

The hydrothermal system prior to a phreatic eruption: The case of the 1873 eruption at La Fossa (Vulcano Island, Italy)

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ABSTRACT

Steam-driven eruptions, such as phreatic and hydrothermal explosions, likely represent some of the most frequent eruptive styles at stratovolcanoes. However, deciphering their timing, dynamics, and underlying mechanisms from eruptive deposits remains a significant challenge, even when, although such deposits are thin, altered, poorly dispersed, and strongly altered, they have not been removed by erosion. Lithic fragments from these eruptions can however preserve valuable information on lithology, pre-eruptive conditions, and the physico-chemical state of the disrupted aquifer. Here we examine the lithic fragments of the “Breccia De Fiore” deposit, emplaced by multiple explosions during a 44-day-long 1873 eruptive phase at La Fossa di Vulcano (Italy). The deposit consists of five poorly sorted lapilli tuff to tuff breccia beds, rich in hydrothermally altered lithics, lacking juvenile material. Petrographic, mineralogical, and geochemical analyses reveal a lithology dominated by silicic and advanced argillic altered particles (44–60 % vol%), together with 23–31 vol% devitrified quartz-bearing fragments hosting vapour-rich fluid inclusions, and 7–27 vol% unaltered material. These features suggest the disruption of a shallow, acid-sulphate hydrothermal system, a rhyolitic plug occupying the shallow crater-conduit system, and unaltered adjacent lithologies. Quartz textures and fluid inclusions point to vapour-dominated conditions and explosions driven by episodic failure of sealed vapour-pockets within the shallow hydrothermal system, repeatedly recharged by magmatic gas flux. We interpret the 1873 steam-driven eruptions as a series of phreatic explosions occurring in a shallow hydrothermal system under conditions of alteration-driven permeability reduction and magmatic gas and heat input. These results underscore the role of alteration and sustained fluid supply into the hydrothermal system in driving prolonged, non-magmatic explosive activity at Vulcano.

1. Introduction

Steam-driven eruptions, encompassing both phreatic and hydrothermal types, are among the most frequent eruptive phenomena observed at stratovolcanoes and caldera systems (Montanaro et al., 2022). Phreatic eruptions occur when shallow groundwater or hydrothermal fluids within an aquifer are rapidly converted to steam by an influx of magmatic heat, causing them to erupt explosively without the incorporation of molten material in the ejected products (Barberi, 1992; Marini et al., 1993; Browne and Lawless, 2001; Stix and de Moor, 2018; Rosi et al., 2018; Gallagher et al., 2020; Montanaro et al., 2022). In

contrast, hydrothermal eruptions are caused by the relatively rapid boiling and discharge of hot, pressurised fluids within a hydrothermal aquifer, often triggered by a drop in confining pressure, and usually occur without direct magmatic input (Mastin, 1995; Browne and Lawless, 2001; Thiéry and Mercury, 2009; Montanaro et al., 2022).

Although often smaller than magmatic eruptions, both types can be highly destructive, as tragically demonstrated by the Ontake (2014) and Whakaari/White Island (2019) eruptions, which caused 63 and 21 fatalities, respectively (Tsunematsu et al., 2016; Dempsey et al., 2020; Miyagi et al., 2020; Burton et al., 2021).

A key factor influencing the likelihood of steam-driven eruptions is

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the effect of hydrothermal alteration. This widespread process occurs in active volcanic systems where circulating hydrothermal fluids—comprising hot mixtures of meteoric water, seawater, and magmatic fluids including gases or supercritical fluids (Giggenbach, 1997; Sharma and Srivastava, 2014; Stix and de Moor, 2018)—chemically and texturally alter the host rocks, modifying their physical and mechanical properties (McPhie, 1993; Browne, 1978; Guilbert and Park, 1986; Pirajno, 2009; Darmawan et al., 2022; Heap et al., 2021, 2022; Poganj et al., 2025). When hydrothermal alteration leads to the precipitation of secondary minerals, fractures and pore spaces become increasingly infilled with minerals such as sulphates, clays, elemental sulphur, and silica (Gurioli et al., 2012; Sutawidjaja et al., 2013; Heap et al., 2019; Gaete et al., 2020; Mick et al., 2021), drastically reducing the permeability of the host rocks (Horwell et al., 2013; Heap et al., 2022; Montanaro et al., 2022). This hinders fluid migration, promoting the build-up of fluid pressurisation that, over time, may “prime” shallow aquifers for sudden failure (Christenson et al., 2010; Mayer et al., 2016; De Moor et al., 2019; Heap et al., 2019; Kennedy et al., 2020; Mick et al., 2021; Montanaro et al., 2022).

Several studies have shown that hydrothermally altered lithic particles within eruptive deposits provide valuable insights into the lithology of the disrupted hydrothermal aquifer. They can also reveal key information about the physico-chemical conditions of involved fluids, the mechanisms that primed the aquifer for explosive failure, and the role played by magmatic fluids in heating and pressurising the aquifer (Mastin, 1991; Browne and Lawless, 2001; Gallagher et al., 2020; Miyagi et al., 2020; Montanaro et al., 2021; Minami et al., 2022; Minami and Geshi, 2025).

At Vulcano Island (Italy), evidence of an active magmatic-hydrothermal system can be observed within the La Fossa Caldera (Fulignati et al., 1998), where intense hydrothermal alteration, a high temperature fumarolic field at the summit of the La Fossa volcano, and widespread soil degassing across its crater and at the base of the cone are well documented (Chiodini et al., 1995, 1996; Fulignati et al., 1998; Granieri et al., 2006; Paonita et al., 2013). Although no explosive eruptions have occurred since the early 20th century, several unrest episodes—the most recent occurred between 2021 and 2023—have been linked to changes in this system (Badalamenti et al., 1988; Barberi et al., 1991; Chiodini et al., 1995; Harris et al., 2012; Capasso et al., 2014; Paonita et al., 2013; Aiuppa et al., 2022; Federico et al., 2023; Di Traglia et al., 2023). Similar instabilities, often recognised in hindsight, have preceded phreatic eruptions at other volcanoes (Kato et al., 2015; Geshi and Itoh, 2018; Heap et al., 2019; Dempsey et al., 2020; Kennedy et al., 2020; Kametani et al., 2021; Mick et al., 2021), highlighting the need for careful studies and interpretation of monitoring data.

Historical records and stratigraphic studies indicate that Vulcano Island experienced at least three phreatic eruptions from La Fossa volcano since 900 CE: the Breccia di Commenda (1250–1300 CE), Forgia 1 (1444 CE), and Forgia 2 (1444–1450 CE) eruptions (Gurioli et al., 2012; Rosi et al., 2018; Di Traglia et al., 2013, 2024). Additional episodes of explosive activity from La Fossa occurred in 1873, 1878/1879, and 1886, culminating in the Vulcanian eruption of 1888–1890—the most recent eruptive phase (Mercalli, 1886; Mercalli and Silvestri, 1891; De Fiore, 1922; Di Traglia et al., 2024; Giansante et al., 2025). The deposits and the dynamics of the 1873 activity were recently discussed in Giansante et al. (2025). These authors named the deposits, mainly dispersed along the northwestern flank of La Fossa, as “Breccia De Fiore”, and interpreted them as the result of a complex eruptive activity characterised by multiple phreatic explosions.

In this study, we investigate the Breccia De Fiore deposits through petrographic and geochemical analyses of the erupted material, with the aim of characterising its composition and the nature of hydrothermal alteration affecting the clasts. The dataset is used to infer the pre-eruptive conditions of the magmatic-hydrothermal system and to identify possible priming mechanisms, contributing to a more comprehensive assessment of phreatic eruption hazards at Vulcano Island.

2. Geological background

2.1. Geological and volcanological framework

Vulcano Island (38°40'N, 14°96'E, 21 km², 500 m a.s.l.) is an active volcanic system of the Aeolian Archipelago in the Southern Tyrrhenian Sea, Italy (Fig. 1a). Subaerial activity started about 120 ky, characterised by both effusive and explosive eruptions from different eruptive centres, interrupted by quiescence periods (Keller, 1980; Frazzetta et al., 1983; De Astis et al., 2013). The activity progressively migrated toward N, strongly controlled by N-S to NNW-SSE extensional and strike-slip structures (Barberi, 1992; Ventura, 2013; Ruch et al., 2016).

The La Fossa composite volcano (391 m a.s.l.), along with the cone of Vulcanello (123 m a.s.l.), is the most recent volcanic centre on the island. It formed over the last 5.5 ka in the northern sector of the island, within the La Fossa Caldera (Frazzetta et al., 1983; Casalbore et al., 2019; Fig. 1a). Eruptive activity ranged from explosive (Vulcanian, phreatomagmatic/phreatic, Strombolian, sub-Plinian) to effusive (Keller, 1980; Frazzetta et al., 1983, 1984; De Astis et al., 2013; Di Traglia et al., 2013, 2024; Selva et al., 2020), producing latitic to rhyolitic and minor shoshonitic products (Keller, 1980; Frazzetta et al., 1983; Gioncada et al., 2003; Boyce et al., 2007; De Astis et al., 2013; Fusillo et al., 2015; Costa et al., 2020).

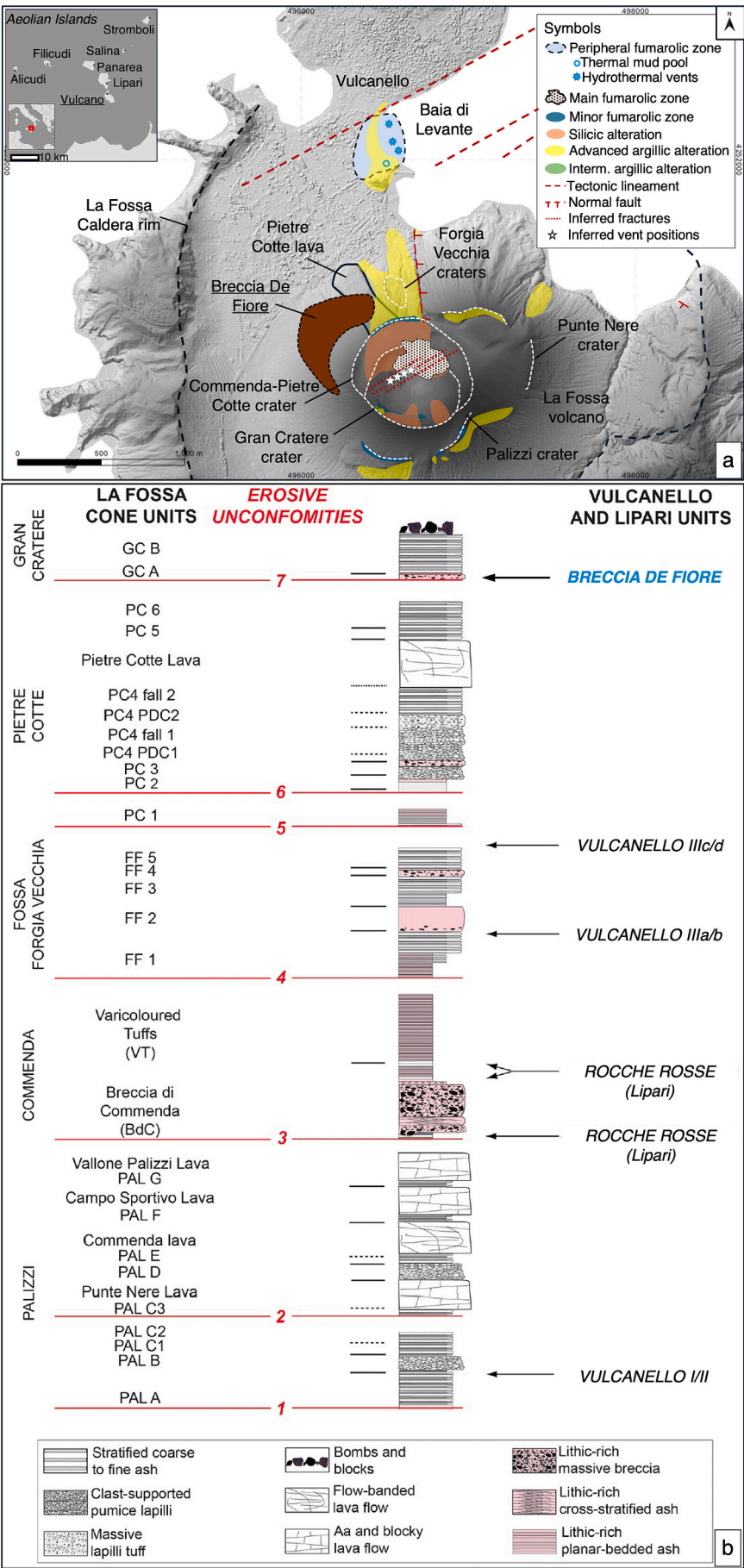
The eruptive history of La Fossa has been thoroughly described by De Astis et al. (2013) and Di Traglia et al. (2013). The post-900 CE stratigraphy has been recently reassessed by Di Traglia et al. (2024), who sub-divided it into five eruptive units: Palizzi, Commenda, Fossa-Forgia Vecchia, Pietre Cotte, and Gran Cratere, separated by four major erosional unconformities (Fig. 1b).

The Palizzi unit (900 CE–13th century) is exposed on the northern and southern flanks of the cone and includes seven sub-units (PAL A to PAL G), composed mainly of dark, parallel-bedded ash layers and two coarse lapilli beds, produced during four explosive phases (Di Traglia et al., 2024). This unit also includes several lava flows: the trachytic Punte Nere (1000–1170 CE), the rhyolitic Commenda lava (1150–1350 CE), the trachytic Campo Sportivo lava (undated), and the trachytic Palizzi lava (1240–1300 CE; Gurioli et al., 2012; Rosi et al., 2018; Di Traglia et al., 2024).

The Commenda unit (1240–1300? CE) includes the Breccia di Commenda deposit (1240–1300 CE) interpreted as the largest phreatic eruption in Vulcano's recent history, with an estimated volume exceeding 2×10^6 m³ (Gurioli et al., 2012; Rosi et al., 2018; Di Traglia et al., 2024). This lithic-rich deposit comprises pyroclastic density current (PDC) deposits, minor fallout layers, and ballistic fragments (Gurioli et al., 2012; Rosi et al., 2018). The Breccia di Commenda deposit is overlain by stratified, reddish ashfall layers known as the “Tufi Varicolori” (Varicoloured Tuffs; Frazzetta et al., 1983; Capaccioni and Coniglio, 1995; Dellino et al., 2011; Rosi et al., 2018).

