Geochemical Methods for Sourcing Lava Paving Stones from the Roman roads of Central Italy

Journal:	*Archaeometry*
Manuscript ID	ARCH-05-0067-2016.R1
Manuscript Type:	Original Article
Date Submitted by the Author:	n/a
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Keywords:	Ancient Roman paving stones, Roman roads, material provenance, volcanic rocks, Trace elements, pXRF, HHpXRF, Geology of Rome, Ancient Rome
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Geochemical Methods for Sourcing Basalt Paving Stones from the Roman roads of Central Italy.

M. Worthing, J. Bannister, R. Laurence, and L. Bosworth

Abstract

This paper documents the results of in-situ analysis of 290 basalt paving stones and 75 possible source rocks using pXRF. Data was collected from sites both in the city of Rome (including the Markets of Trajan); on major roads beyond the city (including the Viae Flaminia, Cassia, Clodia, Praenestina and Appia) and at the city of Ostia. Comparison of the pXRF data with basalt compositional data from the geological literature allows broad identification of possible source areas. 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 of Central Italy.

Key Words: Ancient Roman paving stones; Roman roads; Material provenance; Volcanic rocks; Trace elements; pXRF; HHpXRF; Geology of Rome

Introduction

Black basalt or selce 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 basaltic rocks were readily available for road building. Laurence (1999) gave a detailed account of the historical, cultural, political and economic 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 basalt to the west. However he also presented evidence of movement of material across the Tiber in both directions with selce *diverticula* appearing in road abutments to the east and limestone blocks used in road repairs to the west (Laurence 2004). There is also contemporary historical evidence that selce used in the Via Appia was transported there from 'far away' (Laurence 1999). Black et al. (2004) discussed some of the economic, legal and geographic factors pertaining to basalt extraction and transport for road building in the project area. For example, they discussed the possibility of the use of river transport for the conveyance of building materials and the proximity of possible sources to transport hubs. They pointed out that basalts of several types may be used along single stretches of road and that in some cases the basalts used were not from local sources although the evidence for this appears to be based on petrographic rather than geochemical data. Thus both Laurence (1999) and Black et al. (2004) imply that choices were being made in the selection of basalt sources and that the nature of these choices was complex. 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.

They have suggested that there was a complex supply pattern to Rome that included volcanic deposits associated with Vesuvius in Campania (Lancaster et all 2011) and that there was a trade over a long distance from Pompeii to Rome in lightweight/low density materials (Marra et al 2012). The aims of this paper have been devised to provide a reliable sourcing method for the basalt paving stones (i.e. heavy weight/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 in the building of roads that led from Rome.

Geochemical analysis of rock materials such as basalt is usually done by lab-based equipment such as X-ray fluorescence (XRF) and ICPMS which require 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 northeastern 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 which are protected by regulations relating to the preservation of antiquities which forbid destructive sampling. We have therefore used a non-destructive Niton hand-held X-ray flouresence (HHpXRF) analyzer for data collection. Inevitably this resulted in a loss of resolution when compared with the lab-based analyses but it has still yielded useful information. Standard geochemical variation diagram 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 basalts of the Roman Magmatic Province (RMP). This data was obtained using the accurate lab-based techniques referred to above which raises the issue of the compatibility with the Niton data. 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.

Geological Background

The eastern side of the Italian peninsula is dominated by a line of composite volcanoes lying west of the westward dipping Apennine Front (Conticelli et al. 2007). The volcanic rocks associated with this subduction zone can be 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). In this paper only rocks of the RMP will be considered. We have adopted this approach for two reasons. Firstly, the RMP data seems to fit the paving stone data more closely. Secondly, we think that it is unlikely that a heavy material such as basalt would be transported by land over very large distances, particularly when outcrops of useable basalt would never be far away from road construction sites. This approach will be tested in the following analysis.

The principle volcanoes in the RMP relevant to this report are, from north to south, Vico, Sabatini and the Alban Hills or Colli Albani (Fig. 1). Activity began mainly in the upper Pleistocene (0.63 to 0.02Ma) (Peccerillo 2005). Shallow seismic activity and volcanic gas emissions are still recorded in the Alban Hills suggesting that these volcanoes are quiescent but not extinct (Carapezza et al. 2003, Peccerillo 2005). It is from these composite volcanic centres that voluminous pyroclastic deposits were erupted together with subordinate black basaltic lava flows. The lavas range in composition from tephrites and basanites through to phonolites and trachytes (e.g. Peccerillo 2005). Geochemically they are characterised by high K_2O/Na_2O ratios which is expressed in exclusively volcanic leucite-bearing variably silica-undersaturated alkaline magmas. The high K_2O/Na_2O ratios distinguish them from other magmato-tectonic provinces elsewhere in the world.

