

Renaissance patinas in Úbeda (Spain): mineralogic, petrographic and spectroscopic study

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Abstract Different analytical techniques were used for microstructural and compositional analysis of the ochre-coloured patinas that appear on the calcarenite substrate of monuments in the historical settings of Úbeda and Baeza (Spain). Optical microscopy, scanning electron microscopy–energy dispersive x-ray spectrometry (SEM-EDX), x-ray diffraction, Raman spectroscopy and attenuated total reflection–Fourier transform infrared spectroscopy (ATR-FTIR) were employed and a critical comparison of their experimental requirements, strengths and weaknesses is presented. The study focussed on two churches in Úbeda where patinas were widespread in ornamental elements. These films contained calcite as the principal component, and traces of dolomite and feldspars. Clear identification of calcium oxalate, mainly in the form of whewellite, was achieved by infrared and Raman spectroscopic studies. Results from texture, distribution and composition of the patinas in ornamental elements suggest that ancient treatments were applied for protection of Renaissance façades and consolidation of weathered older façades. The patinas were seldom found on supporting elements. Their different composition,

apatite was found together with oxalates, and location may suggest a biogenic origin here. Gypsum crusts were sometimes found over the patinas.

Keywords Raman · Infrared · Patina · Oxalate · Microscopy · XRD · Monument

Introduction

Dark yellowish, ochre or orange patinas cover external stone surfaces of a large number of monuments [1–5]. Gypsum, calcite, silicates and calcium oxalates are commonly found in this type of patina, which have been classically referred to as Mediterranean patinas [6, 7], *scialbatura* in Italy [8, 9] or oxalate films [7]. Their biological [5, 9–11], artificial or anthropogenic [1, 12–14] origin has been widely discussed and still remains uncertain. It is well known that several treatments have been applied since the Roman age [7] for different purposes: protection against weathering degradations, preparation of the stone substrate prior to the application of polychromy, to produce artificial aging of new architectural elements during conservation, and for maintenance aimed at refreshing the brittleness of the stone surface [7, 12]. Egg, milk, cheese, urine, blood, natural resins, oils, arabic gum and treacle were frequently applied on stone and plaster as conservation treatments. The alterations undergone by these organic products have been regarded as the cause of patina formation [12, 15]. In contrast, theories of the natural origin of the patinas attribute their formation to the metabolic action of living organisms on the stone, like encrusting lichens, algae or fungi [5, 9].

The study of architectural or monumental heritage structures requires the use of minimal sample quantities. This fact and the thinness of the patina layers are the major

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drawbacks for the application of common analytical techniques like x-ray diffraction for identification of the mineral composition. Raman and attenuated total reflection–infrared spectroscopies can be an advantageous choice for the study of patinas, because of the low amount of sample required and the absence of sample preparation [16].

Historical setting

The Renaissance monuments of Úbeda and Baeza (Province of Jaén, Andalusia, Spain) were named World Heritage sites by the United Nations Educational, Scientific and Cultural Organization (UNESCO) in 2003. Two churches, San Pablo and San Isidoro, located in historical Úbeda were selected for this study.

According to various authors [17, 18], San Isidoro's church was built in the thirteenth century in Gothic style over a previous Moorish fortification. Two new Renaissance façades, north and south, were added onto the church in the sixteenth century and the indoor structure was remodelled in keeping with the design of the Cathedral of Jaén [17]. The church has since been remodelled on several occasions. On the other hand, San Pablo's church is one of the oldest parish churches in the city of Úbeda. Its original design has been profoundly transformed so diverse architectural features are easily distinguished on its façades. The western façade was built in the thirteenth century in Romanic-Gothic style; the northern façade was erected in Gothic style at the end of the fifteenth century; the southern façade was decorated in the sixteenth century in a Renaissance style with some Baroque details. Ochre-coloured films have been identified in the southern façade of San Isidoro's church and in the southern, northern and western façades of San Pablo's church.

Geological setting

Most of the monuments in Úbeda and Baeza are built with the Tortonian calcarenite called "Piedra Dorada" [19]. This calcarenite is mainly composed of skeletal grains of calcite, dolomite, quartz and feldspars with some traces of clay minerals and bioclasts. All these grains are bonded by a sparitic or microsparitic carbonate cement. Two basic varieties of Piedra Dorada can be established according to its cementation. A hardener and well-cemented variety (Viva Stone) was usually used as structural support in high-strength areas, whereas a weaker and more porous variety (Franca Stone) had an ornamental function [19–21].

