Trajan's Forum (Hemicycle) and Via Biberatica (Trajan's Markets): An HHpXRF Study of the Provenance of Lava Paving in Ancient Rome (Italy).

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Abstract

The paper reports on geochemical data collected using a He-enabled Hand-Held portable XRF (HHpXRF) from lava paving stones in Trajan's Markets and Trajan's Forum (Rome). Issues relating to HHpXRF field use and calibration are also addressed in detail. Using this instrument 355 analyses of the paving stones were collected and the data was 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 Alban Hills, southeast of Rome. Evidence is also presented pointing to possible source lava flows within the Alban Hills Complex. 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.

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 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 volcanic 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 lab-based XRF data suggesting that selce was transported up to 90 km to construction sites in the Po Plain from sources in the Euganean Hills. But, in general 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 but 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 and only 3% at an on-

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site laboratory and only 15% at an actual excavation. They attribute this partially to scepticism about the analytical performance of HHpXRF machines. In this paper, we have compared our HHpXRF analyses with lab-based XRF analyses of lava flows from the Alban Hills, Sabatini and Vico volcanoes taken from the geological literature. One of the advantages of this approach is that the geological data provides 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 (compare 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.

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 (Conticelli et al. 2010a, Alagna et al. 2010). 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 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. In this paper three volcanoes of the RMP will be discussed: from north to south they are Vico, Sabatini and the Alban Hills but the main focus will be on the latter (Fig. 1).

Vico, Sabatini and the Alban Hills are all characterised 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 characterised by high levels of 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 (e.g. Conticelli et al. 2010a, Alagna et al. 2010, Gaeta et al. 2016). The relative abundance of potassium and the undersaturation with respect to SiO_2 gave rise to the common occurrence of the potassic feldspathoid leucite. 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).

The Alban Hills

This volcanic complex lies 15km southeast 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. 2010a, Gaeta et al 2016). Lava flows are subordinate and the volume of eruptive products 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 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). The Late Tuscalano-Artemisio Phase (Fig. 1) also hosts significant lava flows including the Villa Senni lavas and the lavas of the Pozzolane Rosse 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). These lavas are all 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 Sacrafano together with scoria cones and hydromagmatic maar activity (Conticelli et al. 1997, 2010a, Karner et al.2001, Sottili et al. 2010, Marra et al. 2014) (Fig.1). Activity was dominantly explosive occurring between 800 and 86ka producing voluminous pyroclastic flows and .tuffs. In the south east some of these are interbedded with tuffs from the Alban Hills (Marra et al 2011). Lava flows occur at a number of scattered localities (Fig. 1). The most intense monogenetic activity was concentrated at Trevignano areas to the north of the Bracciano crater, at Monte Maggiore close to the Sacrofano caldera, and at Monte Aguzzo and in the southeast. 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). The magmatic products of Vico have been divided into three main rock Successions (Perini et al. 2000, 2004, Conticelli et al. 2010a). 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 ka – 260 ka) followed by four explosive ignimbrite eruptions which 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 was characterised by tuffs and minor lava flows.

