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Study of vernacular building materials used in cultural heritage as a guide for architectural restoration: Colegio Máximo de Cartuja. Granada-Spain (19th century)

Estudio de materiales de construcción vernáculos empleados en el patrimonio cultural: guía para la restauración arquitectónica del Colegio Máximo de Cartuja. Granada-España (siglo XIX)

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ABSTRACT

Colegio Maximo de Cartuja in Granada (Spain) was built by the Jesuits in 19th century. Using an archaeometric study of the building materials: bricks, glazed tiles, stained glass windows and lime-gypsum mortars (mortar masonry and concrete masonry), the vernacular concept of this construction was established within the geological framework of the "Alhambra formation", and raw materials and techniques first used by the Nasrids in the 13th century have been identified. The results of XRD, XRF and DTA analyzes indicate the use of local clays in the manufacture of bricks and tiles fired at temperatures of $\leq$750 ºC. The clays contained NaCl additives, which improved the ceramic sintering, and traditional Nasrid colours (Cu, Fe, Sn) were used in the glazes and stained glass windows. Local raw materials were also used for air binders. These results have been combined to create a good-practice guide for the sustainable restoration of cultural heritage buildings.

Keywords: Architectural heritage; Conservation; Archeometry study, Vernacular architecture.

RESUMEN

El Colegio Máximo de Cartuja en Granada fue construido por los jesuitas en el siglo XIX. El estudio arqueométrico de sus materiales: ladrillos, azulejos, vidrieras y morteros, define el concepto vernáculo de esta construcción, referenciada en el marco geológico de la "formación Alhambra", junto a la identificación de materias primas y técnicas utilizadas por los nazaríes desde el siglo XIII. Los resultados de XRD, XRF y DTA confirman el uso de arcillas locales para fabricación de ladrillos y losetas que se hornearon a temperaturas de $\leq$750 ºC. Las arcillas debieron contener aditivos de NaCl que beneficiaron la sinterización cerámica, y se comprobó el uso de colores de tradición nazarí (Cu, Fe, Sn) en los esmaltes y vidrieras. Las materias primas locales también se usaron para producir aglomerantes aéreos. Estos resultados se han combinado para crear una guía de buenas prácticas para la restauración sostenible de los edificios del patrimonio cultural.

Palabras clave: Patrimonio cultural arquitectónico; Restauración; Arqueometría; Arquitectura vernácula.

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1. INTRODUCTION

The characterization of building materials has become an important aspect in restoration research, so much so that it forms a perfect symbiosis with the conservation of historical heritage in sites of universal value. Previous studies based on the characterization of materials using quantitative and qualitative techniques (1), (2), (3), (4), (5), (6), (7), (8), (9) confirm the validity of this approach. Also it is necessary highlighting the importance of the analyzes it was performed, which provide precise information about the properties and characteristics of the materials involved (4), (10), (11), (12). It is also important to find out more about the manufacturing process of these materials as this can affect their performance (13), (3) and can help researchers to reach conclusions regarding the possible causes of damage they have suffered (14), (15) guarantee the suitability of the restoration products and ensure that only those with similar or appropriate properties of the materials will be used in the restoration work required by most heritage buildings (16), (17), (18), (19), (20), (21), (22), (23), (24).

Colegio Máximo de Cartuja (Granada-Spain) is situated in the Cartuja campus of the University of Granada, a site that is well-known for a large number of interesting constructions from burial sites from the Neolithic period to the most modern building housing the Mind and Brain Research Centre. Remains from a Roman era pottery workshop have also been discovered (1st and 2nd centuries CE), along with Arabic water channels, necropolises from the Al-Andalus period (7th-9th centuries) and post-Renaissance religious buildings. The site also has an infinite range of examples of its long and interesting history over the centuries as a historic town outside the walls of Granada.

The University of Granada now plans to put all this on display via the restoration and enhancement of these different constructions, which will carry out as a cultural route (25) (see Figure 1A), that includes other buildings of enormous heritage value, such as the Monastery of Cartuja (Cent. 16), the Cathedral (Cent. 16) and the Royal Hospital (Cent. 17). The building studied in this paper, Colegio Máximo de Cartuja (see Figure 1B), which currently belongs to the University of Granada, is situated near the Carthusian Monastery (Monasterio de La Cartuja) which gives the area its name. Colegio Máximo was the first construction built by the Jesuits in this area at the end of the 19th century (1891-1894), on a site that had been highly praised by Muslim chroniclers and poets (26). It was later followed by other buildings, such as the Astronomical, Geophysical and Meteorological Observatory (1901-1902) (27). The building was designed by the architect Francisco Rabanal, who had close links with the Jesuits. It followed various architectural tendencies in vogue in Spain at the time, becoming a clear exponent of the Neo-Mudejar style (28).The use of this neo-Arabic style was something of a departure from the style traditionally used by the Jesuits and deliberately included various decorative features typical of Arabic architecture, such as the Nasrid epigraphic inscription from the Alhambra “Wa lā gāliba illā-llāh” (God is the only Victor), which was transformed into “Ave Maria” (a Catholic prayer). Today Colegio Maximo enjoys the highest possible level of protection for a historic building, after being declared an Asset of Cultural Interest (Bien de Interés Cultural – BIC), and a Historical Artistic Monument by Royal Decree in 1983 (29).

