

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

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14 **Published in *Geochemistry: Exploration, Environment, Analysis*, 18, 2018 [https://](https://doi.org/10.1144/geochem2017-009)**  
15 **[doi.org/10.1144/geochem2017-009](https://doi.org/10.1144/geochem2017-009) © Geological Society of London 2017**

16

17 **Abstract**

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

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

32

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

35

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

40 With the advent of Inductively Coupled Plasma Mass Spectrometry (ICPMS) in the late  
41 twentieth century, analytical chemistry, particularly that of geological and archaeological  
42 materials underwent a major transformation. Within the space of ten years detection limits  
43 for a large number of elements were lowered, in many cases to the part per billion (ppb) level  
44 and simultaneous analysis of solutions containing over 50 elements was able to be undertaken  
45 in less than a minute of analysis time. One of the initial problems encountered was how to

46 dissolve geological solids, and to maintain the analytes in solution for the duration of the  
47 analysis (Hall 1998). Strong acid digests, including aqua regia (AR) were an obvious choice,  
48 although it is of note that for over 50% of elements aqua regia digestion is less than 50%  
49 efficient (e.g. Mann et al 2015), i.e. the analysis is not total. In a partial extraction, in which  
50 less aggressive chemicals are used and for which extraction efficiencies are even lower,  
51 (Stanley and Noble 2008) showed that signal to background contrast ratios in a geochemical  
52 soil survey across mineralisation were increased relative to that for acid digestion. It is likely  
53 that this is due to the fact that high concentrations of non-diagnostic background metal from  
54 within (most) soil mineral grains is not included in the analysis viz. “analytical noise” is  
55 significantly reduced.

56 The Mobile Metal Ion (MMI) solution (Mann 2010) is a neutral-alkaline partial extraction  
57 solution comprising a number of strong complexing ligands which can simultaneously extract  
58 base metals, precious metals, transition metals, lanthanides (rare earths) and some actinides  
59 and non-metals from soil material, and maintain them in solution for ICPMS analysis. As  
60 such it has seen widespread application in mineral exploration (Mann et al, 1998), in  
61 continental surveys (Mann et al, 2012, Reimann et al, 2014) and recently in archaeology  
62 where it has been utilized to define multielement soil geochemical anomalies associated  
63 with Roman metal- processing at a Roman site in Somerset (Sylvester, Mann et al. 2017). In  
64 each of these cases soil sampling was undertaken in the capillary fringe zone, 10-25cm below  
65 surface, and the ability of MMI to discriminate in favour of more recently arrived (in some  
66 cases anthropogenically derived) ions into this layer has been noted (Mann, Birrell et al.  
67 2005).

68 MMI ligand-based partial-extraction soil geochemistry has been shown to be valuable in  
69 defining and delineating multielement anthropogenic anomalies associated with the partially  
70 excavated Roman metal processing site at St. Algar’s Farm, Somerset, UK (Sylvester, Mann

71 et al. 2017). This paper presents results of an MMI soil geochemical sampling programme  
72 carried out within the walls of the Roman town of Calleva Atrebatum in Hampshire, UK,  
73 which has undergone substantial excavation since the late 19<sup>th</sup> century. The purpose of the  
74 work is to determine the existence, persistence, strength and multi-element nature of soil  
75 anomalies produced on site by Roman and pre-Roman metallurgical activities, and in areas  
76 where recent excavation has taken place to examine the effect of that on any pre-existing soil  
77 geochemistry.

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

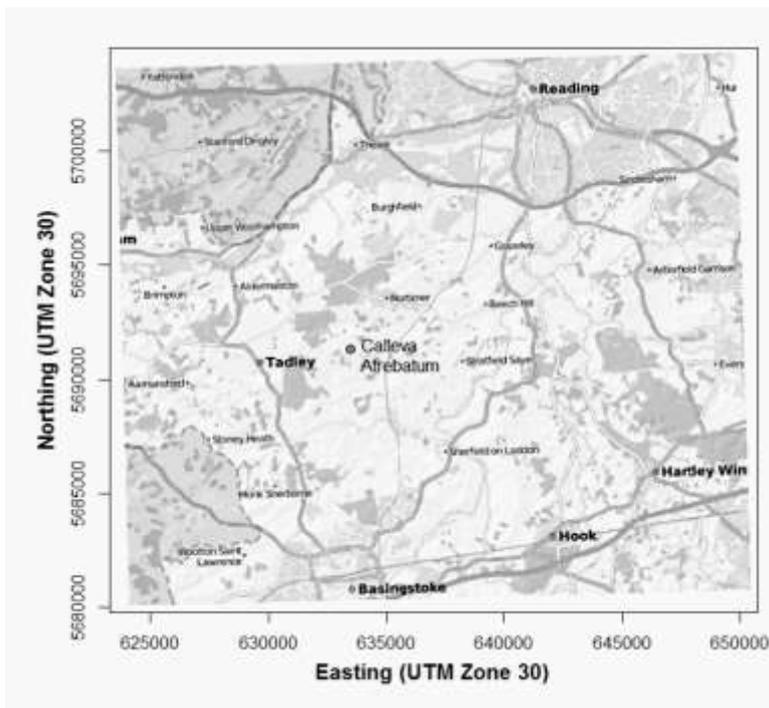
## 82 **MATERIALS AND METHODS**

### 83 *Site description*

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

93 The site consists of two fenced fields separated by an east west farm road. The site is  
94 enclosed by the Roman wall which is intact over most of its length. The wall stands to a

95 height of up to 4.5 m, 3 m wide at the base, narrowing to 2.3 m at the upper level. It is  
96 composed of flint with levelling courses of stone slabs (of a variety of stone types) bound by  
97 a lime mortar. There is a large square area in the northern field where recent archaeological  
98 excavation has been carried out within Insula IX. The greater part of the site has undergone  
99 archaeological excavation in various forms for more than a century. All of those older  
100 diggings have been refilled and repastured.



101  
102 Figure 1. Location map of Calleva Atrebatum

103  
104 The fields in which the Monument and associated archaeology occur are under permanent  
105 grass cover and used for cattle grazing. The site has a maximum elevation of approximately  
106 100m above mean sea level and slopes gently to the south where the elevation is about 90m  
107 a.s.l.

108 The soil at the Calleva site is brown-grey stony loam. It is freely draining, slightly acid, with  
109 low fertility and low carbon. The soils sampled were physically unstratified and below the

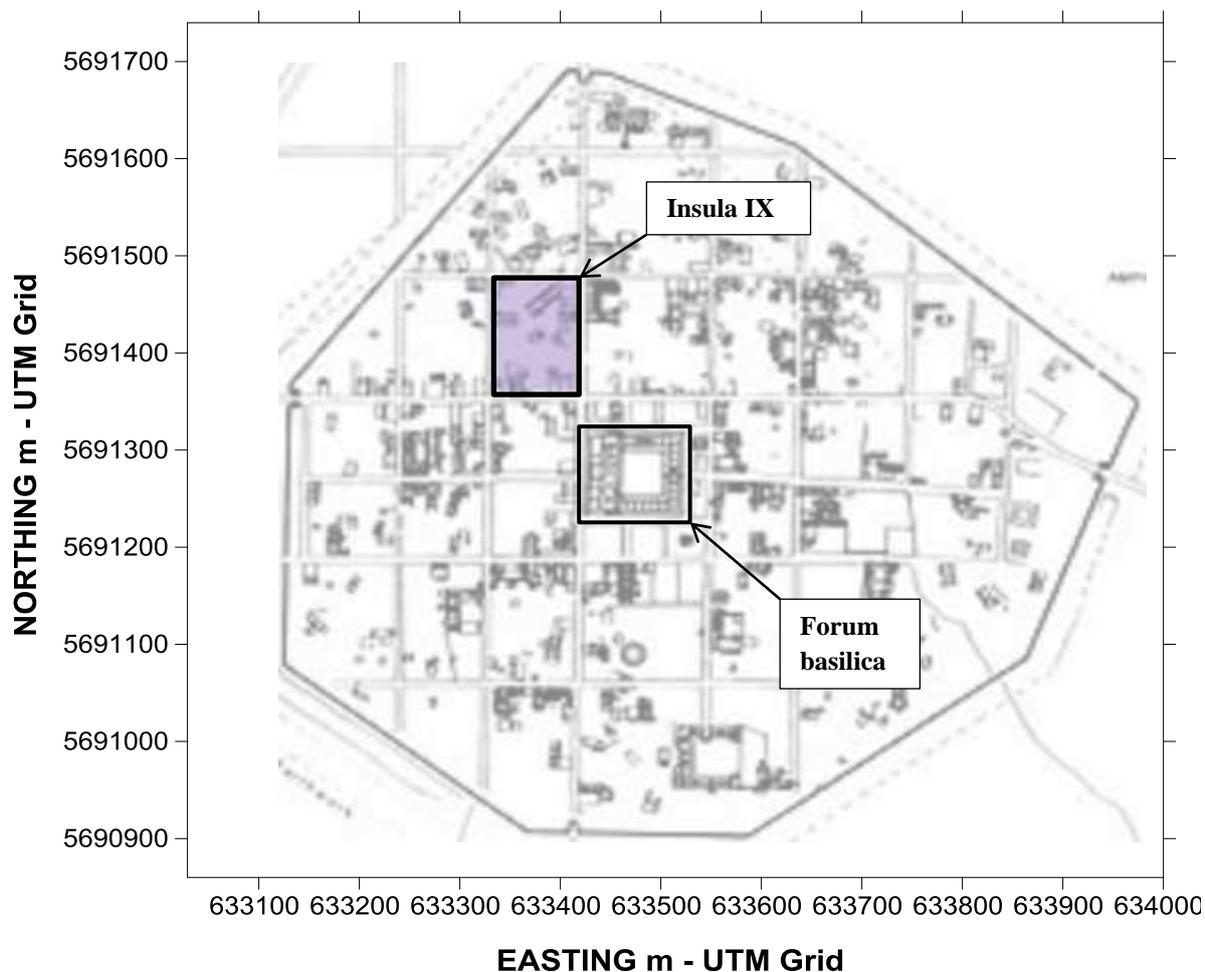
110 grass roots were visually unstructured. Because the site has been ploughed and extensively  
111 excavated and refilled with the plough soil, there is little or no evidence of a humic near  
112 surface layer.