Methodology

Calibration of HHpXRF Equipment

Geochemical data for this paper was collected using a hand held Niton XL3t 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 customised for specific tasks. This was particularly important in this project as determination of paving stone provenance depended on comparisons between Niton data and data sourced from the geological literature of the Roman Volcanic Province. This was obtained on lab-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 twenty seven 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. Firstly 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 cobble stone (COB1) from a modern road in central Rome. This was analysed on a lab-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 K_2O/Na_2O 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 ten analyses of COB1 on a flat sawn surface using the shielded test stand with the Niton set to factory calibrations. Data was 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 ten analyses were averaged and are plotted in Figures 2a-c against the equivalent lab-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 2a shows that MgO, K_2O, CaO and FeO are well calibrated although Al_2O_3 deviates slightly from the 1:1 calibration line. However, SiO_2 is very poorly calibrated. Figure 2b shows that Sr and Ti are also poorly calibrated whereas P, Ba, Ce and Nd are reasonably constrained. In Figure 2c 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 lab-based XRF. These chips had one flat sawn surface which 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 was compared graphically with the equivalent data obtained by the lab-based XRF. The resulting 7 point graph for K and Fe are shown in Figure 3 a and b. They include the straight-line equations for the calibration curve and the R^2 value. The slope and intercept values from all equations were then fed into the CALFAC programme in the Niton software producing an element calibration file which we called BIBROCEL. This was loaded into the Niton memory and 10 analyses of COB1 were collected. An average was calculated from this data and the results are presented in Figures 2d-f alongside the factory calibration files. Figure 2d shows that the major elements are well calibrated. In particular SiO_2 is much improved from the uncalibrated value shown in Figure 2a. There is also some improvement in the trace elements Ba and Sr, particularly the latter (Fig. 2e). Ti is slightly moved on the diagram but not much changed. P is actually worse. Figure 2f 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 this data we produced a second CALFAC file called BIBSTANEL which was saved as a separate file in the CALFAC programme and was used to re-analyse COB1. We found that BIBROCEL yielded the best results and accordingly we used this calibration file in the field.

During field work 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^{o}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 lab-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 SiO_2 values and together with COB1 re-analysed 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 lab-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 was loaded into MinPet 2.02 for analysis.

Sampling and Data Collection

Photographs taken at the time of excavation identified the Hemicycle of Trajan's Forum and theVia Biberatica as sections of ancient paving that had not been restored post-excavation. The tight fit of the paving stones can be seen to be indicative of paving from antiquity, whereas restoration work was characterised by gaps or cement fill (Fig.4a). Three areas of paving stones of the Hemicycle in Trajan's Market were selected for geochemical analysis in 2016 together with re-analysis of some paving stones in 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 on the Via Biberatica. Representative photographs are presented in Figure 4a-f. In addition, vertical photographs were taken of the three Hemicycle areas from overlooking balconies and these were used as accurate maps enabling location and numbering of each paving stone. We used the same numbering system for the Via Biberatica utilised 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. 4c). 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. In order to investigate the effects of cleaning, ten samples were selected at random for analysis of both the cleaned and uncleaned areas. This data shows 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 and emphasised the importance of cleaning prior to analysis

As noted above, geochemical data was collected using a hand held Niton XL3t 950 He GOLDD+ X-ray analyser. The machine has an Au anode (9-50kV, 0-40 :A max) giving a resolution of <185eV. 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 was collected in element % using a livetime of 120 seconds. 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. We also took 10 readings from a number of phenocrysts that characterise most of the lava paving stones.

Paving Stone Petrography

Petrographic analysis was conducted on paving stones from the three areas in the Hemicycle. This data complemented a similar analysis undertaken on the Via Biberatica in 2014. A simple system was devised (modified after Browning unpublished) based on the presence or absence of phenocrysts, their modal percentages, grain size and the presence or absence of flow foliation. Table 1 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 are shown in Figures 5a-d. These histograms show that the three areas of the Hemicycle (Figs 5a-c) are very similar. The dominant rock types are grey porphyritic lavas with phenocrysts ranging between 1 to 5% by volume. (Figs 4b and c). Also all three areas have some stones showing flow foliation (Fig. 4d). 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. 4e). 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. 4e). 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 Figs. 6 a-d. 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 3AC2 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 6 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 3AC2 type is common. These differences may reflect choices made by the stone masons in response to the workability of the different types of lava. The foliated types in Area 1 may have been more susceptible to splitting. Four stones in Area 3 of the Hemicycle contain xenoliths (e.g. Fig.6a), a feature not present in Areas 2 and 3 and the Via Biberatica. They are described in some detail in the study by Tregila et al. (1995) on the geology of the Alban Hills and appear to be particularly common in the Villa Senni eruptive unit.

The geological literature suggests that one of the characteristic features of lavas from the Alban Hills is the ubiquitous presence of leucite phenocrysts (e.g. Tregila et al. 1995). Thus we considered that it was important to confirm the identity of the ubiquitous phenocrysts in the Hemicycle and the Via Biberatica. The crystals are white or cream in colour and are often equant or square-shaped and up to 2cms in diameter.

