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# GEOCHEMICAL METHODS FOR SOURCING LAVA PAVING STONES FROM THE ROMAN ROADS OF CENTRAL ITALY†\*

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*This paper documents the results of in situ analysis of 306 lava paving stones and 74 possible source rocks using pXRF. Data were collected from sites both in the city of Rome—on major roads beyond the city (including the Viae Flaminia, Cassia, Clodia, Praenestina and Appia)—and in the city of Ostia. Comparison of the pXRF data with lava compositional data from the geological literature allows broad identification of possible sources. The results point to quite distinctive patterns of exploitation for the city of Rome and Ostia, utilizing the Alban Hills lava flows, and the roads of the middle Tiber Valley, drawing on lava flows associated with the Vico and Sabatini volcanoes. The results show the potential of pXRF to produce data to elucidate the exploitation of lava flows for paving the Roman roads.*

**KEYWORDS:** ANCIENT ROMAN PAVING STONES, ROMAN ROADS, MATERIAL PROVENANCE, VOLCANIC ROCKS, TRACE ELEMENTS, PXRF, HHPXRF

## INTRODUCTION

Black lava was commonly used as a paving stone in the construction of the roads that radiate out from ancient Rome. These roads traversed three major volcanoes that dominate the landscape of Central Italy, so lava flows were readily available for road building. Laurence (1999) gave a detailed account of the historical factors relating to road construction in Roman Italy. He showed that, in general, geological differences on either side of the River Tiber are reflected in the choice of road construction materials, with limestone and conglomerate used east of the Tiber and black lava to the west. However, he also presented evidence of movement of black lava paving across the Tiber (Laurence 2004). There is also contemporary historical evidence that lava used in the Via Appia was transported there from ‘far away’ (Laurence 1999). Black *et al.* (2004) discussed some of the economic, legal and geographical factors pertaining to lava extraction and transport for road building in the Tiber Valley. They pointed out that lava flows of several types may be used along single stretches of road. However, Laurence (2004) pointed to the presence of paved roads leading from some quarry sites to the Via Flaminia as evidence that local selce sources were being used. Thus Laurence (1999), Black *et al.* (2004) and Laurence (2004) all suggest that choices were being made in the selection of lava sources. These observations should be seen within the context of the provenancing of other volcanic materials for construction, notably the work of Lancaster *et al.* (2010, 2011) on the use of lightweight materials (e.g., scoria and pumice) in concrete vaults, who suggested that there was a complex supply pattern to Rome that included

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volcanic deposits associated with Vesuvius (Lancaster *et al.* 2011; Marra *et al.* 2012). The aims of this paper are to provide a reliable sourcing method for the lava paving stones (i.e., heavyweight/high-density building materials) based on geochemical analysis, and to clarify the exploitation, transportation and trade in this natural resource that was widely utilized in both ancient Rome and its environs.

Geochemical analysis of rock materials such as lava flows is usually done using laboratory-based equipment such as X-ray fluorescence (XRF) and ICPMS, which requires the collection and destruction of some of the rock sample. This equipment is capable of producing highly accurate analyses. Renzulli *et al.* (1999) and Capedri and Grandi (2003) used this approach in their analysis of trachyte paving stones from a network of Roman roads in the Po Plain close to Padua in north-eastern Italy. Capedri and Grandi (2003) sampled 269 paving stones for petrographic and geochemical analysis. The paving stones came from such diverse places as museums, private gardens, public buildings and the remains of roads. Using full XRF whole-rock geochemical analysis, including rare earth elements (REE), they showed convincingly that these paving stones could be sourced to specific quarries in the Euganean Hills complex some 25 km west south-west of Padua. Their work also showed that the paving stones were transported over distances of up to 90 km and that proximity to transport networks including lagoons was a factor determining exploitation.

In this project, we have investigated the geochemistry of *in situ* paving stones that are protected by regulations relating to the preservation of antiquities, which forbid destructive sampling. We have therefore used a non-destructive Niton handheld X-ray fluorescence (HHpXRF) analyser for data collection. Inevitably, this has resulted in a loss of resolution when compared with the laboratory-based analyses, but it has still yielded useful information. Standard geochemical variation diagrams were used for data analysis, and attempts at sourcing were based on comparisons of the Niton data with published analyses taken from the abundant geological literature on the lava flows of the Roman Magmatic Province (RMP). We also discuss the problems associated with this methodology and suggest methods for mitigating them. These solutions will be implemented in future research on a more targeted sample.

#### THE GEOLOGICAL BACKGROUND

The present-day geological and physiographic framework of the central Mediterranean was determined by a complex series of events related to the convergence of the African and Eurasian tectonic plates (Conticelli *et al.* 2007; Alagna *et al.* 2010; Conticelli *et al.* 2010b). The Ionian–Adriatic lithosphere was subducted westwards and north-westwards beneath the Eurasian plate, resulting in the progressive closure of the intervening Tethyan ocean basins. This process began in the Cretaceous and continues to the present day. Convergence resulted in the formation of two principal orogenic belts, the Alps and the Apennines, the latter forming the backbone of the Italian peninsula.

In the Eocene, convergence began in the Apennine orogen as a result of westward subduction of the Adriatic lithosphere beneath the southern European margin (Alagna *et al.* 2010; Conticelli *et al.* 2010b). The progress of these movements was expressed in a complex series of events involving sedimentary basin formation, deformation, and rifting resulting in north–south and north-west–south-east trending extensional basins and varied but widespread subduction-related magmatism. Along the present-day eastern Italian peninsula, magmatic activity began in the Miocene and continues to the present day, migrating diachronously south-westwards (Conticelli

*et al.* 2010b). The resulting volcanic rocks have been assigned to three magmatic provinces; from north to south, the Tuscan Magmatic Province (TMP), the Roman Magmatic Province (RMP) and the Lucanian Magmatic Province (LMP). Activity in the TMP ranged between 5.8 and 0.97 Ma, in the RMP from 760 ka to recent times, and in the LMP between 0.700 and 300 ka (Conticelli *et al.* 2010b; Gaeta *et al.* 2011, 2016).

The spatial definition of the RMP differs between authors (see, e.g., Alagna *et al.* 2010; Conticelli *et al.* 2010b). Here, we have adopted the definition of Alagna *et al.* (2010), who defined it as the region formed by the four large volcanic complexes of Vulsini, Vico, Sabatini and the Alban Hills. These volcanoes lie along the border of the Tyrrhenian Sea, between southern Tuscany and the south-eastern hinterland of the city of Rome. Activity occurred between 760 ka and recent times (Middle Pleistocene to Holocene) (Peccerillo 2005; Alagna *et al.* 2010; Conticelli *et al.* 2010b; Sottili *et al.* 2010). The magmas generated by melting of mantle sources had been modified by fluids in prior subduction events, producing a suite of petrologically unusual potassic and ultrapotassic magmas (Gaeta *et al.* 2006, 2016). They are characterized by high levels of the so-called LILE (Large Ion Lithophile Elements) such as K, Rb, Sr, Ba and Pb relative to HFSE (High Field Strength Elements) such as Nb, Zr and Ti (see, e.g., Alagna *et al.* 2010; Conticelli *et al.* 2010b; Gaeta *et al.* 2016). Magmatic evolution was controlled by assimilation and fractional crystallization processes. In the case of the Alban Hills, this included assimilation of the abundant platform carbonates that underlie the volcano and that also hosted the evolving magma chambers (see, e.g., Marra *et al.* 2009; Gozzi *et al.* 2014). The relative abundance of potassium and the undersaturation with respect to SiO<sub>2</sub> gave rise to the common occurrence of the potassic feldspathoid leucite, which is perhaps the most visible expression of their unusual geochemistry. Texturally, the lavas range from aphyric to strongly porphyritic with leucite, clinopyroxene, plagioclase and olivine as common phenocryst phases. Geochemical classification of these rocks has divided them into two suites; a potassic suite consisting of trachybasalts and trachytes, and an ultrapotassic suite consisting of foidites, leucitites, leucite tephrites and phonolites (Alagna *et al.* 2010). In this paper, three volcanoes of the RMP will be discussed: from north to south they are Vico, Sabatini and the Alban Hills (Fig. 1).

