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Hydrovolcanic vs Magmatic Processes in Forming Maars and Associated Pyroclasts: The Calatrava -Spain- Case History

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1. Introduction

The Calatrava Volcanic Field (CVF) of Castilla-La Mancha is characterised by numerous monogenetic volcanic centres, that erupted mainly foidites, melilitites and carbonatites (ultra-alkaline rock-association sensu, Le Bas, 1981) carrying abundant mantle xenoliths. At CVF, carbonatites have been described by Bailey et al. (2005) and Stoppa et al. (2011). Along with the volcanic field of Eifel of Germany, Limagne basin of France and Intra-mountain Ultra-alkaline Province (IUP) of Italy, the CVF encompasses the most numerous Pliocene-Quaternary extrusive carbonatites in Western Europe in terms of dimension, number and size of volcanoes (Bailey et al., 2005; Bailey et al., 2006). Similar volcanic fields are Toro-Akole and Bufumbira in Uganda (Bailey & Collier, 2000), the Avon district in Missouri (Calliccoat et al., 2008), Mata da Corda in Brazil (Junqueira-Brod et al., 1999) and West Qinling in Gansu Province, China (Yu et al., 2003). In spite of abundant local studies (González Cárdenas et al., 2010; Peinado et al., 2009), the CVF has been mostly neglected by the international audience, although Bailey (2005) outlined the need for a long-term research program on CVF. This work focuses on the role of deep CO₂ at CVF, which is considered an intrinsic component of carbonatitic mantle magmatism (Hamilton et al., 1979). Previous studies of CVF volcanoes considered that the hydrovolcanism is a necessary and sufficient condition to explain the CVF volcanological features, and, as a corollary that the carbonate present in the pyroclastic rocks is remobilised limestones (e.g., López-Ruiz et al., 2002). We propose an alternative hypotheses based on CO₂ violent exsolution and expansion germane to diatremic propagation of ultra-alkaline melts towards the surface and to dry-magmatic origin of the maars (Mattsson & Tripoli, 2011; Stoppa, 1996; Stoppa & Principe, 1998).

2. Volcano-tectonic setting

The CVF volcanoes occur in a circular area of about 3000 km², at the western termination of the SSW-NNE elongated Guadiana valley (Fig. 1), which is one of the largest tectonic basins in central-southern Spain. Most of the CVF centres are nested in the Palaeozoic rocks of the Calatrava and Almagro massifs, composed of quartzite, slate and lesser granite, deformed in E-W and N-S vertical, flexural folds (De Vicente et al., 2007). The massifs are cut by faults striking NW-SE and E-W, which determine a low profile, "horst and graben" -type morphology. The CVF has been subject to a generalised uplift that produced erosion of the

Neogene alluvial and lacustrine sediments filling the "grabens". This erosional phase was followed by paleosol-caliche formation during Lower Pliocene (Peinado et al., 2009). The uplift shortly predates the main volcanic phase. Post-volcanic lacustrine sedimentation, composed of travertine plus epiclastites and diatomite with bioturbation and slumps, has been observed in some maars such as Casa de los Cantagallos, Vega de Castellanos, Hoya de los Muertos (Peña, 1934; Portero García et al., 1988). It is likely that post-volcanic travertines are related to magmatic CO₂ dissolved in the ground-water and/or carbonatite weathering and remobilisation. Lacustrine travertines from Granátula de Calatrava gave C isotopes ratios averaging -5.73‰ $\delta^{13}\text{C}_{\text{PBD}}$ (average of 4 analyses data unpublished courtesy of M. Brillì CNR, Roma) in agreement with values measured from CO₂ emission at Calatrava.

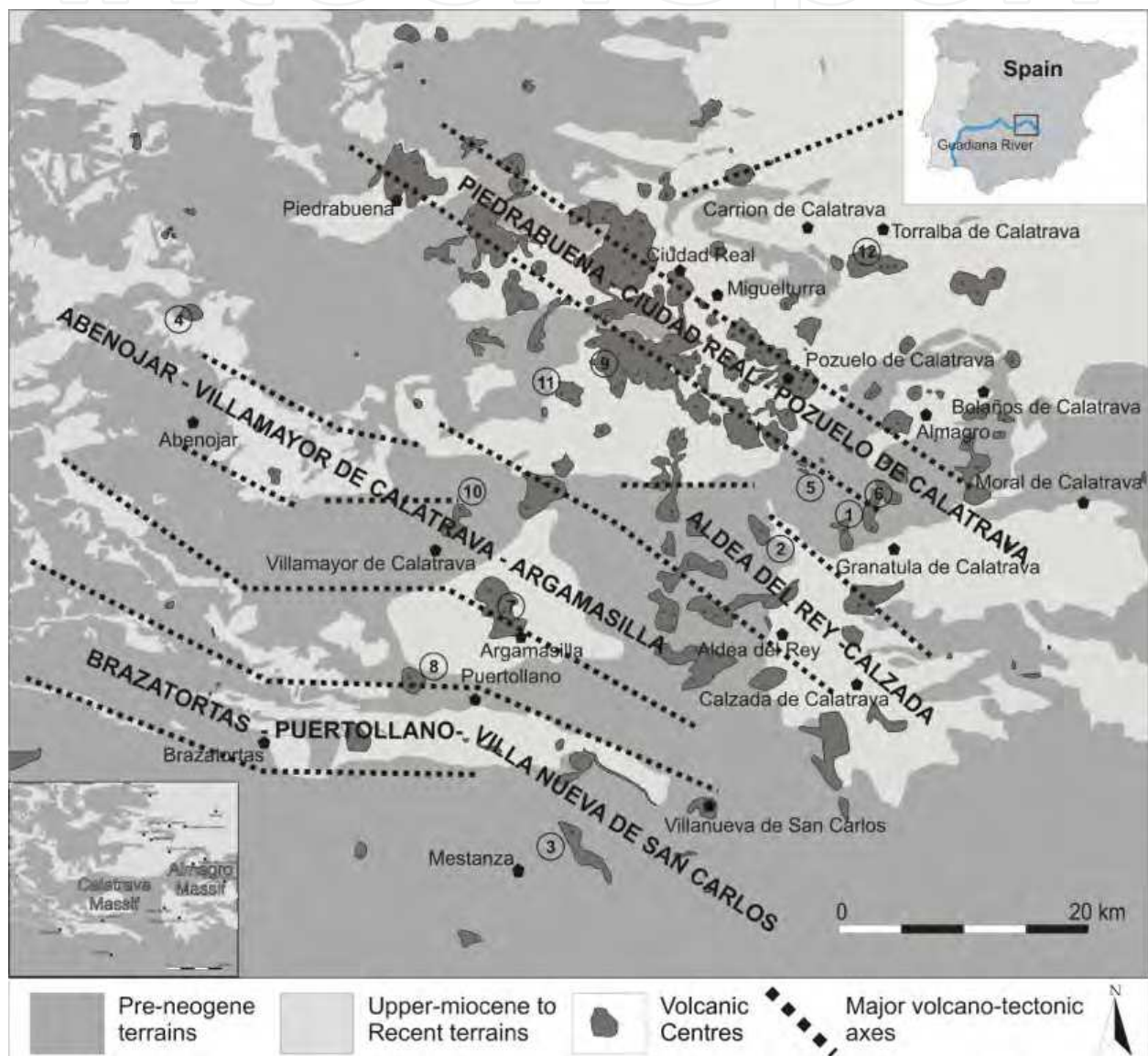


Fig. 1. Geological sketch map of CVF. Left top N 39°10'4.70" W 4°31'10.70" and the right bottom N 38°30'4.80" W 3°31'10.80". 1) La Sima, 2) Hoya de la Cervera, 3) Laguna de la Alberquilla, 4) Laguna Los Michos, 5) La Nava, 6) Cerro Gordo - Barondillo, 7) Laguna Blanca; 8) Laguna Almodovar del Campo, 9) Poblete, 10) Morron de Villamayor, 11) Cabezo Segura II, 12) Cerro San Marcos.

Volcanoes and CO₂ emissions are aligned NW-SE (Fig. 1). This direction corresponds to the elongation of the four major "grabens": a) Piedrabuena-Ciudad Real-Pozuelo de Calatrava, b) Aldea del Rey-Calzada de Calatrava, c) Abenojar-Villamayor de Calatrava-Argamasilla, d) Brazatortas-Puertollano-Villanueva de San Carlos (González Cárdenas & Gosálvez Rey, 2004; Poblete Piedrabuena, 1997). Some seismic activity has been identified east of the CVF. It is very weak, with 2-3 events per year and an average Mw of 2.7. A maximum event of Mw 5.1 occurred in Pedro Muñoz at the NE termination of the upper Guadiana basin, on August 12, 2007. The focal mechanism is compatible with a right, lateral strike-slip fault oriented ENE (data of Instituto Geográfico Nacional de España). The seismological evidence is in agreement with recent stress field estimates in western Spain, indicating pure strike-slip faulting conditions (De Vicente et al., 2007). The volcanic activity has been intense and relatively continuous over a few million years in the CVF (Ancochea, 1982; Cebriá et al., 2011). The subcontinental lithosphere, metasomatised by a rising asthenospheric diapir, has been considered the CVF melt source (Cebriá & López-Ruiz, 1995). However, deep seismic sounding studies on regional scale do not show any notable crustal thinning or upper-mantle upwelling confirming works based on Bouguer anomalies (Bergamín & Carbo, 1986; Díaz & Gallart, 2009; Fernández et al., 2004). If CVF activity is not driven by lithosphere tectonic it could be consequence of a hot finger detached by the megaplume active between the Canary Islands, Azores Islands and the western Mediterranean Sea (Hoernle et al., 1995).

