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RESEARCH ARTICLE

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Chemical-petrographic and isotopic characterization of the volcanic pavement along the ancient Appia route at the Aurunci Mountain Pass, Italy: Insights on possible provenance

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Abstract

The ancient Appia route was built across central-southern Italy between the fourth and second century before the common era (B.C.E.). At the Aurunci Mountain Pass, the route crosses carbonate ridges that provided the raw material used to pave the road in the first century C.E. This material was replaced with lava blocks of unknown origin in the third century C.E. The study area is at least 50 km from the main volcanic centers along the peri-Tyrrhenian side of Italy, such as the Colli Albani, Roccamonfina, and Middle Latin Valley volcanoes. The main objective of this research was the chemical–petrographic and isotopic characterization of rock samples from the Appia flagstones to unravel their possible provenance. The analytical procedure included scanning electron microscope and electron microprobe analyses and $^{87}Sr/^{86}Sr$–$^{143}Nd/^{144}Nd$ isotopic measurements. Samples taken from unknown quarries found in the Middle Latin Valley volcanic field underwent the same analyses. After comparing the analysis results with data from the literature, the most likely source area was identified with the Roccamonfina precaldera ultrapotassic sequence. The availability and use of volcanic resources for the construction and maintenance of the ancient Appia route in the investigated territories are only outlined in this work and deserve further study.

KEYWORDS

Appia route, central Italy, lava flagstones, petrographic analyses, Sr–Nd isotopes

1 | INTRODUCTION

The ancient Appia route (i.e., Via Appia Antica) was built during the Roman Republican period, from 312 B.C.E. until the end of the second century B.C.E., during which the continuous extension of the road track connected Rome to the harbor of Brundisium (Figure 1a). Under Emperor Hadrian (first half of the second century C.E.), an expansion of the road was established to connect Beneventum and Brundisium (Appia Traiana) (Quilici, 1997; Talbert & Bagnall, 2000). Within the southern Latium territory, the Appia route runs straight in an NW-SE direction into the Pontina Plain (Quilici, 1989). Then, the road track enters the central Apennines at the Aurunci Mountain Pass (Figure 1b) between the modern towns of Fondi and Itri (Quilici, 1999; Quilici, 2002; Quilici, 2003; Quilici, 2004; Quilici, 2011), where it overcomes steep carbonate mountain ridges (Figure 2a). Still going SE, the consular road crosses the Garigliano River plain before arriving in the Roccamonfina volcanic area, which extends over the Latium-Campania regional boundary (Figure 1b).

The familiar appearance of the ancient Appia route is stone pavement comprising black lava blocks (Figure 2b), also known as "basoli." The origin of such heavyweight and high-density pavement material has been discussed for the main consular roads near Rome (e.g., Black, Browning, & Laurence, 2004; Laurence, 1999; Laurence, 2004; Worthing, Bannister, Laurence, & Bosworth, 2017). At the Aurunci Mountain Pass, the original stone paving of the road was conducted under Emperor Augustus (44 B.C.E.–14 C.E.) using

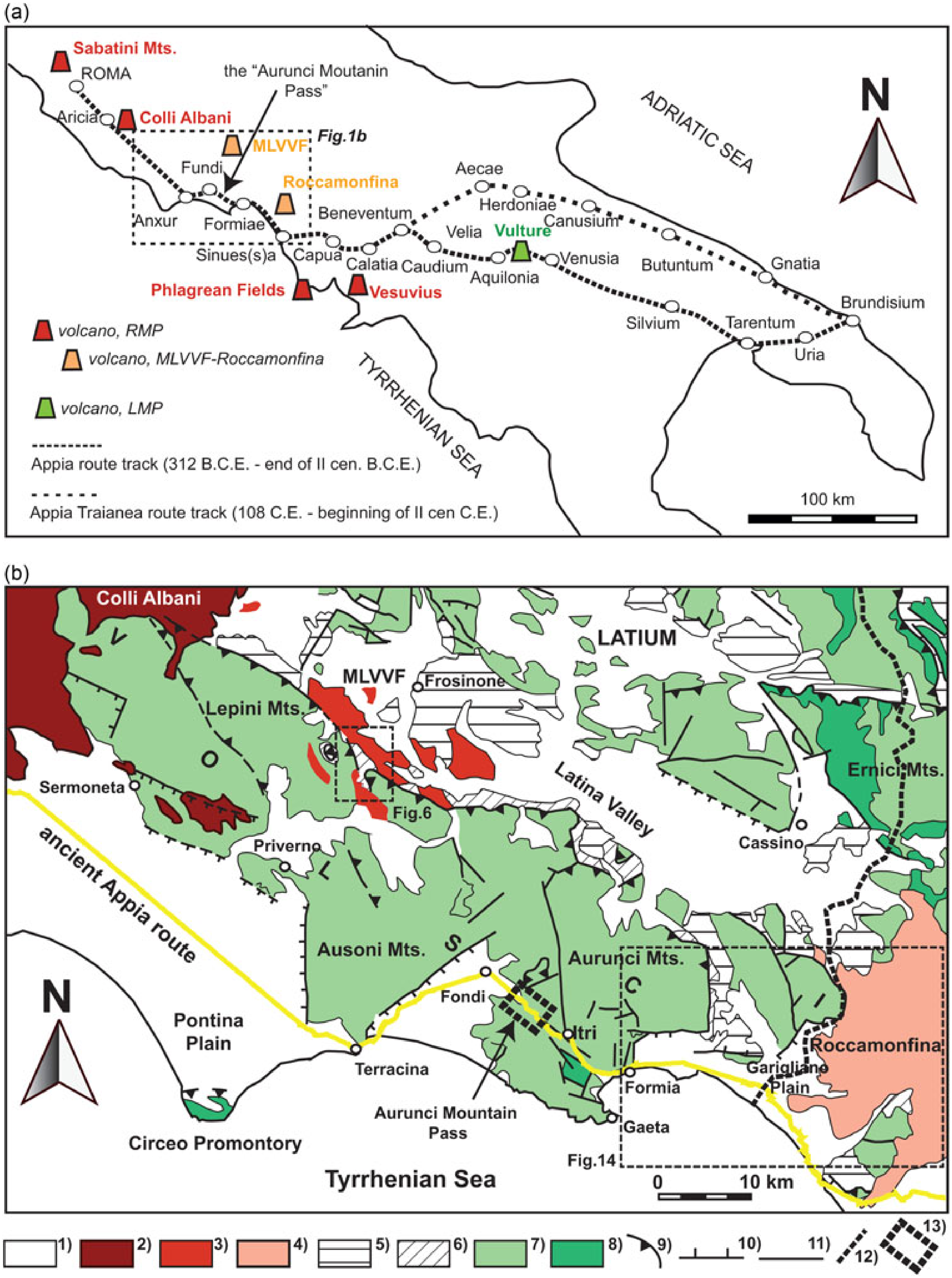

FIGURE 1 (a) Map of central-southern Italy with the ancient Appia route marked. White dots indicate main cities and villages connected by the road. The locations of volcanoes are reported. LMP: Lucanian Magmatic Province; MLVVF: Middle Latin Valley volcanic field; RMP: Roman Magmatic Province. (b) Geological setting of southern Latium and northern Campania (from Parotto & Tallini, 2013, modified). 1) Continental and marine deposits (Holocene-Upper Pleistocene); 2) Colli Albani volcanic deposits (Upper Pleistocene-Holocene); 3) Middle Latin Valley Volcanic Field deposits (Upper Pleistocene); 4) Roccamonfina volcanic deposits (Upper Pleistocene); 5) Syn-orogenic terrigenous deposits (Upper-Middle Miocene); 6) Liguride Unit basinal deposits (Lower Miocene-Oligocene); 7) Carbonate platform deposits (Paleocene-Jurassic); 8) Carbonate platform deposits (Lower Jurassic-Upper Triassic); 9) Thrust fault; 10) Normal fault (dashed when inferred); 11) Strike-slip fault; 12) Latium-Campania regional boundary; 13) Location of the study area. Dashed rectangles indicate boundaries of Figures 6 and 14 [Color figure can be viewed at wileyonlinelibrary.com]

