TRAJAN’S FORUM (HEMICYCLE) AND THE VIA BIBERATICA (TRAJAN’S MARKETS): AN HHPXRF STUDY OF THE PROVENANCE OF LAVA PAVING IN ANCIENT ROME (ITALY)*

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This paper reports on geochemical data collected using a He-enabled handheld portable XRF (HHpXRF) from lava paving stones in Trajan’s Forum (Hemicycle) and the Via Biberatica (Rome). Issues relating to HHpXRF field use and calibration are also addressed in detail. By means of this instrument, 355 analyses of the paving stones were collected and the data were processed using the standard techniques of igneous petrology and petrography. Provenancing was based on comparisons between the HHpXRF data and geological data from the abundant literature on Roman volcanic rocks. These comparisons placed the provenance of the paving stones in the Colli Albani, south-east of Rome. Further analysis using Zr/Y versus Nb/Y discriminant diagrams suggests that the paving stones were quarried from two sources, both of which are represented in Trajan’s Forum and the Via Biberatica. The diagrams suggest that the sources lie within the Faete and Vallerano lava complexes. The latter were probably transported to the construction site by barge on the River Tiber and the former were easily accessible by carts along the Via Appia. The study establishes the potential of HHpXRF equipment for non-destructive analysis of paving stones both in Rome and at other sites in central Italy, and challenges a number of assumptions about the supply of building materials to Rome based on intuition alone.

KEYWORDS: TRAJAN’S FORUM, TRAJAN’S MARKETS, ROMAN ROADS, ANCIENT ROMAN PAVING STONES, MATERIAL PROVENANCE, VOLCANIC ROCKS, HHPXRF

INTRODUCTION

Rome’s hinterland, the middle and lower Tiber Valley, is underlain by a variety of geological lithologies, many of which were quarried in antiquity for construction projects. West of the river, lavas and pyroclastic rocks predominate, whereas to the east of the river, limestone, sandstones and conglomerate are the main rock types. These lithologies were generically known as ‘silex’ in antiquity (Laurence 1999). However, the grey to black lavas, known as ‘selce’ in the archaeological literature, were the preferred rock type for paving in Rome and the roads of central Italy (Laurence 1999, 2004; Black et al. 2004). Intuitively, it might be expected that a heavy material such as lava would be quarried from local sources. However, Capedri and Grandi (2003) presented laboratory-based XRF data suggesting that selce was transported up to 90km by water transport to construction sites in the Po Plain from sources in the Euganean Hills. But, in general,
The provenance of lava paving in ancient Rome

The sourcing of paving stones in the archaeological literature has continued to be based on intuition rather than hard data (e.g., DeLaine 1997).

However, HHpXRF now provides a means of replacing these assumptions with hard data, although few actual scientific studies have been undertaken. For example, Frahm and Doonan (2013) found that only 43% of archaeological papers using so-called pXRF machines used handheld instruments (HHpXRF). These statistics are surprising, particularly when considered against their use in other field-based sciences such as the Earth sciences (73%) and environmental testing (79%). More than four fifths of handheld pXRF analysis in archaeology is done in the laboratory, compared with only 3% at an on-site laboratory and only 15% at an actual excavation. The authors attribute this partially to scepticism about the analytical performance of HHpXRF machines. In this paper, we have compared our HHpXRF analyses with laboratory-based XRF analyses of lava flows from the Colli Albani (Alban Hills), Sabatini and Vico volcanoes taken from the geological literature. One of the advantages of this approach is that the geological data provide a reference standard against which the performance of the Niton HHpXRF can be assessed. This approach has also been enhanced by technological improvements, particularly in the development of He-enabled machines, which permit the collection of a wider range of elements (cf., Worthing et al. 2017). The paper makes a contribution to developing a scientific basis for the provenancing of the lava paving from a major monumental complex in ancient Rome and the implications for the supply of building materials.

THE GEOLOGICAL BACKGROUND

The present-day geological and physiographic framework of the Italian peninsula is a consequence of movements associated with the evolving Apennine Orogenic Belt (Alagna et al. 2010; Conticelli et al. 2010b). These movements began in the Eocene, with convergence and westward subduction of Adriatic lithosphere beneath the southern European margin. This was followed by Miocene subduction-related magmatism along the Italian peninsula, which has continued to the present day. These magmatic 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). In this paper, we will only consider the RMP, which comprises four volcanic complexes: Vulsini, Vico, Sabatini and the Colli Albani. These volcanoes lie along the border of the Tyrrenian Sea, between southern Tuscany and the south-eastern hinterland of the city of Rome. In this paper, three volcanoes of the RMP will be discussed: from north to south, they are Vico, Sabatini and the Colli Albani, but the main focus will be on the latter (Fig. 1).