3. CO₂ emissions and hydrothermalism

CO₂-bubbling springs, locally known as "hervideros" (Poblete Piedrabuena, 1992; Yélamos & Villarroya Gil, 1991), and CO₂ vents (mephites), lethal for animals, are frequent in the CVF. ¹³C/¹²C determination at Granátula de Calatrava and Puertollano CO₂-rich springs gave δ¹³C_{PBD} between -4.9‰ and -5.6‰ similar to primitive mantle values (Redondo & Yélamos, 2005). Mephites at La Sima and Granátula de Calatrava are associated with sporadic H₂S emissions and historical thermal anomalies (Calvo et al., 2010; Gosálvez et al., 2010). Past hydrothermal activity seems to have deposited relatively conspicuous Mn(Co-Fe) concretionary cryptomelane K(Mn⁴⁺, Mn²⁺)₈O₁₆ and litofofite (Li₆Al₁₄Mn₂₁O₄₂(OH)₄₂). These ores are found in La Zarza and El Chorrillo (Fig. 1), about 2 km SSW of Pozuelo de Calatrava (Crespo & Lunar, 1997).

The seismic crisis of August 2007 produced a dramatic increase in gas emissions at La Sima (Peinado et al., 2009). Before the shock of August 12, the CO₂ values were about 0.03 kg/m² per day. After the earthquake new CO₂ vents opened with apparent damage to the surrounding vegetation. A constant increase in the CO₂ emission, up to 324 kg/m² per day and a grand total of 4,86 kg per day only in the La Sima emission area was recorded (González Cárdenas et al., 2007; Peinado et al., 2009).

In CVF shallow well drillings have caused exceptional escapes of CO₂ in Los Cabezos, El Rosario and Añavete. Abrupt large emissions of gas-water are frequent in the area even if not lasting more than a few days. The "chorro" of Granátula de Calatrava in the Granátula-Moral de Calatrava graben has recently released gas, water and debris. After this event, a geophysical study identified a positive gravimetric and thermal anomalies (EPTISA, 2001). On March 2011, the "geyser" of Bolaños de Calatrava swamped an area of about 90,000 m² and issued up to 40 tonnes of CO₂ per day for several days. It spontaneously arose in a vineyard emitting 50,000 cubic meters of water propelled by gases composed 90% vol. of

carbon dioxide plus sulphur compounds (H₂S and HgS). An estimate of the temperature and pressure of the deep seated hydrothermal system is about 118 °C and 63 bar pressure (data Grupo de Investigación GEOVOL de la Universidad de Castilla-La Mancha). These localised activities have been interpreted as ephemeral gas releases along deep fractures. Well-eruption due to drilling confirm that CO₂ is locally accumulated at shallow level (<1km) and any perturbation, either natural or artificial, might lead to the violent release of gas producing water-debris currents. Evidence for a Holocene discrete phreatic eruption, which produced no juvenile ejecta, is recorded in the stratigraphy of the La Columba volcano (González Cárdenas et al., 2007). Future volcanic scenarios can be considered including diatreme formation, volcanian-like explosion, phreatic events, primary lahars, local volcano-seismic crises due to fluids/melt intrusion, potentially fatal CO₂-H₂S rapid emissions. All these phenomena are triggered by the abundant presence of juvenile gases in the magmatic system of Calatrava.

4. CVF magma composition

The entire CVF activity produced no less than 15 km³ of alkaline mafic/ultra-mafic rocks. Rock type occurrences at 33 investigated volcanoes (Fig. 1) are 36% nephelinite, 30% olivine melilitite, 21% leucite nephelinite (leucitite *s.l.*), 6% tephritic nephelinite, 3% melilite nephelinite and 3% carbonatites. It is not possible to calculate rock type in term of individual volume due to their complicate distribution and stratigraphy. However, carbonatite largely dispersed as ash-tuff are probably dominant in volume. Some of the CVF rocks are somewhat similar to ugandite or kamafugite having larnite in the CIPW norms, strong SiO₂ undersaturation and a potassic character with agpaite index (Na+K/Al) of about 0.9. High K content of nepheline suggest that kalsilite, a key mineral for kamafugites, or kaliophyllite occurrence is possible. Worldwide association of melilitite and carbonatite is noteworthy (e.g., Hamilton et al., 1979; Stoppa et al., 2005). This association can be found in many place worldwide and it covers 50% of the occurrences of extrusive carbonatite outcrops (Woolley & Church, 2005). Approximately 50% of the CVF outcrops contain mantle nodules. Plagioclase-bearing rocks are subordinate in all these districts, and in the CVF modal tephrite and basanite are notably absent. CVF nephelinites are depleted in ⁸⁷Sr and enriched in ¹⁴³Nd, whereas leucitite-melilitite and carbonatites are enriched in ⁸⁷Sr and depleted in ¹⁴³Nd (Cebriá & López-Ruiz, 1996). In the CVF peridotitic nodules are spinel-lherzolite to amphibole-lherzolite equilibrated up to 20 kbar and a temperature of 956-1382 °C (Villasca et al., 2010). Possibly different magma sources in the CVF may explain rock associations with different geochemical characteristics: I - melilitite and carbonatite; II - nephelinite-tephritic nephelinite. A level intensely metasomatized with amphibole-carbonate and with phlogopite veins would form the thermal boundary layer. These two components would produce, due to a slightly different partial melting point, the CVF magmatic spectrum. A similar feature has also been found in Italian carbonatites and kamafugites (Stoppa & Woolley, 1997) and is possibly related to reaction of alkali carbonatite with spinel or garnet lherzolite (Rosatelli et al., 2007).

5. Volcanology

Volcanic activity started on the western side of the CVF with the emplacement of melilitite leucite foidites. This early phase is mostly represented at Volcano Morrón de Villamayor (located N 38°49'20'' W 4°07'30''). K/Ar ages are inconsistent, giving a range of 8.7-6.4 Ma

for the same lava cooling-unit of this volcano (Bonadonna & Villa, 1986). Some other deeply eroded emission centres located in the Tirteafuera area may tentatively be related to this first magmatic phase. In the CVF activity lasted till the Quaternary (Ancochea & Ibarrola, 1982; Cebriá & López-Ruiz 1995). However, the dating by K/Ar methods available so far might not be perfectly suitable for the most challenging problems of Recent volcanism in CVF (Balogh et al., 2010). Due to the hundreds of vents, maars, cones and their multiple-clustered pattern in the CVF, it is important to give a general view of the volcanological features of this area and examples of the dominant volcanic forms. As for the definition of volcanic forms as vent, maar, diatrema and scoria cone, we conform to the definition of tab. 2 in White & Ross (2011). We assume, however, that the diatrema "feeder-dike" is very deep and located in the mantle (Stoppa et al., 2011, Fig. 3). In addition, we prefer the term tuffisite (Cloos, 1941) instead of peperite as the latter implies a magma/wet-sediment interaction. For specific discussion about tuffisite definition see Stoppa et al. (2003). CVF volcanoes density ranges from 10 to 15 per 100 km², leading to an estimation of about 250-300 volcanoes in the whole area (Fig. 1). However, volcanic landforms, eruption style and chemical composition are repetitive and are well represented by describing a limited number of volcanoes. Two main areas, located NW and SE of the city of Ciudad Real, can be identified, in terms of density of volcanoes and volume of the deposits. All the other volcanoes are scattered and decrease in size and density with distance from these areas. At least 150 of them have names and are now recognised by local people as volcanoes. The local idiom is very precise and distinguishes between different volcanic forms. *Peña* indicates a cone having a summit covered by blocks, *cabezo* is a small and isolated cone, *laguna* is a maar containing water and *nava* is a maar with a flat dry surface or a marsh, without trees, surrounded by hills, *hoya* and *pozo* are names for a large, deep diatrema. The presence of polygenic volcanoes (Becerra-Ramírez et al., 2010) is questionable from a stratigraphic point of view. In fact, the paleosols delineate the overlap of products of the adjacent volcanoes, rather than polygenic activity. However, co-eruptive vents are frequent and are represented by coalescent, multiple and/or nested vents associated with volcanic complexes of cones and maars. So we prefer the term polyphasic to polygenic. In some cases vents are aligned along NW-SE fissures some kilometres long such as in Miguelturra-Pozuelo de Caltrava (Fig. 1). Exposures of feeding dykes are lacking along these alignments and in general in the CVF.