This emblematic building has not always been occupied and has been used for a range of different purposes. Besides being a school and novitiate for the Society of Jesus from 1894, in 1924 it became one of the most important Jesuit centres in Andalusia with the rank of “Colegio Máximo de la Provincia de Andalucía” (University of the Society of Jesus) (30) and in 1939 towards the end of the Spanish Civil War, it was moved the Theology Faculty there (31). In 1970 the building was acquired by the University of Granada. During the 1980s a number of rehabilitation and restoration projects were carried out to prepare it for use by various university faculties (32). These include the School of Stomatology (1983 until today), the Faculty of Dentistry (1986 until today), the University School of Librarianship and Documentation (1984 until today), the Faculty of Communication and Documentation (2006 until today), the Faculty of Fine Arts (1985-1995) and the School of Road, Canal and Port Engineering (1995-2000) (32). Today it is also home to the University of Granada Press. Managing this highly versatile building is a considerable challenge for the University of Granada in that in addition to combining quite different cultural, institutional, administrative, teaching and research uses, a difficult balance must be struck between the conservation and dissemination of this interesting piece of heritage. The University is obliged to perform this task precisely because these buildings are important historic monuments and surely because of the role that the University plays within the framework of Inter-University agreements in the European Higher Education Area (e. g. the Coimbra Group - an Association of long established European multidisciplinary universities, 1987).

In this research it was characterized the most representative materials from the façades and from the indoor of the neo-Arabic chapel inside the Colegio Máximo, in order to analyze their state of conservation/damage given that this historical building is in need of restoration (Wall bricks show volumetric losses with fractures, fissures and disaggregation. Mortars and concretes on the façades are partially decayed with volumetric and surface losses, on the other hand tiles show fractures and localized efflorescences. The stained glass have fragment losses and bleaching). In particular it was studied the bricks and mortars, materials widely used in the walls (large sections of bricks) and outdoor facings, as well as the glazed tiles and stained glass windows from the neo-Arabic chapel.

2. DESCRIPTION OF THE BUILDING

The building stands alone and has a rectangular floor plan which is organized around four courtyards, two large ones in the front parallel to the main axis of the building and situated around the neo-Arabic chapel, and two other narrower courtyards towards the rear (Figure 1B). The building has three floors. The west, north and south façades (principal and lateral) follow the same lines in terms of composition and use of materials, while the east façade (rear), above all due to the slope of the terrain, is different from the rest of the building in that the ground floor is obscured from view and only the two upper floors are visible. The building occupies an area of 1.2 ha and each façade is over 100 m long. The main façade is flanked by towers situated at either end and there are two more towers framing the main entrance (32).

The façades are composed of large “boxes” of masonry, supported by lines of bricks, corner supports and plain, undecorated brick friezes. In certain areas (main entrance and windows) the bricks are painted dark red (Figure 1C). The whole building is surrounded by brick skirting (although the section on the rear façade is different from the rest), which varies in height between 1.0 and 1.5 metres above the ground. The bricks have similar compositional characteristics and come in two sizes. The bricks used on the main façade measure 6.0 x 11.5 x 23.0 cm, while those used on the sides measure 5.0 x 13.5 x 27.0 cm. Some of them bear the stamp of the factory (see Figure 1F) with the inscription "ROOF TILES AND BRICKS - ALL KINDS OF FLOORS TILES IN JUN"; Jun is a village near Granada in which there are large clay deposits and a long tradition in handcrafted pottery.

Together with the façades of Colegio Máximo, in this study it will also be investigated the chapel, which has various constructed areas. Of particular interest is the ropework ceiling simulating polychrome wood, and the three walls decorated with polychrome plasterwork and striking Nasrid-style epigraphic inscriptions. The walls are crowned by the windows in horseshoe arch shape and trimmed beneath with tiles with geometric and ropework decoration. The tiles are glazed with the typical palette of colours used in Nasrid Islamic architecture, which is based on white colour for solid background made of tin and lead oxides and green, blue and earth colours for geometric decoration made from copper, cobalt and iron oxides, respectively. The windows are made up of 3mm-thick pieces of stained glass which are joined together using soldered strips of lead (Figure 1E). Other interesting features include the glazed tiles on the outside of the building decorated with geometric motifs, and the stamp or hallmark of the brickmaker, which appears on a lot of the bricks used in this building (Figures 1D).

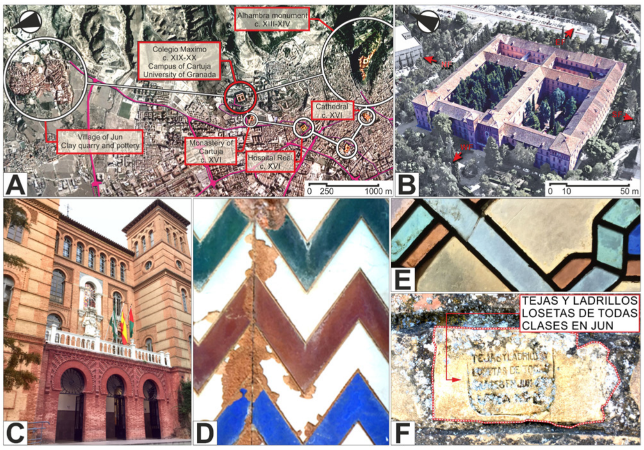

Figure 1. A. Location and current context of the Colegio Máximo de Cartuja. Other historic monuments classified as Assets of Cultural Interest, such as the Monastery of La Cartuja and the Roman Pottery, are also marked. B. Aerial view of the building showing the orientation of the façades. (C). View of the Main Entrance on the West façade. (D). Tiles from the main entrance with colours and geometric motifs characteristic of the Nasrid era. Some fragments have fallen off due to salt efflorescence. (E). Detail of the stained-glass windows from the Neo-Mudejar chapel showing the main range of colours. (F). Detail of a brick from the building with a transcription of the stamp of the manufacturer indicating where it was made

