MMI partial extraction geochemistry for the resolution of anthropogenic activities across the archaeological Roman town of Calleva Atrebatum.

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Abstract

Sixty three soils samples, fourteen samples of previously excavated archaeological material, and five background soil samples taken at the Silchester Roman Town of Calleva Atrebatum in the County of Hampshire, United Kingdom were analysed by the Mobile Metal Ion (MMI) method for a total of fifty three elements. Samples from within the town walls showed considerably higher concentrations than samples outside for many elements; Au, Ag, Cu and

Sn were in extremely anomalous concentrations, Bi, Cd, Hg, Mo, P and Pb were anomalous and Sb and Zn in elevated concentrations. The overall pattern of element distribution is one of an annulus of higher elemental concentrations surrounding a centre of generally lower values centred on the previously excavated Forum basilica. The elements Zr, Ti, Th, Ti, Tl, Nb, Sn, Sc, Cr, Co, Sb, Bi, Ce, Nd (and all other REEs), show similar distributions to one another, and their distribution and that of the noble and base metals, as highlighted by various additive indices, is considered to be the result of metallurgical processing on site. The low values for most elements around the Forum basilica are the result of disturbance of the soil geochemical profile in this area by previous archaeological excavation.

Keywords: soil geochemistry, archaeological prospection, partial extraction, MMI, Roman metal extraction.

Geochemistry has had a small, but growing place in archaeological investigations beginning when it was discovered that phosphate enrichment in Swedish soils was an indicator of prehistoric human occupation and could be connected with prehistoric sites and deserted mediaeval villages (Arrhenius 1931).

With the advent of Inductively Coupled Plasma Mass Spectrometry (ICPMS) in the late twentieth century, analytical chemistry, particularly that of geological and archaeological materials underwent a major transformation. Within the space of ten years detection limits for a large number of elements were lowered, in many cases to the part per billion (ppb) level and simultaneous analysis of solutions containing over 50 elements was able to be undertaken in less than a minute of analysis time. One of the initial problems encountered was how to dissolve geological solids, and to maintain the analytes in solution for the duration of the analysis (Hall 1998). Strong acid digests, including aqua regia (AR) were an obvious choice, although it is of note that for over 50% of elements aqua regia digestion is less than 50% efficient (e.g. Mann et al 2015), i.e. the analysis is not total. In a partial extraction, in which less aggressive chemicals are used and for which extraction efficiencies are even lower, (Stanley and Noble 2008) showed that signal to background contrast ratios in a geochemical soil survey across mineralisation were increased relative to that for acid digestion. It is likely that this is due to the fact that high concentrations of non-diagnostic background metal from within (most) soil mineral grains is not included in the analysis viz. “analytical noise” is significantly reduced.

The Mobile Metal Ion (MMI) solution (Mann 2010) is a neutral-alkaline partial extraction solution comprising a number of strong complexing ligands which can simultaneously extract base metals, precious metals, transition metals, lanthanides (rare earths) and some actinides and non-metals from soil material, and maintain them in solution for ICPMS analysis. As such it has seen widespread application in mineral exploration (Mann et al, 1998), in continental surveys (Mann et al, 2012, Reimann et al, 2014) and recently in archaeology where it has been utilized to define multielement soil geochemical anomalies associated with Roman metal- processing at a Roman site in Somerset (Sylvester, Mann et al. 2017). In each of these cases soil sampling was undertaken in the capillary fringe zone, 10-25cm below surface, and the ability of MMI to discriminate in favour of more recently arrived (in some cases anthropogenically derived) ions into this layer has been noted (Mann, Birrell et al. 2005).

MMI ligand-based partial-extraction soil geochemistry has been shown to be valuable in defining and delineating multielement anthropogenic anomalies associated with the partially excavated Roman metal processing site at St. Algar’s Farm, Somerset, UK (Sylvester, Mann et al. 2017). This paper presents results of an MMI soil geochemical sampling programme carried out within the walls of the Roman town of Calleva Atrebatum in Hampshire, UK, which has undergone substantial excavation since the late 19th century. The purpose of the work is to determine the existence, persistence, strength and multi-element nature of soil anomalies produced on site by Roman and pre-Roman metallurgical activities, and in areas where recent excavation has taken place to examine the effect of that on any pre-existing soil geochemistry.

In the present paper, MMI soil geochemistry is shown to reveal the wide range of metal-processing that has been undertaken, and the effect on soil geochemistry of modern archaeological excavation, at the archaeological Roman town of Calleva Atrebatum, located in the southern United Kingdom.

MATERIALS AND METHODS

Site description

The Atrebates tribe established an oppidum as their capital at Silchester in the first century BCE. It was ditched and occupied an area of about 32 Ha. Subsequent to the Roman conquest in 43 CE the settlement developed into the Roman town of Calleva Atrebatum (Calleva). It was walled and occupied about 40 Ha. The remains of the ruins are situated beneath and to the west of the Parish Church of St. Mary the Virgin. The Silchester Roman Town site has been declared by the state as Scheduled Ancient Monument SAM No. 24336. The site is located about 1.6km east of the village of Silchester, some 14km south west of the town of Reading and about 8km north of Basingstoke in the County of Hampshire, close to the border of Berkshire (Figure 1).

The site consists of two fenced fields separated by an east west farm road. The site is enclosed by the Roman wall which is intact over most of its length. The wall stands to a height of up to 4.5 m, 3 m wide at the base, narrowing to 2.3 m at the upper level. It is composed of flint with levelling courses of stone slabs (of a variety of stone types) bound by a lime mortar. There is a large square area in the northern field where recent archaeological excavation has been carried out within Insula IX. The greater part of the site has undergone archaeological excavation in various forms for more than a century. All of those older diggings have been refilled and repastured.

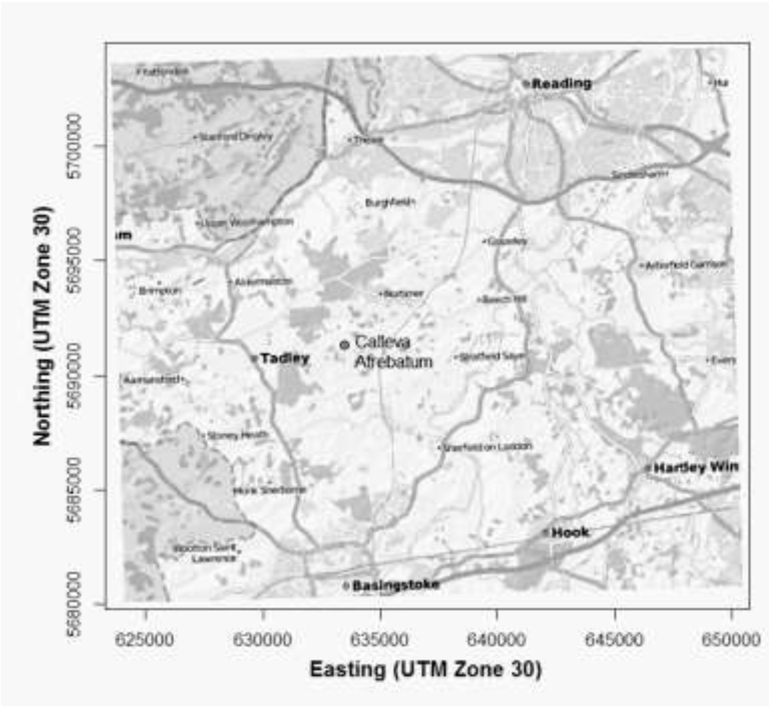


Figure 1. Location map of Calleva Atrebatum

The fields in which the Monument and associated archaeology occur are under permanent grass cover and used for cattle grazing. The site has a maximum elevation of approximately 100m above mean sea level and slopes gently to the south where the elevation is about 90m a.s.l.

The soil at the Calleva site is brown-grey stony loam. It is freely draining, slightly acid, with low fertility and low carbon. The soils sampled were physically unstratified and below the grass roots were visually unstructured. Because the site has been ploughed and extensively excavated and refilled with the plough soil, there is little or no evidence of a humic near surface layer.

The British Geological Survey (BGS) show (in BGS Mapview) the area is underlain by a basement of marine sands and silts of the Palaeogene (34-56 M.Y.) the London Clay Formation and the Bagshot Formation. This basement is overlain by Quaternary Silchester Gravel Member (up to 2 M.Y.) sand, river gravel and alluvial deposits. It is from these Quaternary sediments that the local soil at Silchester appears to have been developed.

A large Roman town site (Calleva) was known to antiquarians from at least medieval times (Norden 1595). Undocumented excavation was carried out on the site before 1864 and then between 1864 and 1878 by Joyce (1881). This was followed by major investigations by the Society of Antiquaries between 1890 and 1909 which revealed a plan of the masonry – founded buildings within the walled town. The results of that work were regularly reported in the journal *Archaeologia* (Fox 1895, Fox and Hope 1905) and were evaluated by Boon (1974).

Detailed scholarly investigations have been carried out on the Roman walls, gates and defences (Boon 1969, Collis 1983, Fulford 1984, Fulford, Rippon et al. 1997), the amphitheatre (Fulford 1989) and the basilica (Fulford and Timby 2000). The excavations at the basilica (Fulford and Timby 2000) also found evidence of metalworking and evidence of iron smelting in the Forum basilica was found by Allen (2013). Excavation on Insula IX developed into the Town Life project (Fulford 2006, Fulford 2011) and included investigations of possible metal- processing hearth sites in House 1 (Cook, Clarke et al. 2005, Cook, Banerjea et al. 2010). A plan of the walled Roman town of Calleva Atrebatum showing the location of Insula IX and the Forum basilica is shown in Figure 2.

The Calleva site contains archaeological evidence of settlement in the Late Iron Age (about first century BCE). Roman settlement is recorded from late first century BCE through until about fifth century CE. (Fulford 2006) present evidence that, whilst the site was substantially abandoned during the fifth century, there was continuity of Romano-British occupation until the later sixth or early seventh century.