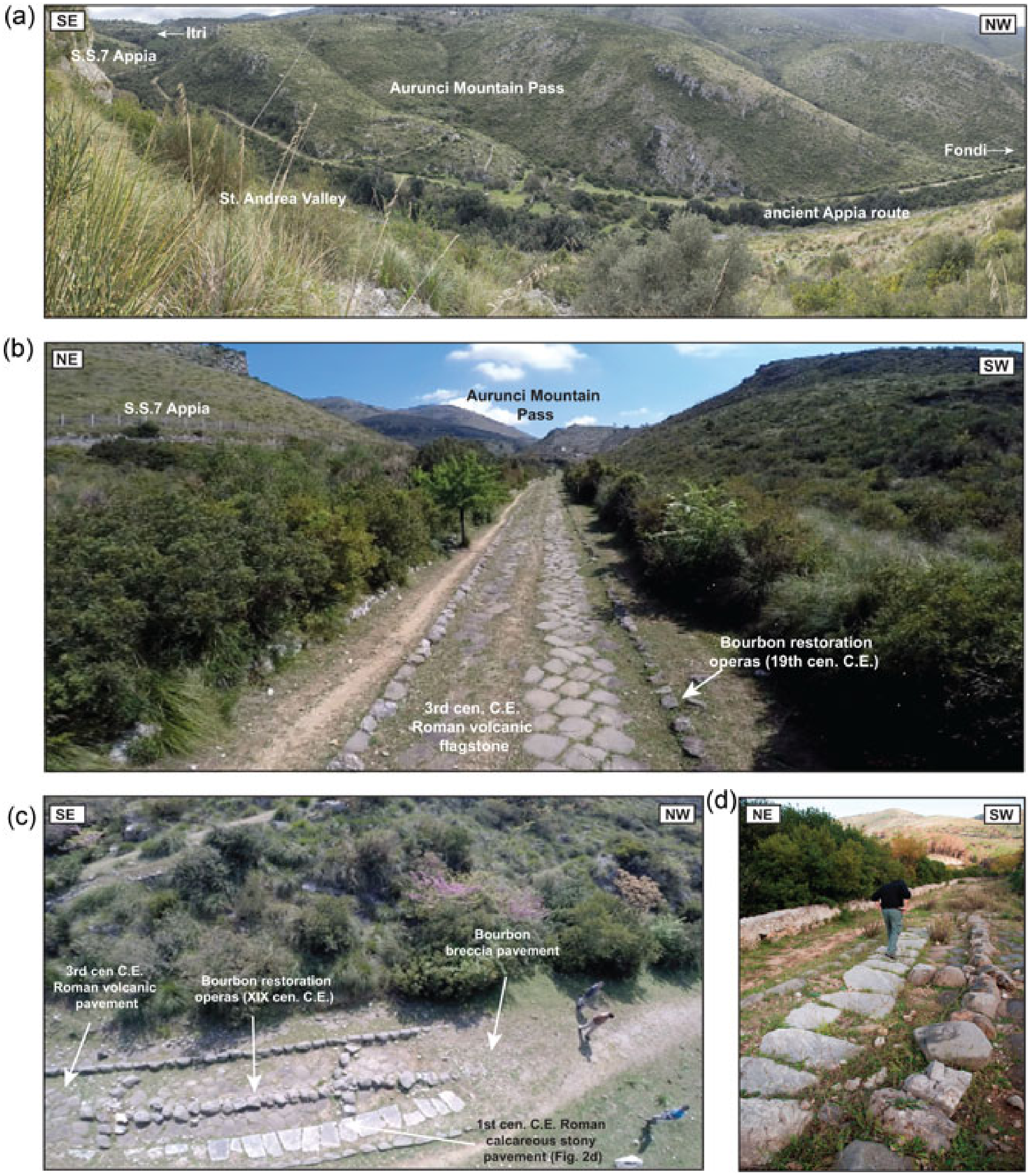

FIGURE 2 (a) Panoramic view of the ancient Appia route at the Aurunci Mountain Pass. (b) UAV (unmanned aerial vehicle) image of the route track with the volcanic stone pavement (third century C.E.) in the St. Andrea Valley. (c) Bourbon restoration works shown by UAV imaging. (c,d) Original stone pavement (first century C.E.) composed of local calcareous rock blocks [Color figure can be viewed at wileyonlinelibrary.com]

calcareous stone (Figures 2c,d) exploited in the local carbonatic Apennine range (Carfora & Di Luzio, 2016; Di Luzio & Carfora, 2018); later, under Emperor Caracalla (216 C.E.), raw volcanic materials from an allochthonous source were exploited to produce lava flagstones. In modern ages, the main restoration efforts (Figure 2b, c) were completed in the 16th century C.E. by the Spanish government of Naples and during the Bourbon period (beginning of the 19th century C.E.) (Quilici, 2004; Quilici, 2007; Quilici, 2011).

In this paper, we present a multimethodological analytical procedure aimed at defining the possible provenance of the volcanic stone pavement on the ancient Appia route at the Aurunci Mountain Pass, a geoarchaeological issue that has not yet been addressed (Quilici, 2002). Identifying the provenance quarry of stones used for the construction of artefacts, buildings, and infrastructures is a common geoarchaeological issue (e.g. Barfod, Freestone, Lichtenberger, Raja, & Schwarzer, 2018; Germinario, Zara et al., 2018; Germinario, Hanchar et al., 2018).

Preliminary hypotheses principally consider the source areas to be the Colli Albani and Roccamonfina volcanic districts (e.g., Conticelli & Peccerillo, 1992; De Rita & Giordano, 1996; De Rita, Faccenna, Funiciello, & Rosa, 1995; Fornaseri, Scherillo, & Ventriglia, 1963; Giordano et al., 2006; Peccerillo, 2005), since they are both traversed by the Appia route (Figure 1a,b); however, both of these areas are more than 50 km away from the Aurunci Mountain Pass, thus implying a lengthy transportation of raw materials from the source location. As a secondary hypothesized source location, the

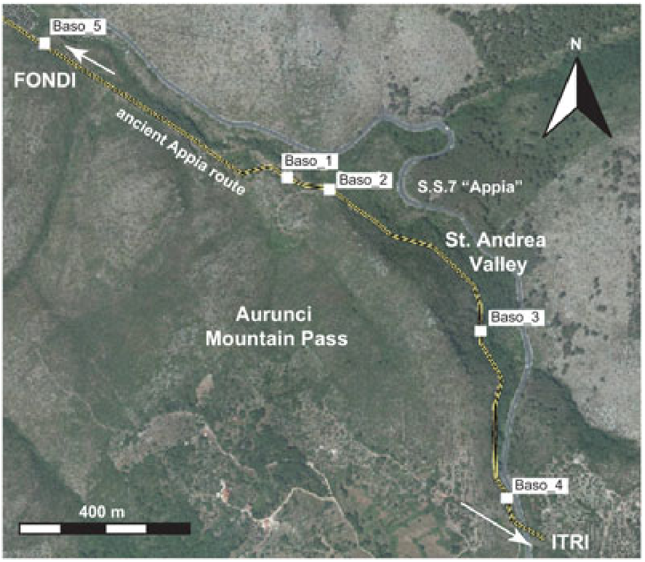

FIGURE 3 Sampling site map [Color figure can be viewed at wileyonlinelibrary.com]

Middle Latin Valley volcanic field (hereafter MLVVF; Frezzotti, De Astis, Dallai, & Ghezzo, 2007; Boari & Conticelli, 2007; Boari, Tommasini, Laurenzi, & Conticelli, 2009) was considered because it falls within the same 50 km radius of interest on the mainland (Figure 1b). While rock quarries of archaeological interest exploiting lava flows are known to be present in the Colli Albani and Roccamonfina areas (Giampaolo, Lombardi, & Mariottini, 2008; Panarello, 2008; Spera, 1999), part of the MLVVF territory was investigated to identify unknown lava quarries, and sites were discovered in the Giuliano di Roma area.

Other volcanic centers, such as the Sabatini Mountains, Vesuvius, and the Phlegraean Fields, were considered less likely sites because they are farther from the Aurunci Mountain Pass (Figure 1a). Finally, overseas resources were not considered because there is no archaeological evidence of a harbor in the Fondi area in the third century C.E. (Cornell & Matthews, 1982).

Volcanic rock samples were taken at five sites along the route track (Figure 3) and underwent a chemical–petrographic laboratory characterization by scanning electron microscope (SEM) and electron microscope probe analyses, which allowed the identification of sample texture, paragenesis, and the quantitative petrochemical composition of main mineral phases. In addition, the $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ isotopic ratios were determined by thermal ionization mass spectrometry. The same analytical procedure was completed for rock samples taken from the Giuliano di Roma quarries.

The results of these analyses were compared with the abundant scientific literature on the petrographic and isotopic signatures of lava products from volcanic districts in central-southern Italy. Different geoarchaeological scenarios were then outlined, opening the scientific debate about the availability and exploitation of geological resources in the Early Imperial ages for the maintenance operations of the ancient Appia route in the territories of southern Latium and northern Campania.

2 | GEOLOGICAL BACKGROUND

In central-southern Italy, the volcanic activity in the Roman Magmatic Province began over a time interval between 0.8 and 0.6 Ma (Peccerillo, 2005) in several volcanic districts (Figure 1a), including clusters of two/three main volcanic edifices (e.g., Sabatini), monogenetic volcanic fields (e.g., Middle Latin Valley and Phlegraean Fields), and districts characterized by a single volcanic edifice with/without a summit caldera and a postcaldera monogenetic activity (e.g., Somma-Vesuvius, Colli Albani, and Roccamonfina volcanoes; e.g., Di Vito et al., 1999; Peccerillo, 2005; Peccerillo & Lustrino, 2005; Conticelli, Melluso, Perini, Avanzinelli, & Boari., 2004; Conticelli, Carlson, Widom, & Serri, 2007; Conticelli et al., 2010; Di Renzo et al., 2007; Alagna, Peccerillo, Martin, & Donati, 2010; Gaeta et al., 2011; Gaeta et al., 2016). In the following sections, brief descriptions of the three volcanic centers hypothesized to be the most likely source areas for the volcanic stone pavement of the ancient Appia route at the Aurunci Mountain Pass will be presented, with an emphasis on lava flows.

2.1 | The Colli Albani volcanic district

Volcanic activity at Colli Albani lasted between 0.6 and 0.04 Ma (De Rita et al., 1995; Karner, Marra, & Renne, 2001; Gaeta et al., 2006a; Gaeta et al., 2016; Giordano et al., 2006; Giaccio et al., 2007; Giordano, 2008), although a quiescent condition has been suggested by new geochronological, gas emission, shallow seismicity, and crustal uplift data (Marra, Anzidei et al., 2016; Marra, Gaeta et al., 2016). The chemical compositions of the pyroclastites and lava flow from the Colli Albani district (Figure 4) are all attributable to the ultrapotassic series (Trigila et al., 1995). Specifically, the Colli Albani eruptive history developed during three main phases of activity (e.g., De Rita et al., 1995; Giordano et al., 2006): (a) the Tuscolano-Artemisio Phase (0.6–0.35 Ma), which consisted of large, caldera-forming eruptive cycles; (b) the Monte delle Faete Phase (0.3–0.24 Ma), characterized by dominant Strombolian and effusive activity, and (c) the recent eruptive activity phase (0.2–0.036 Ma) (Marra et al., 2003; Marra, Karner, Freda, Gaeta, & Renne, 2009; Freda et al., 2006; Freda et al., 2011; Giaccio et al., 2009; Gaeta et al., 2011; Gaeta et al., 2016).

The Capo di Bove lava flow, associated with the Monte delle Faete Phase, is acknowledged as the main source of the paving material of the ancient Appia route (Giampaolo et al., 2008; Spera, 1999; Worthing et al., 2017). Within the ultrapotassic Roman Comagmatic Province, the products from the effusive phases of the Colli Albani district, including the Capo di Bove lava flow, show distinctive petrochemical features, including (a) a K-foiditic composition, with SiO_2 contents as low as 42wt.% (Gaeta et al., 2006b; Palladino, Gaeta, & Marra, 2001; Trigila et al., 1995), that is much lower than those of even basalts; and (b) the absence of plagioclase in the paragenesis (Conticelli et al., 2010; Fornaseri et al., 1963; Gaeta et al., 2016; Trigila et al., 1995).

