

Article

Archaeological and Chemical Investigation on the High Imperial Mosaic Floor Mortars of the Domus Integrated in the Museum of Archaeology D. Diogo de Sousa, Braga, Portugal

Ana Fragata ^{1,*}, Jorge Ribeiro ², Carla Candeias ¹ , Ana Velosa ³ and Fernando Rocha ¹ 

¹ GeoBioTec, Geosciences Department, Campus de Santiago, University of Aveiro, 3810-193 Aveiro, Portugal; candeias@ua.pt (C.C.); tavares.rocha@ua.pt (F.R.)

² Lab2PT, Institute of Social Sciences, Campus de Gualtar, University of Minho, 4710-057 Braga, Portugal; jribeiro@uaum.uminho.pt

³ RISCO, Department of Civil Engineering, Campus de Santiago, University of Aveiro, 3810-193 Aveiro, Portugal; avelosa@ua.pt

* Correspondence: afragata@ua.pt

Abstract: This paper intends to characterize the floor mortar layers (*nucleus*, *rudus* and *statumen*) of the high imperial mosaics of the *domus* integrated in the Museum of Archeology D. Diogo de Sousa, the oldest roman housing testimonies known in Braga, Portugal. It offers an important archaeological and historical contextualization and first chemical characterization attempt on the mortars. The study of 13 mortar samples was carried out at a chemical level through X-ray fluorescence spectroscopy (XRF). All samples presented low lime content when compared to similar studies. A high chemical similarity between nucleus mortars (*opus signinum*) and chemical composition differences between *rudus* and *statumen* mortars was determined, confirmed by statistical analyses. Their composition was distinctly related to the stratigraphic position of each floor mortar layer, following Vitruvius' model, and to the external conditions and treatments (e.g., capillary rise with soluble salts and application of chemical treatments), to which they were submitted.

Keywords: roman mortar; historic mortar; mosaic floors; XRF; *Bracara Augusta*



Citation: Fragata, A.; Ribeiro, J.; Candeias, C.; Velosa, A.; Rocha, F. Archaeological and Chemical Investigation on the High Imperial Mosaic Floor Mortars of the Domus Integrated in the Museum of Archaeology D. Diogo de Sousa, Braga, Portugal. *Appl. Sci.* **2021**, *11*, 8267. <https://doi.org/10.3390/app11178267>

Academic Editors: Anna Galli and Letizia Bonizzoni

Received: 5 August 2021

Accepted: 31 August 2021

Published: 6 September 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Roman mortars are noted for their high durability and complex technological knowledge, related with its composition and execution methods. Their study provides fundamental information regarding the knowledge of the archaeological sites. Some studies have been developed on the characterization of roman mortars in Portuguese archaeological sites, such as Beja-Pisões, Tróia, Conimbriga and Marvão-Anmaia [1–4]. The roman floor mosaics' substrate has several preparatory mortar layers, carefully built (in terms of number, thickness and composition). Specifically, these kind of mortar substrates are under study elsewhere, such as Greece, Italy, Slovenia and Spain [5–12]. However, in *Bracara Augusta*, the Roman name of Braga (Portugal), the roman mortars from its archaeological sites are poorly analyzed and there is no known bibliographic references concerning their characterization.

The Roman city of *Bracara Augusta*, and its evolution between the end of the first century BC and Late Antiquity (V-VII centuries) is known based on the numerous remains recovered by urban archaeology over the last 40 years, in the context of the “Campo Arqueológico de Braga” (CAB; Braga archeological Campus) and the *Bracara Augusta* Project, created in 1976 [13], within the scope of preventive archaeology interventions, conducted by the Archaeology Unit of the University of Minho (UAUM) and the Archaeology Office of the Municipality of Braga (GACMB). In this process, the role of the Museum of Archaeology D. Diogo de Sousa (MDDS), by its contribution in supporting research to the defense and preservation of the archaeological heritage of Braga, must be highlighted. Braga is a city

with more than 2000 years of history, founded by the emperor August, around 16–15 BC, in the context of the administrative reorganization of the Northern Hispania [14,15]. *Bracara Augusta* was one of the most important Roman cities of the *Hispania* northwest, capital of *Conventus*, in the High Empire, of the *Gallaecia*, under Diocletian, and of the Suebic Kingdom, roughly from 411 AD.

Since 1976, dozens of archaeological excavations allowed us to understand the evolution of the city history and the knowledge about its construction techniques and employed materials. In the Stables (Cavalariças, in Portuguese) Archaeological Site of Braga (CVL), in 1991, two mosaic floors were exhumed, covering two compartments belonging to one of the *domus* located to the south of the city *forum*.

1.1. Archaeological Background

Bracara Augusta was an *ex novo* foundation, perfectly planned, and its urban fabric has been recognized through excavations carried out since the 70's [14,15]. The Stables Archaeological Site of the Braga, also known as Zone P1 [16], is located in the southern half of the city, in a prime area (south of the *forum*) on both sides of the maximum *kardo*, east of the blocks occupied by the group of best-known public buildings in the city: the Roman Baths of Alto da Cividade and the Theatre (Figure 1) [17,18].

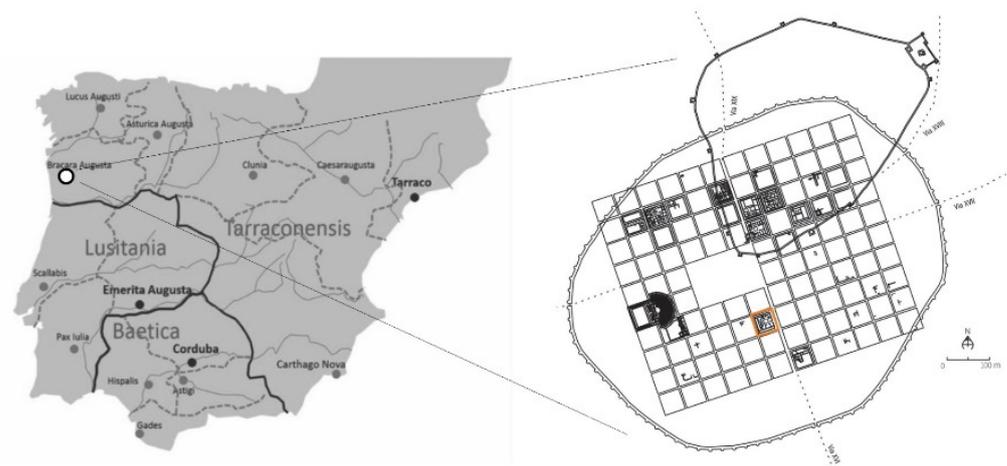


Figure 1. Location of the Stables Archaeological Site in the plan of the Roman city, low imperial and medieval walls. Adapted from [19].

