Evaluation of Thermal Potential of the Amiata geothermal field: Geochemical, Petrologic and Petrophysics data

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INTRODUCTION & AIM

Monte Amiata is a hybrid volcano outpoured between 305 and 231 ka (Laurenzi et al., 2015) during the middle-Pleistocene. Their products consist of a succession of lavas and domes, with composition from trachyte/trachydacite to olivine-latite (Conticelli et al., 2015a; Ferrari et al., 1996; Marroni et al., 2015). The volcanic edifice was built during magma emission from an eruptive fissure aligned along the NNE–SSW direction (Brogi, 2008). The eruptive activity took place in two-short lived episodes (Conticelli et al., 2015a; Ferrari et al., 1996; Marroni et al., 2015), seemingly separated from a level characterised by a strong weathering alteration (e.g., Certini et al., 2006; Principe & Vezzoli, 2021). Key characteristics of lavas and domes encompass abundant rounded magmatic enclaves (Ferrari et al., 1996 and references therein), flat or rounded crustal meta-sedimentary xenoliths (van Bergen, 1983), and the prevalence of sanidine megacrysts (Balducci & Leoni, 1982) within. The area around the volcano underwent a regional uplift of about 2 km, extending from Monte Amiata to Radicofani volcanoes, covering an area of 35 x 50 km caused by an unspecified magma intrusion at a depth of 5-7 km (Acocella & Mulugeta, 2001; Acocella et al., 2002). Geological (van Bergen, 1983; Bigazzi et al., 1981; Calamai, 1970; Mazzuoli & Pratesi, 1963), hydrogeochemical (Magi et al., 2019; Minissale et al., 1995), geochemistry of gasses (Frondini et al., 2009a; Nisi et al., 2014; Sbrana et al., 2020; Vaselli et al., 2013), and geophysical (Girolami et al., 2017; Volpi et al., 2003) studies revealed two significant geothermal reservoirs with high temperatures (> 250°C) and a marked ground CO_2–flux (Frondini et al., 2009b; Sbrana et al., 2021). Despite extensive research, debates persist regarding the stratigraphic relationships among lava flows and domes, the petrogenesis of silicic end-member magma, the magmatic chamber architecture, the petrophysics characteristic of xenoliths and the thermo-chemical interaction with magma. The main objective of this study is to evaluate the thermal energy emitted by the magmatic source and how this propagates into the metamorphic basement as a function of the host country-rock type. Several objectives were achieved, such as the stratigraphic relationship among lavas and domes, the characterisation of the mineral chemistry of crystals from igneous and meta-sedimentary rocks, the investigation of the volatile phase nature trapped by melt inclusions, the determination of a Temperature and Pressure range referred to the magmatic reservoir at the eruption moment, the quantification of the water content, the Fe-redox conditions of brown mica from magmatic rocks and meta-sedimentary xenoliths, and the development of a model outlining the architecture and the evolution of the magmatic reservoir.

This study employs a multidisciplinary approach encompassing a new stratigraphy of volcanic rocks, petrographic investigations, whole-rocks geochemistry, mineral chemistry and isotope chemistry analyses, X-ray diffraction and crystal chemistry of brown micas, microthermometry experiments on melt inclusions and thermobarometry calculations; also, seismic wave velocities propagations and thermal conductivity of basement rocks.

RESULTS & DISCUSSION

A new stratigraphy of volcanic rocks

This study reports a new and original stratigraphy of the Monte Amiata volcano. The new stratigraphic sequence follows the guidelines issued directly by ISPRA according to "Quaderni del Servizio Geologico D'Italia" (Quaderni serie III, vol. 12, fascicolo III, aggiornamento al quaderno n.1/1992).

The "*Bagnore*" synthem (**BGE**) (Fig. 1a) represents the stacking of multiple viscous lava flows all around the volcano, characterised by a flat morphology and the typical sin-depositional structure (i.e., shear zone) in which are hosted major crustal meta-sedimentary xenoliths and minor rounded magmatic enclaves (van Bergen, 1984; Conticelli et al., 2015a). Rocks are porphyritic with major sanidine, brown mica, zoned plagioclase, ortho- and