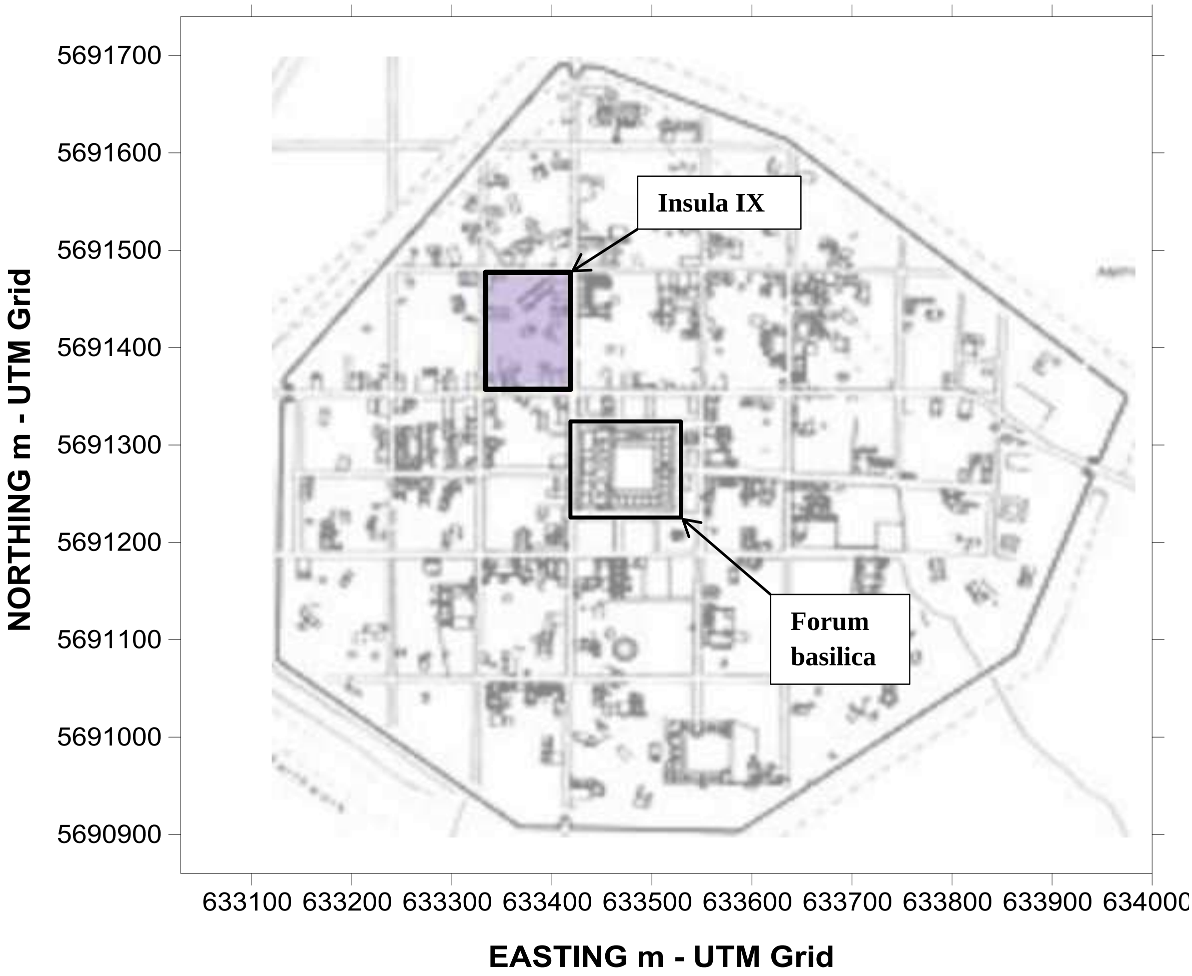


Figure 2. Plan of the Roman town of Calleva Atrebatum

Sampling

A soil geochemical sampling programme, using Mobile Metal Ion (MMI) analysis was undertaken over an area (40ha.) of Silchester Roman Town to obtain a broader knowledge of the relationship between the archaeology and the geochemistry of the site as a whole. Samples were collected at 40m intervals (reduced to 10 m in critical areas) on three north-south lines spaced at 120m with an east-west tie line. The sampling covered an area 600 x 400m and resulted in the collection of 63 samples. Sample locations are shown on Figure 3.

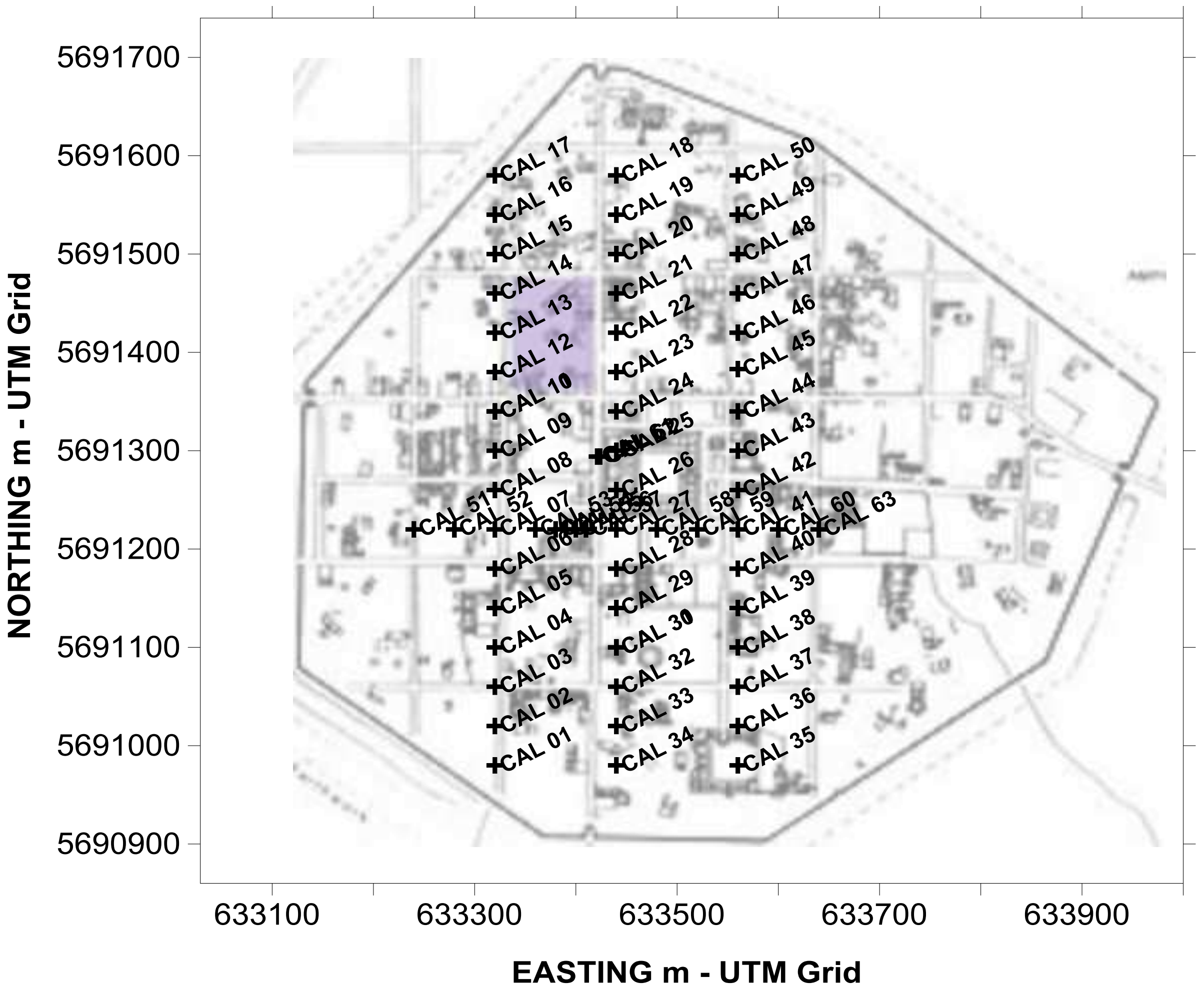


Figure 3. Calleva sample number location plan

The sampling was not representative of the underlying town, as this was a pilot study. The north-south lines run along the edges of town blocks; the single east-west line crosses the middle of some blocks and most blocks are represented by only 3 or 4 samples. The results of the sampling pertain to a 4-500 year urban history and do not relate to any particular points in time. A much greater number of samples, at a higher density will be required to provide more detail of the underlying town.

Splits of fourteen samples of floor debris previously collected during the excavation of House 1 (within Insula IX) were analysed using Mobile Metal Ion (MMI) to further investigate the nature of the geochemical anomalies associated with metal-processing investigated by Cook et al., (2005, 2010). The materials sampled were predominantly clay floor, some with a gravel component (CAH 07, 10, 11, 12, 13, and 14). Some (CAH 02, 03, 08 and 09) were gravel and/or common building material (CBM) mixtures. CAH 01 and 04 were mixtures of slumped materials and building demolition products. Sample CAH 06 was a hearth sample and CAH 05 was heat altered material below a hearth. These groups are labelled the Clay group, the Gravel/CBM group, the Slumped group and the Hearth/Hearth Related group in this document.

Analysis

All samples were treated using the MMI-M Mobile Metal Ion ligand-based partial extraction technique (Mann 2010, Sylvester, Mann et al. 2017) followed by ICP-MS analysis for the concentration of 53 elements. The ICP-MS instrumentation was a Perkin Elmer Elan 9000 DRC II, with an argon plasma.. The solution was analysed for the following elements: Ag, Al, As, Au, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hg, K, La, Li, Mg, Mn, Mo, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, U, W, Y, Yb, Zn and Zr. Quality control and assessment was as recommended by Caritat and Cooper (2011) based on several measures: (1) analysis in a single batch, (2) insertion of blind field duplicates, (3) insertion of blind laboratory replicates, (4) insertion of laboratory standards in the analytical stream at regular intervals and (5) analysis of blank MMI-extraction solution. The elemental values < Lower Detection Limit (LDL) were replaced in the final database with values set to 0.5×LDL. Percentage differences between field duplicates were found to be within acceptable limits.

RESULTS

Five additional samples were collected from outside the Calleva town walls specifically for providing MMI elemental background values and to establish “threshold values”. Speed (2013) demonstrated that the Calleva site, within the town walls, is polluted with a range of elements and that background elemental concentrations could only be obtained by sampling outside the walls.

Determination of background and thresholds for the Calleva soil sample survey

Examination of the analyses of background samples SLB1-5 revealed that SLB1 and SLB4 had significantly (>70%) different concentrations for a number of elements (18 for SLB1 and 16 for SLB4) from the other three samples, which were similar in composition, having mutual ‘r’ correlation co-efficient values ranging from 0.93 to 0.98. As a result the Silchester regional geochemical background (SLB) for each element was defined as the mean of samples SLB2, 3 and 5; the background values for selected elements are shown as Calleva SLB mean in the first column of Table 1.

As a further control, the SLB elemental concentrations were compared with the 1st Quartile Mean (1QM MMI) concentrations obtained from agricultural soil samples taken in south-east England, over rocks of similar age and lithology as part of the Geochemical Mapping of Agricultural Soils (GEMAS) regional soil sampling programme (Reimann, Birke et al. 2014a, Reimann, Birke et al. 2014b). The GEMAS means of 55 samples are shown in column 2 of Table 1. For the elements Ce, Cs, Ga, Nb, Sn and Ti, the background values at Calleva (SLB Mean) are significantly higher (> 10×) than the GEMAS 1QM for SE England, as indicated by the ratios in column 3. The elemental means of the 63 samples within the Calleva walls are shown in column 4 of Table 1 and clearly show that for Ag, Au, Cu, and Sn the background values of columns 1 and 2 are exceeded by a factor of 3. Chen (2016) discuss different methods of determining threshold values in their study which are in general between two and four times when based on the Mean+2STD and Mean+2MAD methods. Given that here we are comparing the mean of all samples at Calleva, not individual anomalies, these backgrounds establish “suitable threshold”.

