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Chemical and mineralogical characterization of historic mortars from the Santa Eulalia de Bóveda temple, NW Spain

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ABSTRACT

Bulk samples of mortars from the Santa Eulalia de Bóveda temple (NW Spain) have been characterized from a chemical and mineralogical point of view, with the aims of contributing technological and provenance inferences, and evaluating possible correlations with the various identified stages along historical periods of construction.

Mortar samples were analyzed by X-ray diffraction and neutron activation analysis.

Mineralogical associations found are similar (quartz, alkali feldspars, calcite and mica) for all samples, only varying in their proportions, mainly calcite. Statistical and geochemical studies allowed the differentiation of two main groups, enhancing definition of the granite nature of the aggregate, and of a significant variation in calcite proportion (lime binder). Two outlying samples were identified: one with higher calcite proportion and other corresponded to a plaster with a different raw material source.

A clear correlation between the chemical groups and the independently defined chronological stages could not be found in this work. However, mortar samples from the earlier stage were associated with a higher aggregate/binder proportion.

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1. Introduction

The restoration of buildings of importance in architectural heritage requires an advanced knowledge of the building materials. The composition of historic mortars can vary dramatically depending on the geographical location and the time period of construction. Their as-found composition is also strongly dependent on levels of alteration/deterioration, due to their high solubility in comparison to brick or stone. Mortars are composed of a binder, aggregate, and sometimes additives. The binder provides consistency. Until the use of Portland cement in the 19th century, lime was the main binder used. Aggregates are normally sand or rock fragments of variable sizes. Considering the two components, the mortar as a whole is morphologically very similar to a sedimentary clastic rock with carbonate cement. Thus, geological methodology is appropriate for their characterization. A reliable restoration and preservation of mortars requires an advanced knowledge of their composition. Mortars of different binder types (lime, gypsum and mud) have been used historically in buildings, but lime mortars are most commonly found. Sand has been widely used as aggregate, although other materials (calcareous and other natural or artificial aggregates, like brick, stone fragments, and pozzolana) have also been employed (Elsen, 2006; Middendorf et al., 2005a,b).

Superficial architectural modifications and restorations introduced in ancient buildings at different times can make it difficult to distinguish the various construction stages, and may hinder the identification of original mortars when similar binder and aggregate have been used. Estimation of proportions of binder/aggregate within mortars is commonly used to characterize them with a view to building conservation (Elsen, 2006); the proportion depends not only on the historical period but also on the mortar type or function (Moropoulou et al., 2000).

Different approaches have been considered to characterize mortars from various points of view. Until 1980 the characterization of historic mortars was mostly based on traditional wet



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Fig. 1. Location of stages I, II, III and IV of Santa Eulalia de Bóveda temple (drawn by A. Rodríguez Paz and P. Mañana-Borrazás).

chemical analyses, and interpretation of results was difficult. Later methods used optical microscope, X-ray diffraction (XRD), scanning electron microscopy (SEM) coupled to energy dispersive X-ray spectroscopy (EDX), simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA), etc. (Elsen, 2006).

Chemical and mineralogical characterization of mortars may be used to understand chronological aspects of the evolution of historical buildings (Vendrell-Saz et al., 1996). Considering a building constructed at different historical stages, the raw materials used in the mortars manufactured during one stage do not necessarily have the same provenance than materials of other stages. If we assume that the same mortar components are used in a same historical stage, its geochemical and mineralogical characterization may enable to establish chronological relationships. However, this method is not useful if the same quarry was used in all periods.

Several studies comprising chemical and mineralogical composition of mortar components have been applied to answer questions related with formulation of repair strategies and replacement of mortars in built monuments, as well as in provenance and technological inferences (Alvarez et al., 2000; Hughes and Cuthbert, 2000; Moropoulou et al., 2000; Ortega et al., 2008; Barba et al., 2009). This compositional approach has been widely used to characterize cultural heritage artifacts, and also mortars in restoration and treatment work and in studies of manufacturing technology and dating (Maravelaki-Kalaitzaki et al., 2003; Casadio et al., 2005; Meir et al., 2005; Nawrocka et al., 2005), particularly by using trace elements.