From a geological point of view, Colegio Máximo de Cartuja and the ceramic production areas in the Albaicín quarter of Granada and in the nearby village of Jun are situated within the Depression of Granada, formed mainly raw by Neogene and Quaternary materials, part of them are located in geological "Alhambra formation" made of conglomerates and sands". The intra-mountain Depression became fully formed during the Late Miocene and a series of rivers appeared on its north-eastern flank. These eroded the reliefs of the Sierra Nevada and the Sierra Arana-Alfacar-Víznar mountain ranges and deposited large amounts of detrital rocks (limestones, travertines, etc.) in a marine basin.

The basin became continental over the period extending from the late Tortonian (at the end of the Miocene) to the Middle Pleistocene, in which an important depressed area developed and was filled by deposits from the River Genil and its various tributaries (River Darro, River Beiro, etc.). This subsidence process has continued until today. The materials commonly found in the geological context of Colegio Máximo de Cartuja and adjacent areas are red clays, gravels, sands and paleosoils from the Quaternary age (Mid-Late Pleistocene), which consist of main clay raw materials for ceramic manufacturing. These materials correspond to what has morphologically been dubbed "Vega Alta", made up of fluvial sediments with a well-developed floodplain. They are ordered in positive sequences which at the base present a channeled layer of gravel and sands with a maximum thickness of 1 m. The rest of the sequence down to 3 m is formed by silts and clays with frequent edaphization processes which in some cases have come to form authentic paleosoils. (33).

3. MATERIALS AND METHODS

3.1. Materials

The samples analyzed are representative of the wide range of building materials (bricks and mortars from the façade, tiles and stained glass windows) used in different parts of the building. A total of 21 samples were characterized, as can be seen in Table 1. The samples were classified into five groups corresponding to the different types of materials studied (masonry concrete, masonry mortar, brick, wall tile and stained glass). The location and the construction feature from which each sample was extracted are also indicated. In all cases, the most important materials extracted (masonry concrete, masonry mortar, brick, wall tile and stained-glass) were found, on a visual inspection, to be in a good condition, and to have a suitable size and weight for transportation and storage (specific plastic bags).

Table 1. List of samples studied in this paper, highlighting location and kind of material

	North façade	**South façade**	**East Façade**	**West Façade**	**Chapel**
Brick	FNB1	FSB3	FEB5	FWB7	
	FNB2	FSB4	FEB6	FWB8	
Glazed tile				FWT1	CHT3
				FWT2	CHT4
					CHT5
Stained glass windows					CHSG1
					CHSG2
					CHSG3
Mortar Masonry	FNMM1			FWMM2	
				FWMM3	
Concrete masonry	FNCM1			FWCM2	

3.2. Methods

Chemical analysis

The samples were analyzed using a PANalytical Zetium X-ray fluorescence spectrometer (XRF) with a ceramic x-ray tube, a 4 KW rhodium anode x-ray generator and a non-coupled goniometer of θ/2 (Granada University Scientific Instruments Centre). The XRF samples were ground mechanically in an agate mortar and then sieved to a grain-size fraction of <0.354 mm (mesh size 45).

X-ray diffraction

The X-ray diffraction samples were analyzed with an MPD Panalytical X'Pert diffractometer, using Cu Kα radiation (1,54056 Å), under working conditions of 45 kV and 40 mA. The diffractograms were recorded between 2θ = 5-600 from a powder sample ground in an agate mortar to a grain size of < 30 μm. The composition was determined with the Xpowder software (34), which takes into account multiple iterations of models of the mixture, so as to guarantee greater precision with the real diffractogram. The samples for the XRD analysis were separated and sieved in a fraction of <1 mm (mesh size 18).

Optical and SEM-EDX microscopy

The mineralogical characterization tests and the tests on the texture and the microstructure of the samples were performed with a polarized optical microscope (Olympus BX-60) and a Zeiss DMS 950 scanning electron microscope (SEM) coupled with Microanalysis Link QX 2000. Apparatus conditions include maximum magnification of 300,000x, acceleration voltage of 1–30 kV, a tungsten filament electron source and SE detector, together with EDX microanalysis Röntec, series M, Edwin, Si (Li), from the University of Granada Scientific Instruments Centre. The samples for SEM observation were prepared for morphological and analytical study by adhering them to the base with colloidal silver and covering them with nano-carbon particles.

Differential thermal analysis

The gravimetric and differential thermal analyzes were performed with a Q-600 TA Instruments equipment (Waters Corporation, Milford, MA, USA), using a platinum sample-holder in an air atmosphere and with a heating speed of 100°C min-1 up to 1000°C min-1.

Ultrasounds

The elastic properties and the degree of compactness of the samples were studied using a PROCEQ PUNDIT PL200 ultrasonic pulse generator with 2 150 kHz transducers in line with ASTM D 2845 (35). 240 samples were mesured (collected and on site). In the samples in which this was possible, the ultrasound propagation velocity (VP) was calculated in three directions with respect to the section of wall from which the samples were taken. VP1 is the direction perpendicular to the wall, VP2 is parallel to the wall and VP3 is perpendicular to the other two.