Geological Data

In order to determine the range of compositions shown by the volcanoes of the RMP, 194 analyses were collected from the geological literature which cover the above volcanoes (Trigila et al. 1995, Conticelli et al. 1997, Conticelli et al. 1998, Di Battistini et al. 1998, Perini et al. 2000, Perini et al. 2004, Peccerillo 2005a, Peccerillo 2005b, Chelazzi 2006, Giordano et al. 2006, Conticelli et al. 2007, Conticelli et al. 2009). The analyses were processed with Minpet petrological software using standard X-Y variation diagrams. The basalts 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 which are commonly used in igneous petrology were plotted. These included Fe, Mn, Zr, Rb and Sr. In order to harmonise the geological and Niton data sets the MnO data in the geological analyses was converted to ppm and where necessary total Fe expressed as Fe_2O_3T was converted to FeOT. In the archaeological data set the Fe expressed as ppm was converted to FeOT.

Figures 2 a-d show plots of the above elements against FeOT 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 generalisation, the Alban Hills data plots at the high FeOT end of the diagram (e.g. Fig. 2a Zr-FeOT). Products from Vico, which make up the largest number of analyses, show a considerable range of compositions with a tendency to concentrate at the low FeOT end with some analyses also plotting at the high FeOT end. The Sabatini data lies in the middle but shows some overlap particularly with the Alban Hills data at the high FeOT end. These data show that there are broad but significant geochemical differences between the volcanoes that may be useful in sourcing the basalt paving stones.

Archaeological Data

The compositional data used in this study was collected by JB from in situ paving stones and possible source basaltic rock outcrops along the Via Flaminia, Via Amerina, Via Cassia, Via Clodia, Via Prenestina Via 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 290 analyses of paving stones and 75 analyses of possible source rocks.

At each locality paving stones and possible source rocks were assigned to defined petrographic groups based on colour, macroscopic mineralogy and textural features. This revealed the presence a considerable range of fabrics from porphyritic to aphanitic. Many porphyritic samples contain leucite crystals up to 2 cms 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 ferromagnesium 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 2cm^2 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 was collected using a hand-held Niton XLt 792 MZ portable XRF. This has a 40keV tube with SiPIN detector with silver filter. Resolution is around 230eV giving detection limits of around 10-15 ppm. Factory calibrations were used during data collection and machine precision was later checked against standards of known composition (Black pers. com.). This instrument is suitable for elements between Ti and Bi on the periodic table and data was collected in ppm (parts per million) 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 basalts and may be significant in sourcing.

For comparative purposes the data (Figs. 2 e-h) are presented next to the geological data in Figures 2 a-d. Each paving stone was assigned a coloured circle symbol based on its geographical location. For the north of the area 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, pink for Via Prenestina, yellow for the City of Rome and grey for the Via Appia. 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-h are somewhat cluttered, it is possible to discern similar patterns between the Niton source data and the geological data. For example, the Alban Hills data tends to cluster at the high FeOT end, Vico data at the low FeOT end and Sabatini data plotting 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 2e-h also show that paving stone data, shows a similar distribution to the source measurements and the geological data. For example, paving stone data from Rome City (yellow circles), Via Appia (grey) and Via Prenestina (pink) plot at the high FeOT or Alban Hills end. The Sabatini data (blue) tends to plot in the middle of the FeOT range although there is considerable overlap at the high FeOT end of the diagram. Similarly the Vico data tends to cluster at the low FeOT end of the diagrams. However there are some significant anomalies. For example comparisons between the Zr-FeOT plots (Figs 2a and 2e) suggest that the published analyses (Fig 2a) have a lower Zr value than the Niton values (Fig. 2e). There are also other mismatches which will be discussed below. The Ostia data (red) forms an anomalous high Zr Cluster and will also be discussed later.

Data Clustering

Paving stone data point clustering is a significant feature of the archaeological data (Fig 2 e-h) although it is somewhat obscured by source data points unrelated to the paving stone clusters. It is evident in all the element plots (Figs. 2e-f) but is particularly well developed in the Zr-FeOT plot (Fig. 2e) which is shown in more detail in Figure 3a. 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. Alkali elements such as Rb and Sr are known to be more mobile during post-magmatic processes. In Figure 3a, data clusters are identified and labeled A-F. Well developed clustering is particularly apparent for the Ostia (red) data (Cluster A) and Cluster B which contains Rome City data (yellow), Via Appia (grey), Via Prenestina (pink). 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 source volcanics it is probable that there will be some points which do not belong to that particular association.

