.    | /      | 9      | 7      | 27     | 35     |
| Clinopyroxene  | tr.    | tr.    | tr.    | 2      | tr.    | 30     | 26     | /      | /      | /      | /      | /      |
| Orthopyroxene  | tr.    | tr.    | tr.    | /      | 4      | 5      | 18     | 14     | traces | traces | traces | traces |
| Amphibole      | /      | /      | /      | 10     | 9      | 5      | 2      | 47     | 39     | 23     | 20     |        |
| Olivine        | tr.    | /      | /      | /      | tr.    | tr.    | 5      | 9      | /      | /      | /      | /      |
| Oxides         | 5      | 3      | 5      | 6      | 5      | 7      | 8      | 2      | 5      | 8      | 6      |
| Amphibole      | /      | /      | /      | 10     | 9      | 5      | 2      | 47     | 39     | 23     | 20     |        |
| Apatite        | tr.    | tr.    | tr.    | tr.    | tr.    | tr.    | tr.    | tr.    | tr.    | tr.    | tr.    | /      |
| Zircon         | tr.    | tr.    | tr.    | tr.    | tr.    | tr.    | tr.    | tr.    | tr.    | tr.    | tr.    | /      |
|                |        |        |        |        |        |        |        |        |        |        |        |        |

tr. = traces amounts; mineral modal percentages are calculated excluding the matrix/vesicles %.

## Table 2. Whole-rock composition of the CPP products from La-ICP MS analyses

| Sample | WP     | CPP-16-11B | CPP-16-11A | P.B.D.D | CPP-PB-PRX | P.N. | BP     | BE     | FBE    | CBE    | CBE    |
|--------|--------|------------|------------|---------|------------|------|--------|--------|--------|--------|--------|
| SiO₂   | 74.30  | 73.40      | 72.70      | 72.01   | 72.18      | 0    | 66.40  | 55.23  | 54.60  | 54.18  | 56.70  | 55.60  | 53.80  | 53.80  |
| TiO₂   | 0.25   | 0.24       | 0.26       | 0.23    | 0.29       | 0.47 | 0.48   | 1.19   | 1.09   | 1.50   | 1.50   | 1.54   | 1.40   | 1.41   |
| Al₂O₃  | 13.75  | 13.55      | 13.57      | 13.57   | 14.29      | 9    | 14.00  | 15.76  | 14.25  | 17.36  | 16.65  | 17.10  | 17.88  | 17.55  |
| Fe₂O₃  | 1.64   | 1.58       | 1.51       | 1.46    | 1.85       | 2.95 | 7.51   | 7.62   | 7.73   | 7.32   | 7.68   | 7.56   | 7.56   | 7.40   |
| FeO    | 1.48   | 1.42       | 1.36       | 1.31    | 1.67       | 2.78 | 2.65   | 6.76   | 6.86   | 6.96   | 6.59   | 6.91   | 6.80   | 6.66   |
| MnO    | 0.05   | 0.05       | 0.06       | 0.06    | 0.06       | 0.07 | 0.12   | 0.14   | 0.13   | 0.13   | 0.13   | 0.13   | 0.13   |        |
| MgO    | 0.38   | 0.36       | 0.52       | 0.35    | 0.62       | 1.76 | 1.47   | 5.22   | 6.65   | 3.97   | 3.85   | 3.63   | 3.31   | 3.22   |
| CaO    | 1.41   | 1.36       | 1.43       | 1.22    | 1.74       | 2.65 | 2.56   | 6.44   | 6.79   | 6.90   | 6.74   | 6.93   | 6.00   | 6.07   |
| Na₂O   | 3.83   | 3.74       | 3.91       | 3.53    | 4.04       | 3.82 | 3.73   | 3.38   | 2.94   | 3.92   | 3.75   | 4.10   | 3.99   | 3.87   |
| K₂O    | 4.81   | 4.78       | 4.91       | 4.87    | 4.62       | 4.24 | 4.13   | 2.74   | 2.56   | 2.70   | 2.64   | 2.95   | 3.15   | 3.03   |
| P₂O₅   | 0.08   | 0.08       | 0.09       | 0.08    | 0.10       | n.a. | 0.17   | n.a.   | 0.29   | n.a.   | 0.50   | 0.49   | n.a.   | 0.66   |
Table 3. Microprobe analyses of the CPPI glass