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 Alban Hills, Sabatini and Vico were loaded into MinPet software. (Trigila et al. 1995, Conticelli et al. 1997, Perini et al. 2000, 2004), Peccerillo 2005, Giordano et al. 2006, Conticelli et al. 2007, Boari et al. 2009, Marra et al. 2009, Alagna et al. 2010, Conticelli et al. 2010 a and b, 2010b, Gozzi et al. 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 Alban Hills. 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 Alban Hills, blue for Sabatini and black for Vico. This data is shown in Figures 7a-f where the major elements TiO_2, Al_2O_3, FeO_T, MgO, CaO, K_2O and P_2O_5 plotted against SiO_2 and Figure 8a-g in which the trace elements Zr, Sr, Ba, Rb, Cu, and Pb are also plotted against SiO_2. The diagrams show the geological data spread across the diagrams with the Alban Hills data at the low SiO_2 end, Vico at the high SiO_2 end and Sabatini in the middle. There is some overlap between the Alban Hills and Sabatini data. In most cases the Alban Hills major and minor elements show elevated values relative to those of Sabatini and Vico. In each diagram the Alban Hills concentrations are enclosed by a field which includes most of the data points.

The Niton data was converted to Wt% oxide for the major elements and ppm for trace elements. Figures 9a-g and 10a-f show the Via Biberatica and Hemicycle data plotted in the same X-Y plots as the geological data above. The Via Biberatica (VB) data is represented by green circles and the Trajan's Market Hemicycle (TM) data as red circles. The VB data tends to cluster whereas the TM data is 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 Alban Hills clusters in Figures 7 and 8 above 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 Alban Hills. There is, however, a note of caution. Close examination of Figures 7 and 8 show that nine Sabatini samples lie within the Alban Hills fields suggesting that they are geochemically identical to some of the rocks from the Alban Hills (see below for discussion).

Phenocryst Compositions

As noted above leucite is a common phenocryst phase in many lavas from the RMP particularly the Alban Hills (e.g. Tregila et al. 1995) We used the Niton in toggle spot mode to obtain ten in situ analyses of some of the larger crystals, five from the Via Biberatica and five from the Hemicycle. The analyses were averaged and are presented in Table 2 together with two microprobe analyses from the Alban Hills (Boari et al. 2009). The VB and TM Niton analyses in Table 2 were obviously measured under less than ideal conditions i.e on uneven pitted surfaces and not *in vacuo*. However the similarities are clear although some of the values such as Al_2O_3 and SiO_2 are low. However given the analytical conditions we conclude that the phenocrysts are leucites.

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 geological data for the Alban Hills. 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 Alban Hills, a process called normalisation. Thus, normalising standards were calculated for each of the effusive phases from the Alban Hills as defined by Gaeta et al. (2016). These standards were calculated as follows: the average of nine samples from the Pozzolane Rosso 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), twenty two 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 placed 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 with the appropriate standard value (i.e. the ratio Sample/Standard was calculated0. 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 1. Thus the similarity to the standard of the selected elements can be visually assessed.

Figure 11a-d shows a series of spiders plotted in which the Via Biberatica (green) and the Hemicycle data (red) are compared with the different Alban Hills standards. They all plot close to the line 1 showing that their geochemistry are very similar to the Alban Hills standards. However the flattest curve is the one for the Vallerano lavas (Fig. 11a) The Pb values are anomalous showing positive spikes (Figs. 11 a-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 11d, the Monte due Torri lava has an unusually low Pb concentration (6ppm) which together with atmospheric contamination, has given rise to the large positive spike. We can therefore conclude that both the X-Y plots (Figs. 9 and 10) and the spiders of Figures 11a-d suggest that the Via Biberatica and the Hemicycle paving stones were sourced in the Alban Hills. 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 normalise the data. We will attempt to address this issue below.

