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València la Vella (Spain) and Late Antique Mortars: A Regional Geochemical Approach

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***Abstract* – The present work deals with the chemical characterisation of the ancient mortars of València la Vella, a Visigothic site dated between the 6th and 8th centuries AD and located in the municipality of Riba-roja de Túria (València, Spain). Thirty-five mortar samples were collected from different masonries and analyzed by portable X-ray fluorescence spectroscopy and inductively coupled plasma mass spectrometry to obtain concentrations of major, minor and trace elements, including Rare Earth Elements. Data from multielement analysis were explored by multivariate statistics to detect the possible presence of different construction phases. Furthermore, the results from València la Vella were compared with a database of chemical data from ancient mortars sampled in historical buildings of València surroundings, spanning from Roman Era to Modern times, to observe differences and similarities with other building materials of the area.**

I. INTRODUCTION

The study of ancient mortars plays a fundamental role in the archaeological interpretation of architectural heritage. Through the analysis of construction materials, it is possible to identify building phases, the provenance of raw materials, technological developments, and even social and economic aspects. Moreover, these studies are essential for developing effective conservation strategies that respect the history and integrity of the monument [1-4].

Various archaeometric techniques have been applied to the study of historical mortars, including optical microscopy (OM), X-ray diffraction (XRD), thermogravimetric and differential scanning calorimetry (TG-DSC), portable X-ray fluorescence (pXRF), and inductively coupled plasma mass spectrometry (ICP-MS) [5-8]. Recently, smartphone imaging colorimetry has been also tested as a preliminary approach [9-10]. These tools allow for the colorimetric, mineralogical and elemental characterisation of mortars, making it possible to distinguish materials made with different manufacturing recipes and raw materials, permitting the identification of different chronological phases [11-15]. The analysis of trace elements and rare earth elements (REEs) is particularly significant, and they have proven to be effective geochemical markers for identifying distinct construction interventions in complex stratigraphic contexts [11, 16-17]. In this context, REE analysis combined with multivariate statistical tools such as principal component analysis (PCA) enables the grouping of samples and identification of affinities related to raw material sources or manufacturing aspects [16, 9]. Furthermore, the use of geochemical databases built from nearby archaeological contexts increases analytical resolution, facilitating the detection of continuities or breaks in local technical traditions [17].

This study presents the results of the chemical characterisation of mortars from the Visigothic fortified settlement of València la Vella (VV). Rediscovered in the late 20th century and currently the focus of a multidisciplinary research project, the site offers an exceptional case for examining large-scale construction practices within a relatively short chronological framework. The techniques used include pXRF and ICP-MS for the precise quantification of major, minor, and trace elements and REEs concentrations. Through comparison with reference materials from other sites in the Valencian region (Sagunto Castle or the Islamic Tower of Silla), the study tries to evaluate construction dynamics within the site. The results contribute to a better understanding of Visigothic and Late Antique building practices and support the creation of a geochemical database of historical mortars from the Valencian territory.

Fig. 1. Map of the sampled structures at València la Vella.

II. ARCHAEOLOGICAL BACKGROUND

Between 570 and 580 CE, a new fortified settlement of ex novo layout emerged 16 km from *Valentia*—València la Vella (Riba-roja de Túria, Spain). Covering 5 hectares and strategically positioned between the Túria River and the Cabrassa Ravine, the site combined strong natural defences with a key communication route between the coast and the interior. Archaeologically rediscovered in the late 1970s during emergency excavations, it has since become a focus of systematic research and heritage preservation.

The settlement features a trapezoidal wall circuit of approximately 1 km, built with double-faced limestone masonry bonded by lime mortar, and interspersed with quadrangular towers. Stratigraphy suggests a single, planned construction phase using local materials [18]. Internally, the site is divided into three sectors: an upper citadel, a central residential-artisanal area, and a lower zone with a bastion and a large civic plaza flanked by monumental buildings. Notably, some structures incorporate reused Roman ashlar blocks, likely sourced from nearby ancient cities such as *Edeta*, *Valentia*, or *Saguntum* [19].

All of these historical and archaeological elements make València la Vella an exceptional site for reconstructing the past of the Valencian territory between the 6th and the 8th centuries CE.