Up to now, little information was available about the Piedra Dorada in these cities. Sebastián et al. [19] performed petrophysical tests on quarry stone from Baeza, whereas Villegas [22] applied some conservation treatments and consolidants. Campos and de la Torre [20, 21, 23] have

recently reported the stone characteristics and the origin of weathering forms in churches of Úbeda and Baeza.

However, although ochre-coloured patinas appear on these calcarenite surfaces, they have not been described or even studied in the historical setting of Úbeda and Baeza. This work aims to characterize the patinas from S. Isidoro and S. Pablo churches (Fig. 1) including a critical discussion of the benefits and drawbacks of the different analytical techniques employed. The elucidation of the origin of the films studied is also attempted.

Experimental

Samples

Extensive sampling was performed at the churches of San Pablo and San Isidoro. Samples were collected from masonry, mortars and ornamental elements at different façades and heights. Diverse pathologies were found in the stone and 20 samples from different locations (Table 1),



Fig. 1 Southern façades of San Isidoro (a) and San Pablo (b) churches in Úbeda (Spain)

Table 1 Description of samples

Church	Sample	Façade	Material	Location
San Isidoro	SIU-15	South	Ornamental element	Exposed column under archivolt
	SIU-16	South	Ornamental element	Sheltered column under archivolt
	SIU-17	South	Ornamental element	Exposed moulding under archivolt
San Pablo	SPU-22	South	Mortar	Outer mortar under pinnable
	SPU-27	South	Ornamental element	Sheltered column under archivolt
	SPU-28	South	Support element	Exposed ashlar under archivolt
	SPU-29	South	Ornamental element	Sheltered moulding under archivolt
	SPU-31	South	Ornamental element	Exposed mullion
	SPU-55	West	Support element	Exposed ashlar next to the columns
	SPU-57	West	Ornamental element	Exposed column under archivolt
	SPU-58	West	Ornamental element	Sheltered column under archivolt
	SPU-59	West	Ornamental element	Sheltered moulding under archivolt
	SPU-61	West	Support element	Exposed ashlar next to the columns
	SPU-62	West	Support element	Exposed ashlar next to the columns
	SPU-65	West	Ornamental element	Sheltered column under archivolt
	SPU-68	West	Support element	(Bio)weathered ashlar
	SPU-69	West	Support element	Weathered ashlar
	SPU-70	North	Mortar	Outer mortar next to the columns
SPU-73	North	Ornamental element	Exposed column under archivolt	
SPU-74	North	Mortar	Outer mortar in columns	

showing the presence of an external ochre-coloured layer, were selected for this study. Considering the historic and cultural importance of both churches, sampling was done with scalpels to minimise damage.

Instruments and methods

The petrographic study of polished, thin sections of samples was carried out using an Olympus BH-2 optical microscope equipped with a digital camera. Samples were prehardened by setting the sample in a mould which was filled with epoxy resin. The obtained sample was cut, top to bottom, in thin parallel sections and stained with alizarin to determinate the nature of the carbonates present [24].

Mineral composition was analysed by using a Siemens D-5000 x-ray diffractometer which was operated at 35 kV and 25 mA, Cu K α radiation (1.5406 Å) and Ni filter. The diffraction patterns were recorded over the range 2–70° at 0.02° intervals in 2 Å. For mineral identification, the obtained diffraction patterns were compared with patterns from the “Powder diffraction file” [25].

Scanning electron microscopic study was carried out at the Centro de Instrumentación Científica (CIC) of the University of Granada with a Carl Zeiss field emission scanning electron microscope (FESEM), model GEMINI-1530, equipped with an INCA-200 microanalyser, working at 20 keV. The samples were premetallised and concretely graphite-sputtered.

A Bruker RFS (FT) Raman spectrometer fitted with a liquid nitrogen-cooled Ge detector was used to record the Raman spectra. The 1,064-nm line of a Nd:YAG laser with

a power of 200 mW was used for excitation. The Raman-scattered radiation was collected at 180° geometry. All spectra were recorded with a resolution of 4 cm⁻¹ and were averaged over 200 scans.