This is the largest excavated area in the southern part of the ancient Roman city and currently houses the facilities of the MDDS, open to the public since 2006. In this place, there were two rectangular buildings, used as stables, dating from the beginning of the 20th century, and located at an elevation of approximately 184 m above sea level. These buildings are surrounded in the west by the Bombeiros Voluntários Street and in the east by an unbuilt area [19,20]. The archaeological work was spread over four excavation campaigns that took place between 1986 and 2002. The first intervention occurred in 1986, to assess the archaeological potential of the area (three surveys) [16]. Between 1988 and 1989, there was a second campaign, covering the entire area of the Museum implantation (24 surveys) [20], followed by a third one, in 1996, extending the intervention to the Museum's gardens [19]. Finally, the fourth and last campaign took place in 2002, at a time when the Museum was already built, in the gardens, on the eastern part of the building [19]. The work carried out allowed the identification of the archaeological remains belonging to several *insulae* of the Roman city, some of which had housing functionalities, chronologically set between the 1st and the 7th century, allowing us to understand the evolution of the city in the blocks located to the south of it. Therefore, it is a large area, which was left out of the medieval city, having certainly been transformed into agricultural spaces, which contributed to the preservation of the existing ruins. Testimonies of the various stages of occupation were

found, such as pavements of *opus signinum*, a pavement of carved stones in the shape of diamonds and rectangles, various mosaics, and walls [16,19,20]. The interpretation of this set allowed the identification of two blocks of the Roman city, designated, respectively, by A and B arranged on each side of the south segment of the maximum *kardo*. Block A was occupied by a *domus*, from which most of the central structures were recovered. From block B, the data collected was more dispersed and complex, and did not allow for a reliable interpretation [19]. The essential part of the exhumed archaeological remains is now buried, apart from the mosaic targeted by this study, which formalized the soil of a room in a house, preserved and musealized in the basement of the MDDS service block [16,20].

1.2. The Bracara Augusta Mosaics and the Findings of the Stables Archaeological Site

Braga's mosaics were studied by Abraços [21,22], in the coordination of a large team. The first set identified was discovered in the "Campo das Carvalheiras" area, in the context of the construction of the new Orphans Seminary; however, most of the documented elements result from the work carried out since 1976, with the formation of the CAB and the UAUM. The large number of archaeological excavations carried out by the UAUM have allowed the identification, registration, safeguarding and collection of materials and a better understanding of the *Bracara Augusta* mosaics. The city has been known, throughout its history, by diverse periods of building construction and economic growth [14,15,23], associated with successive changes in its status, which manifested themselves in various programs for the city's beautification, which integrates the mosaic decoration of many of its public and private buildings. Few of the city's mosaics remain in situ, the majority being deposited in MDDS [22]. A set of 69 mosaic coverings, including elements from Dume and Falperra, essentially decorated with geometric motifs, and some sets decorated with aquatic motifs and vases, were documented. Mosaics from the 1st century are known, however most of these panels date from the 3rd to 4th centuries, as a result of the intense construction and urban renewal program that the city experienced by that time [22].

With specific regard to the mosaics of the CVL archaeological site, there are five records. The first identified set was in 1991, composed of two panels dating from the 1st century, which covered the floor of two rooms of a housing complex. The second, later, dating from the Suevo-Visigothic period, was identified in 1986 in the Museum gardens, and matches a pavement in *opus sectile* and *opus tessellatum*, both preserved in situ. Three fragments were also discovered in works carried out in 1988, testimonies of the *opus tessellatum* technique, whose dating was not possible to specify, given the size of the archaeological discovery and context [22].

The mosaic pavement, analyzed in this present study, and the associated structures, such as walls and pipes, were in a reasonable state of conservation [24]. The rarity of this type of mosaic in the region is due to its size and constitution, and the soil acidity that does not favors its conservation, besides the fact that is considered the oldest Roman housing testimonies known until now in Braga [25], dating from the August period.

1.3. The Presence of Marble and Lime in Bracara Augusta

The raw material most used by the builders of the Roman city was granite, an abundant rock-type in this region (Figure 2).

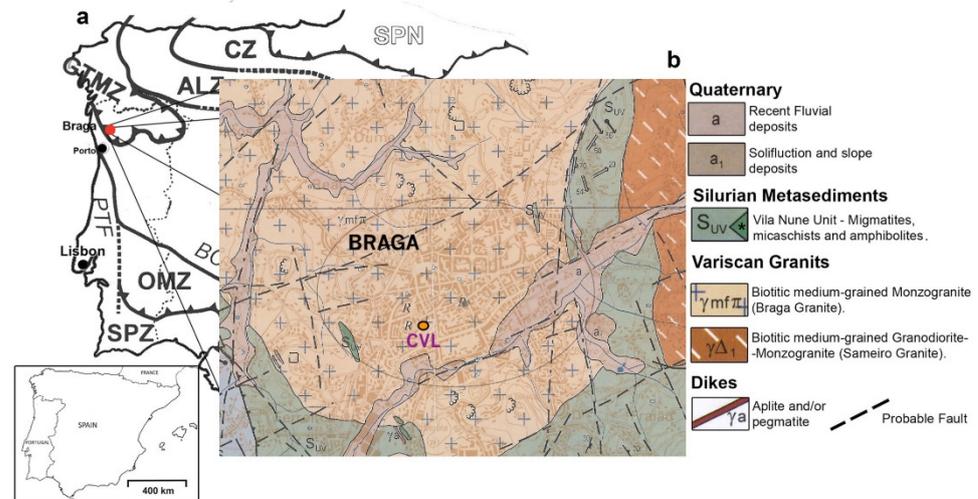


Figure 2. (a) Geological setting of the study area in the Iberian Peninsula; (b) Braga and the Stables Archaeological site geological context [26]. Adapted from [27].

Furthermore, several types of Braga’s ceramics [28], as well as lime and marble [29] were imported from other places in the Roman Empire, such as Lusitania. The importance of marble, one of the most relevant stone resources in the Roman period, from the Marble Triangle (Estremoz, Borba, Vila Viçosa—Portugal), to *Asturica Augusta*, was studied in [30], and referenced therein. These being the marble suppliers of *Bracara Augusta*. However, as documented by a study of the city’s architectural elements [31], in a universe of 356 analyzed pieces, only six were in marble. In addition to the above, its absence may also be justified by the costs associated with its acquisition or, possibly, an economy of reuse, very common in the Roman times and in the medieval world, in the context of the construction of new buildings, or even its reduction to obtain lime, an element of great importance in the Middle Ages. Similar to what was documented in the excavations of the Saint Raymond Museum, in Toulouse [32], there would be kilns for reducing marble pieces, including statuary, to obtain lime. Additionally, the assumptions related to the cost of the material and its reuse are in fact admissible, however the importation of marble and lime to Braga cannot be excluded and could have been superior to the scarce archaeological evidence available.

2. Description and Conservation of the Mosaic’s Pavement

The construction techniques and materials used by the Romans were described, in the 1st century AC, by Vitruvius, in the work entitled “De Architectura” [33], according to the following down to top layers (Figure 3): (a) a first preparatory layer (*statumen*), consisting of rolled pebbles and stones, measuring about 12 cm (the size of a fist); (b) over, the *rudus* layer was placed, consisting of $\frac{3}{4}$ of sand or gravel and small pebbles and $\frac{1}{4}$ of lime in a layer with ~22 cm ($\frac{3}{4}$ of a roman foot), to protect the mosaic against humidity and infiltrations; (c) the *nucleus*, a *opus signinum* layer, consisting of a thin lime mortar with fragments of tile, or ground brick, to level the floor to receive the *tesserae*, in a 1.5 cm layer; finally, (d) the *tesserae* was placed over the *nucleus*, in a layer of 2 to 3 mm, consisting of lime and very fine marble dust, that filled the interstices.