Vico, Sabatini and the Colli Albani are all characterized by large polycentric stratiform complexes with polygenetic calderas (Fig. 1). Their eruptive products are dominated by voluminous explosive pyroclastic rocks such as ignimbrites and tuffs. Lava flows are subordinate. Geochemically, these products are characterized by high levels of large-ion lithophile elements (LILE), such as K, Rb, Sr, Ba and Pb, relative to high field strength elements (HFSE) such as Nb, Zr and Ti (e.g., Alagna et al. 2010; Conticelli et al. 2010b; Gaeta et al. 2016). The relative abundance of potassium and the undersaturation with respect to SiO₂ gave rise to the common occurrence of the potassic feldspathoid leucite. Texturally, the lavas range from aphyric to strongly porphyritic, with leucite, clinopyroxene 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).

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 Colli Albani: details of Colli Albani volcanics modified after Gaeta et al. (2016). The localities of the sites used in the spider diagram normalizations are also shown: volcanic outcrops on Sabatini and Vico after Conticelli et al. (2010b). The yellow stars around Lake Bracciano are localities of Sabatini samples plotting in Colli Albani fields in Figure 2.

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The Colli Albani

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 was dominated in the early phases by polygenetic caldera collapse and the eruption of voluminous explosive products such as ignimbrites and tuffs, some of which are interbedded with coeval tuffs from Sabatini (Conticelli et al. 2010b; Gaeta et al. 2016). Lava flows are subordinate and the volume of eruptive products has decreased with time. In this paper, we have adopted the terminology of Gaeta et al. (2016) to describe the magmatic phases of the volcano. They are an Early Tuscolano–Artemisio Phase (608–500 ka), a Late Tuscolano–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), the Late Tuscolano–Artemisio Phase, the Villa Senni lavas and the lavas of the Pozzolane Rosse, which were erupted on the Vallerano lava plateau. Similarly, the Monte due Torri flow of the Albano Phase is the most recent lava erupted from the Colli Albani and was dated at 40 ka (Gaeta et al. 2011). These lavas are all of the possible sources for some of the paving stones documented in this paper.

Sabatini

The picture here is more complex, mainly because overlapping eruptions occurred from multiple sources including three major caldera complexes—Bracciano, Baccano and Sacrofano—together with scoria cones and hydromagmatic maar activity (Conticelli et al. 1997, Conticelli et al. 2010b; Karner et al. 2001; Sottili et al. 2010; Marra et al. 2014) (Fig. 1). Activity was dominantly explosive, occurring between 800 and 86 ka and producing voluminous pyroclastic flows and tuffs. In the south-east, some of these are interbedded with tuffs from the Colli Albani (Marra et al. 2011). Lava flows occur at a number of scattered localities (Fig. 1). The most intense effusive activity was concentrated in the Trevignano area, to the north of the Bracciano caldera, at Monte Maggiore, close to the Sacrofano caldera, and at Monte Aguzzo and in the south-east, and at San Celso, 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). The magmatic products of Vico have been divided into three main rock successions (Perini et al. 2000, 2004; Conticelli et al. 2010b). 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), followed by four explosive ignimbrite eruptions that destroyed the earlier Vico edifice and formed the current caldera. The Monte Venere Succession was a post-caldera phase ranging in age from 95 to 85 ka, and characterized by tuffs and minor lava flows.

METHODOLOGY

Calibration of the HHpXRF equipment

The geochemical data for this paper were collected using a handheld Niton XLt 950 He GOLDD+ X-ray analyser (hereafter referred to as ‘the Niton’). We learned from our first project, using the earlier Niton XLt 792 MZ machine, that good calibration is vital to the successful use of...
the analyser (Worthing et al. 2017). The XL3t 950 machine comes with factory calibrations that may have to be customized for specific tasks. This was particularly important in this project, as determination of the paving stone provenance depended on comparisons between Niton data and data sourced from the geological literature of the Roman Volcanic Province. These data were obtained on laboratory-based XRF machines and ICPMS, which are both capable of producing highly accurate analyses but require the collection and destruction of some of the rock sample. The paving stones investigated in this paper have a complex geochemistry, consisting of about 27 different detectable elements that are part of a complex silicate matrix. Concentrations range from 20 element% down to 20 ppm. Thus careful calibration was required.

Our calibration protocol involved a number of steps. First, we investigated the accuracy of the factory calibrations. This required a rock standard of known composition against which Niton analyses could be compared. For this purpose, we selected a discarded aphyric lava cobblestone (COB1) from a modern road in central Rome. This was analysed on a laboratory-based XRF machine at the University of Greenwich. Major elements were determined on a fused disc and trace elements on a pressed pellet. Significant geochemical features of this rock included a high K2O/Na2O ratio, suggesting that it was sourced from a local volcano of the RMP and was therefore likely to be compositionally similar to the paving stones that are the subject of this paper.