Infrared spectra were recorded with a Bruker Tensor 27 Fourier transform infrared spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. A horizontal DuraSamplIR single-reflection diamond attenuated total reflection (ATR) (SensIR Technologies) with a torque-limited pressure applicator was employed. All spectra were recorded at a resolution of 4 cm⁻¹ (64 scans). A spectrum of the clean and dry ATR crystal against air was used as background.

No sample preparation was required for either Raman or infrared measurements.

Results and discussion

Optical microscope observation (OM)

The samples from the southern façades of San Isidoro (SIU) and San Pablo (SPU) churches showed a thin continuous superposition of ochre-coloured layers perfectly adhered to the stone surface (Fig. 2). The layers were very homogeneous and 30- to 70- μ m thick. In addition to small grains of calcite, patina appears to be composed (in plane-polarised light) of a micritic matrix in which minerals could not be identified because of their tiny size. Some ferruginous stains could be also distinguished inside. These iron oxides contribute to give the patinas their characteristic ochre colour.

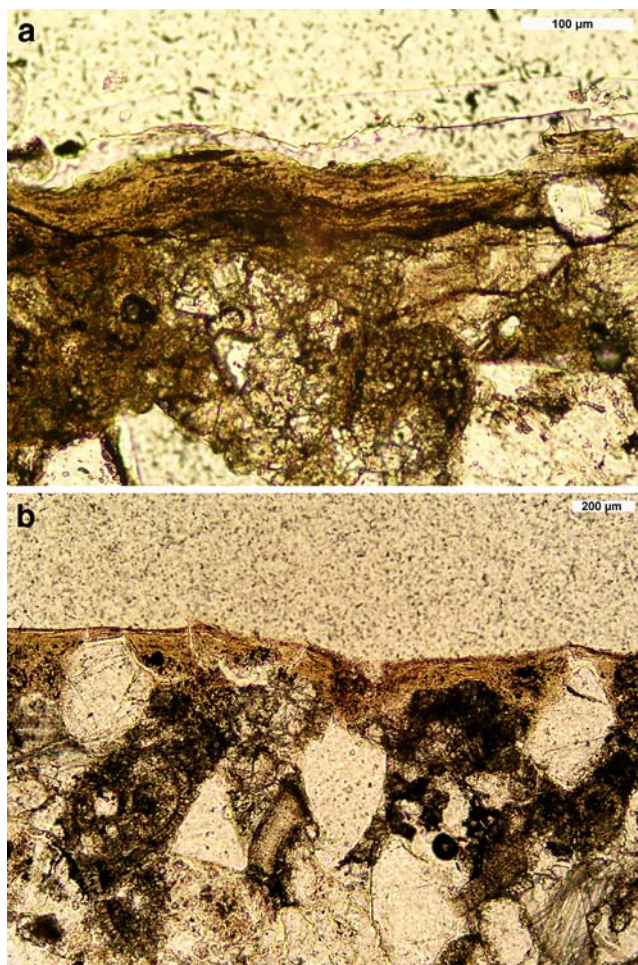


Fig. 2 Ochre-coloured patinas covering ornamental elements in the southern façades of (a) San Isidoro's church (SIU-17) and (b) San Pablo's church (SPU-27). Plane-polarised light. (a) Patina is homogeneous, shows a slight lamination and covers a nonweathered surface. Scale bar 100 µm. (b) The patina is homogeneous, cryptocrystalline and slightly polystratified. The layer–stone contact is sharp but some microfissures can be observed. Scale bar 200 µm

Microfissures were sometimes found perpendicular to the surface of the patinas (see Fig. 2b). The substrate under the layer is a partially cemented Franca stone with traces of gypsum. No traces of biological growth were found.

The patina from the northern and western façades of San Pablo's church showed diffused levels and an irregular borderline as it penetrates inside microcracks and irregularities of the stone (Fig. 3). In these cases, stone substrate was always altered; see for example Fig. 3a where a clear crystallisation of acicular gypsum is observed. Discontinuities between the layer and the stone substrate were detected. Although patinas were mainly found over ornamental elements, few mortars and ashlar seem to be coated by an ochre layer in the northern and western façades (Fig. 3b).