In the present study the mineralogical and chemical composition of mortars from building structures of the Santa Eulalia de Bóveda temple is investigated. It aims to answer questions regarding the technologies employed in their production and finality, and how observed differences may arise from construction using different technologies, and/or from the use of raw materials from different sources. This knowledge may also be useful in restoration and treatment work regarding the materials employed in mortar preparation.

2. Santa Eulalia de Bóveda temple: brief historical overview

The Santa Eulalia de Bóveda monument (Lugo, NW Spain) is an historical building presenting architectural features included in the Romanesque, Paleochristian and Late Medieval architecture. Its origin, construction time and evolution are controversial, as it has been attributed to different historical periods (Montenegro Rúa, 2005; Montenegro Rúa et al., 2008). Although there is still no consensus about its chronology, its utility or its constructive evolution, five constructive phases have been suggested by several authors based on the stratigraphical analysis of their walls and components (Blanco-Rotea, 2008; Blanco-Rotea et al., 2009; Vidal Caeiro, 2003, 2006). The oldest phase has been attributed to the Roman period and/or to late-medieval times. Five construction stages and a theoretical shape of the building at each stage including different stratigraphical units are presented in Fig. 1.

Stage I — this stage includes the oldest remains preserved, comprising the structure of the ground floor, masonry of large ashlars inside the walls, a water pool larger than the present day one, the apse with a vault made of brick walls in the western part and a narthex made of granite ashlars.

Stage II – this comprises two stages that could be contemporary: stage IIa (modifications in the ground floor and the narthex) and stage IIb (construction of a vaulted upstairs floor). However, some architectural elements included in stage II could correspond to stage III, and vice versa. Within stage II the inner space of the ground floor is divided into three naves by two arches aligned East–West, a medication to the front door, and the application of plaster and a painted coating that cover the vault and arches. Utrero Agudo (2006) believes that these elements could correspond to the same late-medieval stage, but other data suggest a series of architectural alterations.

Table 1

Stage, reference, description and location of the mortars samples of Santa Eulalia de Bóveda temple.

Stage	Sample	Description and Location
Ι	MUE 105	Joint mortar — inner wall
	MUE 108	Joint mortar — vault arches
	MUE 109	Joint mortar concrete – between
		vault arches
	MUE 126	Joint mortar — apse vault
II	MUE 83A	Joint mortar — main door horseshoe arch
	MUE 83B	Joint mortar — main door horseshoe arch
	MUE 110	Plaster – inner wall base
III	MUE 013	Joint mortar – upstairs brick vault
	MUE 017	Joint mortar – upstairs brick vault
	MUE 025	Joint mortar — upstairs vault
		extrados (masonry)
IV	MUE 011	Joint mortar – upstairs window
	MUE 014	Plaster — upstairs vault
	MUE 022	Joint mortar — rebuilt upper
		part of upstairs vault

Table 2

Mineralogical associations of mortars of the Santa Eulalia de Bóveda temple obtained by XRD (% wt). (Q – quartz; C – calcite; Kf – potassium feldspar; Pl – plagioclase; Mi – mica; K – kaolinite; Am – amphibole; Gy – gypsum; Tl – talc).

Stage	Sample	Q	С	Kf	Pl	Mi	К	Others
Ι	MUE 105	52	1	32	7	7	1	
	MUE 108	41	3	26	4	24	2	Gy
	MUE 109	45	13	15	6	19	2	Gy, Tl
	MUE 126	20	4	52	3	19	2	Gy
II	MUE 83A	30	11	34	-	20	5	Gy
	MUE 83B	19	22	24	5	20	10	
	MEU 110	20	13	36	2	26	3	Tl
III	MUE 013	25	47	17	1	7	3	Tl
	MUE 017	20	28	36	-	15	2	Tl, Am
	MUE 025	26	21	16	5	28	4	Tl, Am
IV	MUE 011	39	4	30	11	13	3	
	MUE 014	39	16	26	12	6	1	Am
	MUE 022	22	10	39	2	22	5	Gy

Stage III — this stage comprises the lower part wall of the upstairs floor vault (the only one preserved in this floor). Three reconstructive changes may be identified: the addition of a joint mortar in the brick masonry, the restoration in the East side, namely in the upper part of the vault including a window (the latter two are possibly contemporary).