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

118 A large Roman town site (Calleva) was known to antiquarians from at least medieval times  
119 (Norden 1595). Undocumented excavation was carried out on the site before 1864 and then  
120 between 1864 and 1878 by Joyce (1881). This was followed by major investigations by the  
121 Society of Antiquaries between 1890 and 1909 which revealed a plan of the masonry –  
122 founded buildings within the walled town. The results of that work were regularly reported in  
123 the journal *Archaeologia* (Fox 1895, Fox and Hope 1905) and were evaluated by Boon  
124 (1974).

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

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

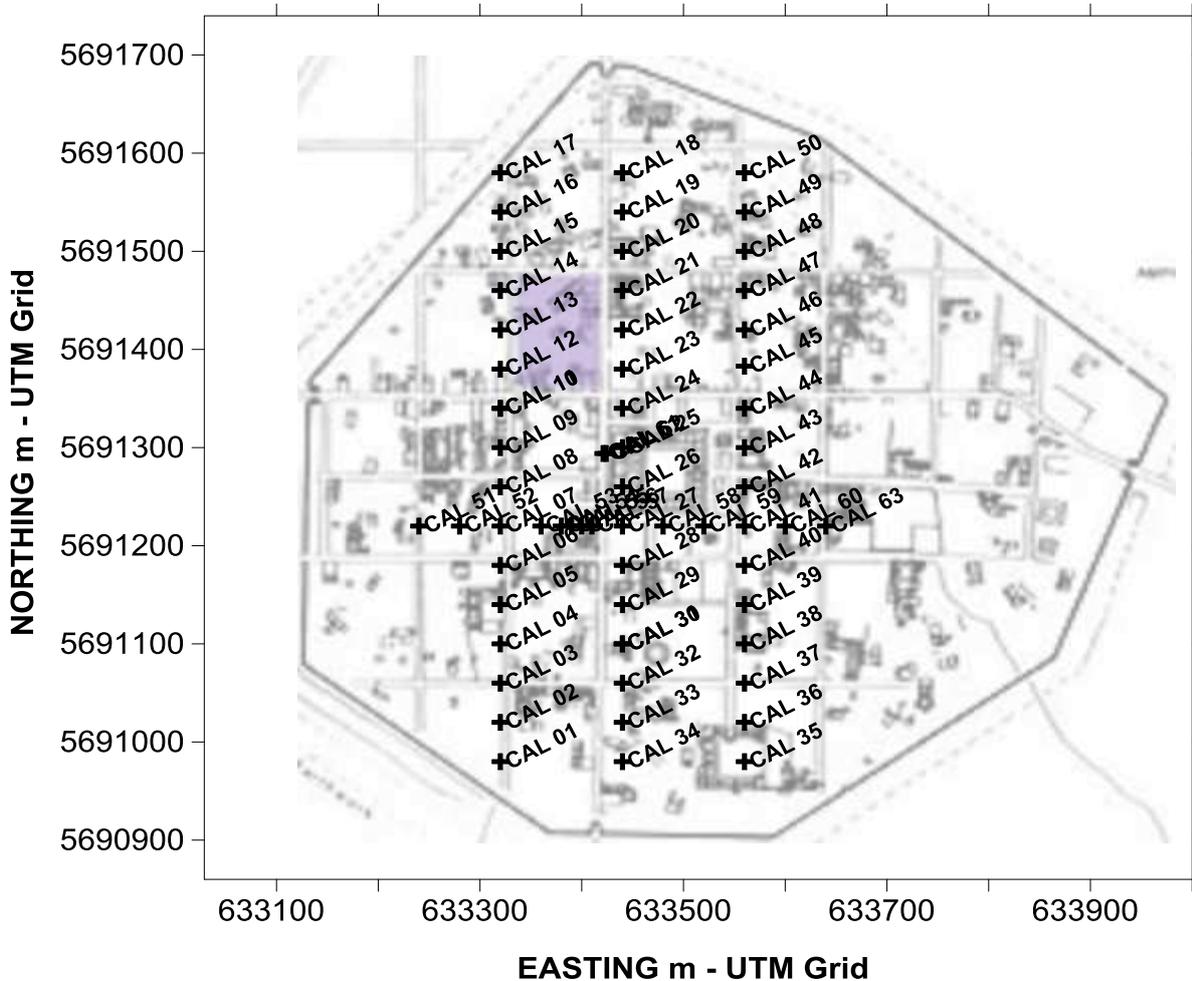


139  
140 Figure 2. Plan of the Roman town of Calleva Atrebatum

141  
142 ***Sampling***

143 A soil geochemical sampling programme, using Mobile Metal Ion (MMI) analysis was  
144 undertaken over an area (40ha.) of Silchester Roman Town to obtain a broader knowledge of

145 the relationship between the archaeology and the geochemistry of the site as a whole.  
 146 Samples were collected at 40m intervals (reduced to 10 m in critical areas) on three north-  
 147 south lines spaced at 120m with an east-west tie line. The sampling covered an area 600 x  
 148 400m and resulted in the collection of 63 samples. Sample locations are shown on Figure 3.



149  
 150 Figure 3. Calleva sample number location plan

151  
 152 The sampling was not representative of the underlying town, as this was a pilot study. The  
 153 north-south lines run along the edges of town blocks; the single east-west line crosses the  
 154 middle of some blocks and most blocks are represented by only 3 or 4 samples. The results of  
 155 the sampling pertain to a 4-500 year urban history and do not relate to any particular points in

156 time. A much greater number of samples, at a higher density will be required to provide more  
157 detail of the underlying town.

158 Splits of fourteen samples of floor debris previously collected during the excavation of House  
159 1 (within Insula IX) were analysed using Mobile Metal Ion (MMI) to further investigate the  
160 nature of the geochemical anomalies associated with metal-processing investigated by Cook  
161 et al., (2005, 2010). The materials sampled were predominantly clay floor, some with a  
162 gravel component (CAH 07, 10, 11, 12, 13, and 14). Some (CAH 02, 03, 08 and 09) were  
163 gravel and/or common building material (CBM) mixtures. CAH 01 and 04 were mixtures of  
164 slumped materials and building demolition products. Sample CAH 06 was a hearth sample  
165 and CAH 05 was heat altered material below a hearth. These groups are labelled the Clay  
166 group, the Gravel/CBM group, the Slumped group and the Hearth/Hearth Related group in  
167 this document.

## 168 *Analysis*

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

180 the final database with values set to  $0.5 \times \text{LDL}$ . Percentage differences between field  
181 duplicates were found to be within acceptable limits.

## 182 **RESULTS**

183 Five additional samples were collected from outside the Calleva town walls specifically for  
184 providing MMI elemental background values and to establish “threshold values”. Speed  
185 (2013) demonstrated that the Calleva site, within the town walls, is polluted with a range of  
186 elements and that background elemental concentrations could only be obtained by sampling  
187 outside the walls.

### 188 *Determination of background and thresholds for the Calleva soil sample survey*

189 Examination of the analyses of background samples SLB1-5 revealed that SLB1 and SLB4  
190 had significantly ( $>70\%$ ) different concentrations for a number of elements (18 for SLB1 and  
191 16 for SLB4) from the other three samples, which were similar in composition, having  
192 mutual ‘r’ correlation co-efficient values ranging from 0.93 to 0.98. As a result the Silchester  
193 regional geochemical background (SLB) for each element was defined as the mean of  
194 samples SLB2, 3 and 5; the background values for selected elements are shown as Calleva  
195 SLB mean in the first column of Table 1.