2.2 | The Roccamonfina volcano

Alternating lava flows, domes, and pyroclastic deposits erupted during three main periods of activity between 600 and 100 ka, forming the

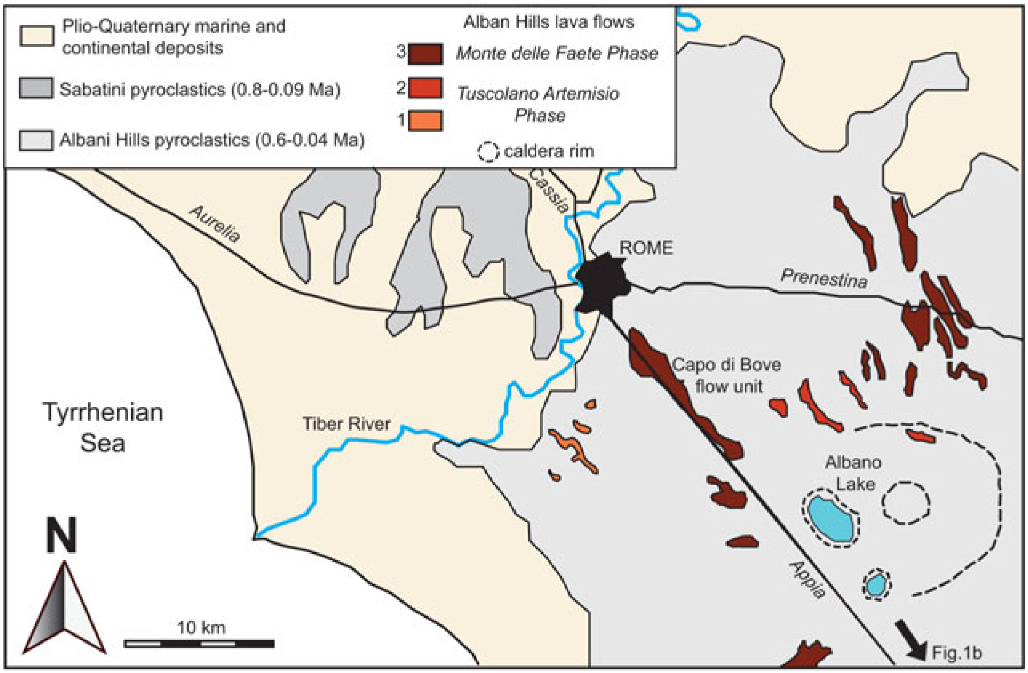

FIGURE 4 Simplified geological map of the Colli Albani volcanic districts with the main consular road routes leaving Rome (modified from Worthing et al., 2017). 1) Pozzolane Rosse eruptive cycle and 2) Villa Senni eruptive cycle *sensu* Freda et al. (2011); 3) Monte delle Faete lavas (including the Capo di Bove flow unit) [Color figure can be viewed at wileyonlinelibrary.com]

Roccamonfina stratovolcano (Figure 5), and are characterized by different geochemical and petrographic signatures (e.g., Ballini, Barberi, Laurenzi, Mezzetti, & Villa, 1989; Conticelli et al., 2009; De Rita & Giordano, 1996).

The first phase of activity (the "pre-caldera period," according to Conticelli et al., 2009) was dominated by the emission of HKS (ultrapotassic series) lava flows (tephrites, phonolites, and plagioclase-bearing leucitites) and subordinate pyroclastites (Giannetti & Ellam, 1994). The following period began after the collapse of the summit caldera ca. 400 ka; pyroclastic and lava flows erupted between 385 and 230 ka (Giannetti & Luhr, 1983; Luhr & Giannetti, 1987; Cole, Guest, & Duncan, 1993; Giordano, 1998a; Giordano, 1998b; De Rita, Giordano, & Milli, 1998), with a KS (potassic series) affinity (trachybasalts, shoshonites, latites, and trachytes). Finally, the last phase of the postcaldera activity spans from 155 to 50 ka (Fornaseri, 1985; Radicati di Brozolo, Di Girolamo, Turi, & Oddone, 1988) and is characterized by the emplacement of subalkaline magmas forming leucite-free mafic lavas and trachytic domes.

2.3 | The Middle Latin Valley volcanic field

The MLVVF is located east of the Volsci ridge (Figure 1b) and it is also known as the Ernici Mts. volcanic district in the Italian geological literature (e.g., Basilone & Civetta, 1975; Civetta, Innocenti, Manetti, Peccerillo, & Poli, 1981; Peccerillo, 2005). Different from the activity of the Colli Albani and Roccamonfina stratovolcanoes, the MLVVF activity occurred through several small scoria, cinder cones, and tuff rings (Figure 6) between 0.7 and 0.37 Ma (Basilone & Civetta, 1975) (or 0.260 Ma in Boari, Tommasini, et al., 2009).

The petrological affinity of these volcanic products indicates a transition from basalt, K-trachybasalt, shoshonite, leucite tephrite, and foidite compositional fields over time. The subalkaline terms display K_2O contents and K_2O/Na_2O ratios within the ranges of calc-alkaline basalts, although the volcanic products are undersaturated in silica (Boari & Conticelli, 2007; Boari, Tommasini et al., 2009; Civetta et al., 1981; Frezzotti et al., 2007; Peccerillo, 2005).

3 | ANALYTICAL METHODS

3.1 | Chemical–petrographic analyses

An environmental SEM (ESEM) analysis was completed at the ESD Electron Microscopy Laboratory of the Earth Science Department of the "Sapienza" University of Rome with a Thermo Scientific QuantaFEI 400 SEM equipped with an EDAX Genesis microanalysis system. SEM microscopes strike small samples with guided electron beams to conduct analyses. Samples were kept under high vacuum ($P = 10^{-5}$ Torr) conditions, as air prevents the production of low-energy electron beams. During the interaction between the primary beam and the sample-forming atoms, numerous particles are emitted, including secondary electrons. For this reason, the sample must first be conductive; otherwise, its production of electrostatic charges disturbs the detection of secondary electrons. To ensure conductivity, all thin sections were covered with a graphite coating. Electrons were then captured by a special detector and converted into electrical pulses sent to a screen that displayed real-time black-and-white high resolution (approximately 5 nm) images. For this work, ESEM analyses were used for qualitative observations on sample texture and main mineral phases.

The quantitative chemical analyses of the main elements of single minerals were performed at the CNR-IGAG (Institute for Environmental Geology and Geoengineering) Electron Microprobe Laboratory via a Cameca SX-50 Electron Microprobe Analyser (EMPA) equipped with five wavelength-dispersive spectrometers and a Link Analytical eXL energy dispersive spectrometer. The EMPA allows the basic chemical composition of a sample to be determined within an area of approximately 10–30 nm^3; chemical elements can be analyzed with a 1% accuracy for major elements or a 3–5% accuracy for trace elements (with a detection limit of approximately 200 ppm). The microprobe measures the characteristic X-rays that each element emits when it is bombarded with an accelerated and collimated electron beam (with a typical energy of 10–30 keV and a current intensity ranging from 2 to 100 nA). The emitted X-rays are detected by a specific device, and the chemical composition of the sample is determined by comparing its X-ray characteristics (wavelength, intensity) with those of reference samples.

The petrographic characterization was completed by a mineralogical modal analysis performed at the Archaeometry Laboratory of the Department of Earth Sciences, Environment and Resources of the "Federico II" University of Naples, which is equipped with a Leica Laborlux 12 Pol transmitted light polarizing microscope. The computer-aided modal analysis outlined the relative proportions of the various mineralogical constituents.

3.2 | Nd–Sr isotopic characterization

The $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ isotope ratios for samples Baso_1–5 were determined by thermal ionization mass spectrometry at the INGV-OV, using a ThermoFinnigan Triton-TI mass spectrometer. After sample

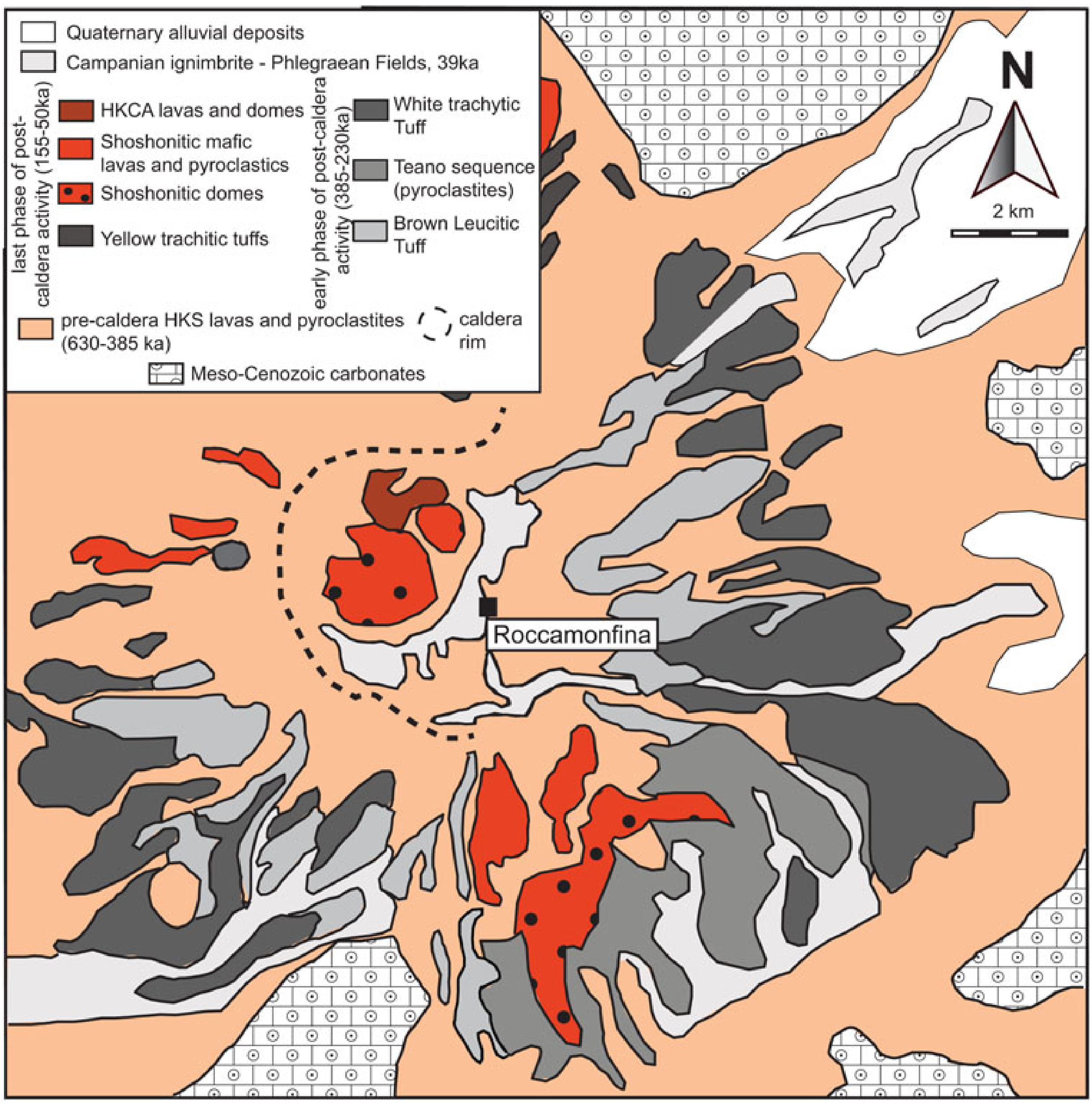

FIGURE 5 Detailed geological map of the Roccamonfina volcano (from Conticelli et al., 2009). HKCA: high-potassium calc-alkaline series; HKS: ultrapotassic series [Color figure can be viewed at wileyonlinelibrary.com]