Stage IV - in this stage, attributed to the Post Medieval period, different modifications and destruction of building components were identified. On the downstairs floor the West wall and the vault were cut to build a door and stairs connecting both floors, in the narthex a half-dome has been built, and in the upstairs floor a vault was modified.

Stage V — this stage includes contemporary interventions between 1929 and 2007.

3. Materials and methods

The sampling of mortars was very restricted even with legal authorization, due to the classification of the temple as National Monument. Therefore, sampling was carried out by taking only a small piece of each mortar (~5 to 6 g) with a chisel, which compromised the study of the binder and the aggregate components separately. Considering the fact that previous studies have already characterized the binder/aggregate proportions (García de Miguel, 2007), and that conservation strategies is not our main purpose but rather a compositional study aiming at chronological considerations, only the bulk sample was used. Thirteen samples have been collected from the four first construction stages (García de Miguel, 2007; Blanco-Rotea, 2008; Blanco-Rotea et al., 2009), four from the first stage and three from the other ones (Table 1).

Mineralogical characterization was based on X-ray diffraction (XRD) with a Philips X'Pert Pro diffractometer equipped with



Fig. 2. X-ray diffraction phase diagram of a bulk sample of the historic mortar MUE 025.

	N	21.3 19.1	10.4	36.9	47.4	30.9	10.3	10.6	14.6	9.34	18.1	9.18	11.1
	Th	11.0	9.05	10.5	9.09	9.11	10.2	7.59	10.0	9.67	12.1	4.05	10.1
	Ta	1.67 1.82	1.54	1.85	1.44	1.39	1.42	1.02	1.68	1.38	1.91	0.43	1.61
	Ηf	2.69 2.71	2.53	2.74	2.29	2.18	2.46	1.83	2.31	2.29	2.84	1.28	2.55
	Lu	0.34 0.24	0.19	0.25	0.18	0.23	0.21	0.15	0.18	0.17	0.22	0.22	0.20
	ЧY	2.75 1.91	1.52	2.00	1.43	1.45	1.59	1.18	1.54	1.37	1.79	1.45	1.55
	Dy	6.42 4.74	2.91	4.21	3.32	3.52	3.46	2.96	4.06	3.44	4.35	2.17	3.97
	τb	1.15 0.75	0.59	0.64	0.62	0.63	0.65	0.51	0.62	0.60	0.85	0.30	0.66
	Eu	0.796 0.553	0.400	0.563	0.375	0.357	0.401	0.316	0.378	0.358	0.468	0.263	0.364
	Sm	7.24 6.08	3.69	5.65	4.56	4.75	3.98	3.12	4.41	4.25	5.77	1.81	4.54
	pN	27.4 24.1	14.1	20.2	17.4	16.8	15.4	12.2	17.3	17.2	22.2	5.40	16.5
	Ce	36.3 40.2	29.1	34.7	30.5	33.5	32.0	24.9	35.4	37.2	43.3	14.1	35.8
	La	22.7 20.4	14.1	16.5	15.2	16.0	14.8	11.1	16.0	16.3	20.2	7.25	16.0
	Ba	157 163	200	254	240	153	223	131	129	124	153	205	128
l otherwise).	Cs	9.64 9.98	8.67	9.62	8.49	7.93	10.0	6.46	8.39	7.48	10.8	7.00	8.94
	Sb	0.27 0.30	0.34	0.77	0.47	0.36	0.35	0.45	0.25	0.97	0.47	0.35	0.22
	Zr	40.00 21.37	47.77	24.15	0.01	0.01	52.88	38.55	20.23	43.51	18.45	20.29	15.01
pecifie	Rb	198 191	187	196	155	147	191	120	174	158	214	144	177
nless s	Br	7.39 6.74	3.85	14.1	9.29	3.78	7.84	7.50	5.81	1.70	2.25	3.09	3.14
n g/gri)	As	6.42 2.07	1.84	4.16	7.16	3.63	2.05	5.99	2.82	1.87	3.16	3.95	1.92
emple.	Ga	20.6 20.5	11.3	21.2	15.1	13.7	17.0	13.1	21.0	12.5	17.9	6.51	18.8
veda t	Co	3.23 2.99	2.67	5.06	1.75	2.49	2.87	1.77	1.82	1.95	4.04	2.10	1.74
ı de Bó	G	7.09 5.27	6.94	8.31	5.25	4.21	6.91	4.98	3.93	4.73	8.18	8.37	1.38
Eulalia	Sc	5.32 5.94	4.42	6.08	4.43	3.84	4.01	2.17	3.27	3.69	5.09	3.18	4.80
the Santa	$Fe_2O_3T\%$	1.93 1.64	1.47	1.87	1.21	1.06	1.50	1.07	1.22	1.25	1.20	0.90	1.27
ortars of	Mn0%	0.19 0.06	0.06	0.04	0.05	0.05	0.04	0.03	0.03	0.03	0.04	0.02	0.03
A of mo	$K_20\%$	4.71 4.44	3.93	3.95	3.48	3.44	3.90	2.81	4.22	3.83	4.88	3.42	4.30
ed by INA	$Na_20\%$	1.26 0.41	0.66	0.93	0.27	0.29	0.52	0.31	0.34	0.44	0.97	1.07	0.42
ıl data obtainı	Sample	MUE 105 MUE 108	MUE 109	MUE 126	MUE 083A	MUE 083B	MUE 110	MUE 013	MUE 017	MUE 025	MUE 011	MUE 014	MUE 022
Table 3 Chemica	Stage	-			Π			Ш			>I		