III. MATERIALS AND METHODS

A. The sampling

Thirty-five mortar samples were analysed and collected from various points of the Visigothic site of València la Vella (Table 1, Figure 1). Twenty-one samples were taken from different segments of the southern wall (WS), two from the eastern wall (WE), and four the northern wall (WN). The remaining fourteen samples were collected from the walls of a rectangular building located at the eastern end of the site (BE).

Table 1. Samples names and provenance.

Sample	Provenance
VV01-15	Southern wall (WS)
VV16-17	Eastern wall (WE)
VV18, VV20-22	Northern wall (WN)
VV23-35	Eastern building (BE)

B. Multielement analysis

Each sample was cleaned with a scalpel to remove weathered surfaces and subsequently broken down using a glass mortar to remove aggregate clasts. The samples were pulverised and homogenised with an agate mortar.

Each sample was analysed twice using a with a Vanta C series Handheld XRF spectrometer by Olympus (Waltham, MA, USA), equipped with a 40 kV rhodium anode X-ray tube and a Silicon Drift Detector (SDD). The Geochem 2-beam method was employed, characterised by 60 s of acquisition time, with the first 30 s to determine heavy elements (Beam 1: 30 s, 40 keV) and the following 30 s to determine light elements (Beam 2: 30 s, 10 keV). Concentration for Al, Si, K, Ca, Ti, Fe and Zr were considered, being above the limits of detection for most of the samples.

The samples were also digested using *aqua regia* [16] and the solution were analyzed with a Perkin Elmer NexION 2000 ICP-MS to determine trace elements, including REE, concentrations of trace elements (Ba, Bi, Co, Cr, Cu, Li, Mo, Ni, Pb, Sr, Tl, V, Sc, Y; REE: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu).

Certified reference materials NCS DC 73375 (Limestone), JDo-1 (Dolostone) SX02-11 (Cement) were used for data quality evaluation.

C. Data analysis

Data exploration was carried out by principal component analysis (PCA) using R [20]. Data were standardised prior to the analysis. Principal component analysis was firstly carried out on València la Vella samples using the concentrations of all the determined elements, and of REE alone as variables. Then, two PCA were also used to compare these mortars to those from Sagunto Castle (SG) [16], from Los Huertos Street (LHS) and railroad station (RS) in Sagunto [17], and from the Islamic Tower of Silla (SIT) [9]. This samples come from Roman Imperial (IMP), Islamic (ISLM), Medieval (MED) and Modern structure (MOD), though the dating of some of them is still uncertain.

IV. RESULTS AND DISCUSSION

A. Analysis of the mortars from València la Vella.

Representative pXRF spectra are shown in Fig. 2.

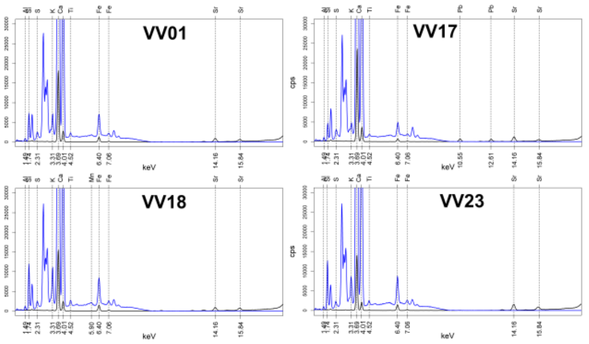

Fig. 2. Representative spectra for WS (VV01), WE (VV17), WN (VV18) and BE (VV23) mortars. Black line: Beam 1 spectrum; blue line: Beam 2 spectrum; cps: counts per second.

Although minor differences have been observed, the spectra from the different mortars are very similar. The most intense peaks are those related to Kα and Kβ lines for Ca. Characteristic X-ray lines for Al, Si, S, K, Ti, Fe and Sr were also detected in all the samples.

Concentrations from pXRF are shown in Table 2, while ICP-MS concentrations are shown in Table 3.

Table 2. Mean elemental concentrations obtained by pXRF.