One of the problems in interpreting Figure 3a is that many of the clusters overlap. This is particularly the case for Cluster B which comprises data mostly from Rome City, and the Viae Appia and Prenestina 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-Sr separated these data sets (Fig. 3b). 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 3a 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 3b showed that they comprise more or less the same samples as in Clusters C, D and E respectively of Figure 3a. Similarly, the data in Cluster F of Figure 3a plots as Cluster F* in Figure 3b. This data plots 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). 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 i.e. 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 summarised in Table 1 which shows the number of paving stones from each cluster and their localities together with possible sources.

Spider Diagrams

In the above section we have used standard two element or X-Y petrological diagrams to analyse the data. 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 resolution. Multi-element or spider diagrams can improve the analytical power of the geochemical data by comparing many more elements against a calculated standard. The more elements used in these plots the better the resolution. Such diagrams are commonly used in igneous petrology. They are prepared by firstly determining the average composition of a standard. In this project the standards were prepared by averaging the composition of lava flows from the geological literature which may represent possible sources. For example, whole rock analyses from the Alban Hills, Sabatini and Vico were averaged to produce standards here called AvALB, AvSAB and AvVic respectively. 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 the archaeological data set with the equivalent standard values and plotted the results on a 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 XY plots and allowed us to interrogate the data in greater detail. They may therefore improve discriminatory comparisons between paving stones and possible sources.

Figure 4a shows a spider diagram for the Rome city, Via Appia and Via Prenestina data normalised to AvALB. The diagram shows that the data plots along an approximately straight line centred on 1. This validates the assertion above that most of the paving stones from the above localities were quarried in the Alban Hills. The Rome City (yellow) Pb data in Figures 4a shows a large range which we suggest is due to environmental pollution not to paving stone geochemistry. This is supported by the fact that the anomaly is not present in paving stones measured in more rural areas. This emphasises the importance of rigorous cleaning of paving stones prior to measurement.

Figures 4b and c represent Sabatini and Vico paving stones normalised to AvSAB and AvVIC respectively. The absence of Pb data in Figure 4b is because this element was not determined in the Sabatini geological analyses (Conticelli et al. 1997). These two diagrams show more complex and ambivalent patterns. For example, the Sabatini data (Fig. 4b) shows slight enrichment in Rb relative to AvSAB and the Vico data (Fig. 4c) shows enrichment in Sr and depletion in Pb relative to AvVIC. Thus an attempt was made to probe more deeply into these data sets. This is not easily done as the volcanic activity in all three volcanoes is episodic and there are subtle geochemical differences between each phase. For example, Vico has three eruptive phases, Sabatini at least two and the Alban Hills has four. Ideally therefore, identification of a local quarry that had been used since Roman times and where published geological analyses were available to calculate a standard is very helpful in identifying possible sources. The quarry at Mount Maggiore (Fig. 1) fulfills the first of these criteria (Laurence pers. Com.) and there are also 6 published geological basalt analyses from there. Cluster C* contains 25 paving stones from Rignano Flaminia which is about 12 km north-north-east of the quarry. There are also 9 from the Nepi area which is about 20km north-north-west from the quarry lying inside the Vico volcanic area (Fig. 1). There are also eight Niton source data points. A standard called AvMAG was calculated using the 6 geological analyses and Cluster C* data was normalised to it (Fig. 4d). The data show a reasonably good fit with slight elevation in Mn compared to AvMAG. This suggests that this quarry was a possible source for some of the paving stones from the local area. Cluster D* data (Fig 4e) shows some similarity to AvMAG but is slightly enriched in Zr and Mn. Most of the paving stones come from inside the Vico volcanic area so it is probable that the source lies inside that area. Cluster E* paving stones (Fig. 4f) are again from inside the Vico area and show some similarities to Cluster D* except for a strong enrichment in Pb. Cluster F* paving stones (Fig. 4g) are quite different to AvMAG showing strong enrichments in Zr and Pb. The paving stones come from northerly localities and it is highly likely that the source lies within the Vico volcanics.

Summary and Conclusions

The distribution of the geological data (Figs. 2a-d) shows that there are broad but significant geochemical differences between the lavas of Vico, Sabatini and the Alban Hills. Alban Hills data tends to display high FeOT values, Vico lower FeOT values Sabatini data tends to plot between the two. Broadly speaking, this geochemical distribution is also mirrored by the Niton source data (Figs. 2e-h) and the Niton paving stone data. The data from the south is relatively consistent and the clusters are well-defined. Cluster A paving stones are however enigmatic. They are abundant in the coastal port of Ostia and a few also occur in Rome city. We have not been able to identify a possible source for them either in the RMP or the TMP. They could have been transported down the Tiber by boat from elsewhere or they may have come in by sea, possibly as ship's ballast. Cluster B paving stones are exclusively found in the south and Niton source data also plots in the Alban Hills field so we conclude that this is their most probable source. This interpretation is supported by spider diagrams (Fig 4a). The widespread distribution of the paving stones however suggests that they may have been quarried from one or more Alban Hills sources and moved over significant distances within the southern area.