We then measured 10 analyses of COB1 on a flat sawn surface, using the shielded test stand with the Niton set to factory calibrations. Data were collected in element% and major elements, except P and Ti were converted to the geological format of wt% oxide. Trace elements, Ti and P were converted to ppm. The 10 analyses were averaged and are plotted in Figures S1 (a) – S1 (c) against the equivalent laboratory-based XRF analyses of COB1. A perfect calibration would show all elements plotting on the 1:1 line, but deviations from this line would indicate faulty calibration. For example, Figure S1 (a) shows that MgO, K2O, CaO and FeO are well calibrated, although Al2O3 deviates slightly from the 1:1 calibration line. However, SiO2 is very poorly calibrated. Figure S1 (b) shows that Sr and Ti are also poorly calibrated, whereas P, Ba, Ce and Nd are reasonably constrained. In Figure S1 (c), Rb and Zr are poorly calibrated, but Cu, Zn, Pb, Y, and Nb are satisfactory. These graphs thus provide a visual check on the accuracy of the factory calibration.

The third recalibration step required a number of standards of known composition. These were kindly provided by Dr Christine Manning, who donated seven small chips of porphyritic Icelandic basalts that had been fully analysed by a laboratory-based XRF. These chips had one flat sawn surface that could be analysed by the Niton in the shielded test stand. Ten analyses of each chip were obtained and an average calculated. The Niton data for each sample were compared graphically with the equivalent data obtained by the laboratory-based XRF. The resulting seven-point graphs for K and Fe are shown in Figures S2 (a) and S2 (b). They include the straight-line equations for the calibration curve and the $R^2$ values. The slope and intercept values from all equations were then fed into the CALFAC program in the Niton software, producing an element calibration file that we called BIBROCEL. This was loaded into the Niton memory and 10 analyses of COB1 were collected. An average was calculated from these data and the results are presented in Figures S1 (d) – S1 (f) alongside the factory calibration files. Figure S1 (d) shows that the major elements are well calibrated. In particular, SiO2 is much improved from the uncalibrated value shown in Figure S1 (a). There is also some improvement in the trace elements Ba and Sr, particularly the latter (Fig. S1 (e)). Ti is slightly moved on the diagram, but not changed much. P is actually worse. Figure S1 (f) shows the other trace elements, Cu, Zn, Y, Pb and Nb, which are well calibrated. Rb and Zr are improved, but still not well constrained.
The whole calibration protocol was repeated with seven basalt and andesite standards used in the XRF machine at the University of Greenwich. These standards were prepared from crushed rock powder mounted in a resin and therefore have a different matrix to the natural rock chips described above. Using these data, we produced a second CALFAC file called BIBSTANEL, which was saved as a separate file in the CALFAC program and was used to reanalyse COB1. We found that BIBROCEL yielded the best results and, accordingly, we used this calibration file in the field.

During fieldwork, a sawn piece of COB1 was used as an external standard to monitor any drift in the Niton’s performance. This exercise suggested that under field conditions of ambient temperatures of around 30°C and relatively high humidity, the Niton drifted from the original BIBROCEL calibration. For example, values for Ti, Fe, Mg and Ca were all high when compared with the laboratory-based XRF values for COB1. Thus, on return to the University of Kent, we repeated the calibration procedure outlined above in modified form. We selected three of the Icelandic basalts representing a range of SiO₂ values and, together with COB1, reanalysed the samples using BIBROCEL. Four analyses of each sample were measured and averages calculated. These values were plotted on the CALFAC calibration graphs against the equivalent laboratory-based XRF values, producing equations for each element. These equations were then used to correct the Rome field data in an EXCEL file. The resulting data were loaded into MinPet 2.02 for analysis.

**Sampling and data collection**

At the beginning of the project, we identified sections of ancient paving in the Hemicycle and the Via Biberatica that had not been restored post-excavation. The tight fit of the paving stones was considered to be indicative of paving in antiquity, whereas restoration work was characterized by gaps or cement fill (Fig. S3 (a)). Three areas of paving stones of the Hemicycle in Trajan’s Market were selected for geochemical analysis in 2016, together with reanalysis of some paving stones in the Via Biberatica. The stones were selected to ensure that the petrographic types identified on the previous visit were represented. It was apparent that the stones in the Hemicycle were more pitted, weathered and dirty than those in the Via Biberatica. Representative photographs are presented in Figure S3. In addition, vertical photographs were taken of the three Hemicycle areas from overlooking balconies, and these were used as accurate maps enabling the location and numbering of each paving stone. We used the same numbering system for the Via Biberatica as utilized in 2014.