Zr/Y vs Nb/Y discriminant diagrams

Rock materials such as lavas, tuffs and pozzolane were used extensively in the architecture of Roman masonry and concretes (e.g. DeLaine 1997, 2000; Marra et al. 2011). These 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 vs Nb/Y and Th/Ta vs Nb/Zr. These elements tend to be immobile during weathering and can thus be used to document both the primary geochemistry of the deposits and the vectors of geochemical change in measured sections in the Alban Hills and Monte Sabatini. They were also used to facilitate sourcing of construction materials

Figure 12a shows a plot of Zr/Y vs Nb/Y for samples identified as belonging to the principle effusive phases of the Alban Hills used in the spider diagrams of Figure 9 (Gaeta et al. 2016). They are as follows: the Monte della Faete lavas, the Monte due Torri lavas, the Vallerano lavas and the Villa Senni lavas (Fig. 1). The data was abstracted from geological analyses and clusters into four overlapping fields. Figure 12 b. shows a plot of the Niton data from the Via Biberatica and the Hemicycle using the same ratios together with the fields from Figure 12a. The vertical linear distribution of the data in Figure 12b is probably a function of the fact that the data for these two elements is close to the detection limits of the Niton. It thus tends to cluster tightly around the small range of 30-40ppm for Y and 20ppm for Nb. However when the data for these two elements is normalised to the geological data in the spiders of Figures 11, they plot close to 1 indicating that their concentrations are close to the values in the geological data set. We consider that this validates their use as described above.

Inspection of Figures 12a and b shows that they do not clearly discriminate between the different possible sources on the Alban Hills. However a number of comments are possible. Firstly the two main data clusters in Fig. 12b suggest that lavas from at least two sources were used in the Via Biberatica and the Hemicycle but their distribution in these sites is numerically different. For example, the higher ratio cluster contains 103 data points of which 68% represent paving stones in the Hemicycle and 32% are from the Via Biberatica. The lower ratio concentration contains 213 data points of which 77% represent paving stones from the Hemicycle and 23% the Via Biberatica. Secondly, although there is no clear association between the data clusters in Figures 12a and 12b, there is a tendency for the higher ratio concentration in Figure 12b to cluster around the Vallerano data in Fig 12a. Similarly there is a less well defined association between the lower ratio concentration in Figure 12b and the Villa Senni lavas in Figure 12a. 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 as the crow flies (Fig.1). In support of this association Worthing et al. (2017) suggested that the Vallerano lavas were a possible source for paving stones in Ostia which is some 18km down stream of the Vallerano outcrops (Fig. 1). A Villa Senni source is slightly more problematic as the lava flows are further from central Rome (Fig.1). If proximity to construction sites was important then the Monte della Faete lavas are closer. Indeed one of them, the Capo di Bove flow, crosses into metropolitan Rome and the Via Appia is in places built on it (Fig.1).

It was noted above that nine samples from Sabatini volcano plot in the Alban Hills field as defined in Figure 7 and 8 above. We have included these samples on Figure 12a where it can be seen that they tend to plot to the left of the lower ratio concentration, 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 in this paper. However they are marginal to the main data points representing the Alban Hills. They also pose a problem of geographical location of these lava flows. Their latitude and longitude readings were abstracted from Conticelli et al. (1997) and their positions are plotted on 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 Alban Hills. We suggest that the latter association is more firmly established by the abundant data presented above.

It was noted above that xenoliths were present in three paving stones in Area 3 of the Hemicycle. Tregila et al. (1995) stated that xenoliths are relatively common in the Villa Senni eruptive unit. One of the Area 3 xenolithic samples plots in the proposed Villa Senni group of Figure 12a and b and two in the proposed Vallerano group. However, these unclear associations lead us to conclude that unequivocal sourcing of the paving stones to individual eruptive phases on the Alban Hills is problematic. Unfortunately we did not have any Ta data so were unable to use the Th/Ta and Nb/Zr ratios to further refine our analysis. However with respect to the Vallerano lavas (Fig. 1), both the geochemistry and the proximity to the Tiber and to central Rome do lend weight to them as the possible source for lavas used in the Via Biberatica and the Hemicycle. Similarly the Vallerano lavas (Fig. 11a) do show the flattest curve in the spider diagrams of Figures 11 a-d. Further support comes from the suggestion of Worthing et al. (2017) that the Vallerano lavas were probably a source for paving stones at Ostia (Fig. 1). These two possible source - construction site associations imply that the paving stones were probably transported by barge (contrary to Delaine 2000: 135).