In sheltered areas of both churches, especially in San Pablo's, patinas seem to be covered by an acicular gypsum layer containing dust and small fragments of calcite and

quartz (see Fig. 3). All these components formed a typical black crust [26] caused by atmospheric weathering.

A thin microcrystalline calcitic layer was seldom observed over the patina. This must be the result of partial dissolution and recrystallisation processes in the abovementioned patina.

X-ray diffraction (XRD)

The ochre-coloured patinas were scratched from the substrate but their thinness and good adherence to the stone hindered their complete isolation. Thus, the samples always contained a high proportion of the underlying calcarenite.

Analysis of masonry and ornamental elements covered by patinas at SIU and SPU shows calcite (CaCO_3) to be the principal component together with lower proportions of

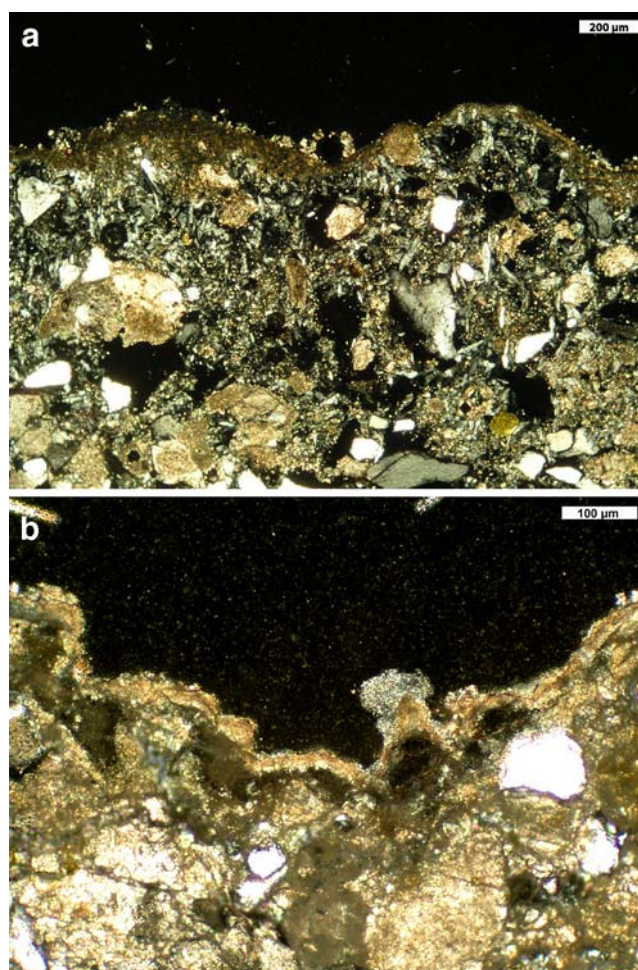


Fig. 3 Patinas (a) SPU-73 and (b) SPU-55 from San Pablo's church. Cross-polarised light. (a) Thin and discontinuous patina covering an ornamental element (northern façade). The stone substrate is completely grain disaggregated and the calcitic cement has been substituted by neoformed acicular crystals of gypsum. Scale bar 200 µm. (b) Irregular patina covering a weathered supporting ashlar on the western façade. The outer stone surface is altered and it shows an increment of porosity and a decrease of calcitic cement. Scale bar 100 µm

quartz (SiO_2) (Fig. 4). Traces of dolomite ($\text{MgCa}(\text{CO}_3)_2$) and feldspars were sometimes detected. The presence of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) was often observed and was especially significant in SPU (Fig. 4b). The gypsum could have originated from black crusts or crystallisation from the mortars. Other soluble salts were also found as traces e.g. halite (NaCl), sylvite (KCl), mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) and nesquehonite ($\text{MgCO}_3 \cdot \text{H}_2\text{O}$). The contribution of niter (KNO_3) was significant only in the samples taken in the ashlar at the bottom of the wall. The presence of niter in the areas with a high capillary rise may be easily attributed to excretion products. Calcium oxalate (weddellite, $\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, and whewellite, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), Fe oxides and phosphates were almost negligible.