A small area of each paving stone was thoroughly cleaned by scrubbing with a plastic brush and clean water. Residues were wiped away with cosmetic wipes. This was followed by further cleaning with 99% ethanol to remove any organic residues and to dry the area prior to analysis. A small adhesive label with the paving stone number was then attached to the stone, with an arrow pointing at the cleaned area (Fig. S3 (c)). Discolouration of the discarded wipes indicated that the stones were generally very dirty. This was particularly the case for stones in the Hemicycle, where pitting sometimes made it difficult to find a suitable flat surface for analysis. We investigated the effectiveness of cleaning by selecting 10 stones at random and comparing analyses of cleaned areas with contiguous areas that had not been cleaned. These data showed that in many cases the analytical values obtained on the uncleaned areas were greater than those on the cleaned area. This was attributed to an accumulation of dust and pollution on the uncleaned surfaces. This observation emphasized the importance of thorough cleaning prior to analysis.
As noted above, the geochemical data were collected using a handheld Niton XL3t 950 He GOLDD+ X-ray analyser. The machine has an Au anode (9–50 kV, 0–40 μA max.), giving a resolution of <185 eV. The He attachment permits determination of lighter elements such as Si, Al, Ca, Mg, P and K as well as elements between Ti and Bi on the periodic table: Zr, Sr, Rb, Ba, Pb, Fe, Mn, As, Zn, Cu, Ni, Nb, S, Pb, Th, La, Ce, Pr and Nd. The data set included 236 analyses from the three areas of the Hemicycle (Areas 1, 2 and 3) plus 119 analyses from the Via Biberatica. During analysis, only matrix compositions were measured; phenocrysts were ignored and data were collected in element% using a livetime of 120 s. The lighter elements accessible with the XLt 950 allow presentation of data in a similar format to that used in the geological literature. This facilitated the comparisons required for sourcing.

Paving stone petrography

Petrographic analysis was conducted on paving stones from the three areas in the Hemicycle. These data complemented a similar analysis undertaken on the Via Biberatica in 2014. A simple system was devised (modified after Browning unpubl.) based on the presence or absence of phenocrysts, their modal percentages, their grain size and the presence or absence of flow foliation. Table S1 describes the petrographic features used to classify the groups present in the sample. The distribution of the different petrographic types among the three areas of the Hemicycle and the Via Biberatica is shown in Figure S4. These histograms show that the three areas of the Hemicycle (Figs S4 (a) – S4 (c)) are very similar. The dominant rock types are grey porphyritic lavas, with phenocrysts ranging between 1% and 5% by volume (Figs S3 (b) and S3 (c)). Also, all three areas have some stones showing flow foliation (Fig. S3 (d)). The distribution of rock types in the Via Biberatica is more complex, although, again, the grey porphyritic types predominate. This complexity may possibly reflect the use of multiple source quarries or reuse of stones from other sites. An unusual group, present only on the Via Biberatica, is coarser grained, with orange weathering, and was classified as Group 4A (Fig. S3 (e)). The coarse grain size suggests that the rock may have been quarried from intrusions such as dykes. A distinctive feature of this rock type is the presence of curved, branching, randomly oriented acicular crystals, probably of clinopyroxene. A few Group 4A stones showed evidence of the coarser-grained rock type in an apparent intrusive relationship with the finer-grained grey leucitic lava type (Fig. S3 (e)). However, the geochemistry of the two types appears to be identical, suggesting that they were derived from the same magma.

The areal distribution of the different petrographic types is shown in Figure S5. These diagrams were prepared from the vertical photographs and reveal some information about the distribution of the different rock types, particularly in the Hemicycle, from which tentative conclusions are drawn. Area 1 contains more of the 3A3 group than Areas 2 and 3. The latter are dominated by the 3A1 and 2 types. There is some evidence of clustering, particularly in Area 1, where 3A3 types are much more common. This may reflect the unloading of a group of similar stones collected, perhaps, from the same part of a lava flow in the source quarry. Foliated types such as 3 AC2 are present in all three areas, but are most abundant in Area 3, where they again tend to show clustering. Again, this may suggest collection and unloading of lava blocks from a particular part of a lava flow.

The diagrams in Figure S5 are all drawn at the same scale and suggest that there are variations in the size of the stones. This was confirmed by numerical computer analysis. Area 1
shows the largest stones and the 3A3 type is common. These differences may reflect choices made by the stonemasons in response to the workability of the different types of lava. The foliated types in Area 1 (3AC2) may have been more susceptible to splitting. Four stones in Area 3 of the Hemicycle contain xenoliths a feature not present in Areas 2 and 3 and the Via Biberatica.