196 As a further control, the SLB elemental concentrations were compared with the 1<sup>st</sup> Quartile  
197 Mean (1QM MMI) concentrations obtained from agricultural soil samples taken in south-east  
198 England, over rocks of similar age and lithology as part of the Geochemical Mapping of  
199 Agricultural Soils (GEMAS) regional soil sampling programme (Reimann, Birke et al. 2014a,  
200 Reimann, Birke et al. 2014b). The GEMAS means of 55 samples are shown in column 2 of  
201 Table 1. For the elements Ce, Cs, Ga, Nb, Sn and Ti, the background values at Calleva (SLB  
202 Mean) are significantly higher ( $> 10\times$ ) than the GEMAS 1QM for SE England, as indicated

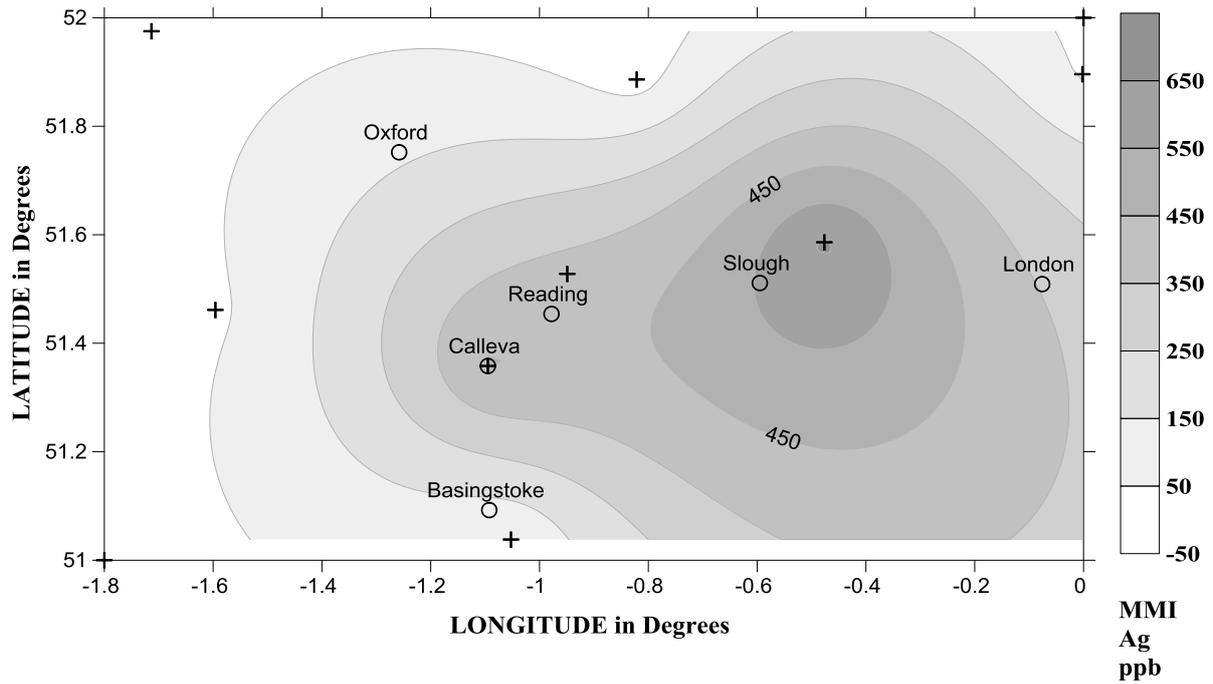
203 by the ratios in column 3. The elemental means of the 63 samples within the Calleva walls  
 204 are shown in column 4 of Table 1 and clearly show that for Ag, Au, Cu, and Sn the  
 205 background values of columns 1 and 2 are exceeded by a factor of 3. Chen (2016) discuss  
 206 different methods of determining threshold values in their study which are in general between  
 207 two and four times when based on the Mean+2STD and Mean+2MAD methods. Given that  
 208 here we are comparing the mean of all samples at Calleva, not individual anomalies, these  
 209 backgrounds establish “suitable threshold”.

210 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	<b>17.9</b>
Cu	5531	613	750	0.8
Cs	5	9	1	<b>9.0</b>
Fe	599365	90000	16000	5.6
Ga	11	24	1.5	<b>16.0</b>
Hg	1.25	0.50	0.5	1.0
Nd	83	148.00	113	1.3
Nb	4.42	10.50	0.25	<b>42.0</b>
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	<b>17.9</b>
Ti	816	2798	12.31	<b>227.3</b>
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

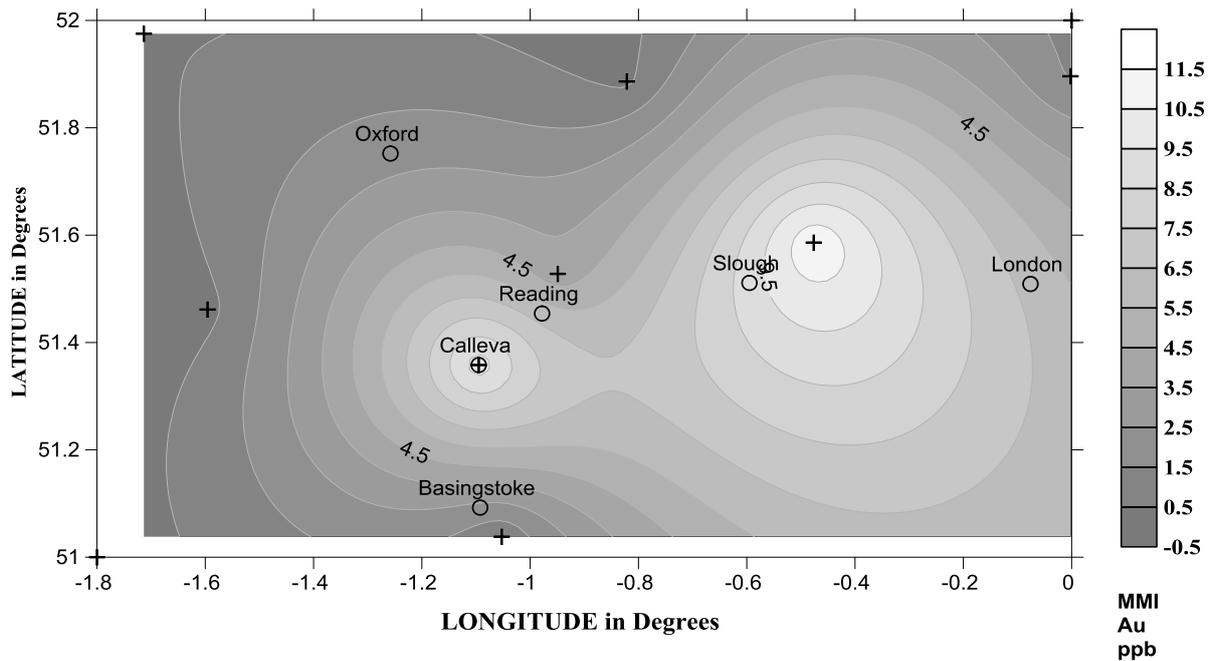
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212 Figures 4 and 5 show the plot of MMI Ag and Au concentrations (respectively) in the  
 213 regional GEMAS samples taken from south east England. When viewed in conjunction with  
 214 Table 1, these distribution maps show that the Calleva sample means for Ag and Au are  
 215 higher than for neighbouring GEMAS samples, except for that near Slough, west of London.  
 216



**Contoured Thames Valley GEMAS MMI and Calleva MMI  
with Sample Locations**

217  
 218 Figure 4. Comparison of Calleva and GEMAS samples - silver



**Contoured Thames Valley GEMAS MMI and Calleva MMI with Sample Locations**

219

220 Figure 5. Comparison of Calleva and GEMAS samples - gold

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

226 The extent of geochemical difference between soils inside and outside the Calleva wall is  
 227 well demonstrated by examination of the elemental log transformed differences between the  
 228 local background sample CAL34 and regional background SLB Mean. The background  
 229 inside the wall is substantially higher in Ag, Al, Au, Ca, Cu, Fe, K, Mg, P and Sn. Silver is  
 230 89× higher, Au is 162×, Cu is 12.6× and Sn is 5.2×.

231

232

233

234 ***Geochemical contrast and Elements of Interest in soils within Calleva walls***