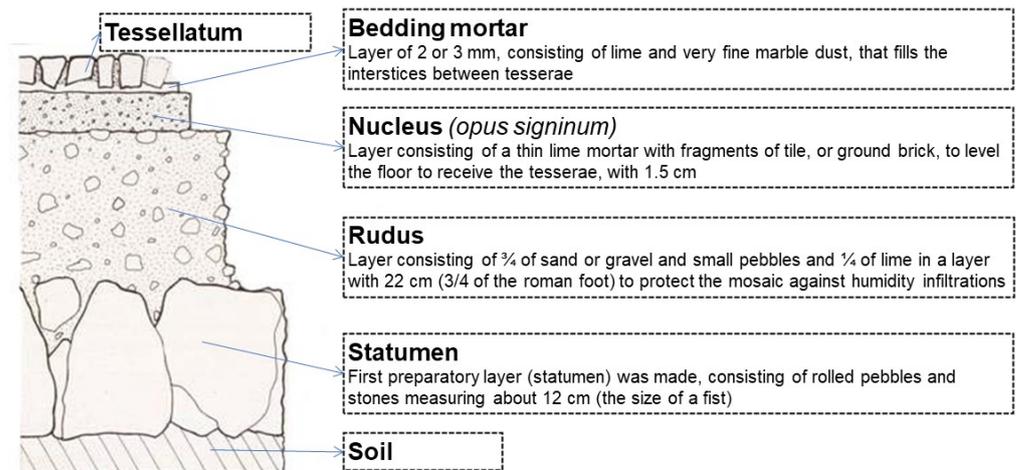


Figure 3. Stratigraphy of Roman mosaic floor according to Vitruvius' description [33].

Many of these Vitruvius model mosaics have subsisted until our days, but this structure was not always strictly respected, leading to a faster deterioration of the mosaic pavement.

In Figure 4, a section of the pavement of the mosaic of the MDDS crypt was drawn, in which can be observed the local adaptation of the different stages of the mosaic construction according to the Vitruvian model. In this case, not all the layers that support the mosaic respect the thickness of the Vitruvius' model. In Figure 5 it is shown the layers corresponding to the *nucleus*, *rudus* and *statumen* of the MDDS crypt mosaic floor.

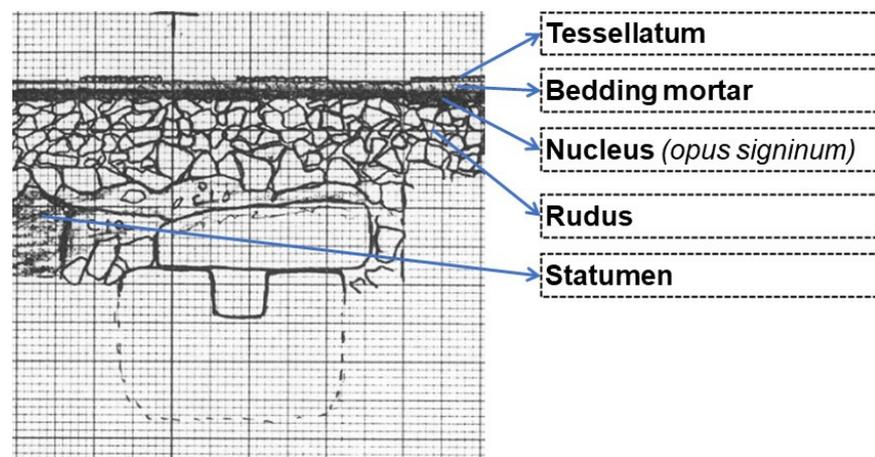


Figure 4. Section of the East profile of the mosaic floor of the Museum crypt [24,34].

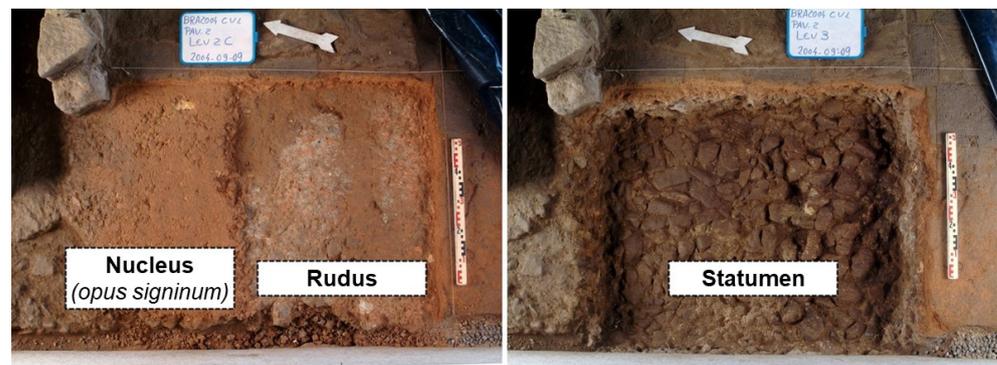


Figure 5. Mosaic floor layers—*nucleus* and *rudus* (left) and *statumen* (right). (Photos generously provided by MDDS).

The protection of the area of the mosaic structure was carried out during the building construction for prior conservation actions (Figure 6a), although it was not efficient in controlling successive floods due to the low quota, at groundwater level, in comparison to the top of the hill located to the west—Hill of Cidade. Archeologists decided, to improve the protection of the area, to bury the mosaic floors until 1997, when the construction of the space that houses the mosaics was finished. The protective materials were removed (except the thin layer of sand that covered the mosaic floors) and some uncovered structures were consolidated and restored with a mortar based on hydraulic lime and gravel and a biocide, applied in the areas with biological colonization. A year later, when the sand was removed it was observed that the *tesserae* as well as other structures (walls, pipes and mortar pavements) were in a reasonable state of conservation. In 2003 and 2004, in order to drain the excess of water that reached the mosaic floors, a gallery was built, although it was not efficient. The floor mosaics were submitted to several treatments to remove the biological colonization [24,33], however it is still present (Figure 6b) due to room unfavorable humidity and temperature conditions. The anomalies in the structure of the crypt's mosaics may be the result of the high accumulation of water due to: (i) capillary rise of groundwater, likely through the more permeable materials of the mosaic structure; and (ii) rising damp due to the accumulation of surface water near the structure surrounding the mosaics. The lack of drainage system around the mosaic floor and lack of ventilation had unfavorable results on the mosaics [35,36].

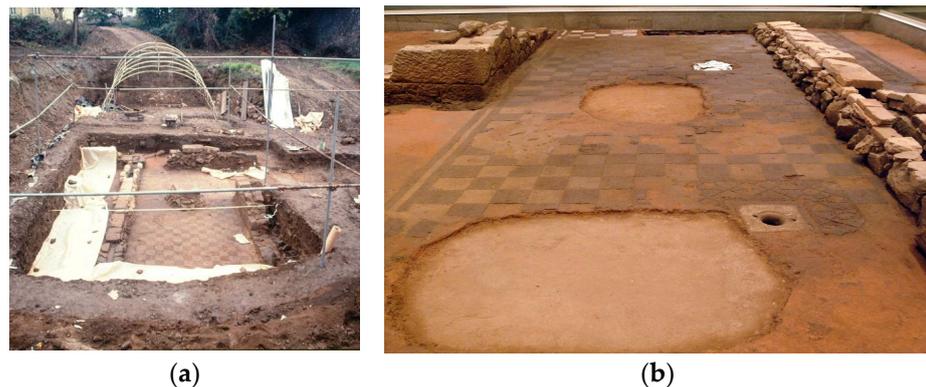


Figure 6. (a) Protection of the area of the structure of the mosaic during the building construction (photo gently provided by MDDS); (b) mosaic floor integrated in the crypt of the Museum of Archeology D. Diogo de Sousa.