## THE VOLCANOES

Vico, Sabatini and the Alban Hills are all characterized by large polycentric stratiform complexes with polygenetic calderas (Fig. 1). The magmas reached the surface in response to extensional movements along north-west to south-east trending basins related to the opening of the Tyrrhenian Sea basin. In the following section, a brief outline of the geology of the three volcanoes will be presented, with an emphasis on the lava flows, using geochronological data from Conticelli *et al.* (2010b) unless otherwise stated.

### *The Alban Hills*

This volcanic complex lies 15 km south-east from the centre of Rome and much of the city is built on its eruptive products (Fig. 1). Activity occurred between 600 and 40 ka (Conticelli *et al.* 2010b; Gaeta *et al.* 2016). However, shallow seismic activity and volcanic gas emissions are still recorded around the volcano, suggesting that it is quiescent rather than extinct (Carapezza *et al.* 2003; Peccerillo 2005). Activity was dominated in the early phases by polygenetic caldera collapse and the eruption of voluminous explosive products such as ignimbrites and tuffs, some

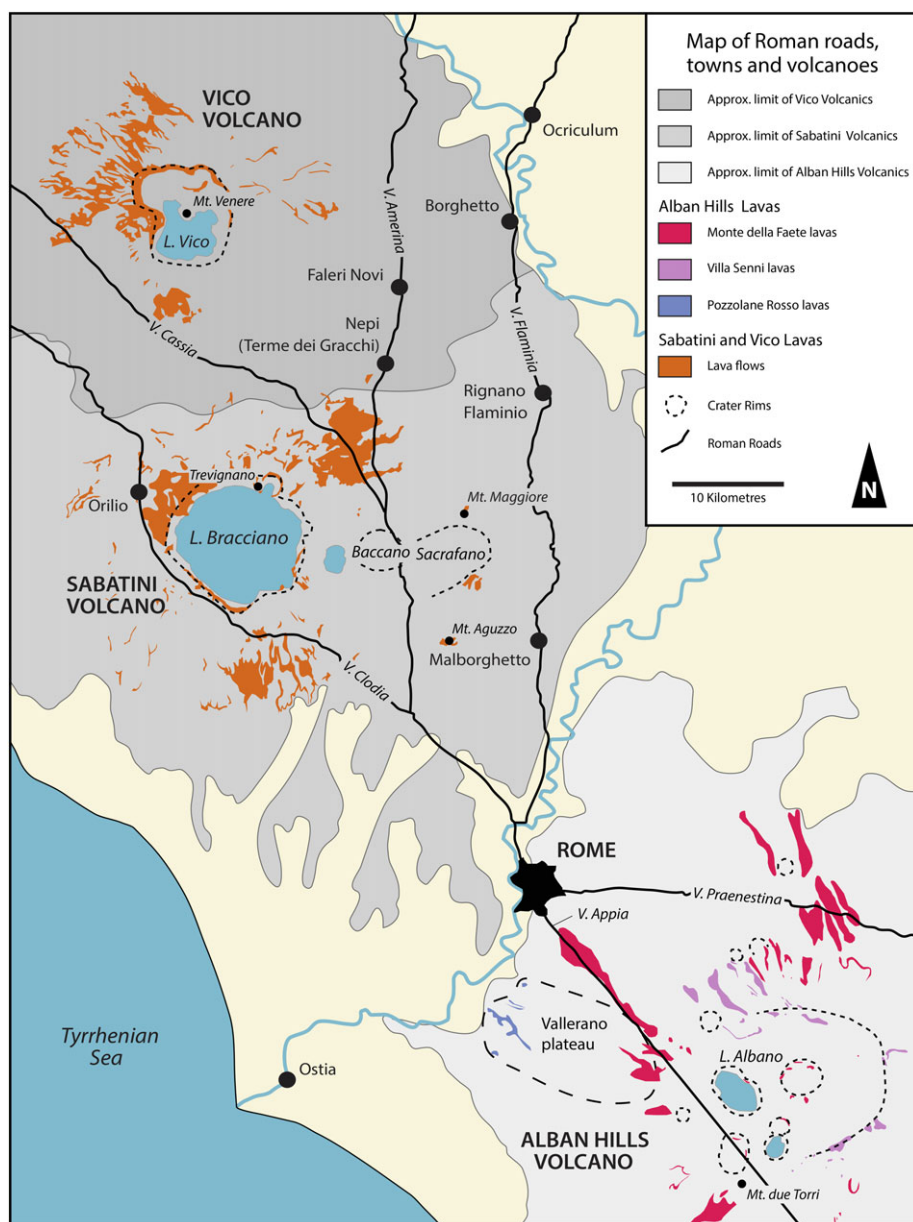


Figure 1 A map showing the Roman roads and towns mentioned in the text and the generalized outcrop of the volcanic rocks of Vico, Sabatini and the Alban Hills. The localities of the sites used in the spider diagram normalizations are also shown.

of which are interbedded with tuffs from Sabatini. However, the volume of eruptive products decreased with time. Lava flows are subordinate, but one flow (Capo di Bove) crosses into the present-day metropolitan area and part of the Via Appia (Fig. 1). There is some variation among authors on the eruptive succession (see, e.g., Giordano *et al.* 2006, 2010; Giaccio *et al.* 2009;

Conticelli *et al.* 2010b), but here we have adopted the subdivision of Gaeta *et al.* (2016), who proposed five phases that were all dated using the  $^{40}\text{Ar}/^{39}\text{Ar}$  method. They are as follows: an Early Tuscalano–Artemisio Phase (608–500 ka), a Late Tuscalano–Artemisio Phase (456–351 ka), the Monte Delle Faete Phase (308–241 ka), a Late Hydromagmatic Phase (201–142 ka) and finally the Albano Phase (69–40 ka).

Of particular interest to this paper are lava flows of the Monte Delle Faete Phase (Fig. 1), which include the Capo di Bove flow referred to above. The Late Tuscalano–Artemisio Phase (Fig. 1) also hosts significant lava flows, including the Villa Senni lavas and the Pozzolane Rosse lavas, which were erupted on the Vallerano lava plateau (Fig. 1). Similarly, the Monte Due Torri flow of the Albano Phase is the most recent lava erupted from the Alban Hills and was dated at 40 ka (Gaeta *et al.* 2011).

### *Sabatini*

The picture here is more complex, mainly because overlapping eruptions occurred from multiple sources, including three major caldera complexes; Bracciano, Baccano and Sacrafano (Fig. 1), together with scoria cones and hydromagmatic maar activity (Conticelli *et al.* 1997, 2010b; Karner *et al.* 2001; Sottili *et al.* 2010) (Fig. 1). Sottili *et al.* (2010) recognized six phases of activity, which began in the east around 800 ka. Subsequently, the focus of activity changed between the different centres, finally ceasing around 86 ka with hydromagmatic maar activity. The most intense monogenetic activity was concentrated in the Monte Rocca Romana and Trevignano areas to the north of Bracciano crater, at Monte Maggiore, close to the Sacrofano caldera, at Monte Aguzzo and Monte Musino in the south-east, and at San Selso, south of Bracciano crater (Fig. 1).

### *Vico*

This consists of a single conic stratiform volcano with a central caldera containing the crater lake of Lake Vico (Fig. 1). In the north, the volcano has largely covered the products of the older Monte Cimino Volcanic Complex, the products of which are geochemically transitional with rocks of the TMP (see, e.g., Aulinas *et al.* 2011). The magmatic products of Vico have been divided into three main rock successions (Perini *et al.* 2000, 2004). The Rio Ferriera Succession began at about 420 ka with the production of pyroclastic fall deposits with interbedded lava flows. The Lago di Vico was a stratovolcano building phase with some interbedded lava flows (300–260 ka). Towards the end of the Lago di Vico Succession, four explosive ignimbrite eruptions were associated with lava flows at Ronciglione, Sutri and Carbognano. The Monte Venere Succession was a post-caldera phase ranging in age from 95 to 85 ka (Conticelli *et al.* 2010b) associated with minor lava flows at Poggio Nibbio, which were erupted around 95 ka along the northern caldera rim (Conticelli *et al.* 2010a) (Fig. 1).