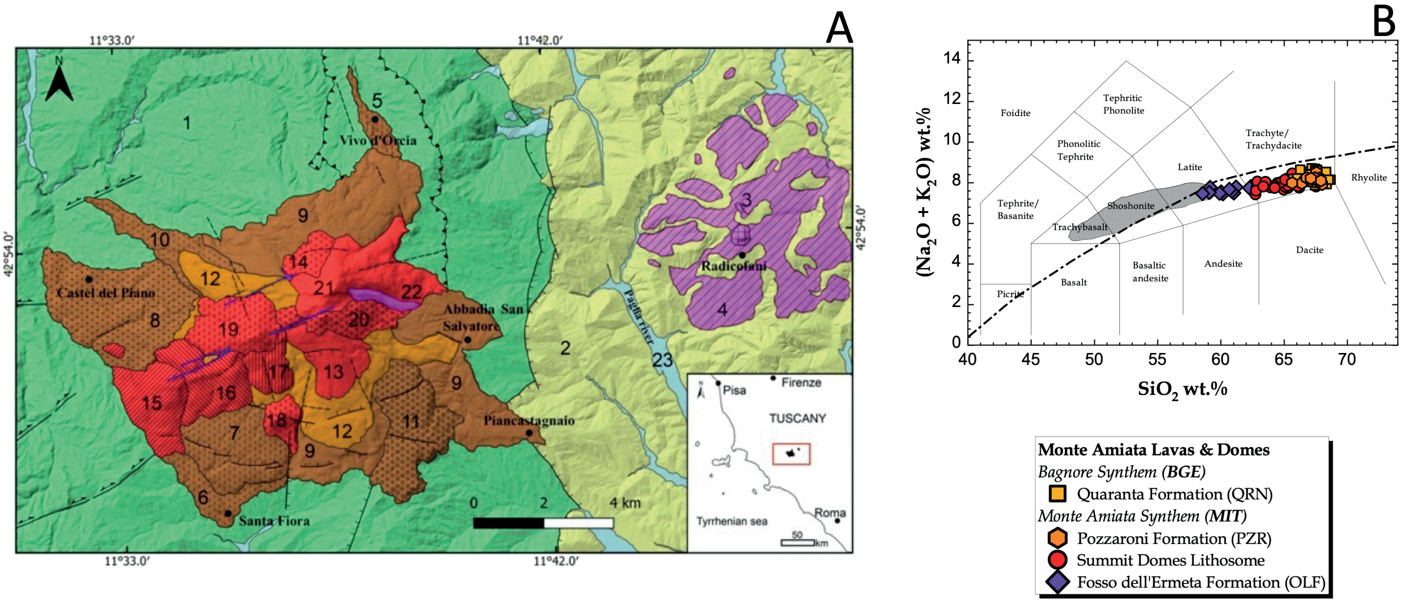

Figure 1 a) *Geographic location and Geological chart of the Monte Amiata–Radicofani volcanic area (courtesy of Sepulveda-Birke J.P.);* ***BGE*** *(5, 6, 7, 8, 9, 10, 11), PZR (12),* ***MIT*** *(13, 14, 15, 16, 17, 18, 19, 20, 21), OLF (22).* ***b)*** *Total Alkali vs. Silica classification diagram of volcanic rocks from Monte Amiata, the grey field represent data of magmatic enclaves from Conticelli et al. 2015a.*

minor clinopyroxenes, set in a glassy groundmass with frequent occurrence of sanidine fragments. The "*Monte Amiata*" synthem (**MIT**) (Fig. 1a) represent the summit domes starting from the "*Pozzaroni*" formation (PZR) and moving toward the East direction along the eruptive fissure. Rocks are porphyritic microcrystalline with major sanidine megacrystals, and phenocrysts of zoned plagioclase, clino- and ortho-pyroxenes, brown mica, all immersed in a groundmass made up of nanolites of plagioclase, pyroxenes, ±olivine and glass. The "*Fosso dell'Ermeta*" formation (OLF) is represented by two small lava flows located on the Eastern flank of the volcano and is already part of the **MIT**, testify the closure moment of the eruption. OLF rocks are porphyritic with microcrysts of zoned plagioclase, brown mica, clino- and ortho-pyroxenes, set in a groundmass of the same phases plus olivine. In the **MIT** lavas and domes, the magmatic enclaves increase the size and the mafic composition, while meta-sedimentary xenoliths are less common.