Scanning electronic microscopy (SEM)

SEM provides useful information about the texture and structure of the patina, as well as information about ele-

mental composition by means of x-ray dispersive energy microanalysis (EDX) [27].

The morphology of the patinas has been previously discussed and our SEM images showed similar results. Figure 5 shows that the outer surface of the patinas was relatively homogeneous and smooth. EDX results (see Fig. 6a) showed that the major component, calcium, was accompanied by minor amounts of aluminium, silicon and iron. This result pointed to calcite being the essential component of the patina. Aluminium and silicon indicated the presence of clay minerals. Iron was attributed to Fe oxides and clay minerals, although it can also appear as atmospheric particulate matter together with bromine, zirconium and lead.

The surface of the patinas was occasionally cracked by microfissures. Perpendicular microfissures (Fig. 6b) which

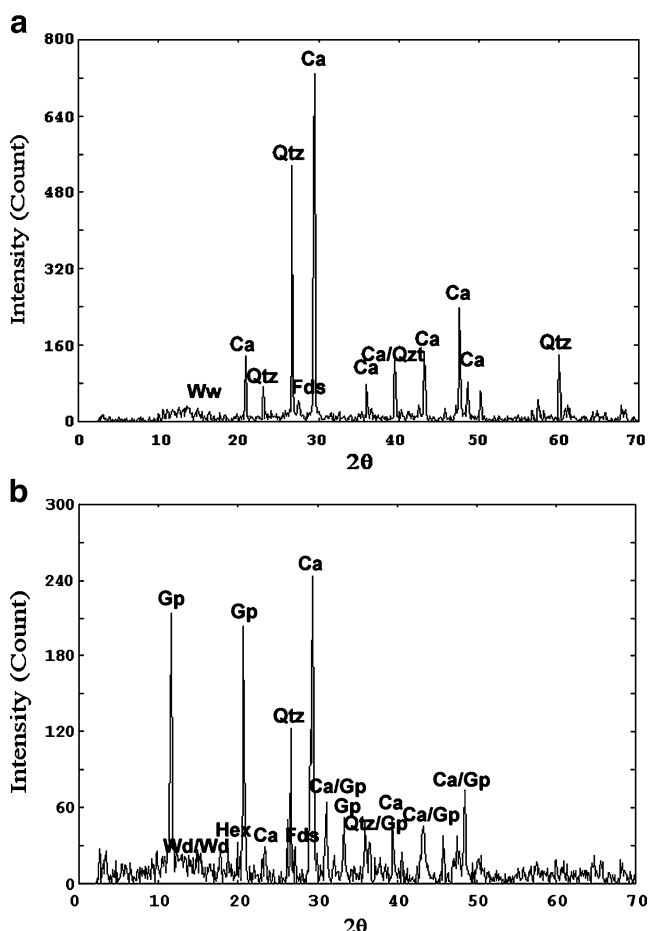


Fig. 4 Characteristic x-ray diffraction pattern of the patinas (a) SPU-29 and (b) SPU-57 samples. *Ca* calcite, *Gp* gypsum, *Do* dolomite, *Qtz* quartz, *Fds* feldspar, *Hex* hexahydrate, *Wd* Weddellite and *Ww* Whewellite peaks have been marked