## THE GEOLOGICAL DATA

In order to determine the range of compositions shown by the volcanoes of the RMP, 205 analyses were collected from the geological literature covering the above volcanoes (Trigila *et al.* 1995; Conticelli *et al.* 1997, 2007, 2009, 2010a,b; Di Battistini *et al.* 1998; Conticelli 1998; Perini *et al.* 2000, 2004; Peccerillo 2005; Chelazzi *et al.* 2006; Giordano *et al.* 2006; Boari *et al.* 2009; Marra *et al.* 2009; Alagna *et al.* 2010; Gozzi *et al.* 2014; Gaeta *et al.* 2016). The



analyses were processed with MinPet petrological software using standard  $X$ - $Y$  variation diagrams. The lavas are identified on the diagrams by colour-coded triangles specific to the volcano from which they were erupted: green for the Alban Hills, blue for Sabatini and black for Vico. To facilitate comparison with the archaeological data, only elements obtained by the Niton and that are commonly used in igneous petrology were plotted: these included Fe, Mn, Zr, Rb and Sr. In order to harmonize the geological and Niton data sets, the MnO data in the geological analyses were converted to parts per million (ppm) and where necessary total Fe expressed as  $\text{Fe}_2\text{O}_{3\text{T}}$  was converted to  $\text{FeO}_{\text{T}}$ . In the archaeological data set, the Fe expressed as ppm was converted to  $\text{FeO}_{\text{T}}$ .

Figures 2 (a)–2 (d) show plots of the above elements against  $\text{FeO}_{\text{T}}$ , which is a crude measure of magmatic evolution and thus spreads the data points across the diagram. One of the significant features of these diagrams is the compositional overlap between lava flows from the different volcanoes. Such overlaps are considered normal in igneous petrology, but are not helpful for the provenance studies required by this project, which would be facilitated by compositional clustering. However, there are some useful patterns present. As a broad generalization, the Alban Hills data plot at the high- $\text{FeO}_{\text{T}}$  end of the diagram (e.g., Fig. 2 (a), Zr vs.  $\text{FeO}_{\text{T}}$ ). Products from Vico show a considerable range of compositions, with a tendency to concentrate at the low- $\text{FeO}_{\text{T}}$  end, with some analyses also plotting at the high- $\text{FeO}_{\text{T}}$  end. The Sabatini data lie in the middle, but show some overlap, particularly with the Alban Hills data at the high- $\text{FeO}_{\text{T}}$  end. These data show that there are broad but significant geochemical differences between the volcanoes that may be useful in sourcing the paving stones.

#### THE ARCHAEOLOGICAL DATA

The compositional data used in this study were collected by JB from *in situ* paving stones and possible source rock outcrops along the Viae Flaminia, Amerina, Cassia, Clodia, Praenestina and Appia, as well as historical sites in the city of Rome and Ostia Antica (Fig. 1). These ancient roads cross the major volcanic centres of Vico and Sabatini to the north of Rome and the Alban Hills to the south (Fig. 1). JB collected 306 analyses of paving stones and 74 analyses of possible source rocks.

Field petrographic analysis revealed the presence of a considerable range of fabrics, from porphyritic to aphanitic. Many porphyritic samples contain leucite crystals up to 2 cm in diameter, which may comprise up to 50% of the mode. These striking rocks are locally known as '*occhio di pesce*', or 'fish eyes', and occur at Vico, Sabatini and the Alban Hills. Phenocrysts of pyroxene, plagioclase and sanidine were also recorded. Aphanitic samples occur throughout, with varying ratios of felsic to ferromagnesian components. The field study suggested that in most cases more than one of the petrographic groups was present in the paving stones examined at each locality. From an analytical standpoint, the presence of abundant phenocrysts is not helpful. The Niton window is 2 cm<sup>2</sup>; thus only a small area of the sample is irradiated. If phenocrysts are abundant, they will partition a significant part of the magma chemistry, making groundmass measurements unrepresentative of the bulk composition of the rock. Thus aphanitic rocks were preferred, or those with a relatively low phenocryst content.

Paving stones and potential source rocks were washed and dried prior to analysis and compositional data were collected using a handheld Niton XLt 792 MZ portable XRF. This has a 40 keV tube and a SiPIN detector with a silver filter. The resolution is around 230 eV, giving detection limits of around 10–15 ppm. Factory calibrations were used during data



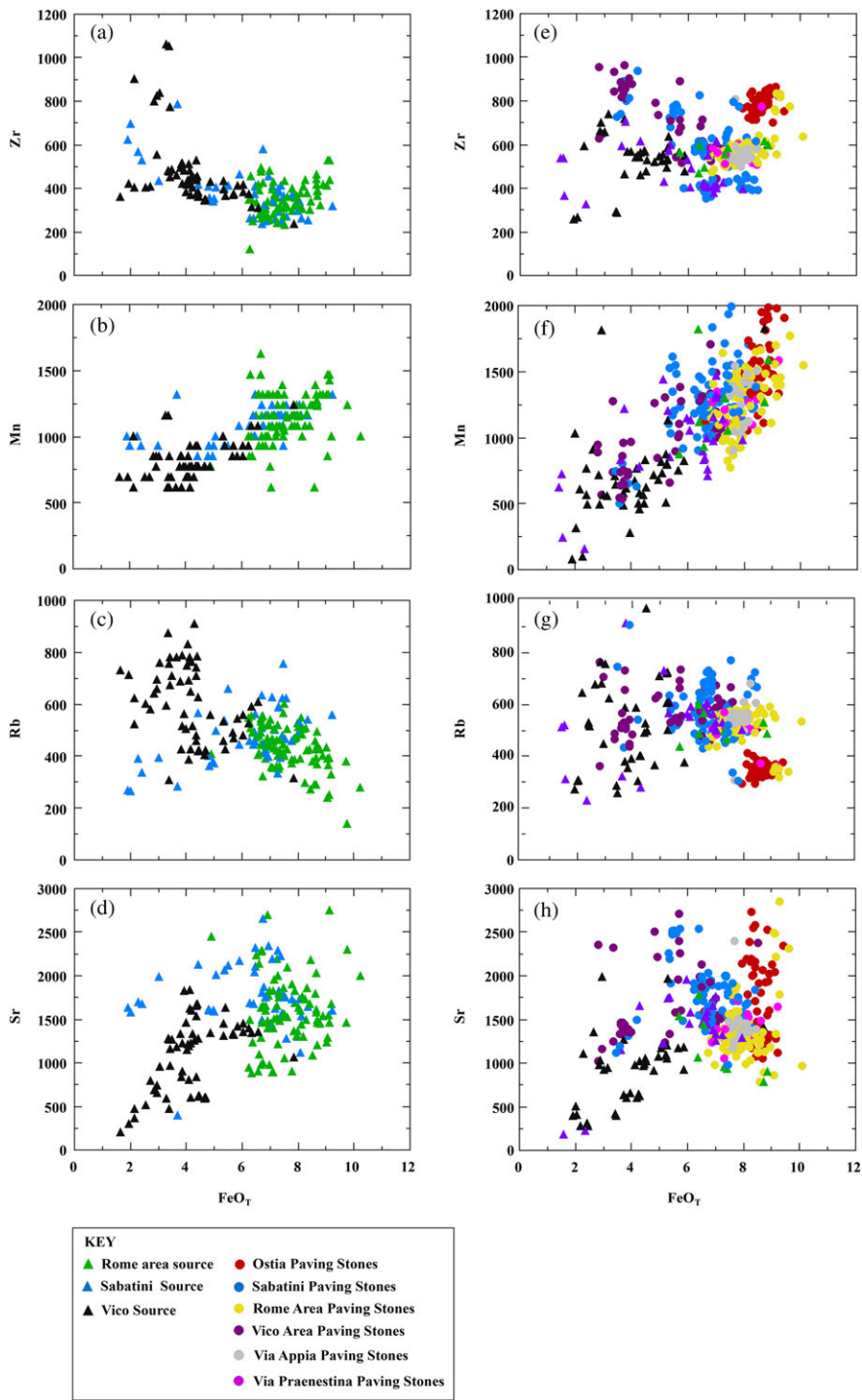


Figure 2 (a–d) Published geological analyses versus  $FeO_T$ ; (e–h) Archaeological data versus  $FeO_T$ .

collection and the machine precision was later checked against standards of known composition (Black pers. comm.). This instrument is suitable for elements between Ti and Bi on the periodic table and data were collected in ppm for Zr, Sr, Rb, Pb, Fe, Mn, Se, As, Zn, Hg, Cu, Ni, Co, Cr and U. Lighter elements such as, Mg, Al, Si, P, K and Ca could not be determined by the above instrument, but are now accessible with later helium-enabled Niton analysers. Geologically, they are important major elements in these volcanic rocks and may be significant in sourcing.