5.1 Maar/diatreme systems

At CVF there are no geophysical data or exposure allowing direct observation of diatremes. Circular depressions sharply excavated into the Palaeozoic crystalline hard-rocks with steep internal escarpment and without significant accumulation of volcanics outside the rims, are considered here as the surface expression of eroded diatremic conduits. The few remnants of volcanics may indicate the presence of a former maar. When a pyroclastic ring is found around these depressions, it is classified as a maar (Martín-Serrano et al., 2009). La Hoya de la Cervera (Figs. 1, 2a,b) is located north of the Aldea del Rey, along a NW-SE alignment, which links with the CO₂-rich springs. Less than 3 km NE is the large maar of Finca la Nava (Fig. 3). La Hoya de la Cervera is a depression with diameter of about 300 m, totally excavated into the hard Palaeozoic rocks. The depression bottom is at about 675 m a.s.l., while the rim is between 750 and 825 m above sea level (a.s.l.). Sparse remains of lapilli tuffs and breccias are exposed along the depression rim in the NE section. These deposits are characterised by occurrence of tuffs, containing concentric-shelled cored lapilli, along with heterolithic breccias which are hardened by carbonate matrix (Fig. 8c). The diatrema of La Hoya de La

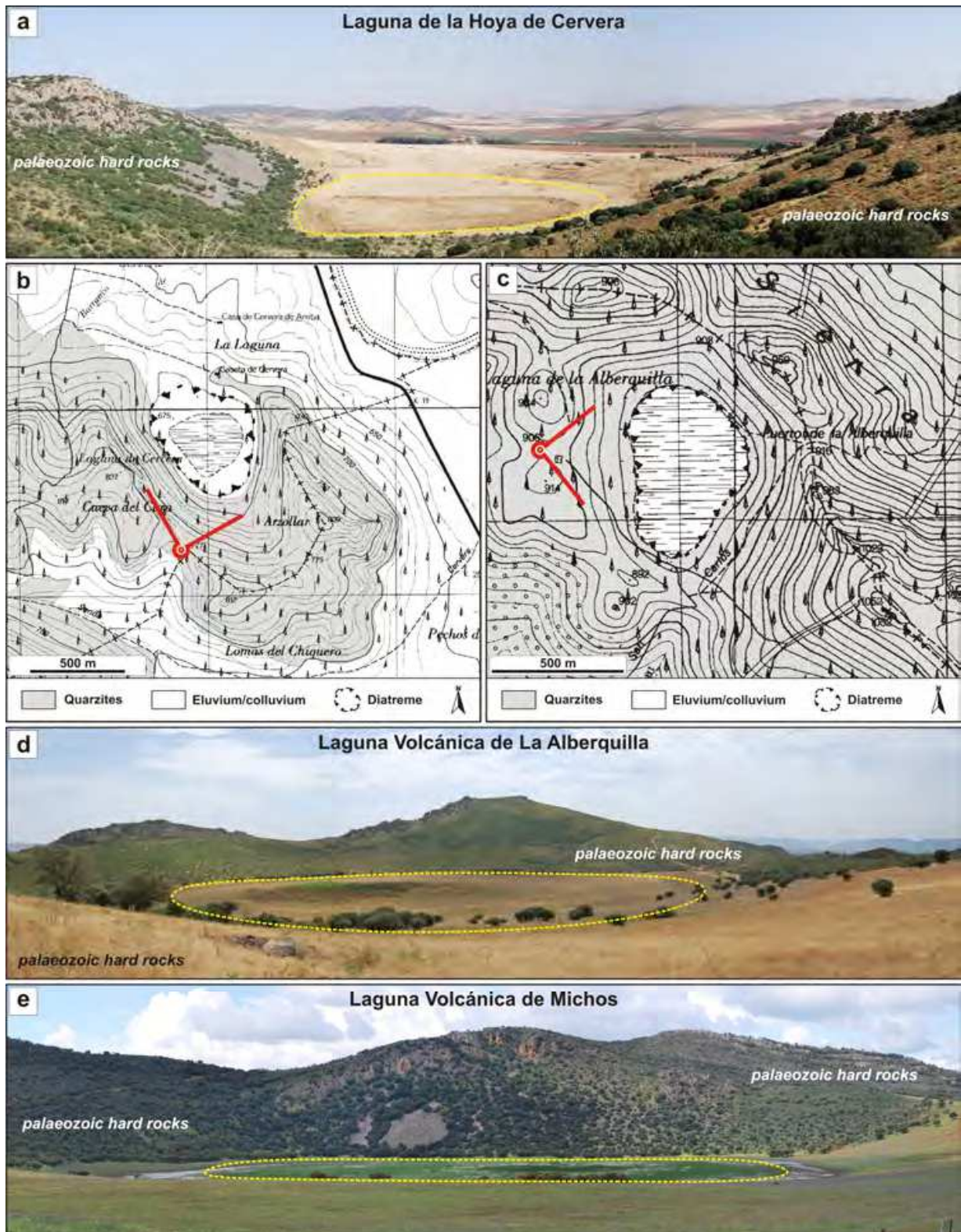


Fig. 2. Surface expression of CVF diatremes: a) general view of Hoya de la Cervera and b) geological sketch map, c) geological sketch and d) general view of Laguna de la Alberquilla, e) general view of Los Michos diatreme. Red symbol in this and other figures are outlook points from where the pictures were taken. In the yellow dashed line is indicated the rim of the eroded diatreme.

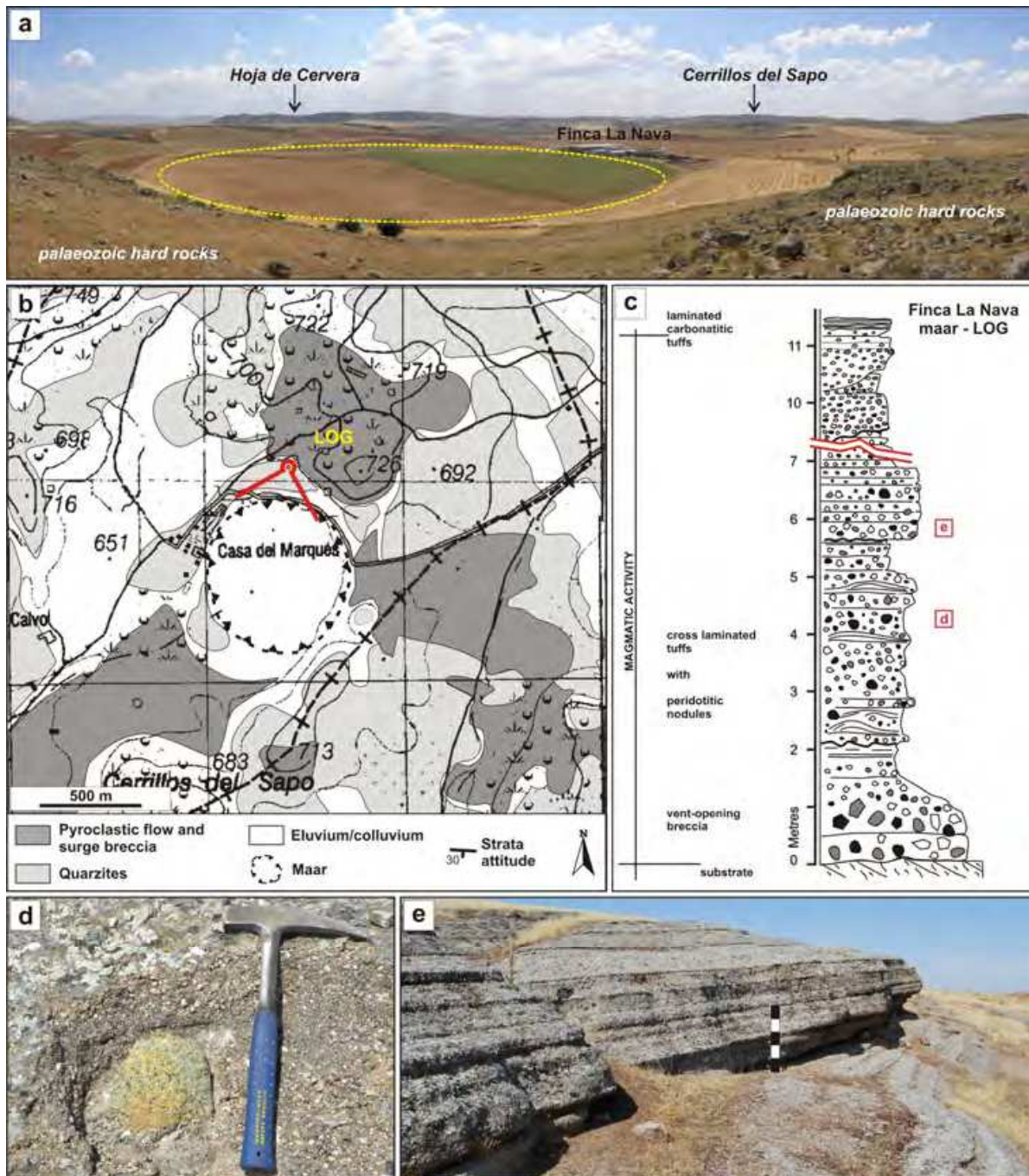
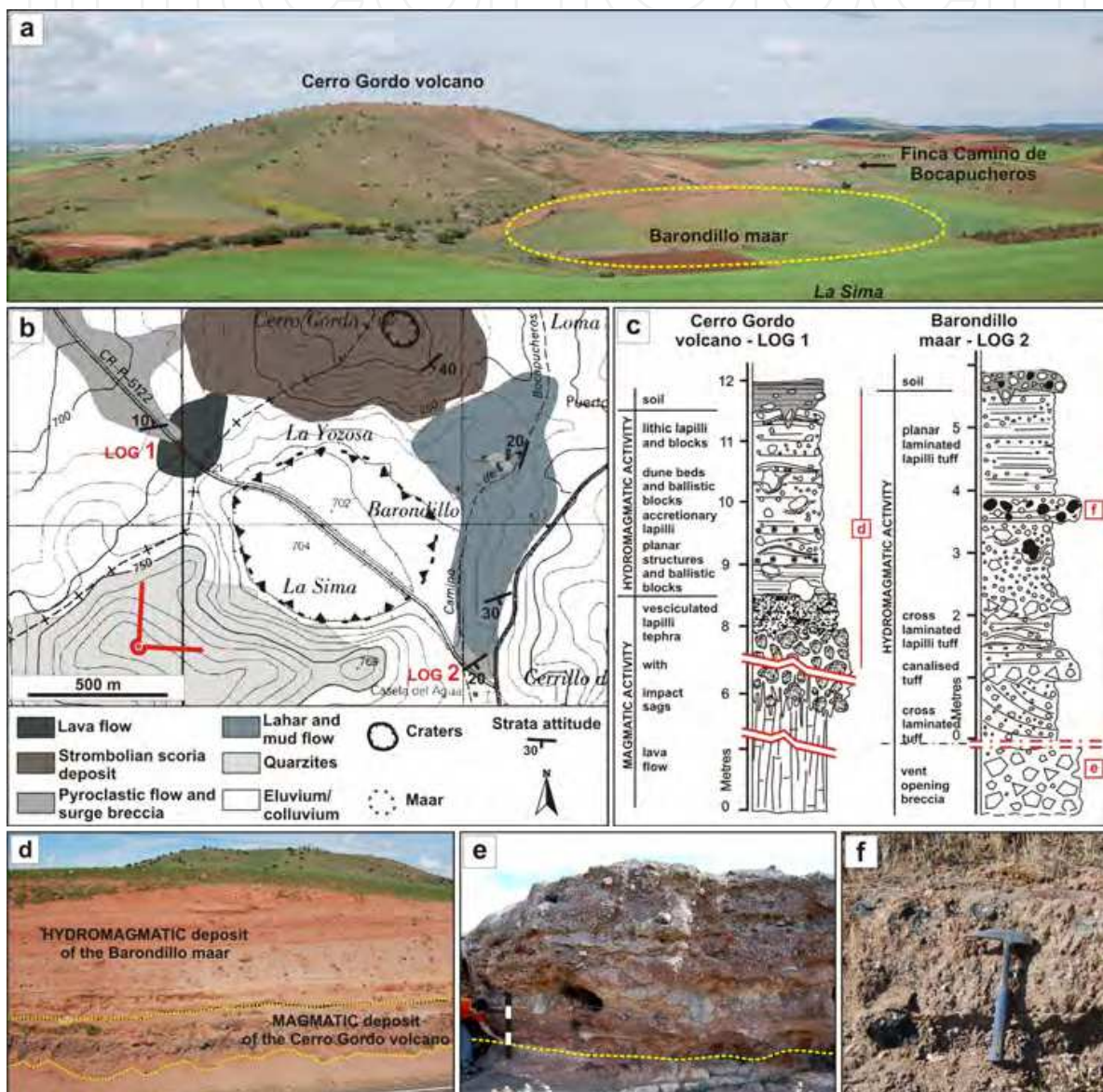