dissolution with high-purity acid solutions, Sr and Nd were separated from samples Baso_1–5 by conventional ion-exchange chromatographic techniques. The Sr blank was 0.15 ng during the chemistry processing period. The measured $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ isotope ratios were normalized to $^{87}Sr/^{86}Sr = 0.1194$ and $^{146}Nd/^{144}Nd = 0.7219$, respectively, for within-run isotopic fractionation. The $2\sigma_{mean}$, that is, the standard error for $N = 180$, was better than ±0.000012 for the Sr measurements and ±0.000007 for the Nd measurements. During the collection of isotopic data, replicate analyses of NIST SRM 987 ($SrCO_3$) and La Jolla standards were performed to check for external reproducibility. The external reproducibility (2σ, where σ is the standard deviation of the standard results, according to Goldstein, Deines, Oelkers, Rudnick, & Walter, 2003), was 0.710230 ± 0.000019 (2σ, $N = 120$) and 0.511845 ± 0.00001 (2σ, $N = 70$) for $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$, respectively. The Sr and Nd isotope ratios of the present work, as well as those from the literature considered for comparison purposes, were normalized to the recommended values of NIST SRM 987 ($^{87}Sr/^{86}Sr = 0.71025$) and La Jolla ($^{143}Nd/^{144}Nd = 0.51185$) standards, respectively (Thirlwal, 1991).

3.3 | Field survey

As previously mentioned, there is no information in the literature about lava quarries within the MLVVF territory that have a clear significance from an archaeological point of view. Therefore, preliminary field investigations were carried out to identify such quarries. These investigations were limited to the Tyrrhenian (SW) side of the Lepini watershed (Figure 6) because this last has been considered a morphological obstacle for raw material transportation.

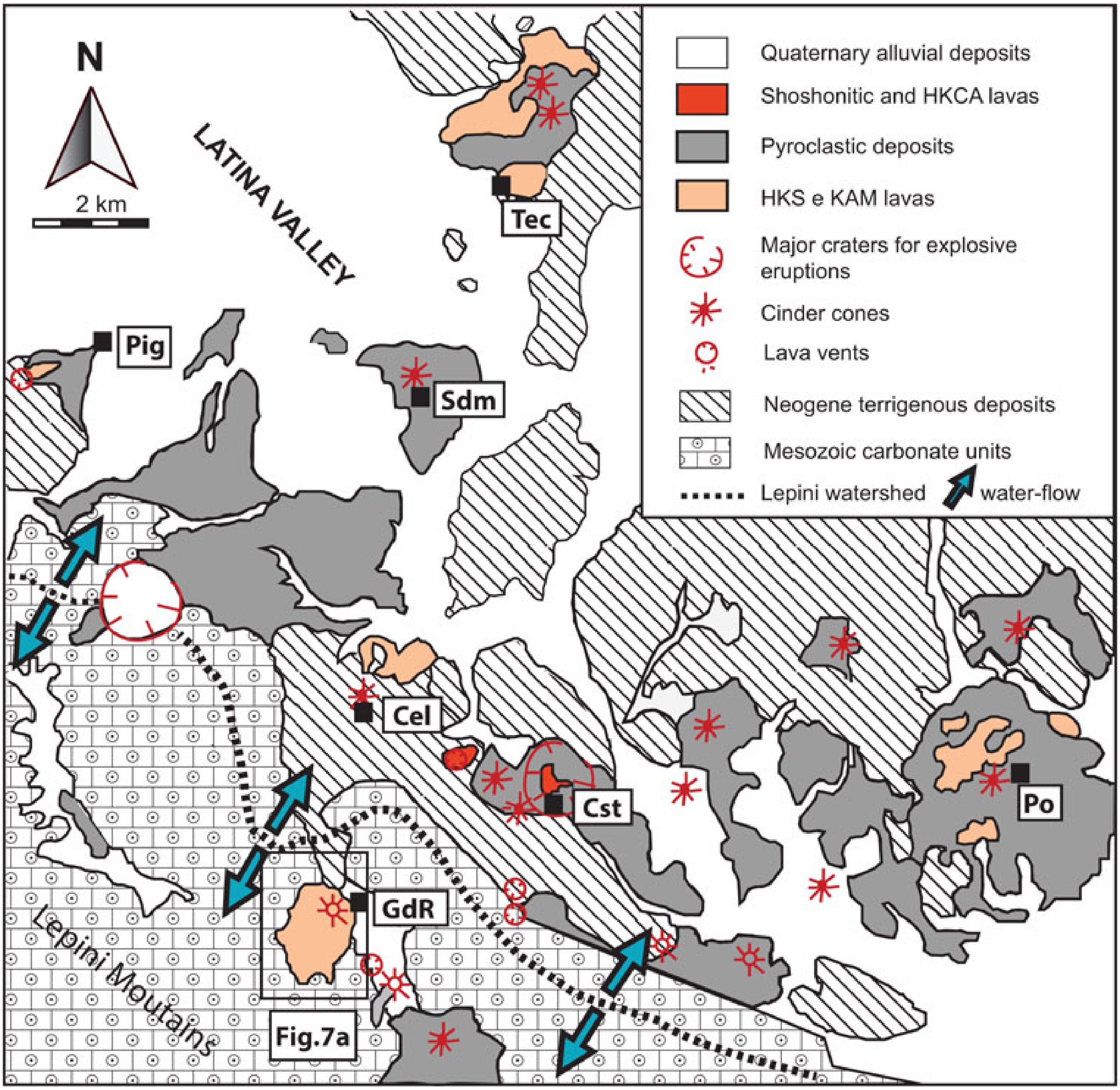

FIGURE 6 Detailed geological map of the Middle Latin Valley volcanic field (MLVVF) (from Boari, Tommasini et al., 2009). Cel: Celleta; Cst: Colle St. Arcangelo; Gdr: Giuliano di Roma; HKS: ultrapotassic series; KAM: kamafugitic series; Pig: Piglione; Po: Pofi; Sdm: Selva dei Muli; Tec: Tecchiena [Color figure can be viewed at wileyonlinelibrary.com]

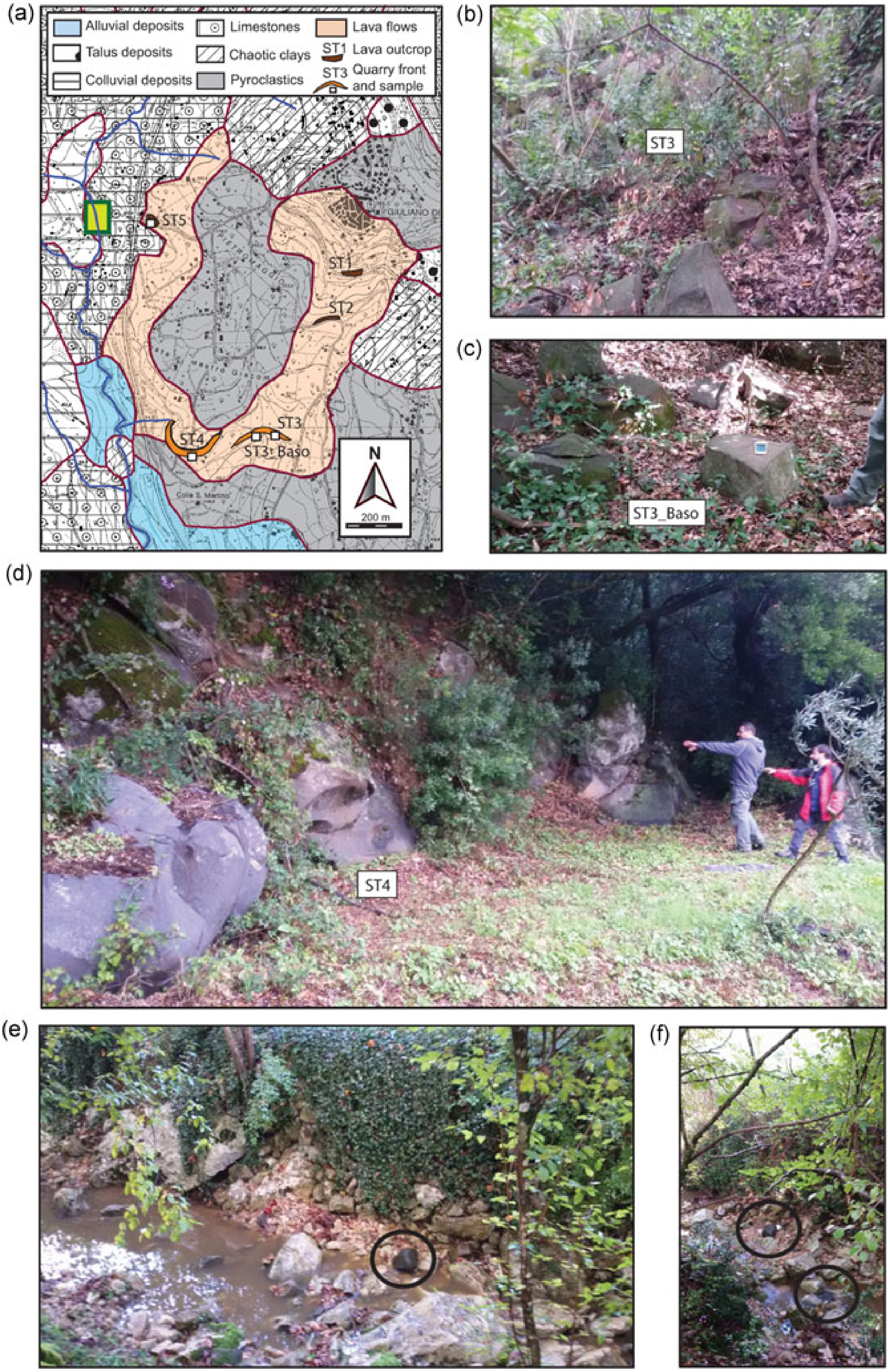

FIGURE 7 Field survey near the Giuliano di Roma village: (a) geological map of the investigated outcrops and stone quarry fronts; (b) quarry edge with detached rock blocks at site ST3; (c) reworked rock block from which sample ST3_Baso was taken; (d) quarry edge at site ST4; (e,f) evidence of semifinished volcanic blocks abandoned in an N–S flowing stream located west of the volcanic quarries (panel a for location) [Color figure can be viewed at wileyonlinelibrary.com]