For comparative purposes, the data (Figs 2 (e)–2 (h)) are presented next to the geological data in Figures 2 (a)–2 (d). Each paving stone was assigned a coloured circle symbol based on its geographical location. For the north of the area, the colours were based on the volcano on which the paving stone data was collected: blue for Sabatini and black for Vico. In the south, the picture is more complicated and symbols were assigned based on a particular Via or geographical locality: red for Ostia, yellow for the city of Rome, grey for the Via Appia and magenta for Via Praenestina. The city of Rome data included paving stones from Trajan's Market, the Arch of Titus and the Via Sacra. Coloured triangles were used for sources: green for the Alban Hills, blue for Sabatini and black for Vico. These data points represent actual outcrops measured in the field and are thus specific to the volcano indicated by the colour code.

Although Figures 2 (e)–2 (h) are somewhat cluttered, it is possible to discern similar patterns between the Niton source data and the geological data. For example, data from the Alban Hills area tend to cluster at the high-FeO<sub>T</sub> end and Vico data at the low-FeO<sub>T</sub> end, while Sabatini data plot in the middle. This, of course, is to be expected, as the data points represent measurements taken from *in situ* lava flows. However, it is interesting to note that, broadly speaking, Figures 2 (e)–2 (h) suggest that the paving stone data show a similar distribution to the source and geological data. For example, the paving stone data from the city of Rome (yellow circles), the Via Appia (grey) and the Via Praenestina (magenta) plot at the high-FeO<sub>T</sub> or Alban Hills end. The Sabatini data (blue) tend to plot in the middle of the FeO<sub>T</sub> range, although there is considerable overlap at the high-FeO<sub>T</sub> end of the diagram. Similarly, the Vico data tend to cluster at the low-FeO<sub>T</sub> end of the diagrams. However, there are some significant anomalies. For example, comparisons between the Zr versus FeO<sub>T</sub> plots (Figs 2 (a) and 2 (e)) suggest that the published analyses (Fig. 2 (a)) have a lower Zr value than the Niton values (Fig. 2 (e)).

#### DATA CLUSTERING

Paving stone data point clustering is a significant feature of the archaeological data (Figs 2 (e)–2 (h)), although it is somewhat obscured by source data points unrelated to the paving stone clusters. Such clustering is evident in all the element plots (Figs 2 (e)–2 (h)), but is particularly well developed in the Zr versus FeO<sub>T</sub> plot (Fig. 2 (e)), which is shown in more detail in Figure 3 (a). Zr is considered to be relatively immobile during post-eruption alteration and weathering, and may thus be a more reliable indicator of primary magma chemistry. In Figure 3 (a), data clusters are identified and labelled A–F. Well-developed clustering is particularly apparent for the Ostia (red) data (Cluster A) and for Cluster B, which contains city of Rome (yellow), Via Appia (grey) and Via Praenestina (magenta) data. Cluster B is overlapped by Cluster D, which contains both Vico and some Sabatini data points. In addition, there are also several minor clusters, particularly of the Sabatini data (blue) (e.g., Cluster C). However, given the spread of data and the overlap in compositions of the sources, it is probable that there will be some points that do not belong to that particular association.

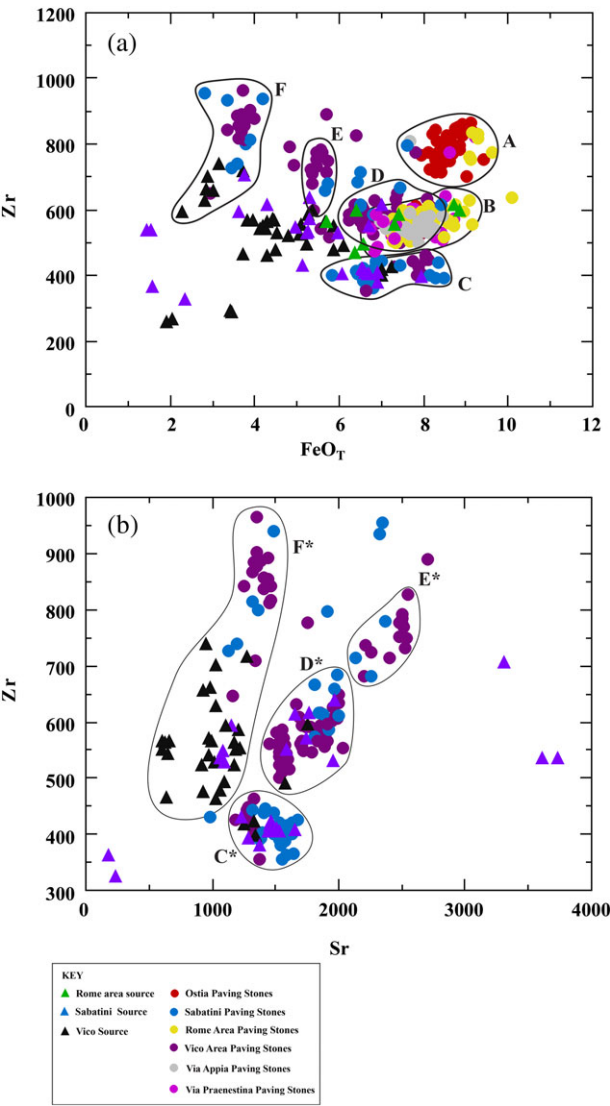


Figure 3 (a) A plot of Zr versus FeO<sub>T</sub>, showing clustering of data. (b) A plot of Zr versus Sr, showing data clustering.

One of the problems in interpreting Figure 3 (a) is that many of the clusters overlap. This is particularly the case for Cluster B, which comprises data mostly from the city of Rome and the Viae Appia and Praenestina, and Cluster D, which comprises mostly Vico data. Such overlaps obscure geochemical relationships that may facilitate sourcing. Thus other geochemical parameters were sought to get round this problem. For example, Cluster D paving stones tend to show elevated levels of Sr relative to Cluster B. Thus a plot of Zr versus Sr separates these data sets (Fig. 3 (b)). This figure shows a plot of the Sabatini and Vico data only and reveals three contiguous fields defining a linear trend. These new clusters are equivalent to Clusters C, D and E of Figure 3 (a) and have thus been named C\*, D\* and E\*, respectively, to avoid confusion.

Comparison of the sample numbers in Clusters C\*, D\* and E\* in Figure 3 (b) shows that they comprise more or less the same samples as in Clusters C, D and E, respectively, of Figure 3 (a). Similarly, the data in Cluster F of Figure 3 (a) plot as Cluster F\* in Figure 3 (b). These data plot as a more diffuse linear trend at lower Sr and higher Zr values. These relationships clearly validate the geochemical coherence of the observed clusters. The trends defined by the Sabatini data in Clusters C\* and D\* may be partly related to the high-Ba and a low-Ba series recorded by the geological data of Conticelli *et al.* (1997).

