

PETROLOGICAL CHARACTERISATION OF THE ‘BARXETA CREMA’ AND ‘BUIXCARRÓ ROSA’ LIMESTONES (VALENCIA, SPAIN)

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ABSTRACT: *The two analysed rocks in this study are located in the municipalities of Barxeta (“Barxeta crema”) and Quatretonda (“Buixcarró rosa”; Mountain range of Buixcarró) in the southern part of the Valencia province. These massive, mostly recrystallised, Campanian limestones (Late Cretaceous, ~70-84 Ma) were deposited on the southern margin of the Iberian plate during the alpine cycle. This zone is characterised by a great tectonostratigraphic complexity and is situated at the limit of the Betic (external Pre-Betic) and the SE Iberian Mountain Belt and, therefore, is less affected by the alpine deformation.*

Quarrying for architectonic, sculpture and ornamental use began in Roman times (Augustus), but due to present-day exploitation of the quarry it is difficult to identify their old excavation faces. The limestones, thanks to the ease with which they can be worked (scant porosity, uniform grain size, hardness etc.), were especially used for architectonic decoration. In the Valencia Community examples can be found in monuments such as the Claustrillo Alto del Palacio del Abad, within the Cistercian complex of the Monastery of Santa Maria (Valldigna), as in the Cathedral, Lonja, and the Basílica de la Virgen de los Desamparados (Valencia).

The petrological characterisation of the host rocks has been performed in the laboratory of the “Instituto de Restauración del Patrimonio de la Universidad Politécnica de Valencia”. Hence, scanning electron microscopy (energy dispersive x-ray microanalysis, SEM/EDX), Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD) and voltammetry of microparticles were used to determine the chemical and structural composition of the two rock types, “Barxeta crema” and “Buixcarró rosa”.

KEYWORDS: Limestone, Barxeta, Buixcarró, Late Cretaceous, scanning electron microscopy, FTIR, XRD, voltammetry of microparticles

1. INTRODUCTION

The identification of materials in façades, sculptures or ornaments (natural as well as repaired rocks and mortars) and their mineralogical distribution (degree of heterogeneity), are two of the most important jobs in the documentation required for the conservation and restoration of historical buildings as they allow us to define the rock and optimise the restoration of the individual monument or sculpture. Besides characterising the fresh rock, the study of the physically and chemically altered rock by pure laboratory research is necessary to achieve a sufficient knowledge base and understand how to handle untreated as well as altered rocks in historical monuments.

Valencia (‘Valentia’ original Latin name) was founded by Romans in 137 BC. Like most of the towns at that time, the economic necessities because of the high costs of the transportation of construction materials meant that Valencia was predominantly supplied by rock from the surrounding areas. From this point of view it seems to be quite reasonable, that travertines from the municipalities of Rocafort and Godella were used in the construction of the first monuments in the town of Valencia (Cavanilles, 1795-1797). Later,

with the growing demand for architectonic decoration in the Valencia Community, it became necessary to exploit and use marbles from farther afield, e.g. near Xàtiva (Barxeta). The quarrying of these rocks began during the Reign of Emperor Augustus, while this material began to be incorporated into Valencian monuments during the Flavian dynasty (69-96 CE) and was probably shipped from *Portus Sucronensis* (Cullera) to Valencia (Cebrián and Escrivá, 2001; Mayer and Rodá, 1991).

In this paper we will focus on the petrological characterisation of two recrystallised limestones, Barxeta crema and Buixcarró rosa, that were directly extracted from the quarries. Because both rocks are fine-grained, compact and very easily polished, they, especially Buixcarró rosa, have been widely used in architectonic decoration throughout the Valencia Community. On the other hand, one main problem of these consolidated carbonate rocks are their crosscutting clay minerals that contain veins causing preferential disruption planes, an impediment to sophisticated treatments. Examples can be found in the Valencia Community in monuments such as the *Claustrillo Alto del Palacio del Abad*, within the Cistercian complex of the Monastery of Santa Maria (Valldigna), as well as in the Cathedral, *Lonja*, and *Basílica de la Virgen de los Desamparados*.



Figure 1. Barxeta crema extraction front near (~3km to the east) the village Barxeta.