Table 1 shows that the situation further north is more complex. Cluster C* contains paving stones from both Vico and Sabatini but the majority come from Rignano Flaminia which lies within the Sabatini area (Fig. 1). The limited data suggests a source in either Mt Maggiore or Terme dei Gracchi which is close to Nepi. Spider diagrams however support a Mt Maggiore source (Fig. 4d). The origin of Cluster D* paving stones is more consistent. They come mostly from mostly from Faleri Novi and Nepi (Terme dei Gracchi) which lie within the Vico volcanics. Source data is minimal but similarity to AvMAG suggests that Mt Maggiore is also a possible source. Data for Cluster E* is minimal and there is no source data. Cluster F* paving stones are from far north localities such as Ocriculum and Faleri Novi. The Cluster F* spider diagram is very different from AvMAG suggesting a source within the Vico volcanic area. We conclude that data for the northern area is more difficult to interpret but again suggests the presence of multiple sources with paving stones moved over significant distances.

The research also confirmed that paving materials were not sourced from the Vesuvian region, in contrast to the lightweight materials studied by Lancaster et al (2011) and Marra et al (2012). Underlying the pattern of sourcing, determined above, is the fundamental limitation of transportation with the city of Rome utilizing sources from the Alban Hills rather than from Sabatini or Vico.

Future Research

Hand-Held portable XRF (HHpXRF) equipment clearly has potential for applications in the study of the provenancing of paving materials derived from volcanic sources. Like other applications of HHpXRF in archaeology, we have found advantages and constraints (Frahm and Doonan 2013). The key issue for the future is to develop a robust method for the application of this technology that has the ability to increase our knowledge-base and to generate new data, whilst recognizing the limitations of the data derived using HHpXRF for archaeological questions (most recently Killick 2015).

- We suggest that a future project should be more focused perhaps on a single locality. Investigation of the geochemistry of individual flows within the volcanic edifices may also allow identification of sources with the help of spider diagrams. It may also be possible to identify and visit known basalt quarries from the Roman period. We plan to collect rock samples from these outcrops. They can be analysed at the analytical facilities at the University of Greenwich in collaboration with Professor David Wray. The results could be used to calculate possible standards and, in so doing, address the widely reported skepticism in the utilization of HHpXRF (compare Grave et al 2012).

- Future research should utilize a more recent Niton machine, particularly one that is helium enabled, which will allow collection of light element data as well as the elements used above and perform to a higher degree of analytical precision. The latter would permit greater geochemical discrimination particularly in spider diagrams.

- The calibration of handheld portable XRF spectrometers (pXRF) is a key challenge (Charlton 2013). This issue emerged in the data presented above where there was some evidence that the Niton data for Zr was slightly different from the published geological data. This was identified as a probable calibration problem. Such problems can probably be resolved by consultation with the manufacturers and comparison of Niton data with lab-based XRF analyses obtained on the same rock material. See Goodale et al 2012 and the debate over use of data from pXRF in archaeology – see especially Speakman and Shackley (2013) on Frahm (2013a) and Frahm's response (2013b) and also in Frahm (2014).

- There is also a need to investigate possible environmental contamination. of paving stones surfaces. For example, it was noted above that there was a very high Pb content in paving stones from metropolitan Rome suggests that there is a problem with air pollution contamination. A surface film of pollution will attenuate the X-ray signal. This problem can of course be mitigated by thorough cleaning. Further investigation is also needed on the effects of weathering on paving stone surfaces over the 2000 years since quarrying.

- Create a robust field procedure for the use of HHpXRF taking into account recent findings with regard to count time (Newlander et al 2015) alongside the resolution of issues of calibration, and establishment of number of readings taken per paving stone. This procedure will be applied in-situ at a range of sites including the Markets of Trajan (Rome) and other preserved sections of paving from sites associated with construction in the second century AD.

- The above suggestions are key to the development of the potential of HHpXRF as a technology for the analysis of the provenancing of Roman volcanic paving stones in central Italy. With their resolution, the potential to use HHpXRF more widely for the analysis of not just paving materials, but also other building materials associated with Roman standing remains.

Acknowledgements.

This project formed part of the British School at Rome's Tiber Valley project. We wish to acknowledge the support of the British School at Rome JB and RL wish to thank Dr Stuart Black (University of Reading) and Dr Helen Patterson (British School at Rome) for their support. RL acknowledges the support of the University of Birmingham and, in particular, Prof. Vince Gaffney (now University of Bradford). MW, LB, and RL have gained support from the University of Kent that included the purchase of pXRF equipment and wish to thank John Hurley and Ken Grainger at Niton UK for additional support in relation to calibration issues. MW and RL acknowledge the on-going support of Professor David Wray (University of Greenwich).