The mosaic 1 feature squares were made of granite *tesserae* alternated with squares made of white limestone *tesserae* (Figure 7). The tray included, to this end, a drainage opening also covered with mosaic but with small squares with about 8 to 9 cm on the side. Mosaic 2 was decorated with squares of hourglass lines, equally made with granite and limestone *tesserae* (Figure 7). The mosaic covered a room whose maximum dimensions are 2.23 m in width and 3.22 m in length, with squares of approximately 20 cm on each side. In both cases, the limestone *tesserae* is poorly preserved [22] and only the granitic features remain preserved. The characterization of the *tesserae* composition determined that the white ones are composed of limestone, and the dark ones by granite, possibly pink granite from the Conde area, in Braga, assuming that this mosaic was made with local raw material [24].

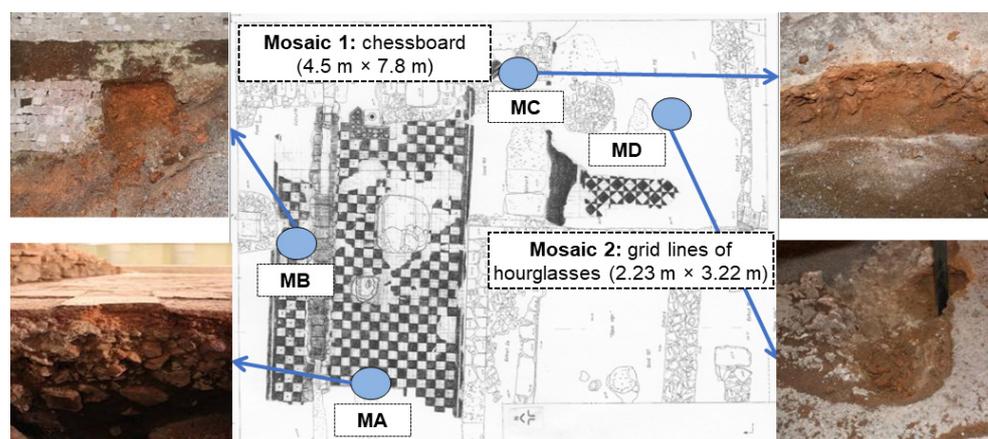


Figure 7. Schematic representation of the mosaic floor of the Museum crypt and sampling areas (Schematic representation gently provided by MDDS).

The durability of the floor mortars that supports those mosaic pavements is remarkable, although some conservation actions may be needed, as some cohesion loss was observed in those renders. No prior studies considering chemical characterization of those mortars in Braga were found. To achieve this, a study on those mortars was handle in this paper.

3. Materials and Methods

3.1. Materials

The study was conducted in the four different areas of the mosaic floor integrated in the crypt of the MDDS building. Micro-sampling was performed and carefully removed to prevent contamination and following the protocol of the technicians of MDDS.

This investigation was based on the characterization of 13 samples collected from the different mortar layers of the mosaic floor considering four different areas (MA, MB, MC, MD) of the mosaic floors (Figure 7). The samples were collected from original and well-preserved floor mortars (although some cohesion loss was observed during sampling, mainly in nucleus layer) and were macroscopically grouped, considering the color and the removal depth, in five different layers: layer 1—five samples from *nucleus* upper zone (MA2, MA3, MB1, MC1, MD1), layer 2—five samples from *nucleus* lower zone (MB2, MC2, MC3, MC4, MD2), layer 3—one sample between *nucleus* and *rudus* (MA4), layer 4—one sample from *rudus* (MD3) and layer 5—one sample from *statumen* (MA1) (Table 1).

The bedding mortar, a very thin layer consisting of lime and very fine marble (Figure 2), was not visible and, if it existed, may be below the original *tesselatum*; it was not possible to collect samples from this layer. Samples from the *nucleus* layer were removed from the *nucleus* upper layer (layer 1, close to the outer surface that previously was in contact with bedding mortar) and from the *nucleus* lower layer (layer 2, close to the *rudus* layer) to investigate compositional differences. Additionally, it was only possible to collect one sample from the interface between *nucleus* and *rudus* (MA4), and from *rudus* (MD3) and from *statumen* (MA1) layers; these samples need to be removed from deep and only one zone at the mosaics' floor mortars was defined by the museum technicians, to avoid as much damage as possible. The thickness of floor mortar layers varies. During nucleus sampling it was difficult to identify which group the samples belonged to in some cases.

Table 1. Studied samples and their characteristics.

Layer 1: Nucleus—Opus Signinum (Upper Zone of the Layer)					
Description	Removal depth: ~1.0/3.0 cm; color: reddish.				
					
Sample	MA2	MA3	MB1	MC1	MD1
Layer 2: Nucleus—Opus Signinum (Lower Zone of the Layer)					
Description	Removal depth: ~3.0/5.0 cm; color: reddish.				
					
Sample	MB2	MC2	MC3	MC4	MD2
Layer	Layer 3: Between Nucleus and Rudus		Layer 4: Rudus	Layer 5: Statumen	
Description	Removal depth: ~5 cm; color: pinkish		Removal depth: ~5/10 cm; color: brown	Removal depth: ~25/30 cm; color: dark brown	
					
Sample	MA4	MD3	MA1		

3.2. Methods

This present study aims to characterize the chemical composition of the mosaic floor mortars. The chemical analyses were performed on finely crushed mortar samples by X-ray fluorescence spectroscopy (XRF) through a Panalytical Axios spectrometer PW4400/40 X-ray (Marvel Panalytical, Almelo, The Netherlands) equipped with Rh tube under argon/methane, at University of Aveiro (UA), using Omnian37 and Pro-Trace2021 software for major and minor elements analyses, respectively. The loss of ignition (LOI) was determined by heating the mortars samples at 1000 °C, using an electric furnace for 3 h. The major elements analyzed were Al₂O₃, CaO, Cl, Fe₂O₃, K₂O, MgO, MnO, Na₂O, P₂O₅, SiO₂, SO₃, and TiO₂ with detection limit of 1%. The detection limits of the trace elements analyzed were: As = 4.06 mg/kg, Ba = 6.90 mg/kg, Br = 0.78 mg/kg, Co = 4.54 mg/kg, Cr = 1.96 mg/kg, Cs = 4.78 mg/kg, Cu = 2.84 mg/kg, Ga = 0.94 mg/kg, Nb = 0.84 mg/kg, Ni = 2.00 mg/kg, Rb = 0.64 mg/kg, Sn = 3.02 mg/kg, Sr = 0.72 mg/kg, Th = 2.52 mg/kg, V = 2.78 mg/kg, Zn = 1.28 mg/kg and Zr = 0.80 mg/kg. Precision and accuracy of analyses and procedures were monitored using UA internal standards, certified reference material and quality control blanks. Results were within the 95% confidence limits. The relative standard deviation was between 5% and 10%.

All statistical analyses were performed using IBM SPSS® statistics v25. The normality of the data was verified (Shapiro–Wilk’s test, $p > 0.05$). ANOVA, Tukey’s test, t-student, K-means, cluster and discriminant analysis were used to determine groups and statistically significant differences ($p < 0.05$).

4. Results and Discussion

The chemical compositions, related to the binder and aggregates of the mosaic floor mortars samples, are detailed in Tables 2 and 3. The K-Means Cluster analysis of all samples identified two sets of samples in both major and trace elements, with MA1, MA4 and MD3 forming a cluster clearly separated from the remaining samples. The ANOVA 1-way analysis showed that the variables with significant influence to define these two groups were Al_2O_3 , K_2O , SiO_2 , Ba, Cs, Ga, Nb, Rb, Sn ($p = 0.00$), MgO, Zr ($p = 0.001$), P_2O_5 ($p = 0.002$), Ni ($p = 0.003$), Br, Sr ($p = 0.006$), Na_2O ($p = 0.007$), and Fe_2O_3 ($p = 0.015$).