Summary and Conclusions

Sections of paving stones from the Via Biberatica and Trajan's Market Hemicycle 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 XY plots. Comparisons with geological data for the Alban Hills, Sabatini and Vico on the same XY plots also show that both major and trace elements show a close association with the Alban Hills geological data. This association is confirmed by spider diagrams that normalise paving stone analyses to lava flow analyses for the four main effusive units of the Alban Hills: 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 Alban Hills. 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 these sources are represented in the Via Biberatica and the Hemicycle. A tentative association was also made between the Vallerano lavas and the Villa Senni lavas as possible sources. The former is considered to be a stronger candidate as the 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. This conclusion posits a data-led alternative to the intuited assumption that the Capo di Bove lava flow was the source of paving and opens up questions of the use of the Tiber as a means of supplying paving stones to Rome contrary to assertions in the modern literature (DeLaine 2000: 135).

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 field work. However the Niton window is about $2cm^2$ 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 stone need to be measured during fieldwork. Thus we conclude that finer grained aphyric rocks should be selected but this is not always possible. The other issue, we encountered was instrument drift during fieldwork. We used COB1 to monitor Niton performance during fieldwork 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 lab-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 for the Icelandic basalts used in the BIBROCEL calibration which were slightly porphyritic. Thus comparing Niton analyses with analyses obtained by lab-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 lab-based data and that 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), and there is an abundance of material available for further study and the production of data-led conclusions.