Fig. 3. Bivariate plot of La versus Sc for mortar samples of the Santa Eulalia de Bóveda temple.

a goniometer PW $3050/6 \times$ with CuK α radiation, operating at 45 kV and 40 mA. Non-oriented aggregates of pulverized bulk material were measured between 4 and $70^{\circ}2\theta$ using a step of 0.02° and 1.5 s scanning time in each step. Semi-quantitative analyses were obtained by measuring both the main peak area and the thickness at half height of each mineral (full width at half maximum). The ratio of this value by the reflector power gives the semi-quantitative proportion of each mineral (Schultz, 1964; Biscaye, 1965; Martin-Pozas, 1968; Galhano et al., 1999). The total percentage of phyllosilicates was determined by considering the d = 4.48 Å peak. The percentage of various clay minerals was determined by the maximum reflection intensity of each one, and then recalculated to a phyllosilicate percent.

Chemical analyses of bulk samples have been performed by neutron activation analysis (NAA) to obtain the concentration of Na, K, Fe, Mn, Sc, Cr, Co, Ga, As, Br, Rb, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, Lu, Hf, Ta, Th and U. Irradiations were done in the core grid of the Portuguese Research Reactor (RPI, ITN, Sacavém). All powdered samples were prepared for irradiation by weighing 200-300 mg of powder into cleaned high-density polyethylene vials. Two standard multi-element materials were used (GSS4 and GSD9) from the Institute of Geophysical and Geochemical Prospecting (IGGE) for chemical analysis (comparative method), taking as reference values data tabulated by Govindaraju (1994). Long irradiations (6 h) were carried out in packets including samples and standards into the reactor core at a heat flux of $3.96 \times 10^{12} \,\mathrm{cm}^{-2} \,\mathrm{s}^{-1} \varphi \mathrm{epi} / \varphi \mathrm{th} = 1.03\%; \quad \varphi \mathrm{th} / \varphi \mathrm{fast} = 29.77.$ Short irradiations were performed (2 min), at a flux of $4.4 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. Both Fe and Au flow monitors were also irradiated to correct flow variations. Two gamma ray spectrometers were used to measure elemental composition: a coaxial Ge detector of 150 cm³ and a low-energy photons detector (LEPD), both connected to a multichannel analyzer Accuspec B (Canberra) through a Canberra 2020 amplifier. The first system has a FWHM of 1.9 keV at 1.33 MeV and the second one a FWHM of 300 eV at 5.9 keV and 550 eV at 122 keV. The relative error of the method is less than 5% and occasionally 10% (Gouveia and Prudêncio, 2000).