Colorimetry

All the samples were subjected to a colorimetric assessment so as to establish colour patterns for the main building materials used in Colegio Máximo de Cartuja (masonry concrete, masonry mortar, bricks, wall tiles and stained glass), in order to facilitate standard restoration tasks (cleaning, consolidation, replacement or filling in cracks and holes with specific mortars). 400 samples were mesured on site (20 for each group). The diffuse spectral reflectance curves for the different materials studied were measured in the visible range using a Konica Minolta CM-2500c spectrophotometer, with a wavelength of 360 nm to 740 nm, a 2° and 10° observer, CIE 1931/2, CIE 1964/10 (36), (37) and a D65 illuminant.

4. RESULTS AND DISCUSSION

XRD

The XRD results of brick fragments (FEB5 and FWB7) from two different façades of the building (east and west) can be seen in Figure 2. The significant presence of calcite without thermal alteration suggests that brick samples FEB5 and FWB7 were fired at temperatures ≤ 750 ° C as the studies show (38), (39) (40). The presence of dolomite may be due to the raw materials used in the manufacture of the bricks, the vast majority of which come from the Paleosoils (Pleistocene) geological formation based on red clays, gravels and sands, composed of calcareous, ferruginous and dolomitic clays, together with illite minerals and lime, and dolomitic grogs (33). The presence of feldspars and muscovites was found in the geological formation and the quarries from which the raw materials used in pottery and brickmaking were extracted. In addition, the presence of analcime in the diffractogram could be due to the clay raw materials of geographical context that could contain sodium, or due to the alteration by soluble salts coming from subsoil, deposited in the bricks once laid in the building (41), (42). Another interpretation of the provenance of analcime in these bricks may be due to the addition of sodium chloride in raw bodies by brickmakers, which, as has been proved, improves its plasticity and workability, as well as reduces the sintering temperature and provides greater compaction and mechanical strength of the ceramic materials obtained (39), (43). All of this verify that the clay raw materials used are of low temperature, a fact which coincides with the geological chart of the area that indicates the presence of sediments and red clays, which chemical composition does not allow high temperature firing (33), (44).

The XRD results for mortar and concrete (FWMM3 and FNCM1) samples from the Colegio Máximo indicate that they were made from mixes based on lime-based air binder with gypsum additives (hybrid mixes), particularly in the case of the concretes. Gypsum is normally added to the mixes to ensure quicker setting, thus improving the workability of the mortars and concretes (45). The remaining components (quartz and muscovite) are local aggregates from the river. Likewise, the calcite in the sample is a result of aggregates from fragments of local marbles, limestones, dolomites and travertines found in geological sediments or river basins (River Beiro and River Genil).

Figure 2 shows also the diffractograms for the ceramic body or biscuit of the wall tiles (FWT1 and FWT2). These materials have different characteristics from those of the bricks because they must have been fired at higher temperatures of around 1000ºC, in particular in the second firing in which the thick glazes coating the tiles are melted. The XRD peaks for calcite are less frequent, suggesting greater presence of calcium oxide, which is obtained at temperatures of over 900ºC. The analcime (FWT2) may result from the decomposition of the vitreous phase of the tiles (as noted in samples from archaeological sites in Switzerland (42), (46), (47), (48), or preferably of the use of NaCl as an additive to make the body more fluid. The remaining components observed in the analysis, such as anhydrite, are typically found in local clayey soils and/or in efflorescence.