Table 2. Chemical concentrations of the major components of the mortars samples (in %).

Sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	LOI
MA2	0.34	1.10	30.93	35.42	2.98	0.24	0.13	2.60	5.11	1.25	0.06	8.38	11.24
MA3	0.30	1.16	32.49	37.07	1.50	0.40	0.10	2.68	3.65	1.30	0.07	8.48	10.62
MB1	0.27	1.35	32.68	38.53	3.45	0.86	0.04	3.43	2.14	1.35	0.13	8.62	6.93
MC1	0.33	0.97	29.27	31.87	4.64	3.82	0.11	2.46	5.48	1.12	0.10	7.58	11.96
MD1	0.43	1.11	33.02	32.90	4.57	0.41	0.19	2.76	3.85	1.27	0.11	8.63	10.53
MB2	0.18	1.28	34.97	36.16	3.46	0.35	0.03	2.86	1.52	1.37	0.09	8.91	8.59
MC2	0.26	0.99	34.09	34.63	4.35	0.32	0.10	2.52	2.41	1.22	0.17	8.09	10.63
MC3	0.22	1.14	34.03	35.65	3.87	0.26	0.03	3.35	1.46	1.62	0.10	11.07	6.84
MC4	0.19	1.35	35.93	36.42	3.50	0.17	0.07	2.70	1.70	1.28	0.16	8.50	7.78
MD2	0.43	1.47	34.08	34.91	3.39	0.23	0.15	3.26	2.41	1.38	0.08	8.69	9.22
MA4	1.11	2.25	22.27	47.31	0.74	0.21	0.07	6.70	5.60	1.37	0.10	7.01	4.83
MD3	1.74	1.70	20.71	54.06	1.98	0.07	0.03	7.07	2.01	1.22	0.07	6.22	2.76
MA1	0.23	1.56	26.11	47.56	0.86	0.13	0.03	4.73	1.11	1.54	0.13	7.80	7.77

Table 3. Chemical concentrations of the trace elements of the mortars samples (in mg/kg).

Sample	As	Ba	Br	Co	Cr	Cs	Cu	Ga	Nb	Ni	Pb	Rb	Sn	Sr	Th	V	Zn	Zr
MA2	23.1	350	60.2	5.6	45.4	18.6	23.7	36.0	31.4	11.6	59	270	28.4	85	36.4	50.4	77	300
MA3	17.3	360	52.4	5.1	47.4	22.2	27.0	37.1	32.3	13.3	51	250	23.2	65	37.0	56.1	87	300
MB1	51.9	520	30.6	8.4	46.4	20.8	67.2	34.5	29.2	13.8	71	290	21.0	160	42.2	67.9	170	340
MC1	55.6	420	67.4	8.6	40.1	20.6	55.8	33.3	29.9	11.2	240	240	21.9	87	34.2	60.6	78	250
MD1	24.9	440	85.8	8.4	50.0	18.6	57.5	37.3	32.2	14.3	56	250	23.6	90	37.9	57.3	190	280
MB2	76.6	380	35.1	8.8	51.8	19.8	55.7	38.1	33.5	13.7	61	260	24.4	70	40.9	63.6	120	310
MC2	58.5	330	65.0	15.2	45.6	18.9	71.4	36.1	32.2	12.4	170	250	23.6	67	36.2	69.6	130	270
MC3	61.5	560	38.1	8.0	58.3	22.2	58.9	44.7	37.6	14.6	660	290	29.6	88	48.1	87.5	130	400
MC4	45.7	370	42.1	15.6	48.4	20.5	62.5	38.0	34.3	13.2	77	250	25.1	59	36.8	68.0	200	300
MD2	25.3	440	65.4	4.9	48.2	19.9	64.0	36.1	31.3	15.0	53	270	21.3	89	39.2	65.7	190	340
MA4	4.9	950	20.3	7.3	32.9	17.5	35.3	21.2	18.6	7.8	44	380	10.5	210	37.8	62.5	170	450
MD3	14.4	970	12.5	<LOD	41.0	15.0	36.8	20.1	16.0	8.6	38	400	10.7	260	36.5	61.8	82	400
MA1	42.1	560	23.4	7.3	60.9	12.5	57.8	22.0	19.0	12.1	44	330	9.4	92	41.7	77.2	83	540

LOD: Limit of detection.

All samples were characterized by low CaO content (1.1–5.5%) and high concentration in F_2O_3 (6.2–11.1%) and Al_2O_3 (20.7–35.9%), when compared with the same elements from other studies on roman mortars [8,10,37]. A study on Pompeii mortars [38] found low percentages of CaO (3.81%) and attributed this low content to the high content of volcanic rock fragments as well as to the to the chemical composition of the binder composed by a mixture of lime and clay. Another possible explanation can be related to the degradation of those present study mortars (some cohesion loss was observed) as a result of the unfavorable humidity conditions to which the mosaic floor has been submitted that may lead to the leaching of the lime, as cohesion loss was observed during sampling [39]. The SiO_2 content was higher than Al_2O_3 in all samples, although in samples MA4 (between *nucleus* and *rudus*), MD3 (*rudus*) and MA1 (*statumen*), this difference was much more evident, with over 2X's. The highest SiO_2 content was found in samples MA4, MD3 and MA1, with 47.3%, 54.1% and 47.6%, respectively. These samples showed lower Al_2O_3 and higher K_2O content than nucleus ones (layers 1 and 2). MD3 showed the lowest Al_2O_3 (20.7%) and

LOI (2.7%) concentrations, among all samples. The low LOI (2.7–11.2%) in all samples, when compared to other studies, e.g., [8,40], can be related to the high percentage of clay minerals and its release of OH⁻ and calcite release of CO₂ [41].

Nucleus renders (layer 1—*nucleus* upper zone, and layer 2—*nucleus* lower zone) also displayed higher content of Fe₂O₃ (8.1–11.2%, except in sample MC1 with 7.6%), Al₂O₃ (29.3–36.0%) and lower SiO₂ content (31.8–38.5%), when compared to *rudus* (MD3) and *statumen* (MA1) render samples, which may be the result of ceramic powder presence in nucleus render composition. The higher content of Fe₂O₃ is responsible for the rose ochre color, that can be associated with the brick fragments or powder mixed in the mortar [38], and may indicate that iron is in its oxide form. Additionally, layer 1 showed higher CaO content (3.6–5.5%, except in sample MB1 with 2.1%) than layer 2 (1.5–2.4%). The higher CaO content in layer 1 may result from the influence of the composition of the bedding mortar that previously existed above the nucleus layer (although was not visible during sampling) and could be mixed in the nucleus upper zone. According to Vitruvius [33], it was composed by lime and very fine marble dust. In layer 1, MA2 and MC1 samples showed the highest CaO content, with 5.1% and 5.5%, respectively. The highest content in Al₂O₃ was observed in layer 2 (34.1–36.0%). The higher Cl content was found on the *nucleus* upper layer (layer 1), which may be the result of capillary rise with chloride soluble salts through the mosaic floor and evaporation occurring at the outer surface of the outer layer, and as a result higher Cl concentration was observed in this layer [42].