More specifically, a region with lava outcrops near the Giuliano di Roma village, which has an ultrapotassic signature (Boari, Tommasini et al., 2009) and is SW of the Lepini watershed, represents a possible source area for paving materials (Figure 7a). In two lava outcrops south of the village (ST3 and ST4), sharp, subvertical cuts that identify quarry fronts were observed (Figure 7b,d). In addition, there were some observed instances of unfinished quarrying activity products with a rough shaping similar to that of the volcanic flagstones usually set along Roman consular roads (Figure 7b,c). The discovery of reworked lava stones within the bed of a river flowing toward the Tyrrhenian coast was particularly interesting (Figure 7e,f). The use of the river courses as transportation routes for

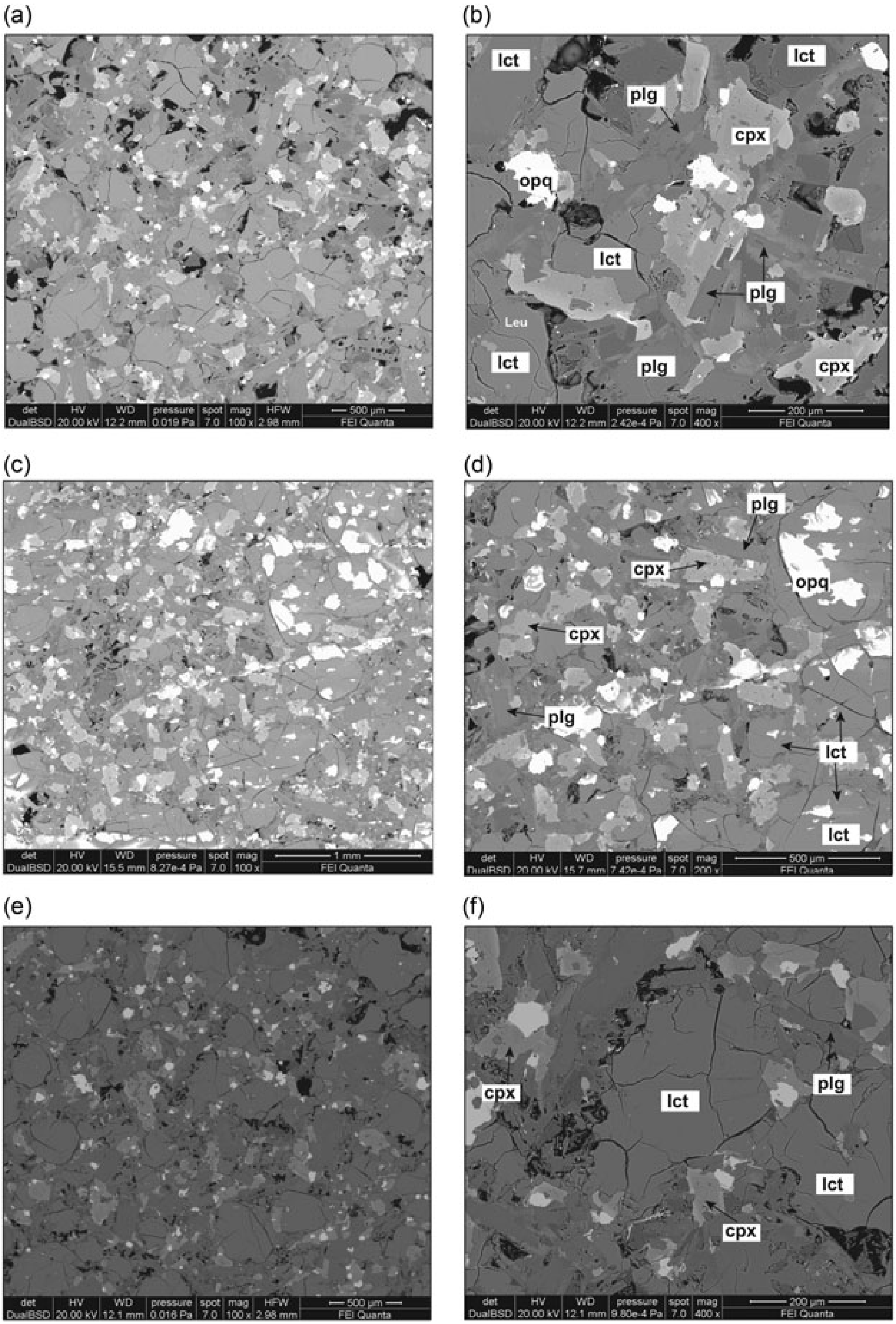

FIGURE 8 Backscattered SEM-EDS images of the ancient Appia samples at different magnifications: (a,b) Baso_1; (c,d) Baso_2; and (e,f) Baso_3. cpx: clinopyroxene; lct: leucite; opq: opaques; plg: plagioclase

raw volcanic materials was hypothesized in the area of the Fiora River (southern Tuscany, Italy) by Marra & D'Ambrosio (2012) with respect to the exploitation of the products of the Onano eruption and their transportation to the ancient town of Vulci and the seaport of Regisvilla.

Lava rocks at sites ST3, ST4, and ST5, which were identified as quarry fronts and isolated fallen blocks (ST3_Baso) were sampled.

4 | RESULTS

4.1 | Chemical–petrographic and isotopic analyses of samples from the ancient Appia route

The SEM images and petrographic EMPA analysis results for all rock samples collected from the ancient Appia route (Baso_1-5) indicate a moderately porphyric (or aphyric) texture with leucite and secondarily

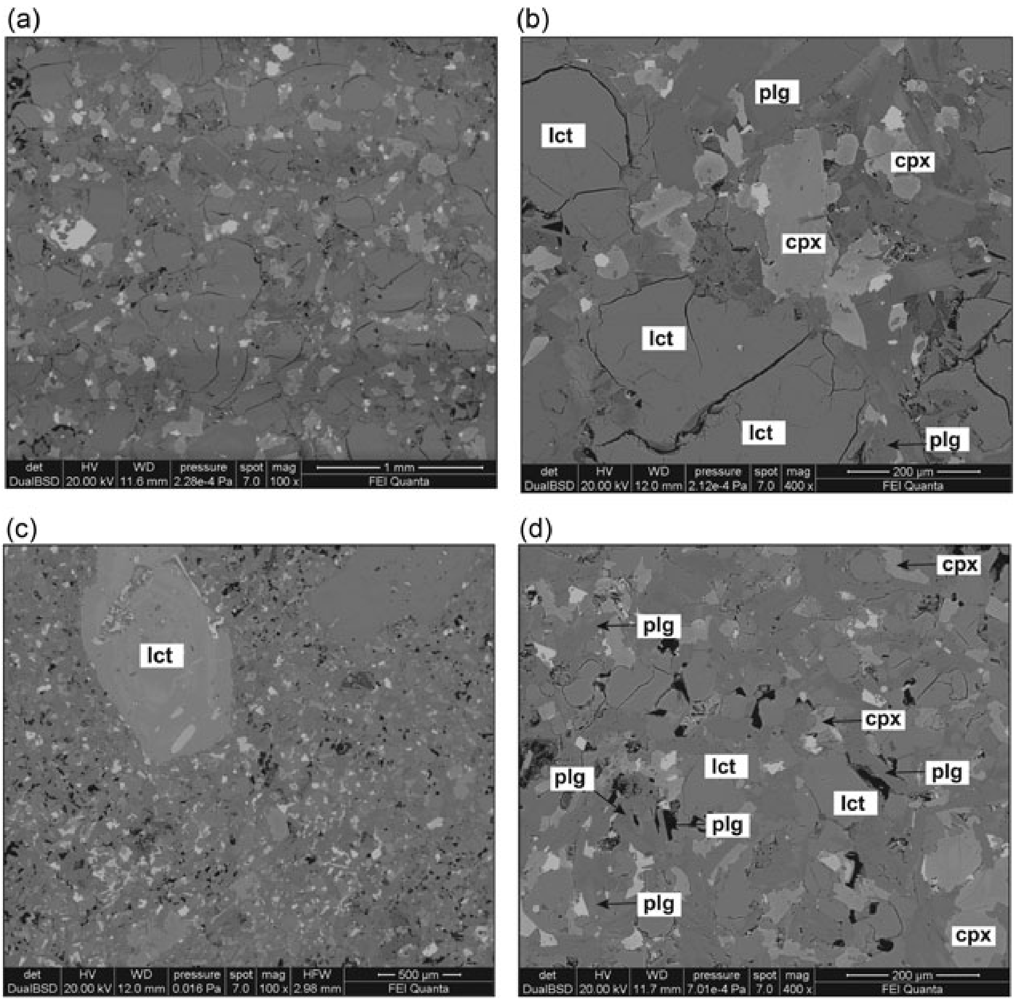

FIGURE 9 Backscattered SEM-EDS images of the ancient Appia samples at different magnifications: (a,b) Baso_4; (c,d) Baso_5. cpx: clinopyroxene; lct: leucite; opq: opaques; plg: plagioclase

TABLE 1 EMPA determinations on the mineral phases of samples Baso_1-5

Sample	X (utm)	Y (utm)	Paragenesis
Baso_1	373483.45	4574700.67	**lct**, **cpx**, **plg**; lct, cpx, plg; *ol*, *apa*, *opq*, *amph*
Baso_2	373559.02	4574675.12	**lct**, **cpx**, **plg**;, lct, cpx, plg; *ol*, *ne*, *apa*, *opq*, *bio*, *gl*
Baso_3	373839.33	4574411.36	**lct**, **cpx**, **plg**; lct, cpx, plg; *ol*, *apa*, *opq*,
Baso_4	373887.543	4574097.23	**lct**, **cpx**, **plg**, lct, cpx, plg; *ol*, *apa*, *opq*, *amph*, *kf*.
Baso_5	373029.58	4574951.92	**plg**, **cpx**; lct, cpx, plg; *opq*, *amph*, *apa*, *gar*

Note. Mineral secondary species in the groundmasses are in italics, and phenocrystals are in bold. amph: amphibole; apa: apatite; bio: biotite; cpx: clinopyroxene; gar: garnet; gl: glass; Kf: K-feldspar; lct: leucite; ne: nepheline; o: olivine; opq: opaques (Fe, Ti-oxide); plg: plagioclase.