#### SPIDER DIAGRAMS

In the above section, we have used standard two-element or  $X$ – $Y$  petrological diagrams to analyse the data (Figs 2 (a)–2 (h)). These diagrams are useful but have the drawback that only two elements or element ratios can be used for analysis. The results show that the method is broadly capable of sourcing paving stone clusters to a particular volcano. However, they depend on the amount and quality of the data, which in many cases, particularly in the northern area, is inadequate. Consequently, the diagrams lack sufficient discriminatory power. Multi-element or spider diagrams can improve the analytical resolution of the geochemical data by comparing many more elements against a calculated standard. Such diagrams are commonly used in igneous petrology, and the more elements used the better. They are prepared by first determining the average composition of a standard, which may, for example, be calculated from a number of analyses of a common type of lava from a particular locality. In this paper, the standards were prepared by averaging the composition of a number of lava flows from the geological literature that may represent possible sources.

In this study, six geologically significant elements were selected for comparison with the standards. They were Zr, Sr, Rb, Pb, Fe and Mn and they were arranged at the bottom of the diagram. MinPet software divided the concentrations of these elements in each paving stone analysis with the appropriate standard value. This can be simply expressed as the ratio Sample/Standard and this is plotted against a vertical logarithmic scale. Elements having the same concentrations as the standard will plot as a value 1. Thus the similarity to the standard of the selected elements can be visually assessed. Spider diagrams thus facilitate direct comparison of more elements than the two normally represented in  $X$ – $Y$  plots and allowed us to interrogate the data in greater detail. They may therefore improve discriminatory comparisons between paving stones and possible sources. This will be tested in the following section.

#### Groups A and B

Figure 4 shows spider diagrams for paving stones from the southern area, which includes Group A paving stones from Ostia (red) (Figs 4 (a)–4 (d)) and Group B paving stones represented by three subgroups: city of Rome (yellow) (Figs 4 (e)–4 (h)), the Via Appia (grey) (Figs 4 (i)–4 (l)) and the Via Praenestina (magenta) (Figs 4 (m)–4 (p)). In the interest of clarity, where group clusters contain paving stones from other areas—for example, Group A (Fig. 3 (a))—only the dominant group is included in the spider diagrams. This applies particularly where paving stone numbers are high.

The vertical column on the left of Figure 4 shows the different groups of lavas from the Alban Hills that were used as standards. The locality of these flows is shown in Figure 1 (Gaeta *et al.* 2016). The normalizing standards were calculated as follows: the average of nine samples from the Pozzolan Rosso lavas from the Vallerano Plateau (Gaeta *et al.* 2006; Boari *et al.* 2009;

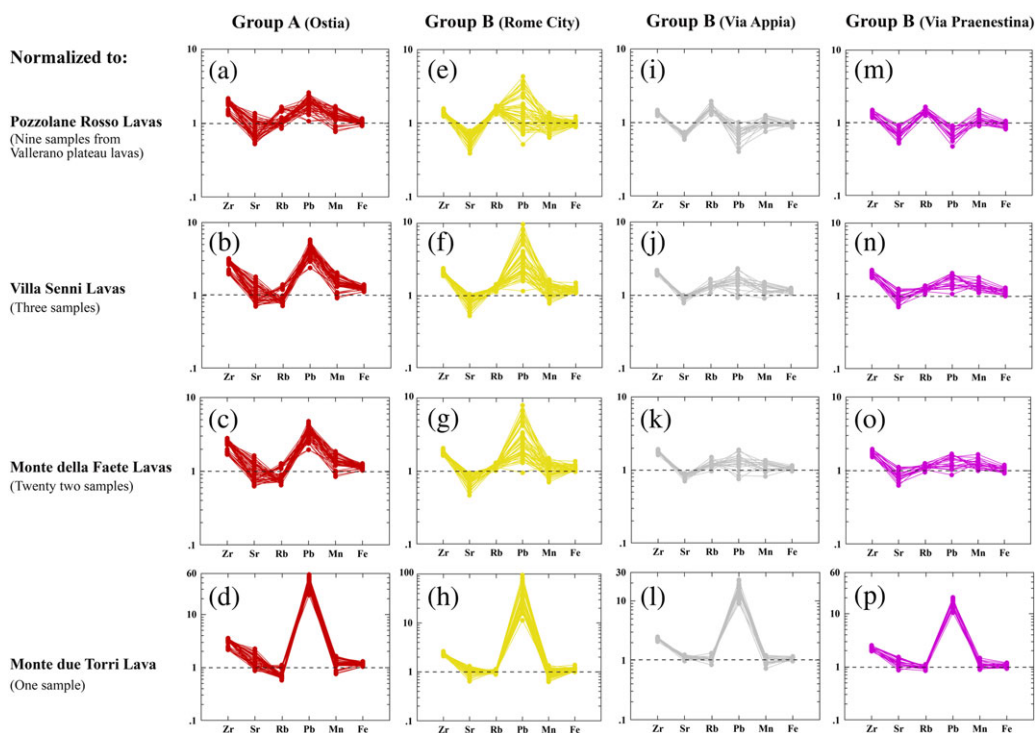


Figure 4 Spider diagrams showing Groups A and B normalized to various Alban Hills lavas: explanation in text.

Marra *et al.* 2009; Gozzi *et al.* 2014), three samples from the Villa Senni lavas (Marra *et al.* 2009; Gozzi *et al.* 2014; Gaeta *et al.* 2016), 22 samples from the Monte della Faete lavas (Boari *et al.* 2009; Marra *et al.* 2009; Gozzi *et al.* 2014; Gaeta *et al.* 2016) and one sample from the Monte due Torri lavas (Gaeta *et al.* 2011). The horizontal rows show spiders for each group normalized to these standards.

Inspection of Figure 4 shows some interesting patterns. Group A paving stones (red) from Ostia have high Zr and low Rb values (Fig. 2 (a)). Inspection of Figure 2 (a) shows that there are no published analyses that have Zr values comparable to those shown by the archaeological data (Fig. 2 (e)). We have thus regarded Group A as problematic. However, the spider in Figure 4 (a) does suggest that there may be some relationship with lavas from the Vallerano plateau (Fig. 1), although the fit is relatively poor. This observation merits further investigation, as the outcrops of the Vallerano lavas are close to the River Tiber and barely 12 km from the ancient port city of Ostia. There may also be more than one source represented at Ostia, which will tend to obscure relationships in Figure 4 (a). We intend to investigate this in a future project. The city of Rome paving stones (Figs 4 (e)–4 (h)) (yellow) do not show a relationship with any of the standards, suggesting that they were quarried from a yet unknown source or sources. It is also interesting that the Pb data in (Figs 4 (e)–4 (h)) show a large range, which we suggest may be due to environmental pollution rather than paving stone geochemistry. This is supported by the fact that the anomaly is not present or is much reduced in paving stones measured in more rural areas. This emphasizes the importance of rigorous cleaning of paving stones prior to measurement.

The spiders for the Viae Appia (grey) and Praenestina (magenta) (Fig. 4) show much clearer relationships. Both display relatively flat plots when normalized to the Villa Senni lavas (Figs 4 (j) and 4 (n)) and the Monte della Faete lavas (Figs 4 (k) and 4 (o)). The data suggest, therefore, that the paving stones for each of these two VIAE were quarried from at least two sources; one from the Villa Senni lavas and the other from the Monte della Faete lavas. With respect to the latter, it is significant that the Capo di Bove flow, which is part of the Monte della Faete lavas (Gozzi *et al.* 2014), crosses into what is now metropolitan Rome and that the Via Appia is, in places, built on it (Fig. 1). This can be observed at the Tomb of Caecilia Metella. An interesting feature of all of these diagrams is the elevation of the Zr values, imparting a 'Zr kick' to the spiders. We will address this presently.

Samples normalized to the Monte due Torri lavas clearly suggest that this flow could not have been a source for any of the paving stone groups (Figs 4 (d), 4 (h), 4 (l) and 4 (p)). The very low Pb levels in this flow (Gaeta *et al.* 2011) are diagnostic and necessitated a change of scale in the spiders.