Petrology and Geochemistry

Whole-rocks geochemistry investigations of the volcanic rocks indicate a wide compositional spread passing from trachydacite to latite (Fig. 1b), whereas trace elements indicate the important role played by sediments during the subduction suggesting a primary recycling of a sedimentary component within the upper mantle (Conticelli & Peccerillo, 1992; Avanzinelli et al., 2008; Conticelli et al., 2015b).

Isotope chemistry reveals a similar isotopic composition for the different lava tongues of (**BGE**) ($^{87}Sr/^{86}Sr$ = *0.713019*) all around the volcano, which begins to change from the "*Pozzaroni*" formation (PZR) (*0.71301–0.71292*) and continues to vary in the Sr-ratio towards the summit domes (**MIT**) (*0.712905*) and the final lavas (OLF) (*0.71161*). The "*Pozzaroni*" formation was placed temporally and spatially between the basal complex (i.e., "*Bagnore*" synthem) and summit domes (i.e., "*Monte Amiata*" synthem), representing an intermediate outcrop with similar features between **BGE** and **MIT** rocks (Fig. 1a).

The whole-rock geochemistry of thermo-metamorphic xenoliths indicates a generic SiO_2- and Al_2O_3-rich rock typical of a pelite, with enrichment in barium and strontium. Isotope chemistry reveals an $^{87}Sr/^{86}Sr$ ratio of *0.71675*.

Mineral Chemistry

Mineral chemistry investigations are carried out on plagioclase, sanidine, brown mica, clino- and orthopyroxenes, and glass from groundmass and melt inclusions (MIs). In particular, brown micas from igneous and meta-sedimentary suites exhibited different geochemical signatures suggesting distinct growth environments that slightly interact with each other (Fig. 2a), followed similarly by the geochemical signature of sanidine; clinopyroxenes record a transition from sub-alkaline to alkaline affinity of his hosted rocks (Fig. 2b). μSr-Isotope investigation on sanidine megacrysts indicate a high-radiogenic core (*0.71338*) and a less-radiogenic rim (*0.71305*) (Fig. 2c) suggesting a strong disequilibrium condition during the growth and the nucleation set in a complex magmatic environment and starting from an ancient sub-crustal mantle-derived magma, which gradually begins to undergo a magma mixing with a more mafic and less radiogenic magma. Also, brown mica, plagioclase and sanidine record the presence of peraluminous component released from magmatic fluids during a near-soli-