References

Black, S., Browning, J., 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: Coarelli, F., Patterson, H. British School at Rome.

Capedri, S., 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.

Charlton, M.F. 2013. Review of Handheld XRF for Art and Archaeology (Studies in Archaeological Sciences 3). Journal of Archaeological Science 40, 3058-3059.

Conticelli, S., Francalanci, L.,Manetti, P., Cioni, R., 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, 107-136.

Conticelli, S., Carlson RW., Widom E., 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., Boari E, Avanzinelli, De Benedetti, A.A., Giordano, G., Mattei, M, Mellusco L, Morra V. 2010. Geochemistry, isotopes and mineral chemistry of the Colli Albani volcanic rocks: contraints on magma genesis and evolution. From: Funiciello, R. and Giordano, G. (eds) The Colli Albani Volcano. Special Publications of IAVCEI, 3, 107-139. Geological Society of London, London.

Frahm, E. 2013a. Validity of “off-the-shelf” handheld portable XRF for sourcing near eastern Obsidian chip debris. Journal of Archaeological Science 40, 1080-1092.

Frahm, E. 2013b. Is obsidian sourcing about geochemistry or archaeology? A reply to Speakman and Shackley. Journal of Archaeological Science 40, 1444-1448.

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, 105-125.

Frahm, E. and Doonan, R.C.P. 2013. The technological versus methodological revolution of portable XRF in archaeology. Journal of Archaeological Science 40, 1425-1438.

Giordano, G., De Benedetti, A.A., Diana, A., Diano, G., Gaudioso, F., Marasco, F., Miceli, M., Mollo, S., Cas, R.A.F., Funiciello, 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: 875-883.

Grave, P., Attenbrow, V., Sutherland, L. Pogson, R. and Forster, N. 2012. Non-destructive pXRF of mafic stone tools. Journal of Archaeological Science 39, 1674-1686.

Killick, D. 2015. The awkward adolescence of archaeological science. Journal of Archaeological Science 56: 242-247.

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, 949-961.

Lancaster, L.C., Sottili, G., Marra, F. and Ventura, G. 2010. 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, pp 221.

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: Patterson, H. Archaeological Monographs of the British School at Rome.

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, 556-577.

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, 534-548.

Peccerillo, A. 2005. The Roman Province. In: Plio-Quaternary Volcanoes in Italy. Petrology, Geochemistry, Geodynamics. Springer, pp 70-106.

Perini, G., Conticelli, S., Francalanci, L., 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, 247-272.

Perini, G., Francalanci, L., Davidson, J.P., Conticelli, S. 2004. Evolution and Genesis of Magmas from Vico Volcano, Central Italy: Multiple Differentiation pathways and Variable Parental Magmas. Journal of Petrology, 45, 139-182.

Renzulli, A., Antonelli, F., Santi, P., Busdraghi, P., Luni, M. 1999. Provenance Determination of Lava Paving stones from the Roman 'Via Consolare Flaminia' Pavement (Central Italy) using Petrological Investigations. Archaeometry 41, 209-226.

Speakman, R.J. and Shackley, M.S. 2013. Silo science and portable XRF in archaeology: a response to Frahm. Journal of Archaeological Science 40: 1435-1443.

Trigila, R., Agosta, E., Currado, C., De Benedetti, A.A., Freda, C., Gaeta, M., Palladino, D.M., Rosa, C. 1995. Petrology. In: The Volcano of the Alban Hills. Tipografia SGS, Roma, 95-165.