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

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

245 Table 2. *Geochemical Contrast for Calleva soil samples*

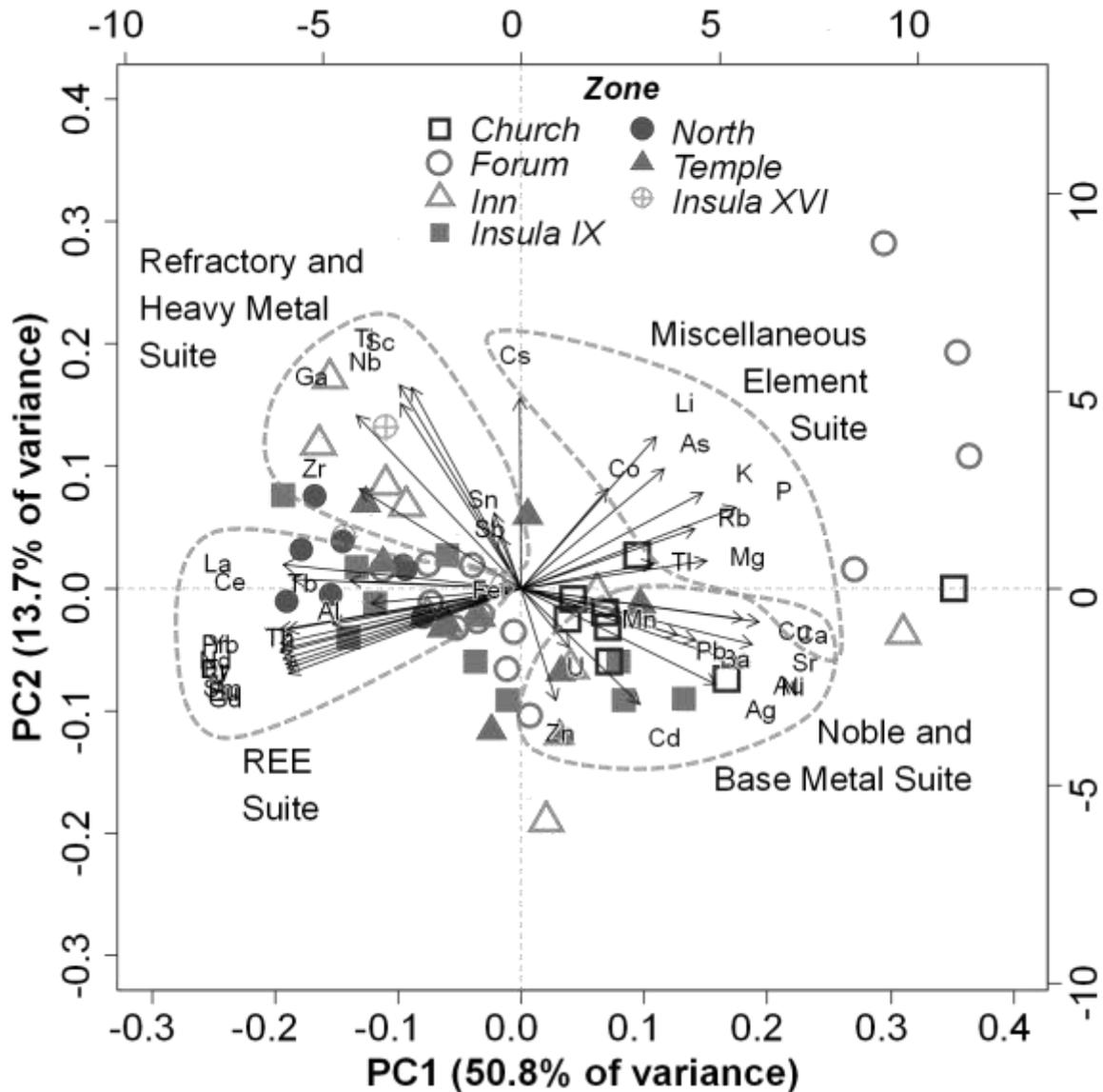
ELEMENT	GEOCHEMICAL CONTRAST CALLEVA 4QM/SLB Mean	246 247
<b>Ag</b>	<b>87.1</b>	
<b>Au</b>	<b>141.7</b>	
<b>Bi</b>	2.0	248
<b>Cd</b>	2.1	
<b>Cs</b>	1.1	
<b>Cu</b>	<b>12.7</b>	249
<b>Fe</b>	1.0	
<b>Ga</b>	0.9	
<b>Hg</b>	6.3	250
<b>Mo</b>	2.1	
<b>Nb</b>	0.8	251
<b>Nd</b>	1.1	
<b>P</b>	2.9	
<b>Pb</b>	2.0	252
<b>Sb</b>	1.7	
<b>Sn</b>	<b>12.0</b>	
<b>Ti</b>	0.6	253
<b>Tl</b>	1.2	
<b>Y</b>	0.8	
<b>Zn</b>	1.7	254
<b>Zr</b>	1.0	

255

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

261 ***Component Analysis (PCA) of Calleva soils***

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



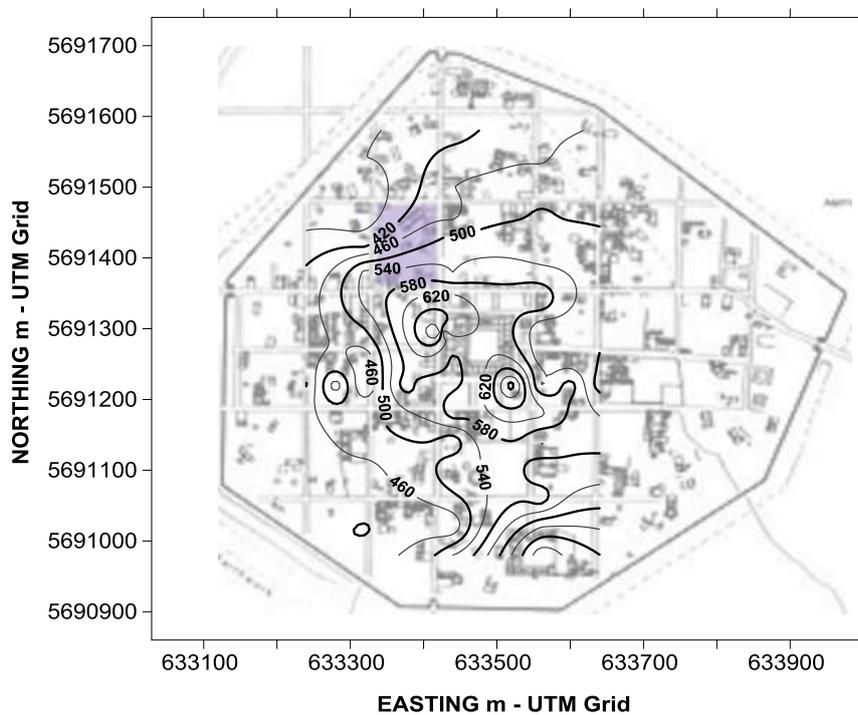
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265 Figure 6. PCA biplot Calleva

266 The PCA confirmed and better defined the elemental associations deduced from correlation  
 267 analysis and demonstrated a credible relationship between the spatial location of samples and  
 268 their elemental suites. Five components explained > 80% of the multivariate variance with  
 269 two components individually explaining more than 10% of the multivariate variance (PC1  
 270 50.8%; PC2 13.7%). The PC1-PC2 space provided adequate discrimination of element suites  
 271 and observations, and higher order components are not presented. Chen (2016) note that the  
 272 first two components are normally used and provide commentary on the use of ilr  
 273 transformed data. PC1 was dominated by positive loadings for the elements Au, Ag, Ca, Cu,

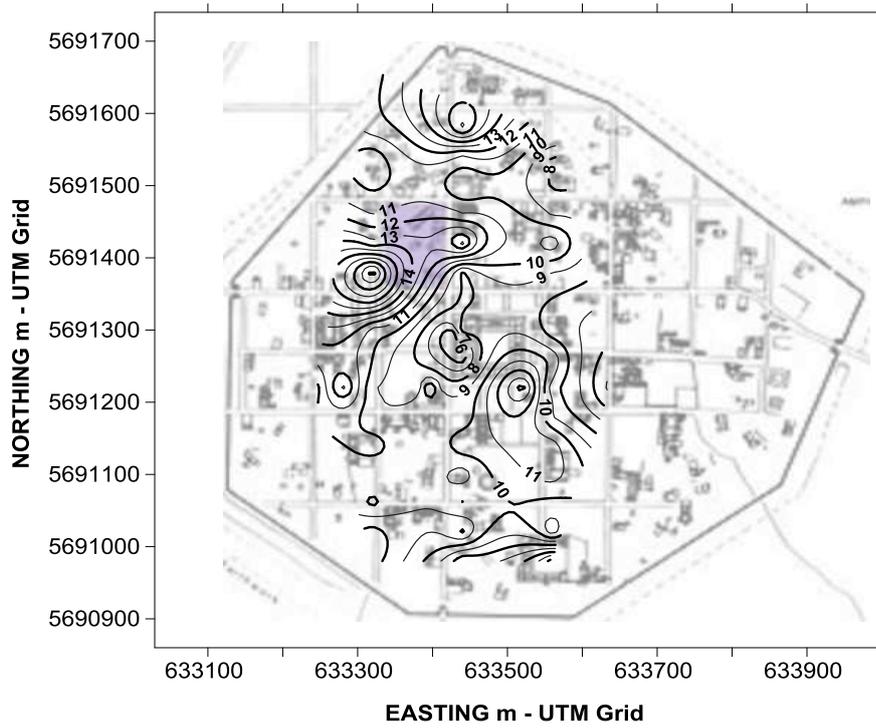
274 Ni and Sr and negative loadings for REEs and Th. PC2 was dominated by positive loadings  
275 for the refractory elements Ga, Nb, Sc and Ti and negative loadings for Ag, Cd and Zn. Four  
276 elemental groupings were inferred from the PCA vectors and these are shown in Figure 6. A  
277 group characterized by Ag, Au, Ba, Ca, Cu, Mn, Ni, Pb, Sr and possibly Cd, Zn and U has  
278 been named the Noble and Base Metal Suite. The elements Ga, Nb, Ti, Sc Sb and Sn have  
279 been designated the Refractory and Heavy Metal Suite. The REEs, Al, and Th form the REE  
280 Suite and a Group of elements consisting of Li, As, Co, K, P, Rb, Tl and Mg has been named  
281 the Miscellaneous Element Suite. Samples from some areas at Calleva (*e.g.* the Church, and  
282 the northern part of the walled area) plot close together on the PCA biplot and are therefore  
283 geochemically similar. Other groups of samples are spread across the PC1-PC2 space,  
284 representing intra-group compositional variability.