Table 1. *Calleva sample and background means*

	CALLEVA MEAN	CALLEVA SLB Mean	GEMAS 1QMean	SLBM/GEMAS 1QMean
ELEMENT	ppb	ppb	ppb	
Ag	458	5.33	2.64	2.0
As	17	21	8.23	2.6
Au	10	0.10	0.5	0.2
Ba	520	716	246	2.9
Ca	524000	501670	552140	0.9
Cd	63	52	60	0.9
Ce	104	217	12.12	**17.9**
Cu	5531	613	750	0.8
Cs	5	9	1	**9.0**
Fe	599365	90000	16000	5.6
Ga	11	24	1.5	**16.0**
Hg	1.25	0.50	0.5	1.0
Nd	83	148.00	113	1.3
Nb	4.42	10.50	0.25	**42.0**
P	8183	3970	1729	2.3
Pb	1227	1183	150	7.9
Sb	2.1	2.67	2.59	1.0
Sn	32	4.67	0.26	**17.9**
Ti	816	2798	12.31	**227.3**
Tl	0.81	1.05	0.25	4.2
Y	107	296.00	187	1.6
Zn	2594	2853	460	6.2
Zr	66	121	71	1.7

Figures 4 and 5 show the plot of MMI Ag and Au concentrations (respectively) in the regional GEMAS samples taken from south east England. When viewed in conjunction with Table 1, these distribution maps show that the Calleva sample means for Ag and Au are higher than for neighbouring GEMAS samples, except for that near Slough, west of London.

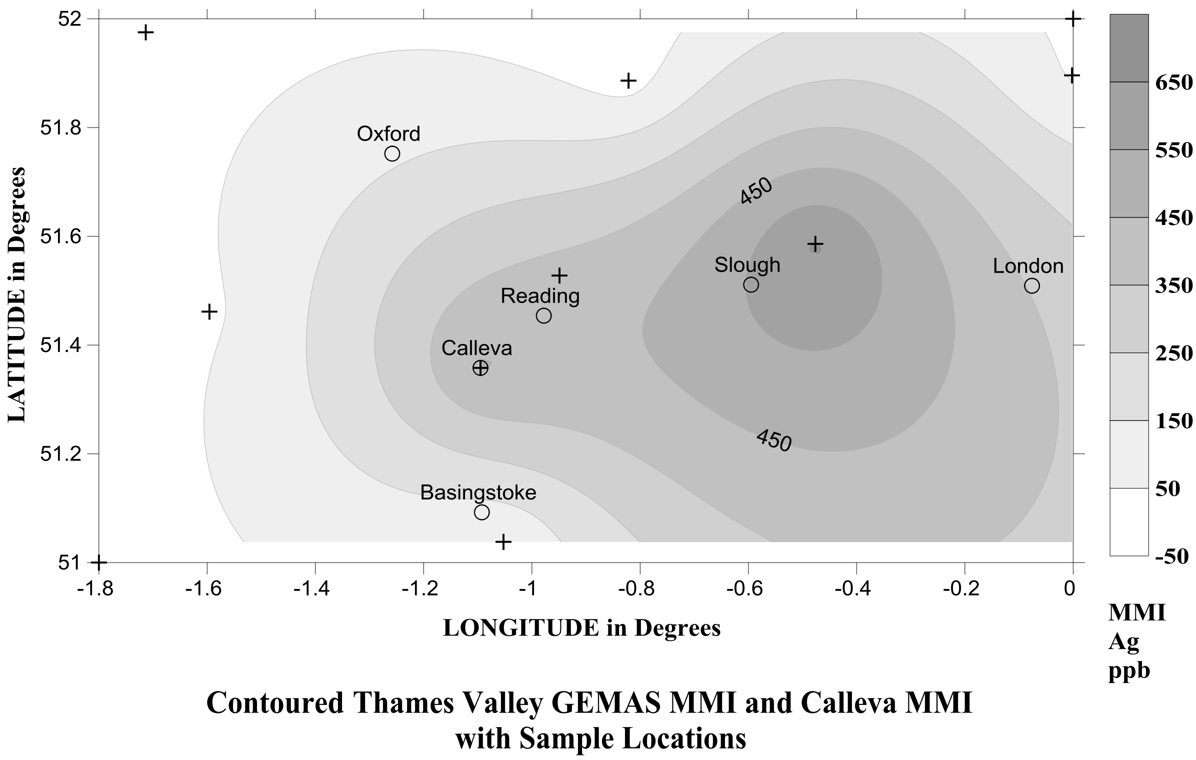


Figure 4. Comparison of Calleva and GEMAS samples - silver

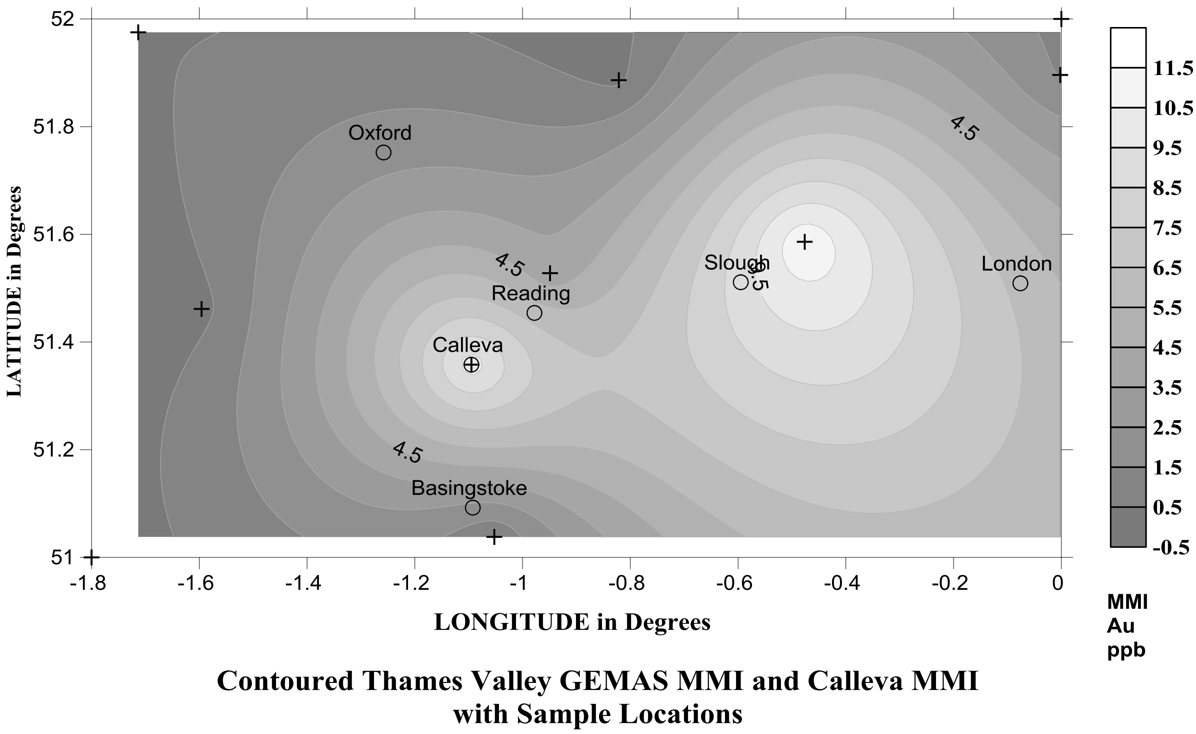


Figure 5. Comparison of Calleva and GEMAS samples - gold

The choice of CAL34 as representative of the local background sample within the Calleva walls was made after consideration of the location of the samples with low elemental concentrations. CAL34 was chosen as it is located at the margin of the survey area and is adjacent to sample CSINT1, which was collected by Speed (2013) to determine the strong acid digestion backgrounds.

The extent of geochemical difference between soils inside and outside the Calleva wall is well demonstrated by examination of the elemental log transformed differences between the local background sample CAL34 and regional background SLB Mean. The background inside the wall is substantially higher in Ag, Al, Au, Ca, Cu, Fe, K, Mg, P and Sn. Silver is 89× higher, Au is 162×, Cu is 12.6× and Sn is 5.2×.

Geochemical contrast and Elements of Interest in soils within Calleva walls

For this study, the Geochemical Contrast (GC) for each element has been defined as the value of the Mean of the 4th quartile (4QM) divided by the SLB Mean (which were not included in the calculation of the quartiles).

The elements Au (GC 141.7), Ag (GC 87.1), Cu (GC 12.7) and Sn (GC 12.0) are present in extremely anomalous (GC > 10) concentrations, Hg (GC 6.3) is strongly anomalous (GC > 5) whilst P (GC 2.9), Mo and Cd (GC 2.1), Bi and Pb (GC 2.0 which is low because the SLB samples are enriched in this element) are anomalous (GC 2 – 5). Both Sb and Zn are present in elevated concentrations. Whilst not consistently present in high concentrations, Cs, Ga, Nb and Ti were present in high concentration in a number of samples. Geochemical Contrast for a range of elements from Calleva soil samples is shown in Table 2.

Table 2. *Geochemical Contrast for Calleva soil samples*

ELEMENT	GEOCHEMICAL CONTRAST CALLEVA 4QM/SLB Mean
Ag	**87.1**
Au	**141.7**
Bi	2.0
Cd	2.1
Cs	1.1
Cu	**12.7**
Fe	1.0
Ga	0.9
Hg	6.3
Mo	2.1
Nb	0.8
Nd	1.1
P	2.9
Pb	2.0
Sb	1.7
Sn	**12.0**
Ti	0.6
Tl	1.2
Y	0.8
Zn	1.7
Zr	1.0

The very high Geochemical Contrast and elevated elemental mean for Au (mean 10.1 ppb), Ag (mean 459 ppb), Cu (5531 ppb) and Sn (31.6 ppb) clearly show that the Calleva town site is much enriched in these elements. Other 'elements of interest' considered to be of potential anthropogenic importance at Calleva are Bi, Cd, Cs, Ga, Hg, Mo, Nb, Nd, P, Pb (mean 1227 ppb), Sb, Ti, Tl, Y, Zn (2594 ppb) and Zr.

Component Analysis (PCA) of Calleva soils

To further investigate the potential association of different elements at Calleva, a Principal Component Analysis (PCA) was carried out (Figure 6).