Fig. 3. a) General view of Finca la Nava maar and, on the skyline, Hoya de la Cervera and Cerrillos del Sapo indicated by an arrow, b) geological sketch of Finca la Nava maar, c) stratigraphy of La Nava volcanic products (log position located on the map and written in yellow), d) discrete mantle nodule in the La Nava tuffs (hammer is 30 cm long) and e) picture showing the intermediate part of the La Nava volcanic sequence (the bar scale is 1 m long).

Alberquilla (Figs. 1, 2c,d) is located on the escarpment of the Puertollano graben, and is part of a NW-SE elongated cluster of volcanoes, east of the village of Mestanza. The graben shoulders are made of Palaeozoic quartzite. The depression hosts a laguna at 865 m a.s.l., while the rim is at 950-1000 m a.s.l.; the shape of the depression is elliptical (500 x 300 m). The Los Michos diatreme (Figs. 1, 2e) is one of the best preserved and hosts a temporary

lake at 700 m a.s.l.. It has a diameter of about 450 m and is sharply cut through crystalline rocks. There are no above ground, pyroclastics rocks preserved around it. La Nava maar is about 1 km wide and is located on the NE side of the Río Jabalón valley, at 620 m a.s.l., and is excavated in the Palaeozoic hard-rock substrate (Figs. 1, 3). Pyroclastic rocks outcrop discontinuously around the maar, especially at the north side, where a maximum thickness of about 11 metres was observed. They are mostly roughly layered, cross-laminated strata about 7 m thick overlying 2 m thick, vent opening breccia. Vent opening breccias are pyroclastic rocks composed largely of country rock blocks (up to 80%) which are inferred to have been deposited during the initial crater formation (Stoppa, 1996).



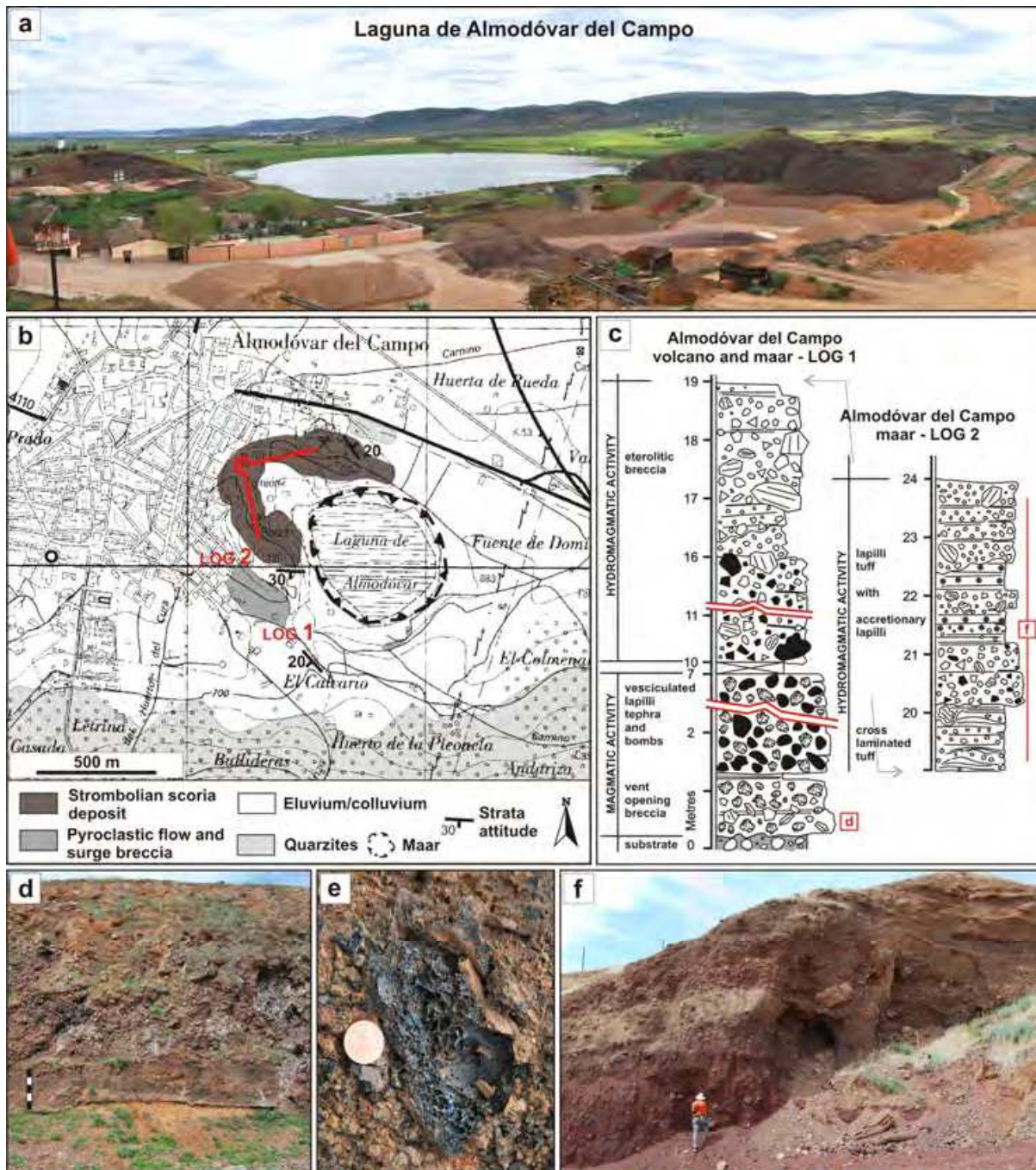


Fig. 5. Almodóvar del Campo: a) General view of Laguna de Almodóvar maar; b) geological sketch map of the area, c) stratigraphy of the volcanic sequence (logs indicated in inset b), d) Palaeosol and vent opening breccia, the bar scale = 1 metre, e) detail of vent opening breccia, showing a large mafic pumice, f) general view of the hydro-volcanic layers corresponding to the upper part of the sections of inset c, LOG 2.