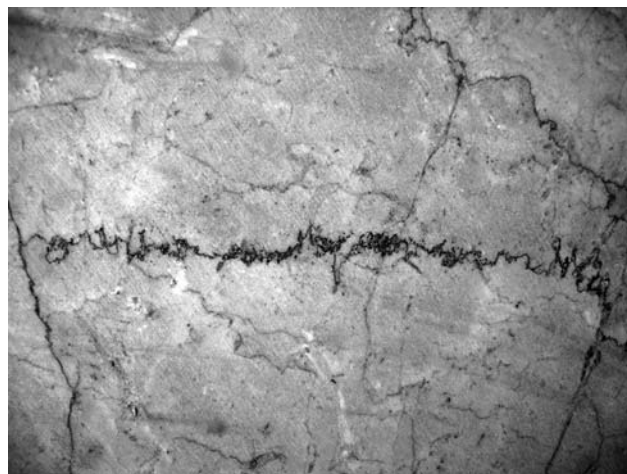


Figure 2. Host rock Buixcarró rosa closeup. (width of image 1m)



Figure 3. Buixcarró rosa. Column within Basílica de la Virgen de los Desamparados (Valencia).

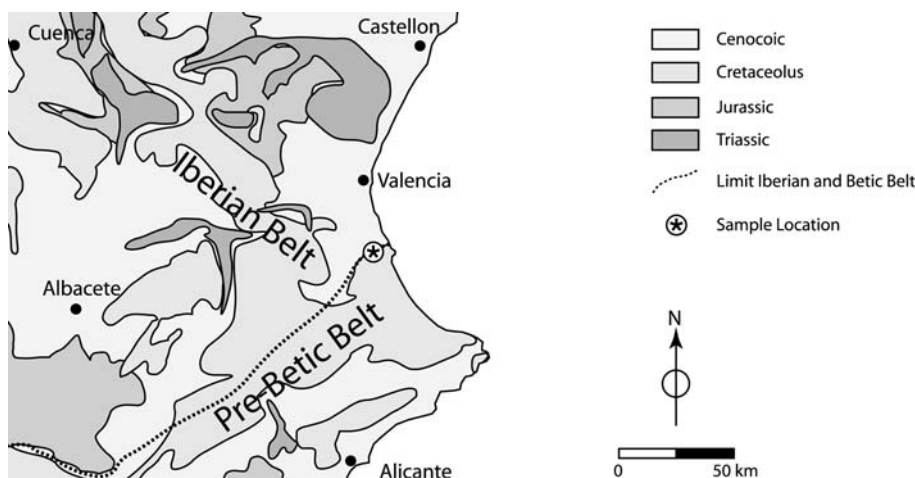


Figure 4. Simplified geological map with sample location.

2. REGIONAL GEOLOGICAL SETTING

Valencia Province, within the boundaries of the Valencian Community, is basically characterised by Mesozoic and Cenozoic sediments, whereas the Palaeozoic is almost entirely absent. In the northern part Triassic, Jurassic and Cretaceous sediments can be found while, south of Valencia, Cretaceous sediments predominate (Fig. 4). This area is characterised by two major cordilleras: the NW-SE Iberian Belt in the north and the SW-NE Betic Belt in the south. The Iberian Cordillera is squeezed in between the Pyrenees and the Betic Belt and owes its tectonic complexity to the emergence of these mountain ranges. The limestones we analysed are located about 50 km south of Valencia on the boundary between the external Pre-Betic and the SE Iberian mountain range. According to the geological map (1:50 000, sheet 771, *Instituto Geológico y Minero de España*, 1972), both rock types are Upper Cretaceous (Campanian ~70-84 Ma), belong to the same stratigraphic unit and the strata dip about 10° to the SSW. There is a normal NW fault on the southern boundary of the Barxeta crema quarry that raises up these massive limestones.

3. EXPERIMENTAL

3.1. Scanning Electron Microscope (SEM/EDX)

We used a a Jeol JSM 5410 scanning Electron Microscope, operating with a Link-Oxford-Isis microanalysis system for the morphological examination of the limestones and to obtain their chemical composition.

The analytical conditions were: 20 kV accelerating voltage, 2×10^{-9} A beam current and 15 mm working distance. The unpolished samples were carbon-coated to eliminate charging effects.

3.2. Fourier transform infrared Spectroscopy (FT-IR)

A representative amount of a fresh rock sample obtained directly from the quarry was crushed in an agate mortar and pestle by hand. IR absorption spectra were performed in the attenuated total reflectance mode (ATR) with a Vertex 70 Fourier transform infrared spectrometer and with a fast FR-DGTS (fast recovery deuterated triglycine sulphate) temperature-stabilised coated detector. The number of co-added scans was 32; resolution: 4 cm^{-1} . The analysed limestones contain more than 99% CaCO_3 , and the rocks were treated with 3M HCl to identify the rest of the minerals.