Previous studies about the chemical characterization of archaeological and ceramic materials used the hierarchical cluster analysis on chemical data to obtain a more robust interpretation [43,44]. The cluster analyses (Ward linkage) of layers 1 and 2, separated sample MC1 from the others, and defining two other subgroups, one with MA3, MB1, and MA2 samples, and a second one with MB2, MC4, MC3, MC2, MD2, and MD1 samples (Figure 8a). The variables cluster analysis also revealed that Al₂O₃ and SiO₂ present a distinct concentration pattern from the other major elements, in agreement with previous analysis (Figure 8b). An ANOVA 1-way analysis of these two groups revealed significant statistical differences in Al₂O₃ and CaO ($p < 0.05$). The groups descriptive statistics showed that Al₂O₃ concentration mean for layer 2 (36.62%) was higher than for layer 1 (31.68%), and that CaO mean for layer 1 was higher than for layer 2, with 4.04% and 1.90%, respectively. Despite differences identified, all the other variables did not present significant differences. Additionally, discriminant analysis based on the chemical composition of each nucleus layer (1 and 2) revealed that samples MC2 and MC4 from layer 2 showed more affinity with layer 1, and samples MA2 and MD1 from layer 1 revealed more affinity with layer 2. This may result from sampling contamination due to the small thickness of this layer. As this roman pavement is an archaeological heritage integrated in a museum, it is not possible to collect more samples.

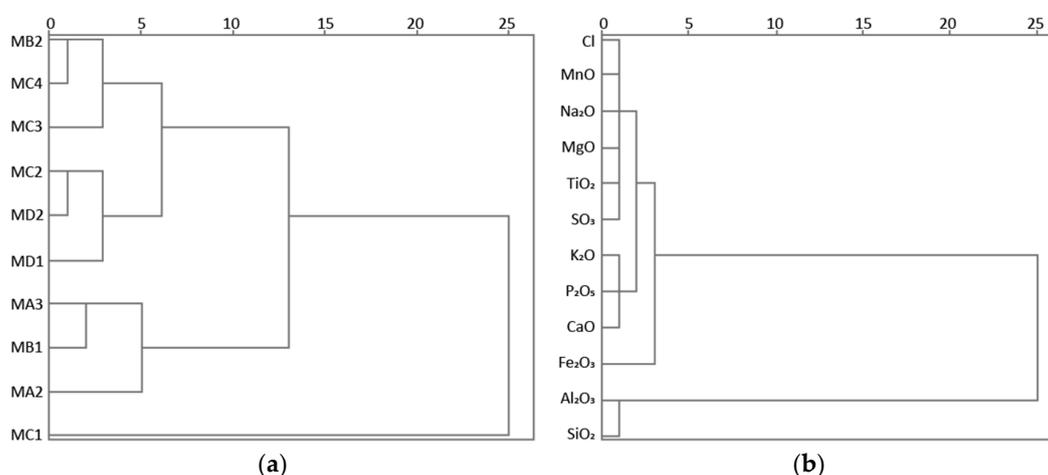


Figure 8. Cluster analysis of layer 1 and 2: (a) samples; (b) major elements.

Relatively high trace elements As, Pb and Cu contents (Table 3), when compared to other studies [38,40], were found. In most of the nucleus samples, the considerably higher As concentration might be attributed to the application of biocides to remove the biological colonization of the mosaic floor (e.g., [40]). The relatively high content in Cl, Pb and Cu (Table 2) can be due to the considerable degree of exposure to modern construction (concrete and Portland cement), considering that the mosaic floor is integrated in the new cement and concrete building of MDDS (e.g., [40]).

The dendrogram obtained by cluster analysis on the trace elements chemical data for all samples is presented in Figure 9. T-student test revealed significant differences between all variables in layers 1 and 2. An ANOVA 1-way analyses showed significant statistical differences between the 2 layers in V ($p < 0.05$) content. The descriptive statistics showed that the V mean in layer 2 (70.88 mg/kg) was higher than in group 1 (58.46 mg/kg). All the other variables did not present significant differences between groups. Moreover, discriminant analysis of layers 1 and 2 trace elements content suggested that samples MC2, MC3 and MC4 from layer 2 revealed more affinity with layer 1, and samples MC1 and MD1 from layer 1 showed more affinity with layer 2.

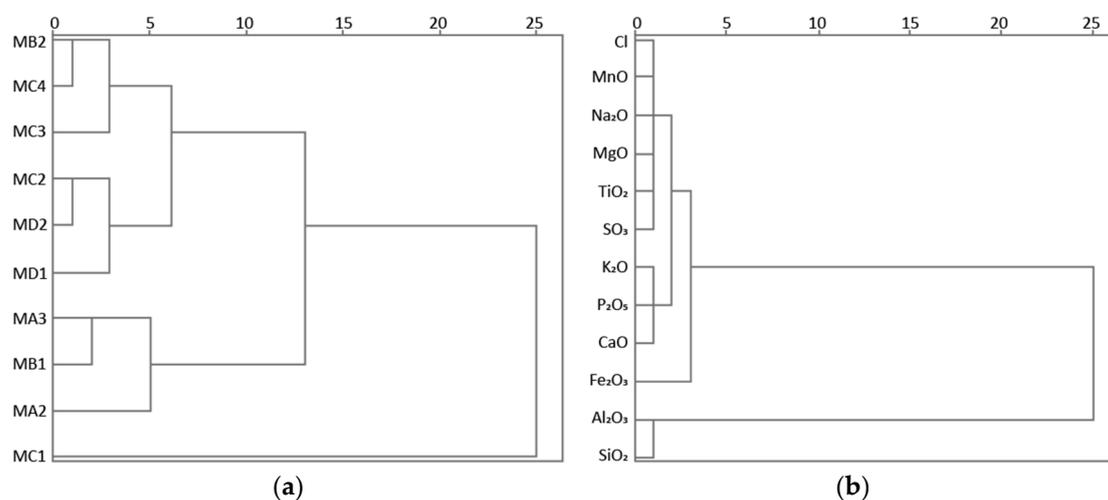


Figure 9. Dendrogram obtained by cluster analyses: (a) samples; (b) trace elements—all groups.

These mortars were characterized by low content in CaO and high content of Fe₂O₃ and Al₂O₃. The *nucleus* (layers 1 and 2) was characterized by higher Fe₂O₃ and Al₂O₃ than *rudus* and *statumen*. *Rudus* and *statumen* showed higher SiO₂ content than *nucleus*. Comparing layers 1 with 2: layer 1 showed higher CaO content and layer 2 higher Al₂O₃ content. These layers showed relatively high As, Pb and Cu contents.

The statistical analyses enabled the differentiation of the two main *nucleus* layers (layers 1 and 2) from the three outlier samples: between *nucleus* and *rudus*, *rudus* and *statumen*. The descriptive statistics revealed differences among layers 1 and 2 concerning mainly Al₂O₃, CaO and V contents. Considering layers 1 and 2 major elements statistical analyses, MC2 and MC4 from layer 2 shows more affinity with layer 1 and MA2 and MD1 from group 1 shows more affinity with layer 2; analyses on trace elements revealed that samples MC1 and MD1 from layer 1 presented more affinity with layer 2 and MC2, MC3 and MC4 from layer 2 more affinity with layer 1.

5. Conclusions

The results obtained on the 13 mortars samples from different floor layers of the high imperial mosaics of the *domus* integrated in the crypt space of Museum of Archaeology D. Diogo de Sousa showed that there are differences on the chemical elements analyzed from the different layers: nucleus upper layer (layer 1), nucleus lower layer (layer 2), between *nucleus* (layer 3) and *rudus* (layer 4), *rudus* and *statumen* (layer 5) layers.