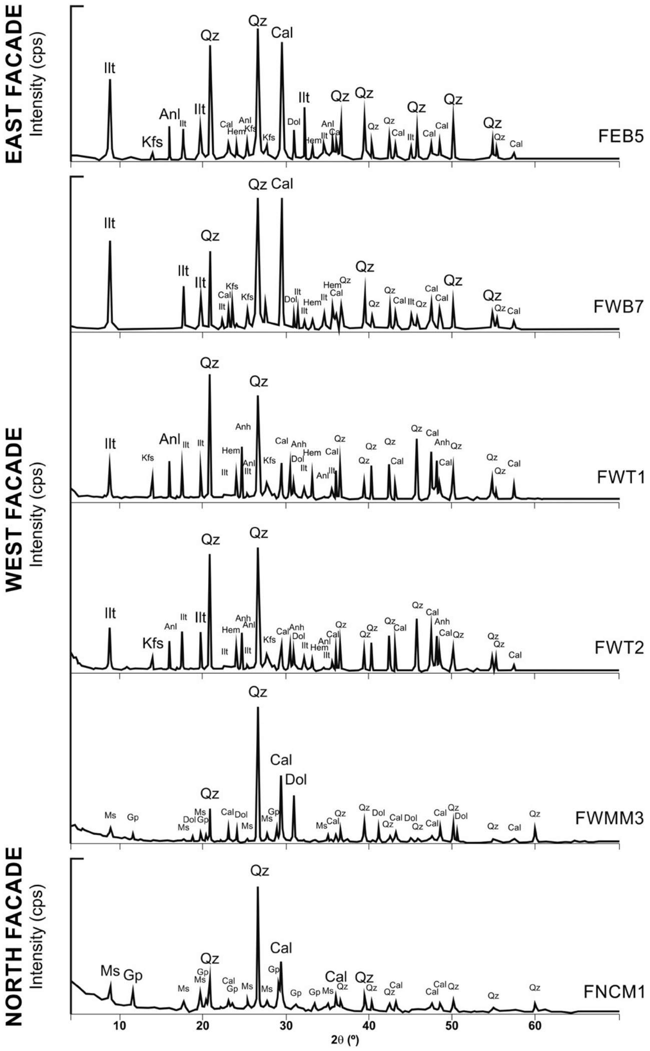

Figure 2. X-ray diffractograms for the bricks from the East and West façades of the Colegio Máximo de Cartuja. Sample FEB5 and Sample FWB7. X-ray diffractograms for the tiles from the West or Main façade. Samples FWT1 and FWT2. X-ray diffractograms of the samples (masonry concrete (FNCM1) and masonry mortar FWMM3). Sample FNCM1, composed above all of calcium and gypsum binders with quartz and muscovite aggregate. Sample FWMM3 composed of a lean air lime (dolomite) binder and gypsum with quartz and muscovite aggregates. Abbreviations for names of rock-forming minerals (49). Legend: Ilt= illite; Qz = quartz; Dol = dolomite; Cal = calcite; Hem = hematite; Kfs = K-feldspar; Anl = analcime

XRF

The chemical analysis of the samples (Table 2) confirms the XRD results set out above. Silicates are the main component of all the brick and tile (biscuit) samples. The mortars and concretes with a high CaO content are a binder consisting of air lime and carbonated aggregates. The presence of MgO suggests that this is lean air lime, while that of SO3 indicates that gypsum was added to the mixes to make them set more quickly. The results for the glass sample confirm that it is a "cathedral"-type soda lime glass (50) with a lead melting agent. The chromophore for this glass (light blue) has a cobalt and iron base.

Table 2. Chemical composition by XRF analysis (wt %) of bricks (FEB5, FWB7), glazed tiles (FWT1, FWT2), concrete masonry (FNCM1), mortar masonry (FWMM3) and stained glass (CSHG1). Data normalized to 100% (LOI-free).

	SiO_2	CaO	Al_2O_3	MgO	Fe_2O_3	Na_2O	K_2O	PbO	SO_3	CoO	LOI
FEB5	73.80	0.93	14.65	1.29	4.51	0.17	3.03				0.67
FWB7	72.99	0.55	14.44	1.33	5.57	0.50	2.90				0.71
FWT1	72.35	1.11	14.14	1.59	3.85	1.45	3.76				0.94
FWT2	74.22	0.98	13.92	1.35	2.32	1.92	3.94				0.89
FNCM1	1.05	72.53	1.95	0.10	0.02	0.10	0.04		0.70		23.20
FWMM3	0.98	68.92	1.90	3.02	0.04	0.07	0.04		0.59		24.50
CHSG1	70.10	6.30	1.47	0.25	0.28	5.80	0.66	15.50		0.03	

OPTICAL MICROSCOPY

The ceramic materials studied have matrixes composed of clays and tempers made of crushed rock (mixed into the base pastes) and other ceramic residues (grogs). The relative compactness of these ceramics suggests low sintering and low firing temperature. Pores of 10-20 µm can be observed. The brick fragment from the east façade (FEB5) can be seen in Figure 3 (image A). It has large pores throughout the matrix, which is based on phyllosilicates and large amounts of quartz grogs of varying size ranging from very small (250 µm) to the largest measuring around 3 mm. The laminar illite-type grogs are highlighted in red, together with the carbonate grains. The temper was hardly altered by heating, as can be seen in the quartz with well-defined, clear-cut edges. Mineralizations can be detected which coincide visually with analcime (highlighted in red). Image B of sample FWB7 from the west façade shows a ceramic material with high porosity and low compactness, with a hardly sintered clay matrix, dominated by illite grogs and schist fragments from the geological area, which range in size from 70 µm to 2 mm. A large number of unaltered quartz grogs can also be observed, marked in red in the image. Feldspar is also present as part of the clayey material from the quarry.

The mortar sample (FNCM1) from the north façade, seen in Figure 3 image C, is a very porous mortar-concrete material, with a pore size ranging from >250 µm down to micropores of ≈20 µm. The matrix is calcareous with well-carbonated lumps and fragments of aggregate of muscovite and quartz (marked in red) of between 40-50 µm in size. Image D shows sample FWMM3 from the west façade. This is an air lime mortar with a very porous matrix in which retraction fissures and isolated carbonate lumps can be observed. Acicular lumps of gypsum can also be seen, marked in red in the Figure 3 (image D).

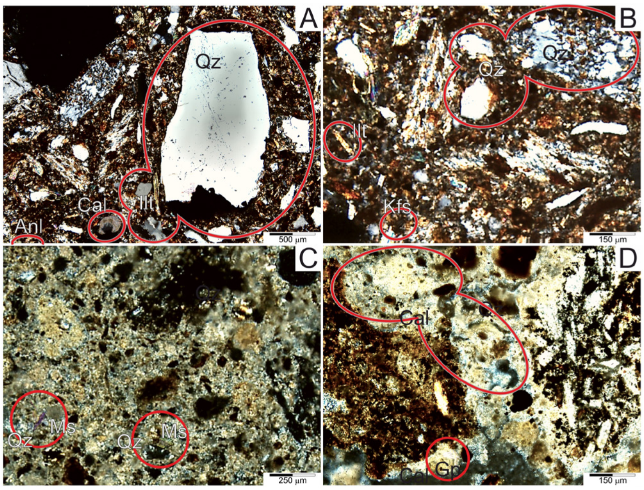

Figure 3. OM micrographs of bricks and mortars. Micrographs taken with a polarized light optical microscope (A). Ceramic material (FEB5), 20X, crossed nicols, with detail of the matrix and the pores, and of fine grogs. (B). Crushed ceramic fragments can also be seen in image B. Ceramic material (FWB7), 40X, crossed nicols, with quartz, illite and feldspar grogs. Image E, concrete mortar (FNCM1), 40X, crossed nicols, the presence of quartz and muscovite aggregates is marked in red. Images F, lime mortar (FWMM3), 40X, crossed nicols. The carbonation of Ca(OH)2 to calcite and acicular gypsum crystals is marked in red.