Close to the top, there are about 2 m of laminated, carbonatitic tuffs containing melilitite lapilli concentric-shelled lapilli with a central kernel of amphibole and phlogopite xenocrysts or mantle nodules. Tuff layers are hardened by carbonate and show lapilli plastically moulded each other (Fig. 8). Large discrete peridotitic nodules are scattered as impacting blocks in the tuffs.

The Barondillo maar is adjacent to Cerro Gordo volcano located near La Sima volcano, currently the most significant CO₂ emission centre in CVF. This small maar, located at 700 m a.s.l., has a diameter of 80 m and is partially excavated in the quartzite of the Almagro massif (Figs. 1, 4a,b). Road-cut exposures along CR-P-5122 road, towards Valenzuela de

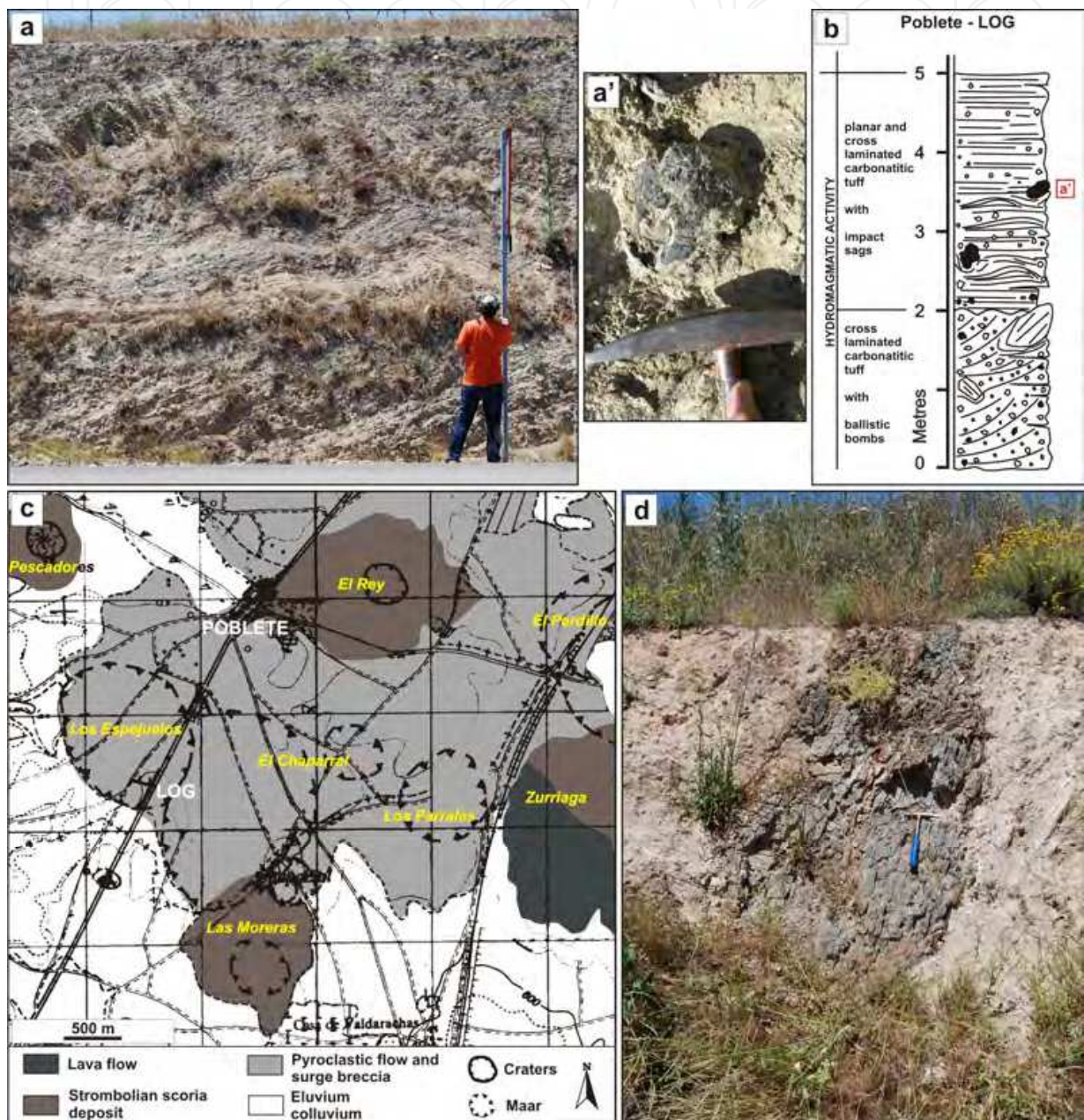


Fig. 6. Pyroclastic deposits in the Poblete area: a) carbonatite dune layers on a road cut, a') ballistic block composed of an amphibole mega-crystal, b) stratigraphy at the road cut (see map for reference), c) sketch map of the area, d) large country-rock ejecta in carbonatitic ash tuff. The names of other volcanic centres are in yellow in the sketch map.

Calatrava and near Mina de San Carlos, offer a good view of volcanic deposits (LOG 1, Fig. 4c,d). South and SW of Ciudad Real, pyroclastic units have unique carbonatitic features. They have been substantially neglected so far because not clearly related to a volcanic centre. These pyroclastic deposits are located 3 km south of the village of Poblete and close to the Los Espejuelos maar. The scoria cones of Cabezo Segura and Volcán de la Zurriaga are to the SE and SW; the maars of Hoya del Pardillo, El Chaparral and Hoya del Mortero are 2 km to the E, the small edifice of Volcán de Cabezo de Pescadores is 2 km to the NW, while a cluster of others maars and the scoria cones are located north (Fig. 6c). The exposures show lapilli tuffs and dune layers with juvenile mafic lapilli immersed in a carbonate matrix (Figs. 6a,a'). Metre-sized ballistic block of country-rocks impacted this soft substrate and produced notable impact sags (Fig. 6d). Sedimentation interference between impact blocks and carbonate layers emplacement indicate a rapid accumulation in a turbulent volcanic regime (surge). Centimetre-sized clinopyroxene crystals are scattered in the tuff. The size of the blocks suggests that the sequence is very proximal to the emission centre (Los Espejuelos?). More distal outcrops show lapilli tuffs organised in co-sets of layers with the ash matrix being composed of carbonate but large ballistic blocks are absent and only mafic bombs are visible (Fig. 6a').

5.2 Scoria cones and lava flows

The Volcán Morrón de Villamayor (Fig. 1) is associated with lava flows of olivine leucite melilitite (Humphreys et al., 2010). The vent area shows two necks having columnar jointing; the largest neck is located north and represents the highest point of the volcano at 840 m a.s.l.. The south flank of the pyroclastic edifice is covered by spatter bombs indicating a lava fountain activity. Two lava flows originated from this area and, after a short travel, flooded the area where the Cantera del Morrón quarry is located. The two lava flows have different modal composition, mostly due to abundant country rocks lithics in the lower flow and olivine in the upper flow. Columnar jointing cutting through the two lava flows indicates that they form a single cooling-unit. The pyroclastic rocks and lava flows cover about 2 km².

The Volcán Cabeza Segura II has an olivine melilitite-carbonatite and nephelinite composition (Stoppa et al., 2011). It consists of a 100 m-thick accumulation of massive or layered agglomerate that become a lapilli tuffs towards the top (Fig. 7b). Distinctive layers of inverse graded, ovoid concentric-shelled lapilli and bombs (Carracedo Sánchez et al., 2009), intercalated with undulated beds of carbonatitic lapilli tuff, occur in the middle of the volcanic pile (Stoppa et al., 2011). Towards the top there are cross-laminated, carbonate-rich beds, 20-30 cm thick (Fig. 7b,e,f). They contain melilititic lapilli with internal concentric layers of carbonatitic melilitite (Fig. 8b). Lava a few metres wide and about one metre thick lava sheets are repeated in the volcanic sequence, while a thicker tabular lava flow close the eruptive cycle. The upper part of the sequence surrounding the lava is a layered, reddened scoriaceous lapilli fall deposit with a thin palaeosol on the top.

The Cerro San Marcos (Fig. 1) is an isolated scoria cone of olivine melilitite composition. The volcano is located about 2 km south of Torralba de Calatrava. The volcanic deposit is an inverse-graded agglomerate of spherical bombs and lapilli (Fig. 8a,b) with a few cm thick ash levels. Some bombs are nucleated by large lithics. On top of the sequence, ribbon-bombs and pumiceous lapilli prevail over other pyroclasts and lithics. Torralba lapilli have distinct concentric lava shells (Fig 8a,b).