The chemical characterization of the studied floor mortar layers indicated that their composition was distinctly related to their stratigraphic position in the substrate, according to Vitruvius' model, and to the external conditions and treatments to which each layer was submitted (e.g., capillary rise with soluble salts and application of chemical treatments). Mosaic floor mortars showed low content of CaO and high F₂O₃, Al₂O₃, Cl, As, Pb and Cu contents. The statistical analyses using the chemical data on major and trace elements was robust and confirmed the clear separation between the *nucleus* layer (layers 1 and 2) and the other layers.

This study offers an important archaeological and historical contextualization and a first chemical characterization on the roman mortars of *Bracara Augusta*. Additionally, it is focused on mortar investigation of the oldest Roman housing testimonies of *Bracara Augusta* musealized in Museum of Archaeology D. Diogo de Sousa, Portugal.

Future studies will focus on the mineralogical analyses of the mosaic floor layers, and correlate them with the results of the chemical analyses discussed in this present study.

Author Contributions: Conceptualization, A.F., J.R. and F.R.; methodology, A.F. and F.R.; statistical analysis, C.C.; validation, A.F. and F.R.; formal analyses, A.F., J.R., C.C. and A.V. and F.R.; investigation, A.F., J.R.; writing—original draft preparation, A.F., J.R. and C.C.; writing—review and editing, A.F., J.R., C.C. and F.R.; supervision, A.F. and F.R. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by GeoBioTec Research Centre (UIDB/04035/2020), funded by FCT—Fundação para a Ciência e a Tecnologia, FEDER funds through the Operational Program Competitiveness Factors COMPETE and by national funds (OE), through FCT, in the scope of the framework contract foreseen in the numbers 4, 5 and 6 of the article 23, of the Decree-Law 57/2016, of 29 August, changed by Law 57/2017, of 19 July.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank the Museum of Archaeology D. Diogo de Sousa (MDDS), in Braga, Portugal, for sampling permission. We are very grateful to Vitor Hugo Torres from MDDS for his support and assistance in mortars sampling and to Cristina Sequeira for her assistance in mortars chemical analyses at Geosciences Department from University of Aveiro (UA).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Silva, A.S.; Paiva, M.; Ricardo, J.; Salta, M.M.; Monteiro, A.M.; Candeias, A.E. Characterisation of Roman mortars from the archaeological site of Tróia (Portugal). *Mater. Sci. Forum* **2006**, *514–516*, 1643–1647. [[CrossRef](#)]
2. Cardoso, I.; Macedo, M.F.; Vermeulen, F.; Corsi, C.; Santos Silva, A.; Rosado, L.; Candeias, A.; Mirão, J. A multidisciplinary approach to the study of archaeological mortars from the town of Ammaia in the Roman province of Lusitania (Portugal)*. *Archaeometry* **2014**, *56*, 1–24. [[CrossRef](#)]
3. Borsoi, G.; Santos Silva, A.; Menezes, P.; Candeias, A.; Mirão, J. Analytical characterization of ancient mortars from the archaeological Roman site of Pisões (Beja, Portugal). *Constr. Build Mater.* **2019**, *204*, 597–608. [[CrossRef](#)]
4. Velosa, A.L.; Coroado, J.; Veiga, M.R.; Rocha, F. Characterisation of roman mortars from Conímbriga with respect to their repair. *Mater. Charact.* **2007**, *58*, 1208–1216. [[CrossRef](#)]
5. Pacht, V.; Stefanidou, M. Technology of multilayer mortars applied in ancient floor mosaic substrates. *J. Archaeol. Sci.* **2018**, *20*, 683–691. [[CrossRef](#)]
6. Izzo, F.; Arizzi, A.; Cappelletti, P.; Cultrone, G.; De Bonis, A.; Germinario, C.; Graziano, F.; Grifa, C.; Guarino, V.; Mercurio, M.; et al. The art of building in the Roman period (89 B.C.–79 A.D.): Mortars, plasters and mosaic floors from ancient *Stabiae* (Naples, Italy). *Constr. Build. Mater.* **2016**, *117*, 129–143. [[CrossRef](#)]
7. Kramar, S.; Zalar, V.; Urosevic, M.; Körner, W.; Mauko, A.; BMirtič, B.; Lux, J.; Mladenović, A. Mineralogical and microstructural studies of mortars from the bath complex of the Roman *villa rustica* near Mošnje (Slovenia). *Mater. Charact.* **2011**, *62*, 1042–1057. [[CrossRef](#)]
8. Ergenç, D.; Fort, R. Multi-technical characterization of Roman mortars from Complutum, Spain. *Measurement* **2019**, *147*, 106876. [[CrossRef](#)]