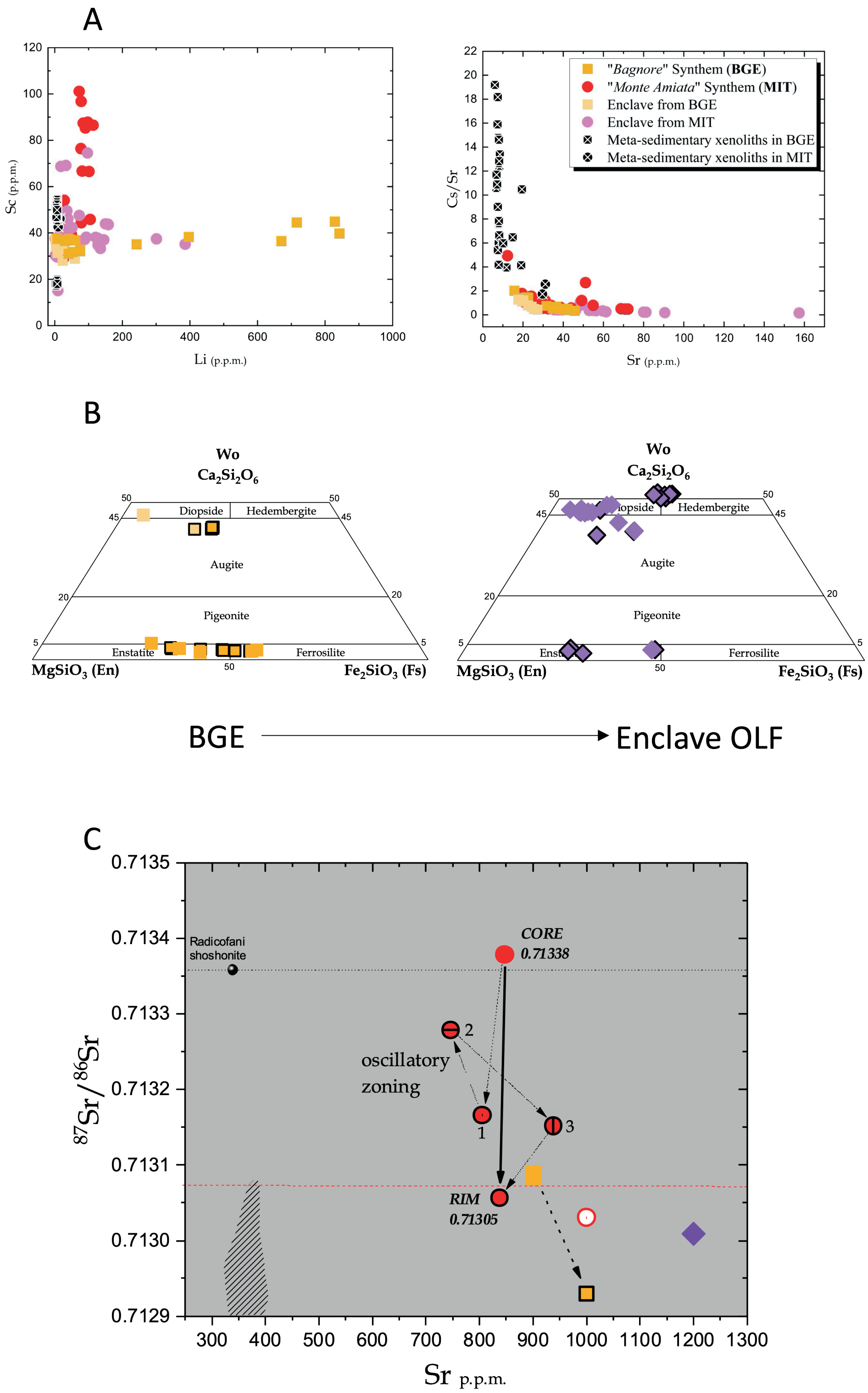

Figure 2 a) *Brown Micas trace-elements chemistry denotes an enrichment in lithium for samples from BGE while an enrichment in scandium for crystals from MIT (left graph); it also suggests a mutual interaction between magma and crustal xenolith (right graph).* ***b)*** *Clinopyroxene major-elements chemistry from* ***BGE*** *(left) and OLF magmatic enclaves (right) rocks suggesting a change in the magmatic affinity passing from sub-alkaline to alkaline.* ***c)*** *μSr-isotope chemistry of sanidine megacrysts exhibits characteristic oscillatory zoning and suggests a combination of fractional crystallisation plus magma mixing processes, revealing the chaotic nature of the system.*

dus condition, suggesting by: *i)* the partial melting of xenoliths associated with a release of Rb, Al, and Fe-rich peraluminous melts, and *ii)* the signature in lithium is interpreted as an indicator that characterises the marginal zone of the magmatic chamber, where the crystallisation is pushed toward the limit of the melt-impregnated regime condition (i.e., < 20 – 50 vol.% of melt; Koyaguchi & Kaneko, 2000). Textural and mineral chemistry evidence supports the process of continuous fractional crystallization followed by numerous injections of hot and mafic magmas. Also, there is compelling information about an active interaction between magmas and meta-sedimentary xenoliths indicated by mineral reactions and compositional signatures and by the circulation of hydrothermal-magmatic fluids in the marginal shell zone of the magmatic chamber. Such isotopic disequilibrium within individual sanidine megacryst samples provides compelling evidence of dynamic magma interactions in a chaotic environment, highlighting the potential coexistence of distinct magma sources, or stages, within the magmatic system. This suggests a possible co-genetic relationship between the trachytic magma (HKCA) of Monte Amiata (Conticelli et al., 2015a) and a common mantle source component with the nearby Radicofani volcano (Conticelli et al., 2011).

Thermobarometry calculations

Different thermobarometric methods, as machine learning and traditional calculation, are applied using the chemistry investigations carried out on plagioclase, clinopyroxene and glass. In particular, the automatised calculations are made by Thermobar (Wieser et al., 2022) and GAIA (Chicchi et al., 2023), with the capability of being able to use a wide range of thermodynamic equations from experimental literature (e.g., Putirka et al., 2003; Putirka, 2008; Waters & Lange, 2015; and references therein). Temperature, pressure and water content investigated reveal a volcanic condition represented by a shallow hypabyssal magmatic reservoir with deep mafic roots, characterised by a *T-P-*X_{H2O} range of 900 – 1160°C, 1 – 9 kbar, and H_2O wt.% between 0.8 – 2.1, respectively (Fig. 3a-b).