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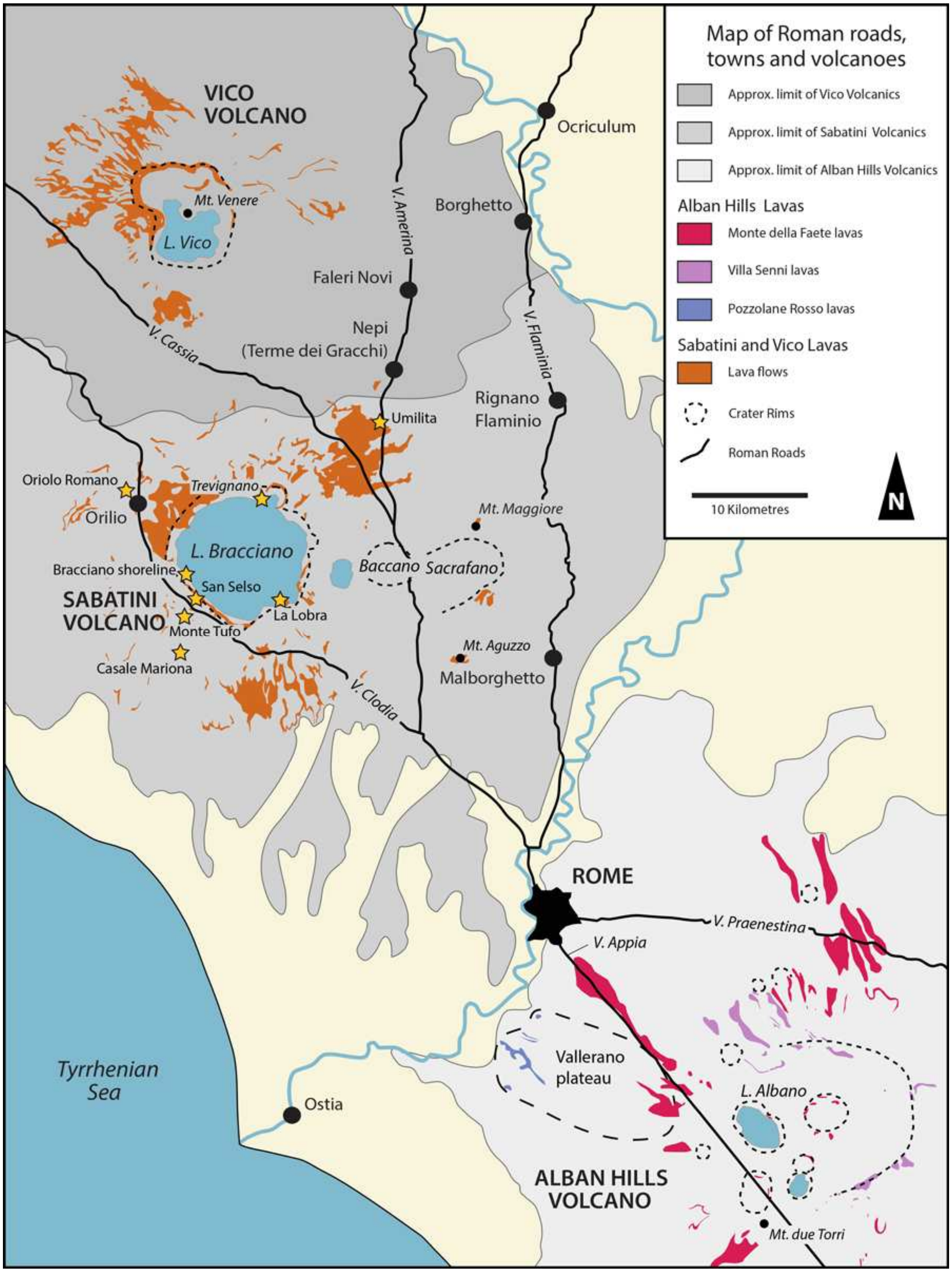
Map of Roman roads, towns and volcanoes
Approx. limit of Vico Volcanics
Approx. limit of Sabatini Volcanics
Approx. limit of Alban Hills Volcanics
Alban Hills Lavas
Monte della Faete lavas
Villa Senni lavas
Pozzolane Rosso lavas
Sabatini and Vico Lavas
Lava flows
Crater Rims
Roman Roads
10 Kilometres
N
VICO VOLCANO
Mt. Venere
L. Vico
Ocriculum
V. Amerina
Borghetto
Faleri Novi
Nepi
(Terme dei Gracchi)
V. Cassia
V. Flaminia
Rignano Flaminio
Umilita
Oriolo Romano
Orilio
Trevignano
Mt. Maggiore
L. Bracciano
Baccano
Sacrafano
Bracciano shoreline
San Selso
SABATINI VOLCANO
La Lobra
Monte Tufo
Casale Mariona
Mt. Aguzzo
Malborghetto
V. Clodia
ROME
V. Praenestina
V. Appia
Vallerano plateau
Tyrrhenian Sea
Ostia
L. Albano
ALBAN HILLS VOLCANO
Mt. due Torri

Fig.1.