The geological literature suggests that one of the characteristic features of lavas from the Colli Albani is the ubiquitous presence of leucite phenocrysts (e.g., Trigila et al. 1995). The crystals are white or cream in colour and are often equant or square-shaped and up to 2 cm in diameter. This mineral is ubiquitous in the paving stones studied at both localities (Fig. S3).

RESULTS AND ANALYSIS

The aim of the research was to determine the composition of the paving stones and to use this information to establish their possible source or sources. Thus, as a first step, the composition of rocks from the three volcanoes close to Rome was investigated, using the abundant geological literature on the Roman Magmatic Province (RMP). Thus, 188 analyses from the Colli Albani, Sabatini and Vico were loaded into the MinPet software (Trigila et al. 1995; Conticelli et al. 1997, 2007, Conticelli et al. 2010a; Conticelli et al. 2010b; Perini et al. 2000, 2004; Peccerillo 2005; Giordano et al. 2006; Boari et al. 2009; Marra et al. 2009; Alagna et al. 2010; Gozzi 2012; Gozzi et al. 2014; Gaeta et al. 2016).

All of these volcanoes have complex histories, and in the case of Sabatini there are several eruptive phases and two major geochemical suites, a high-Ba and a low-Ba suite (Conticelli et al. 1997). The latter do not contain leucite, so they were eliminated from the data set, leaving 25 analyses. These are supplemented by 73 analyses from Vico and 90 from the Colli Albani. The analyses were processed with Minpet petrological software using standard X–Y variation diagrams. The leucitic lavas are identified on the diagrams by colour-coded triangles specific to the volcano from which they were erupted; green for the Colli Albani, blue for Sabatini and black for Vico. These data are shown in Figures 2 (a)–2 (g), where the major elements TiO2, Al2O3, FeO, MgO, CaO, K2O and P2O5 are plotted against SiO2, and in Figure S6, in which the trace elements Zr, Sr, Ba, Rb, Cu and Pb are also plotted against SiO2. The diagrams show the geological data spread across the diagrams, with the Colli Albani data at the low-SiO2 end, Vico at the high-SiO2 end and Sabatini in the middle. There is some overlap between the Colli Albani and Sabatini data. In each diagram, the Colli Albani concentrations are enclosed by a field that includes most of the data points.

The Niton data were converted to wt% oxide for the major elements and ppm for trace elements. Figures 3 and 4 show the Via Biberatica and Hemicycle data plotted in the same X–Y plots as the geological data above. The Via Biberatica (VB) data are represented by green circles and the Trajan’s Market Hemicycle (TM) data by red circles. The VB data tend to cluster, whereas the TM data are slightly more spread. The linear trends shown in these diagrams are probably related to magmatic differentiation (e.g., Boari et al. 2009; Gozzi et al. 2014). In addition, the fields defining the Colli Albani clusters in Figures 2 and S6 are also included. It is clear that these fields contain some or most of the VB and TM data. This is compelling evidence that the paving stones were sourced in the Colli Albani. There is, however, a note of caution. Close examination of Figures 2 and S6 shows that nine Sabatini samples lie within the Colli Albani fields, suggesting that they are geochemically identical to some of the rocks from the Colli Albani (see below for discussion).
Figure 2  Geological data for the Colli Albani (green triangles), Sabatini (blue triangles) and Vico (black triangles).
Figure 3  Major elements versus $SiO_2$ for the Via Biberatica data (green circles) and Trajan’s Market Hemicycle (red circles): $n = 331$. 

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In the above section, we have shown that standard $X-Y$ petrological diagrams reveal a close relationship between the geochemistry of the Hemicycle and Via Biberatica paving stones and the geological data for the Colli Albani. However, the restriction of these diagrams to comparisons between two elements or element ratios limits their discriminatory power, in this case to a particular volcano. In igneous petrology, multi-element diagrams called spider diagrams are frequently

Figure 4  Selected trace elements from the Via Biberatica and Trajan’s Market Hemicycle plotted against wt% SiO$_2$: trace element values in ppm and symbols as in Figure 3.