### Groups C\*, D\*, E\* and F\*

The majority of the paving stones from the above groups come from roads crossing Vico (88) as compared to Sabatini (43) (Table 1). These paving stones fall into well-defined groups and the geological literature yielded 108 analyses that are potential standards (see, e.g., Conticelli *et al.* 1997; Perini *et al.* 2004). Despite these apparent advantages, sourcing has proved to be problematic. There are three main reasons for this. First, lava flows are relatively abundant in both Sabatini and Vico, and some of them come from isolated monogenetic centres (Fig. 1). This relative abundance of choice complicates the selection of standards. Second, and related to this, we were unable to find information about the locations of quarries that were used in the Roman period with the exception of those at Monte Maggiore and Monte Aguzzo (Laurence 2004) (Fig. 1). Such information would have allowed us to narrow down the choice of lava flow standards. Third, although the Vico area hosts the largest number of paving stones, the Niton geochemical data for Groups E\* and F\* is inadequate (Table 1). Despite these complications, we have attempted to source the different groups by calculating standards from the following Vico lava flows: Mt Venere, Poggio Nibbio, Ronciglione and Lago di Vico (Fig. 1) (Perini *et al.* 2004). On Sabatini, we selected Monte Maggiore, Monte Aguzzo and Trevignano (Fig. 1) (Conticelli *et al.* 1997, 2010b). Unfortunately, there are no data for Pb in Conticelli *et al.* (1997), which leaves diagrams based on this data incomplete. Many of the resulting spiders do not reveal any clear source – paving stone relationships, so we have selected four that do; two from Vico and two from Sabatini, and they are presented in Figure 5. In each case, the distance between the possible source and the road construction site is considered, as overland transport of very heavy lava blocks must have been an issue. However, we have no hard information on the importance of this matter. Indeed, definitive answers to such questions would be clarified by unequivocal identification of paving stone – source associations.

There is a reasonably good Group C\* fit for the Monte Venere lavas (Fig. 5 (a)). However, the paving stones with this signature come mostly from Nepi, Terme di Gracchi and Rignano Flaminia (Table 1). The latter is some 30 km to the south-east of Monte Venere, which casts some doubt on this association. Groups D\*, E\* and F\* show no relationship with the Monte Venere lavas (Figs 5 (e), 5 (i) and 5 (m)). The Lago di Vico lavas correlate reasonably well with Groups E\* and F\* (Figs 5 (j) and 5 (n)), although the sample numbers are low for Group F\*. However, geographically this seems possible, as Faleri Novi and Nepi are some 15 km to the south-east of



Table 1 A composite table summarizing data from clusters defined by paving stones in Figures 3 and 4. The localities on the left are arranged geographically from north to south. The figures in the columns are paving stones within each cluster and these are colour coded using the scheme in Figures 2–5; black for Vico, blue for Sabatini and green for the Alban Hills

Paving stone Locality	A		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B		B	
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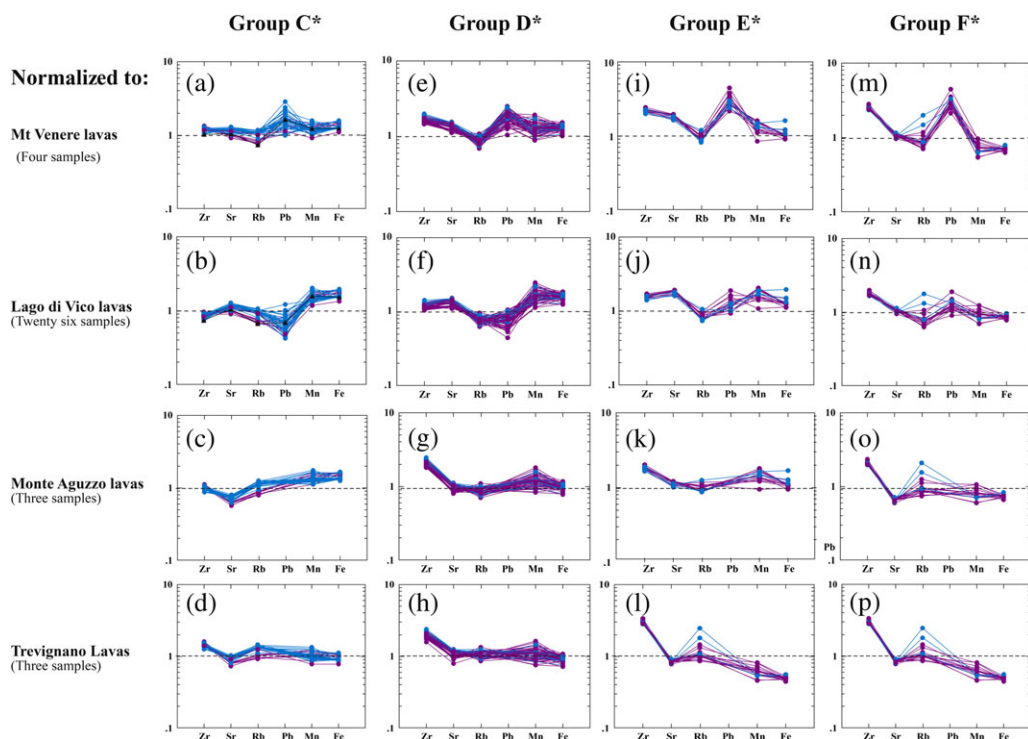


Figure 5 Spider diagrams showing Groups C\*, D\*, E\* and F\* normalized to Sabatini and Vico lavas: explanation in text.

Lago di Vico, although Oriculum is some 30 km to the east-north-east (Table 1). The two possible Sabatini sources at Monte Aguzzo and Trevignano (Fig. 1) are regarded as incomplete because of the absence of Pb data. However, there appears to be a possible association between Monte Aguzzo (Fig. 1) and Groups D\* and E\* (Figs 5 (g) and 5 (k)) and between Trevignano (Fig. 1) and Groups C\* and D\* (Figs 5 (d) and 5 (h)). It is interesting to note that all of these diagrams show the characteristic 'Zr kick' mentioned above. From a geographical standpoint, the Trevignano association is possible for Groups C\* and D\*, but the Monte Aguzzo association seems less likely, as Monte Aguzzo is in the south, close to the confluence of the Viae Clodia and Flaminia.

#### SUMMARY AND DISCUSSION

Compositional data were collected using a handheld Niton portable XRF from *in situ* lava paving stones along the Viae Flaminia, Amerina, Cassia, Clodia, Praenestina and Appia, as well as historical sites in the city of Rome and Ostia Antica. These viae cross three volcanoes of the RMP, the Alban Hills, Sabatini and Vico. The Niton archaeological data were compared graphically on *X–Y* plots with analyses of lava flows taken from the geological literature. Six geologically significant elements were plotted against  $\text{FeO}_T$ . As a broad generalization, both the geological and the archaeological data from viae around the Alban Hills and historical sites in Rome plot at the high- $\text{FeO}_T$  end of the diagrams. The Vico data, despite showing a considerable compositional range, tend to concentrate at the low- $\text{FeO}_T$  end and the Sabatini data

plot in the middle. These diagrams therefore suggest a crude method of sourcing paving stones to a particular volcano. They also suggest that paving stones were quarried from a local volcanic source and were not transported over large distances.

A significant feature of the archaeological data is the tendency towards clustering of data points. Our analysis recognized six such clusters (Groups A, B, C\*, D\*, E\* and F\*), which maintained their integrity on both Zr versus FeOT plots and Zr versus Sr plots. Such clustering is perhaps to be expected, as lava blocks collected at different quarries will reflect the limited range of compositions present in that quarry. On the other hand, the geological data plots will tend to reflect the regional data spread present in the whole volcano. We therefore conclude that where large numbers of paving stones and sources occur together in a cluster, it is likely that this represents a source association; that is, a group of paving stones from a common source. In this sense, the word 'source' is used broadly to suggest a particular volcano. These paving stone – source – geographical associations are summarized in Table 1, which shows the number of paving stones from each cluster and their localities, together with possible sources. Another interesting feature of the clusters is that most contain paving stones from at least one other source area (see Table 1). For example, in Figure 3(a) the Group A cluster (Ostia) contains stones the compositions of which were determined in the city of Rome (yellow). This suggests that the road builders used paving stones from specific sources at different road construction sites; in this case, either Ostia or the city of Rome.