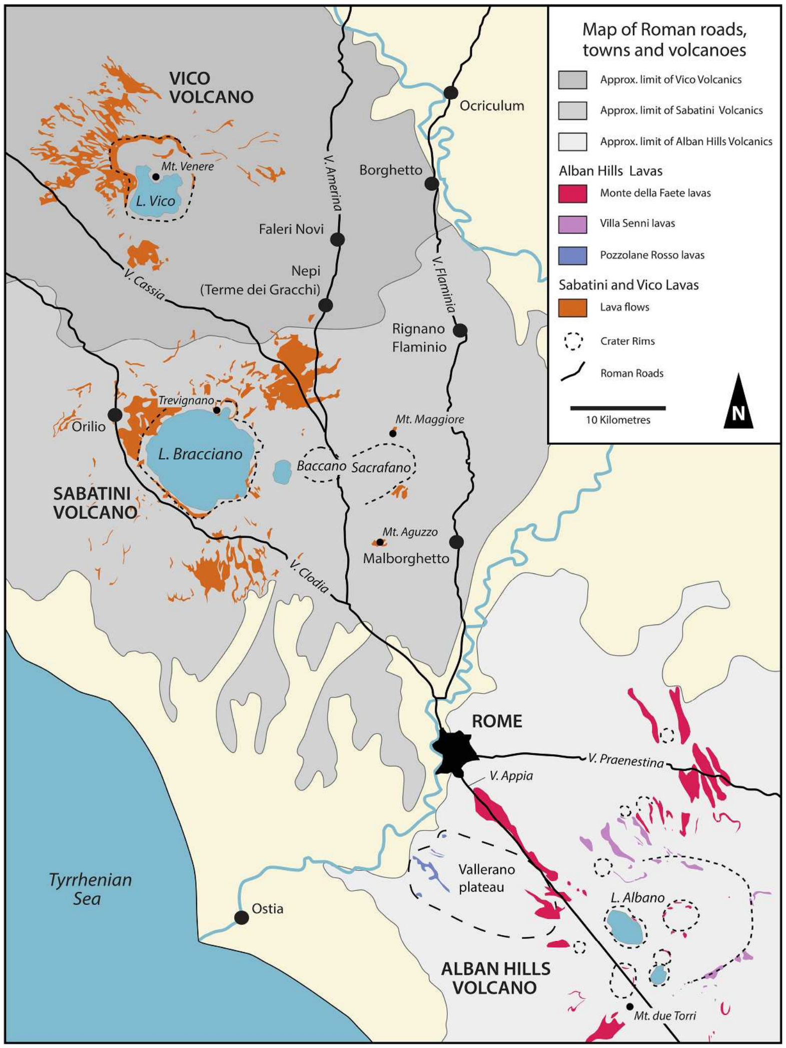

Fig.1. Map showing the Roman roads and towns mentioned in the text and the generalised outcrop of the volcanic rocks of Vico, Sabatini and the Alban Hills. Details of Alban Hills volcanics modified after Gaeta et al. (2016). The localities of the sites used in the spider diagram normalisations are also shown.

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Fig. 1

199x293mm (300 x 300 DPI)

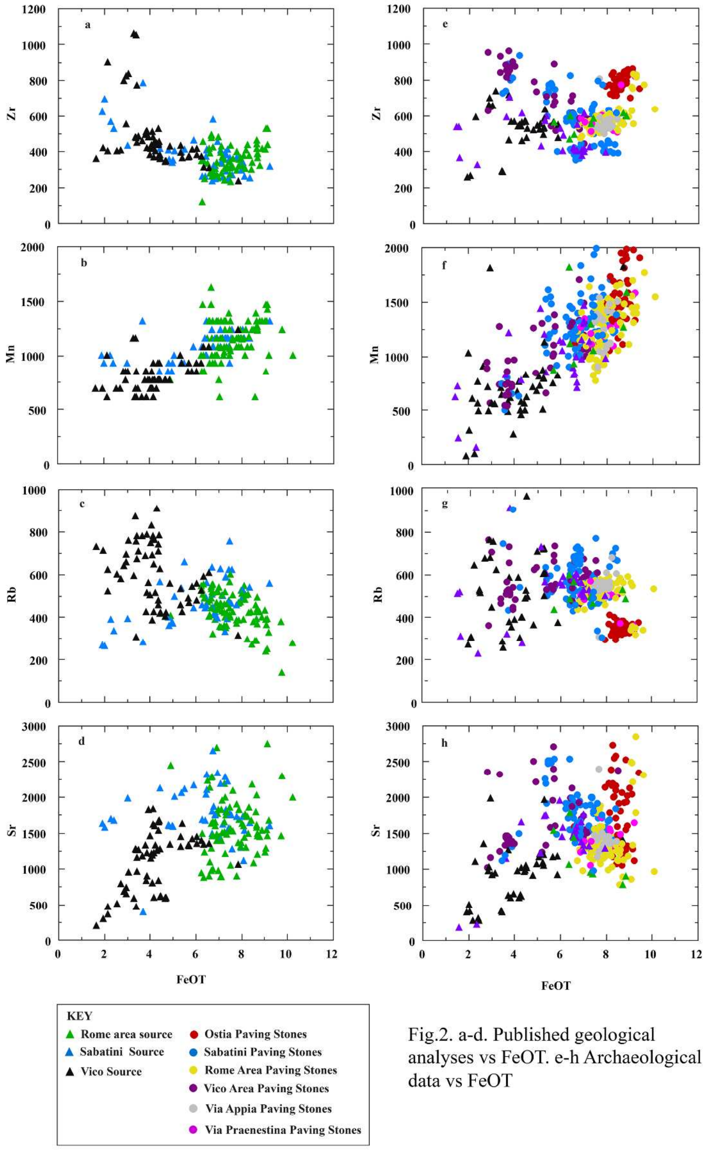

Fig.2. a-d. Published geological analyses vs FeOT. e-h Archaeological data vs FeOT
Fig. 2
199x326mm (300 x 300 DPI)