3.3. X Ray diffraction XRD

X-ray powder diffraction analysis was carried out using a Siemens DMP 2000 X-ray diffractometer with $\text{CuK}\alpha$ radiation at the wavelength of 1.5405 Å.

3.4. Voltammetry of microparticles

Voltammetric experiments were performed in 0.10 M HCl using paraffin-impregnated graphite electrodes (PIGEs, Scholz and Meyer 1998; Grygar et al 2002: 163) where 10-20 μg of powdered samples were abrasively transferred, as has already been described in detail (Doménech and Doménech 2005). Electrochemical experiments were performed at

Wavenumbers [cm ⁻¹]				
Limestones				Assignment
Barxeta crema	Buixcarró rosa	Ref. 1	Ref. 2	
712	711	712	712	ν_4 -Symmetric CO ₃ deformation
873	871	874	876	ν_2 -Asymmetric CO ₃ deformation
1407	1405	1425	1435	ν_3 -Asymmetric CO ₃ stretching
1796	1795	1798	1812	$\nu_1 + \nu_4$
2511	2508	2414	2545	$2\nu_2 + \nu_4$
2877	2875		2873	$2\nu_3$

Table 1. Main IR absorption bands (ν) of infrared bands of limestones and assigned modes. Ref. 1: Gunasekaran et al. 2006; Ref. 2: Gaffey (1986)

ambient temperature in a deoxygenated three-electrode cell, using CH 420 I piece of equipment.

4. RESULTS AND DISCUSSION

4.1. FTIR Spectroscopy

The untreated limestones show the typical IR absorption spectrum of calcium carbonate composed rocks. A typical calcite group carbonate spectrum includes three major absorption bands between 600 and 1500 cm⁻¹ and each can be assigned to particular deformation modes of the CO₃²⁻ ion (Adler, 1963). These bands have been related to ν_4 -symmetric planar bending mode at low wavelength numbers, ν_2 -asymmetric out-of plane bending and ν_3 -symmetric stretching at higher wavelengths. The ν_1 -symmetric stretching mode is also characteristic of carbonate rocks, but can normally only be detected by Raman spectroscopy and is inactive at infrared (Adler, 1963; Gunasekaran et al. 2006). Besides these first-order internal modes, combination modes can be identified ($\nu_1 + \nu_4$, $2\nu_2 + \nu_4$, $2\nu_3$; Gunasekaran et al. 2006)

The analysis of both rocks, Barxeta crema and Buixcarró rosa, resulted in the same spectrum with bands at 712 (711), 873 (871), 1407 (1405), 1796 (1795) and 2511 (2058) cm⁻¹. These bands are in accordance with the data predicted in the literature (Tab. 1, Fig. 5a,b. Adler, 1963; Shoval, 2003; Gunasekaran et al. 2006). The minor shift in the position of the ν_3 band to lower wavelengths might be due to impurities such as trace metals and/or the presence of clay minerals.

The composition of the two rock types is more than 99% CaCO₃ and the characteristic infrared absorption bands of calcium carbonate are very strong. To reveal the other remaining minerals we dissolved the rocks with HCl and the residue was measured with the FTIR method.

The absorption bands that were obtained indicate the dominance of typical clay minerals. Clay minerals are hydrated aluminium silicates with a layered structure of two-dimensional sheets of corner-sharing SiO₄ and AlO₄ tetrahedra, (Al,Si)₃O₄. In clays the tetrahedral sheets are always bonded to octahedral sheets (e.g. by Al, Mg), coordinated by six oxygen atoms. The unshared vertex from the tetrahedral sheet forms part of one side of the octahedral sheet but an additional oxygen atom is located above the gap in the tetrahedral sheet forming an OH group in the clay structure. The clay minerals can be subdivided into three main groups: the kaolinite, the smectite and the illite group.

Clay minerals are characterised by typical inner hydroxyl groups between the tetrahedral and octahedral sheets, resulting in a band in the region of 3620 cm⁻¹ (Keeling 1963; Stuart 2004). At around 915 cm⁻¹ OH deformation bands (AlAlOH) while absorption lines in the 1120-1000 cm⁻¹ range are due to Si-O stretching bands. Si-O-Si deformation occurs at 523 and 468 cm⁻¹. Kaolinite has two characteristic bands at ~3694 and 694 cm⁻¹ and peaks at 780-800 cm⁻¹ are characteristic for the quartz doublet. OH-stretching and bending vibrations of water cause absorption bands near 3635 and 1637 cm⁻¹, respectively.