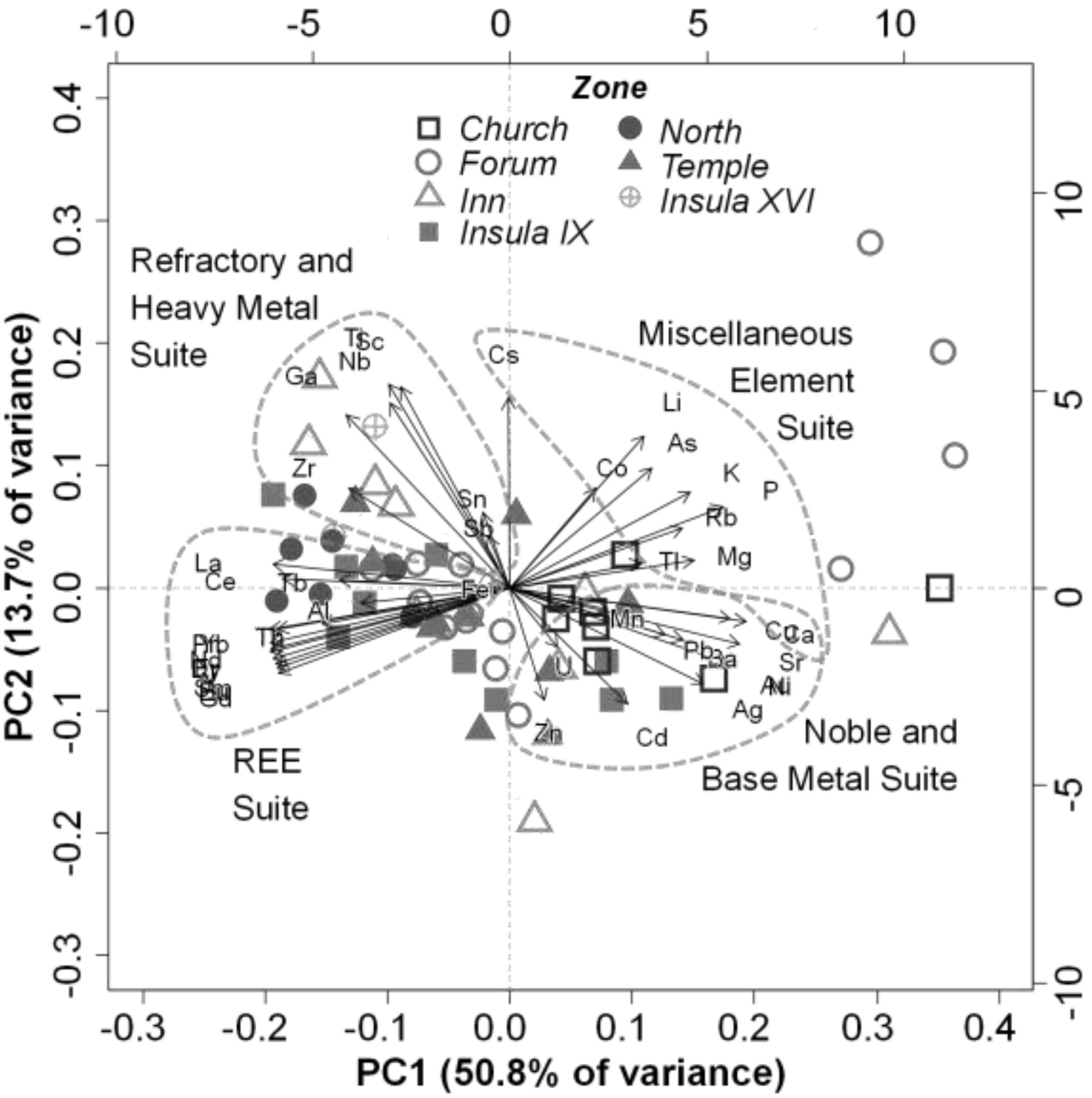


Figure 6. PCA biplot Calleva

The PCA confirmed and better defined the elemental associations deduced from correlation analysis and demonstrated a credible relationship between the spatial location of samples and their elemental suites. Five components explained > 80% of the multivariate variance with two components individually explaining more than 10% of the multivariate variance (PC1 50.8%; PC2 13.7%). The PC1-PC2 space provided adequate discrimination of element suites and observations, and higher order components are not presented. Chen (2016) note that the first two components are normally used and provide commentary on the use of ilr transformed data. PC1 was dominated by positive loadings for the elements Au, Ag, Ca, Cu, Ni and Sr and negative loadings for REEs and Th. PC2 was dominated by positive loadings for the refractory elements Ga, Nb, Sc and Ti and negative loadings for Ag, Cd and Zn. Four elemental groupings were inferred from the PCA vectors and these are shown in Figure 6. A group characterized by Ag, Au, Ba, Ca, Cu, Mn, Ni, Pb, Sr and possibly Cd, Zn and U has been named the Noble and Base Metal Suite. The elements Ga, Nb, Ti, Sc Sb and Sn have been designated the Refractory and Heavy Metal Suite. The REEs, Al, and Th form the REE Suite and a Group of elements consisting of Li, As, Co, K, P, Rb, Tl and Mg has been named the Miscellaneous Element Suite. Samples from some areas at Calleva (*e.g*. the Church, and the northern part of the walled area) plot close together on the PCA biplot and are therefore geochemically similar. Other groups of samples are spread across the PC1-PC2 space, representing intra-group compositional variability.