Melt inclusions microthermometry constrain

Two types of MIs are present within sanidine mega- and phenocrysts: *i*) a *euhedral* type, ranging in size from 200 to 25 μm, displaying a regular geometry of rooms. The colour of glass ranges from brown to colourless, from nanocrystalline to glassy matrix. Bubbles are present in large and small specimens, appearing mostly black in transmitted light, occupying ½ and ¼ of the total volume of the MI. *ii*) An *anhedral* type frequently show a size up to 200 μm, the colour of the glass ranging from brown to colourless and the bubble is large and accompanies the irregular shape of the MIs. Microthermometric experiments are held on MIs extracted from megacrysts core and rim zone, in which no differences in temperature are recorded between them. According to the guidelines of Frezzotti (2001), results of heating experiments reveal an observed average T_1 of 994°C, and an average T_2 of 1114°C, while T_3 is never reached. During the increase in temperature, the bubble is never reabsorbed by the melt.

CO_2-dominated plumbing system

Raman spectroscopy investigations are conducted on the bubble of heated MIs. Analyses reveal the presence of pure CO_2, showing the typical peaks at 1387.05 cm^{-1} and 1283.67 cm^{-1} with a constant Fermi diad (Fermi, 1932) of 103.4 cm^{-1}. The amount of carbon dioxide observed within sanidine MIs aligns with the low water content measured indirectly by plagioclase–liquid hygrometer (Waters & Lange, 2015) and by the crystal-chemistry investigation on brown mica.

Magma-Crust interaction

The degree of interaction between the magmatic intrusion and the metamorphic basement can be understood using the crustal meta-sedimentary rocks that could be found in lavas and domes as xenoliths. A detailed study on petrography, geochemistry, seismic wave velocity propagation and thermal propagation of crustal xenoliths is mandatory to understand how the heat is released from the magmatic intrusion through the metamorphic rock basement. Meta-sedimentary rocks show a wide spectrum of facies and textures typically of contact metamorphosed pelites passing from *slate* (500-570°C; Fig. 4a), *semi-hornfels* (600-650°C; Fig. 4b) to *hornfels* (700-750°C; Fig. 4c-d), changing progressively the mineralogic assemblage. The observed transition indicates an increase in temperature, which may represent the thermo-metamorphic shell surrounding the magma cham-