The Fossa-Forgia Vecchia unit (1403?–1550 CE) is characterised by alternating phreatic and magmatic eruptions, following a quiescence period marked by an erosional unconformity (EU4 in Fig. 1b; Di Traglia et al., 2024). It includes phreatic breccia deposits from the FF2 (1444 CE) and FF4 (1444–1550 CE) eruptions, associated with the Forgia Vecchia craters located on the northern upper flank of the La Fossa cone (Fig. 1a, b; Di Traglia et al., 2024).

The Pietre Cotte unit (1631–1786 CE) lies above either an erosional unconformity (EU5 in Fig. 1b) or on top of a 3–7 m thick sequence of reworked volcanoclastic material, indicating several decades of quiescence (Di Traglia et al., 2024). The sequence comprises at least six eruptive phases, beginning with the southward-dispersed PC1 ash layer. The subsequent deposits (PC 2–PC 6) include fallout and PDC, pumice- and obsidian-rich deposits, showing variable dispersal directions and multiple erosional surfaces. The thickest and most complete exposures are found along the walls of the 1888–1890 crater (Di Traglia et al., 2024). The sequence is capped by the Pietre Cotte rhyolitic lava flow,



(caption on next page)

Fig. 1. a) Map of the northern sector of Vulcano Island (Aeolian archipelago, southern Tyrrhenian Sea, Italy) showing the La Fossa volcano within the La Fossa Caldera. The map identifies the main crater (Gran Cratere) and older craters of Commenda-Pietre Cotte, Forgia Vecchia (two lateral craters), Palizzi, and Punte Nere. Major fumarolic zones within the crater (high-temperature field) and peripheral emissions at Baia di Levante are shown. The Pietre Cotte lava flow is also mapped. The location of the Breccia De Fiore deposit and the inferred vent(s) responsible for its emplacement (white stars) are shown. Zones of hydrothermal alteration within the La Fossa Caldera are indicated: silicic alteration (orange), advanced argillic alteration (yellow), and intermediate argillic (green; Fulignati et al., 1998; Boyce et al., 2007). The main structural and tectonic features are also traced (De Astis et al., 2013); **b)** Stratigraphic succession of La Fossa volcano (last 900 years) characterised by four eruptive units: Palizzi (900 CE–13th century), Commenda (1240–1300? CE), Fossa-Forgia Vecchia 1403?–1550 CE), Pietre Cotte (1631–1786 CE), and Gran Cratere (1786–1890 CE), separated by erosive unconformities (in red; modified from Di Traglia et al., 2024). The Palizzi unit includes seven sub-units (PAL A–G) consisting mainly of plane-parallel ash and lapilli layers, and several lava flows (Punte Nere, Commenda, Campo Sportivo, and Palizzi). The Commenda unit includes the Breccia di Commenda (BdC) phreatic deposit, which is composed of pyroclastic density currents (PDCs) and minor fallout layers, as well as reddish ashfall deposits (Varicoloured Tuffs, VT). The Fossa-Forgia Vecchia unit consists of both phreatic (FF2, FF4) and magmatic (FF1, FF3, FF5) deposits from eruptions at the two Forgia Vecchia craters. The Pietre Cotte unit includes ash fallout and PDC deposits, together with the rhyolitic Pietre Cotte lava flow. The Gran Cratere unit comprises sub-unit GCa, composed of lithic-rich deposits, including the Breccia De Fiore deposit, and sub-unit GCB, marked by parallel-bedded ash and lapilli layers with bombs from the 1888–1890 Vulcanian eruption. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

which is still visible on the northern flank of the La Fossa cone (Fig. 1a).

The Gran Cratere unit (1786–1890 CE) overlies the erosional unconformity EU7 and is subdivided into two main sub-units: GCa and GCB (Di Traglia et al., 2024). The GCa sub-unit comprises lithic-rich breccia layers, cropping out mainly on the northern upper flank of the cone and over the Pietre Cotte lava (Di Traglia et al., 2024). These clast- to matrix-supported deposits include altered flow-banded rhyolitic lava blocks (15–20 cm in diameter) and are laterally variable in both thickness and composition. They reach several tens of centimetres near the summit but rapidly thin out downslope. At the same stratigraphic level, these deposits are encountered also on the eastern and southern slopes of La Fossa (Di Traglia et al., 2024). The GCB sub-unit is characterised by parallel-bedded alternations of ash, lapilli, and bombs from the 1888–1890 Vulcanian eruption. The most complete and proximal tephra sequence, located about 500 m east of the present crater, reaches 230 cm in thickness (Di Traglia et al., 2024).

Since the end of the 1888–1890 CE eruption, Vulcano Island has not experienced any further eruption. Volcanic activity has been limited to continuous fumarolic emissions and soil degassing, mainly concentrated within the La Fossa crater and at the base of the cone in the Baia di Levante area (Fig. 1a; Selva et al., 2020; Inguaggiato et al., 2022; Aiuppa et al., 2022; Federico et al., 2023).

2.2. The La Fossa hydrothermal system: From magmatic degassing to surficial alteration facies

High-resolution, electrical resistivity tomography (ERT), along with self-potential, soil CO₂, temperature measurements, and 3D magnetotelluric surveys recognised the main hydrothermal system of Vulcano Island focused beneath the La Fossa volcano, between the Commenda-Pietre Cotte and Gran Cratere craters (Fig. 1a; Revil et al., 2008, 2010; Di Giuseppe et al., 2023). The system is characterised by a conductive anomaly beneath the central cone, likely associated with an active hydrothermal system confined into the shallowest 500 m of depth, bounded by resistive zones aligning with the caldera rims. Below the Gran Cratere structure, another high-resistivity anomaly likely marks a conduit-like structure extending to depths exceeding 2500 m, through which magmatic fluids ascend toward the surface (Revil et al., 2008, 2010; Di Giuseppe et al., 2023).

The La Fossa active magmatic-hydrothermal system is characterised by the continuous uprise of magmatic fluids mixed in variable proportions with those from the hydrothermal system (Paonita et al., 2013 and reference therein). These fluids are released at surface through the high temperature fumarolic field inside and along the northern rim of the La Fossa crater (Fig. 1a). Discharged fluids reached temperatures up to 700 °C in early 1990 and around 400 °C during the 2021–2023 unrest (Barberi et al., 1991; Chiodini et al., 1995; Harris et al., 2012; Capasso et al., 2014; Inguaggiato et al., 2022; Federico et al., 2023).

At depth, these fluids contribute to alteration, hydrothermal mineral precipitation, and metasomatism of the volcanic and sub-volcanic rocks

forming the conduit system (Fulignati et al., 1998). Near the surface, fluids rich in SO₂, HCl, HF, H₂S, partly emerge from fumarolic vents and partly condense into groundwater, forming very acidic solutions with pH < 2. These acidic solutions interact with the surrounding rocks, causing an acid-sulphate surficial alteration (Fulignati et al., 1998; Boyce et al., 2007) characterised by a mineralogical zoning reflecting the progressive neutralisation of the extremely acidic fluids and resulting in a sequence of alteration facies. A zone dominated by silicic alteration, composed almost exclusively of residual silica due to the extensive leaching of original rocks, surrounds the high temperature fumarolic field (Fig. 1a). The advanced argillic facies develops adjacent to the silicic alteration zone and mainly consists of minerals of the alunite group. Intermediate argillic alteration, characterised by the presence of kaolinite group minerals, occurs sporadically (Fig. 1a; Fulignati et al., 1998; Boyce et al., 2007).

2.3. The Breccia De Fiore (BDF) deposit

Following nearly 85 years without significant eruptive activity after the Pietre Cotte cycle, aside from a few minor eruptions in 1812, 1822, and 1832 (De Fiore, 1922), La Fossa volcano resumed its activity in 1873 with a 44-day-long explosive phase (Salino, 1874; Mercalli, 1883, 1886; Mercalli and Silvestri, 1891; De Fiore, 1922). This period was marked by multiple explosions occurring at intervals ranging from minutes to several days and of varying intensity: some ejected only ash-sized particles, while others produced coarser material including blocks (Mercalli and Silvestri, 1891; De Fiore, 1922; Giansante et al., 2025). Mercalli and Silvestri (1891) indirectly described these products when comparing them with those of the first two days of activity of the 1888–1890 eruption, reporting that they were identical and formed by variably altered fragments, with no evidence of clear fresh, glass-rich magmatic material.

The products of this eruptive phase are preserved in the geological record and exposed along the northwestern flank of the La Fossa cone (Fig. 1a), where they lie stratigraphically between the underlying Pietre Cotte deposits and the overlying materials of the 1888–1890 eruption, placing them within the GCa unit as defined by Di Traglia et al. (2024) (Fig. 1b). Their limited spatial distribution is interpreted as the result of a combination of factors, including non-deposition, intense erosion (especially on the northern flank; Ferrucci et al., 2005), and the location of the eruptive vent(s) (Giansante et al., 2025). The inferred vent location(s) (Fig. 1a), located inside the La Fossa crater near its northern rim, along with an inclined vent geometry, likely contributed to the asymmetrical dispersal of the deposits (Fig. 1a; Giansante et al., 2025).

The deposit has an overall texture ranging from massive to laminar and stratified. The presence of a substantial block fraction in specific beds of the sequence (up to 47 %; see SM1), the marked heterogeneity of clast types, and the widespread occurrence, in the most proximal outcrops, of zones where coarse lapilli and blocks dominate, would support its classification as a tuff breccia (Le Maitre et al., 2005). However,

basing on the most distinctive facies of the deposits of these eruptions, Giansante et al. (2025) used the general term “breccia” (Breccia De Fiore, BDF) not only to refer this part of the sequence but for the whole deposit, also in analogy with the nomenclature adopted for the older Breccia di Commenda deposit, which, despite including finer-grained intervals, was defined by its most diagnostic breccia-rich layers (Gurioli et al., 2012; Rosi et al., 2018).

The BDF comprises a stratified sequence of five distinct layers (A–E), each containing clasts that display evidence of hydrothermal alteration and oxidation, as indicated by yellow, reddish, brown, and white hues in ash, lapilli, and block-sized fragments (Fig. 2a, b). With a total average thickness of 45 cm, the BDF is poorly sorted and composed of relatively coarse material with a bimodal total grain-size distribution (TSGD) showing peaks at -4 to -3ϕ and 0 to 1ϕ (Fig. 2c; Giansante et al., 2025). Based on isopach maps, the estimated volume of the entire deposit ranges from 3.7 to $4.6 \times 10^3 \text{ m}^3$, while individual layers vary between 6.4×10^3 and $1.9 \times 10^4 \text{ m}^3$ (Giansante et al., 2025).

In the field, the five layers are separated by sharp boundaries and can be distinguished based on differences in grain size, sedimentary

structures, and macroscopic colour (Giansante et al., 2025). The basal layer (A) is a 3–30-cm-thick grey, matrix-supported bed predominantly composed of lapilli (17–71 wt%), particularly at proximal sites, where also distinct, open-framework zones enriched in blocks are present. Particularly in its upper portion, layer A becomes enriched in coarse lapilli and blocks (average diameter 11–15 cm), where the matrix content is reduced or completely absent. The block content, expressed as a percentage relative to the ash-lapilli fraction (see SM1), ranges from 31 to 36 % (Fig. 2d), with a marked increase observed at proximal sites near the northern crater rim compared to the base of the cone. Laterally, the layer passes from massive to stratified, reflecting topographic influence on deposition.

Layer B (1–18 cm of thickness) is a reddish to brownish, ash-rich bed (77–85 wt%) composed mostly of fine to medium ash. It varies from weakly laminated to stratified and, in this case, it is formed by alternating, well-sorted ash and lapilli layers.

Layer C is grey in colour and 2–35 cm thick. It contains fine to coarse lapilli (13–58 wt%) and ash (42–87 wt%) arranged in massive to stratified beds. The stratified portions display alternating layers of ash and

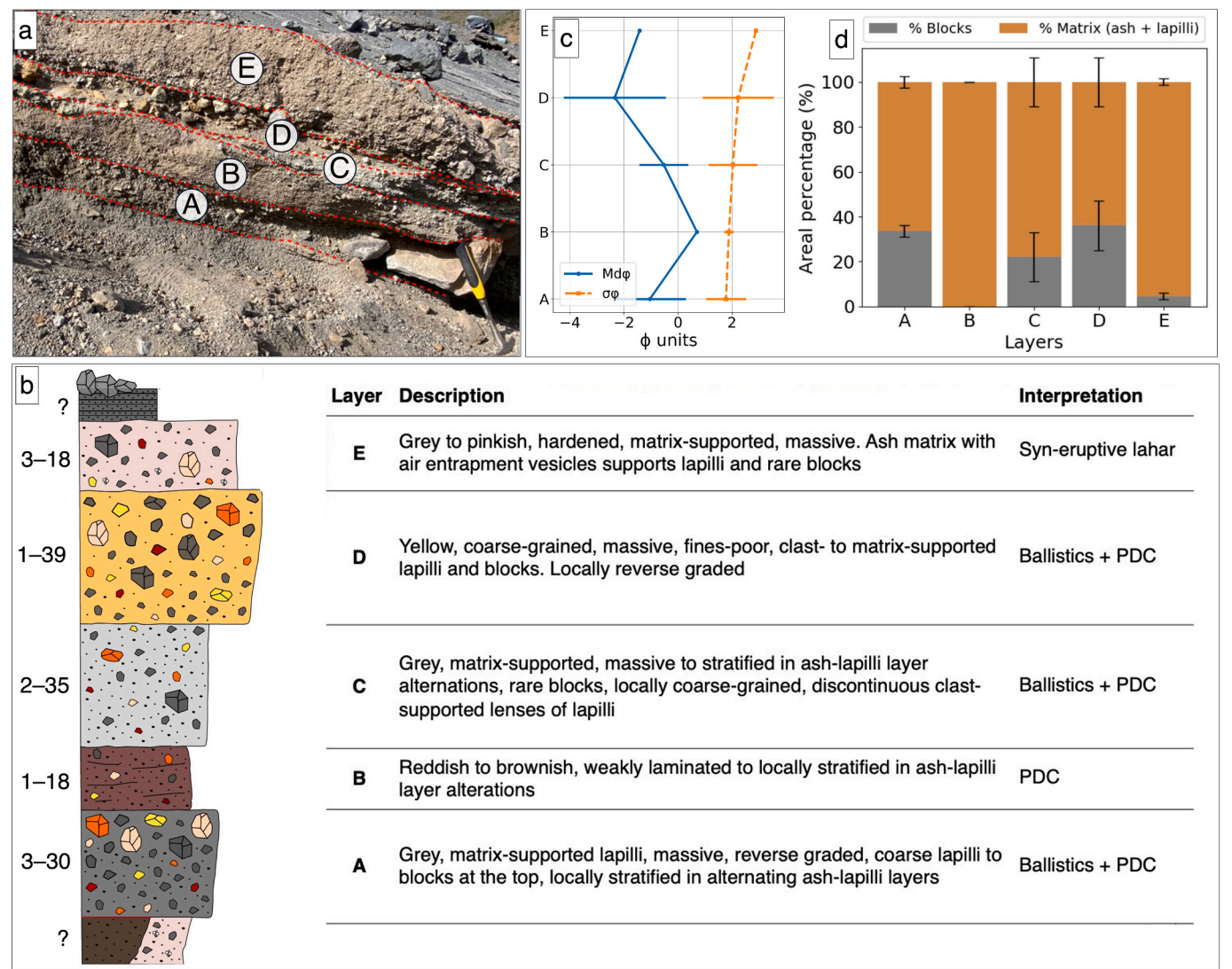


Fig. 2. a) Outcrop photograph of the Breccia De Fiore deposit, displaying layers A to E of the sequence; b) Reference stratigraphic section of the Breccia De Fiore deposit. The unit typically overlies an erosional surface (in red) cut into a brown ash layer or lahar deposits (in pink) above the Pietre Cotte unit. It is overlain by parallel-bedded ash and lapilli layers (in dark grey) of the 1888–1890 eruption; c) Areal percentage of blocks (grey) and matrix (ash + lapilli; orange) for layers A to E. Each bar represents the mean value, with error bars showing the full range (min–max) obtained from image analysis; d) Median diameter ($Md\phi$) and sorting ($\sigma\phi$) across the Breccia De Fiore sequence. Error bars indicate the estimated range (min–max; Giansante et al., 2025). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

lapilli, commonly showing matrix-poor lenses of coarse lapilli and larger clasts measuring 5–10 cm in diameter. The block content ranges from 11 to 33 % relative to the ash-lapilli fraction (Fig. 2d).