Class		Al	Si	K	Ca	Ti	Fe	Zr
WS	m	0.20	2.8	0.049	20	0.053	0.43	64
	s	0.06	1.1	0.020	3	0.015	0.11	18
WE	m	0.24	1.4	<LD	26.8	0.038	0.29	52
	s	0.06	0.3		0.9	0.018	0.06	11
WN	m	0.22	4.1	0.12	19	0.072	0.53	75
	s	0.02	0.7	0.09	2	0.011	0.17	11
BE	m	0.19	3.6	0.04	20	0.054	0.43	48
	s	0.05	0.7	0.03	2	0.015	0.10	16

Note: Elemental concentrations are expressed as percentage by mass from Al to Fe and as mg kg^{-1} for Zr; m: mean; <LD: below the limit of detection.

The PCA analysis of the mortars from València la Vella (Fig. 3), based on the concentration of major, trace, and REE show a certain homogeneity in the composition of the mortars, as suggested also by the ellipsis (95%) for BE and WS distributions, though some slight compositional differences that could indicate distinct construction phases and building practices within the site could be pointed out (Fig. 3a). The first three PCs represent 64% of the overall variance in the dataset.

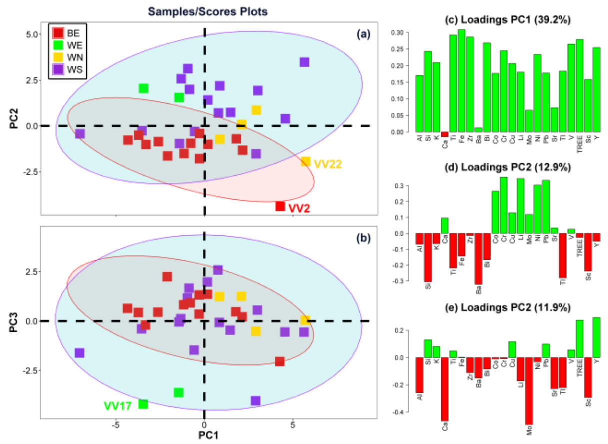

Fig. 3. Principal component analysis of the mortars from VV employing all the elements as variables. Samples/scores plots for PC1 vs PC2 (a) and PC1 vs PC3 (b) and loadings for PC1 (c), PC2 (d) and PC3 (e). Ellipses represent normal distribution (95%) for BE and WS.

BE samples are clustered relatively tightly in PCA plots, indicating notable compositional homogeneity. This suggests a single construction phase or the consistent use of a coherent mortar recipe in terms of both raw materials and proportions. The WS group is concentrated in the upper section of the PCA and is compositionally distinct from BE. These samples show relatively higher contents of Al, Fe, and elements such as Zn, Cu, and Ti. However, five mortars from WS fall together with BE samples. The WN samples exhibit moderate dispersion on the positive side of PC1 (Fig. 3a). VV22 diverges from the main cluster due to its high PC1 score. Finally, it is worth noticing that although the WE group includes only two samples, they have slightly low PC3 scores (Fig. 3b), indicating a singular composition. Its relatively high content of Ca and lower levels of Al and Fe suggest a more calcitic mortar or one with a lower proportion of terrigenous components.

All the analysed elements are positively correlated with PC1 (39.2%) except for Ca (Fig. 3c), suggesting that on this axis the terrigenous component of the mortars is represented. On the other hand, Si, Ba, Tl and Sc are the most influential variables in PC2 negative direction (Fig. 3d), while Co, Cr, Li, Ni and Pb are the most influential in the positive one. Finally, Ca and Mo are the most important variables for the third PC, and they are negatively correlated to PC3 (Fig. 3e), indicating that samples with lower scores are characterised by a more important calcitic component.

PCA results suggest the presence of minor differences, supporting the hypothesis of a settlement constructed over a short time span, though the compositional variability among sectors and the presence of outlier mortars (e.g.:

VV2 and VV17) could indicate repairs or later modifications. However, the present data and the substantial homogeneity of the samples, pointed out also by the distribution in the PCA space of the main groups of mortars, do not permit to detect clearly different construction phases.

The above quoted observations are broadly confirmed by the PCA carried out using just REE as variables (Fig. 3). PC1 and PC2 account for 89.7% and 5.7% of the overall variance respectively.