285 ***Elemental distribution in Calleva soils***



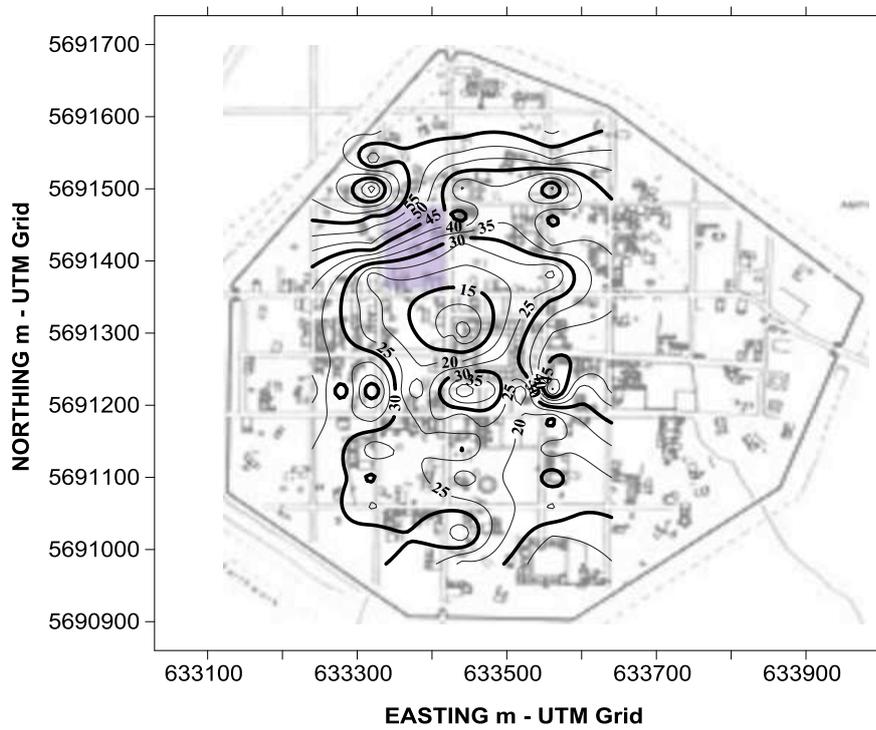
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287 Figure 7. Element distribution plots - Ca ppm



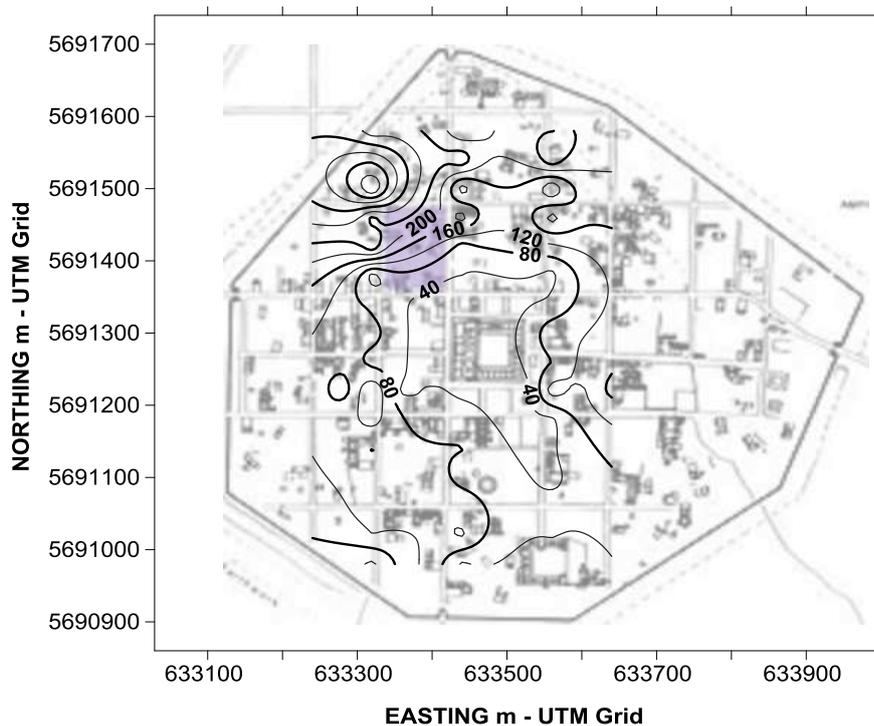
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289 Figure 8. Element distribution plots - Au ppb



290

291 Figure 9. Element distribution plots - Sn ppb



292

293 Figure 10. Element distribution plots - Ce ppb

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

304 The overall pattern of element distribution is one of an annulus of higher elemental  
 305 concentrations surrounding a centre of generally lower values (except for Mo which exhibits  
 306 a spot high in this area). The centre low is located over and around the Forum basilica, an

307 area that was excavated and refilled after each field season in the 1980's and where previous  
308 excavation of this area and much of the rest of the Calleva site in the late 19<sup>th</sup> Century were  
309 not refilled for more than half a century after excavation. This phenomenon is well  
310 displayed by the distribution plots for Ca, Au, Sn and Ce which are shown in Figures 7, 8, 9,  
311 and 10.

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

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

331 The less elevated (but still quite high) Ag and Au concentration locations may represent  
332 different types of occurrence of the two metals (perhaps Ag coin manufacturing locations, Ag  
333 votives in temples) or may represent the widespread contamination of the site as a whole  
334 from the various forms of human activity that has taken place on the site and which is  
335 commonly recorded in soils (Acosta, Gabarrón et al. 2015, Mann and Sylvester 2015). The  
336 simple fact that Boon (2000) in Fulford and Timby (2000, p. 127) records the discovery of  
337 575 Roman and Pre-Roman coins and (Fulford 2011) which documents the entire  
338 Antiquarian collection (over 12,000 coins) and lists the coin hoards (Ag and Cu-alloy) attest  
339 to the widespread distribution of Ag and Au at Calleva.

340 The overall content of MMI extractable Sn on the site is high (Figure 9), Sn has a  
341 Geochemical Contrast of 12, a mean concentration of 31.6 ppb and a concentration range of  
342 5-89 ppb. Many of the higher Sn concentration samples are present in the north of the area  
343 along with several incompatible elements (an incompatible element is one that is unsuitable  
344 in size and/or charge to enter the cation sites of the minerals of which it is included. One  
345 group includes elements having large ionic radius such as K, Rb, Cs, Sr, and Ba. A second  
346 group includes elements of large ionic valences (or high charges), such Zr, Nb, Hf, REEs, Th,  
347 U and Ta). There are also additional, more widespread, higher Sn concentration samples,  
348 which are also high in Cu, Pb, Ag and Zn, to the east and south of the Forum Basilica.  
349 Northover and Palk (2000; pp 417, 419 *in* Fulford and Timby 2000) stated that tin was  
350 produced by the melting of bronze and the cupellation of silver from coinage containing tin in  
351 the area of the basilica. Tin was also used in the manufacture of pewter at the Forum basilica  
352 (Fulford 2011). It is therefore possible that at least some of the elevated concentrations for  
353 these elements may result from material dumped here during the excavations of the Forum  
354 basilica. However, it is likely that the treatment of Sn containing alloys was far more  
355 widespread across the site as shown, for example, by Cook et al. (2005), who recorded

356 elevated Sn concentrations (90 ppm) from a hearth site within House 1 at the Insula IX  
357 excavation. The relatively wide-spread and elevated concentrations of Sn in the Calleva  
358 samples may be an indication of widespread Sn processing on the site, or of the presence of  
359 Sn bearing iron-smelting slag as was noted for German slags (Dill 2009) and also at Calleva  
360 (Fulford 2006, Fulford 2011, Fulford 2012).

361 Copper, Pb and Zn are elements that were of importance in the daily life activities at Calleva  
362 as made clear by Fulford and Timby (2000) and by Northover and Palk (in Fulford and  
363 Timby 2000, pp. 415-420) who described the bronze and pewter residues from the site.  
364

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

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

374 Copper is also highly elevated in the Au rich samples CAL12, 13 and 52, located to the west  
375 of the Forum Basilica on Insulae X, XIV and XVI. Lead is enriched in the samples in the  
376 northwest of the area and especially in CAL15 (highest Nb) and CAL13 (high Au) and in two  
377 samples in the south. Zinc shows little spatial association with either Cu or Pb and is not  
378 recorded as being a metal of importance at Calleva by Fulford and Timby (2000). Analyses of  
379 crucible residues and silver alloy samples returned Zn concentrations almost always < 0.1%.