The absorption spectra for both rocks are quite similar. Several OH-vibrations and a water vibration were observed (Table 2, Fig. 6a,b). The

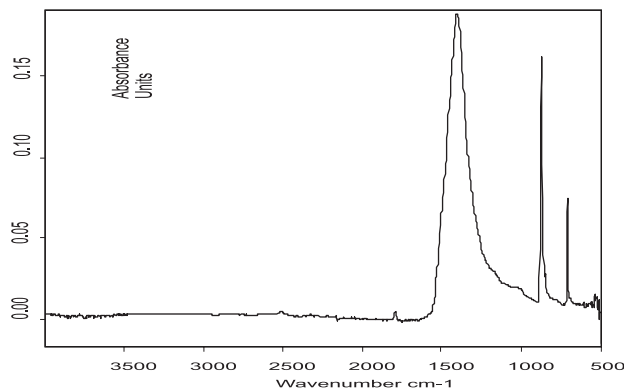


Figure 5a. IR absorption spectra of the Barxeta crema limestone.

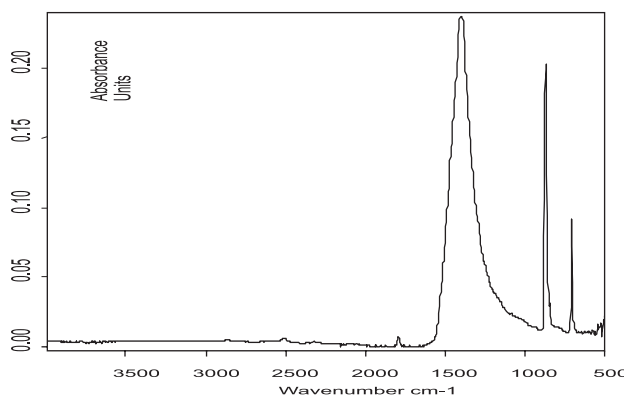


Figure 5b. IR absorption spectra of the Buixcarró rosa limestone.

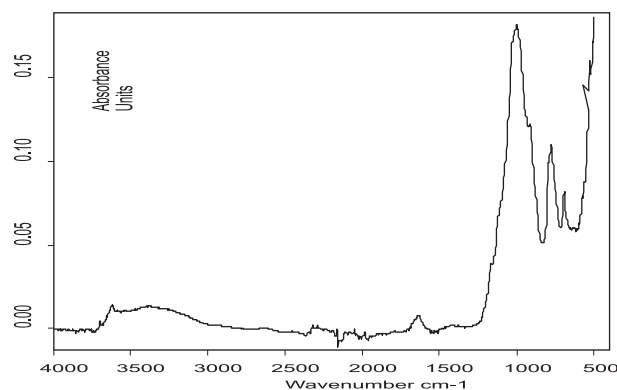


Fig. 6a. IR absorption spectra of the Barxeta crema after HCl treatment.

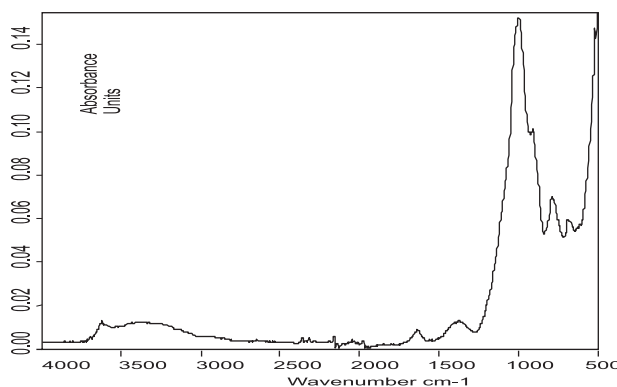


Fig. 6b. IR absorption spectra of the Buixcarró rosa after HCl treatment.