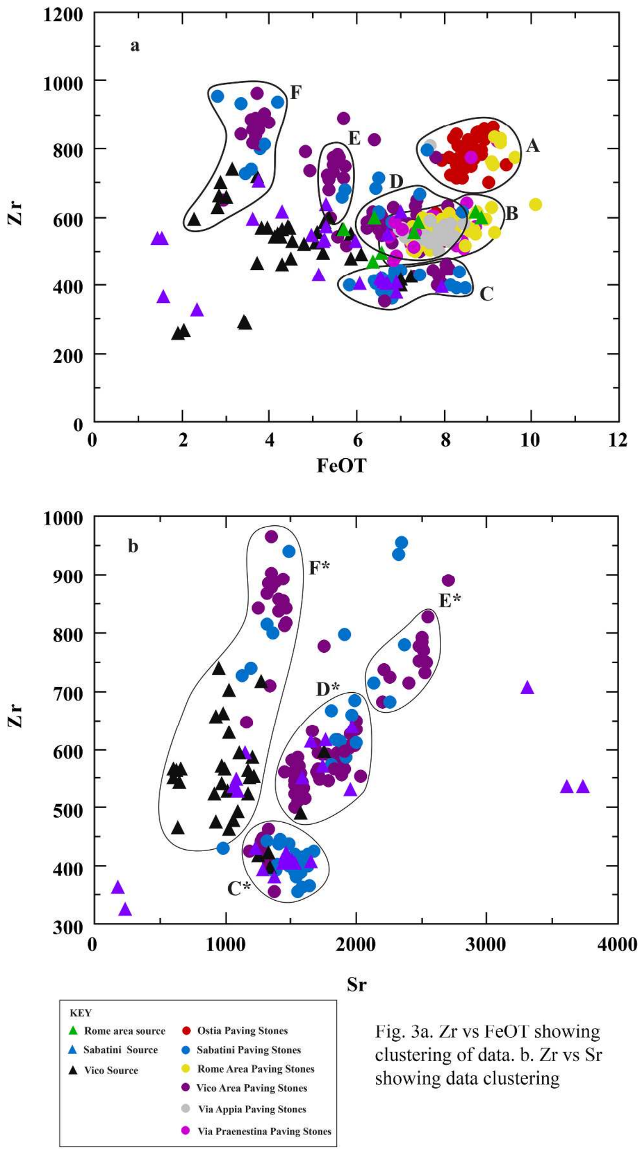

Fig. 3a. Zr vs FeOT showing clustering of data. b. Zr vs Sr showing data clustering.
Fig. 3
199x359mm (300 x 300 DPI)

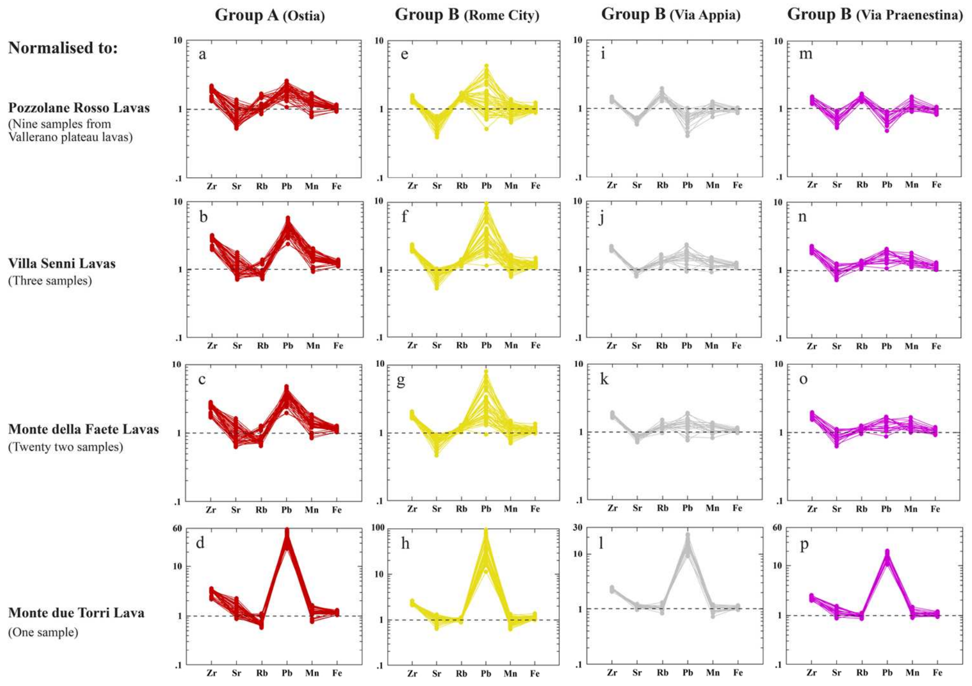

Fig. 4. Spider diagrams showing Groups A and B normalised to various Alban Hills lavas. Explanation in text.