SEM-EDX

Figure 4A (sample FNB1) shows a ceramic material with no sintering (a barely compacted clay matrix) and large quantities of pores. There are no signs of particle melting, as can be seen for example in the illite (marked in red), which has clearly defined edges with no visual signs of sintering. The EDX results confirm that ceramics are rich in illite, due to presence of magnesium, potassium and iron. In addition it can be inferred that presence of sodium is due to analcime. Image 4B (sample FEB-6) shows a ceramic material with no sintering, suggesting the use of low-temperature clay raw materials. Packages of illite without softening thermal can be observed due to the low firing temperature. The EDX analysis is coherent with calcareous and illite clays (Fe-K), fired at low temperatures and with traces of magnesium and sodium, the latter probably a consequence of the addition of plasticizers or melting agents. In both cases the results obtained are coherent with raw materials from local clay quarries in the different geological strata.

Image 4C (sample FNCM1) is a high porosity mortar concrete composed of lime and gypsum binder, and an aggregate of muscovite and probably ceramic fragments. Image 4D (sample FWMM3) is a rendering mortar. According to EDX analysis the binder is made of lime and gypsum, with siliceous and/or ceramic aggregates. The transformation-carbonatation of the air binder from Ca(OH)2 to CaCO3 is shown in red (small image).

For glazed tiles and glasses from stained glass window, the results see Figure 5A (CHT4), shows a green glazed tile. The SEM image shows that the glaze is approximately 0.20-0.25 mm thick with some fissures and microbubbles well adhered to the ceramic biscuit. A certain number of pores can be observed in the biscuit. The EDX analysis confirms the composition of a low temperature ferrous-calcareous body with potassium melting agents. The analysis of the glaze shows that it is a lead glaze which melted into the base at a temperature in the range of 900-1000ºC. Chromophore elements in the copper and iron glaze also stand out together with zinc opacifiers. Figure 5B (FWT1) shows a white tile with an approximate glaze thickness of 0.2 mm and small microbubble defects. Although the unglazed ceramic base is porous, it has an acceptable level of compactness due to the fact that the tiles were fired a second time so as to melt the glaze into the base. The EDX analysis of the ceramic base coincides with the previous sample in that it has a ferrous-calcareous type composition with potassium, typical of the raw materials from the geological area in which Colegio Máximo de Cartuja and the nearby quarries are located. The glaze (sample FWT1) is a cream-white glaze of Nasrid tradition with a lead melting agent and a tin-based opacifier-chromophore.

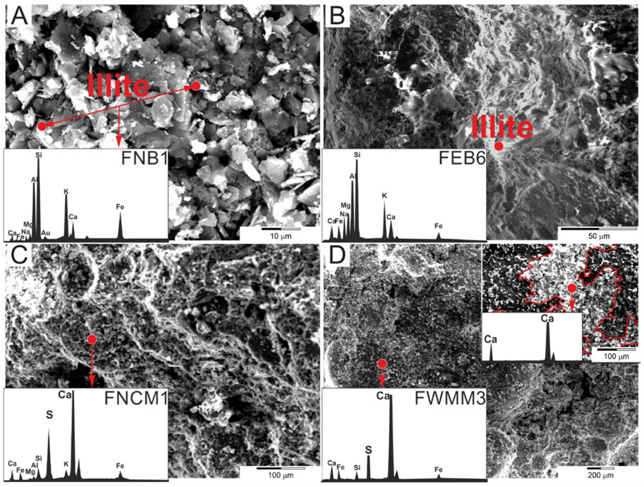

Figure 4. Examples of SEM images and EDX analyzes. A. Sample FNB1. Ceramic fired at low temperature (FNB-1). B. Sample FEB6. Ceramic fired at low temperature, with high porosity and no fusion between particles. C. (FNCM1). High porosity mortar-concrete. D. (FWMM3). Rendering mortar containing gypsum.

Figure 5C (CHSG2) shows a piece of glass with an approximate thickness of 3 mm. Dust has accumulated on the surface. The EDX analysis shows the characteristic composition of this kind of glass (a soda-lime glass with a lead melting agent).

DTA

The average results for the bricks are in line with the XRD results. All temperature values were calculated by means of the program with which the DTA/TGA graphs were processed. In these analyzes endothermic peaks can be observed in the 80-140ºC range, probably due to a loss of water which is physically adsorbed. These peaks are accompanied by a loss of weight. Subsequent endothermic peaks at 728ºC (sample FEB5) and 773ºC (sample FWB7) are due to the reaction of the calcite (CaCO3), which is very abundant in both samples. This reaction also leads to a fall in weight after which it stabilizes. The fact that this endothermic effect was registered in the analyzes of both ceramic materials indicates that the calcite was intact in both; in other words: they could have been fired at a lower temperature to that of thermal decomposition of the calcite. The graph of figure 6 indicates that the firing temperature could have been <730ºC (FEB5) and 770ºC (FWB7), respectively. This confirms the results deduced from the X-ray diffractograms. It is important to emphasize the heterogeneity of the ceramic bodies and above all the heterogeneity of the firing process, since the firing