Table 3. Mean elemental concentrations measured by ICP-MS

Class		Ba	Bi	Co	Cr	Cu	Li	Mo	Ni
WS	m	33	0.221	0.7	3.2	26	3.1	0.35	1.7
	s	16	0.017	0.4	0.8	10	0.8	0.09	0.6
WE	m	60	0.211	0.651	3.05	12.0	3.6	0.490	2.2
	s	7	0.003	0.006	0.09	1.9	1.0	0.018	0.7
WN	m	63	0.24	0.7	3.1	21	3.4	0.39	2.2
	s	6	0.02	0.4	0.2	4	0.5	0.07	0.4
BE	m	60	0.22	0.4	2.6	23	2.1	0.31	1.4
	s	12	0.02	0.2	0.4	7	0.4	0.05	0.3

Class		Pb	Sr	Tl	V	TREE	Sc	Y
WS	m	4	280	0.23	5.2	20	2.3	2.7
	s	3	160	0.03	0.9	5	0.5	0.5
WE	m	1.1	242	0.219	4.61	13	2.13	1.5
	s	0.9	61	0.003	0.12	3	0.11	0.3
WN	m	4.1	197	0.237	5.4	27	2.22	3.4
	s	0.5	28	0.007	0.4	3	0.09	0.3
BE	m	1.7	187	0.23	5.2	21	2.3	2.8
	s	0.3	20	0.04	1.1	3	0.4	0.4

Note: Elemental concentrations are expressed as mg kg^{-1}. TREE: sum of the REE (La-Lu); m: mean.

Although some mortars fall slightly separated in the samples/scores plot (Fig. 4a), the PCA does not point out the presence of outliers or isolated clusters. The first PC shows positive correlations with all the REE (Fig. 4b), suggesting that this direction essentially indicates the richness in these elements. On the other hand, PC2 loadings (Fig. 4c) suggest that this axis indicates a fractionation between lighter REE, showing positive coefficients, and heavier REE, showing negative coefficients.

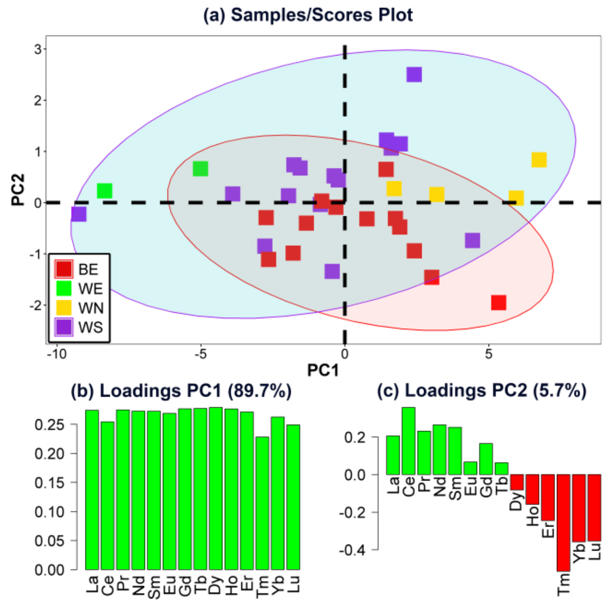

Fig. 4. Principal component analysis of the mortars of VV employing REE as variables. Samples/scores plot for PC1 vs PC2 (a) and loadings of PC1 (b) and PC2 (c). Ellipses represent normal distribution (95%) for BE and WS.

B. Building a chemical database of the historical mortars of Valencia surroundings

Multivariate statistical analysis PCA has been used to compare samples from VV with the mortars from other monuments of Valencia surroundings.

The PCAs have revealed a clear compositional differentiation of the mortars from VV with respect to other samples in the database which allows us to outline both technological and chronological interpretations.

In the PCA based on all the elements (Fig. 5), the VV samples appear in a very defined cluster in the upper left quadrant, significantly distancing themselves from the other chronotypological groups (Fig. 5a). PC1 and PC2 explain 40.5% and 16.4% of the variance respectively, and the loading of elements such as Al, Si, Fe, and Ti in PC1 reinforces their differentiating role (Fig. 5b).

When the REE are considered exclusively (Fig. 6), this separation intensifies: the VV samples form a compact cluster that is clearly located in a separate sector of the graph (Fig. 6a).

PC1 explains 85.5% of the variance and is correlated in positive direction with the REEs (Fig. 6b). While PC2, explaining 9.7% of the variance, shows diverse loadings and a particularly intense positive correlation with Lu (Fig. 6b).