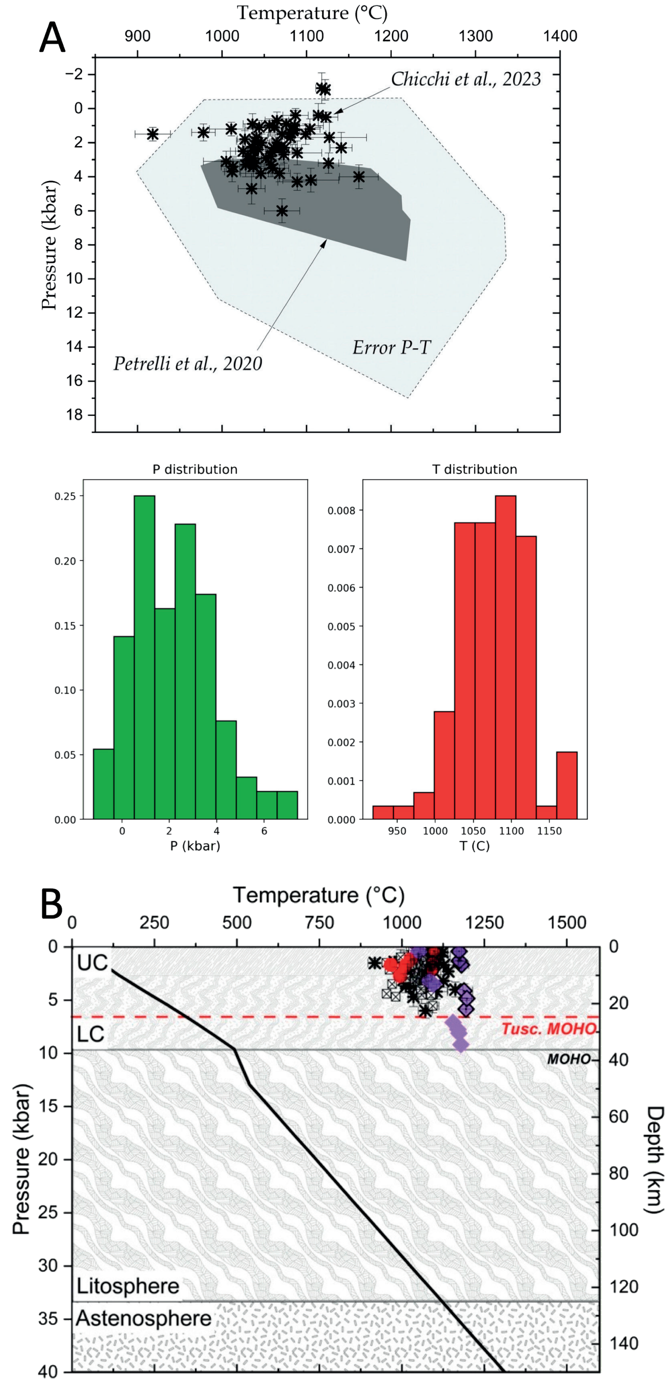

Figure 3 a) *Pressure and Temperature space calculated by Machine Learning.* ***b)*** *Schematic representation of the magmatic intrusion in an ideally reconstructed lithospheric mantle structure.*

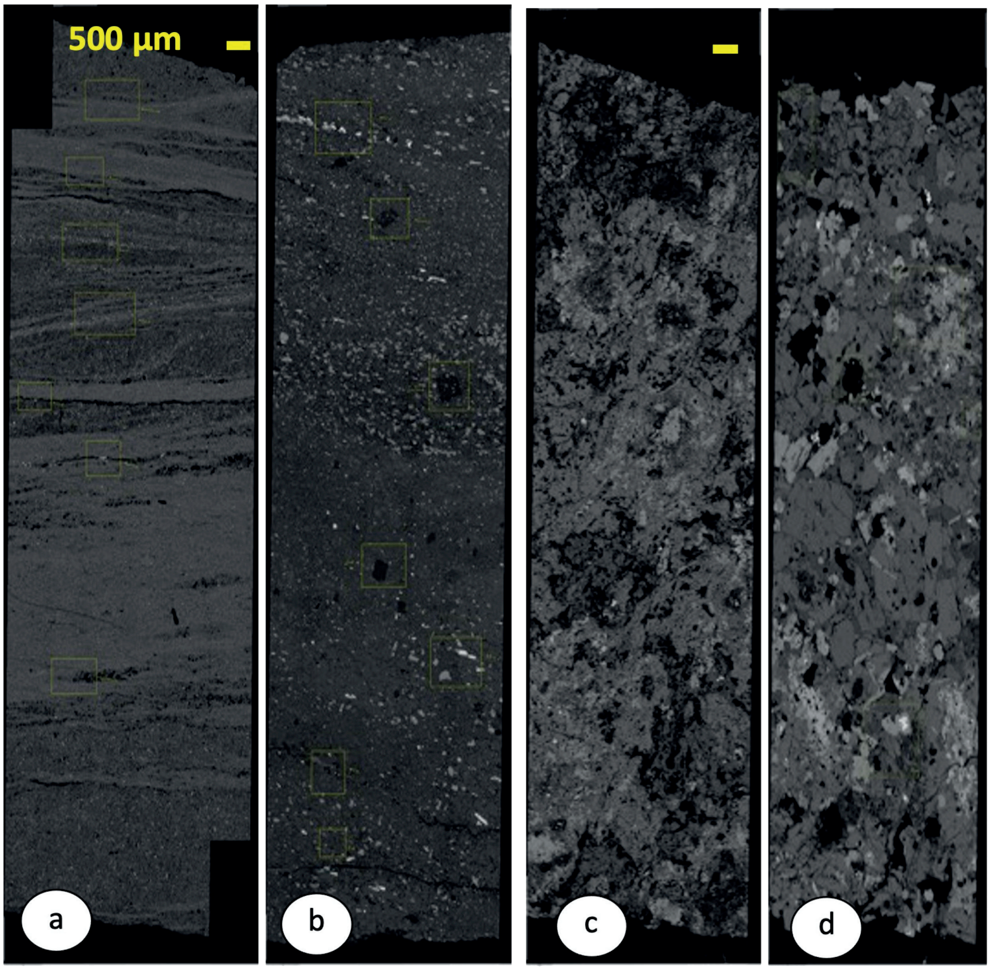

***Figure 4** SEM-BSE image of crustal meta-sedimentary xenoliths hosted by lavas and domes. Following the fabric and mineral features of xenoliths, it is possible to recognise an order related to the thermo-metamorphism of pelitic rocks, sketchily representing the contact aureole around the magmatic reservoir. The recognised facies are **a)** slate; **b)** semi-hornfels; **c-d)** hornfels.*