The *X–Y* plots referred to above are, in one sense, a blunt instrument as a sourcing tool, as they require only two elements or element ratios and thus lack discriminatory power. Spider diagrams are widely used in igneous petrology and have the advantage that they utilize many more elements than the *X–Y* plots. Analysis using these diagrams suggested that Group A (Ostia) could have been sourced on the Vallerano Plateau of the Alban Hills (Fig. 1), although the fit is not particularly good. We were unable to source Group B from the city of Rome (yellow). However, the Group B spiders for the *Viae Appia* (grey) and Praenestina (magenta) give a good fit for both the Villa Senni lavas and the Monte della Faete lava flows, which erupted on the north-western flanks of the Alban Hills (Fig. 1). The picture for Groups C\*, D\*, E\* and F\* is much more complex. There are possible fits for Group C\* and Monte Venere lavas, Group F\* and Lago di Vico, Monte Aguzzo and Groups D\*, E\* and F\*, and Trevignano and Groups C\* and D\*. However, the latter two associations are compromised by the absence of Pb data. Clearly, some confusion is introduced where the same groups normalize to widely differing geographical localities. Thus attempts to source Groups C\*, D\*, E\* and F\* were unsatisfactory.

Several conclusions may be derived from the analysis and methodology presented above. First, it is clear that more element data would have added analytical rigour to the spider diagrams. However, our choice of elements was determined by the capability of the Niton machine. More recent machines, especially helium-enabled models, permit the collection of more elements, particularly the lighter ones, which were inaccessible to the machine used in this paper. Second, the location of the quarries used in Roman times would have assisted in the choice of standards, particularly with respect to Vico and Sabatini. One of the consistent features of the spiders in Figures 4 and 5 is the elevated values of Zr, which manifests in the spider diagrams as a 'Zr kick'. It was noted above that there were some significant anomalies in the Zr values between the geological and archaeological data (compare Figs 2 (a) and 2 (e)). We suggest that this was probably caused by a calibration error that has resulted in an overestimation of the Zr values in the paving stones, which in turn would produce the 'Zr kick' in the spiders. If this is the case, a correct calibration would have reduced the measured Zr values, bringing them more into line with the geological values and thus flattening the curves. This emphasizes the importance of

correct calibration of the Niton, rather than the use of factory calibrations. We conclude, in this preliminary account, that if some of the issues noted above are resolved, then the method shows considerable promise in the sourcing of Roman lava paving stones.

#### FUTURE RESEARCH

As others have found, HHpXRF has enormous potential (Frahm and Doonan 2013), but it comes with some limitations (most recently, Killick 2015). We suggest that future projects on paving materials focus on a specific archaeological location to calculate possible standards and, in so doing, address the widely reported scepticism in the utilization of HHpXRF (compare Grave *et al.* 2012), utilizing an up-to-date helium-enabled machine to allow for the collection of light elements. This approach would also inform the effective calibration of HHpXRF, when compared to laboratory-derived results (Charlton 2013): for example, our Niton data for Zr were slightly elevated relative to the published geological data. This is a subject debated in relation to the study of obsidian: see Goodale *et al.* (2012), Speakman and Shackley (2013) on Frahm (2013a) and Frahm's response (2013b), and also Frahm (2014). Allied to this issue, a robust field procedure for HHpXRF needs to be created, taking into account recent findings with regard to count time (Newlander *et al.* 2015) and the establishment of the number of readings taken per paving stone.

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#### REFERENCES

- Alagna, K., Peccerillo, A., Martin, S., and Donati, C., 2010, Tertiary to present evolution of orogenic magmatism in Italy, in *The geology of Italy: tectonics and life along plate margins* (eds. M. Beltrando, A. Peccerillo, M. Mattei, S. Conticelli and C. Doglioni), *Journal of the Virtual Explorer*, **36**(20), paper 18, <https://doi.org/10.3809/jvirtex.2010.00233>.
- Aulinas, M., Gasperini, D., Gimeno, D., Macera, P., Fernandez-Turiel, J. L., and Cimarelli, C., 2011, Coexistence of calc-alkaline and ultrapotassic alkaline magmas at Mount Cimini: evidence for transition from the Tuscan to the Roman Magmatic Province (Central Italy), *Geologica Acta*, **9**, 103–25.
- Black, S., Browning, J., and Laurence, R., 2004, From quarry to road: the supply of basalt for road paving in the Tiber Valley, in *Mecator placidissimus: the Tiber Valley in antiquity* (eds. F. Coarelli and H. Patterson), Quasar: Rome.
- Boari, E., Avanzinelli, R., Melluso, L., Giordano, G., Mattei, M., Arnaldo, A., De Benedetti, A. A., Morra, V., and Conticelli, S., 2009, Isotope geochemistry (Sr–Nd–Pb) of leucite-bearing volcanic rocks from 'Colli Albani' volcano, Roman Magmatic Province, Central Italy: inferences on volcano evolution and magma genesis, *Bulletin of Volcanology*, **71**, 977–1005.
- Capedri, S., and Grandi, R., 2003, Trachytes used for paving Roman roads in the Po Plain: characterization by petrographic and chemical parameters and provenance of paving stones, *Journal of Archaeological Science*, **30**, 491–509.
- Carapezza, M. M., Badalamenti, B., Cavarra, L., and Scalzo, A., 2003, Gas hazard assessment in a densely inhabited area of Colli Albani Volcano (Cava dei Selci, Roma), *Journal of Volcanology and Geothermal Research*, **123**, 81–94.