Spider diagrams

In the above section, we have shown that standard $X-Y$ petrological diagrams reveal a close relationship between the geochemistry of the Hemicycle and Via Biberatica paving stones and the geological data for the Colli Albani. However, the restriction of these diagrams to comparisons between two elements or element ratios limits their discriminatory power, in this case to a particular volcano. In igneous petrology, multi-element diagrams called spider diagrams are frequently
used to discriminate between rocks from different tectonic settings. These diagrams employ large numbers of elements, thus greatly improving their analytical power. They are based on comparisons between a geochemical data set and a calculated standard. For example, in this paper we wished to compare the Niton data sets from Trajan’s Market Hemicycle and the Via Biberatica with the different rock units from the Colli Albani, a process called normalization. Thus, normalizing standards were calculated for each of the effusive phases from the Colli Albani, as defined by Gaeta et al. (2016). These standards were calculated as follows: the average of nine samples from the Pozzolane Rosse lavas from the Vallerano Plateau (AvVal) (Gaeta et al. 2006; Boari et al. 2009; Marra et al. 2009; Gozzi et al. 2014), three samples from the Villa Senni lavas (AvSen) (Marra et al. 2009; Gozzi et al. 2014; Gaeta et al. 2016), 22 samples from the Monte della Faete lavas (AvFaet) (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 (AvTorri) (Gaeta et al. 2011).

The elements to be compared with the standards were arranged at the bottom of the diagram. They are Si, Ti, Al, Fe, Mg, Ca, K, P, Rb, Sr, Zr, Ba, Pb, Y and Nb. The MinPet software divided the concentrations of these elements in the paving stones by the appropriate standard value (i.e., the ratio sample/standard was calculated). This value was plotted above each element on a vertical logarithmic scale. Thus elements with the same concentrations as the standard will plot as a value of 1. Thus, the similarity between the selected elements and the standard can be visually assessed.

Figure 5 shows a series of spiders in which the Via Biberatica (green) and the Hemicycle data (red) are compared with the different Colli Albani standards. They all plot close to the line 1, showing that their geochemistry is very similar to the Colli Albani standards. However, the flattest curve is the one for the Vallerano lavas (Fig. 5 (a)). The Pb values are anomalous, showing positive spikes (Figs 5 (a)–5 (c)). However, we have suggested before (Worthing et al. 2017) that paving stones from urban areas appear to be contaminated with atmospheric lead, giving rise to anomalous Pb spikes. In the case of Figure 5 (d), the Monte due Torri lava has an unusually low Pb concentration (6 ppm) which, together with atmospheric contamination, has given rise to the large positive spike. We can therefore conclude that both the X–Y plots (Figs 3 and 4) and the spiders of Figure 5 suggest that the Via Biberatica and the Hemicycle paving stones were sourced in the Colli Albani. However, it is clear that the similarity of the diagrams means that they fail to discriminate between the different effusive units that were used to normalize the data. We will attempt to address this issue below.

Zr/Y versus Nb/Y discriminant diagrams

Rock materials such as lavas, tuffs and pozzolane have been recognized by scholars to have been used extensively in the architecture of Roman masonry and concretes (e.g., DeLaine 1997, 2000; Marra et al. 2011). Authors showed that in many cases the primary geochemistry of these rocks, particularly of tuffs and pozzolane, has been modified by element mobility during Quaternary weathering and pedogenesis. Clearly, these changes in geochemistry complicate the sourcing of these materials. In response, Marra et al. (2011) devised a set of discriminant diagrams based on the trace elements ratios Zr/Y versus Nb/Y and Th/Ta versus Nb/Zr. These elements tend to be immobile during weathering, and were thus used to document both the primary geochemistry of the deposits and the vectors of geochemical change in measured sections in the Colli Albani and Monte Sabatini. They were also used to facilitate sourcing of construction materials.

Figure 6 (a) shows a plot of Zr/Y versus Nb/Y for samples identified as belonging to the principle effusive phases of the Colli Albani used in the spider diagrams of Figure 3. They are as
follows: the Monte della Faete lavas, the Monte due Torri lavas, the Vallerano lavas and the Villa Senni lavas (Fig. 1) (Gaeta et al. 2016). The data were abstracted from geological analyses and cluster into four overlapping fields. Figure 6 (b) shows a plot of the Niton data from the Via Biberatica and the Hemicycle using the Zr/Y and Nb/Y ratios together with the fields from Figure 6 (a). The vertical linear distribution of the data in Figure 6 (b) is probably a function of the fact that the values for these two elements are close to the detection limits of the Niton. They thus tend to cluster tightly around the small range of 30–40 ppm for Y and 20 ppm for Nb. Also, when the data for these two elements were normalized to the geological data in the spiders of Figure 5, they plotted close to 1. This suggests that their concentrations are close to the values in the geological data set. We consider that this validates their use as described below.