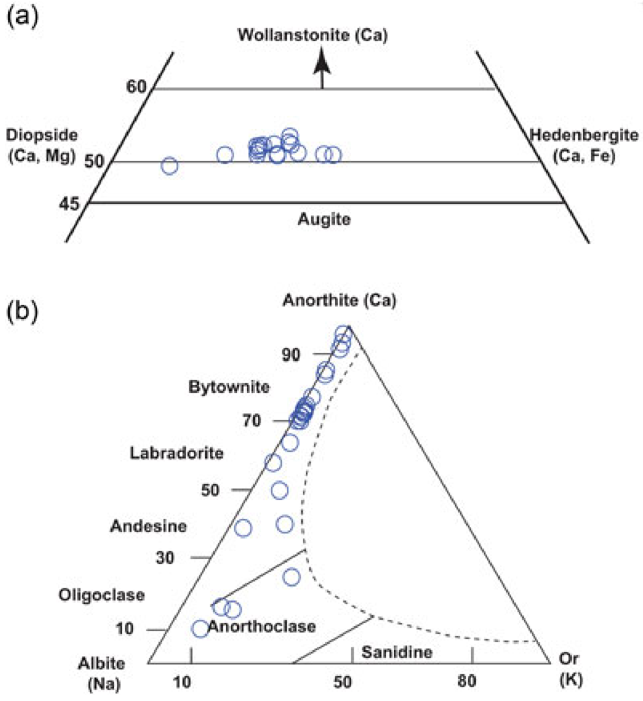

FIGURE 10 (a) Clinopyroxene compositions (17 EMPA analyses) from the Baso_1–5 samples (diagram as in Morimoto, 1988); (b) plagioclase compositions (25 EMPA analyses) from the Baso_1–5 samples. EMPA: electron microprobe analyzer [Color figure can be viewed at wileyonlinelibrary.com]

clinopyroxene crystals and few plagioclase crystals immersed in a microcrystalline to hypocrystalline groundmass (no significant amount of interstitial glass is present) including the same main minerals and rare olivine, apatite, opaques (Fe- and Ti-oxides), amphibole, biotite, K-feldspar, garnet, and nepheline (Figure 8, Figure 9, and Table 1). The chemical–petrographic characterization of the mineral phases for samples Baso_1–5 outlined the typical paragenesis of ultrapotassic series, with dominant leucite and clinopyroxene components.

The EMPA quantitative chemical analyses allowed the compositional analysis, expressed in oxides, of the mineral phases. In particular, attention was focused on the characterization of the clinopyroxenes and plagioclases; the clinopyroxene composition (Morimoto, 1988) was plotted in the diopside field, with a prevailing hedenbergite term (Figure 10a); the plagioclase composition is predominantly bytownitic, with a prevalent anorthitic fraction and only a small amount of observed orthoclase (Figure 10b).

The modal analyses of the thin sections from samples Baso_1–5 (Table 2) show that samples Baso_1–4 are composed of 50–60% leucite, 20–25% clinopyroxene, and 10–20% plagioclase; the olivine and nepheline compositions are each approximately 5%. Sample Baso_5 has a high plagioclase percentage (≥65%), approximately 25% percentage of clinopyroxene, a minor percentage of amphibole (≤5%) and Fe–Ti oxides (≤3%), and approximately 5% leucite. According to the classification of Le Bas (1989) and Innocenti, Rocchi, and Trigila (1999), Baso_1–4 rock samples can be considered tephritic leucitites, whereas the Baso_5 sample is a basanite.

The $^{87}Sr/^{86}Sr$ isotope ratios determined for the Baso_1–4 samples are similar, within the range of analytical errors, and range from 0.71018 to 0.71019, whereas the Baso_5 sample is characterized by a different and significantly lower $^{87}Sr/^{86}Sr$ value (0.70946). The Nd isotope ratios are inversely correlated to the Sr isotope abundances, with the Baso_1–4 samples characterized by $^{143}Nd/^{144}Nd$ ratios of approximately 0.51212–0.51213 and the Baso_5 sample demonstrating the highest Nd isotope ratio (0.51216) (Table 3).

4.2 | Chemical–petrographic and isotopic analyses of lava samples from the MLVVF

Results of the chemical–petrographic (SEM–EMPA), modal, and isotopic analyses for the rock samples collected from the Giuliano di Roma area are shown in Figure 11a,b and Table 4. The rock textures of samples ST3, ST3_Baso, ST4 and ST5 are highly porphyric with millimeter-sized phenocrystals of clinopyroxene, which are also present in the groundmass with microphenocrystals of leucite and, in smaller quantities, olivine, plagioclase, nepheline, Fe–Ti oxides (opaques), amphiboles, and biotite (Table 4). Both the EMPA and modal analyses indicate a paragenesis dominated by clinopyroxenes (≥45%) and leucite (25–45%); a small amount of olivine (5–10%) was found in samples ST3, ST4, and ST5, whereas a very low amount of plagioclase (5%) was identified only in samples ST3_Baso and ST4. Still adopting the classification methodology of Le Bas (1989) and Innocenti et al. (1999), samples ST3, ST3_Baso, and ST5 can be classified as phonolitic tephrites, while sample ST4 is a leucitite (with lct ≥ 40%). Finally, both the $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ isotope ratios

TABLE 2 Results of modal analyses for samples Baso_1–5

Sample	X (utm)	Y (utm)	Relative percentage
Baso_1	373483.45	4574700.67	lct 55–60%; cpx 20–25%; plg 20%; ol 5%
Baso_2	373559.02	4574675.12	lct 55%; cpx 20%; plg 10%; ol 10%; ne 5%
Baso_3	373839.33	4574411.36	lct > 50%; cpx 20%; plg 10%, ol 5%;
Baso_4	373887.543	4574097.23	lct 55–60%; cpx 20–25%; plg 20%; ol 5%
Baso_5	373029.58	4574951.92	plg ≥ 65%; cpx 25%; leu~5%; amph ≤ 5%; opq ≤ 3%;

Note. amph: amphibole; cpx: clinopyroxene; lct: leucite; ne: nepheline; ol: olivine; plg: plagioclase.

TABLE 3 Results of the $^{86}Sr/^{87}Sr$ and $^{143}Nd/^{144}Nd$ isotopic analyses for samples Baso_1–5

Sample	X (utm)	Y (utm)	$^{86}Sr/^{87}Sr$	$^{143}Nd/^{144}Nd$
Baso_1	373483.45	4574700.67	0.710176	0.512128
Baso_2	373559.02	4574675.12	0.710176	0.512125
Baso_3	373839.33	4574411.36	0.710192	0.512122
Baso_4	373887.543	4574097.23	0.710187	0.512118
Baso_5	373029.58	4574951.92	0.709464	0.512165

display limited variations, ranging from 0.70967 to 0.70972 and 0.51214 to 0.51215, respectively (Table 4).

5 | DISCUSSION

Archaeometric analyses are usually performed via chemical and minero-petrographical techniques to characterize and provide useful information on the provenance of ancient materials, which, in the present case, are volcanic flagstones set on the ancient Appia route at the Aurunci Mountain Pass in the third century C.E. In this respect, the isotopic analyses of $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios, which demonstrate significant variations at both regional and local scales within the context of the peri-Tyrrhenian Quaternary magmatism (e.g., D'Antonio, Tilton, & Civetta, 1996; Conticelli et al., 2004; Conticelli et al., 2007; Peccerillo, 2005; Peccerillo & Lustrino, 2005; Boari, Tommasini et al., 2009; Boari, Avanzinelli et al., 2009; Giaccio et al., 2013), may help draw a distinction among different source areas for the flagstones. In the last decade, a further method has been developing and used to fingerprint volcanic rocks and establish their provenance, that is the trace-element (i.e., Zr, Y, Nb, Th, Ta) signature (e.g., Lancaster, Sottili, Marra, & Ventura, 2010; Marra & D'Ambrosio, 2012; Marra et al., 2013; D'Ambrosio, Marra, Cavallo, Gaeta, & Ventura, 2015; Farr, Marra, & Terrenato, 2015; Marra, D'Ambrosio, Gaeta, & Mattei, 2017; Marra, Anzidei et al., 2016; Marra, Gaeta et al., 2016).