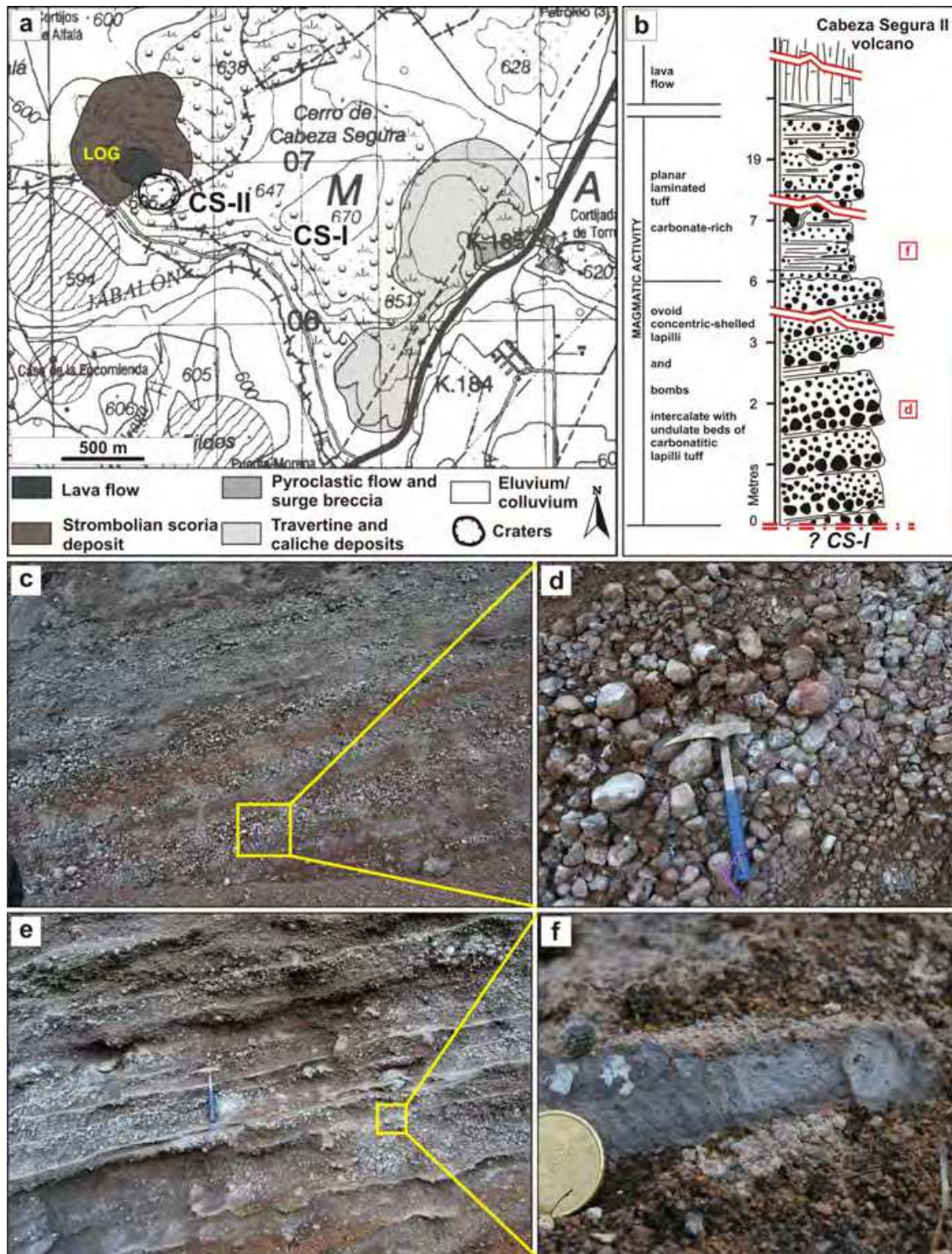


Fig. 7. Cabezo Segura II: a) geological sketch map of the area and b) stratigraphic of the volcanic sequence, c) pyroclastic layers alternating inverse graded tephra and agglomerate, d) detail of spheroidal bombs and lapilli, e) agglomerate layers with carbonatitic ash-tuff showing cross lamination and undulated layers (dunes) and f) detail of carbonatite tuff.

6. Features of CVF pyroclastites

6.1 Lapilli

Concentric-shelled lapilli are juvenile pyroclasts specifically associated with maar/diatreme deposits as discussed in a number of study to which we remand for details (Junqueira-Brod, 1999; Mitchell, 1997; Stoppa & Wolley, 1997). These peculiar lapilli have been described from recent African and other European provinces (Bailey, 1989; Bednarz & Schmincke, 1990; Hay, 1978; Lloyd, 1985; Lloyd et al., 2002; Riley et al., 1996; Stachel et al., 1994; Stoppa et al., 2003). Stoppa & Principe 1998) described similar lapilli in maar deposit at Monte Vulture Italy and defined them "concentric-shelled lapilli". Concentric-shelled lapilli are associated with ultra-alkaline rocks such as carbonatites and melilitites found in intracratonic settings and, to our knowledge, they have not been found in any other volcanic rock association or tectonic settings (Calliccoat et al., 2008; Cloos, 1941; Ferguson et al., 1973; Gurney et al., 1991; Keller, 1981; Mitchell, 1997; Stoppa & Lupini, 1993; Stoppa, 1996). They have been interpreted to have formed as sub-volcanic, fluid, "spinning droplets" in a conduit by Junqueira-Brod et al. (1999). A similar model has been discussed by Stoppa et al., at CVF (2011).

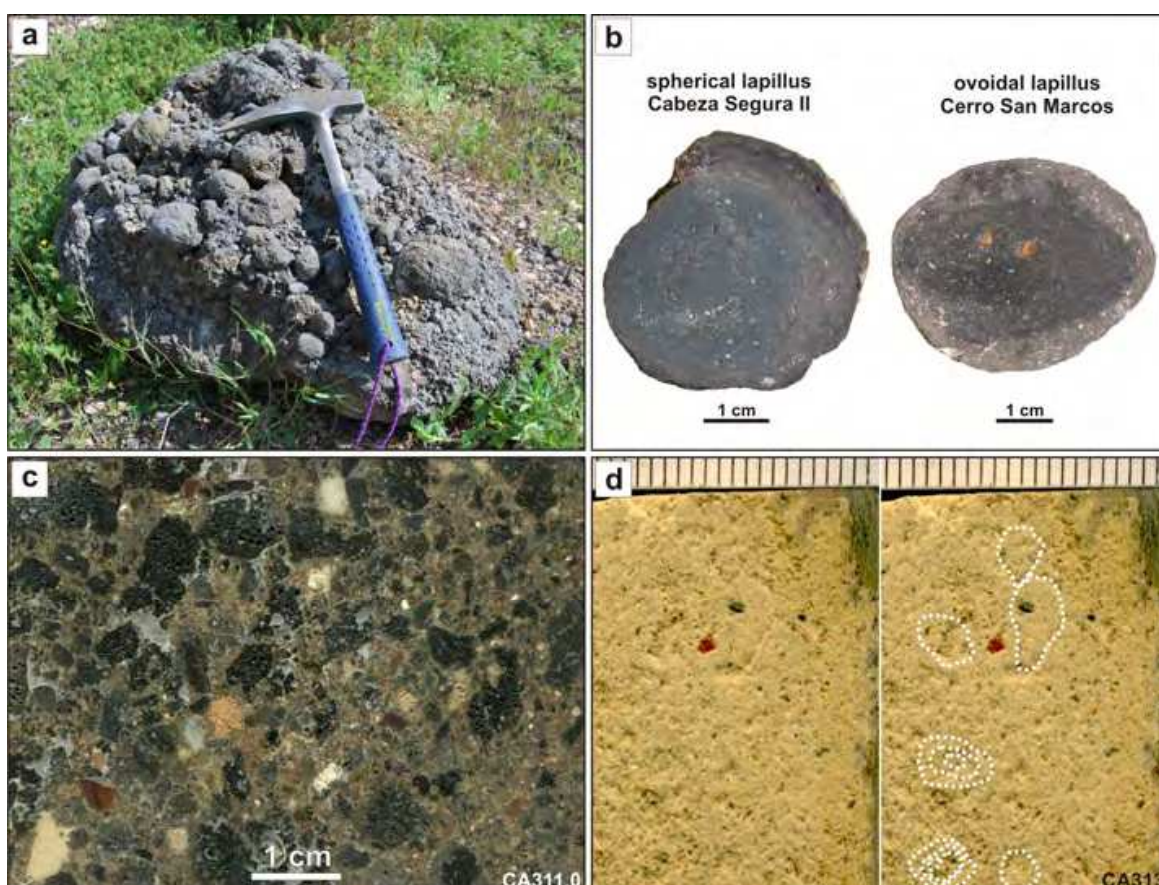


Fig. 8. a) Agglomerate of spheroidal lapilli from Cerro San Marcos-Torralba volcano; b) sectioned concentric-shelled lapilli from CVF (Stoppa et al., 2011), c) Laguna Blanca tuff: juvenile lapilli and angular crustal lithics suspended in a carbonate matrix, d) carbonatite ash-tuff showing teardrops lapilli.