Elemental distribution in Calleva soils

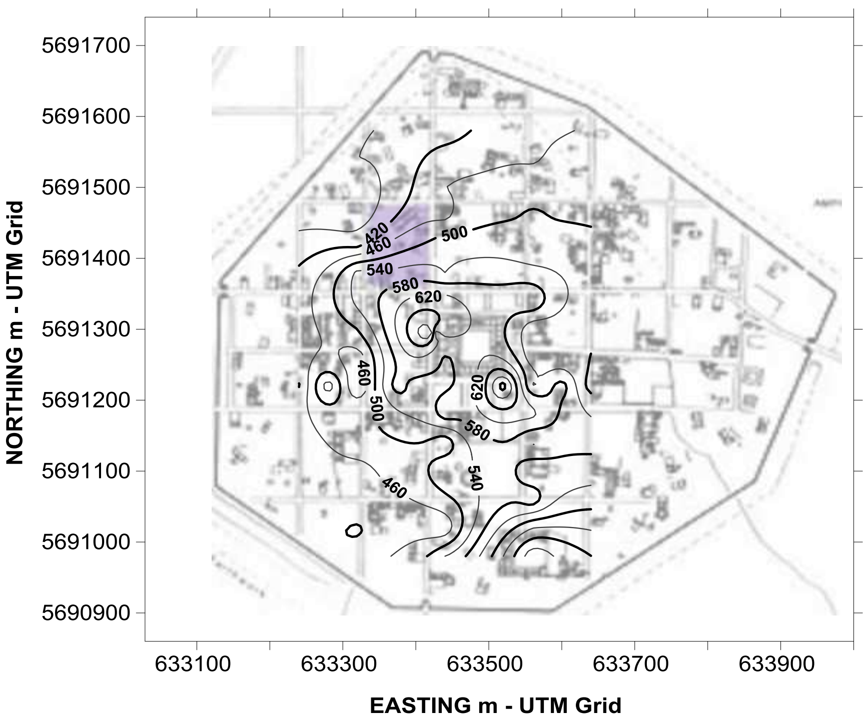


Figure 7. Element distribution plots - Ca ppm

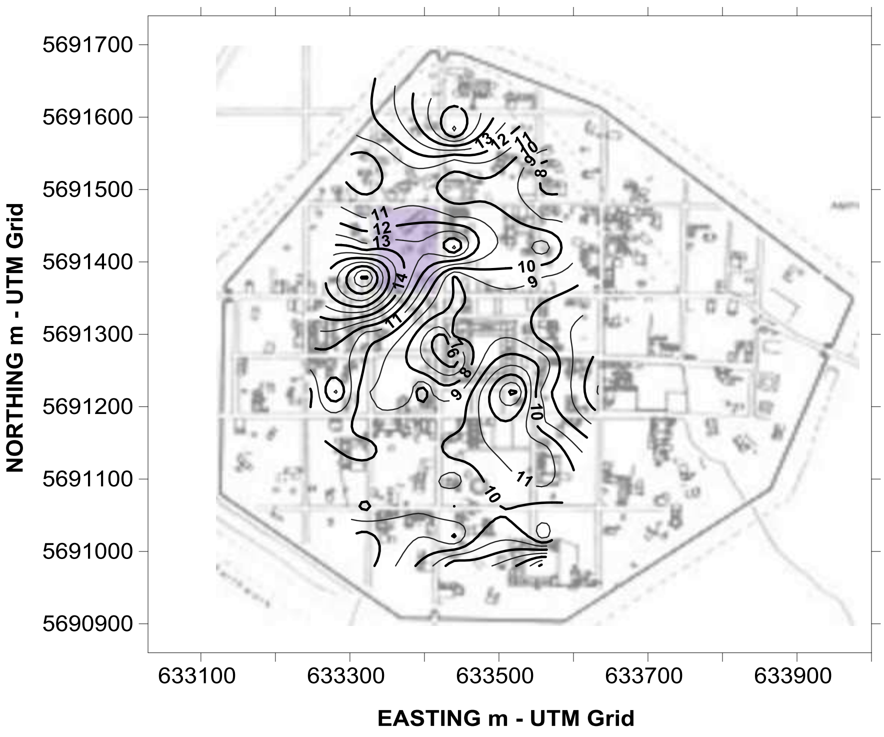


Figure 8. Element distribution plots - Au ppb

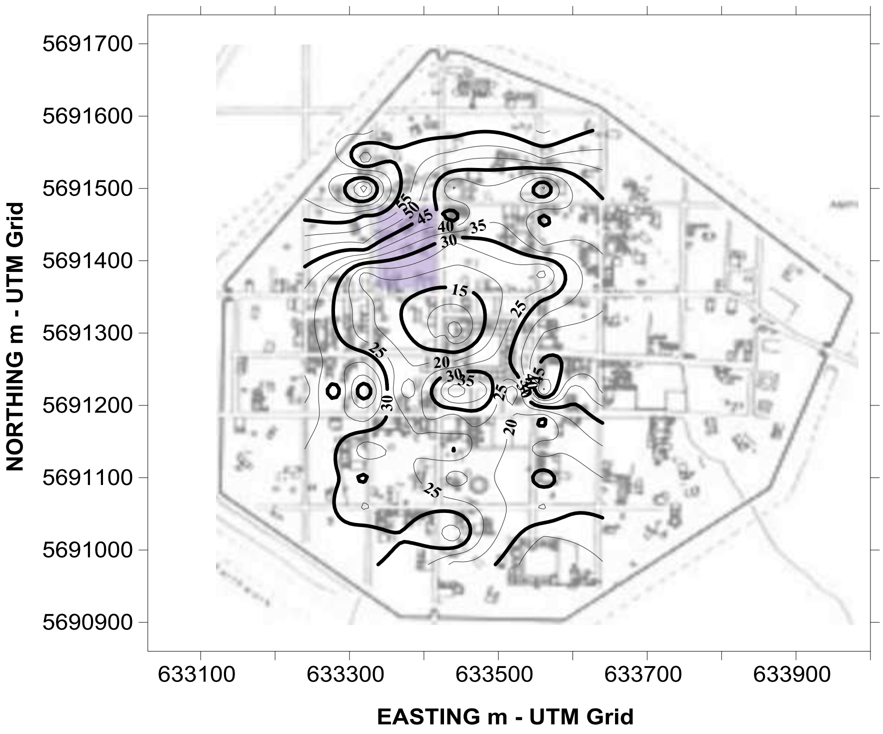


Figure 9. Element distribution plots - Sn ppb

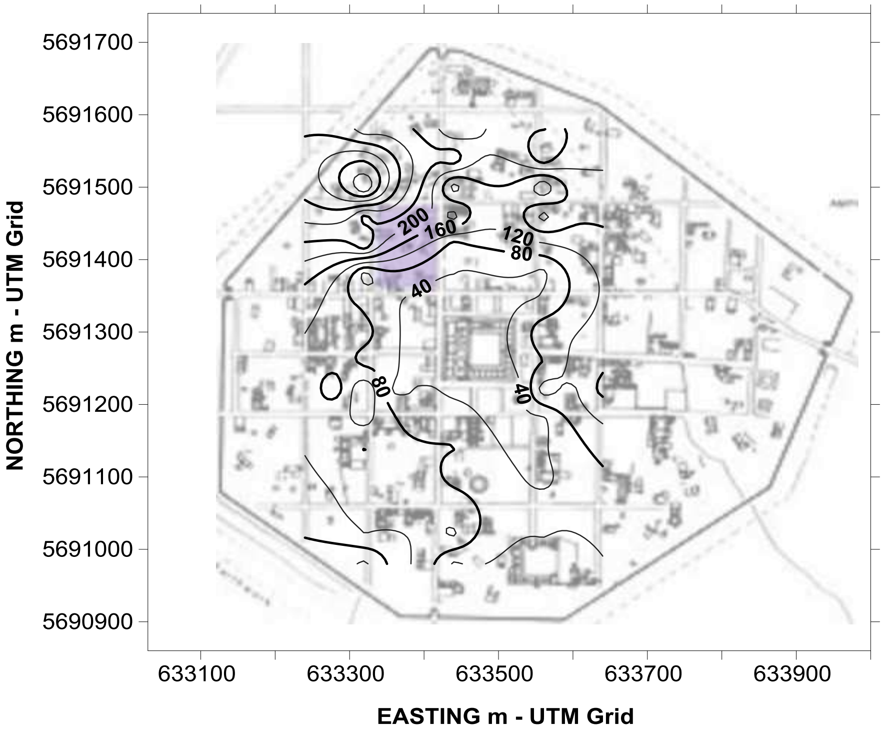


Figure 10. Element distribution plots - Ce ppb

To examine the patterns of areal distribution of the elements of interest and to visualise the correspondence between elemental concentrations and archaeological features, the raw data for each element were plotted as contours of concentrations. Plots for Ca, Au, Sn and Ce are shown in Figure 7, 8, 9 and 10. Contours were generated from point data using simple kriging with exponential variogram models, implemented using the R package 'geoR' (Ribeiro Jr. and & Diggle 2015). Variables to be predicted were log-transformed where necessary to remove skewness, and kriged predictions were made on a grid with 5 m spacing across the area sampled. Variogram models were fitted by Cressie's weighted least-squares after fitting a first-order polynomial trend surface, and with the maximum distance restricted to 40% of the greatest inter-sample distance, as recommended by Reimann et al. (2008).

The overall pattern of element distribution is one of an annulus of higher elemental concentrations surrounding a centre of generally lower values (except for Mo which exhibits a spot high in this area). The centre low is located over and around the Forum basilica, an area that was excavated and refilled after each field season in the 1980's and where previous excavation of this area and much of the rest of the Calleva site in the late 19th Century were not refilled for more than half a century after excavation. This phenomenon is well displayed by the distribution plots for Ca, Au, Sn and Ce which are shown in Figures 7, 8, 9, and 10.

Calcium is distributed fairly evenly across the site (Figure 7) in concentrations below that (MMI Ca<800ppm) normally attributed to calcium carbonate lithology. It is consistent with a basement of marine sands and silts of the Palaeogene (34-56 M.Y.), London Clay Formation and the Bagshot Formation. Both Ag and Au are present at Calleva in anomalously high concentrations and both display extremely elevated Geochemical Contrast (GC) values (Au = 142, Ag = 87). Silver shows a concentration range of 151- 1740 ppb, Au ranges from 0.05 - 20.6 ppb in concentration. The highest concentrations of Ag and Au are in samples CAL12 (Ag 1740 ppb, Au 20.6 ppb) and CAL18 (Ag 899 ppb, Au 17.3 ppb), both in the north of the site and near the Insula IX excavation where evidence of precious metal smelting in House1 has previously been investigated (Cook, Clarke et al. 2005, Cook, Banerjea et al. 2010, Cook, Clarke et al. 2014). The distribution map for Au is shown in Figure 8.

Whilst there is spatial coincidence between the higher values of both elements, the linear relationship between the two elements was found to be only moderate ($R^2 = 0.58$). The higher values are very likely to be a signature for buried precious metal-working hearths and /or smelting/cupellation products. This contention is supported by Northover and Palk (in Fulford and Timby 2000, pp. 395-420) who described crucibles related to the refining of Ag and Au on the site. Northover and Palk have also documented the occurrence of Ag coin moulds of late pre-Roman Age at Calleva.

The less elevated (but still quite high) Ag and Au concentration locations may represent different types of occurrence of the two metals (perhaps Ag coin manufacturing locations, Ag votives in temples) or may represent the widespread contamination of the site as a whole from the various forms of human activity that has taken place on the site and which is commonly recorded in soils (Acosta, Gabarrón et al. 2015, Mann and Sylvester 2015). The simple fact that Boon (2000) in Fulford and Timby (2000, p. 127) records the discovery of 575 Roman and Pre-Roman coins and (Fulford 2011) which documents the entire Antiquarian collection (over 12,000 coins) and lists the coin hoards (Ag and Cu-alloy) attest to the widespread distribution of Ag and Au at Calleva.

The overall content of MMI extractable Sn on the site is high (Figure 9), Sn has a Geochemical Contrast of 12, a mean concentration of 31.6 ppb and a concentration range of 5-89 ppb. Many of the higher Sn concentration samples are present in the north of the area along with several incompatible elements (an incompatible element is one that is unsuitable in size and/or charge to enter the cation sites of the minerals of which it is included. One group includes elements having large ionic radius such as K, Rb, Cs, Sr, and Ba. A second group includes elements of large ionic valences (or high charges), such Zr, Nb, Hf, REEs, Th, U and Ta).There are also additional, more widespread, higher Sn concentration samples, which are also high in Cu, Pb, Ag and Zn, to the east and south of the Forum Basilica. Northover and Palk (2000; pp 417, 419 *in* Fulford and Timby 2000) stated that tin was produced by the melting of bronze and the cupellation of silver from coinage containing tin in the area of the basilica. Tin was also used in the manufacture of pewter at the Forum basilica (Fulford 2011). It is therefore possible that at least some of the elevated concentrations for these elements may result from material dumped here during the excavations of the Forum basilica. However, it is likely that the treatment of Sn containing alloys was far more widespread across the site as shown, for example, by Cook et al. (2005), who recorded elevated Sn concentrations (90 ppm) from a hearth site within House 1 at the Insula IX excavation. The relatively wide-spread and elevated concentrations of Sn in the Calleva samples may be an indication of widespread Sn processing on the site, or of the presence of Sn bearing iron-smelting slag as was noted for German slags (Dill 2009) and also at Calleva (Fulford 2006, Fulford 2011, Fulford 2012).

Copper, Pb and Zn are elements that were of importance in the daily life activities at Calleva as made clear by Fulford and Timby (2000) and by Northover and Palk (in Fulford and Timby 2000, pp. 415-420) who described the bronze and pewter residues from the site.

Copper, Pb and Zn are all present in elevated concentration on the Calleva site as shown by their means (Cu 5531 ppb, Pb 1227 ppb, Zn 2594 ppb). The elevated Cu is consistent with its Geochemical Contrast of 12.7, whereas both Pb (GC 2.0) and Zn GC 1.7) display only modest Geochemical Contrast because the background levels of both of these elements are high and probably indicate some widespread local regional elevation in concentration, as noted above.

Copper and Pb are strongly concentrated in a group of samples to the east and southeast of the Forum Basilica. These samples also show elevated concentration of Ag, Sn and to a lesser extent Zn and may be indicative of bronze, pewter and silver processing in this area.

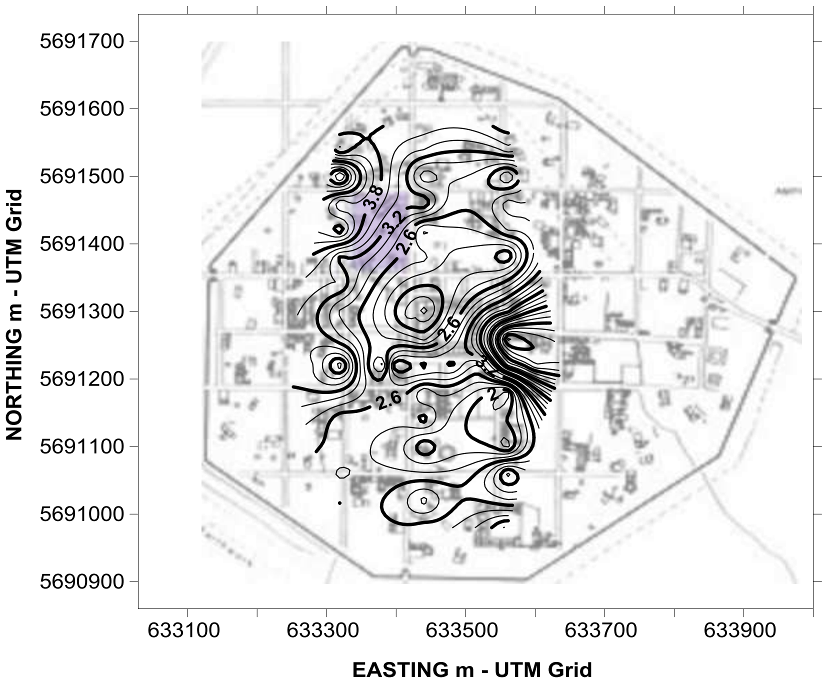
Copper is also highly elevated in the Au rich samples CAL12, 13 and 52, located to the west of the Forum Basilica on Insulae X, XIV and XVI. Lead is enriched in the samples in the northwest of the area and especially in CAL15 (highest Nb) and CAL13 (high Au) and in two samples in the south. Zinc shows little spatial association with either Cu or Pb and is not recorded as being a metal of importance at Calleva by Fulford and Timby (2000). Analyses of crucible residues and silver alloy samples returned Zn concentrations almost always < 0.1%. It is possible that the high concentrations of Zn may be related (in part at least) to the dissolution of high Zn containing slags derived from the processing of base and precious metal materials (Dill 2009).

The elements Zr, Ti, Th, Ti, Tl, Nb, Sn, Sc, Cr, Co, Sb, Bi, Ce, Nd (and all other REEs), many of which are incompatible elements (Brownlow 1996) , show a very close similarity in their spatial distribution. The distribution of Ce, which is representative of this suite of elements, is shown in Figure 10. The locus of enrichment for these elements is on, or around sample CAL15 which is located immediately northwest of the Insula IX excavation. This sample was taken from a location about 5m north of the soil dump from the Insula IX excavation and it is possible that at least some of the elemental enrichment noted may have come from material leached from the soil dump. Whilst the elements Cr, Th, Cs, Zr, Sb as well as Hg and Mn are concentrated around CAL15, others (Nb, Ti, Th, Ce as well as W and Li) display a broader spread of higher concentrations across the north of the sampled area.