4. Results and discussion

The mineralogical compositions obtained by X-ray diffraction of the mortar samples are presented in Table 2. Quartz is the main component of the mortars, associated with potassium feldspars, calcite and mica in different proportions, and plagioclase and kaolinite as accessory minerals. In Fig. 2 a diffraction pattern of sample MUE 025 is shown.

Samples from stage I consist mainly of quartz, K-feldspars and mica. The quotient quartz/feldspars is always higher than one, except in one sample (MUE 126). Calcite, plagioclase, mica and gypsum are accessory minerals.

Samples from stage II present almost equal proportions of quartz, K-feldspars and mica. Calcite, plagioclase and kaolinite are accessory minerals. Sample MUE 083B is richer in calcite and kaolinite than the others from this stage. The quartz/feldspar ratio is always lower than one.

Samples from stage III are the richest in calcite, associated with quartz, K-feldspars and micas. Sample MUE 013 differs from all the others due to a dominance of calcite (around 50%). Plagioclase, kaolinite, talc, gypsum and amphibole are accessory minerals.

Samples from stage IV present a relationship between quartz and feldspars higher than one, except in one sample, and the same accessory minerals.

A previous work using petrography showed that the aggregate component of the mortars is of granitic origin, comprising abundant quartz, K-feldspars and mica, and the binder consist of micritic calcite, in some cases with organic matter or clay materials (García de Miguel, 2007).

In the present work the aggregate and the binder proportions were estimated based on XRD results. We assume that the aggregate proportion corresponds to the quartz and feldspars sum, and the binder to the calcite percentage. This assumption derives from the previous petrographic study, which points to a granitic origin of the aggregate and showed the presence of micritic calcite only as binder (García de Miguel, 2007). According to Middendorf et al. (2005a,b), XRD cannot distinguish between carbonate in the aggregate and in the lime paste from the binder, and only detects crystalline phases resulting from carbonation and hardening. Also, amorphous phases like calcium silica gel are not detected. However, in the present work we consider that the semi-quantification obtained by XRD gives an idea of the aggregate/binder proportion.

In general the quotient aggregate/binder determined in the mortars are higher than one, with the exception of sample MUE 013, which corresponds to a plaster. Thus, results point to lower aggregate/binder proportion in all samples of stage III and in one sample of stage II. Samples from stage I present the highest



Fig. 4. Bivariate plot of La versus Th for mortar samples of the Santa Eulalia de Bóveda temple.

 Table 4

 Rare earth elements parameters of mortars of the Santa Fulalia de Bóveda temple

Stage	Sample	Ce/Ce*	Eu/Eu*	(La/Yb) _N	(La/Sm) _N	Sum REE
I	MUE 105	0.71	0.33	5.69	1.97	105
	MUE 108	0.88	0.29	7.37	2.10	98.9
	MUE 109	0.95	0.32	6.40	2.40	66.6
	MUE 126	0.93	0.32	5.69	1.83	84.7
II	MUE 083A	0.90	0.25	7.33	2.09	73.6
	MUE 083B	0.96	0.23	7.61	2.11	77.3
	MUE 110	0.99	0.30	6.42	2.33	72.5
III	MUE 013	1.02	0.30	6.49	2.23	56.4
	MUE 017	1.01	0.26	7.17	2.27	79.9
	MUE 025	1.05	0.26	8.21	2.40	80.9
IV	MUE 011	0.97	0.25	7.78	2.19	99.2
	MUE 014	0.95	0.43	3.45	2.51	33.0
	MUE 022	1.03	0.24	7.12	2.21	79.5

aggregate/binder proportions. In samples presenting higher amounts of feldspars relative to quartz and calcite, feldspars (Kfeldspars mainly) may have been used as fluxes.