The most striking thing about Figure 6 (b) is that the data plot as two distinct groups (A and B), suggesting that the lavas were quarried from at least two sources. Each of these sources is represented in both the Hemicycle and the Via Biberatica. For example, Group A contains 213 data points, of which 77% represent paving stones from the Hemicycle and 23% are from the Via Biberatica. Group B contains 103 data points, of which 68% represent paving stones in the Hemicycle and 32% are from the Via Biberatica. However, considerable overlap between the data points in Figure 6 (a) obscures attempts to link the geochemistry of the paving stones in Figure 6 (b) with potential sources in Figure 6 (a). This makes definitive sourcing problematic.
There is, however, a tendency for Group B in Figure 6 (b) to coincide with the Vallerano data cluster in Figure 6 (a). Some support for this relationship comes from the fact that the Vallerano paving stone spider (Fig. 5 (a)) shows the flatter curve compared with the others in Figure 6. The relationship between Group A in Figure 6 (b) and the data points in Figure 6 (a) is unclear. Despite this lack of clarity, closer examination of the Nb/Y and Zr/Y ratios does provide further information. The Nb/Y value for Group B in Figure 6 (b) (0.65) is very similar to the average composition of the Vallerano lava field (LVa-a’) in Figure 8 of Marra et al. (2011). Similarly, the Nb/Y value of Group A in Figure 6 (b) (0.48) is very similar to the average composition of the Faete lava field (LVb) of Figure 8 of Marra et al. (2011). The distribution of data points on the Zr/Y axis also tends to support these relationships. The vertical spread of the data points suggests that the supposed Vallerano lavas (Group B) have a slightly higher Zr/Y ratio than the supposed Faete lavas (Group A). This is exactly the relationship shown in Figure 8 of Marra et al. (2011). Unfortunately, we did not have any Ta data, so we were unable to use the Th/Ta and Nb/Zr ratios to further refine our analysis. We may tentatively conclude, therefore, that the best fit for the two...
groups is that the stones of Group A were quarried from the Faete lavas and those of Group B from the Vallerano lavas.

DeLaine (1997, 2000) noted that proximity of source quarries to construction sites and the availability of transport were important factors in major Roman monumental building projects. She discussed the merits of water transport in such large projects and described the relative economies of scale resulting from it. She also described the types of boats used, including those in possible use on the Tiber. She thus considers water transport to be a viable means of moving building materials from source to site. From a proximity point of view, a Vallerano source is possible, as the quarries are close to the Tiber and are barely 12 km from central Rome (Fig. 1). Material could thus have been moved up the Tiber by barge. In support of this, Worthing et al. (2017) proposed that the Vallerano lavas were a possible source for paving stones in Ostia, which is some 12 km downstream of the Vallerano outcrops (Fig. 1).

The Monte della Faete lavas are closer to Trajan’s Forum than any other source. Indeed, the Capo di Bove flow crosses into metropolitan Rome and in places the Via Appia is built on it (Fig. 1). Current outcrops of this flow are only 8 km from Trajan’s Forum and half that distance from the Baths of Caracalla. Based on this proximity, DeLaine (1997) appears to assume that this flow was the source of the selec used in the construction of the Baths of Caracalla. The geochemical evidence presented above does not allow us to go that far in respect of Trajan’s Forum. Instead, we prefer to identify one of the sources with the more generic Faete lavas, of which the Capo di Bove flow is one member.

It was noted above that nine samples from Sabatini volcano plot in the Colli Albani field as defined in Figures 2 and S6. We have included these samples in Figure 6 (a), where it can be seen that they tend to plot to the left of Group A: two in the Villa Senni field, three in the Monte della Faete field and three outside. This does not eliminate them completely as representing a possible source for the paving stones described in this paper. However, they are marginal to the main data points representing the Colli Albani. The geographical location of these lavas also poses a problem. Their latitude and longitude readings were abstracted from Conticelli et al. (1997) and their positions are plotted in Figure 1. They cluster around Lake Bracciano, some 35 km north-west of Rome. We suggest that that this lack of proximity to Rome makes them a less likely source for the paving stones at Trajan’s Market compared to the Colli Albani. We also suggest that the latter association is more firmly established by the abundant data presented above.