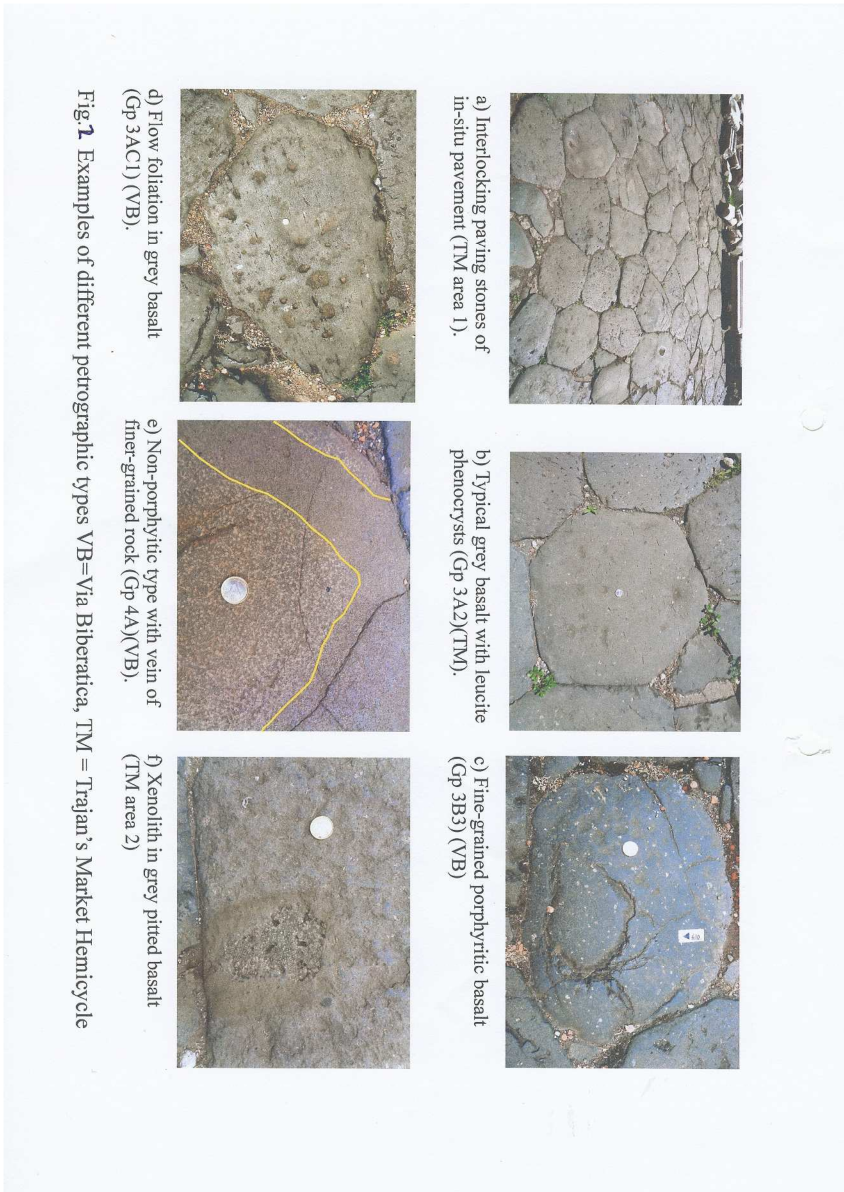

Fig. 4. Photographs of different petrographic types VB = Via Biberatica, TM = Trajan's Market Hemicycle. Key to symbols in Table 1.

208x293mm (300 x 300 DPI)