The chemical–petrographic characterization (SEM, EMPA, and modal analyses) of samples Baso_1–5 from the Appia pavement, which show dominant leucite and clinopyroxene characteristics associated with a significant amount of plagioclase (between

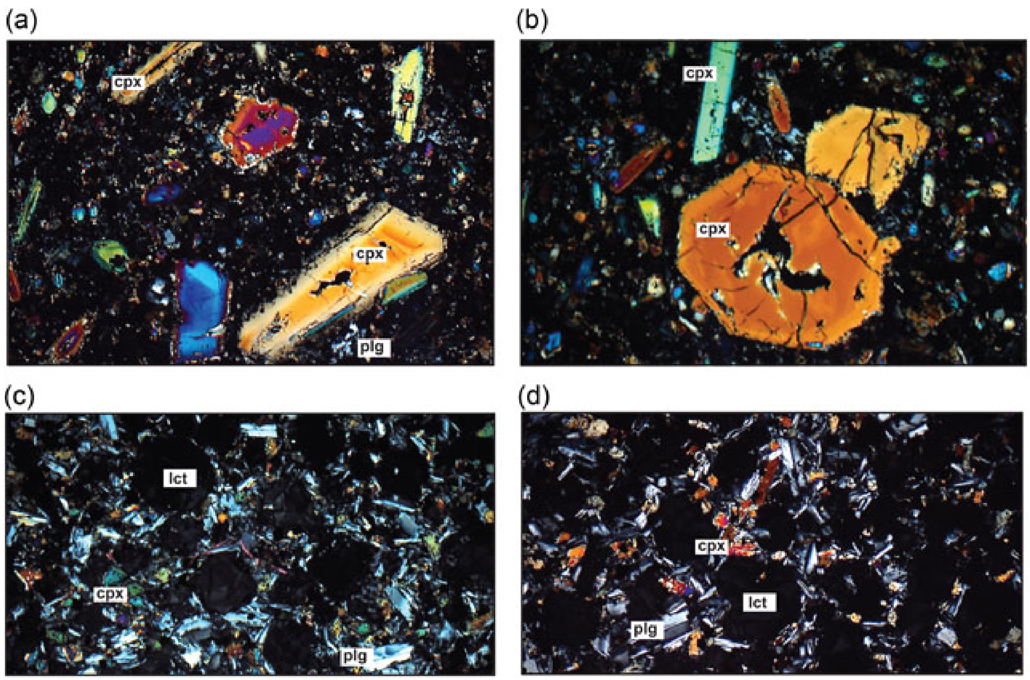

FIGURE 11 Transmitted light polarizing microscope images (crossed nicols, magnification 5×) of samples: (a) ST3_baso; (b) ST5 (both ST3_baso and ST5 are from the Giuliano di Roma area); (c) Baso_3; (d) Baso_4 (from the ancient Appia route). cpx: clinopyroxene; lct: leucite; plg: plagioclase [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 4 Results of the chemical–petrographic and isotopic analyses for the lava samples collected in the Giuliano di Roma area (Figure 7a)

Sample	X (utm)	Y (utm)	$^{87}Sr/^{86}Sr$	$^{143}Nd/^{144}Nd$	Paragenesis (EMPA analysis)	Relative percentage (modal analysis)
ST3	33356157	4599048	0.709687	0.512149	**cpx;** cpx; lct; *ol; ne; opq*	cpx ≥ 50%, lct ≤ 30%, ol ≈ 10%
ST3_Baso	33356119	4599090	0.709673	0.512143	**cpx;** cpx; lct; *plg; amph*	cpx ≥ 50%, lc ≤ 30%, plg ≈ 5%, amph < 5%
ST4	33355688	4598849	0.709672	0.512143	**cpx;** cpx; lct; *ol;bio*	cpx ≥ 45%, lc ≥ 40%, ol 5% plg ≈ 5%, bio ≈ 2%
ST5	33355464	4600001	0.709717	0.512133	**cpx;** cpx; lct; *plg; opq*	cpx > 50%, lct ≤ 30%, ol 10%

Note. cpx: clinopyroxene; EMPA: electron microprobe analyzer; lct: leucite; ol: olivine; opq: opaques; plg: plagioclase.

10–25% and 65%), is in agreement with the typical paragenesis of HKS rocks of the ultrapotassic volcanism in central Italy. Two petrographic rock types with different isotopic signatures (Table 3) were identified for the five samples (Baso_1–4 and Baso_5, see Table 2), suggesting the exploitation of at least two different quarries.

Regarding the possible provenance of the volcanic raw material, the results of the isotopic analysis (Figure 12a) allow the exclusion of Campania volcanoes (Vesuvius and Phlegraean fields) and overseas areas, such as the Aeolian Arc, Sicily, and Sardinia (as already indicated on an archaeological basis). Among the remaining initially hypothesized source regions, the results of the chemical–petrographic characterization (Tables 1,2) rules out the Colli Albani volcanic district because of the presence of plagioclase in the paragenesis of all the analyzed material from the Appia route. Therefore, based on an initial approximation, the Roccamonfina and MLVVF districts and, to a lesser extent, the Mt. Sabatini volcanic district remain possible source areas. Such significant evidence coming from the petrographic and isotopic analyses have suggested to postpone the investigation of the trace-elements signature to further works.

Focusing on the isotopic characterization more in detail (Figure 12b), the $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios for samples Baso1–4 and partly sample Baso_5 show clear similarities with those from the Roccamonfina precaldera effusive phase of activity (Conticelli et al., 2009) and the MLVVF-HKS sequence (Boari, Tommasini et al., 2009), whereas the Roccamonfina postcaldera products and the MLVVF shoshonitic lavas show much higher $^{143}Nd/^{144}Nd$ ratios and lower $^{87}Sr/^{86}Sr$ ratios, and the $^{87}Sr/^{86}Sr$ ratios of MLVVF kamafugitic rocks are very much higher. The

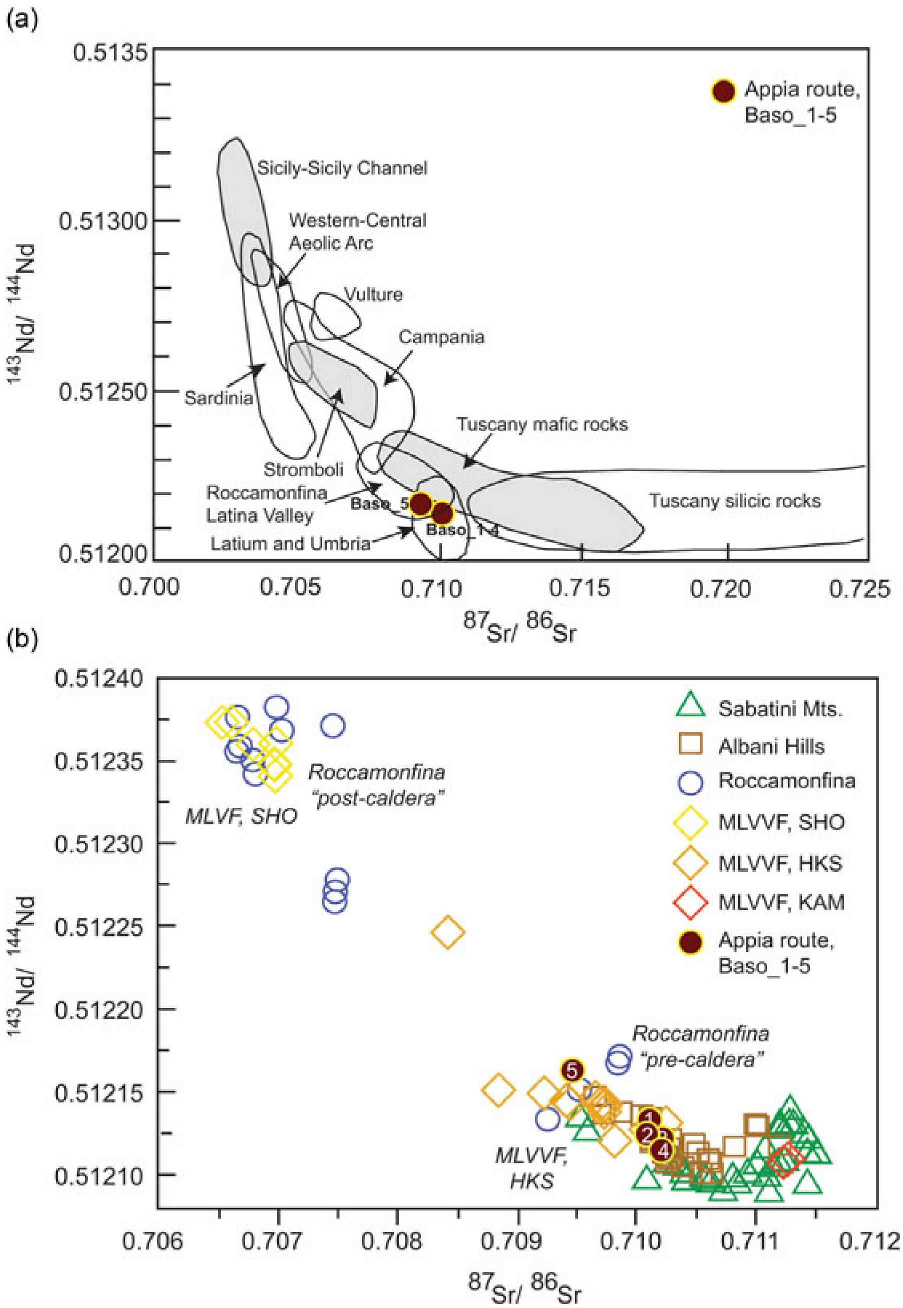

FIGURE 12 (a) $^{87}Sr/^{86}Sr$ versus $^{143}Nd/^{144}Nd$ isotopic plot for the Plio-Quaternary mafic volcanic rocks from central Italy, slightly modified after Peccerillo (2005); (b) $^{87}Sr/^{86}Sr$ versus $^{143}Nd/^{144}Nd$ plot, magnified from (a) and showing the isotopic ratios determined for the Baso_1–5 samples. The error bars for $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ are included in symbols. HKS: ultrapotassic series; KAM: kamafugitic series; MLVVF: Middle Latin Valley volcanic field; SHO: shoshonitic series [Color figure can be viewed at wileyonlinelibrary.com]