380 It is possible that the high concentrations of Zn may be related (in part at least) to the

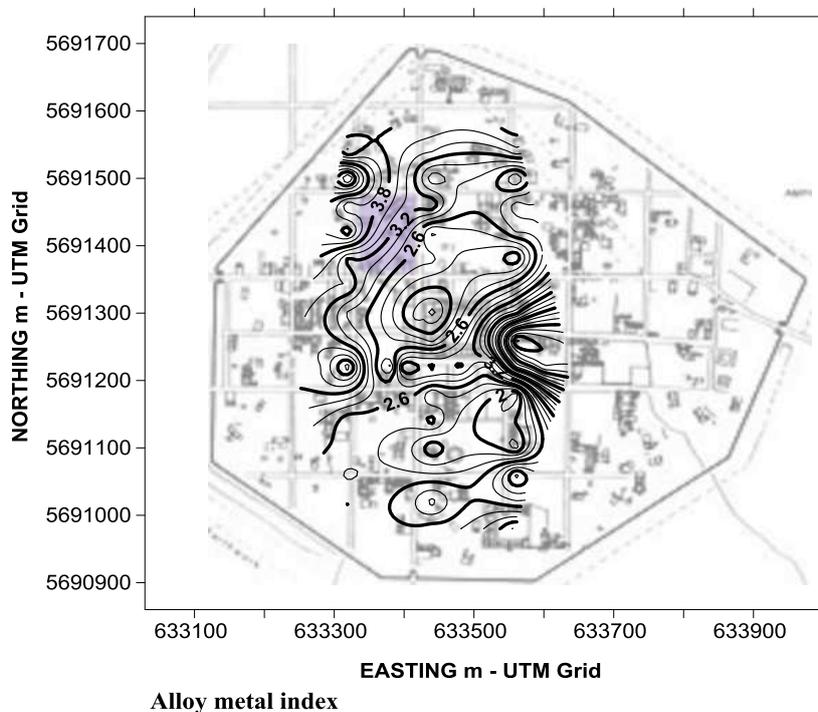
381 dissolution of high Zn containing slags derived from the processing of base and precious  
382 metal materials (Dill 2009).  
383 The elements Zr, Ti, Th, Ti, Tl, Nb, Sn, Sc, Cr, Co, Sb, Bi, Ce, Nd (and all other REEs),  
384 many of which are incompatible elements (Brownlow 1996) , show a very close similarity in  
385 their spatial distribution. The distribution of Ce, which is representative of this suite of  
386 elements, is shown in Figure 10. The locus of enrichment for these elements is on, or around  
387 sample CAL15 which is located immediately northwest of the Insula IX excavation. This  
388 sample was taken from a location about 5m north of the soil dump from the Insula IX  
389 excavation and it is possible that at least some of the elemental enrichment noted may have  
390 come from material leached from the soil dump. Whilst the elements Cr, Th, Cs, Zr, Sb as  
391 well as Hg and Mn are concentrated around CAL15, others (Nb, Ti, Th, Ce as well as W and  
392 Li) display a broader spread of higher concentrations across the north of the sampled area.

### 393 *Soil sample indices at Calleva*

394 Whilst individual elements in a suite can be used to define an area of particular interest,  
395 examination of an elemental group (a composite index) can commonly provide better detail  
396 and definition of the phenomenon giving rise to the anomalous suite (Smith, Campbell et al.  
397 1984, Mann, de Caritat et al. 2012). The analysis of the Calleva MMI data – correlation  
398 analysis, PCA and multi-element plots – leads logically to the construction and use of three  
399 such indices. The index points can be plotted and contoured to produce an Index plot. Plots  
400 for three suites; the Alloy Metal Suite, the Incompatible Element Suite (Incompatibles) and  
401 the Noble Metal Suite are shown in Figures 11, 12 and 13.

402 The Alloy Metal Index (AM) is an additive index composed of the sum of the normalized to  
403 the mean concentrations of Cu, Pb and Sn. Contours of the AM data points (CPM) are shown  
404 in Figure 11. They display three areas of high values. The highest are immediately east of the  
405 Forum Basilica, covering parts of Insulae V, VI and XXXIV. Sample CAL42, from this area,

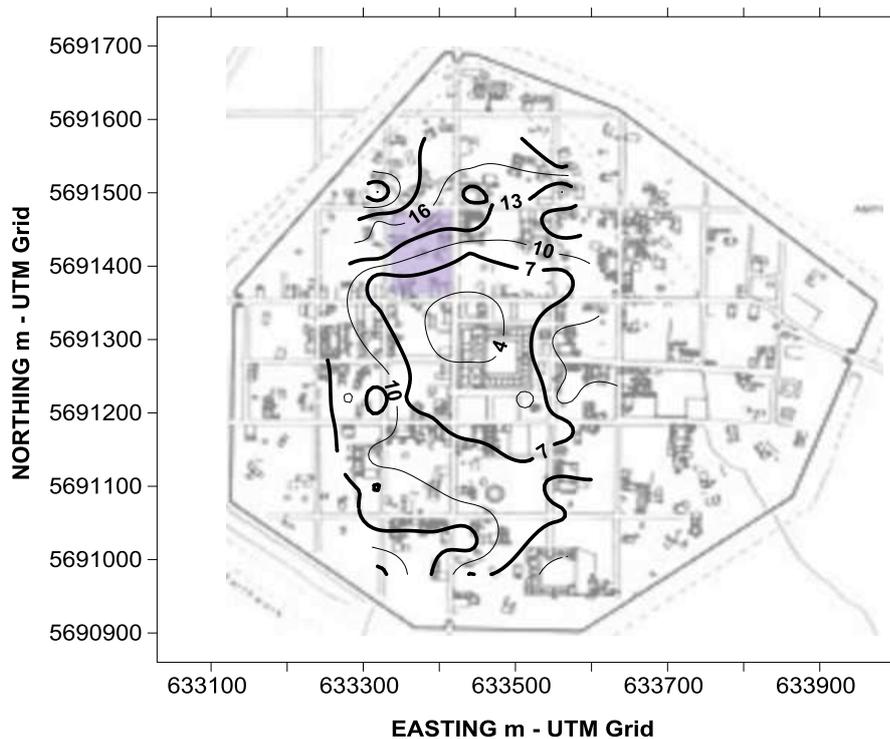
406 has the highest concentration of both Cu and Pb and also a high Sn content. The second area  
 407 of elevated AM indices largely overlaps that of the major Incompatible Element (ICE) index  
 408 zone, across the north of the site. The AM index peaks over sample CAL15 as does the ICE  
 409 index. This is in part because CAL15 has the highest Sn content of all samples on the site and  
 410 Sn is a component of both indices. The highest Cu value in this area is not in CAL15,  
 411 although it does have a high Cu (and Pb) concentration, but is in CAL16 located 40m to the  
 412 north. The third area of elevated AM values lies at the western margin of the sampled area. It  
 413 is centred on CAL7 and is characterized by moderately high Cu and Sn concentrations.  
 414 It is notable that the AM index values are low over the area of the Forum basilica.