ber, also known as the contact aureole. The progressive change in their mineral fabric denotes variations in the petrophysics proprieties, such as the V_P/V_S ratio and the thermal conductivity/diffusivity. Using all information, from thermobarometry, geochemistry and petrophysics, is possible to quantify the thermal propagation between the magmatic body and the surrounding crustal country rocks.

The geothermal potential calculation

The search for geothermal energy in the Monte Amiata area began in the 1950s (Barelli et al., 2010; Bertini et al., 1995), and together with the active Larderello geothermal field (Parri & Lazzeri, 2016 and references therein), it constitutes a strategic national and regional energy hub. The work carried out in this study attempts to go beyond the classic approach of studying a geothermal field but attempts to theorize a very-deep reservoir within Tuscany basement rocks, and beneath the Monte Amiata area, integrating all the information derived from investigations of crustal and volcanic material. Theoretically, it is possible to create multiple synthetic reservoirs through the application of Hot Dry Rock (HDR) technology (Rummel, 2005; U.S. Department of Energy, 1997), bypassing the shallow (Barelli et al., 2010) and the deepest (Bertini et al., 1995) geothermal reservoirs currently used for the energetic production. The calculation was made bypassing all problems related with the engineering application of HDR technology in a complex geothermal field such as Monte Amiata. The present-day thermal emission from the magmatic heat source is characterised by a temperature of 820°C (i.e., calculated using a ratio of 100°C/100 ka; González et al., 2022; Zambra et al., 2022), quantifiable by 10^{24} calories emitted per km^3. Considering the possibility of being able to create and exploited, by means of high-pressure fluids, a reservoir of fractured rocks at a depth of about 5 km and with a volume of 10 km^3 with a maximum theorical energy production of 3277 MW/year or 0.33 GW_{yt}.

CONCLUSIONS

Results of stratigraphy, petrography, geo- and mineral-chemistry, and isotope chemistry suggest a single extrusive eruption involved in the setting of lavas and domes. The petrogenesis of high-silica magmas could be explained by an intrusion of sub-crustal mantle-derived HKCA/SHO magmas (i.e., Tuscany-type; Conticelli et al., 2010; Peccerillo, 2017) in the lithospheric crust, which undergoes a process of R_xMFC due to the progressive injection of a hot and mafic silica-undersaturated potassic mantle-derived magma (i.e., Roman-type; Conticelli et al., 2010; Peccerillo, 2017) (Fig. 5a-b). The geochemical model performed on the groundmass glasses of trachydacitic rocks and the mineral chemistry investigations supports the presence of a micro-assimi-