| Sample | WP | BP | BE | FBE | CBE |
|--------|----|----|----|-----|-----|
| Oxide  |    |    |    |     |     |
| SiO₂   | 77.51 | 77.31 | 75.51 | 71.76 | 72.55 | 70.87 | 73.38 | 69.83 | 72.64 | 70.63 | 68.36 |
| TiO₂   | 0.03  | 0.11 | 0.16 | 0.16 | 0.19 | 0.31 | 0.14 | 0.40 | 0.32 | 0.45 | 0.64 |
| Al₂O₃  | 13.05 | 12.53 | 13.20 | 15.27 | 15.67 | 16.10 | 15.27 | 15.46 | 15.51 | 16.86 | 16.56 |
| FeO    | 0.31  | 0.45 | 0.95 | 0.84 | 0.28 | 0.37 | 0.52 | 0.67 | 0.43 | 1.36 | 1.09 |
| MnO    | 0.00  | 0.00 | 0.05 | 0.18 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| MgO    | 0.03  | 0.00 | 0.07 | 0.10 | 0.05 | 0.04 | 0.04 | 0.05 | 0.04 | 0.27 | 0.27 |
| CaO    | 0.35  | 0.26 | 0.81 | 1.35 | 1.27 | 1.17 | 1.26 | 1.27 | 1.23 | 1.32 | 1.22 |
| Na₂O   | 3.02  | 2.87 | 3.56 | 3.82 | 2.52 | 2.59 | 2.78 | 3.05 | 4.23 | 2.61 | 2.42 |
| K₂O    | 5.98  | 6.19 | 5.66 | 5.42 | 5.33 | 5.36 | 5.37 | 5.22 | 5.06 | 5.15 | 5.09 |
| P₂O₅   | 0.00  | 0.00 | 0.04 | 0.01 | 0.11 | 0.03 | 0.05 | 0.06 | 0.07 | 0.09 | 0.12 |
| F      | 0.00  | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.06 | 0.14 |
| Cl     | 0.00  | 0.00 | 0.15 | 0.20 | 0.08 | 0.08 | 0.08 | 0.21 | 0.17 | 0.21 | 0.18 |
| Total  | 100.28 | 99.71 | 100.15 | 99.10 | 98.06 | 96.91 | 98.91 | 96.21 | 99.70 | 99.01 | 96.15 |
| A/CNK  | 1.08  | 1.05 | 0.98 | 1.05 | 1.28 | 1.32 | 1.20 | 1.19 | 1.06 | 1.37 | 1.41 |
| A/NK** | 1.14  | 1.10 | 1.10 | 1.26 | 1.58 | 1.60 | 1.47 | 1.45 | 1.25 | 1.71 | 1.74 |

* = molar (Al₂O₃/(CaO+Na₂O+K₂O))
** = molar (Al₂O₃/(Na₂O+K₂O))

Table 4. Representative microprobe analyses of CPPI feldspar crystals

| Sample | WP plagioclase | BP | BE groundmass | BE phenoey | BE sieve-textured crystals* | FBE phenoey crystals** | CBE phenoey crystals** |
|--------|----------------|----|---------------|-------------|---------------------------|------------------------|------------------------|
| WP K-feldspar | BP | BE |              |             |                          |                        |                        |
### Table 5. Microprobe analyses of CPPI clinopyroxene and orthopyroxene grains

| Sample | WP | BP | BE | BE megacrystal | CBE crystal-rich inclusion | BE cpx | WP | BP |
|--------|----|----|----|----------------|---------------------------|--------|----|----|
| Oxide  | 106A-3b | PB16-A12 | 112a1-lco | 112a3-1loc | 112a4-2bcu | 106A2-2bcu | 112a1-3c | 112a2-1loc | 112A1-lc | 112A6-1c | 106A2-1lc |
| SiO₂   | 56.31  | 53.29 | 55.22 | 54.35 | 55.15 | 52 | 54.71 | 51.96 | 52.30 | 53.50 | 53.59 | 51.12 |
| TiO₂   | 0.07   | 0.35  | 0.18 | 0.21 | 0.30 | 0.41 | 0.05 | 0.33 | 0.75 | 0.09 | 0.21 | 0.76 |
| Al₂O₃  | 0.84   | 2.76  | 1.41 | 2.03 | 2.13 | 4.55 | 0.30 | 3.28 | 3.44 | 0.98 | 0.94 | 4.44 |
| FeO    | 13.7   | 16.53 | 11.68 | 11.32 | 12.49 | 17.15 | 16.99 | 7.05 | 6.77 | 9.18 | 8.91 | 7.57 |
| MnO    | 0.60   | 0.36  | 0.26 | 0.24 | 0.30 | 0.37 | 3.95 | 0.20 | 0.18 | 1.12 | 1.24 | 0.21 |
| MgO    | 27.54  | 25.15 | 29.28 | 27.69 | 29.21 | 25.01 | 20.7 | 16.06 | 16.34 | 12.78 | 12.76 | 14.95 |
| CaO    | 0.61   | 1.06  | 1.62 | 1.85 | 1.34 | 1.43 | 1.53 | 20.38 | 20.48 | 21.68 | 21.40 | 20.25 |
| Na₂O   | 0.00   | 0.11  | 0.03 | 0.05 | 0.03 | 0.04 | 0.16 | 0.38 | 0.39 | 0.46 | 0.48 | 0.51 |