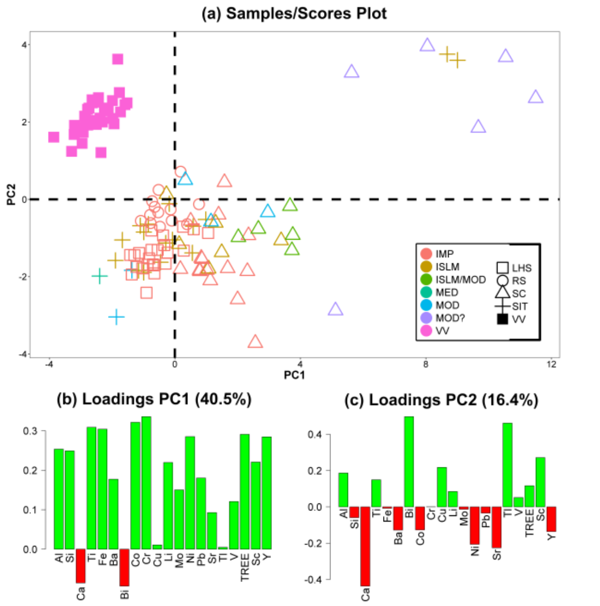

Fig. 5. Principal component analysis of the mortars from VV and those from historical buildings in the surroundings of Valencia employing all the elements as variables. Samples/Scores plot for PC1 vs PC2 (a) and loadings of PC1 (b) and PC2 (c).

These results point out a marked chronological differentiation between the mortars from the Visigothic site and the rest, as the samples from VV do not overlap with other chronological groups such as Roman-Imperial, Islamic or Modern. This differentiation is even more marked in the analysis of REE. This behaviour suggests a systematically distinct geochemical signal which points out the use of different raw materials compared to those of the other buildings which were taken into account.

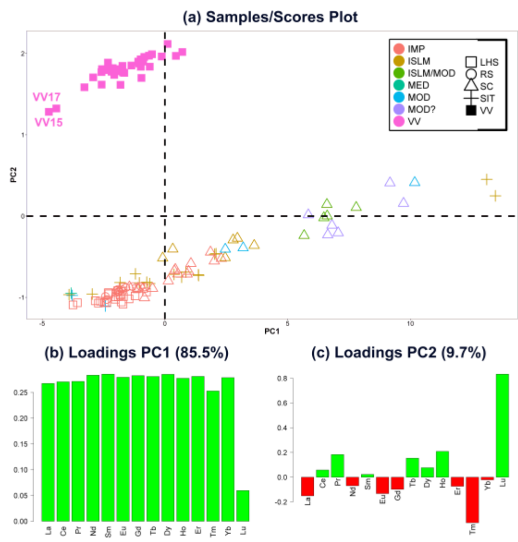

Fig. 6. Principal component analysis of the mortars from VV and those from historical buildings in the surroundings of Valencia employing REE as variables. Samples/Scores plot for PC1 vs PC2 (a) and loadings of PC1 (b) and PC2 (c).

V. CONCLUSION

The multi-analytical study of mortars València la Vella, integrating pXRF, ICP-MS, and multivariate statistical analysis enabled the chemical characterisation of the building materials, providing key information for their chronological interpretation.

PCA reveals compositional homogeneity, indicative of the use of a consistent mortar recipe and maybe a single construction phase. Nevertheless, slight variations among architectural sectors such as between the possible basilica (BE) and the outer wall (WS), and the presence of few atypical samples (VV2, VV17, and VV22) may reflect later interventions, but these differences are not pronounced enough to define clearly distinct building phases.

Comparison with a regional chemical database of historical mortars has shown a significant compositional differentiation between the València la Vella and other contexts of the region (Roman, Islamic, Modern). In particular, REE suggested a distinctive geochemical signature. The results support the hypothesis of a specific tradition, maybe linked to the exploitation of local raw materials or construction practices particular to the Visigothic period or possibly to this particular area, though more specific analyses should be carried out to characterise the different mortar phases and better understand the different recipes and raw materials used in the region within this large historical timeframe.

Overall, this study contributes to the development of a regional geochemical database, reaffirming the potential of the multi-analytical and statistical approach to discriminate mortar recipes and phases of intervention, strengthening its applicability in the study of historic architectural heritage.

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