Layer D, the coarsest and most distinctive bed in the sequence, is yellow in colour and ranges from 1 to 39 cm in thickness. It is clast- to matrix-supported and composed of moderately to well-sorted lapilli (42–90 wt%), with the highest block contents reaching 25–47 % relative to the ash-lapilli fraction (Fig. 2d) and increasing at proximal sites. The layer is generally massive, occasionally showing reverse grading.

The topmost layer E (3–18 cm thick) consists of a massive, hardened, grey to pinkish matrix-supported bed. The matrix, which is composed of ash embedding fine to coarse lapilli and minor blocks (3–6 % relative to the ash-lapilli fraction; Fig. 2d), is cohesive and shows syndepositional vesicles related to air entrapment, concentrated near the base of the layer. At proximal sites, the lapilli content reaches up to 55 wt%, while the matrix content visibly decreases at distal sites near the base of the cone.

The overall stratigraphy suggests unsteady deposition from turbulent PDCs, ballistic fallout, and water-related processes such as syn-eruptive lahars (Fig. 2b; Giansante et al., 2025). According to Giansante et al. (2025), the BDF deposit formed from a series of shallow, low-energy phreatic eruptions occurring at shallow depths disrupting the La Fossa hydrothermal system. While historical chronicles detail the eruptive events during this period allowing to set it during 1873, it is not possible to confidently correlate specific phases of the described eruptions during the 44-day-long eruptive phase with the individual stratigraphic layers identified in the field.

3. Materials and methods

Scanning electron microscope (SEM) observations were carried out on carbon-coated samples from layers A, B, C, and D of the BDF at the MEMA Laboratories of the University of Florence (Italy) and at the CISUP laboratories of the University of Pisa (Italy). At MEMA Laboratories, a ZEISS EVO MA15 SEM equipped with an OXFORD AZTEC 5.0 energy dispersive microanalytical system (EDS) was used for the analysis, operating at 15 kV with a beam current of up to 2 nA. A FEG-SEM-EDS FEI Quanta 450 apparatus, equipped with a Bruker-Quantax energy dispersive spectrometer (EDS), was used at CISUP Laboratories, operating at 15 kV acceleration voltage and 10 nA beam current. Analysed samples included eight polished grain mounts (six on the 1–1.4 mm and two on the 1.40–2 mm fractions) and three stubs with dispersed ash grains (0.250–0.355 mm fraction). The polished grain mounts were prepared by randomly picking a subset of fragments from a larger sample. Each stub was divided in 2 halves: one half composed of randomly picked fragments, and the other half containing a selection of macroscopically altered clasts (i.e., white, brownish, yellow, reddish fragments, and clasts characterised by a brownish to orange and red translucent patina).

Clasts from the 2–2.8 mm size fraction of layers B and D were embedded in resin and four thin sections prepared for petrographic analysis. For each layer, one section was prepared using randomly picked fragments, and the other by selecting highly altered-looking fragments, following the same criteria used for stub preparation.

The identification and quantification of the components along the BDF sequence was based on a microscopic approach to better evaluate the type and extent of hydrothermal alteration by looking at the interior of clasts. A total of 250 to 300 clasts on each of four polished mounts, amounting to approximately 1000 clasts in total, was classified combining observations using a binocular microscope with petrographic and SEM analyses.

Geochemical analyses were carried out on very fine ash (<4φ) of layers A, B, and D to derive information, given the high area/volume ratio, on the trace elements transported by the magmatic-hydrothermal fluids involved in the eruptions. Major element composition of the fine ash was analysed by ICP-OES at Actlabs laboratories (Canada), while

trace elements were determined by ICP-MS using a Perkin-Elmer NEXION 300× spectrometer at the Earth Sciences Department of the University of Pisa (DST-UNIP). The samples were manually ground in an agate mortar, previously cleaned with diluted HCl. The powder samples were dissolved using the “acid digestion” method, both via total and partial digestion. The total digestion method was applied to determine Li, Be, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Ag, Sb, Cs, Ba, Hf, Ta, W, Tl, Pb, Bi, Th, U and Rare Earth Elements (REE). Approximately 50 mg of powdered sample were treated with HNO₃ and HF (1:4 ratio) followed by HNO₃ and H₂O (1:2 ratio), and subsequently evaporated on a hot plate. Certified standards of basalt (“BE-N”) and dolerite (“WSE”) were used to calibrate and evaluate the results of the analyses. A second procedure, according to the Environmental Protection Agency (EPA) method, involved partial dissolution in a microwave system: about 50 mg of powdered sample were treated with reverse Aqua Regia (7.5 mL HNO₃ + 2.5 mL HCl) at 180 °C and 1800 W. This method was applied to determine the concentration of Cd, As, Sn, Se, and Mn. The REE element concentrations were normalised to chondritic values (Sun and McDonough, 1989). The Hg content in the fine matrix of the deposit was analysed in parallel with the other trace elements using the Direct Mercury Analyzer DMA-80 m at the DST-UNIP.

To assess metal and metalloid enrichment in fine ash, enrichment factors (EF) for elements such as Ag, Cu, Bi, Tl, Th, Mo, Pb, Zn, As, Sb, Be, Li, Se, and Mn were calculated using the method of Zoller et al. (1983):

$$EF_{sample} = \frac{\left(\frac{X}{R}\right)_{sample}}{\left(\frac{X}{R}\right)_{reference}}$$

where X/R represents the ratio of a specific element (X) to a reference immobile element (R , in this case Th) in the sample and the reference fresh rock.

X-ray diffraction (XRD) data on mineral phases from selected particles were collected using a Bruker D8 Venture single-crystal diffractometer equipped with a Photon III CCD area detector (CISUP, University of Pisa, Italy), to check for different silica phases.

4. Results

4.1. Macroscopic description of the BDF fragments

The BDF particles, as observed both macroscopically and under a binocular microscope, displayed a thin surface coating of fine, dusty material ranging in colour from reddish to pinkish. Based on their visual characteristics under the microscope, the particles were broadly distinguished primarily by hue into two groups: coloured particles and grey to black particles.

Coloured particles showed a wide range of hues, including red, orange, yellowish, white (opaque or translucent), and shiny metallic coatings varying from red to dark brown (Fig. 3a). These particles, subrounded with low sphericity, suggest extensive interaction with hydrothermal fluids, which has completely obscured their original lithology and texture. Similar characteristics—such as white or yellowish coatings attributed to prolonged exposure to hot fluids—were documented in the descriptions by Mercalli and Silvestri (1891) of the ejecta from the 3–5 August 1888 eruptions and were also observed in earlier eruptions between 1873 (the focus of this study) and 1886.

In contrast, grey to black particles, which constitute the majority, showed limited or no surface alteration. They tend to preserve their original lithology and texture, apart from localised modifications, yet never showing the typical features of fresh juvenile material. Partial alteration was evidenced by discontinuous patinas in shades of yellow, orange, or reddish-brown, confined to specific surface areas (Fig. 3b, c). These particles varied from dense to vesicular. Dense particles were non-

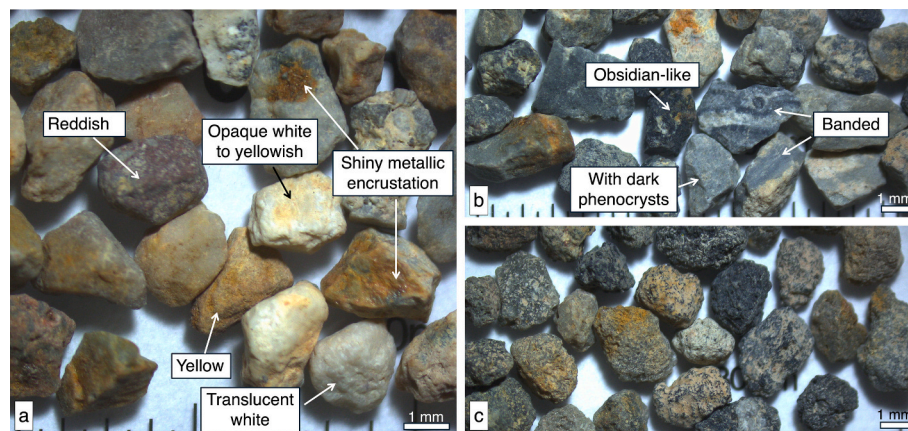


Fig. 3. Photographs of the BDF lithic particles under a binocular microscope: **a)** Particles showing intense surface alteration, with a range of colours including yellow, orange, reddish, white (either opaque or translucent), and shiny metallic encrustations; **b)** Dense, grey to black particles showing partial to slight surface alteration. Examples include particles with dark phenocrysts, obsidian-like, and banded textures; **c)** Grey to black vesicular particles showing localised alteration, with patinas strongly concentrated along vesicle walls. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

vesicular or slightly vesicular, angular to sub-angular in shape, and consisted of lava fragments of variable origin. Some contained sparse dark to lighter phenocrysts and reveal a porphyritic texture. Others appeared as dark, obsidian fragments or as banded fragments with alternating dark and light grey bands (Fig. 3b), which are interpreted as banded rhyolites. Vesicular particles (Fig. 3c) exhibited a range of vesicle size and shapes, from spherical to elongated. They usually lacked glassy lustre, appeared opaque, and were frequently affected by yellow to orange surface patinas, particularly concentrated along vesicle walls (Fig. 3c).

Additional observations on coarse material (in particular, the medium to coarse lapilli fraction between 16 and 32 mm was investigated in detail to have a reliable statistics) further support this classification. Nearly all analysed clasts were lava fragments, except for a vesicular clast from layer B. Two dominant lithotypes were identified: dark to black fragments containing light to dark phenocrysts within a nearly black groundmass, and grey, often flow-banded clasts with alternating black, grey, and whitish laminae (Fig. SF1). These clasts had low to medium sphericity and sub-angular to sub-rounded shapes. Surface alteration was highly variable: some clasts displayed extensive orange to brownish alteration rims, while others remained relatively unaltered. In some cases, alteration was pervasive, producing yellowish alteration zones and vugs.

While colour variations were observed across layers A to E of the BDF deposit, the particle types described above were consistently present throughout the sequence, with no apparent significant changes in their relative abundance. Although not providing a detailed quantification, a quantitative assessment of particle types and abundances for layers A through D, which are attributed to similar eruption dynamics (Giansante et al., 2025), is presented in the following section.

4.2. Petrography and SEM-EDS analysis of the BDF fragments

Petrographic analysis and SEM-BSE imaging revealed that macroscopic features—such as reddish, brownish, or grey to dark colouration described above—were not consistently reliable indicators for distinguishing particle types or assessing the extent of hydrothermal alteration. Consequently, macroscopic observations were not used for componentry classification. Instead, the relative abundance of particle types was determined through a micro-scale approach that integrated petrography, SEM analyses, and observation of polished mounts under a binocular microscope.

This integrated method allowed for the identification of three distinct particle groups: hydrothermally altered, unaltered, and

microfelsitic particles (Fig. 4).

Hydrothermally altered (Type 1) particles displayed a wide range of colours, including light grey, white, yellowish, orange, reddish, and brownish hues (Fig. 4), and were characterised by pervasive hydrothermal alteration. This alteration extended beyond the surface into the interior of the particles, although the degree of internal alteration might vary, being less intense in some cases. These particles exhibited diffuse porosity in the form of irregular void spaces and internal fractures. Based on their dominant mineral assemblage, Type 1 particles were further subdivided into two subtypes: Type 1a and Type 1b. Type 1a ranged in colour from light grey to white and might appear opaque or translucent (Fig. 4). They were characterised by quartz and possibly amorphous silica according to XRD analyses (see SM2) distributed throughout the particle, either completely (Fig. 5a, b) or partially replacing the original texture. In some particles, silica polymorphs formed pseudomorphs after primary minerals of clinopyroxenes and feldspars (300–500 μm), or plastered internal fractures (Figs. 5a–d, 6a–d). Relicts of primary minerals revealed an original porphyritic texture with very low phenocryst content (<2–5 %) (Figs. 5c, d, and 6c, d). In many of these particles, phenocrysts replaced by silica polymorphs were embedded in a groundmass that shows limited signs of alteration, usually composed of volcanic glass surrounding euhedral to subhedral clinopyroxene, feldspar, and rounded Fe–Ti oxides (Fig. 6a–d). Otherwise, the groundmass was microcrystalline, composed of lath-shaped and acicular feldspars (Fig. SF2). Other Type 1a particles exhibited a vuggy (Fig. 6e) to a more massive texture (Fig. SF3), with a groundmass dominated by fine silica phases, usually displaying poorly defined crystal boundaries, and irregular voids (Fig. SF3). In some cases, the groundmass also contained an association of quartz and sanidine (see SM2) microlites. Microlites are observed as irregular patches forming distributed throughout the particle and ranging from rounded to squared shapes, similar to spherulites, or lacking a defined shape (Fig. SF2). Elemental mapping of Type 1a particles (e.g., Fig. 6e–g) revealed strong silica enrichment and aluminium depletion, consistent with intense acid leaching.