Wavenumbers [cm^{-1}]		
After HCl treatment, Remaining clay minerals		Assignment
Barxeta crema	Buixcarró rosa	
525	523	Si-O-Si deformation
694	694	δ (Al-O-Al) kaolinite
793	795	Qtz-doublet
912	912	OH-deformation bands (AlAlOH)
1005	1004	Si-O stretching bands
1409	1384	(residual CO_3 stretching of undissolved carbonate)
1633	1630	bending vibration of water
3395	3395	OH-stretching
3620	3620	Inner hydroxyl groups, stretching vibrations
3698		ν (OH) vibrations at the octahedral surface of the layers

Table 2. Main IR absorption bands (ν) of infrared bands of residual rocks and assigned modes.

BC	BR	BC	BR	BC	BR			
2θ [°]	2θ [°]	d [Å]	d [Å]	Intensity [%]	Intensity [%]	h	k	l
29,543	29,452	3,02115	3,03021	100	100	1	0	4
36,105	36,004	2,48569	2,49244	8,2	12,5	1	1	0
39,535	39,500	2,27754	2,27949	11,1	18,2	1	1	3
43,300	43,208	2,08784	2,09207	10,8	15,3	2	0	2
47,642	47,586	1,90719	1,90931	12,5	15,7	0	1	8
48,653	48,556	1,86990	1,87341	12,4	17,9	1	1	6

Table 3. Indexed powder XRD pattern for limestones. BC=Barxeta crema; BR=Buixcarró rosa.

OH-deformation bands of AlAlOH could be identified. An absorption band at 840 cm^{-1} indicates partial substitution of octahedral Al by Mg and Fe (Šucha, et al. 2001) and this could not be observed. The Si-O stretching bands at 1005 (1004) and the quartz doublet at 793 (795) cm^{-1} were detected. In both samples a peak at 694 cm^{-1} (δ Al-O-Al) was identified, but, in addition, a weak band at 3698 cm^{-1} (ν -OH stretching vibrations) in the Barxeta crema suggests a small amount of kaolinite, while the overall spectrum favours an illite composition. In the system these impurities are likely (Alvarez-Puebla, 2005). The overall high baseline at low wavelengths and the rise is interpreted to be the result of iron oxides and hydroxides.

4.2. XRD

Mineralogical characterisation was also determined by XRD. This technique is often used to determine the mineralogical composition as well as qualitative and quantitative phase analysis. The main reflections in the limestones Barxeta crema (and Buixcarró rosa) occur at d -spacings 3.02115 (3.03021), 2.48569 (2.49244), 2.27754 (2.27949), 2.08784 (2.09207), 1.90719 (1.90931) and 1.86990 (1.87341) Å (Table 3). The XRD-diagrams that were obtained show quite sharp peaks and not much background absorption (Fig. 7a,b). The reflections confirm calcite structure in the limestones, excluding the presence of dolomite. The additionally peak at $2\theta=26.800$ ($d=3.32381$ Å) in the Barxeta crema indicates the presence of a small amount of quartz.

4.3. Field observations combined with SEM/EDX results

The general aspect in the field at outcrop size of the Barxeta crema limestone can be described as follows: banked cream- to orange-coloured compact rock without any recognisable depositional structures. The calcite minerals are small-sized and flattened clay-filled veins without any preferred orientation crosscut the host rock. The veins developed after calcite recrystallisation and the colour is predominantly reddish, suggesting the presence of iron oxides.

The overall appearance in the quarry of the Buixcarró rocks is very similar to that of the Barxeta crema: compact banked limestone without any obvious depositional structures, traversed by randomly distributed clay-