415  
 416 Figure 11. Composite Index plots for Alloy metals

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

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



431 **Incompatible element index**

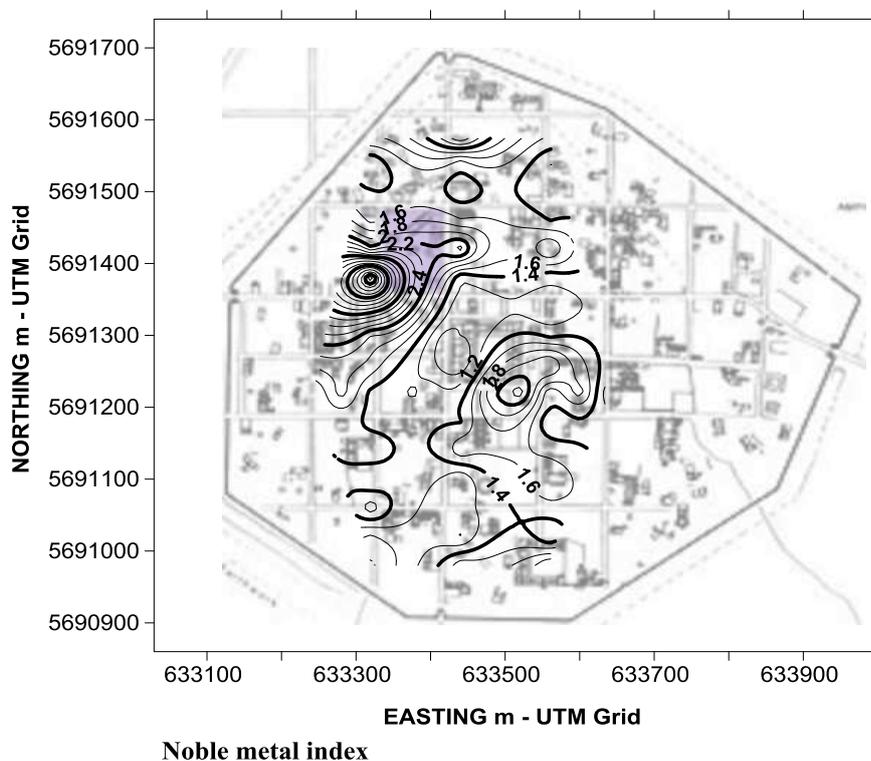
432

433 Figure 12. Composite Index plots for Incompatible elements

434

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

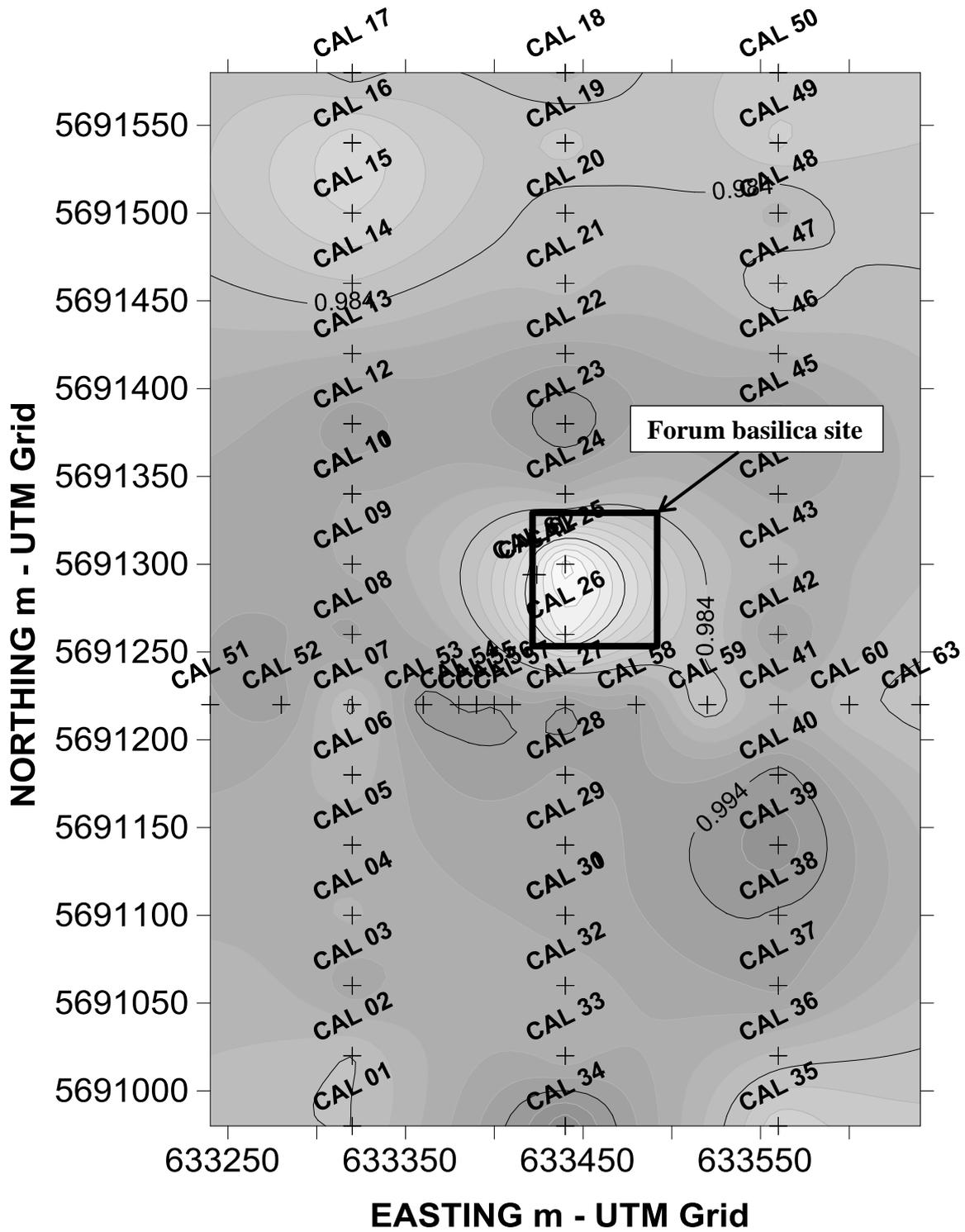
440 The Noble Elements Ag and Au have been compiled into the simple additive (elements  
441 normalized to the mean) Noble Metal Index (NM), the contoured values of which are shown  
442 in Figure 13.



443 Noble metal index  
444 Figure 13. Composite Index plots for Noble metals

445  
446 The NM index contours are centred primarily around three sites; sample CAL12 southwest of  
447 the Insula IX excavation, over a road between Insulae IX and X; sample CAL18 over vacant  
448 land in Insula XXIII and over what is depicted as a Church, south of the Forum basilica, in

449 sample CAL59 (also elevated in Cu). The CAL12 anomaly is by far the strongest and its  
450 location close to the intersection of the major east-west and north-south Roman roads (which  
451 lead directly to the North and West town gates) indicates its importance. It is very likely to be  
452 a precious metal smelting/cupellation site. The NM Index values are low over the Forum  
453 basilica.



455

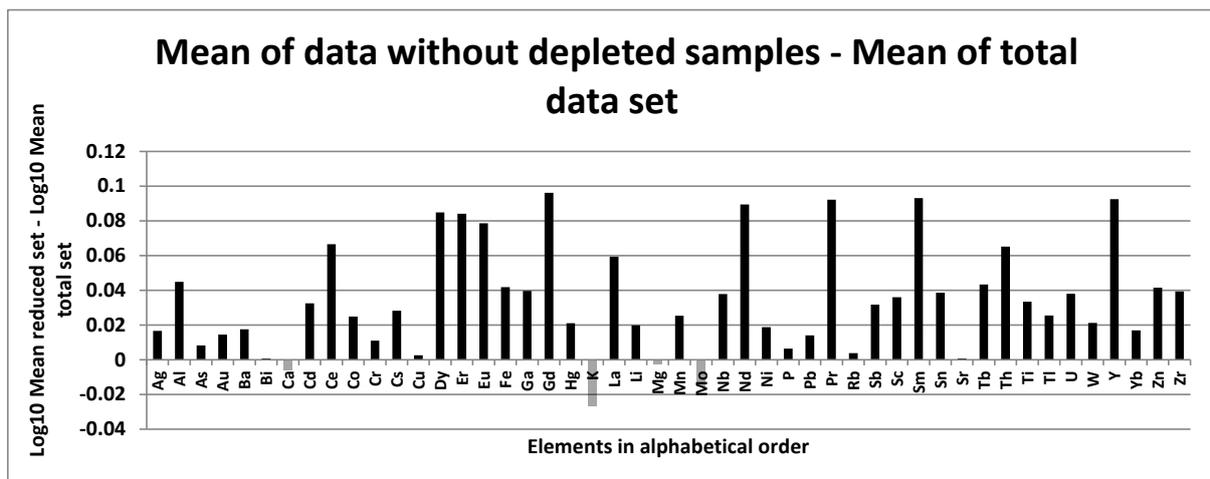
456 Figure 14. Degree of Geochemical Similarity

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

461

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

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



472

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

474

475 **MMI analysis of material from previous House 1 floor samples**

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

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

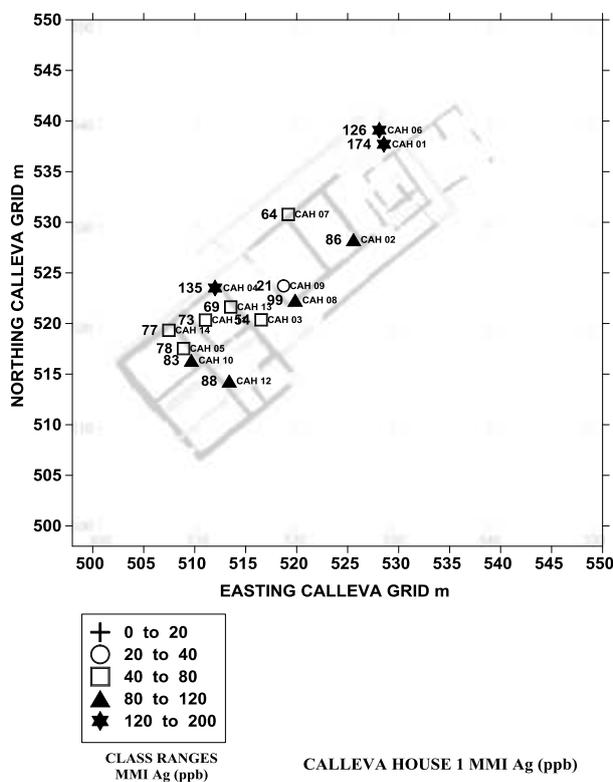
MEAN GEOCH. CONT. 4QM/1QM	Ag	Au	Cd	Ce	Co	Cu	Ga	Gd	Hg	La	Mg	Mn	Mo	Nd	Ni	Pb	Sm	Sr	Y	Yb	Zn
		87	9.4	37	28	22	6785	2.9	6	2.5	5.4	24	16275	5.8	17	980	181	4.6	2375	23	1.1
	1.9	2.3	3	3.3	2.9	2.4	2.5	2.2	4	2.9	3	2.1	4.4	3.4	5.5	4.5	2.7	2.6	5.7	4	3
<b>MEANS</b>																					
Clay rich	76	10	34	39	29	6145	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
<b>MEAN RATIOS</b>																					
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

482  
 483 The elevated concentration of Ag, Au, Cd, Cu, Hg, Mn, Mo, Ni, Pb, and Zn in the Slumped  
 484 and Hearth/Hearth Related groups is indicative of the metal processing known to have been  
 485 carried out in this area (Cook, Clarke et al. 2005). The elemental mean ratios of both of these  
 486 groups when compared with the Gravel/CBM group are very high in REEs. This may be  
 487 indicative of the presence of furnace slag or other metal processing by products as was noted  
 488 for particular sites during the course of the Calleva reconnaissance MMI work. The enhanced  
 489 value of most of these elements is partially explained by the nature of the materials in the  
 490 various sample groups. The Gravel/CBM material consists predominantly of flint fragments  
 491 (Gravel) and refractory brick/ceramic (CBM) both of which have little capacity to adsorb the  
 492 ionic elemental species extractable by MMI. In contrast, the Slumped and Hearth/Hearth  
 493 Related groups contain finer and more adsorbent materials. This feature is further

494 demonstrated by the greater concentration of the elements in the Clay group than the  
 495 Gravel/CBM group.