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Fig. 4
151x114mm (300 x 300 DPI)

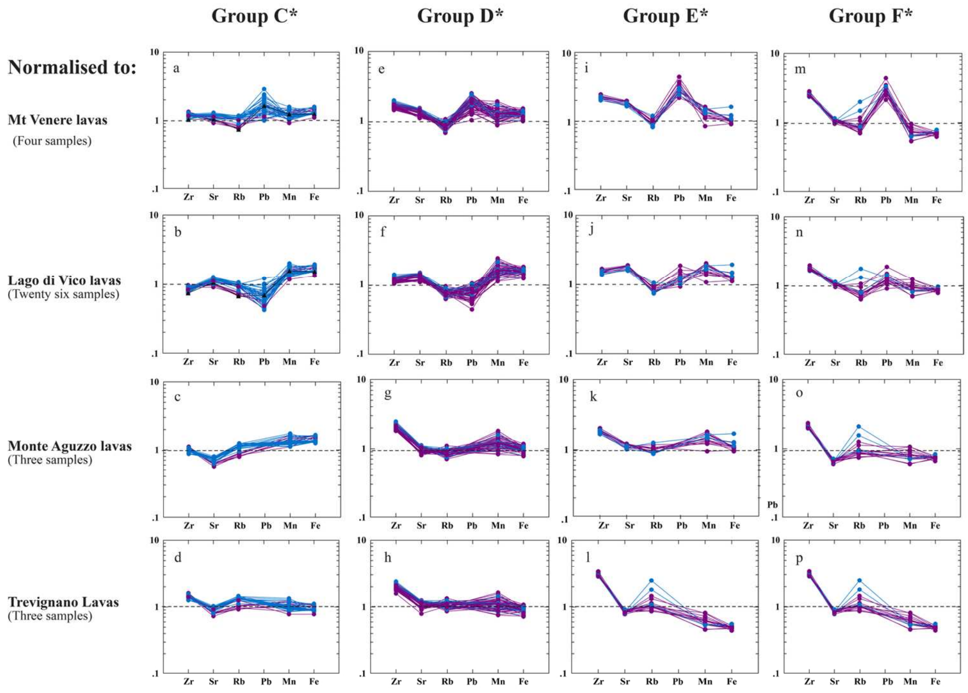

Fig. 5 Spider diagrams showing Groups C*, D*, E* and F* normalised to Sabatini and Vico lavas. Explanation in text.

Fig. 5 Spider diagrams showing Groups C*, D*, E* and F* normalised to Sabatini and Vico lavas.
Explanation in text.

Fig. 5

153x118mm (300 x 300 DPI)

Paving stone Locality	A Ostia Rome City	B Rome City Ostia	B Via Appia	B Via Praenestina	C*	D*	E*	F*
Ocriculum								11
Borghetto								
Faleri Novi						14	3	2
Nepi	1				1	21	10	
Terme dei Gracchi					8	18		
Rignano Flaminio					25			
Orilio					1	5	3	
Bracciano						2		
Malborghetto	1				3			3
Rome City	6	52						
Via Praenestina				22				
Via Appia			21					
Ostia	45	13						
Sources plotting within Clusters	0	Alban Hills	Alban Hills	Alban Hills	Mt. Maggiore 8 Terme dei Gracchi 3 Bracciano 1	Terme dei Gracchi 1 Bracciano 2	0	Vico 5 Borghetto 2 Tre Croce 3
Sources from Spidergrams	Vallerano Plateau Lavas?	Unknown	Villa Senni or Monte della Faete lavas	Villa Senni or Monte della Faete lavas	Monte Venere? Trevignano?	Monte Aguzzo? Trevignano?	Monte Aguzzo? Lago di Vico?	Lago di Vico?

Table 1. Composite table summarising data from clusters defined by paving stones in Figures 3 and 4. Localities at left are arranged geographically from north to south. Figures in columns are paving stones within each cluster and these are colour coded using the scheme in Figs 2-4; black for Vico, blue for Sabatini and green for the Alban Hills.

Table 1

94x44mm (300 x 300 DPI)