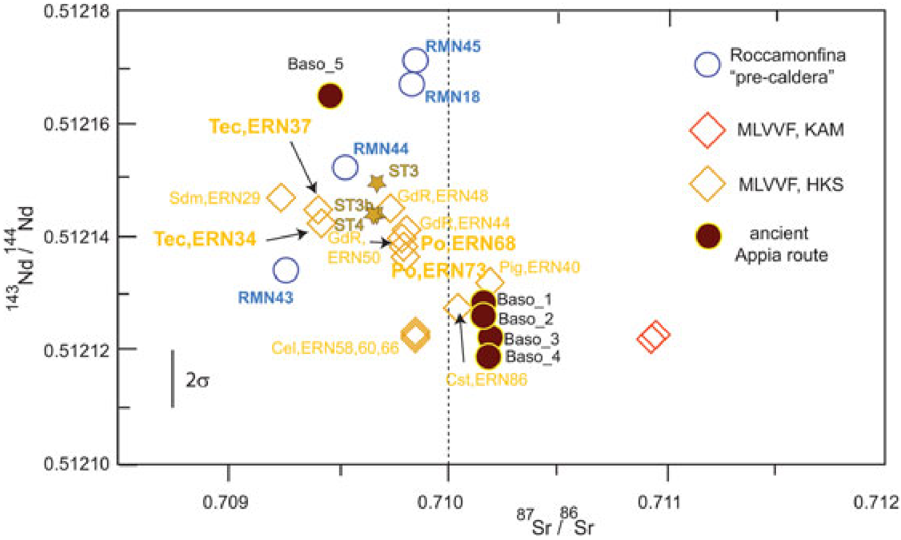

FIGURE 13 $^{87}Sr/^{86}Sr$ versus $^{143}Nd/^{144}Nd$ plot focusing on the values reported exclusively for HKS rocks from the MLVVF territory by Boari, Tommasini et al. (2009) (bold indicates the presence of plagioclase) and HKS rocks from the Roccamonfina district by Conticelli et al. (2009). The error bar for $^{87}Sr/^{86}Sr$ is included in symbols. Cst: Colle St. Arcangelo; ERN: Ernici; Gdr: Giuliano di Roma; HKS: ultrapotassic series; KAM: kamafugitic series; MLVVF: Middle Latin Valley volcanic field; Pig: Piglione; Po: Pofi; RMN: Roccamonfina; Sdm: Selva dei Muli; Tec: Tecchiena [Color figure can be viewed at wileyonlinelibrary.com]

Sabatini Mountains volcanic district generally shows significantly higher $^{87}Sr/^{86}Sr$ ratios and cannot be considered as the provenance area.

Figure 13 shows further insights into the form of reported isotopic values for HKS lavas from the MLVVF and Roccamonfina precaldera sequence, as described by Boari, Tommasini et al. (2009) and Conticelli et al. (2009), respectively. Isotopic analyses do not unambiguously address the geoarchaeological issue, since the $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios that were determined for samples Baso_1–5 are

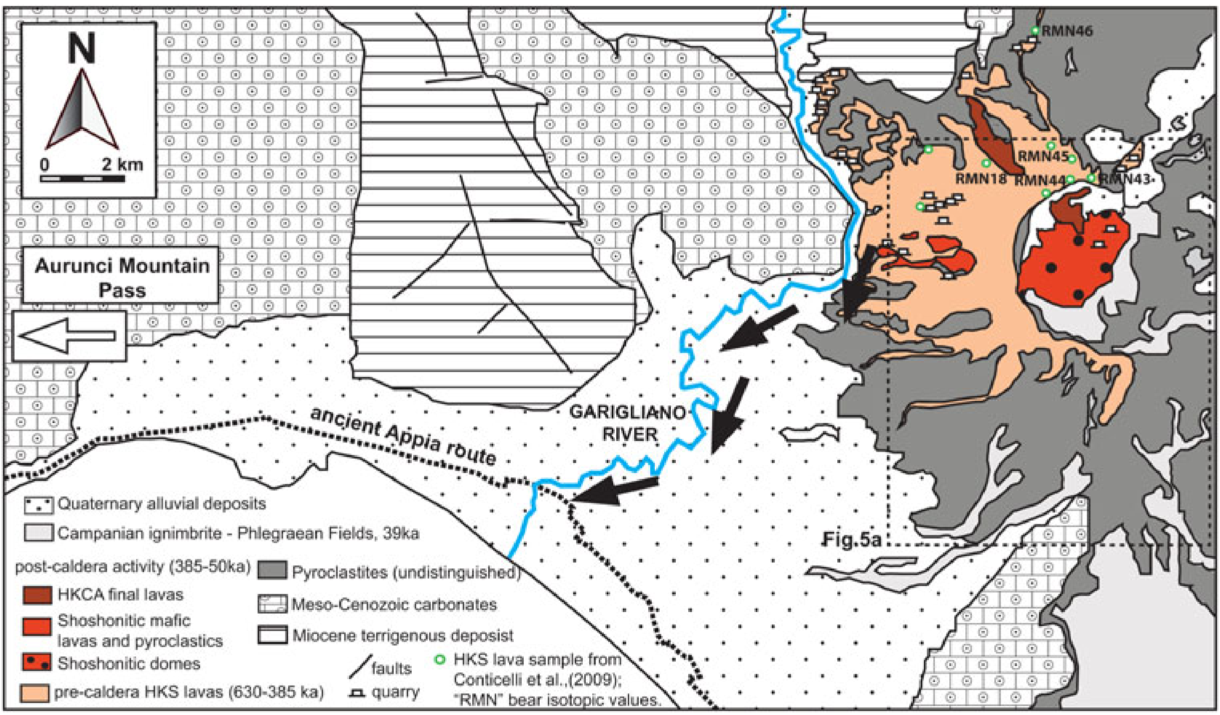

FIGURE 14 Geological map of the western side of the Roccamonfina volcanic area, the Garigliano Plain and the south-eastern edge of the Aurunci Mountains (modified from sheet no 171 "Gaeta" of the Italian Geological Map edited by ISPRA). The map reports i) locations of precaldera leucite-bearing ultrapotassic rock samples, also featuring the $^{87}Sr/^{86}Sr$ $^{143}Nd/^{144}Nd$ isotopic ratios (RMN18, RMN43–46) reported by Conticelli et al. (2009); ii) rock quarries carved into lava flows, as described in Panarello (2008). Black arrows suggest the direction of possible fluvial transportation of raw material. ISPRA; Istituto Superiore per la Protezione e la Ricerca Ambientale (i.e. Higher Institute for Environmental Protection and Research) [Color figure can be viewed at wileyonlinelibrary.com]

consistent with those reported for both HKS series. At a first glance, the $^{87}Sr/^{86}Sr$ ratio of 0.710 seems a threshold value for the Roccamonfina HKS lavas, and this would lead to an origin from the MLVVF for samples Baso_1–4. Anyway, the small amount of data available for the Roccamonfina area (e.g., Conticelli et al., 2009; see also Figure 14) could explain the lack of $^{87}Sr/^{86}Sr$ values greater than 0.710 in Figure 13, and this does not allow to support the last hypothesis.

However, a provenance from the ultrapotassic rocks of the MLVVF is considered here unlikely because of the different paragenesis between samples Baso_1–5 and samples taken from the San Giuliano di Roma area (Tables 2,4; Figure 10a–d). Although field survey and sampling efforts in the MLVVF territory should be intensified and increased, it is worthwhile to emphasize that the ultrapotassic rocks studied by Boari, Tommasini et al. (2009), which contain plagioclase (bold codes in Figure 13), are located northeast of the Lepini watershed (Figure 6).

A reliable hypothesis considers the lava flows that erupted during the Roccamonfina precaldera sequence as the most likely source rocks for the volcanic flagstones set on the ancient Appia route at the Aurunci Mountain Pass in the third century C.E. The paragenesis of samples Baso_1–5 is consistent with those of the HKS plagioclase leucitites reported in Conticelli et al. (2009), which are characterized by clinopyroxene and plagioclase phenocrystals; the latter, in a few cases, is the predominant phase (similar to the Baso_5 sample).

Stone quarries carved into lava flows have been identified in the Roccamonfina territory (Panarello, 2008), and their location is shown in Figure 14 with the position of the HKS precaldera lava samples analyzed by Conticelli et al. (2009) and, in a few cases (RMN), the $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios. Most of these quarries are on the western half of the Roccamonfina volcano, within outcrops of the precaldera ultrapotassic lava flows. Not by chance, they are located near the N–S-oriented course of the Garigliano River, the main water stream flowing toward the Tyrrhenian Sea.

The results of this work set the basis for further research investigating the Roccamonfina territory for a thorough characterization of its quarries in terms of their dimensions, shapes, extraction techniques, and other features. Additional petrographic and/or isotopic analyses of lava samples will be necessary to make comparisons with those from the ancient Appia route, both at the Aurunci Mountain Pass and the Garigliano Plain. New research will benefit greatly from the application of trace elements analyses since, as demonstrated by Marra, D'Ambrosio, Sottili, and Ventura (2013), results of this method can distinguish lavas from the Roccamonfina volcano (on the base of Th/Ta values) or the Campanian areas (basing on the coupled Th/Ta vs Nb/Zr signature).

Likewise, the meaning of the quarry system discovered in the San Giuliano di Roma area (MLVVF) should be better described; the evidence of quarries near a N–S flowing river (Figure 7e,f) is an interesting similitude with the Roccamonfina territory and the Garigliano River. The role of flowing water in raw material transportation must be argued in an archaeological context considering commercial relationships between Latin Valley and the peri-Tyrrhenian territories in the third century C.E.

6 | CONCLUSIONS

This paper describes a multidisciplinary analytical procedure applied to investigate the provenance of the volcanic stone pavement set along the ancient Appia route at the Aurunci Mountain Pass in the third century C.E. under Emperor Caracalla. Within the context of the Quaternary volcanic districts found along the peri-Tyrrhenian side of peninsular Italy, initial working hypotheses were discarded or corroborated based on the results of integrated chemical–petrographic and $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$ isotopic analyses.

The lava flagstones were derived from volcanic raw material possibly belonging to the Roccamonfina precaldera effusive phase of activity (630–385 ka), during which ultrapotassic leucite-bearing lavas were emitted. This conclusion is based on the results of SEM, EMPA, and modal analyses on samples from the Appia route, which were compared with data from the literature.

The paragenesis of the samples allowed us to exclude the Colli Albani volcanic district as a possible material source. The isotopic ratios are consistent with those reported in the literature for ultrapotassic lavas from both the Roccamonfina precaldera sequence and the Middle Latin Valley Volcanic Filed. A preliminary investigation within the latter territory identified an unknown quarry system near the Giuliano di Roma area. However, despite compatible isotopic fingerprints, the Giuliano di Roma samples are plagioclase-free lavas that do not match with the plagioclase-enriched samples from the ancient Appia flagstones.

Further investigations will be necessary to characterize the quarry system in the Roccamonfina and MLVVF territories and understand the role and importance of the fluvial transportation of raw materials from source areas to the ancient Appia route running along the Tyrrhenian coast.

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