In addition, XRD allowed us to establish that no high temperature phases were attained in the technological procedure of the making of mortars, so the burning of the calcareous stone to obtain the lime paste formed from the binder, was done at temperatures lower than 800-900 °C (presence of micas), and may be lower than 500 °C, due to the presence of kaolinite. However, this clay mineral is present in low amounts, and part may be neoformed due to alteration of feldspars.

The chemical composition of mortar bulk samples is reported in Table 3. Chemical composition appears to be related with the geological nature of the aggregate and binder. Chemical results show that samples with higher amounts of K and Rb have higher proportions of alkali feldspars and mica. Low Cs values were found in carbonate rich samples (see Table 2).

Among the chemical elements studied, Th shows a positive correlation with other poorly soluble elements such as K, Rb, Cs and La, and other REE. Samples from stage I present higher contents of Fe. Chemical and mineralogical results suggest a more felsic source for aggregates in the case of samples MUE 105, MUE 108, MUE 126 (stage I) and MUE 011 (stage IV), and a more mafic source for sample MUE 014 from stage IV. Samples with lower aggregate/ binder proportion present high contents of As, pointing to the preferential presence of this element in calcite (see Tables 2 and 3).



Fig. 5. Chondrite-normalized rare earth patterns for mortar samples from the Santa Eulalia de Bóveda temple. Normalization values from Korotev (1996) resulting from multiplying Anders and Grevesse (1989) values by a factor of 1.36.



Fig. 6. Chemical element distribution patterns of samples normalized to the average of G1.

Multivariate statistical analysis using all determined chemical elements as variables points to the existence of two main groups and two outliers: Group 1 (G1) comprises samples MUE 109 (stage I), MUE 083A, MUE 083B, MUE 110 (stage II), MUE 017, MUE 025 (stage III) and MUE 022 (stage IV); Group 2 (G2) comprises samples MUE 105, MUE 108, MUE 126 (stage I) and MUE 011 (stage IV); and the two defined outliers are sample MUE 013 (stage III) and sample MUE 014 (stage IV).

Group 2 with higher aggregate/binder proportion presents higher contents of all studied elements in general. The opposite behavior was found for samples MUE 013 and MUE 014. This is respectively related to higher carbonate content in the bulk sample (lower aggregate/binder proportion) and to a more mafic source. This tendency can be seen in Figs. 3 and 4, where biplot graphs of La *vs* Sc and La *vs* Th are shown.

Regarding rare earth elements (REE), group 2 presents higher contents. In sample MUE 105 a negative Ce anomaly was also found (Table 4 and Fig. 5). Sample MUE 013 presents lower REE contents and a small positive Ce anomaly. MUE 014 presents a different REE pattern, with the lowest degree of differentiation between light REE and heavy REE (Table 4).

The descriptive and multivariate statistical analyses showed that among the chemical elements studied, the best discriminates are the less mobile in surface environments (K, Sc, Ga, Rb, Cs, REE, Hf, Ta and Th). These elements can be used to differentiate the original materials of mortars particularly related with the aggregate. Based on the higher chemical homogeneity found for group 1, the average values of the above-referred chemical elements for the samples of this group were used as references for normalization of the chemical contents of other samples from group 2, and the outliers. The chemical distribution patterns obtained after this procedure are shown in Fig. 6. Group 2 is enriched in all studied elements, relative to the average concentration of the main group of mortars analyzed (G1). On the other hand, sample MUE 013 is depleted in all studied elements, most probably due to a dilution effect of the calcite proportion in this sample, which is around 50%. The same type of raw material may have been used for the aggregate, but for some reason a greater proportion of binder appears to have been included in the recipe. Sample MUE 014 differs from all the others. It exhibited clear depletion of studied elements relative to the group 1 average, presented more heterogeneous and higher REE fractionating. This indicates use of different raw material. This sample also presents strong depletion of Ga, REE (especially Nd and Tb) and Ta, elements usually strongly correlated with each other. Indeed, MUE 014 is not a joint mortar, like almost all the other samples (except MUE 110), but corresponds to remains of the plaster of the upstairs building. The MUE 014 sample also presents a mineralogical distinction, with higher plagioclase proportion, in similar amount to calcite, and the lowest mica percentage (see Table 2). Geochemical patterns point to a more mafic source for the raw material of this sample.