Concentric-shelled lapilli invariably cored by mantle material, xenocryst or peridotite nodule, are typical of the CVF pyroclastic rocks. This structure has been observed also in bombs which have a larger mantle nodule in the core (Carracedo Sánchez et al., 2009). They occur in maar deposits such as Almodóvar del Campo, la Nava, La Hoya de la Cervera, Laguna Blanca as well as scoria cone such as Cabeza Segura II, Cerro Gordo and Cerro San Marcos (Fig. 8a,b; Plate 2a,b in Stoppa et al., 2011). The lapilli shells are formed by densely packed, welded, glassy spherules of melilitite containing microphenocrysts of olivine, clinopyroxene, melilite, nepheline, h a yne, opaques, plus glass. In some spherules, melilite laths are abundant and concentrically arranged around a core which is a mafic xenocrysts (Fig. 9a,b). Concentric-shelled lapilli at the CVF contain up to 50% of primary carbonate in the form of coalescent globules having menisci necks and amoeboid shape which testify segregation under liquid condition (Fig. 9c,d) (Rosatelli et al., 2007). Primary features of igneous carbonate are largely targeted by geochemical studies and have been the specific object of several papers (e.g., Rosatelli et al., 2010; Stoppa et al., 2005). Detailed geochemical studies are outside the aim of this paper and the textural criteria, well known from previous papers, are used to assess a primary igneous origin of carbonates. Primary calcite composition in the CVF lapilli is given in Stoppa et al. (2011).

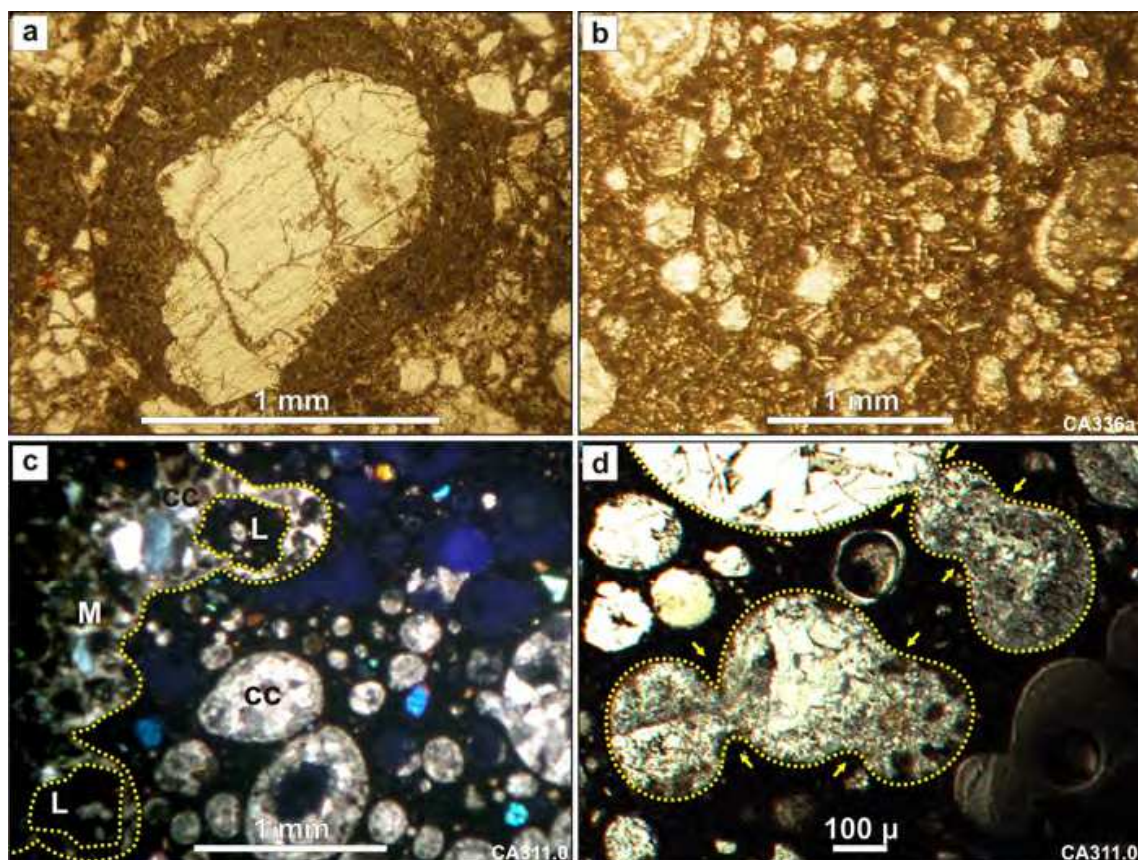


Fig. 9. a) Hoya de la Cervera melilitite cored ash-sized lapillus in thin section, b) Cerro Gordo melilitite ash-sized lapillus showing concentric internal structure, c) and d) Laguna Blanca tuff in thin section, melilitite lapillus-carbonatitic matrix contact and coalescent calcite globules preserving menisci (indicated by yellow arrows). Key symbols: CC - carbonatitic matrix; L - lapillus; M - matrix.

6.2 Matrix

At CVF the matrix of concentric-shelled lapilli tuff is composed of particles having distinctive morphology and arrangements which are shown in Fig. 9. We consider as matrix the <2 mm clastic component of tuffs. At CVF, ash-sized particles are very often composed of turbid, micro or cryptocrystalline calcite. Ash-sized particles structure, have often with two or more concentric shells, shells, resembling that of the lapilli irrespectively of the size (Fig. 8c,d). Their sub-spherical shape and "teardrops" reveals that they quenched from a melt under surface-tension condition (Keller, 1981). In spite of the strong agglutination and compaction the faint contours of the spherules can be easily distinguished (Fig. 9a,b). Carbonate spherules can be in contact or moulded with melilitite spherules.

The interstices among larger particles, which are in general melilitites, are filled by progressively smaller, densely packed spherules which are in general carbonatitic. Intragranular spaces are filled by amoeboid turbid cryptocrystalline carbonate (micrite). Similar textural occurrences at CVF and elsewhere were proven to be primary igneous or re-crystallised primary carbonate, by geochemistry (Hay, 1978; Stoppa & Lupini, 1993; Stoppa et al., 2005; Stoppa et al., 2011). Calcite globules in the melilitites spherules are broken towards their host spherule rim, indicating that their content was poured out and incorporated in the matrix, which is in fact composed of smaller melilititic fragments and carbonate having very similar composition with respect to those in the spherules (Fig. 9g). Patches of mosaic textured limpid carbonate and vugs with sparitic calcite are also present and represent secondary calcite and cement.

6.3 Dry and wet pyroclastic deposits

Dry-magmatic deposits at CVF are composed of juvenile, spherical or ovoidal, concentric-shelled lapilli and bomb and/or high vesiculated fragments, variable in size. They generally form agglomerate or lapilli layers devoided in fine-ash component. Presence of abundant lithics gives to many deposits a brecciated aspect (vent opening facies). These "breccia" layers are interbedded by hardened carbonate-rich lapilli tuffs. The lapilli-tuffs have compacted matrices formed by isotropic or nucleated spherules of carbonatites and melilitite which can maintain a spherical shape or mould each other (Fig. 9). This matrix structure is conducive of dry high temperature deposition at least able to produce welding and agglutination of smaller spherules in the matrix. Deposits made by these juvenile pyroclasts are found at CVF both in the maars and the scoria cone. Layer attitude, volcano sedimentary structures and texture indicate they have been deposited mainly by pyroclastic surge and ballistic fall related to moderate to strong vulcanian to strombolian activity.

Hydro-volcanic deposits in the CVF are dominated by lava blocks interbedded with vesiculated fine-ash matrix, where vesicles are probably produced by expansion of water vapour in a muddy matrix, and other cold-emplaced, wet pyroclastic deposits. Microscopic features reveal abundance of sharp-cut glass fragments, specific alteration and zeolite cement related to interaction with a magma/water interaction. In addition, condensed water is reflected by mud-flows formation and fall-out deposits composed of accretionary lapilli that often plastically mould each other. Dominant emplacement mechanism is surge, wet pyroclastic flow and mud flow possibly linked to moderate collapse of hydrovolcanic strombolian column.

7. Discussion

7.1 Sub-surface vs surface fragmentation mechanism

The CVF provides the opportunity to highlight and to contrast different mechanisms of magma fragmentation associated to maar-related pyroclasts including deep-seated gas exsolution, sub-surface magma vesiculation and superficial hydrovolcanic phenomena. Juvenile pyroclasts at CVF varies from highly vesiculated scorias (pumices) to mostly unvesiculated concentric-shelled bombs, lapilli and ash sized spherules. These juvenile pyroclasts have morphology and structure indicating they reached the final shape when still plastic and hot. This process has to occur at magmatic temperature as it involves co-eruptive carbonatite and melilitite, the latter composition having high liquidus temperature (Brey and Green, 1977). A high degree of vesiculation indicate high content of juvenile volatiles and possible dry magmatic fragmentation in sub-surface condition (e.g., Mattsson & Tripoli, 2011) but unvesiculated concentric-shelled lapilli fragments require different origin.