Soil sample indices at Calleva

Whilst individual elements in a suite can be used to define an area of particular interest, examination of an elemental group (a composite index) can commonly provide better detail and definition of the phenomenon giving rise to the anomalous suite (Smith, Campbell et al. 1984, Mann, de Caritat et al. 2012). The analysis of the Calleva MMI data – correlation analysis, PCA and multi-element plots – leads logically to the construction and use of three such indices. The index points can be plotted and contoured to produce an Index plot. Plots for three suites; the Alloy Metal Suite, the Incompatible Element Suite (Incompatibles) and the Noble Metal Suite are shown in Figures 11, 12 and 13.

The Alloy Metal Index (AM) is an additive index composed of the sum of the normalized to the mean concentrations of Cu, Pb and Sn. Contours of the AM data points (CPM) are shown in Figure 11. They display three areas of high values. The highest are immediately east of the Forum Basilica, covering parts of Insulae V, VI and XXXIV. Sample CAL42, from this area, has the highest concentration of both Cu and Pb and also a high Sn content. The second area of elevated AM indices largely overlaps that of the major Incompatible Element (ICE) index zone, across the north of the site. The AM index peaks over sample CAL15 as does the ICE index. This is in part because CAL15 has the highest Sn content of all samples on the site and Sn is a component of both indices. The highest Cu value in this area is not in CAL15, although it does have a high Cu (and Pb) concentration, but is in CAL16 located 40m to the north. The third area of elevated AM values lies at the western margin of the sampled area. It is centred on CAL7 and is characterized by moderately high Cu and Sn concentrations. It is notable that the AM index values are low over the area of the Forum basilica.

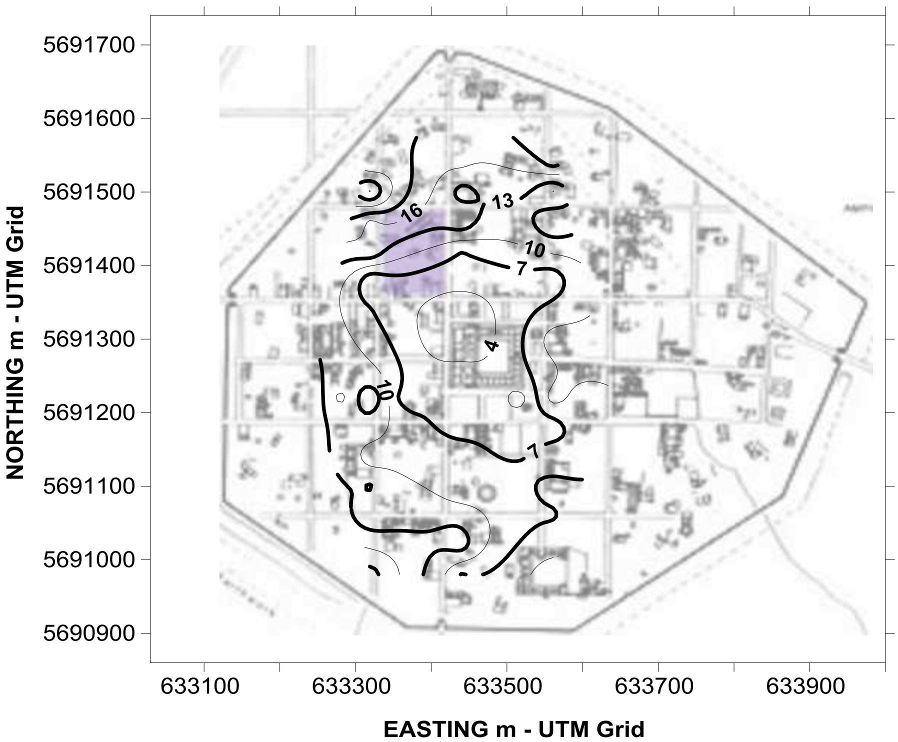


Alloy metal index

Figure 11. Composite Index plots for Alloy metals

The Incompatible Element Suite (Incompatibles) suite has been compiled into the contoured Incompatibles Element Index (ICE) and is shown in Figure 12. It is an additive index constructed by summing the normalized-to-the mean values for the elements Cs, Ga, Nb, Sc, Sn, Th, Ti, Tl, Y and Zr.

The ICE Index shows a strong focus on the area to the northwest of the Insula IX excavation and has a peak in sample CAL15. Elevated ICE index values extend in a broad zone from the CAL15 high in the northwest, east across the site (CAL 49, 50), north of Insula IX. There are also spot highs in the very south (CAL1) and west of the area (CAL51). This is reflective of the individual elemental distribution plots. CAL15 and samples immediately to the north (CAL16, 17) are located over Insula XXVI. The CAL1 anomaly is underlain by vacant land in Insula XXVIII whilst CAL51 appears to be coincident with a north-south road between Insulae XV and XVI. It is possible that the buildings beneath the elevated ICE Index points may have housed metal processing facilities. The ICE Index values are low over the area of the Forum basilica.

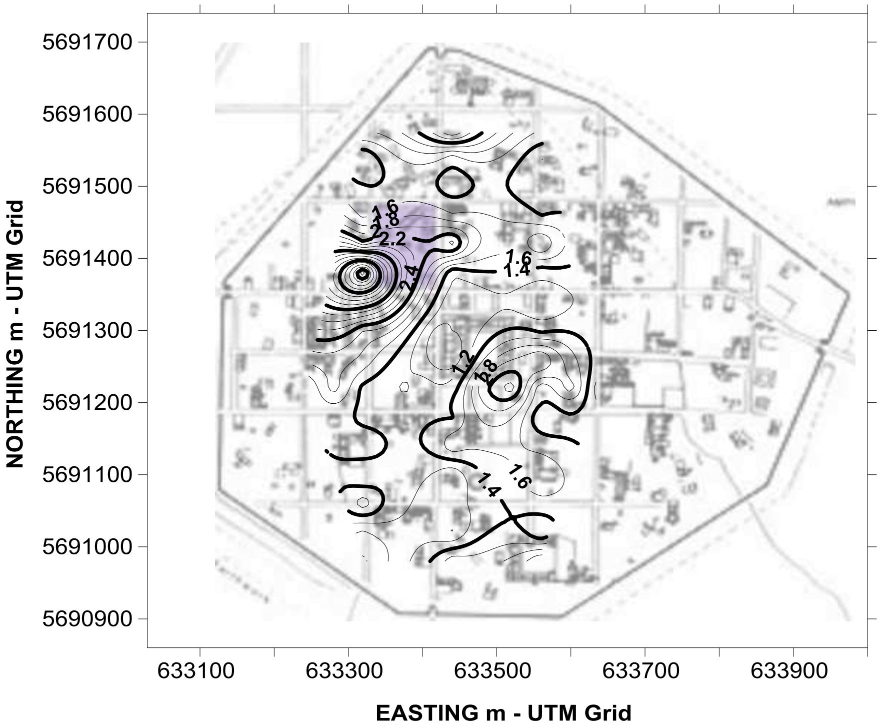


Incompatable element index

Figure 12. Composite Index plots for Incompatible elements

The separation of the distribution of the ICE and AM index anomalous areas as well as their overlap in one area is an indication that Sn is probably associated with at least two different metallurgical contexts at Calleva. The association of Cu with the Noble Metals , as for example in CAL59, is perhaps further evidence that various metal processing activities, together with a range of metals, were being treated at one site, either contiguously or at different times.

The Noble Elements Ag and Au have been compiled into the simple additive (elements normalized to the mean) Noble Metal Index (NM), the contoured values of which are shown in Figure 13.



Noble metal index

Figure 13. Composite Index plots for Noble metals

The NM index contours are centred primarily around three sites; sample CAL12 southwest of the Insula IX excavation, over a road between Insulae IX and X; sample CAL18 over vacant land in Insula XXIII and over what is depicted as a Church, south of the Forum basilica, in sample CAL59 (also elevated in Cu). The CAL12 anomaly is by far the strongest and its location close to the intersection of the major east-west and north-south Roman roads (which lead directly to the North and West town gates) indicates its importance. It is very likely to be a precious metal smelting/cupellation site. The NM Index values are low over the Forum basilica.

The Calleva Basilica Forum geochemical 'hole'

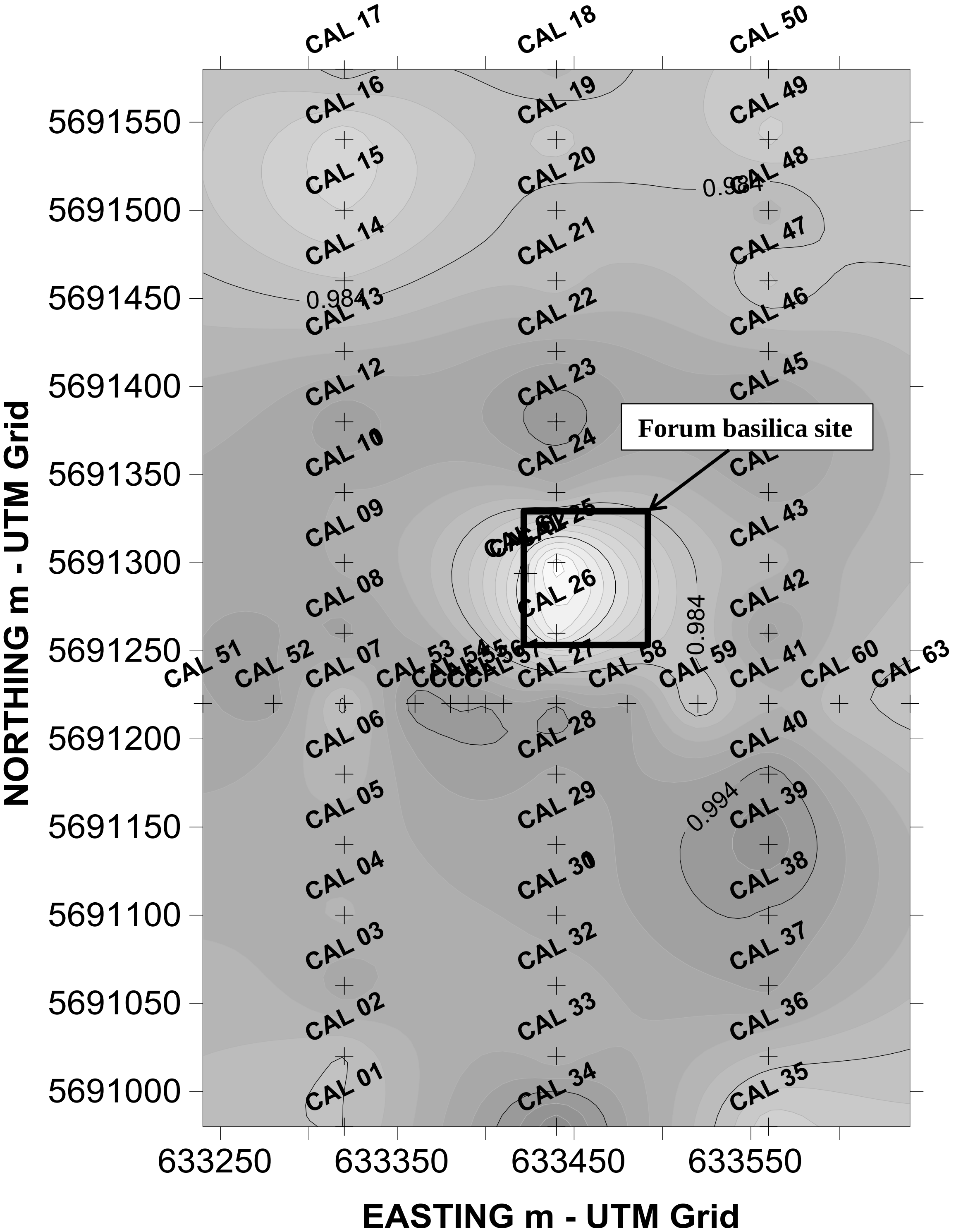


Figure 14. Degree of Geochemical Similarity

The elemental distribution plots and those for the spatial distribution of element indices reveals an area of relatively low concentration for almost all elements over the area where the excavation of the Forum basilica was undertaken (Fulford and Timby 2000). There are four samples in this geochemical 'hole'.