An = anorthite; Ab = albite; Or = orthoclase

*b = fresh overgrowth; ** c = core; b = rim
| Oxide         | 112a2l-1c | 112a2-2c | 112a9-1c | 112a1-2 | 112b8-2 | 106A4-x |
|--------------|-----------|----------|----------|---------|---------|---------|
| SiO<sub>2</sub> | 39.16     | 38.65    | 39.22    | 38.28   | 38.35   | 41.02   |
| TiO<sub>2</sub> | 0.00      | 0.09     | 0.00     | 0.16    | 0.02    | 0.02    |
| Al<sub>2</sub>O<sub>3</sub> | 0.03     | 0.01     | 0.03     | 0.00    | 0.03    | 0.03    |
| FeO          | 19.87     | 19.61    | 23.64    | 22.42   | 22.08   | 18.94   |
| MnO          | 0.32      | 0.27     | 0.21     | 0.43    | 0.34    | 0.55    |
| MgO          | 40.61     | 41.21    | 38.02    | 39.08   | 38.23   | 38.57   |
| Na<sub>2</sub>O | 0.01     | 0.00     | 0.05     | 0.00    | 0.02    | 0.00    |
| K<sub>2</sub>O | 0.00      | 0.02     | 0.01     | 0.00    | 0.00    | 0.07    |
| CaO          | 0.12      | 0.12     | 0.14     | 0.27    | 0.11    | 0.07    |
| P<sub>2</sub>O<sub>5</sub> | 0.06     | 0.04     | 0.04     | 0.05    | 0.00    | 0.08    |
| F            | 0.00      | 0.00     | 0.00     | 0.02    | 0.16    | 0.00    |
| Cl            | 0.03      | 0.01     | 0.01     | 0.00    | 0.00    | 0.02    |
| Total       | 100.20    | 100.02   | 101.39   | 102.51  | 99.35   | 99.31   |

Cation (apfu)

| Element | BE          | WP          | BP          |
|---------|-------------|-------------|-------------|
| Si      | 1.01        | 1.01        | 1.01        |
| Ti      | 0.00        | 0.00        | 0.00        |
| Al      | 0.00        | 0.00        | 0.00        |
| Cr      | 0.00        | 0.00        | 0.00        |
| Fe<sup>3+</sup> | 0.00 | 0.00 | 0.00 |
| Fe<sup>2+</sup> | 0.43 | 0.41 | 0.57 |
| Mn      | 0.01        | 0.01        | 0.01        |
| Mg      | 1.56        | 1.58        | 1.29        |
| Ca      | 0.00        | 0.00        | 0.00        |
| Mg#     | 0.78        | 0.79        | 0.69        |
| Te      | 0.35        | 0.29        | 0.28        |

Wo = % wollastonite; En = % enstatite; Fs = % ferrosilite Wo = % wollastonite; En = % enstatite; Fs = % ferrosilite.

Table 6. Microprobe analyses of the CPP olivine crystals
Table 7. Representative compositions of CPPI amphibole and biotite crystals, and amphibole thermo-baro-hygrometric results from Ridolfi and Renzulli, (2012) method

| Sample | FBE amp | FBE c | CBE core | CBE rim | BP core | BP rim |
|--------|---------|-------|----------|---------|---------|--------|
| Oxide  | DD-1b   | DD-3b | DD-1c    | DV2-F11c| DV-11c  | DV-A2b |
| SiO$_2$| 42.24   | 41.8  | 39.03    | 40.18   | 41.02   | 41.60  |
| TiO$_2$| 3.19    | 3.25  | 4.98     | 3.54    | 4.73    | 3.7    |
| Al$_2$O$_3$| 11.01 | 10.94 | 13.66    | 12.9    | 12.47   | 12.37  |
| FeO   | 14.09   | 14.63 | 15.21    | 13.1    | 12.42   | 12.3   |
| MnO   | 0.28    | 0.41  | 0.28     | 0.27    | 0.18    | 0.38   |
| MgO   | 12.46   | 12.33 | 10.67    | 12.39   | 12.75   | 13.59  |
| CaO   | 11.35   | 11.65 | 11.94    | 11.49   | 11.71   | 11.48  |
| Na$_2$O| 2.11   | 2.36  | 2.51     | 2.5     | 2.70    | 2.44   |
| K$_2$O| 1.23    | 1.25  | 1.01     | 1.03    | 0.94    | 0.96   |
| F     | 0.16    | 0.30  | 0.05     | 0.22    | 0.00    | 0.03   |
| Cl    | 0.12    | 0.10  | 0.06     | 0.02    | 0.05    | 0.05   |
| H$_2$O$_{calc}$| 1.80 | 1.80  | 1.80     | 1.80    | 1.80    | 1.80   |
| Anhydrous Total | 98.25 | 99.01 | 99.35    | 97.64   | 98.19   | 99.74  |
| Mg/(Mg+Fe$^{2+}$)| 0.67  | 0.66  | 0.63     | 0.69    | 0.72    | 0.72   |
| Fe/(Fe+Mg)     | 0.33  | 0.34  | 0.37     | 0.32    | 0.28    | 0.28   |
| T Rid12$^*$ (°C) | 940  | 953   | 1033     | 1003    | 1013    | 994    |
| P Rid12$^*$(Kbar)| 923  | 955   | 1007     | 994     | 1035    | 1012   |
| H$_2$O$^*$ Rid12 (wt %) | 4.73 | 4.22  | 4.66     | 4.87    | 4.84    | 5.13   |