Despite the fact that crustal debris far outweighs the proportion of mantle fragments in the CVF pyroclastic rocks, the concentric-shelled pyroclasts have only mafic crystal or peridotite fragment as kernels (Fig. 9a). Clearly, at the CVF the concentric lapilli were formed before crustal fragment incorporation in the rising magma. They formed before that other process may modify eruptive style, as they are found in both maar and scoria cones. Lack of vesicularity need not necessarily indicate that their magma was low in initial juvenile volatile component, but rather that the juvenile gases have been concentrated as the fluidising medium in the subvolcanic genetic environments after magma fragmentation (Stoppa et al., 2011 and references therein).

The shell structure suggests that the lapilli do not form by separation of discrete lumps of melt. They are obviously produced by agglutination of very small spherules of melt (Stoppa et al., 2011) - a mechanism which favours the CO₂ exsolution due to the very large surface of the spherules with respects the lapilli (Junqueira-Brod et al., 1999; Stoppa et al., 2003). Concentric-shelled lapilli found into maars are important because they represent the interface between the erupting magma and the volatile component. This is germane to the concept of sub volcanic fluidisation of tuffisite which implies pristine exsolution of large amount of juvenile gases (see discussion in Lloyd & Stoppa, 2003).

The CVF concentric-shelled lapilli and spherules are completely different from particles produced by Zimanowski et al. (1997) experiment because experimental spherules lack concentric structure and a core. Instead, Kelvin-Helmholtz instability is produced by liquids having different densities moving at various speeds. The Kelvin-Helmholtz instability occurs when shear is present within a continuous fluid, or when there is sufficient velocity difference across the interface between two fluids. This can start lapilli formation in a conduit where carbonatite and silicate liquids may be physically separated according their immiscibility predicted by experiments of Kjarsgaard & Hamilton (1989) and formed according the "spin-lapilli" model proposed by Junqueira-Brod et al. (1999). Textural study of tuffisites and related extrusive deposits suggest that the immiscible carbonate fraction can be incorporated in the lapilli or form the external carbonatite layers of them and the rest sprayed as ash-sized fragments and spherules (Stoppa et al., 2003). Lapilli in tuffisite and related extrusive deposits are typically shelled by a smooth cover of very fine-grained

carbonate (Carracedo Sánchez et al., 2009; Stoppa & Woolley, 1997). This may explain why concentric shelled lapilli are restricted to rocks containing igneous carbonate and spinning lapilli are found also deep-inside diatremes. Notably, concentric-lapilli and dense welded matrix composed of melt spherules are not found in natural hydrovolcanic tuffs.

Concentric-shelled lapilli and accretionary lapilli formation require totally different genetic conditions. Accretionary lapilli have low density (1.2 gr/cm³, Schumacher & Schmincke, 1991) and can be sustained in suspension by vigorous convective cells in the eruptive column. Concentric lapilli and bombs, have much higher density and formation in the same condition of accretionary lapilli is unrealistic. Stoppa et al. (2011) report terminal velocity (V_t) curves built using measured density and size for accretionary lapilli and concentric-shelled lapilli from Calatrava and Monte Vulture Italy. They argue that concentric shelled lapilli and bombs cannot be generated in the convective region of a volcanic plume as are accretionary lapilli and require V_t similar to that required to transport mantle nodules. Owing their deep origin it is clear that concentric- shelled lapilli and mantle nodules are not carried to the surface by hydrovolcanism.

7.2 Role of H₂O

There is a general agreement in the previous Spanish literature that CVF eruption style was influenced by heterogeneous ground permeability producing interaction of a low-viscosity, high-temperature melt feeding system with a spatially restricted aquifer, i.e. hydrovolcanism (Sheridan & Wohletz, 1983). If groundwater-flow rates are insufficient to maintain persistent hydro-volcanic eruption, activity evolves towards strombolian activity or hawaiian fountains and lava flows (Peinado et al., 2009). We note, that in CVF this may be restricted to high hydraulic conductivity facies in the basin sedimentary infilling as there are no remarks of "impure coolants" such as wet sediments in the deposits. In addition, hydrovolcanic activity often ends the eruptions (e.g., Almodóvar del Campo, Fig. 5c-h) suggesting that water entered the conduit late owing the dropping of pressure in the conduit itself. In these rocks, hydrous phases such as phlogopite and amphibole indicate minor juvenile H₂O as well. It was argued that ultramafic melts (e.g., kimberlite magma) may contain high amount of juvenile H₂O rather than CO₂. In the latter case, it is important to note that the presence of juvenile water, inferred for kimberlitic magma, which also contain spin-lapilli and abundant mantle nodules but not concentric-shelled lapilli, does not affect CO₂-triggered diatresis and cannot be confused with hydrovolcanic feature because it does not imply a contribution of external water.

7.3 Role of CO₂

There is general consensus that carbonatite and associated silicate melts (foidite melilitite) are near-primary melts generated in the mantle (e.g., Bailey, 1993). Carbon dioxide is the major volatile phase in carbonatites and melilitites where concentric-shelled lapilli have been reported (Junquera-Brod et al., 1999; Lloyd & Stoppa, 2003). Low viscosity, high temperature, ultramafic carbonate-rich magma needs rapid ascent to erupt both silicate liquid and mantle xenoliths from the asthenospheric depths (Humphreys et al., 2010). A conduit flow mechanism is sufficient; diapiric ascent and melt percolation are too slow (Anderson, 1979; Spera, 1987). Initial carbonatitic percolating melts start out with high CO₂ and those that follow an eruptive adiabat will exsolve gases and pass through Olafsson & Eggler's (1983) carbonate-out boundary, leading to massive CO₂ exsolution (Bailey, 1985). At

the same time, the melt temperature approaches the liquidus where major gas foaming (CO_2) occurs. In the CO_2 diatresis model of Bailey (1985), foaming at mantle depth in near conjunction with the carbonate-out boundary has three effects: (i) production of minute spherules when melt is fragmented; (ii) very rapid quenching of these spherules, (iii) concentration of the juvenile gases largely as the fluidising medium. If a firm link between deep-seated CO_2 , diatresis and tuffisite formation is established, no other model is required to explain the formation of these maars. In fact, the diatresis phenomena responsible for diatrema formation is well able to excavate the maar itself and to fragmentate the country rocks. This hypotheses confirmed by several studies on maar associated to ultra-alkaline melts poses the problem to classify this peculiar volcanic activity which may be considered a form of strombolian to sub-plinian activity modified by physical proprieties of CO_2 instead of H_2O vapour/gas. High density of CO_2 probably prevents the formation of high buoyant volcanic column and favours later expansion of surges. Diatrema formation is also important in the formation of a maar crater which is considered here the superficial expression of the growing of a diatrema beneath it. We suggest the term “diatremic eruption” for this kind of CO_2 related maar formation.

8. Conclusions

1. At CVF, hydrovolcanic deposits are clearly distinguishable from magmatic deposits in terms of volcano sedimentary structures, texture, grain-size and lapilli key features. The accretionary lapilli found in hydro-volcanic deposit originate in the convective region of an eruptive column by wet ash-particles accretion and require passage from vapour to condensed water. The formation of concentric-shelled lapilli, which are typical of CVF maars and scoria cones as well as many other carbonatitic maars, cannot be realistic in a volcanic column for these high density, high temperature pyroclasts.
2. Concentric-shelled lapilli are ubiquitous; accretionary lapilli are limited to hydrovolcanic deposit. We deduce that hydrovolcanism at CVF was neither necessary, nor sufficient condition for concentric shelled lapilli. In fact, the concentric-shelled lapilli formation cannot be explained by hydrovolcanic process.
3. Highly vesiculated fragments in CVF maars indicate abundant presence of juvenile volatiles. On the other hand, agglutinated spherule of melilitite and carbonatite forming concentric shells around a mantle-rock kernel are considered as evidence of deep seated magma fragmentation in a diatrema. The coincidence of their sampling depth of the mantle kernel with the depth of CO_2 exolution (diatresis) strongly suggest that the magma propulsion and eruption was triggered and sustained by mantle CO_2 and not juvenile or external water.
4. We interpret the carbonate matrix of the CVF tuffs as the quench of an immiscible carbonatitic liquid separated by the eruptive carbonatitic melilitites magma. The matrix is composed of carbonatite spherules sprayed directly as a physically separated magmatic liquid. This process is documented by carbonatite liquid blebs in the melilitite pyroclasts.
5. CO_2 diffused and climatic emissions are at present the most notable activity in CVF. We argue that due to the carbonatitic nature of CFV magma CO_2 was the dominant gas in the volcanic system. Diatresis is here preferred as boosting maar formation as also suggested by Mattsson & Tripoli (2011). Maar formation at CVF is interpreted as mainly

due to magmatic mechanisms. Passage from maar stage to strombolian/effusive stage is interpreted as the consequence of the dropping of volatiles concentrated on the top of the magmatic column in the conduit.

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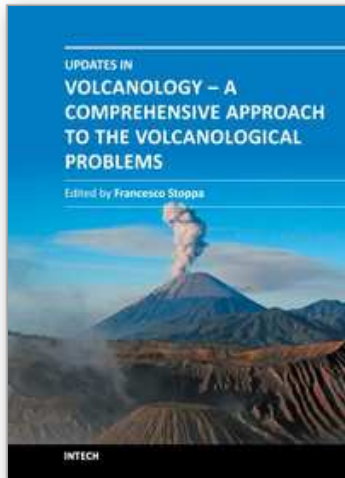
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