SUMMARY AND CONCLUSIONS

Sections of paving stones from the Via Biberatica and Trajan’s Market Hémicycle were selected for geochemical analysis, based on the geometric fit of the stones. The selected stones were then classified according to their petrographic features, based on the presence or absence of phenocrysts, their modal composition and the presence of flow foliation. This analysis suggests significant petrographic differences between the paving stones from the Via Biberatica and Trajan’s Market, which can be explained by quarrying from different positions in the same lava flow or from different quarries, or both. Clustering of the different petrographic types also allows some tentative conclusions to be drawn about the loading and unloading of stones from different parts of the source quarry or quarries. Geochemical analysis of the paving stones shows that that they plot in well-defined overlapping fields on $X-Y$ plots. Comparisons with geological data for the Colli Albani, Sabatini and Vico on the same $X-Y$ plots also show that both major and trace elements display a close association with the Colli Albani geological data. This association is confirmed by spider diagrams that normalize paving stone analyses to lava flow analyses for...
the four main effusive units of the Colli Albani: the Monte della Faete lavas, the Monte due Torri lavas, the Vallerano lavas and the Villa Senni lavas. However, these spiders do not allow a definitive association to be established between the paving stones and any of the above effusive units. They simply confirm their overall connection with the Colli Albani. Further analysis using the ratios Zr/Y and Nb/Y (Marra et al. 2011) suggests that the paving stones were quarried from at least two sources, and that both of these sources are represented in the Via Biberatica and the Hemicycle. These diagrams also suggest that the two sources lie within the Vallerano and Faete lava complexes. The Vallerano outcrops are close to the Tiber and to central Rome. In support of this, previous research suggested that a Vallerano source was used for paving stones at Ostia (Worthing et al. 2017). If this is the case, it is probable that the paving stones were transported by barge to both Ostia and Rome. The Faete lavas, including the Capo di Bove flow, are also considered to be strong candidates due to their close proximity to Trajan’s Forum. These conclusions posit data-led alternatives to previous intuited assumption and open up questions of the use of the Tiber as a means of supplying paving stones to Rome.

The utility of HHpXRF for this project and others of a similar type also needs some final discussion. It is clear from the above procedure that calibration of the Niton analyser is far from straightforward. Apart from the analytical capability of the machine, there are two main problems that may influence the accuracy of the calibration. The first relates to the grain size of the standards and the paving stones. Normally, groundmass analyses are measured when the Niton is used during calibration and fieldwork. However, the Niton window measures about 2 cm², which means that only a small area of the rock is irradiated. Thus the presence of phenocrysts or a coarser grain size may mean that some chemical components may not be included in the analysis, which may therefore be unrepresentative of the bulk composition of the rock. The modal abundance of minerals hosting trace elements may also affect the measured concentrations of these elements. For example, Zr is usually partitioned in the mineral zircon (ZrSiO₄), which may occur in very low modal abundance, scattered throughout the rock matrix. Thus some zircons may be missed by a Niton analysis, which will, of course, underestimate the concentration of Zr. A possible remedy is multiple analyses of the same rock, but this is impossible when hundreds of paving stones need to be measured. Thus we conclude that finer-grained aphyric rocks should be selected, but that this is not always possible. The other issue we encountered was instrument drift during fieldwork. We used COB1 to monitor the Niton performance, noting departures from expected values, but we did not do this systematically. For example, we could have referred to COB1 at fixed times of the day, which may have revealed a temperature effect. However, it is unclear what corrections could have been applied if this information had been available.

The calibration issues are also compounded by the analytical procedure used in laboratory-based XRF machines. This involves grinding the whole rock into a fine powder, which is then melted with a flux to produce a fused glass disc for analysis. Thus the whole rock, including the phenocrysts, is represented in the analysis and trace elements are also homogenized in the fused disc. These differences are relevant in the case of the Icelandic basalts used in the BIBROCEL calibration, which were slightly porphyritic. Thus, comparisons between Niton analyses and analyses obtained by laboratory-based XRFs can be problematic and may introduce errors in calibration. This may go some way to explaining some of the issues in making comparisons between laboratory-based data and those obtained with HHpXRF. Calibration protocols, taking averages of a number of readings, may partly compensate for these effects. However, we conclude that it is very difficult to obtain a perfect 1:1 calibration, particularly with respect to trace elements. BIBROCEL is thus a best-fit calibration.
To end on a more positive note; it is clear that when large amounts of Niton data obtained from volcanic rocks of known provenance are compared with literature-based geological data of the same rocks, the agreement is good (e.g., Worthing et al. 2017). There is an abundance of material available for further study and the production of data-led conclusions.

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Figure S1. Niton calibration diagrams. Figs. a-c represent factory calibrations, Figs. d-f BIBROCEL calibrations.

Figure S2. Niton calibration curves for K and Fe based on data collected during machine calibration. $R^2$ values are also shown.

Figure S3. Photographs of different petrographic types VB = Via Biberatica, TM = Trajan’s Market Hemicycle. Key to symbols in Table S1.
Figure S4. Histograms of the petrographic groups represented in the four investigated areas of Trajan’s Market. Key to symbols in Table S1.
Figure S5. Areal distribution of the different petrographic types in the four areas of Trajan’s Market under investigation. Key to symbols in Table S1.
Figure S6. Selected trace element geological data plotted against Wt% SiO2. Trace element data in ppm and symbols as in Fig 7.
Table S1. Examples of criteria for paving stone petrographic classification.