The 'depth' of this multi-element 'hole' is evident on the Degree of Geochemical Similarity (DOGS) (Mann, de Caritat et al. 2016) r correlation coefficient plot (Figure 14) using the local background sample CAL34 as the Comparator. This plot shows that the 'hole' is a distinct area of relatively low DOGS r values which coincides with the area of the Forum basilica excavation.

The histogram difference plot of the log transformed elemental means of the data set without the four 'hole' samples minus the log transformed elemental means of the full data set in shown in Figure 15. It demonstrates clearly that samples over the Forum Basilica excavation area are depleted in all except four elements (Ca, K, Mo and Mg). This accounts for the 'hole'. The reason why this 'hole' exists is discussed below.

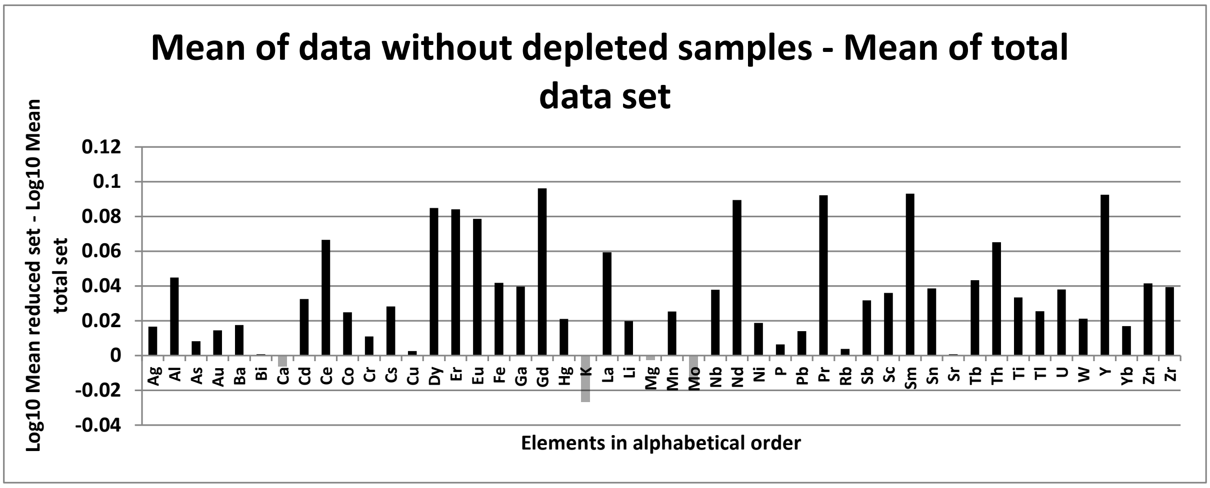


Figure 15. Difference plot - full data and no Forum samples

MMI analysis of material from previous House 1 floor samples

Elevated concentrations of many elements were measured across the sample suite as indicated by commonly high Mean value and the relatively low values for Geochemical Contrast for most elements shown in Table 3. There appears to be a general contamination of the House1 area by many elements and in particular Ag, Au, Cd, Cu, Hg, Mn, Ni, Pb, Sr, Y and Zn. This is consistent with elemental concentrations over the whole Calleva site.

Table 3. *Calleva House1 MMI Means and Geochemical Contrast*

	Ag	**Au**	**Cd**	**Ce**	**Co**	**Cu**	**Ga**	**Gd**	**Hg**	**La**	**Mg**	**Mn**	**Mo**	**Nd**	**Ni**	**Pb**	**Sm**	**Sr**	**Y**	**Yb**	**Zn**
MEAN	**87**	**9.4**	**37**	**28**	**22**	**6785**	**2.9**	**6**	**2.5**	**5.4**	**24**	**16275**	**5.8**	**17**	**980**	**181**	**4.6**	**2375**	**23**	**1.1**	**1439**
GEOCH. CONT. 4QM/1QM	**1.9**	**2.3**	**3**	**3.3**	**2.9**	**2.4**	**2.5**	**2.2**	**4**	**2.9**	**3**	**2.1**	**4.4**	**3.4**	**5.5**	**4.5**	**2.7**	**2.6**	**5.7**	**4**	**3**
MEANS																					
Clay rich	76	10	34	39	29	6145	3.3	7.5	3	6.8	28	18267	6.2	21	986	157	5.7	2472	28	1.1	1133
Gravel-CBM	65	5.5	16	6.6	8	3545	1.4	1.8	1.6	2.3	8.3	6613	2.5	4.8	216	95	1.5	1383	7	0.5	955
Slump	155	16	61	42	28	13305	4.5	9.5	2.5	8.5	30	28250	11	29	1460	185	7.5	3125	37	2	1940
Hearth	102	7.1	60	24	21	8665	3	6.5	3.5	4.5	36	17650	6.5	15	2012	420	4.5	3320	27	1.3	2825
MEAN RATIOS																					
Hrth/Grvl-CBM	1.6	1.3	4	3.4	2.6	2.4	2.2	3.7	2.8	2	4.3	2.7	2.6	3.1	**9.3**	4.4	3	2.4	2.4	2.5	3
Slmp/Grvl-CBM	2.4	3	4	**6.3**	3.5	3.6	3.3	**5.4**	2	3.8	3.6	4.3	4.2	**6.1**	**6.8**	2	**5**	2.3	2.3	4	2
Hrth/Clay	1.4	0.7	2	0.6	0.7	1.4	0.9	0.9	1.2	0.7	1.3	1	1.1	0.7	2	2.7	0.8	1.3	1	1.2	2.5
Slmp/Clay	2	1.6	2	1.1	1	2.2	1.3	1.3	0.8	1.2	1.1	1.6	1.7	1.4	1.5	1.2	1.3	1.3	1.3	1.9	1.7

The elevated concentration of Ag, Au, Cd, Cu, Hg, Mn, Mo, Ni, Pb, and Zn in the Slumped and Hearth/Hearth Related groups is indicative of the metal processing known to have been carried out in this area (Cook, Clarke et al. 2005). The elemental mean ratios of both of these groups when compared with the Gravel/CBM group are very high in REEs. This may be indicative of the presence of furnace slag or other metal processing by products as was noted for particular sites during the course of the Calleva reconnaissance MMI work. The enhanced value of most of these elements is partially explained by the nature of the materials in the various sample groups. The Gravel/CBM material consists predominantly of flint fragments (Gravel) and refractory brick/ceramic (CBM) both of which have little capacity to adsorb the ionic elemental species extractable by MMI. In contrast, the Slumped and Hearth/Hearth Related groups contain finer and more adsorbent materials. This feature is further demonstrated by the greater concentration of the elements in the Clay group than the Gravel/CBM group.

The associations between the elements in the House 1 floor samples have been examined by Pearson correlation analysis using the $\log_{10}$ transformed MMI data. Significant associations were observed despite the relatively low sample size (14 samples). There are strong correlations between Ag, Cd and Cu ($r > 0.80$). Copper also correlates strongly with Mn ($r = 0.86$) and moderately strongly with Mo ($r = 0.71$) and Ni ($r = 0.76$). Cadmium also correlates very strongly with Ni ($r = 0.93$) and strongly with Pb ($r = 0.81$) and Zn ($r = 0.88$). Lead shows a very strong association with Zn ($r= 0.90$), and a strong correlation with Cd ($r = 0.81$) and Ni ($r = 0.88$). Gold does not show significant correlations with other elements.

To examine the location of the areas of significant metal enrichment, individual element plots were made on the plan of the excavated buildings as shown in Cook, Clarke et al. (2005). Plots of Ag, Au, Cu and Hg are shown in Figures 16, 17, 18 and 19.