5. Conclusions

The study of the mortars and plasters from the Santa Eulalia de Bóveda monument by using chemical and mineralogical data of bulk material is presented. This methodological approach was adopted due to constraints on sample size (<5 g), which limited our ability to apply the usual methods (mechanical or chemical) to separate aggregate and binder.

Chemical and mineralogical results confirm an aggregate of granitic nature and a calcite binder. Mineralogical associations and proportions indicate a technological procedure involving the burning of the calcareous stone at temperatures lower than 800–900 °C to obtain the lime paste. The chemical results obtained enable the differentiation of two main groups and two outliers. A clear correlation between geochemical groups and chronological stages was not found. However, most mortars of the earlier stage present a similar chemical pattern (Group 2) and a higher aggregate/ binder proportion. The majority of the samples was relatively similar from a chemical point of view (Group 1), and enriched in calcite. Some of the chemical differences of the outliers can be explained by the calcite amount, except in one case (plaster) where geochemical pattern points to a different source of the raw material (more mafic).

The results obtained in this work, by studying the bulk material, show how this approach can be useful for the characterization and differentiation of mortars. Indeed a multivariate statistical analysis using chemical data, enhance the role of the elements with the lower mobile behavior in surface environments (potassium, scandium, gallium, rubidium, cesium, rare earth elements, hafnium, tantalum and thorium) for the differentiation of mortars. In this way, these elements can also be used for provenance issues, avoiding the effect of modifications in the chemical composition due to alteration processes. Results permit to establish different groups of mortars that can help to a better understanding of the building history, as well as in restoration and treatment work strategies.

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References

- Alvarez, J.I., Navarro, I., Martín, A., García Casado, P.J., 2000. A study of the ancient mortars in the north tower of Pamplona's San Cernin church. Cement and Concrete Research 30, 1413–1419.
- Anders, E., Grevesse, N., 1989. Abundances of the elements meteoric and solar. Geochimica et Cosmochemica Acta 53, 197–214.