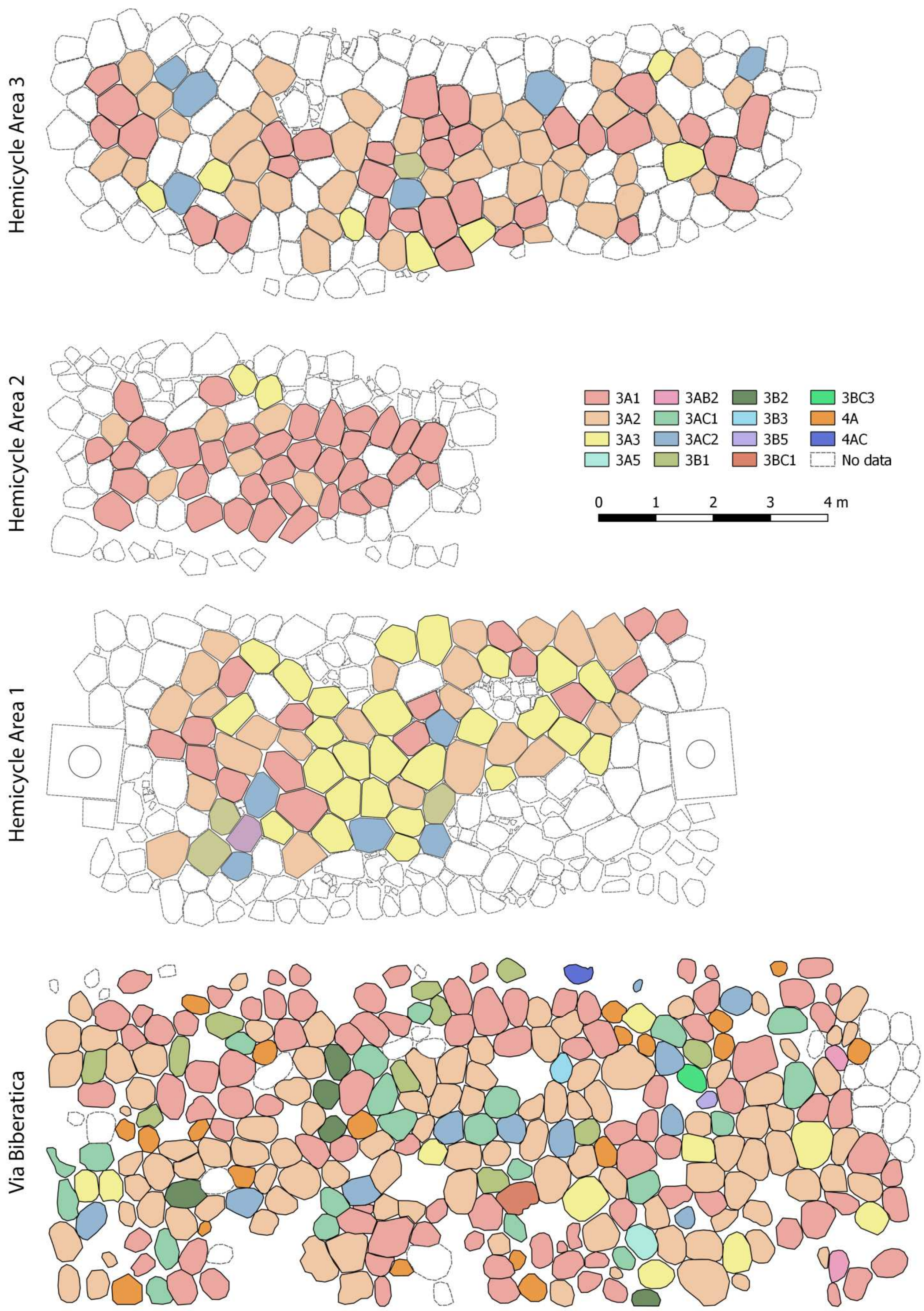

Fig..4. Areal distribution of the different petrographic types in the three areas of the Hemicycle and the Via Biberatica.

Group	Symbol	Definition
3Ax	3	Porphyritic
	A	Groundmass visible with naked eye
	x = 1-5	Percentage of phenocrysts
3ACx	3	Porphyritic
	A	Groundmass visible with naked eye
	C	Flow foliation present
	x = 1-3	Percentage of phenocrysts
3Bx	3	Porphyritic
	B	Groundmass not visible with naked eye
	x = 1-5	Percentage of phenocrysts
3BCx	3	Porphyritic
	B	Groundmass not visible with naked eye
	C	Flow foliation present
	x = 1-3	Percentage of phenocrysts
4A	4	Phenocrysts absent
	A	Groundmass visible with naked eye

Table 1. Examples of criteria for paving stone petrographic classification.

	Alban Hills*		VB	TM
SiO_2	54.80	54.90	50.41	49.86
TiO_2	0.05	0.05	0.35	0.30
Al_2O_3	22.90	23.30	15.40	15.53
Fe_2O_3	0.71	0.67	1.11	0.69
MgO	bdl	bdl	0.01	0.00
CaO	bdl	bdl	1.49	0.98
Na_2O	0.1	0.08	nd	nd
K_2O	21.00	21.30	16.30	16.56
P_2O_5	nd	nd	0.28	0.45
Sr ppm	2114	423	286	116
Ba ppm	182	2180	626	544

Table 2. Leucite analyses (*after Boari et al. 2009), bdl = below detection limits, nd = not determined. VB = Via Biberatica, TM =Trajan's Market Hemicycle. VB and TM are averages of 5 analyses.

Table 2. Niton leucite analyses (VB and TM) compared with microprobe analyses of leucites from the Alban Hills after Boari (2009).