- Charlton, M. F., 2013, Review of handheld XRF for art and archaeology (Studies in Archaeological Sciences 3), *Journal of Archaeological Science*, **40**, 3058–9.
- Chelazzi, L., Bindi, L., Olmi, F., Peccerillo, A., Menchetti, S., and Conticelli, S., 2006, A lamproitic component in the high-K calc-alkaline volcanic rocks of the Capraia Island, Tuscan Magmatic Province: evidence from clinopyroxene crystal chemical data, *Periodico di Mineralogia*, **75**, 75–94.
- Conticelli, S., 1998, The effect of crustal contamination on ultrapotassic magmas with lamproitic affinity: mineralogical, geochemical and isotope data from the Torre Alfina lavas and xenoliths, *Central Italy*, *Chemical Geology*, **149**, 51–81.
- Conticelli, S., Carlson, R. W., Widom, E., and Serri, G., 2007, Chemical and isotopic composition (Os, Pb, Nd and Sr) of Neogene to Quaternary calc-alkalic, shoshonitic and ultrapotassic mafic rocks from the Italian peninsula: inferences on the nature of their mantle sources, *Geological Society of America, Special Paper*, **418**, 171–202.
- Conticelli, S., Francalanci, L., Manetti, P., Cioni, R., and Sbrana, A., 1997, Petrology and geochemistry of the ultrapotassic rocks of the Sabatini Volcanic District, Central Italy: the role of evolutionary processes in the genesis of variably enriched alkaline magmas, *Journal of Volcanology and Geothermal Research*, **75**, 107–36.
- Conticelli, S., Marchionni, S., Rosa, D., Giordano, G., Boari, E., and Avanzinelli, R., 2009, Shoshonite and sub-alkaline magmas from an ultrapotassic volcano: Sr–Nd–Pb isotope data on the Roccamonfina volcanic rocks, Roman Magmatic Province, southern Italy, *Contributions to Mineralogy and Petrology*, **157**, 41–63.
- Conticelli, S., Boari, E., Avanzinelli, R., De Benedetti, A. A., Giordano, G., Mattei, M., Melluso, L., and Morra, V., 2010a, Geochemistry, isotopes and mineral chemistry of the Colli Albani volcanic rocks: constraints on magma genesis and evolution, in *The Colli Albani volcano* (eds. R. Funicello and G. Giordano), 107–39, Special Publications of IAVCEI, 3, Geological Society of London, London.
- Conticelli, S., Laurenzi, M. A., Mattei, M., Avanzinelli, R., Melluso, L., Tommasini, S., Boari, E., Cifelli, F., and Perini, G., 2010b, Leucite bearing (kamafugitic/leucitic) and free lamproitic ultrapotassic rocks and associated shoshonites from Italy: constraints on petrogenesis and geodynamics, in *The geology of Italy: tectonics and life along plate margins* (eds. M. Beltrando, A. Peccerillo, M. Mattei, S. Conticelli and C. Doglioni), *Journal of the Virtual Explorer*, **36**(20), paper 20, <https://doi.org/10.3809/jvirtex.2010.00251>.
- Di Battistini, G. D., Montanini, A., Vernia, L., Bargossi, G. M., and Castorina, F., 1998, Petrology and geochemistry of ultrapotassic rocks from the Montefiascone Volcanic Complex (Central Italy): magmatic evolution and petrogenesis, *Lithos*, **3**, 169–95.
- Frahm, E., 2013a, Validity of ‘off-the-shelf’ handheld portable XRF for sourcing near eastern obsidian chip debris, *Journal of Archaeological Science*, **40**, 1080–92.
- Frahm, E., 2013b, Is obsidian sourcing about geochemistry or archaeology? A reply to Speakman and Shackley, *Journal of Archaeological Science*, **40**, 1444–8.
- Frahm, E., 2014, Characterizing obsidian sources with portable XRF: accuracy, reproducibility, and field relationships in a case study from Armenia, *Journal of Archaeological Science*, **49**, 105–25.
- Frahm, E., and Doonan, R. C. P., 2013, The technological versus methodological revolution of portable XRF in archaeology, *Journal of Archaeological Science*, **40**, 1425–38.
- Gaeta, M., Freda, C., Christiansen, J. N., Dallai, L., Marra, F., Karner, D. B., and Scarlato, P., 2006, Time-dependent geochemistry of clinopyroxene from the Alban Hills (Central Italy): clues to the source and evolution of ultrapotassic magmas, *Lithos*, **86**, 330–46.
- Gaeta, M., Freda, C., Marra, F., Arienzo, I., Gozzi, F., Jicha, B., and Di Rocco, T., 2016, Palaeozoic metasomatism at the origin of Mediterranean ultrapotassic magmas: constraints from time dependent geochemistry of Colli Albani volcanic products (Central Italy), *Lithos*, **244**, 151–64.
- Gaeta, M., Freda, C., Marra, F., Di Rocco, T., Gozzi, F., Arienzo, I., Giaccio, B., and Scarlato, P., 2011, Petrology of the most recent ultrapotassic magmas from the Roman Province (Central Italy), *Lithos*, **127**, 298–308.
- Giaccio, B., Marra, F., Hajdas, I., Karner, D. B., Renne, P. R., and Sposato, A., 2009,  $^{40}\text{Ar}/^{39}\text{Ar}$  and  $^{14}\text{C}$  geochronology of the Albano maar deposits: implications for defining the age and eruptive style of the most recent explosive activity at the Alban Hills Volcanic District, Italy, *Journal of Volcanology and Geothermal Research*, **185**(3), 203–13.
- Giordano, D., Polacci, M., Papale, P., and Caricchi, L., 2010, Rheological control on the dynamics of explosive activity in the 2000 summit eruption of Mt. Etna, *Solid Earth*, **1**, 61–9.
- Giordano, G., De Benedetti, A. A., Diana, A., Diano, G., Gaudioso, F., Marasco, F., Miceli, M., Mollo, S., Cas, R. A. F., and Funicello, R., 2006, The Colli Albani mafic caldera (Roma, Italy): stratigraphy, structure and petrology, *Journal of Volcanology and Geothermal Research*, **155**, 49–80.
- Goodale, N., Bailey, D. G., Jones, G. T., Prescott, C., Scholz, E., Stagliano, N., and Lewis, C., 2012, pXRF: a study in inter-instrument performance, *Journal of Archaeological Science*, **39**, 875–83.
- Gozzi, F., Gaeta, M., Freda, C., Mollo, S., Di Rocco, T., Marra, F., Dallai, L., and Pack, A., 2014, Primary magmatic calcite reveals origin from crustal carbonate, *Lithos*, **190–1**, 191–203.

- Grave, P., Attenbrow, V., Sutherland, L., Pogson, R., and Forster, N., 2012, Non-destructive pXRF of mafic stone tools, *Journal of Archaeological Science*, **39**, 1674–86.
- Karner, D. B., Marra, F., and Renne, P., 2001, The history of Monti Sabatini and Alban Hills volcanoes: groundwork for assessing volcanic-tectonic hazards for Rome, *Journal of Volcanology and Geothermal Research*, **107**, 185–219.
- Killick, D., 2015, The awkward adolescence of archaeological science, *Journal of Archaeological Science*, **56**, 242–7.
- Lancaster, L. C., Sottili, G., Marra, F., and Ventura, G., 2010, Provenancing of lightweight volcanic stones used in Roman concrete vaulting: Evidence from Turkey and Tunisia, *Archaeometry*, **52**, 949–61.
- Lancaster, L. C., Sottili, G., Marra, F., and Ventura, G., 2011, Provenancing of lightweight volcanic stones used in Roman concrete vaulting: evidence from Rome, *Archaeometry*, **53**, 707–27.
- Laurence, R., 1999, *The roads of Roman Italy: mobility and cultural change*, Routledge, London.
- Laurence, R., 2004, The economic exploitation of geological resources in the Tiber Valley: road building, in *Bridging the Tiber, approaches to regional archaeology in the Middle Tiber Valley* (ed. H. Patterson), Archaeological Monographs of the British School at Rome: London.
- Marra, F., D'Ambrosio, E., Sottili, G., and Ventura, G., 2012, Geo-chemical fingerprints of volcanic materials: identification of a pumice trade route from Pompeii to Rome, *Geological Society of America Bulletin*, **125**, 556–77.
- Marra, F., Karner, D. B., Freda, C., Gaeta, M., and Renne, P., 2009, Large mafic eruptions at Alban Hills Volcanic District (Central Italy): chronostratigraphy, petrography and eruptive behaviour, *Journal of Volcanology and Geothermal Research*, **179**, 217–32.
- Newlander, K., Goodale, N., Jones, G. T., and Bailey, D. G., 2015, Empirical study of the effect of count time on the precision and accuracy of pXRF data, *Journal of Archaeological Science*, **43**, 534–48.
- Peccerillo, A., 2005, The Roman Province, in *Plio-Quaternary volcanism in Italy: petrology, geochemistry, geodynamics*, 70–106, Springer, Berlin.
- Perini, G., Conticelli, S., Francalanci, L., and Davidson, J. P., 2000, The relationship between potassic and calc-alkaline post-orogenic magmatism at Vico volcano, Central Italy, *Journal of Volcanology and Geothermal Research*, **95**, 247–72.
- Perini, G., Francalanci, L., Davidson, J. P., and Conticelli, S., 2004, Evolution and genesis of magmas from Vico volcano, Central Italy: multiple differentiation pathways and variable parental magmas, *Journal of Petrology*, **45**, 139–82.
- Renzulli, A., Antonelli, F., Santi, P., Busdraghi, P., and Luni, M., 1999, Provenance determination of lava paving stones from the Roman 'Via Consolare Flaminia' pavement (Central Italy) using petrological investigations, *Archaeometry*, **41**, 209–26.
- Sottili, G., Palladino, D. M., Marra, F., Jicha, B., Karner, D. B., and Renne, P., 2010, Geochronology of the most recent activity in the Sabatini Volcanic District, Roman Province, Central Italy, *Journal of Volcanology and Geothermal Research*, **196**, 20–30.
- Speakman, R. J., and Shackley, M. S., 2013, Silo science and portable XRF in archaeology: a response to Frahm, *Journal of Archaeological Science*, **40**, 1435–43.
- Trigila, R., Agosta, E., Currado, C., De Benedetti, A. A., Freda, C., Gaeta, M., Palladino, D. M., and Rosa, C., 1995, Petrology, in *The volcano of the Alban Hills*, 95–165, Tipografia SGS, Roma.

# SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

Data S1. Supplementary material