Type 1b particles appeared white to yellowish or orange (Fig. 4) and shared textural similarities with Type 1a particles, including the silica-rich groundmass (Fig. 6i, k). However, unlike Type 1a, these particles were enriched in aluminium and potassium sulphates, notably alunite and jarosite, with minor kaolinite. These secondary minerals commonly filled pores and veins, only rarely replaced primary phenocrysts (Fig. 6i–m). Sulphur-enriched zones were frequently observed in voids and cross-cutting veins, corresponding to areas of sulphate concentration (Fig. 6j, l).

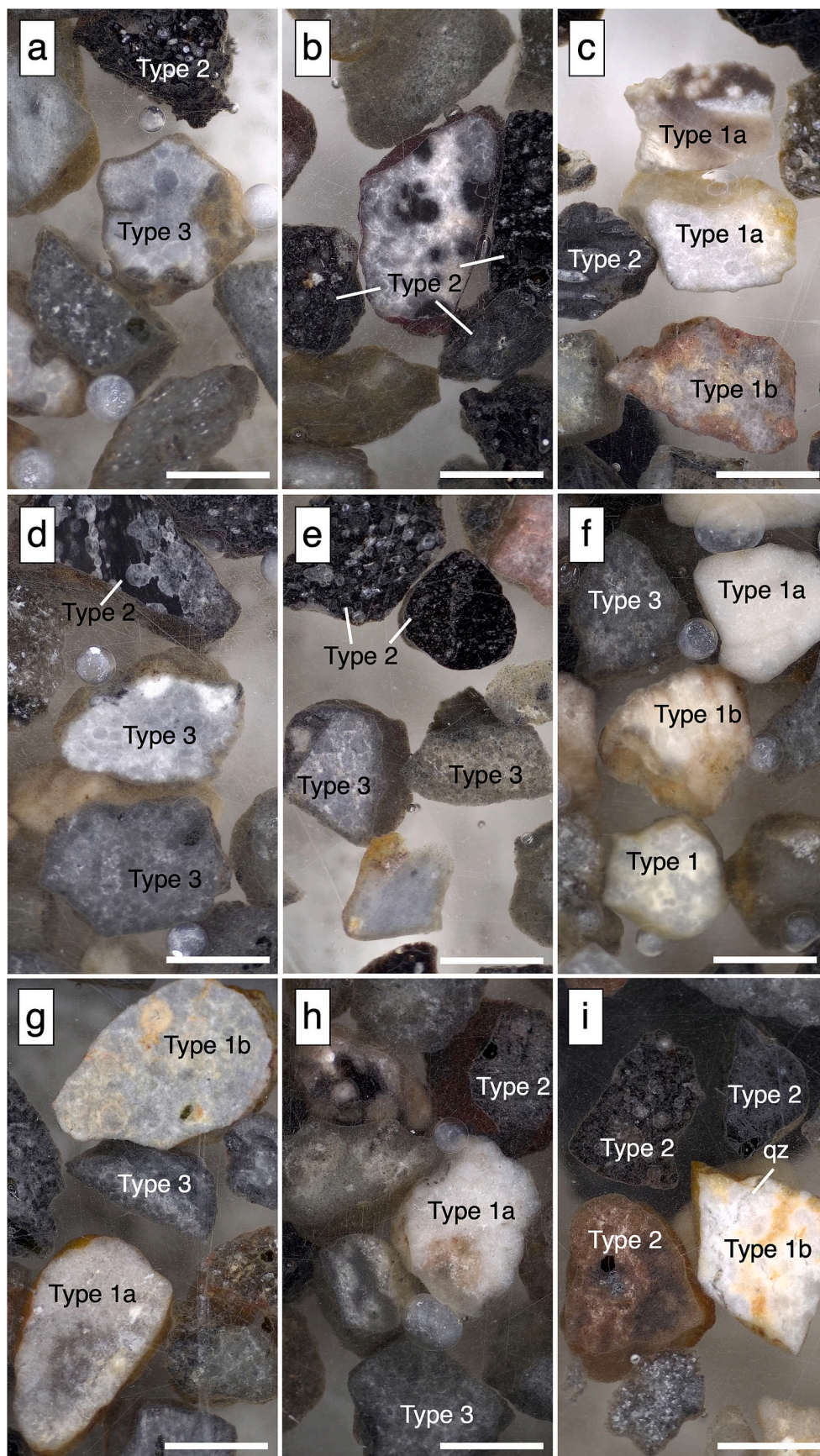


Fig. 4. Photographs of the three different particle types under a binocular microscope: hydrothermally altered (Type 1a, silicic alteration, Type 1b, advanced argillic alteration), unaltered (Type 2), and microfelsitic (Type 3). Scalebar: 1 mm.

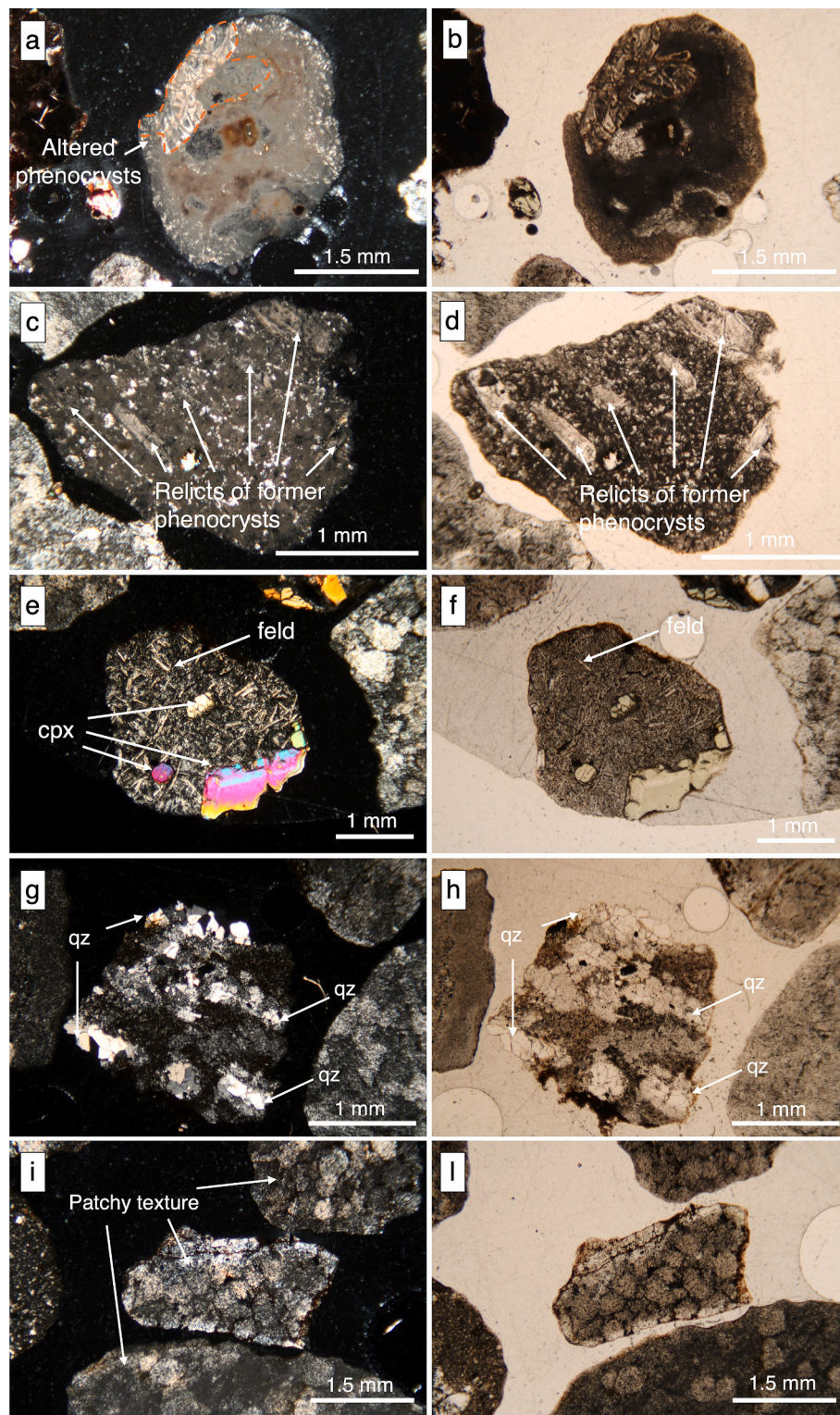


Fig. 5. Photomicrograph of the BDF lithic fragments under crossed polars (left) and plane-polarised light (right): **a-b**) Hydrothermally altered particle (Type 1a) entirely replaced by amorphous silica; **c-d**) Hydrothermally altered particle (Type 1a) showing relicts of primary phenocrysts replaced by silica polymorphs; **e-f**) Unaltered particle (Type 2) with rare clinopyroxene phenocrysts in a microcrystalline groundmass dominated by lath-shaped feldspars; **g-h**) Microfelsitic particle (Type 3) displaying quartz crystals in bands and a devitrified (quartz-feldspar microlites) groundmass; **i-l**) Microfelsitic particle (Type 3) showing the characteristic patchy texture of rounded quartz-feldspar spherulites.

Unaltered (Type 2) particles showed no clear evidence of hydrothermal alteration, although surface alteration might occasionally be present (Fig. SF4). These particles exhibited a porphyritic texture with a low phenocryst content (< 2–5 %) set within a microlite-rich glass-

bearing groundmass. Phenocrysts consisted of euhedral to subhedral clinopyroxene and feldspar crystals. The groundmass textures of Type 2 particles varied considerably. Some displayed a dark, highly microcrystalline groundmass composed of densely packed, lath-shaped

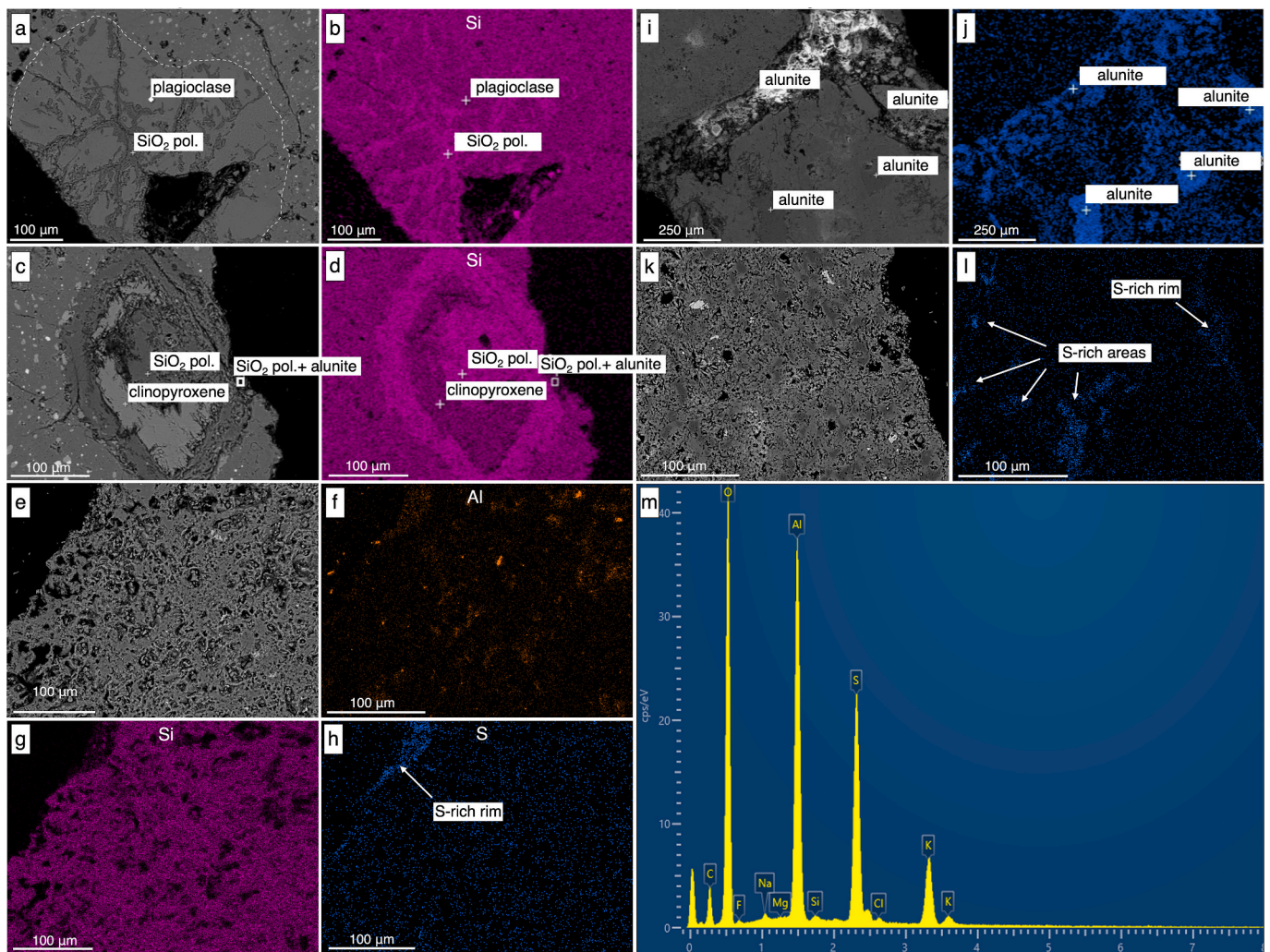


Fig. 6. SEM photomicrographs of hydrothermally altered particles of Type 1a (a–h) and Type 1b (i–m): **a)** BSE image showing silica (SiO_2) polymorphs plastering fractures; **b)** Si-elemental map at the same location of a) showing Si-enrichment areas; **c)** BSE image showing silica (SiO_2) polymorphs replacing a former clinopyroxene; **d)** Si-elemental map at the same location of c) showing Si-enrichment within the replaced phenocryst; **e)** BSE image of a highly porous, completely leached particle; **f)** Al-elemental map at the same location of e) showing strong Al depletion; **g)** Si-elemental map at the same location of e) showing strong Si-enrichment; **h)** S-elemental map at the same location of e) showing S-rich particle rim; **i)** BSE image showing highly porous zones filled with alunite; **j)** S-elemental map at the same location of i) showing S-rich areas where alunite concentrates; **k)** BSE image of a porous particle; **l)** S-elemental map at the same location of k) showing S enrichment in pore spaces; **m)** Alunite EDS spectrum characterising the advanced argillic alteration.

feldspars (Fig. 5e, f). Others were light-coloured, incipiently vesicular (elongated to cusate vesicles), and composed of a microcrystalline groundmass dominated by tabular and acicular feldspars (Fig. SF5). Additional examples were characterised by a light brown, less densely microcrystalline groundmass, composed of tabular and acicular feldspars (Fig. SF5). Some particles exhibited a dense to poorly vesicular, dark- to brown-coloured groundmass, containing scattered feldspar microcrystals and phenocrysts of clinopyroxene and feldspar. The dark zones within the groundmass corresponded to spherulitic textures (Fig. SF5). Other Type 2 particles show a banded groundmass, transitioning from pale to light brown tones (Fig. SF5).