Note: Te = tephroite; Fo = forsterite; Fa = fayalite; Ca-Ol = calcic olivine
| Sample | BE microcx | BE corona | BE phenocx | WP biotite | BP CB-2c2-5 | BE 112a4-2c | FBE DD1lc | CBE DV1-2ot | DV1.Bt2crx* |
|--------|------------|-----------|------------|------------|-------------|-------------|----------|-------------|-------------|
| Oxide  |            |           |            |            |             |             |          |             |             |
| SiO2   | 40.34      | 43.04     | 41.47      | 36.12      | 36.83       | 36.06       | 36.11    | 36.58       | 35.81       |
| TiO2   | 4.74       | 2.34      | 2.70       | 5.48       | 4.78        | 5.50        | 5.71     | 5.87        | 5.43        |
| Al2O3  | 13.03      | 11.2      | 12.99      | 13.16      | 13.42       | 14.32       | 14.25    | 14.73       | 14.86       |
| FeO    | 12.95      | 12.63     | 11.27      | 17.94      | 16.94       | 17.02       | 15.29    | 14.03       | 14.19       |
| MnO    | 0.18       | 0.24      | 0.17       | 0.47       | 0.13        | 0.26        | 0.29     | 0.11        | 0.17        |
| MgO    | 13.12      | 14.32     | 14.09      | 12.71      | 13.32       | 13.64       | 14.36    | 15.19       | 15.10       |
| CaO    | 11.45      | 11.05     | 11.79      | 0.00       | 0.03        | 0.00        | 0.01     | 0.00        | 0.01        |
| Na2O   | 2.14       | 2.16      | 2.45       | 5.00       | 0.74        | 0.61        | 0.74     | 1.03        | 1.09        |
| K2O    | 2.06       | 0.91      | 1.07       | 9.39       | 10.74       | 8.68        | 8.66     | 8.29        | 8.40        |
| F      | 0.16       | 0.16      | 0.12       | 0.43       | 0.00        | 0.21        | 0.29     | 0.00        | 0.21        |
| Cl     | 0.05       | 0.05      | 0.05       | 0.13       | 0.00        | 0.07        | 0.10     | 0.07        | 0.06        |
| H2Ocalc| 1.80       | 1.80      | 1.80       | 3.72       | 3.96        | 3.88        | 3.84     | 4.02        | 3.87        |
| Anhydrous Total | 99.12 | 98.10     | 98.17      | 96.33      | 96.92       | 96.38       | 95.82    | 95.90       | 95.33       |
| Mg/(Mg+Fe2+) | 0.70 | 0.73      | 0.76       | 0.56       | 0.58        | 0.59        | 0.62     | 0.66        | 0.65        |
| Fe/(Fe+Mg) | 0.30 | 0.27      | 0.24       | 0.44       | 0.42        | 0.41        | 0.38     | 0.34        | 0.35        |
| T Rid12a (°C) | /      | /         | 1000      |           |             |             |          |             |             |
| P Rid12b (Kbar) | /      | /         | 988       |           |             |             |          |             |             |
| H2Oc Rid12 (wt %) | /      | /         |           |           |             |             |          |             |             |

\[14\] a = calculated amphibole temperatures from the Ridolfi and Renzulli, (2012) thermometer

\[15\] b = calculated amphibole pressures from the Ridolfi and Renzulli, (2012) barometer

\[16\] c = calculated H2Oliq from the Ridolfi and Renzulli, (2012) hygrometer

\[17\]

\[18\]

\[19\]
Highlights

• Pleistocene rhyolitic ignimbrite with multi-banded pumice clasts (mafic enclaves)

• Chemical hybridization of rhyolite and basalt to form dacitic rocks

• Enclave amphibole zoning reflecting re-equilibration in the rhyolitic reservoir

• Pre-eruptive cooling stage of rhyolitic melt to 800 °C at a depth of 2.6 kbar
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Declaration of interest “none”