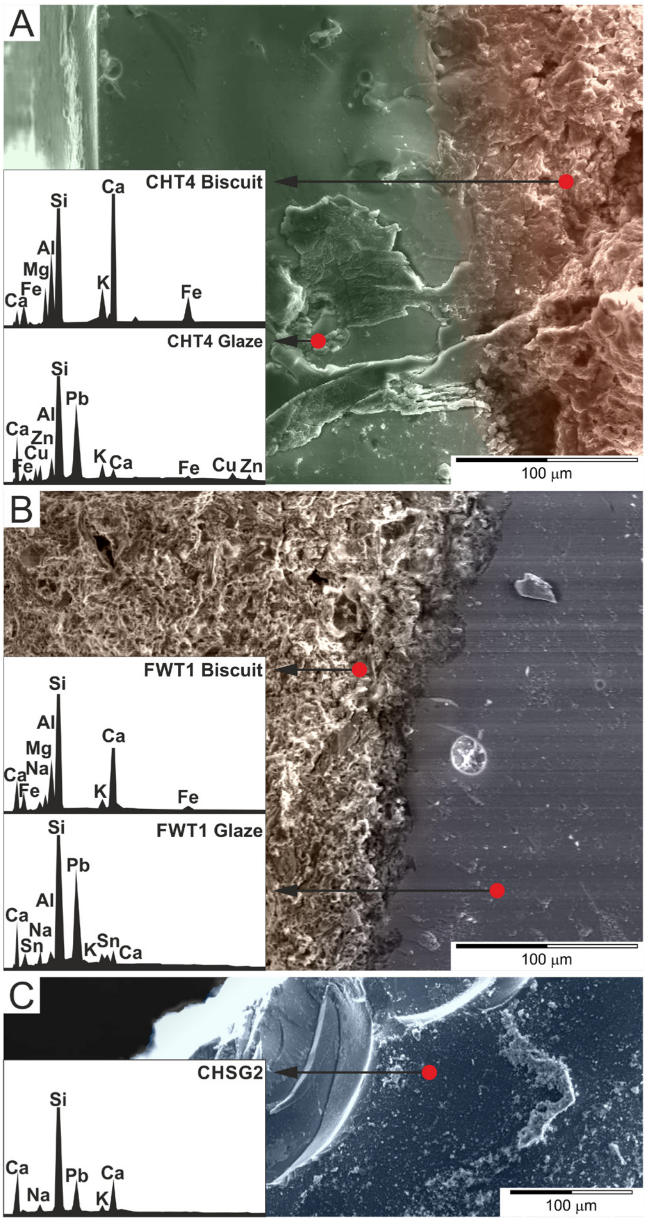

Figure 5. (A) Green glazed tile from the Chapel of the Colegio Máximo highlighting the presence of bores on the ceramic bisque and cracks in the glaze. (B) White glazed tile from the east façade with lead melting agents and tin opacifiers. (C) Fragment of blue glass from the soda-lime type stained-glass windows and lead melting agents, characteristic of "cathedral windows" (50).

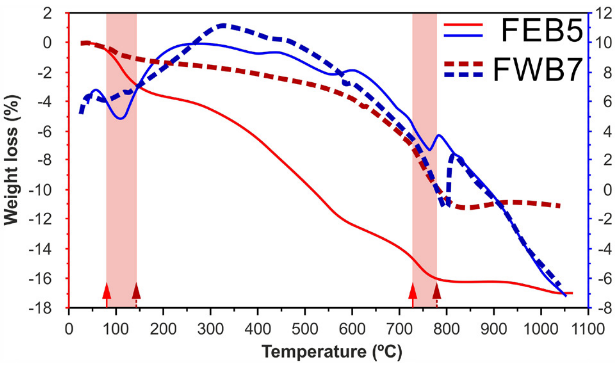

Figure 6. Graphic representation of TG/DTA values (detached fragments) for FEB5 and FWB7 brick samples.

was artisanal, rather than industrial, and the manufacturers had limited technical resources at their disposal.

ULTRASOUNDS

Table 3 sets out the average values for the bricks and mortars measured at different locations with average velocity and standard deviation data. The ceramic materials show similar values to other ceramics fired at low temperatures of ≤750ºC. Some authors report similar values for common pottery type ceramics fired at low firing temperatures at which the clay bodies do not reach sintering (38). In addition, the mortars, concretes and renders made with air lime show expected values for this kind of material (51) both in air lime mortars and in those containing gypsum additives.

Table 3. Average/standard deviation values of ultrasound transmission speed of masonry bricks, masonry concrete and masonry mortar

		Masonry brick			**Masonry concrete**			**Masonry mortar**		
Site	**m/s**	**V_{p1}**	**V_{p2}**	**V_{p3}**	**V_{p1}**	**V_{p2}**	**V_{p3}**	**V_{p1}**	**V_{p2}**	**V_{p3}**
N FACAD	$\bar{x}$	1738	1926	1491	1880	1861	1776	1988	1963	1971
	σ	82	84	79	80	92	79	71	78	100
S FACAD	$\bar{x}$	1075	1302	1188	1217	1198	1113	1490	1512	1645
	σ	89	91	95	77	93	89	79	72	85
E FACAD	$\bar{x}$	1985	1340	1292	2127	1238	1208	1602	1552	1522
	σ	85	72	87	79	76	81	89	84	82
W FACAD	$\bar{x}$	2438	1792	1545	2050	1943	1985	1933	1991	1904
	σ	92	91	82	76	69	73	84	93	76

COLOUR

The colour of the samples was also studied showing a wide palette of different tones. Figure 7 shows the chromatic coordinates L*, a* and b*, according to the CIELab1976 system (Hoffmann, 2010). The colours of the mortars, concretes and bricks from the building can be seen in image 7A. All the materials studied have a tonal position in the yellow and red quadrant except for group 2CM, which has yellow and green hints. Colorimetric heterogeneity over unpainted bricks is due to craft firing and can undergo selective oxidation reductions in kiln. The mortars and concretes have very low saturation and high levels of lightness, which results in the colour being perceived as off-white. The bricks in general are more saturated in yellow and red tones and also have high levels of lightness.