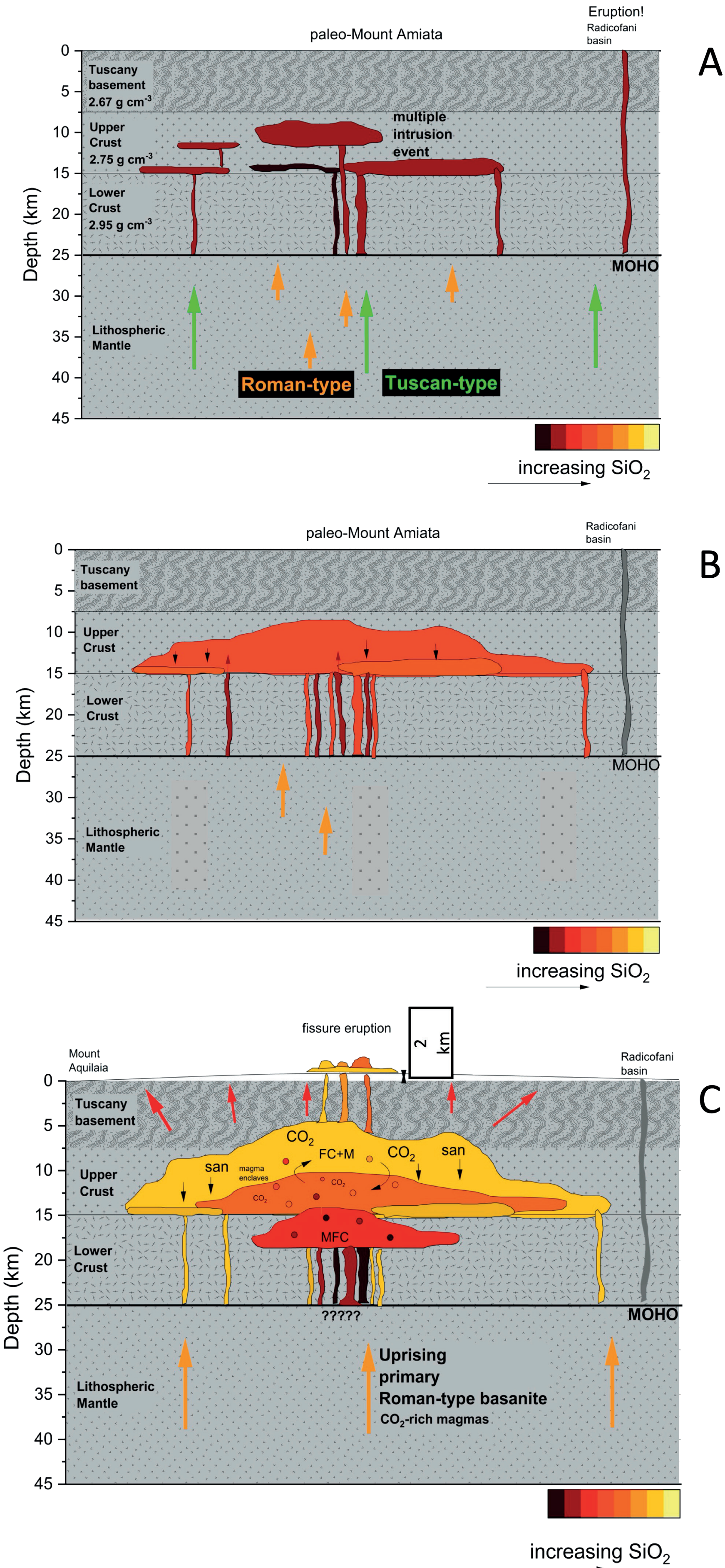

Figure 5 *Reconstruction of the magmatic intrusion beneath the studied area.* ***a)*** *The eruption event of Radicofani volcano signing the moment of the first intrusion of HKCA/SHO mantle-derived magmas (i.e., 1.2 Ma).* ***b)*** *The continuous Fractional Crystallisation process plus a magma mixing with Roman-type mantle-derived magmas involves the evolution and the increase in size of the magmatic reservoir.* ***c)*** *In the last stage, prior to the eruption of Monte Amiata volcano (i.e., 0.30 – 0.23 Ma), the magmatic reservoir was characterised by a zoned magmatic chamber with different levels, a mafic magma roots in depth and a differentiated magmas on the top.*

lation process of peraluminous melts/fluids release from pelitic xenoliths, undergoing pyrometamorphic processes during the last stage of the magmatic differentiation. The application of geothermobarometers revealed a volcanic temperature range from 900 to 1160°C, with a largely variable storage pressure between 0.1 and 0.9 GPa. Microthermometry experiments on sanidine melt inclusions confirm these volcanic temperatures in the range between 900 and 1075°C. The Pressure and Temperature found suggest volcanic conditions during the eruption event, supporting the idea of mantle-derived magmas and a storage depth from ≈3 to ≈20 km (Fig. 5c). The large amount of CO_2 indicates mantle processes as the main players, furthermore, influencing the amount of water dissolved in magma and, additionally, opens the way on the potential release of carbon-rich fluids from thermo-metamorphosed crustal xenoliths directly into the magmatic reservoir. The architecture of the magma chamber of Monte Amiata volcano can be idealised with a batholith-shape divided into two zones with different thermo-chemical features, characterised by a differentiated rock in the most marginal inner zone of the magmatic reservoir and a contact aureole in the outer zone, and mafic roots deep down (Fig. 5c). The calculated present-day temperature emitted by the heat source is about 820°C, quantifiable by 10^{24} calories emitted per km^3, and a maximum theoretical energy production of 3277 MW/year or 0.33 GW_{yt}.

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