Microfelsitic (Type 3) particles were grey coloured (Fig. 4), occasionally bordered by oxidised rims. Their texture was similar to that of hydrothermally altered particles, marked by complete devitrification of the original groundmass into irregular spherulites composed of intergrowths of quartz and sanidine (see SM2). These microlitic structures are dispersed throughout the particle, forming a distinctive “patchy” texture (Figs. 4, 5g–l, 7). Under crossed polars, these patches exhibited low birefringence, appearing pale (white to light grey) in contrast to the surrounding darker glassy or cryptocrystalline groundmass (Figs. 5, 7).

In some of the microfelsitic particles, phenocrysts of euhedral to subhedral unaltered alkali-feldspar (possibly sanidine), clinopyroxene, Fe–Ti oxides, and apatite, with rare microcrystals of Fe-rich clinopyroxene and fayalite mineral associations were observed.

A distinctive feature of microfelsitic particles was the presence of large silica crystals (up to 100–500 μm) within the groundmass, as well as occurring in veins, vugs, and pore spaces (Fig. 7). XRD analysis of the vein-filling crystals confirmed that the silica mineral is quartz (SM2). Zircon grains (<20 μm) were also found in pore spaces.

Many quartz crystals contained nearly monophase, vapour-rich fluid inclusions with ellipsoidal shapes (Fig. 7j, k), usually smaller than 10 μm , rarely reaching ~20 μm . These inclusions were randomly distributed to form small clusters. Due to their small size, a systematic determination of the salinity and trapping temperature of these fluid inclusions was not possible.

Only in rare cases, interstitial glass and silicate melt inclusions were observed within quartz crystals. They displayed high SiO_2 content (~78 wt%) and Cl concentrations below the detection limit.

Regardless of type, most particles were coated with a thin, irregular rim composed of fine (<10 μm) alunite and jarosite crystals (Fig. 6h, 8).

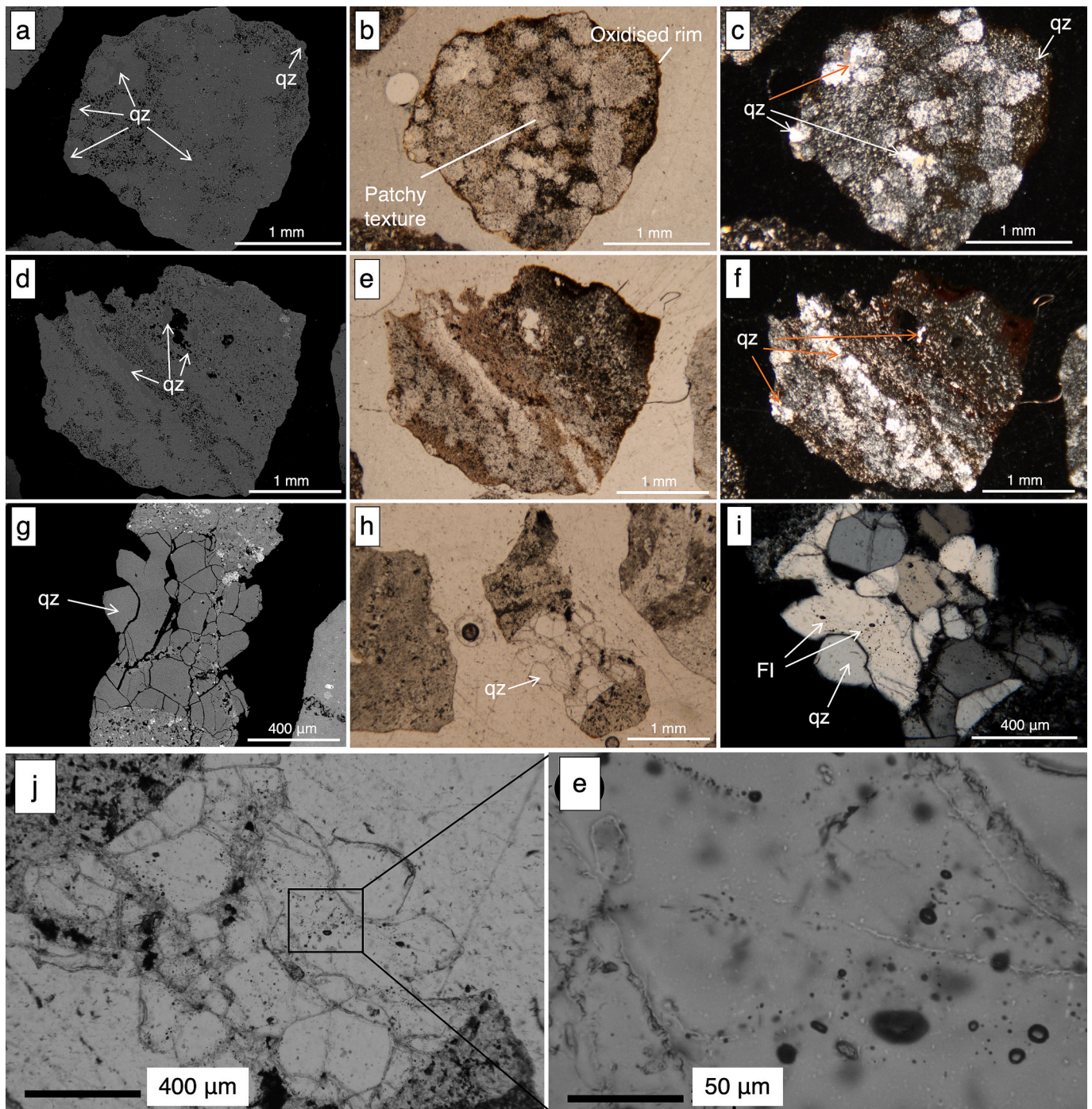


Fig. 7. Photomicrographs of microfelsitic particles (Type 3). **a)** BSE image showing spherulites and quartz crystals (dark grey); **b)** Fragment a) under plane polarised light showing a red oxidised rim; **c)** Fragment a) under cross polarised light; **d)** BSE image showing quartz crystals along a vein and in pores; **e)** Fragment d) under plane polarised light; **f)** Fragment d) under cross polarised light; **g)** BSE image showing a fractured quartz crystal (~800 μm); **h)** fragment g) under plane polarised light; **i)** Focus of fragment g) under crossed polarised light showing fluid inclusions (FI); **j-k)** Fluid inclusions in fragment g). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The relative abundances of hydrothermally altered, microfelsitic, and unaltered particles across the BDF sequence, performed coupling direct microscopic observations on polished surfaces of the grains and thin sections, are presented in Fig. 9. Hydrothermally altered particles are the most prevalent, comprising 44–60 % of the total, with their proportions increasing from layer A to D. Microfelsitic particles account for 23–31 %, with higher proportions in layers A and C. Unaltered particles represent the smallest fraction and the largest relative variation in abundance of all the particles, ranging from 7 to 26 %, and show a

general decrease from layer A to E, except for a slight increase in layer B. Table ST1 details the proportions of the different particle types for each BDF layer, expressed as mean $\pm$ range deviation to account for inherent challenges in particle classification, including overlapping features and potential misidentification.

4.3. Fine ash geochemical composition

The geochemical composition of the fine ash fraction ($<4\phi$) from the

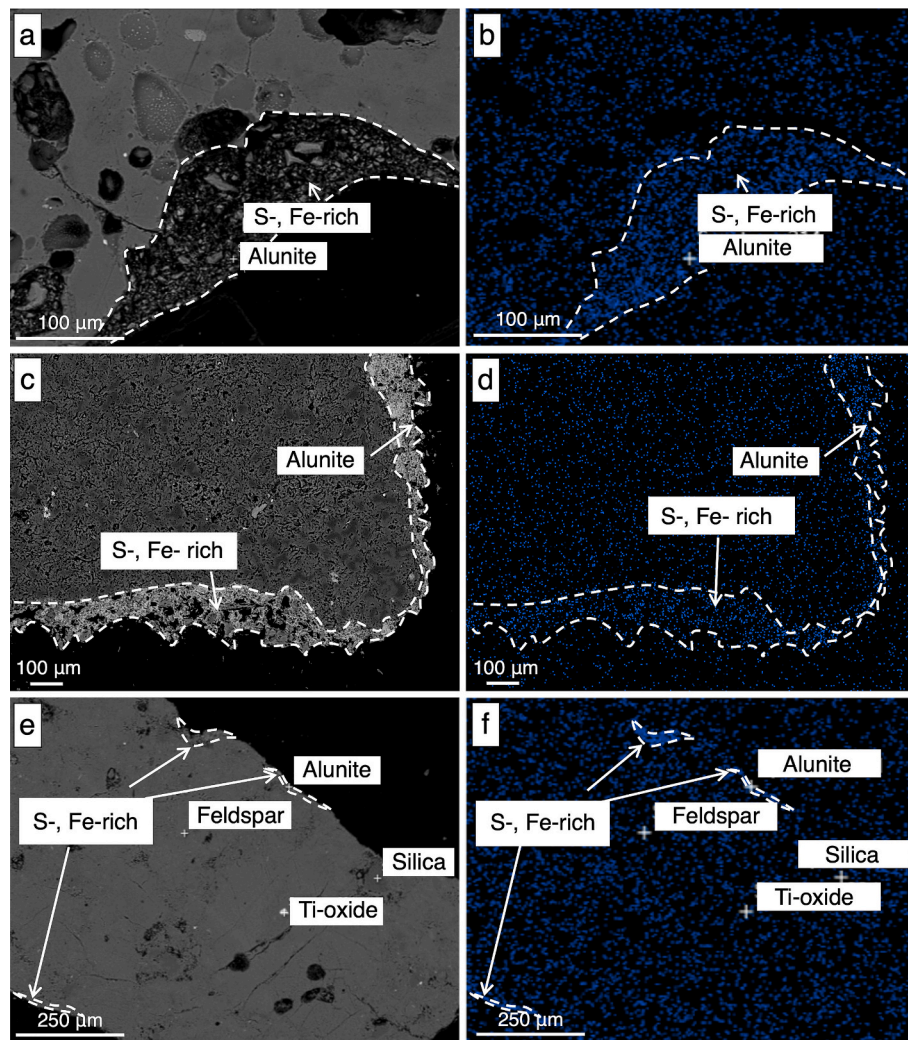


Fig. 8. SEM microphotographs showing sulphur (S)- and iron (Fe)-rich areas (white dashed line) on particle rims, where very fine (<10 µm) alunite crystals are found. **a)** SEM-BSE image of an “unaltered” particle (Type 2) from layer B of the BDF sequence; **b)** Sulphur elemental map of the same particle; **c)** SEM-BSE image of a “hydrothermally altered” particle (Type 1a) from layer D of the BDF sequence; **d)** Sulphur elemental map of the same particle; **e)** SEM-BSE image of a “hydrothermally altered” particle (Type 1a) from layer B of the BDF sequence; **f)** Sulphur elemental map of the same particle.

BDF deposit was investigated for both major and trace elements (Table 1). The fine matrix showed SiO₂ concentration of 60–63 wt%, placing it within the latitic-trachytic fields of the Total Alkali–Silica (TAS) diagram (Fig. 10a).

Compared to fresh lava samples from Palizzi (trachyte) and Pietre Cotte (rhyolite), considered as unaltered rock equivalents, the chondrite-normalised REE pattern of the BDF fine ash displayed a higher ratio light REE (LREE)/heavy REE (HREE). LREE concentrations are higher than those observed both in the Palizzi trachyte and in the Pietre Cotte rhyolite, while HREE are impoverished with respect to the Pietre Cotte rhyolite (Fig. 10b).

This fractionation pattern is also evident in the chondrite-normalised La/Sm and La/Lu ratios diagram (Fig. 10c). The BDF samples showed higher ratios than the unaltered reference lavas of Pietre Cotte and Palizzi, with La/Sm values ranging from 6.9 to 9.7 and La/Lu values from 27.0 to 40.7. These compositions fall within the field defined for advanced argillic-altered rocks from Vulcano by Fulignati et al. (1998) and Boyce et al. (2007).

The enrichment factor (EF) analysis of the BDF fine ash, calculated relative to the rhyolitic Pietre Cotte lava (Fig. 10d) and the trachytic Palizzi lava (Fig. 10e), showed enrichments in elements such as Ag, Cu, Bi, Se, Tl, Mo, and As, while Mn, Li, Be, and Zn are depleted. Antimony (Sb) had no significant enrichment or depletion relative to the reference

rocks. Mercury (Hg) concentrations in the BDF fine ash, listed in Table ST2, range from 5.7 to 11.4 ppb.

5. Discussion

5.1. The hydrothermal system before the BDF eruptions

The lithic particles in the BDF deposit record the state of the hydrothermal system before the 1873 eruptions. As illustrated in Fig. 11, this system is here schematised as a rhyolitic plug emplaced within the shallow conduit system of La Fossa possibly during the preceding Pietre Cotte cycle, surrounded by halos of hydrothermal alteration and permeated by fractures acting as preferential fluid pathways.