- Barba, L., Blancas, J., Manzanilla, R., Ortiz, A., Barca, D., Crisci, G.M., Mirello, D., Pecci, A., 2009. Provenance of the limestone used in Teotihuacan (Mexico): a methodological approach. Archaeometry 51, 525–545.
- Biscaye, P.E., 1965. Mineralogy and sedimentation of recent deep-sea clay in the Atlantic Ocean and adjacent seas and oceans. Geological Society of America Bulletin 76, 803–832.
- Blanco-Rotea, R., 2008. Mirando hacia el futuro: conocer para conservar. La evolución constructiva de Santa Eulalia de Bóveda. In: Montenegro Rúa, E., Blanco-Rotea, R., Benavides, R., Portela, C. (Eds.), Santa Eulalia de Bóveda. Santiago de Compostela. Xunta de Galicia, Spain.
- Blanco-Rotea, R., García, R.B., Sanjurjo Sanchéz, J., Mosquera, D.F., 2009. Evolución constructiva de Santa Eulalia de Bóveda (Lugo, Galicia). Arqueología de la Arquitectura 6, 149–198.
- Casadio, F., Chiari, G., Simon, S., 2005. Evaluation of binder/aggregate ratios in archaeological lime mortars with carbonate aggregate: a comparative assessment of chemical, mechanical and microscopic approaches. Archaeometry 47 (4), 671–689.
- Elsen, J., 2006. Microscopy of historic mortars a review. Cement and Concrete Research 36, 1416–1424.
- Galhano, C., Rocha, F., Gomes, C., 1999. Geostatistical analysis of the influence of textural, mineralogical and geochemical parameters on the geotechnical behaviour of the 'Argilas de Aveiro' formation (Portugal). Clay Minerals 34, 109–116.
- García de Miguel, J.M., 2007. Informe sobre el estudio de muestras de morteros y sales de Santa Eulalia de Bóveda (Lugo). Inedit Report. Tomos Conservación Restauración, Lted, Vigo, Spain.
- Gouveia, M.A., Prudêncio, M.I., 2000. New data on sixteen reference materials obtained by INAA. Journal of Radioanalytical and Nuclear Chemistry 245 (1), 105–108.
- Govindaraju, K., 1994. Compilation of working values and sample description for 383 geostandards. Geostandards Newsletter 18, 1–158 (Special Issue).
- Hughes, J.J., Cuthbert, S.J., 2000. The petrography and microstructure of medieval lime mortars from the west of Scotland: implications for the formulation of repair and replacement mortars. Materials and Structures 33, 594–600.
- Korotev, R.L., 1996. A self-consistent compilation of elemental concentration data for 93 geochemical reference samples. Geostandards Newsletter 20, 217–245.
- Maravelaki-Kalaitzaki, P., Bakolas, A., Moropoulou, A., 2003. Physico-chemical study of Cretan ancient mortars. Cement and Concrete Research 33, 651–666.
- Martin-Pozas, J.M., 1968. El analisis mineralógico cuantitativo de los filosilicatos de la arcilla por difracción de rayos X. Ph.D. thesis, Granada, Spain: University of Granada.
- Meir, I.A., Freidin, C., Gilead, I., 2005. Analysis of Byzantine mortars from the Negev Desert, Israel, and subsequent environmental and economic implications. Journal of Archaeological Science 32, 767–773.
- Middendorf, B., Hughes, J.J., Callebaut, K., Baronio, G., Papayianni, I., 2005a. Investigative methods for the characterization of historic mortars – part 1: mineralogical characterization. Materials and Structures 38, 761–769.
- Middendorf, B., Hughes, J.J., Callebaut, K., Baronio, G., Papayianni, I., 2005b. Investigative methods for the characterization of historic mortars – part 2: chemical characterization. Materials and Structures 38, 771–780.
- Montenegro Rúa, E.J., 2005. El descubrimiento y las actuaciones arqueológicas en Santa Eulalia de Bóveda (Lugo). Estudio historiográfico y documental de los avatares de un bien de interés cultural. Concello de Lugo, España.
- Montenegro Rúa, E.J., Blanco Rotea, R., Benavides, R., Portela, C., 2008. Sta Eulalia de Bóveda. Xunta de Galicia, Santiago de Compostela, Spain (in Spanish and English).
- Moropoulou, A., Bakolas, A., Bisbikou, K., 2000. Investigation of the technology of historic mortars. Journal of Cultural Heritage 1, 45–58.
- Nawrocka, D., Michniewicz, J., Pawlyta, J., Pazdur, A., 2005. Application of radiocarbon method for dating of lime mortars. Geochronometria 24, 109–115.
- Ortega, L.A., Zuluaga, M.C., Alonso-Olazabal, A., Insausti, M., Ibañez, A., 2008. Geochemical characterization of archaeological lime mortars: provenance inputs. Archaeometry 50, 387–408.
- Schultz, L.G., 1964. Quantitative Interpretation of Mineralogical Composition X-ray and Chemical Data for the Pierre Shale. United States Geological Survey, Professional Paper, 391-C, 1–31 pp.
- Utrero Agudo, M.A., 2006. Iglesias tardoantiguas y altomedievales en la Península Ibérica: Análisis arqueológico y sistemas de abovedamiento. In: Anejos de Archivo Español de Arqueología, XL. CSIC, Madrid, Spain.
- Vendrell-Saz, M., Alarcon, S., Molera, J., Garcia-Valles, M., 1996. Dating ancient lime mortars by geochemical and mineralogical analysis. Archaeometry 38 (1), 143–149.
- Vidal Caeiro, L., 2003. Santa Eulalia de Bóveda: Análisis de los ladrillos. Gallaecia 22, 225–252.
- Vidal Caeiro, L. 2006, Arqueología de Santa Eulalia de Bóveda, III Premio de investigación Manuel Vázquez Seijas, Lugo, 11–122 pp.