9. Moreno-Alcaide, M.; Compañia-Prieto, J.M. Roman plasters and mortars from ancient Cosa (Tuscany-Italy). Mineralogical characterisation and construction from *domus* 10.1 (House with *Cryptoporticus*). *J. Archaeol. Sci.* **2018**, *19*, 127–137. [[CrossRef](#)]
10. Starinieri, V.; Papayianni, I.; Stefanidou, M. Study of materials and technology of ancient floor mosaics' substrate. *Conservar. Património* **2008**, *7*, 29–34. [[CrossRef](#)]
11. Miriello, D.; Barca, D.; Bloise, A.; Ciarallo, A.; Crisci, G.M.; De Rose, T.; Gattuso, C.; Gazineo, F.; La Russa, M.F. Characterisation of archaeological mortars from *Pompeii* (Campania, Italy) and identification of construction phases by compositional data analysis. *J. Archaeol. Sci.* **2010**, *37*, 2207–2223. [[CrossRef](#)]
12. Leone, G.; De Vita, A.; Magnani, A.; Rossi, C. Characterization of archaeological mortars from Herculaneum. *Thermochim. Acta* **2016**, *624*, 86–94. [[CrossRef](#)]
13. Martins, M.; Carvalho, H. Roman city of *Bracara Augusta* (Hispania Citerior Tarraconensis): Urbanism and territory occupation. *Agri Centuriate* **2017**, *14*, 79–98.
14. Martins, M. *Bracara Augusta*: A Roman town in the Atlantic area. In *Journal of Roman Archaeology*; JRA Supplementary Series 62; Thomson-Shore: Dexter, MI, USA, 2006; pp. 213–222.
15. Martins, M.; Braga, C.; Magalhães, F.; Ribeiro, J. Constructing identities within the periphery of the Roman Empire: North-west Hispania. In *Rome and Barbaricum. Contributions to the Archaeology and History of Interaction in European Protohistory*; Curcă, R.G., Rubel, A., Symonds, R., Voß, H.U., Eds.; Archaeopress: Oxford, UK, 2020; pp. 135–154.
16. Delgado, M.; Gaspar, A.M. Intervenção arqueológica na Zona P1 (Antigas cavaliariças do regimento de infantaria de Braga)—Archaeological intervention in zone P1 (Old stables of the Braga infantry regiment). *Cad. Arqueol.* **1986**, *3*, 155–167.
17. Martins, M.; Carvalho, H. *Bracara Augusta* and the changing rural landscape. In *Changing Landscapes. The Impact of Roman Towns in the Western Mediterranean, Proceedings of the International Colloquium, Castelo de Vide, Marvão, Portugal, 15–17 May 2008*; Corsi, C., Vermeulen, F., Eds.; Ante Quem: Bologna, Italy, 2010; pp. 281–298.
18. Martins, M.; Mar, R.; Ribeiro, J.; Magalhães, F. The Roman theatre of *Bracara Augusta*. In Proceedings of the XVIII CIAC: Centre and Periphery of the Ancient World, Mérida, Spain, 13–17 May 2013; pp. 861–864.
19. Magalhães, F. The Roman Domus on the NO Peninsula. Architecture, Construction and Sociability. Ph.D. Thesis, University of Minho, Braga, Portugal, 2019. (In Portuguese).
20. Delgado, M.; Martins, M. Intervenção arqueológica na Zona P1 (Antigas cavaliariças do regimento de infantaria de Braga)—Archaeological intervention in zone P1 (Old stables of the Braga Infantry Regiment). *Cad. Arqueol.* **1988**, *5*, 79–93.
21. Abraços, F.; Wrench, L. The Roman mosaics of *Bracara Augusta*: Re-reading and reinterpretation of decorative motifs. *J. Mosaic Res.* **2017**, *10*, 9–26. [[CrossRef](#)]
22. Abraços, F.; Lima, A.M.C.; Mourão, C.; Limão, F.; Wrench, L.; Pinto, M.M.; Gomes, P.D.; Lopes, R. *The Corpos of the Roman Mosaics of Conventus Bracaraugostanus*; Centro de Estudos Históricos: Lisbon, Portugal, 2019.
23. Martins, M.; Magalhães, F.; Peñín, R.; Ribeiro, J. The housing evolution of Braga between late Antiquity and the early Middle Ages. In *Arqueologia Medieval. Hàbitats Medievais*; Sabaté, F., Brufal, J., Eds.; Pagès Editors: Lleida, Spain, 2016; pp. 35–52.
24. Abraços, F. Conservation et restauration des mosaïques romaines au Portugal—Quelques exemples dans les collections de musées. In *Lessons Learned: Reflecting on the Theory and Practice of Mosaic Conservation; Proceedings of the 9th ICCM Conference, Hammamet, Tunisia, 29 November–3 December 2005*; Khader, B., Abed, A.B., Demas, M., Roby, T., Eds.; Getty Publications: Los Angeles, CA, USA, 2008; pp. 69–74.
25. Martins, M.; Carvalho, H. Transforming the territory: *Bracara Augusta* and its Roman cadaster. *Rev. Historiogr.* **2016**, *25*, 219–243.
26. Ferreira, N. *Geological Chart of Portugal in Scale 1:50,000—Sheet 5-D, Braga*; Ministério da Economia, Instituto Geológico Mineiro, Departamento de Geologia: Lisboa, Portugal, 2000.
27. Antunes, I.M.H.R.; Gonçalves, L.M.B. The “Sete Fontes” groundwater system (Braga, NW Portugal): Historical milestones and urban assessment. *Sustain. Water Resour. Manag.* **2018**, *5*, 235–248. [[CrossRef](#)]
28. Prudêncio, M.I. Ceramic in ancient societies: A role for nuclear methods of analysis. In *Nuclear Chemistry: New Research*; Koskinen, A.N., Ed.; Nova Science Publishers, Inc.: Hauppauge, NY, USA, 2008; Volume 2, pp. 51–81.
29. Ribeiro, J.; Martins, M. Os materiais de construção em *Bracara Augusta*. In *História da Construção—Os Materiais*; Melo, A., Ribeiro, M.V., Eds.; CITEM: Braga, Portugal, 2012; pp. 15–34.
30. Taelman, D.; Elburg, M.; Smet, I.; De Paepe, P.; Lopes, L.; Vanhaecke, F.; Vermeulen, F. Roman marble from Lusitania: Petrographic and geochemical characterisation. *J. Archaeol. Sci.* **2013**, *40*, 2227–2236. [[CrossRef](#)]
31. Ribeiro, J. *Arquitectura em Bracara Augusta. Uma análise das Técnicas Edilícias*; Afrontamento: Porto, Portugal, 2013.
32. Cazes, Q.; Aremond, J.C. Les fouilles du musée Saint Raymond à Toulouse (1994–1996). In *Mémoires de la Société Archeologique du Midi de la France*; Conseil Général de La Haute-Garonne; Centre Atio Al D'études Spatiales: Toulouse, France, 1997; pp. 35–53.
33. Perrault, C. *Les Dix Livres d'Architecture de Vitruve*; Pierre Mardaga Editeur: Liège, France, 1996.
34. Fragata, A. Study of the mortar support of the mosaics of the imperial domus integrated in the space crypt of the regional museum of archaeology D. Diogo de Sousa (MDDS). In Proceedings of the XIV A.D. Saeculum Augustum—The Age of Augustus International Conference, Lisbon, Portugal, 24–26 September 2014. (In Portuguese).
35. Fragata, A. Compatible Renders for Masonries Submitted to Severe Water Action. Ph.D. Thesis, University of Aveiro, Aveiro, Portugal, 2013. (In Portuguese).
36. Veiga, R.; Fragata, A.; Tavares, M.; Magalhães, A.; Ferreira, N. Inglesinhos convent: Compatible renders and other measures to mitigate water capillary rising problems. *J. Build. Apprais.* **2009**, *5*, 171–185. [[CrossRef](#)]

37. Alonso-Olazabal, A.; Ortega, L.A.; Zuluaga, M.C.; Ponce-Antón, G.; Jiménez Echevarría, J.; Fernández, A.C. Compositional characterization and chronology of roman mortars from the archaeological site of Arroyo de la Dehesa de Velasco (Burgo de Osma—Ciudad de Osma, Soria, Spain). *Minerals* **2020**, *10*, 393. [[CrossRef](#)]
38. Miriello, D.; Bloise, A.; Crisci, G.M.; De Luca, R.; De Nigris, B.; Martellone, A.; Osanna, M.; Pace, R.; Pecci, A.; Ruggieri, N. New compositional data on ancient mortars and plasters from *Pompeii* (Campania—Southern Italy): Archaeometric results and considerations about their time evolution. *Mater. Charact.* **2018**, *146*, 189–203. [[CrossRef](#)]
39. Lubelli, B.; Nijland, T.; Hees, R. Self-healing of lime based mortars: Microscopy observations on case studies. *Heron* **2011**, *56*, 75–91.
40. Ontiveros-Ortega, E.; Rodríguez-Gutiérrez, O.; Navarro, A. Mineralogical and physical-chemical characterization of Roman mortars used for monumental substrates on the hill of San Antonio, in the Roman city of Itálica (prov. *Baetica*, Santiponce, Seville, Spain). *J. Archaeol. Sci. Rep.* **2016**, *7*, 205–223.
41. Daoudi, L.; Rocha, F.; Costa, C.; Arrebei, N.; Fagel, N. Characterization of rammed earth materials from the XVIth century. Badii palace in Marrakech, Morocco to ensure authentic and reliable restoration. *Geoarchaeology* **2017**, *33*, 529–541. [[CrossRef](#)]
42. Fragata, A.; Veiga, R.; Velosa, A. Substitution ventilated render systems for historic masonry: Salt crystallization tests evaluation. *Const. Build. Mater.* **2016**, *102*, 592–600. [[CrossRef](#)]
43. Liritzis, I.; Xanthopoulou, V.; Palamara, E.; Papageorgiou, I.; Iliopoulos, I.; Zacharias, N.; Vafiadou, A.; Karydas, A. Characterization and provenance of ceramic artifacts and local clays from late Mycenaean Kastrouli (Greece) by means of p-XRF screening and statistical analysis. *J. Cult. Herit.* **2020**, *46*, 61–81. [[CrossRef](#)]
44. Papageorgiou, I. Ceramic investigation: How to perform statistical analyses. *Archaeol. Anthropol. Sci.* **2020**, *12*, 210. [[CrossRef](#)]