The silicic alteration facies, represented by Type 1a particles, occurs in the innermost part of the fluid ascent pathways (Fig. 11b). These particles show pervasive leaching, with silica phases (quartz, amorphous silica) replacing original clinopyroxene and feldspar phenocrysts and groundmass. Their massive and vuggy textures, alongside a general aluminium depletion, indicate intense alteration and leaching by hot, strongly acidic hydrothermal fluids (Stoffregen, 1987; Hedenquist et al., 2000; Pirajno, 2009; Sillitoe, 2010, 2015). Similar textural features have been reported from other active volcanic systems where hydrothermal fluids extensively modify host rocks, including as Ontake, Aso,

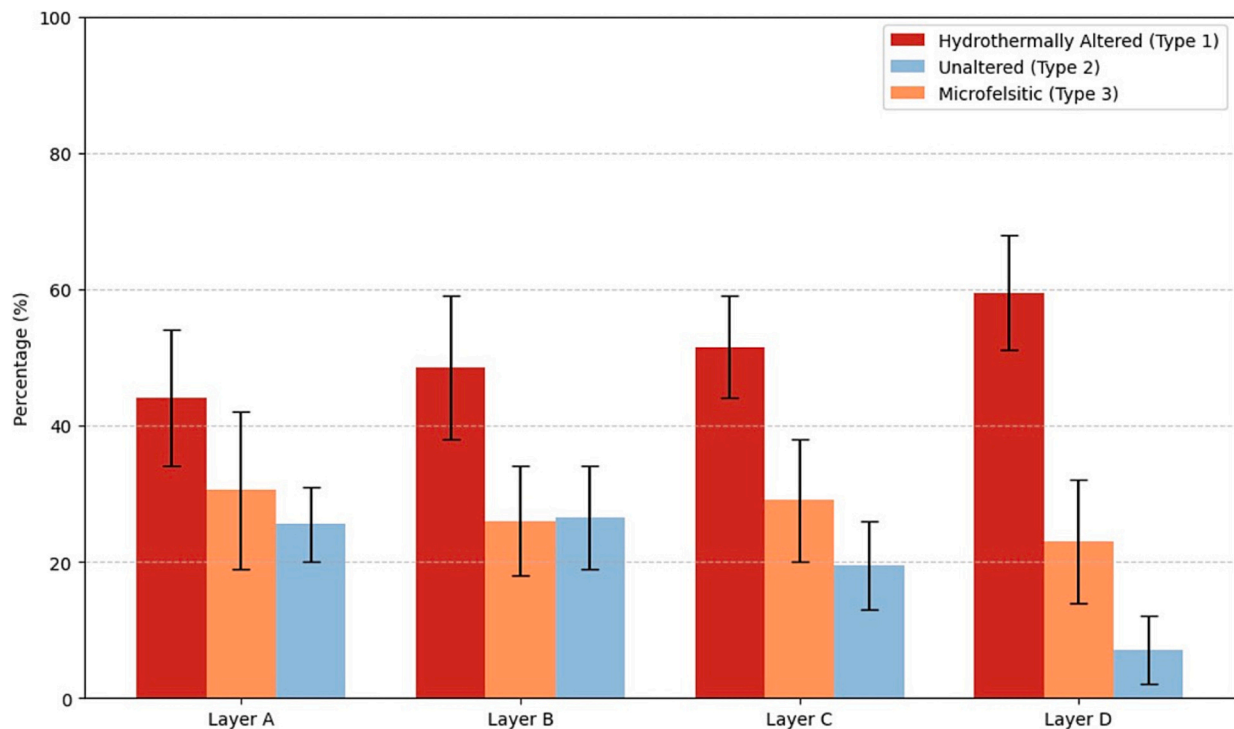


Fig. 9. Percentage of hydrothermally altered -Type 1 (red), unaltered -Type 2 (blue), and microfelsitic -Type 3 (orange) particles in layers A, B, C, and D of the BDF sequence. Histogram height reflects the estimated central tendency of each particle group, while vertical black bars indicate the full extent classification variability observed during visual assessment. The error is due to uncertainties in classifying some individual particles. The proportions of different particle types expressed as ranges are listed in Supplementary Table ST1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Kuchinoerabujima, and Meakandake volcanoes (Minami and Geshi, 2025). These features are consistent with alteration under temperatures of 200–250 °C and pH <2 (Stoffregen, 1987).

Adjacent to the silicic zone is the advanced argillic alteration facies, recorded by Type 1b particles (Fig. 11b). These particles contain secondary alunite group minerals (alunite and jarosite) filling pores and crosscutting veins, suggesting precipitation from a less acidic, sulphur-rich hydrothermal fluids (Stoffregen, 1987; Hedenquist et al., 2000; Pirajno, 2009; Sillitoe, 2010). This alteration halo develops where progressive neutralisation of fluids raises pH values in the range 2–4.5 (Fulignati et al., 1998; Boyce et al., 2007).

The geochemical signature of the BDF fine ash further supports this interpretation. Relative to unaltered trachytic and rhyolitic reference lavas, the fine ash exhibits LREE enrichment and HREE depletion, consistent with advanced argillic alteration (Fulignati et al., 1998, 1999). This reflects the lower mobility of LREE in acidic environments, where they are more easily incorporated into sulphate minerals such as those of the alunite group, which preferentially accommodate LREE in their large A-site. Conversely, HREE are more effectively removed by acid leaching (Fulignati et al., 1999). Elevated La/Sm and La/Lu ratios place the BDF within the compositional field of advanced argillic-altered rocks from Vulcano (Fulignati et al., 1998, 1999), confirming a strong hydrothermal overprint.

The dominance of advanced argillic alteration in the BDF fine ash is interpreted as a cause of mechanical weakening, due to alteration involving sulphate minerals or clays that allow a more efficient fragmentation than silica-cemented rocks (Heap et al., 2020; Montanaro et al., 2022). Decompression experiments on similarly altered rocks from Solfatara volcano at Campi Flegrei—where acidic fluids transformed the host material into amorphous silica and alunite—have demonstrated that such rocks have low mechanical strength and produce large amounts of fine particles, with alunite-rich material contributing most significantly to the fine fraction (Mayer et al., 2016).

The presence of alunite coatings and pore fillings on BDF ash particles further supports their derivation from fragmentation of pyroclastic hydrothermally altered rocks during the eruptions.

Together, the advanced argillic and the silicic alteration facies are indicative of a shallow, acid-sulphate environment (White and Hedenquist, 1990; Hedenquist and Lowenstern, 1994; Hedenquist et al., 2000; Fulignati et al., 1998), interpreted as the result of pre-eruptive circulation of acidic hydrothermal fluids through the shallow bedrock and, possibly, the clastic crater infill at La Fossa. This scenario reflects a pre-1873 hydrothermal system characterised by physico-chemical conditions similar to those observed today (Fulignati et al., 1998; Boyce et al., 2007).

Based on their heterogeneous textures, textural resemblance to variably hydrothermally altered particles (Type 1 particles; Fig. SF2), and mineralogical and textural similarity to deposits from the Pietre Cotte eruptive cycle (Piochi et al., 2009; Rossi et al., 2019; Costa et al., 2020), the unaltered particles (Type 2) are interpreted as fragments recycled mainly from that earlier phase rather than juvenile material from the 1873 eruptions.

Microfelsitic particles (Type 3), with quartz-feldspar spherulites in the groundmass, are interpreted as rhyolitic in composition and possibly derived from the partial fragmentation of the pre-1873 rhyolitic plug (Fig. 11b). This plug may represent a remnant of the earlier Pietre Cotte eruptive cycle, which ended with the emplacement of the homonymous rhyolitic lava flow on the northern flank of the cone (De Astis et al., 2013; Di Traglia et al., 2013, 2024).

Within these particles, silica phases occur both as quartz-feldspar microlite intergrowths and quartz infilling pore spaces, veins, and fractures. Quartz has never been reported as a magmatic phenocryst in Vulcano's rhyolitic products (Gioncada et al., 1998; Piochi et al., 2009; De Astis et al., 2013; Costa et al., 2020), and previous reports of quartz-bearing clasts have attributed them to crustal xenoliths undergoing partial melting (Clocchiatti et al., 1994; Zanon et al., 2003). In our

Table 1Major and trace element composition of the BDF fine ash fraction (< 4 ϕ).

Element	Unit	Detection limit	Analysis method	Samples					
				BDF 1.1	BDF 1.2	BDF 1.4	AT 4	AT 6	AT11
SiO ₂	wt%	0.01	FUS-ICP	–	–	–	56.41	57.49	60.96
Al ₂ O ₃	wt%	0.01	FUS-ICP	–	–	–	14.67	16.34	14.73
Fe ₂ O ₃ (T)	wt%	0.01	FUS-ICP	–	–	–	8.84	7.12	6.74
MnO	wt%	0.001	FUS-ICP	–	–	–	0.10	0.11	0.10
MgO	wt%	0.01	FUS-ICP	–	–	–	1.46	1.56	1.25
CaO	wt%	0.01	FUS-ICP	–	–	–	3.55	3.93	3.15
Na ₂ O	wt%	0.01	FUS-ICP	–	–	–	3.61	3.50	3.62
K ₂ O	wt%	0.01	FUS-ICP	–	–	–	5.29	5.25	5.19
TiO ₂	wt%	0.001	FUS-ICP	–	–	–	0.42	0.50	0.39
P ₂ O ₅	wt%	0.01	FUS-ICP	–	–	–	0.41	0.42	0.33
LOI	wt%		GRAV	–	–	–	4.43	4.11	3.39
Total	wt%	0.01	FUS-ICP	–	–	–	99.19	100.30	99.86
Ba	ppm	2	FUS-ICP	–	–	–	741	894	613
Sr	ppm	2	FUS-ICP	–	–	–	832	968	693
Y	ppm	1	FUS-ICP	–	–	–	27.0	26.0	28.0
Sc	ppm	1	FUS-ICP	–	–	–	9.00	10.0	8.00
Zr	ppm	2	FUS-ICP	–	–	–	217	232	224
Be	ppm	1	FUS-ICP	–	–	–	5.00	5.00	6.00
V	ppm	5	FUS-ICP	–	–	–	107	124	97
Li	ppm		ICP-MS	53	47	50	52	46	56
Be	μg/g		ICP-MS	5.9	5.3	5.7	5.4	5.3	5.7
V	μg/g		ICP-MS	116	111	105	98	113	81
Cr	μg/g		ICP-MS	19.3	11.4	14.0	20.3	17.0	15.6
Co	μg/g		ICP-MS	11.9	11.3	10.2	10.0	11.1	8.3
Ni	μg/g		ICP-MS	14.8	7.9	12.2	9.8	8.6	12.9
Cu	μg/g		ICP-MS	134	126	125	147	151	95
Mn	μg/g		ICP-MS (p.d.)	n.d.	n.d.	n.d.	176	158	209
Se	μg/g		ICP-MS (p.d.)	n.d.	n.d.	n.d.	3.3	2.9	2.9
Cd	μg/g		ICP-MS (p.d.)	n.d.	n.d.	n.d.	0.04	0.04	0.03
Sn	μg/g		ICP-MS (p.d.)	n.d.	n.d.	n.d.	3.60	3.20	3.50
Zn	μg/g		ICP-MS	93	65	72	64	62	55
Ga	μg/g		ICP-MS	19.8	18.5	19.1	18.4	18.7	17.6
Rb	μg/g		ICP-MS	223	210	216	226	202	230
Sr	μg/g		ICP-MS	770	850	775	813	936	637
Y	μg/g		ICP-MS	33	29	32	29.0	28.6	27.6
Zr	μg/g		ICP-MS	215	220	216	205	226	197
Nb	μg/g		ICP-MS	29	27	29	26.3	26.4	27.3
Mo	μg/g		ICP-MS	16.6	10.7	14.8	19.8	13.1	14.5
Ag	μg/g		ICP-MS	1.25	1.14	1.11	1.27	1.31	1.12
As	μg/g		ICP-MS (p.d.)	n.d.	n.d.	n.d.	28.20	26.2	17.8
Sb	μg/g		ICP-MS	1.44	0.96	1.35	1.40	0.93	1.47
Cs	μg/g		ICP-MS	14.6	14.9	15.5	15.2	13.5	16.0
Ba	μg/g		ICP-MS	703	843	759	694	847	578
La	μg/g		ICP-MS	164	135	126	167	153	126
Ce	μg/g		ICP-MS	259	217	212	255	257	206
Pr	μg/g		ICP-MS	23	19.4	20	23.0	24.3	19.1
Nd	μg/g		ICP-MS	69	60	66	71	78	61
Sm	μg/g		ICP-MS	10.9	9.7	11.8	11.8	12.5	10.7
Eu	μg/g		ICP-MS	1.13	1.27	1.24	1.16	1.33	1.06
Gd	μg/g		ICP-MS	7.4	7.9	10.5	9.5	8.9	8.7
Tb	μg/g		ICP-MS	1.07	1.15	1.39	1.29	1.17	1.14
Dy	μg/g		ICP-MS	6.0	6.3	7.2	6.4	6.0	5.8
Ho	μg/g		ICP-MS	1.18	1.14	1.31	1.12	1.05	1.04
Er	μg/g		ICP-MS	3.3	3.0	3.6	3.11	3.02	3.00
Tm	μg/g		ICP-MS	0.49	0.45	0.53	0.46	0.44	0.45
Yb	μg/g		ICP-MS	3.2	2.9	3.5	3.01	2.84	2.98
Lu	μg/g		ICP-MS	0.47	0.43	0.50	0.44	0.43	0.44
Hf	μg/g		ICP-MS	5.9	5.9	6.0	5.7	5.9	5.6
Ta	μg/g		ICP-MS	1.81	1.68	1.82	1.69	1.66	1.79
W	μg/g		ICP-MS	6.4	4.4	5.2	5.4	4.2	5.1
Tl	μg/g		ICP-MS	1.51	1.96	2.2	1.73	2.97	1.57
Pb	μg/g		ICP-MS	87	49	68	55	61	46
Bi	μg/g		ICP-MS	0.56	0.41	0.47	0.49	0.87	0.39
Th	μg/g		ICP-MS	69	51	62	61	55	53
U	μg/g		ICP-MS	11.5	11.0	12.3	10.5	12.4	11.7