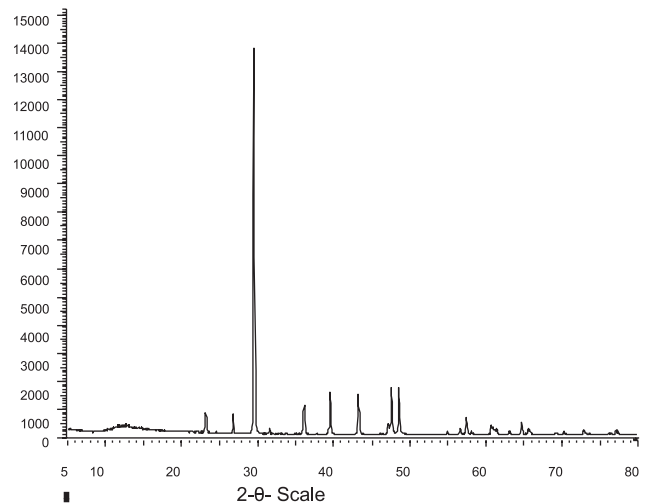


Figure 7a. Powder XRD pattern of Barxeta crema limestone

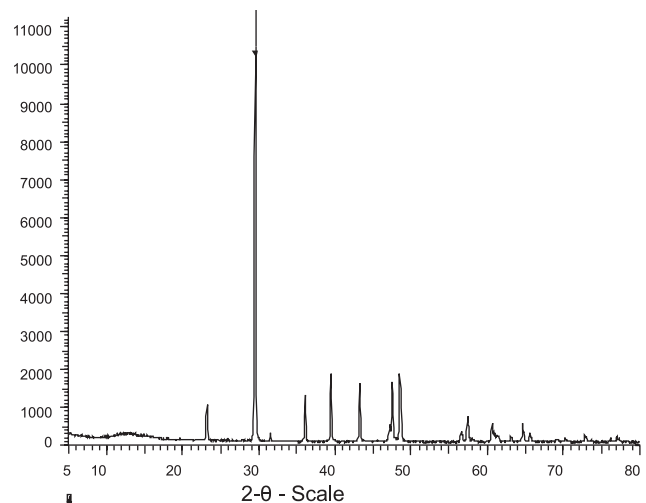


Figure 7b. Powder XRD pattern of Buixcarró rosa limestone.

filled veins. But, in contrast to the Barxeta crema, the colour is varying very strongly. Within the same extraction front red-, pink-, cream- and flesh-coloured limestones can be observed. Both rocks are fine grained (micritic to sparitic) and calcite is almost completely recrystallised.

The scanning electron microscope analysis (SEM) was able to confirm the observations of the hand specimens. The rocks are almost entirely composed of equant microcrystalline calcite (micrite, Fig. 8a). The compact appearance in the field can be confirmed and only intercrystalline microporosity of microcrystalline areas can be observed. The electron microscope study demonstrates that the micrite is not homogeneous but has areas of finer and coarser crystals, and intracrystalline boundaries that might be planar, irregular or sutured (Fig. 8a,b,d and e) and which, according to Tucker (2001), is quite normal.

Most of the calcite crystals show a compact anhedral habit and suggest aggrading neomorphism of micrite to sparite (Folk 1965, increasing crystal size, Fig. 8a,b). This is supported by the irregular curved intracrystalline boundaries and penetration of microcrystalline groundmass material into phenocrysts, making their normal euhedral boundaries incomplete (embayments, Fig. 8b; Tucker, 2001).

Furthermore clay minerals could be detected. As mentioned above, clay minerals are sheet silicates (phyllosilicates) with parallel sheets of silicate