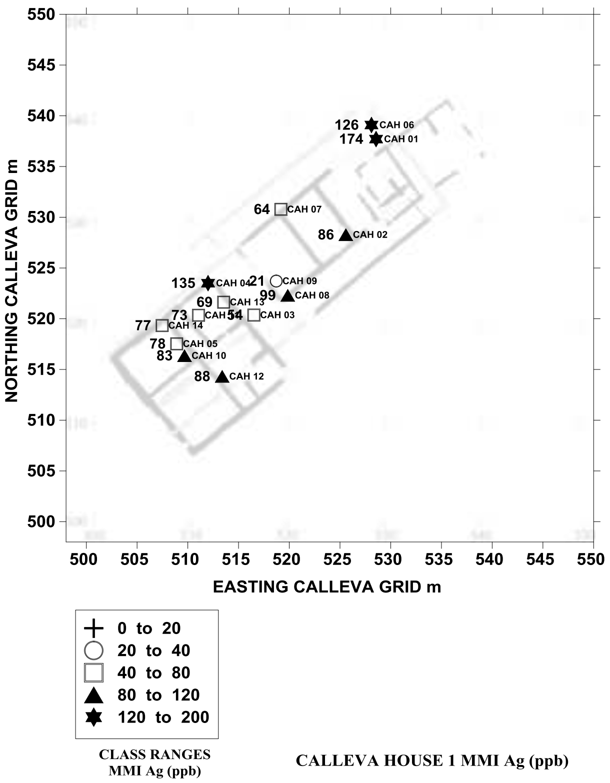


Figure 16. House 1 floor samples - MMI Ag

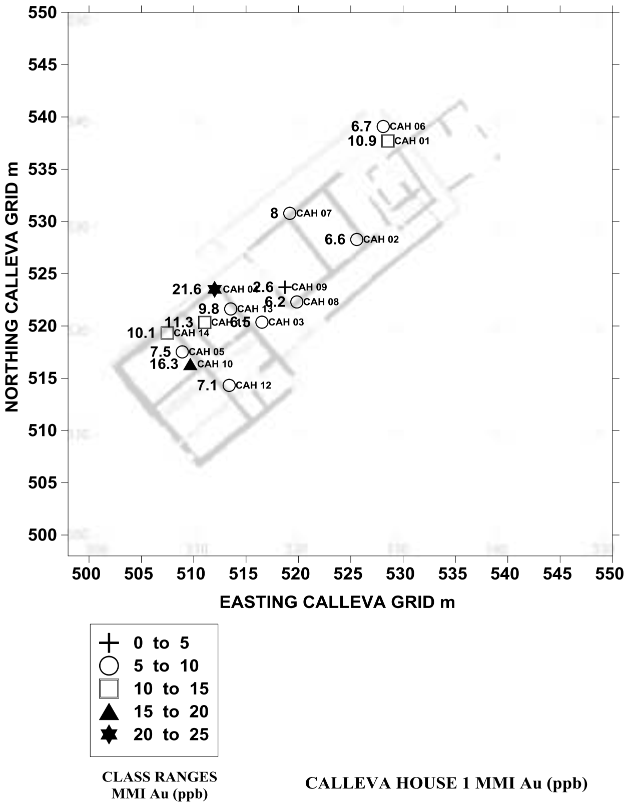


Figure 17. House 1 floor samples – MMI Au

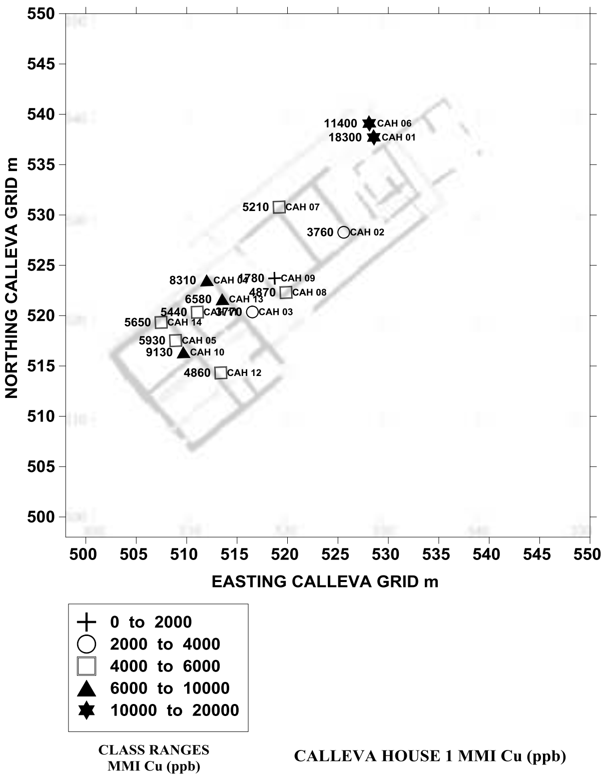


Figure 18. House 1 floor samples – MMI Cu

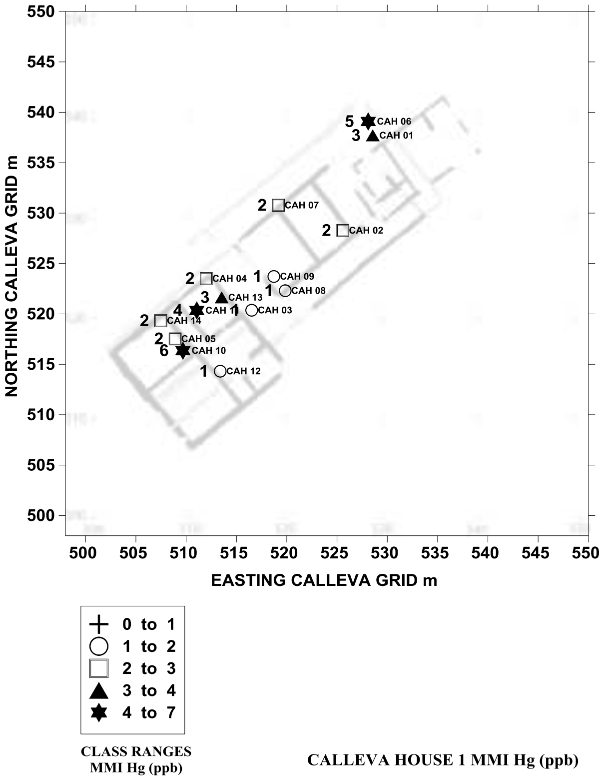


Figure 19. House 1 floor samples – MMI Hg

These plots show that hotspots for all the elements (except Au) occur around samples CAH01 and CAH6 at the northern margin of House1. There are two other significant hotspots in the southwest of the building. One is around CAH4 which is strongly anomalous in Ag and Au and also Cu, Cd, Cd, Mo, Ni and Mn. The second is centred on CAH10 which is enriched in Ag and Au as well as Cu, Cd, Hg, Mo, Ni, Mn, Pb, Sb and Sr. A number of other samples in this section of House1 are elevated in some elements (e.g. CAH11 is elevated in Hg, Mo, Ni, Pb and Sr) and it appears that this area was one of the active areas of metal-processing. Zinc is present in substantially elevated concentrations only in the multi-element anomalous samples CAH01 and CAH06. Samples CAH01 (Slump group) and CAH06 (Hearth group) are very close together and the signatures provided by these two samples are corroborative of the finding of Cook et.al. (2005) that this was the site of Hearth 3681, ‘a feature…0.94 m in diameter with a shallow depth of 0.05 m and a flat base. It was oriented north-east/south-west and produced within it an ash layer which contained numerous iron nails and some ironsmithing slags'. It was believed by Cook et al. (2005, pp 808-809) that this site was used for the working of Cu alloys (probably brass) in addition to iron-working.

DISCUSSION OF RESULTS

The high concentrations of Ag and Au observed in this study of soils at Calleva are remarkable. It is not a site where either of these two metals was mined. The soil anomalies are a clear demonstration that late Iron Age and Roman occupation brought with it quantities of these two noble metals. The soil and floor material composition suggests that metallurgical procedures were carried out at Calleva, probably producing jewellery and coinage. It is evident that the amount of attrition was significant, certainly enough to be easily detectable by modern analytical techniques. Mann and Sylvester (2015) showed that the amount of gold mined by the Romans was enough to explain the concentrations of gold in present-day European soils, at least over the extent of the former Empire, and that physical attrition (normal wear and tear) over a period of two thousand years is likely as the mechanism of redistribution. Interestingly in the GEMAS MMI study of European agricultural soils (Mann et al, 2015), high concentrations of gold and silver were not just observed at Slough west of London as depicted in Fig 4, but also at the GEMAS site nearest Paris, the former Roman town of Lutetia. Neither London nor Paris have geology normally associated with the mining of gold, but both have been sites of metallurgical re-working, accumulation and display of the precious metals over considerable periods of time.

The Calleva site also shows anomalous concentrations of base metals, HFSE's and other incompatible elements. The AM index, comprising Cu, Pb and Sn has three areas with anomalies, immediately to the east of the Forum basilica, and on the northern and western margins of the sampled area at Calleva. The Incompatible Elements Index, comprising Cs, Ga, Nb, Sc, Sn, Th, Ti, Tl, Y and Zr is high NW of Insula IX where it overlaps a high in the

AM index, suggesting a common source from anthropogenic activity. The Noble Metals Index comprising Ag and Au displays three anomalies, the highest of which is close to the E-W and N-S road intersection and suggestive of a smelting/cupellation site. The index plots as a whole provide substantial support for the hypothesis that the MMI multi-element geochemistry has detected signatures characteristic of metal processing from a number of specific sites at Calleva. In particular, the sites around samples CAL12, CAL15, CAL 42 and CAL59 are strongly indicative of metal processing and require follow-up using closer spaced sampling, followed by archaeological investigation.

The MMI soil analysis technique is based on sampling at the top of the capillary fringe, 10-25cm below ground surface where maximum accumulations of mobile ions have previously been observed (Mann, Birrell et al. 2005). Evidence from the glacial tills of Canada suggests that anomalies in this soil zone concentrate in a relatively short time (<8500 years) compared to most geological processes (Mann, Birrell et al. 2005). Much of the Calleva site has been disturbed in the last century or so, and more comprehensively over the Forum basilica area some 40 years ago by the Fulford archaeological team (Fulford & Timby, 2000). It is interesting and instructive that in the Forum basilica area, four MMI samples taken at 10-25cm showed very significantly reduced signals for most elements compared to the remainder of the Calleva site. This suggests that the recent comprehensive overturning of the soil profile has redistributed material from the horizon of ion accumulation; segregation within the profile has not recovered within a 40 year period. That the signals at or near surface are derived from capillary rise and evaporation from primary material beneath, is also demonstrated by the experiment in which samples from the floor of excavated House 1 were subjected directly to MMI analysis.

Correlation analysis results of these floor samples strongly indicate that the processing of Ag, Au and Cu (with their geochemically coherent associates Cd, Hg, Mo, Mn, Ni and Zn) was carried out in and around House1 during the Roman Period. The lack of association of Pb with Ag or Au or other elements (except its geochemical associate Sb) is indicative that there was probably no cupellation of Pb, for the extraction of Ag, carried out on this site in association with the other metal processing works. The enrichment of Au, Ag, Cu, and Hg in hearth slump sites is indicative of metal processing, whilst enrichment of REEs in hearth /slump sites is suggestive of slag, in an overall process which has similarities to fractionation of elements from melts during geological processes.

Whilst comparable data on individual samples are not available, in general the spatial distribution of MMI results are comparable with XRF and acid digest results of Cook et al (2005) with respect to the anomalous elements and distribution of anomalies associated with old hearths.

CONCLUSIONS

Calleva Atrebatum is a relatively well-documented archaeological site. Despite this, or perhaps in some cases as a result of this, a number of conclusions regarding the present study can be made.

The work has demonstrated that MMI soil analysis provides high geochemical contrast and definition of soil geochemical anomalies for Au, Ag, Cu, Sn and Hg. These anomalies provide prime targets for further investigation at this archaeological site.

The noble metals Au and Ag have been shown to display discrete, high concentration soil geochemical anomalies at locations in the centre of the Roman town which are underlain by Roman buildings, and which may have been metal processing sites. In addition, these elements show widespread elevated concentrations both within and just outside the town walls in a manner consistent with well-established human occupation. This is probably indicative of dispersal of detrital material produced during metal processing as well as attrition of these elements from jewellery and coinage and confirms a strong Roman connection with the soil anomalies.

The presence of well-defined base metal anomalies and surrounding anomalies for incompatible elements, possibly slag derived, is indicative of significant smelting operations on site. Further investigation of these anomalies is warranted as it may provide evidence of much greater and more widespread metal processing on this site than has hitherto been considered.

The low concentration of many elements in the four samples from the discrete, disturbed area encompassing the Forum basilica suggests that >40 years is required for re-establishment of MMI anomalies in the soil surface zone after the disruption caused by excavation and strongly suggests that sampling of soils for MMI analysis should be done prior to their disturbance, not after archaeological excavation

This work has demonstrated that ligand-based partial extraction geochemistry provides useful diagnostic evidence of anthropogenic activity of various types within and around the Calleva archaeological site.

The use here, for the first time, of MMI analysis to provide useful archaeological information of excavated material (rather than soil) such as building floor detritus, dust and debris derived from metal working is a new and potentially very significant medium for application of MMI technology.

ACKNOWLEDGEMENTS

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