p.d. = partial dissolution method

n.d. = not determined

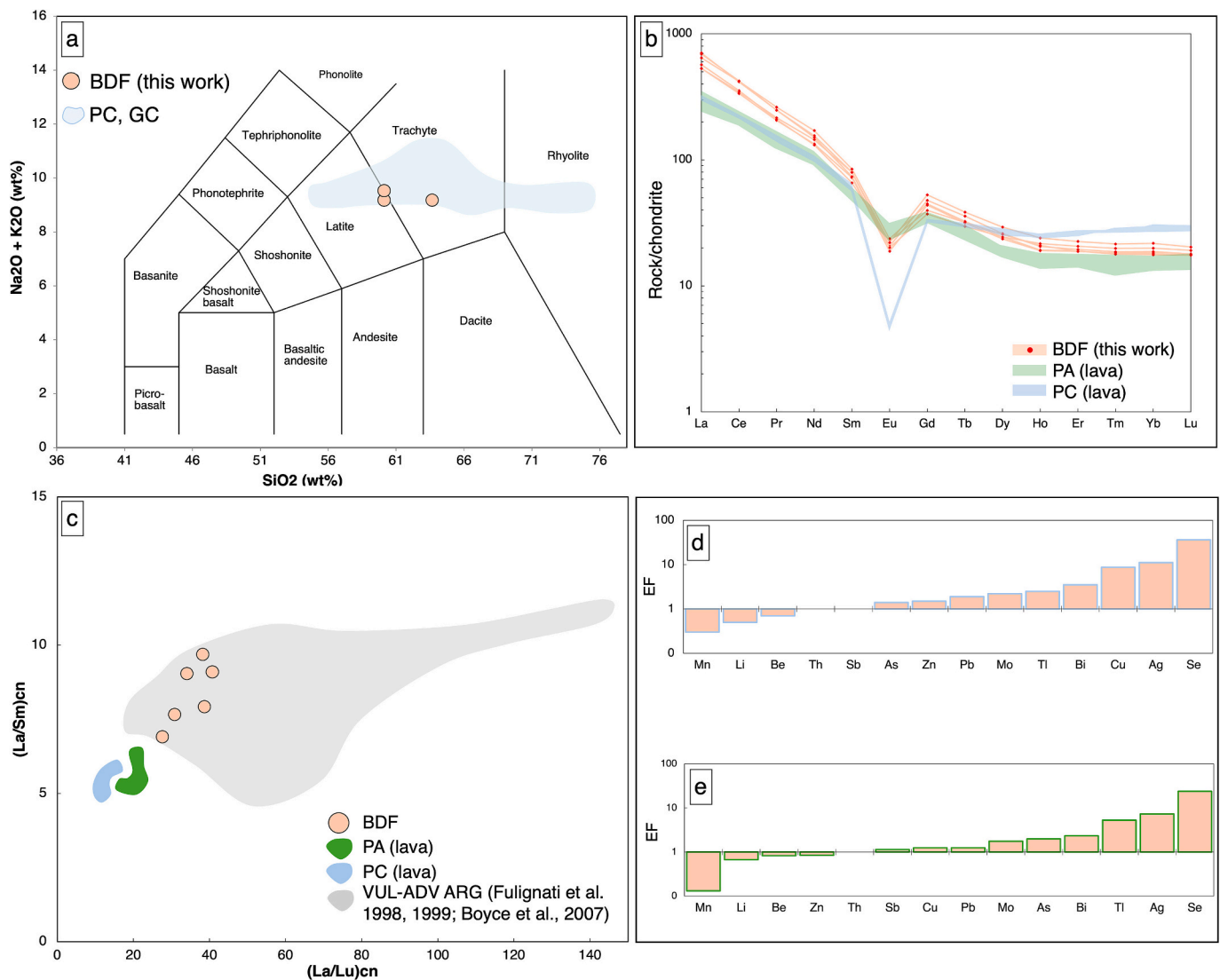


Fig. 10. a) Total alkali vs silica (TAS) diagram of the Breccia De Fiore (BDF) fine ash, Pietre Cotte (PC) and Gran Cratere (GC) sequences (Clocchiatti et al., 1994; Del Moro et al., 1998; De Astis et al., 1997, 2013; Bullock et al., 2019; Pinarelli et al., 2019; Costa et al., 2021). Analyses LOI-free to 100; b) Chondrite-normalised (Sun and McDonough, 1989) REE pattern of the Breccia De Fiore (BDF) fine ash, trachytic Palizzi lava (PA; Nicotra et al., 2018; Costa et al., 2021), and rhyolitic Pietre Cotte lava (PC; Bullock et al., 2019; Costa et al., 2021); c) Chondrite-normalised (Sun and McDonough, 1989) La/Sm and La/Lu ratios for the Breccia De Fiore (BDF) fine ash, trachytic Palizzi lava (PA; Nicotra et al., 2018; Costa et al., 2021), rhyolitic Pietre Cotte lava (PC; Bullock et al., 2019; Costa et al., 2021), and the hydrothermally altered (advanced argillic) rocks of Vulcano (VUL-ADV ARG; Fulginiti et al., 1998, 1999; Boyce et al., 2007); d) Enrichment Factor (EF) for the Breccia De Fiore (BDF) fine ash with respect to the Pietre Cotte reference rock (rhyolitic lava; Rudnick and Gao, 2003; Costa et al., 2021); e) Enrichment factor (EF) for the Breccia De Fiore (BDF) fine ash with respect to the Palizzi reference rock (trachytic lava; Rudnick and Gao, 2003; Costa et al., 2021).

samples, mineralogy and texture (e.g., Fig. 7) support a secondary origin.

Quartz-feldspar microlite associations documented by Horwell et al. (2013) in dome samples from Soufrière Hills volcano (Montserrat) were attributed to complete devitrification of volcanic glass. By analogy, we propose that intense devitrification of the groundmass could account for the development of spherulitic quartz-feldspathic textures (Lofgren, 1971). Previous studies (Simons, 1962; Lofgren, 1971; Tuffen and Castro, 2009; Breikreuz, 2013; Zheng et al., 2018; Breikreuz et al., 2021) have shown that spherulites can form either during reheating of rhyolites or through hydrothermal alteration at temperatures ranging from <40 to ~ 400 °C. We interpret the devitrification textures in BDF microfelsitic particles as the result of prolonged exposure of the rhyolitic plug to high-temperature magmatic gas flux within the La Fossa conduit, which enhanced silica mobility and promoted chemical and textural reorganisation of the rhyolitic glass. This interpretation is consistent with present-day evidence of a conduit-like structure beneath La Fossa

crater permeated by magmatic gases (Di Giuseppe et al., 2023), which we consider analogous to conditions preceding the 1873 eruptions.

Under protracted conditions of high temperatures (>250 °C, based on crater fumarolic field measurements since 1900; e.g., De Fiore, 1922; Barberi et al., 1991; Chiodini et al., 1995; Harris et al., 2012; Capasso et al., 2014; Federico et al., 2023) within the plug, hydrothermal alteration is likely inhibited, as SO_2 does not disproportionate into H_2SO_4 and H_2S , and acids like HCl reduce their dissociation, preventing hydrolysis reactions (Sakai and Matsubaya, 1977; Ruaya and Seward, 1987). This may explain the absence of hydrothermal alteration in the microfelsitic particles and supports the inference that these particles were sourced from the central and/or deeper, hotter zones beneath the La Fossa plug, in contrast to hydrothermally altered or unaltered fragments which may derive from upper and lateral zones surrounding the plug, potentially developed into the Pietre Cotte unit (Fig. 11b). Additionally, interaction with alkali-rich, magmatic gases may explain the presence of atypical mineral phases in microfelsitic particles, including

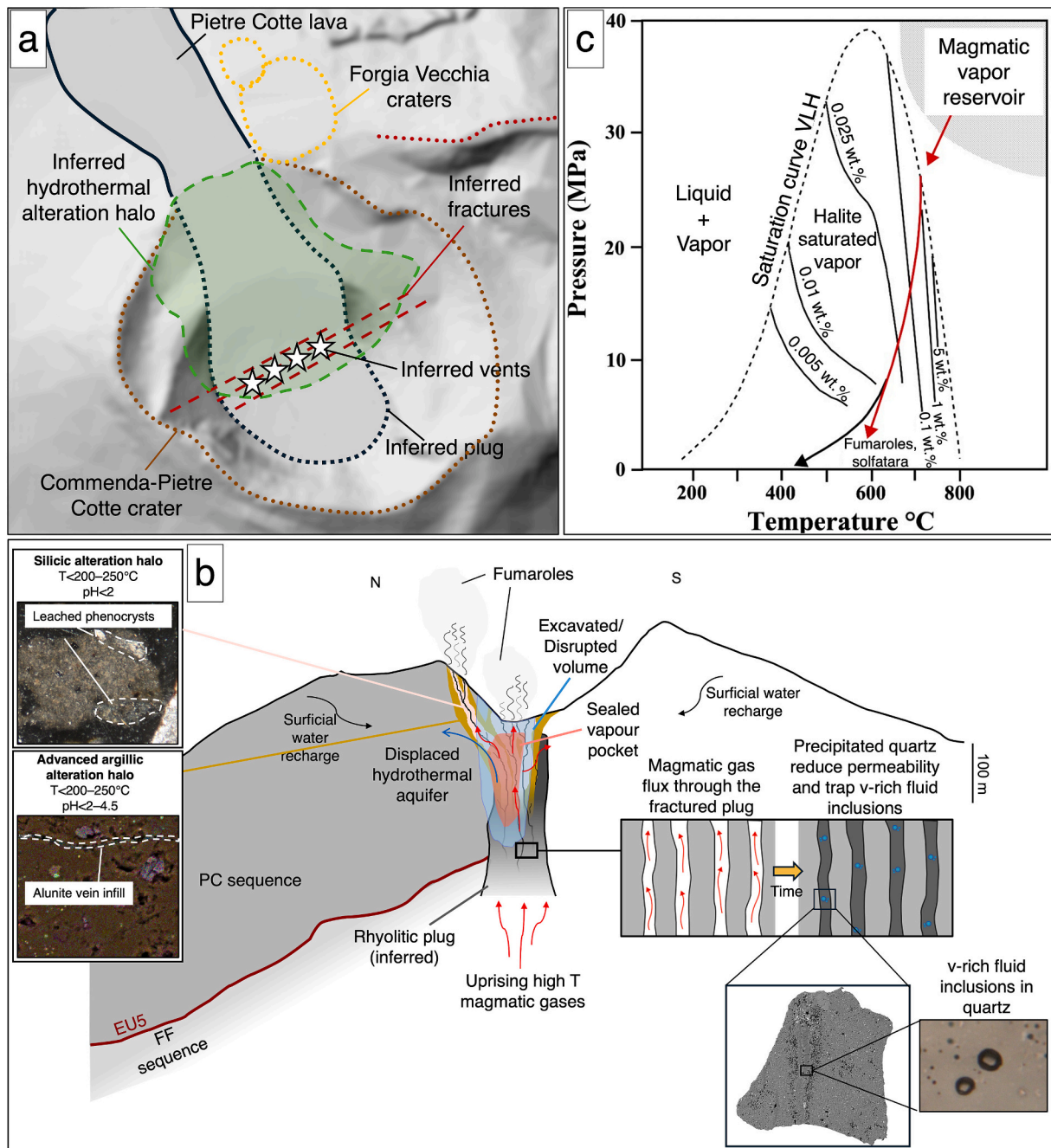


Fig. 11. **a)** Plan-view map of the inferred pre-eruptive setting at La Fossa volcano, including the main morphological and geological structures, eruptive vent(s) of the BDF eruptions, fractures, hydrothermal alteration zones, and the location of the rhyolitic plug; **b)** Conceptual model of the pre-1873 magmatic-hydrothermal system at La Fossa volcano (vertical scale approximate, geometry and features schematic, not to scale). Due to acidic fluid circulation, silicic and advanced argillic alteration developed in the shallow subsurface adjacent to fluid migration pathways at temperatures (T) < 250 °C and pH $< 2-4.5$, reducing rock permeability. A shallow, cooled rhyolitic plug occupying the upper crater-conduit system of La Fossa was subjected to increased, high-temperature magmatic gas flux that displaced the pre-existing hydrothermal aquifer at shallow depth and enlarged a vapour-dominated zone. Magmatic gas ascent through the fractured plug promoted its devitrification and quartz precipitation, trapping vapour-rich (v-rich) fluid inclusions. Silica deposition within the plug, together with surrounding hydrothermal alteration, progressively reduced permeability and generated sealed vapour pockets. Overpressurisation led to explosive failure of these pockets, fragmenting portions of the plug as well as adjacent altered and unaltered lithologies, largely derived from the previous Pietre Cotte eruptive cycle; **c)** Pressure-temperature diagram (modified from [Henley and Berger, 2011](#)) illustrating the quasi-isenthalpic expansion (red path) of a saline magmatic vapour under low-pressure conditions, used to infer the salinity of vapour-rich fluid inclusions in quartz precipitated within the plug. At pressures < 10 MPa (depths $< \sim 400$ m, consistent with explosion depths inferred by [Giansante et al., 2025](#)), the vapour phase has very low salinity (< 0.005 wt% NaCl). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

fayalite, Fe-rich clinopyroxene, and zircon.

A separate mechanism—vapour deposition from silica-rich volatile fluids—can also generate silica phases, especially cristobalite, in fractures, pores, and veins via either local redistribution or bulk transport

([Horwell et al., 2013](#); [Damby, 2012](#); [Kushnir et al., 2016](#)). While our samples predominantly contain quartz crystals, the presence of cristobalite cannot be entirely excluded, especially where pore-filling silica exhibits the characteristic “fish-scale” texture (see Fig. SF6; [Horwell](#)

et al., 2013; Damby, 2012). We suggest that quartz within pores, veins, and fractures formed primarily via bulk transport from silica-bearing gases migrating through different sectors of La Fossa magmatic-hydrothermal system, although local redistribution may have also contributed.

High-temperature gas flux through the plug is evidenced by the presence of vapour-rich fluid inclusions in quartz within microfelsitic particles. These inclusions, occurring as small clusters, are interpreted as primary with respect to quartz growth (Roedder, 1984). Their occurrence is consistent with formation during quartz precipitation from silica-rich, vapour-dominated fluids infilling open spaces (veins, pores, fractures), where irregular crystal faces trapped pockets.

Such vapour-rich fluid inclusion assemblages have been reported in near-surface environments of the high-sulphidation epithermal-porphyry copper systems (e.g., Red Mountain, USA; Lecumberri-Sanchez et al., 2013), where their occurrence is linked to intense boiling or flashing of hydrothermal fluids that transform systems from liquid-dominated to vapour-dominated (Lecumberri-Sanchez et al., 2013). In our case, the absence of coexisting liquid-rich inclusions and the lack of textural evidence for boiling in host quartz (e.g., feathery, plumose, colloform textures) or steam-flashing (e.g., colloform amorphous silica, secondary fluid inclusions; Moncada et al., 2012; Yasami and Ghaderi, 2019; Guzman et al., 2025), lead us to interpret the system as vapour-dominated, not necessarily experiencing boiling. Nevertheless, we do not exclude that boiling and/or flashing of liquid water may have occurred in lateral or localised sectors of the magmatic-hydrothermal system.

Although the exact composition of these fluid inclusions could not be directly measured due to their small size, their salinity can be inferred through the quasi-isenthalpic expansion of saline magmatic vapour under low-pressure conditions (Fig. 11c; Henley and Berger, 2011). At pressures below ~10 MPa—corresponding to depths shallower than ~400 m, consistent with conditions inferred for the BDF eruptions (Giansante et al., 2025)—the vapour phase retains very low salinity (<0.005 wt% NaCl). This is in agreement with the observed single-phase fluid inclusions and supports the interpretation of a low-salinity, vapour-rich magmatic fluid at shallow depth beneath La Fossa.

The Ag, Cu, Bi, Se, Tl, Mo, and As enrichment in the BDF fine ash further suggests the influx of hot, magmatic gases capable of transporting volatile and metal elements (Henley and Berger, 2011; Edmonds et al., 2022), in agreement with previous works showing that most of those elements are commonly present in La Fossa fumaroles and are directly sourced from a degassing magma (Allard et al., 2000; Mandon et al., 2025). The mercury (Hg) content of the BDF fine ash is comparable to soil Hg concentrations previously determined by Barghigiani et al. (1990). We acknowledge that post-eruptive alteration and fumarolic overprinting can modify geochemical signatures. However, the location and the consistent enrichment patterns of the sampled deposit may suggest that such effects were limited, supporting our interpretation of magmatic gas flux.