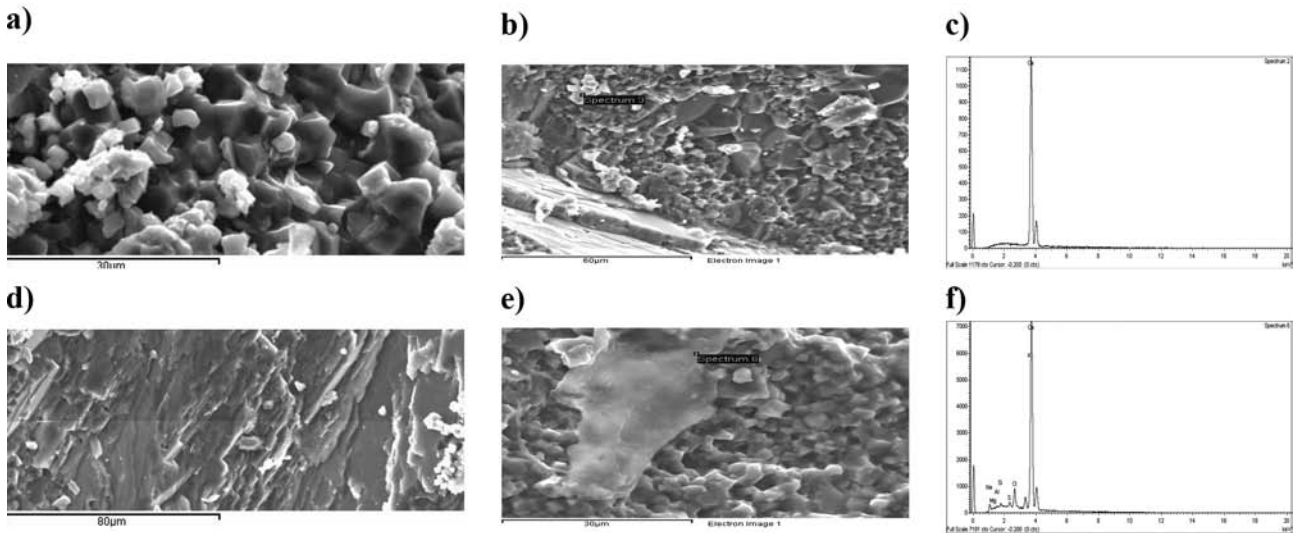


Fig. 8. a+b) Secondary electron image obtained by SEM of micritic to sparitic calcite habits of the Barxeta crema stone. c) X-ray spectrum obtained in spot mode in a calcite grain of the Barxeta stone (see 8b). d) Secondary electron image obtained by SEM in the Buixcarró rosa stone. e) Secondary electron image of weathered clay mineral in the Buixcarró rosa stone. f) X-ray spectrum in a clay aggregate (see 8e)

tetrahedra. Illite is the predominant mineral in many shales, which is a mica-like clay mineral, but differs from micas in having less substitution of Al for Si, having K partly replaced by Ca and Mg, and in containing more water and Fe. The chemical formula is $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$. Illite formation can be the result of muscovite and feldspar alteration in weathering and hydrothermal environments as well as in some low grade metamorphic rocks. In SEM imaging sheet minerals could be identified and, combined with the FTIR results, weathered illite seems to be the predominant phyllosilicate (Fig. 8e,f).

4.4. Voltammetry of microparticles

Marble samples were also studied by means of solid state electrochemical methods, using the voltammetry of microparticles approach, developed by Scholz et al. (1998). This methodology has previously used to study iron pigments (Doménech et al. 2001; Grygar et al. 2002: 1100; Doménech and Doménech 2007) and iron components in raw materials (Doménech and Doménech 2005).

Figure 9 shows the square wave voltammetric response of: a) Barxeta, and, b) Buixcarró samples in contact with 0.10 M HCl. Voltammograms of Barxeta show reduction peaks at +0.60 and +0.18 V vs. AgCl/Ag while for Buixcarró the peak at +0.60 V is accompanied by overlapping signals at +0.18 and +0.38 V. The process at +0.18 V can be attributed to the reduction of interstitial Fe^{3+} ions passing to the solution, a process favoured by the use of an acidic electrolyte. The electrochemical processes at +0.60 and +0.38 V can be attributed to the reduction of unidentified iron minerals accompanying calcium carbonate in marbles. Accordingly, marbles from Barxeta and Buscarró exhibit significant differences in their composition with respect to: i) the abundance of interstitial iron ions, and, ii) the presence of clay minerals accompanying calcium carbonate in the marble.

5. CONCLUSIONS

In the field of stone conservation and restoration, it is necessary to have a detailed characterisation of both altered stone within the monument as well as unaltered rock from the quarry in order to be able to apply the appropriate method of intervention. The petrological characterisation of the two unaltered limestones in this work is aimed at obtaining solid knowledge about the rocks employed in Valencian historical monuments.

The presence in the studied marbles of accessory minerals associated with calcium carbonate was confirmed by voltammetry of microparticles, FTIR and SEM/EDX.

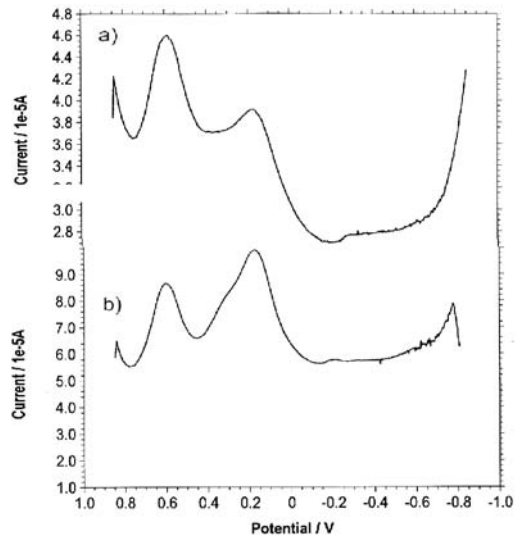


Fig. 9. SQWVs of marble specimens from: a) Barxeta, b) Buscarró, attached to PIGEs in contact with 0.10 M HCl. Potential scan initiated at +0.85 V in the negative direction. Potential step increment 4 mV; square wave amplitude 25 mV; frequency 5 Hz.