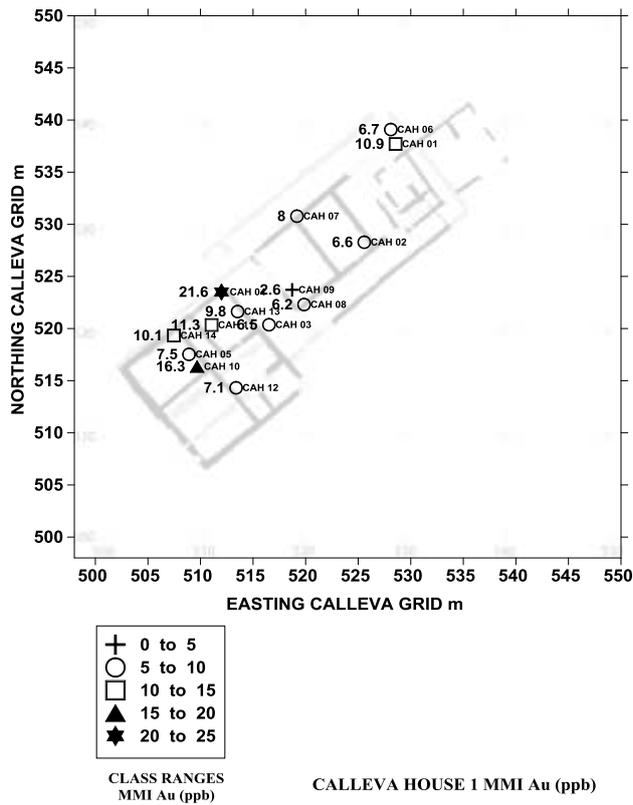
496 The associations between the elements in the House 1 floor samples have been examined by  
 497 Pearson correlation analysis using the log<sub>10</sub> transformed MMI data. Significant associations  
 498 were observed despite the relatively low sample size (14 samples). There are strong  
 499 correlations between Ag, Cd and Cu ( $r > 0.80$ ). Copper also correlates strongly with Mn ( $r =$   
 500  $0.86$ ) and moderately strongly with Mo ( $r = 0.71$ ) and Ni ( $r = 0.76$ ). Cadmium also correlates  
 501 very strongly with Ni ( $r = 0.93$ ) and strongly with Pb ( $r = 0.81$ ) and Zn ( $r = 0.88$ ). Lead  
 502 shows a very strong association with Zn ( $r = 0.90$ ), and a strong correlation with Cd ( $r = 0.81$ )  
 503 and Ni ( $r = 0.88$ ). Gold does not show significant correlations with other elements.

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



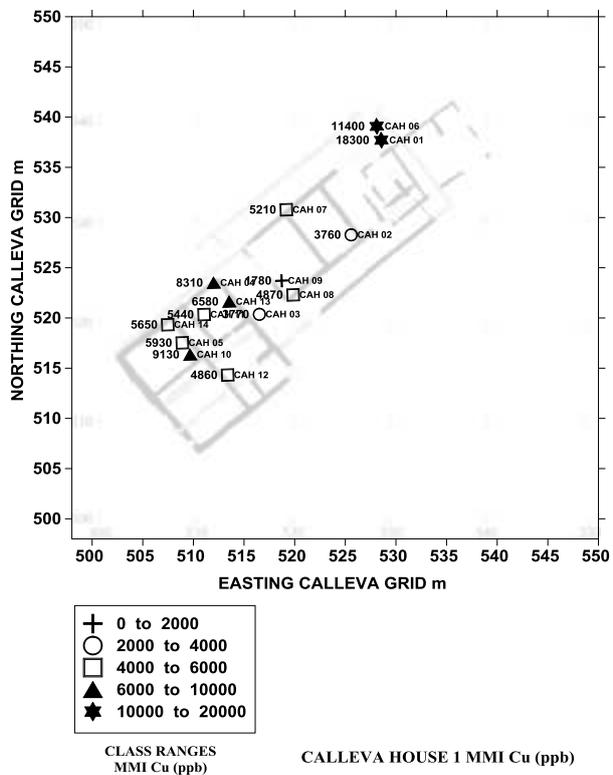
507

508 Figure 16. House 1 floor samples - MMI Ag



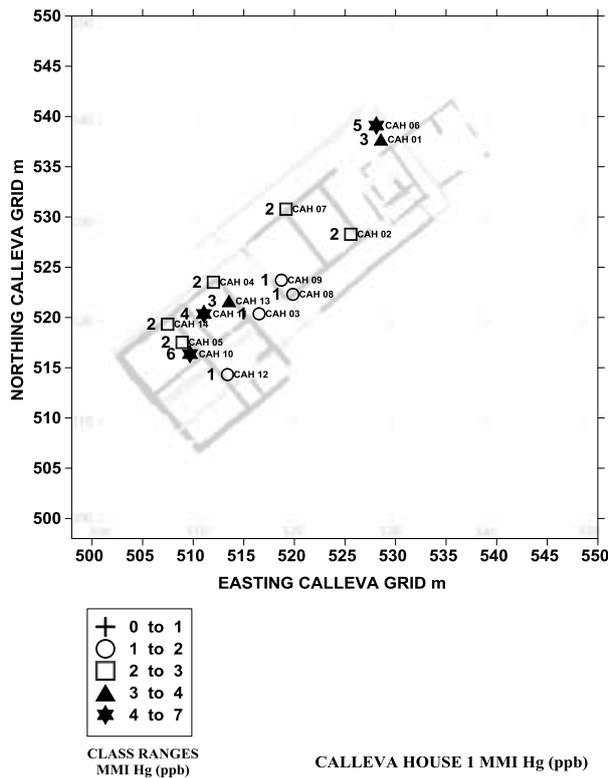
509

510 Figure 17. House 1 floor samples – MMI Au



511

512 Figure 18. House 1 floor samples – MMI Cu



513

514 Figure 19. House 1 floor samples – MMI Hg

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

528 smithing slags'. It was believed by Cook et al. (2005, pp 808-809) that this site was used for  
529 the working of Cu alloys (probably brass) in addition to iron-working.

## 530 **DISCUSSION OF RESULTS**

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

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

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

560 The MMI soil analysis technique is based on sampling at the top of the capillary fringe, 10-  
561 25cm below ground surface where maximum accumulations of mobile ions have previously  
562 been observed (Mann, Birrell et al. 2005). Evidence from the glacial tills of Canada suggests  
563 that anomalies in this soil zone concentrate in a relatively short time (<8500 years) compared  
564 to most geological processes (Mann, Birrell et al. 2005). Much of the Calleva site has been  
565 disturbed in the last century or so, and more comprehensively over the Forum basilica area  
566 some 40 years ago by the Fulford archaeological team (Fulford & Timby, 2000). It is  
567 interesting and instructive that in the Forum basilica area, four MMI samples taken at 10-  
568 25cm showed very significantly reduced signals for most elements compared to the  
569 remainder of the Calleva site. This suggests that the recent comprehensive overturning of the  
570 soil profile has redistributed material from the horizon of ion accumulation; segregation  
571 within the profile has not recovered within a 40 year period. That the signals at or near  
572 surface are derived from capillary rise and evaporation from primary material beneath, is also  
573 demonstrated by the experiment in which samples from the floor of excavated House 1 were  
574 subjected directly to MMI analysis.

575 Correlation analysis results of these floor samples strongly indicate that the processing of  
576 Ag, Au and Cu (with their geochemically coherent associates Cd, Hg, Mo, Mn, Ni and Zn)

577 was carried out in and around House1 during the Roman Period. The lack of association of  
578 Pb with Ag or Au or other elements (except its geochemical associate Sb) is indicative that  
579 there was probably no cupellation of Pb, for the extraction of Ag, carried out on this site in  
580 association with the other metal processing works. The enrichment of Au, Ag, Cu, and Hg in  
581 hearth slump sites is indicative of metal processing, whilst enrichment of REEs in hearth  
582 /slump sites is suggestive of slag, in an overall process which has similarities to fractionation  
583 of elements from melts during geological processes.

584 Whilst comparable data on individual samples are not available, in general the spatial  
585 distribution of MMI results are comparable with XRF and acid digest results of Cook et al  
586 (2005) with respect to the anomalous elements and distribution of anomalies associated with  
587 old hearths.

## 588 **CONCLUSIONS**

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

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

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

601 attrition of these elements from jewellery and coinage and confirms a strong Roman  
602 connection with the soil anomalies.

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

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

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

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

## 620 **ACKNOWLEDGEMENTS**

621 Professor Michael Fulford and his colleagues in the Archaeology Department of the University  
622 of Reading are thanked for their considerable assistance and advice and SGS Minerals are  
623 sincerely thanked for their generous contribution to the analyses. Our thanks are also

624 extended to Associate Professor Andrew Rate for his assistance and advice and to the  
625 anonymous reviewers of our paper for their selfless contributions.

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