The rare melt inclusions and interstitial glass hosted in quartz crystals exhibit exceptionally high SiO₂ contents (~78 wt%), exceeding previously reported values for Vulcano rhyolites (e.g., Piochi et al., 2009; De Astis et al., 2013; Rossi et al., 2019; Costa et al., 2020). We suggest these crystals most likely formed at high temperature deeper in the system, possibly near intrusion zones, and were later remobilised during episodes of rapid or transient heating, when batches of vapour-dominated fluids and/or localised fluid flashing events fractured the surrounding rocks. Such events could have created new permeable pathways or wall fragmentation of existing fractures, enabling upward migration of fluids. The originated fragments may then have been entrained and transported toward the surface, a process consistent with conduit evolution and fragment recycling described in previous studies (Ross and White, 2006; Valentine et al., 2014; Sweeney and Valentine, 2015; Montanaro et al., 2021). We exclude the alternative hypothesis of quartz crystallisation under near-melting conditions within a partially

molten rhyolitic plug, as there is no evidence of juvenile rhyolitic material in the BDF deposit and magmatic quartz has never been documented at Vulcano. Instead, the observed pervasive devitrification of microfelsitic particles, together with hydrothermal alteration leading to precipitation of silica phases, supports an origin through secondary thermal and chemical alteration of pre-existing glass-bearing material from the rhyolitic plug.

The macroscopic and microscopic banded textures in microfelsitic particles (e.g., Figs. 3b, 7d, e) are interpreted as primary flow banding in the plug, enhanced by internal, localised fracturing (Stasiuk et al., 1996), which increased vertical permeability and facilitated gas flow (Farquharson et al., 2016). In this context, secondary quartz may have precipitated along these porous gas-escape channels.

Synthesising the evidence from the BDF lithic fragments, we reconstruct a pre-1873 scenario beneath La Fossa where sustained magmatic degassing progressively “dried out” the shallow hydrothermal aquifer, expanding an existing vapour-dominated zone at shallow depth (Fig. 11b). Such thermal conditions likely persisted within the plug and along its margins since its emplacement, based on historical reports of continuous fumarolic activity following the Pietre Cotte cycle (De Fiore, 1922), and intensified approximately two months before the first 1873 explosion (Mercalli and Silvestri, 1891; De Fiore, 1922).

5.2. Conditions leading to the 1873 eruptions

Historical descriptions indicate that, prior to the 1873 eruptions, fumarolic activity at La Fossa was relatively low, largely confined to a prominent fumarole on the northern crater rim (Salino, 1874; Mercalli, 1883; Mercalli and Silvestri, 1891; De Fiore, 1922). By mid-July 1873—approximately two months before the eruptive onset—miners working within the crater reported a marked intensification of outgassing, unusual subterranean noises, and a widening of the fumarolic field (Salino, 1874; Mercalli and Silvestri, 1891; De Fiore, 1922). These phenomena are indicative of a significant increase in subsurface permeability through and fluid migration, likely reflecting the formation of new pathways for gas escape or a pressure increase in the hydrothermal system possibly related to the combined effect of mass and heat advection from the deep. Precursory escalations in superficial activity have been documented before recent steam-driven eruptions, such as those at Ebinokogen Ioyama (Japan, 19 April 2018), Hakone (Japan, 29 June 2015), and La Soufrière de Guadeloupe (1976–1977) (Komorowski et al., 2005; Mannen et al., 2018, 2021; Tajima et al., 2020; Ohba et al., 2021).

At Vulcano, unrest episodes have been generally attributed to pressurisation of the shallow hydrothermal system by magmatic gas accumulation, without necessarily requiring the ascent of magma—except for the 2021–2023 crisis (Montalto, 1994, 1996; Alparone et al., 2010, 2019; Cannata et al., 2012; Aiuppa et al., 2022; Stissi et al., 2023). We interpret the 1873 eruptions as driven by enhanced and sustained flux of heat and magmatic gases from depth. This is supported by fumarolic emission increase, the prolonged character of explosive activity, and the occurrence of vapour-rich fluid inclusions indicative of high-temperature fluid circulation. Whether this activity reflected degassing of a stationary, shallow magma body—potentially through destabilisation of a foam layer (Aiuppa et al., 2022)—or actual magma migration to shallower depths remains difficult to resolve with the available observations. However, the fact that the 1873 eruptions initiated a prolonged, 15-year period of volcanic crisis culminating in the 1888–1890 Vulcanian eruption may support the latter scenario, suggesting the onset of magma ascent beneath La Fossa.

As magmatic gases rose, they preferentially exploited the permeability zones within the densely fractured plug and surrounding lithologies (Fig. 11b). Approaching the surface, they enlarged a shallow vapour-dominated zone beneath La Fossa, displacing the aquifer, and intensified the magmatic signature of fumaroles.

Hydrothermal alteration progressively reduced the permeability of

the system: deposition of silica, alunite-group minerals and clays at the top of the plug and in adjacent lithologies likely created low-permeability zones surrounding fluid pathways that trapped vapour beneath them, facilitating the build-up of shallow overpressure (Fig. 11b). Experimental and field studies at Merapi (Heap et al., 2019) demonstrate how acid-sulphate alteration decreases rock permeability, fostering pore pressure build-up sufficient to fragment dome rocks and drive explosions (Heap et al., 2019). In addition, enhanced quartz deposition within pores and fractures may have progressively contributed to reduce plug permeability (Pirajno, 2009; Mayer et al., 2016; Heap et al., 2017; Horwell et al., 2013; Montanaro et al., 2022). These zones possibly acted as a cap-rock similar to lava dome structures described at Merapi (e.g., Heap et al., 2019) and the lava cap proposed for the Breccia di Commenda eruption at Vulcano (Rosi et al., 2018). The sealing effect could have critically reduced the system's ability to discharge gas and thus release pressure, priming it for explosive failure. Similar permeability-reducing processes have been recognised at the Soufrière Hills dome at Montserrat (Horwell et al., 2013), and during the 2021–2023 unrest at La Fossa, when an initial increase in permeability was followed by sealing linked to intense steam flux and mineral precipitation within subsurface rocks (Pailot-Bonnétat and Harris, 2024).

The inferred low salinity in primary vapour-rich fluid inclusions hosted in quartz within the plug suggests entrapment of a predominantly vapour phase at shallow depths, consistent with magmatic vapour injection into a shallow, vapour-dominated environment. The absence of crack-seal microtextures—usually diagnostic of repeated cycles of decompression, boiling, or flashing (Henley and Ellis, 1983; Pirajno, 2009; Becker et al., 2010; Henley and Berger, 2011; Moncada et al., 2012; Henley and Seward, 2018)—further supports this interpretation.

In this framework, the cyclic explosions that characterised the 1873 activity can be explained without invoking large volumes of liquid water flashing to steam. Instead, pressure is thought to have developed from continuous magmatic gas supply accumulating beneath sealed or semi-sealed zones, forming discrete vapour pockets (Mendieta et al., 2025; Mannen et al., 2025). When the overpressure exceeded host rock tensile strength and the lithostatic load, failure occurred, producing explosions that fragmented both hydrothermally altered and unaltered lithologies from the hydrothermal systems, the confining rocks, and portions of the plug itself. Decompression could have also destabilised adjacent vapour pockets, amplifying the explosive sequence. Although the eruptions appear predominantly driven by vapour pocket failure, localised flashing of liquid water cannot be completely ruled out during decompression—particularly within aquifer zones retaining liquid water close to boiling conditions (Revil et al., 2008, 2010; Di Giuseppe et al., 2023; Pailot-Bonnétat et al., 2023)—potentially amplifying the explosivity of certain events (Montanaro et al., 2022).

The repetitive nature of the explosions is therefore explained by localised destabilisation within the shallow hydrothermal system in zones of vapour accumulation, sustained by a continuous input of hot fluids from depth. Fallback of erupted material into the crater may have further promoted sealing, enhancing overpressure, and facilitating the repetition of explosions. Additional evidence in support of this interpretation includes the description of the opening of at least four distinct vents within the La Fossa crater during the 1873 activity (Mercalli, 1886; De Fiore, 1922; Giansante et al., 2025), suggesting lateral migration of eruption sources over time. Crater formation likely involved both altered and unaltered portions of the Pietre Cotte pyroclastic sequence as well as the rhyolitic plug (Fig. 11b).

Experimental studies have shown that explosions driven by steam-flashing tend to yield higher proportions of very fine particles (<63 μm ; Montanaro et al., 2016). In the BDF, this fraction is consistently low and commonly <3 wt% (Giansante et al., 2025). Combined with the polymodal distributions dominated by particles <2 ϕ (Giansante et al., 2025), and the abundance of blocks, these features may appear to be broadly compatible with explosions driven by vapour expansion, which generally favours coarser grain-size distributions (Montanaro et al.,

2022). On the other hand, although the sorting of the BDF deposit is poor to very poor, varying from 1 to $\sim 4\phi$, sorting alone cannot be used to discriminate between explosions driven predominantly by vapour expansion (“dry” explosions) and those involving partial to complete steam-flashing, since both processes have been observed to produce poorly sorted deposits (Montanaro et al., 2016). Nevertheless, significant uncertainties remain. The original lithology involved in fragmentation strongly influences the final grain-size spectrum, and our dataset may be affected by the absence of very proximal and more distal deposits (Giansante et al., 2025). These limitations hinder a robust reconstruction of the fragmentation process. As such, while the available evidence may point to vapour expansion as the dominant driving mechanism, the role of steam flashing cannot be completely excluded.

The explosions are inferred to have occurred at shallow depths (100–150 m below the crater; Giansante et al., 2025) based on: i) the presence of lithic fragments showing alteration consistent with near-surface hydrothermal conditions (Fulignati et al., 1998; Boyce et al., 2007); ii) the absence of high-temperature alteration minerals associated with deeper zones, such as those found in older deposits like the Breccia di Commenda (Fulignati et al., 1998); iii) the occurrence of vapour-rich fluid inclusions in quartz crystals, indicative of low-pressure, vapour-dominated conditions; and iv) the possible disruption of poorly consolidated, porous rocks similar to those present in crater fillings, as evidenced by the diffuse alunite-bearing alteration on particle surfaces.

Although the combined mechanism of sealing and pressurisation repeated over a prolonged period is rarely, if ever, invoked to explain deposits from past eruptions, similar long-lasting steam-driven eruption styles may have occurred at La Soufrière de Guadeloupe (Komorowski et al., 2005) and Whakaari/White Island (Letham-Brake, 2013). While our model does not fully align with the most recent classification of phreatic eruptions (Montanaro et al., 2022), it remains consistent with the broader conceptual framework of phreatic activity, where magmatic gas input plays a critical role in destabilising a shallow hydrothermal system. For this reason, we suggest retaining the term “phreatic” to describe the 1873 eruptions.

At Vulcano Island, phreatic eruptions remain a recognised and possibly impending hazard—as underscored by the 2021–2023 hydrothermal crisis—but no such activity have occurred since the 1888–1890 Vulcanian eruptions. Observations from recent unrest episodes (Milluzzo, 2012; Aiuppa et al., 2022; Inguaggiato et al., 2022, 2023; Federico et al., 2023; Di Traglia et al., 2023) indicate that surface outgassing is currently efficient. This may suggest that sealing conditions comparable to those inferred for the pre-1873 system have not reformed, despite evidence for mineral precipitation and hydrothermal alteration processes (Fulignati et al., 1998; Boyce et al., 2007; Madonia et al., 2019; Harris and Pailot-Bonnétat, 2024), processes known to reduce rock permeability. Instead, the persistence of fractured, permeable pathways—likely sustained by the continuous interaction of magmatic-hydrothermal fluids with host rocks (Stissi et al., 2023)—appears to inhibit significant pressure-build up. However, as highlighted by the deformation observed during the 2021 crisis, the system ultimately depends on the balance between deep magmatic input and surface output: a sudden and substantial increase in gas flux from depth could still exceed the system's ability to release fluids, recreating conditions for overpressurisation.

6. Summary and conclusions

The study of lithic clasts from the BDF deposit provides new insights into the state of the hydrothermal system at La Fossa di Vulcano prior to the 1873 phreatic eruptions. The main findings of this study can be summarised as follows:

- The 1873 eruptive phase produced the BDF, a sequence of five poorly sorted lapilli tuff to tuff breccia beds that are rich in hydrothermally altered lithics and lack juvenile material.
- Pre-eruptive conditions at shallow levels were dominated by hot, acidic fluids ($T < 200\text{ }^{\circ}\text{C}$ – $250\text{ }^{\circ}\text{C}$, pH 2–4.5, locally <2) producing silicic and advanced argillic alteration along pathways for fluid migration, contributing to reduce rock permeability.
- Hydrothermal alteration developed along the margins and possibly above a densely fractured and devitrified rhyolitic plug occupying the shallow conduit system of La Fossa. Prior to the 1873 eruptions, this plug was fluxed by high temperature silica-rich magmatic gases that promoted secondary quartz precipitation in its pore spaces and fractures, reducing its permeability.
- Primary vapour-rich fluid inclusions in precipitated quartz within the plug document magmatic gas supply and the presence of a vapour-dominated environment in the shallow hydrothermal system.
- The interplay between sealing conditions and enhanced magmatic gas input favoured the formation of overpressured, partially isolated vapour pockets above and within the plug at shallow depths, following the system's permeability. The sequence of small-scale phreatic explosions was likely triggered by the episodic failure of these pockets, sustained by persistent magmatic gas input. Therefore, explosion repetition reflects alternating sealing-rupture processes, with sealing potentially enhanced by fallback material.
- The explosions were shallow and excavated parts of the rhyolitic plug, as well as the above and surrounding unaltered and hydrothermally altered rocks.

This study emphasises the complex interplay between magmatic gas/heat inputs, hydrothermal alteration, and permeability evolution in controlling shallow pressurisation and eruption potential. The clear role of an active magmatic degassing in activating the 1873 sequence of phreatic explosions, which preceded by 15 years the 1888–1890 Vulcanian activity of the La Fossa cone, represents an important warning about the possible scenario for a future reactivation at this volcano. By refining our understanding of these dynamics, we can contribute to more effective monitoring strategies and hazard assessment at Vulcano and in comparable volcanic settings worldwide.

CRediT authorship contribution statement

Silvia Giansante: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Conceptualization. **Paolo Fulignati:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Conceptualization. **Anna Gioncada:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Conceptualization. **Marco Pistolesi:** Writing – review & editing, Validation. **Tomaso Esposti Ongaro:** Writing – review & editing, Validation. **Antonio Tazzini:** Writing – review & editing, Writing – original draft, Investigation. **Raffaello Cioni:** Writing – review & editing, Writing – original draft, Validation, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jvolgeores.2025.108445>.

Data availability

All data needed to evaluate the conclusions in the paper are present in the paper and/or in the Supplementary material.

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