FTIR spectra obtained from samples subjected to prior HCl treatment make it possible to identify Illite/ Kaolinite clays. These clay minerals, localised in veins, form discrete disruption planes that impede sophisticated treatments. Recrystallisation processes of calcite minerals and the presence of sheet silicates could be confirmed by SEM analyses. It was also possible to verify the absence of open porosity (only intracrystalline) and compact micritic composition of the limestones. In addition, voltammetry of microparticles enables the identification of interstitial iron ions from the aforementioned clay minerals.

Pure limestones or marbles ($CaCO_3$) should be white but impurities are responsible for colour variations. Organic matter in limestones gives them a grey-black appearance, while limonite gives them a yellowish-brown colour and hematite, a reddish pink.

Limonite is a mixture of hydrated iron(III) oxide-hydroxide of varying composition. The formula can be written as $FeO(OH) \cdot nH_2O$, although this is not entirely accurate as limonite often contains a varying proportion of oxide to hydroxide. Hematite is the mineral form of Iron(III) oxide and the formula is written as Fe_2O_3 . Nonetheless, the origin of the homogeneous pinkish colouring of the Buixcarró rosa is not that obvious. Detrital iron from climate

change alteration would result in a large quantity and variability of particle size, which could not be observed in the analysed samples. Pigmentation found in the studied marbles could tentatively be associated with the dispersion of submicrometric (hydro)oxides generated by iron-bacteria as proposed by Mamet and Pr eat (2005 and 2006) for red marbles from different regions (France, Belgium, Czech Republic and Italy). To be able to answer the still open questions concerning the generation and mineralogical composition of these limestones, further selective research methods will be implemented.

ACKNOWLEDGMENTS

We would like to acknowledge the financial support we have gratefully received from the Spanish MEC Innovation, Research and Development Project CTQ 2005-09339-L03-01, as well as the FEDER foundation and the *grant for doctors attending centres of research excellence in the Valencia Community* (Generalitat Valenciana R+D program, DOGV 17/11/2006). The authors would also like to give thanks for the use of the facilities and to the technical supervisors Dr. Jos e Luis Moya L opez and Mr. Manuel Planes Insausti of the Scanning Electron Microscopy Service of the UPV.

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Versi n espa ola

TITLE: *Caracterizaci n petrol gica de las rocas calizas "Barxeta Crema" y "Buixcarr  Rosa" de Valencia*

ABSTRACT: *Las dos rocas analizadas est n localizadas en los municipios de Barxeta (Barxeta crema) y Quatretonda (buixcarr  rosa; Sierra de Buixcarr ) en la parte sur de la provincia de Valencia. Estas macizas y en su mayor a recristalizadas rocas calizas Campanienses (cret ceo superior, ~70-84 Ma) fueron depositadas en el margen sur de la placa ib rica durante el ciclo alpino. Esta zona est  caracterizada por una gran complejidad tectonoestratigr fica y est  situada en el limite de la cordillera B tica (Pre-B tica externa) y sureste Ib rica y, por lo tanto, no tan afectada por la deformaci n alpina.*

La extracci n de rocas para uso arquitect nico, escult rico y ornamental empez  en tiempos romanos (Augustea), pero debido a la presente explotaci n de la cantera es dif cil identificar sus antiguos frentes de excavaci n. Las rocas calizas, gracias a la facilidad para trabajar con ellas (baja porosidad, tama o de grano uniforme, dureza, etc.), fueron especialmente utilizadas para la decoraci n arquitect nica. Los ejemplos en la comunidad Valenciana pueden encontrarse en monumentos como el Claustro Alto del Palacio del Abad, dentro del conjunto cisterciense del Monasterio de Santa Mar a de la Valldigna, as  como la Catedral, la Lonja y Bas lica de La Virgen de los Desamparados de Valencia.

La caracterizaci n petrol gica de las rocas fuente ha sido llevada a cabo en el laboratorio del Instituto Universitario de Restauraci n del Patrimonio. Para ello se han aplicado: microscop a electr nica de barrido (microan lisis de rayos x, SEM/EDX), espectro de absorpci n infrarrojo (FTIR), difracci n de rayos x (XRD) y voltametr a de micropart culas, con el objetivo de determinar la composici n qu mica y estructural de las dos rocas (Barxeta crema y Buixcarr  rosa).

KEYWORDS: *Roca caliza, Barxeta, Buixcarr , Cret ceo superior, microscop a electr nica de barrido, FTIR, XRD, voltametr a de micropart culas*