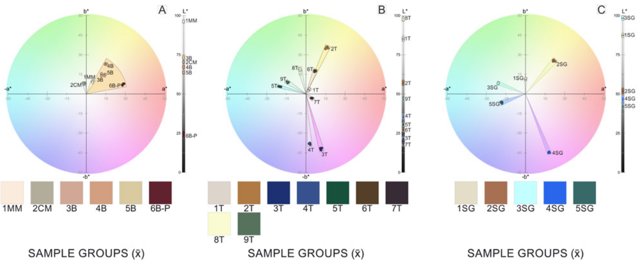

Figure 7. Graphic representation of CIELab 1976 (53) values for different building materials used in the Colegio Maximo of Cartuja (37). (A) (MM), mortar masonry; (CM), concrete masonry; (B), bricks; (B-P), painted bricks. (B) (T), glazed tiles. (C) (SG), stained glass.

The colours of the glazed area of the tiles (Figure 7B) have very heterogeneous positions in all the chromatic quadrants together with a range of lightness values, so recovering in detail the palette of colours characteristic of Granada ceramics of Nasrid tradition (52). Figure 7C displays the range of colours in the glass from the stained glass window from the Chapel of Colegio Máximo de Cartuja. In general, these are simple colours (blue, green and ochres), which are technically easy to produce.

5. CONCLUSIONS

1. The archaeometric study of the construction materials used in Colegio Maximo de Cartuja highlights the use of locally sourced materials, as confirmed by references from geological area.
2. The techniques used to produce these materials were semi-artisanal, which means that they are not totally uniform. There are variations for example in the colour of the bricks as a result of both the heterogeneous nature of the raw materials and also of the firing processes (unintentional changes in the oxidizing and/or reducing conditions inside the kiln).
3. The unusual presence of analcime in this kind of ceramic materials fired at low temperatures suggests that common salt (NaCl) could be used as an additive in the unfired ceramic bodies used to make the bricks. In the right proportions, this additive can improve the workability and plasticity of clay-based ceramic bodies and reduces the thermal maturity temperature and the sintering temperature of the ceramics. This is a very important factor in the semi-artisanal production of ceramic materials when it comes to reducing costs.
4. The choice of local raw materials was another important aspect in the construction of this building. The proximity and ready availability of raw materials makes a possible restoration work easier, as does the long tradition of manufacturing building materials on the site itself, in the Albaicín neighbourhood and in villages nearby, as well as possible reuse of quarries for clays and grogs, quarries for the production of binders (air lime or hydraulic) or for the extraction of aggregates. All of this would enable the use of suitable conservation materials and techniques, thus reducing the impact of previous restoration works on heritage buildings of singular value.
5. The results of the colorimetric study were used to create a colour chart for the main building materials used in the construction of Colegio Máximo, thus facilitating future restoration work on heritage buildings of this kind.
6. All the materials used in the construction of this building are an integral part of the overall concept of the Jesuit architect, who sought to recover much of the Arabic legacy still present on the hill of La Cartuja. The result was a Neo-Mudejar design for the main parts of Colegio Máximo (Theology Faculty) together with a selection of colours that had a long, extended tradition in the Arab world (54), (55). In this sense the use of colours based on earths, iron, copper or cobalt was a clear tribute to the culture of Al-Andalus, ever present in the city of the Alhambra.
7. The recovery and enhancement of the architectural cultural heritage in different types of buildings and structures in different places poses a real challenge for those researching in the field of materials science and for those working in conservation. The composition of these materials, the way they are used in the building and their state of damage and deterioration are key aspects in the necessary analysis required prior to any restoration work. Furthermore, from the point of view of the restoration of historical buildings, the main focus of this research, when these buildings are part of the architectural and cultural heritage of a particular geographical area, they have their own unique features at a strictly conceptual, formal or compositional level and from the materials point of view, when it comes to construction, conservation, restoration, recovery and enhancement.
8. This research has shown that when building Colegio Maximo de Cartuja (C. 19), the Jesuits acted in much the same way as the Carthusians had when they built the nearby Monastery of Cartuja (C. 16), and the Iberian and Roman settlers had done in the construction of their pottery workshops (C. 1 and 2 C. E), using techniques involving “water and clay” from the hill itself and from the River Beiro that flowed alongside.
9. Analytical results of construction materials reveal the historical tradition of “water and clay” in Albaicin quarter, Cartuja Hill and Beiro River, from Roman times to the present, as well as the use of sodium chloride in ceramics for better vitrification at lower temperatures. Recovering of vernacular materials and techniques in the area can generate a culture of sustainable restoration that will result an economic dynamization of this area for touristic sector. In addition, related to conservation works the mandatory restoring proposals would be surface cleaning, joining and replacement of detached parts, consolidation of materials and final protection.

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