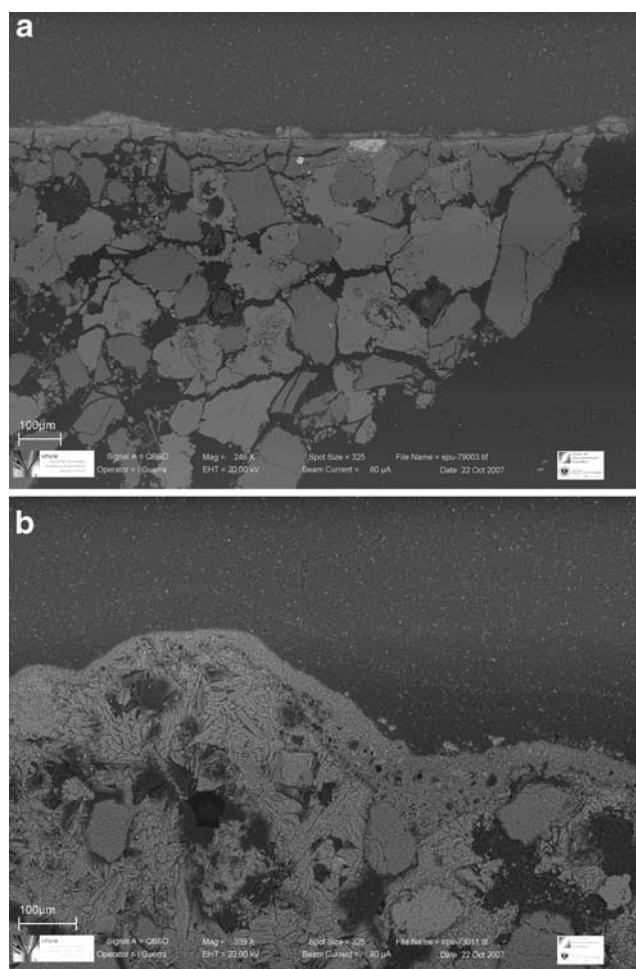
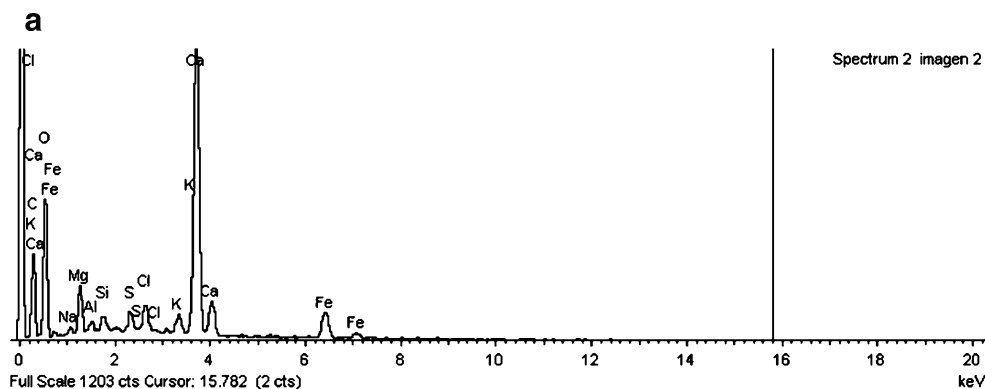


Fig. 5 SEM-BSE (backscattered electron mode) image of thin sections of patinas in ornamental elements. Scale bar 100 μm . (a) SPU-31: thin and regular patina develops on calcarenite, in which an ochre micritic layer can be seen in direct contact with the rock. The ochre layer appears microlaminated. (b) SPU-73: the patina covers the surface and adapts to the irregular underlying surface. Gypsum fills underlying pores and cavities

Fig. 6 Typical EDX-SEM analysis of the surface of a patina sample (a). SEM-BSE images of the surface of samples (b) SPU-22 showing retraction microcracks. Scale bar 200 μm ; (c) SIU-17. Small crystals of Na/K chloride crack the continuity of the patina as efflorescences. Scale bar 3 μm ; and (d) SPU-73. The surface of patina shows chloride and sulfate efflorescences. Scale bar 100 μm



seem to be produced by retraction of the original paste and parallel microfissures produced by the growing of crystalline salts (e.g. gypsum, halite, sylvite, mirabilite or hexahydrite) (Fig. 6c). EDX microanalysis provided information about their constituents being the more important sodium, potassium, magnesium, calcium, sulfur and chlorine. Soluble salts, especially Na–K chloride and Ca–Mg sulfates, crystallise as subflorescences and cryptoefflorescences. Most of these ions came from adjacent mortars and were distributed by the high capillary rise. The efflorescences promoted the loss of calcitic cement and the grain disintegration of the underlying calcarenite (Fig. 6d).

Other salts such as phosphates and nitrates could indicate the presence of biological activity or an organic compound [12].

Sulfur, chlorine, nitrogen, sodium, potassium, magnesium, and rarely bromine, zirconium and lead were found on the surface of the patinas.

Sometimes, patinas were covered by black crusts of gypsum (see Fig. 7). These crusts had already been observed by OM and also contained dust particles (calcite, quartz, carbonaceous particles). EDX microanalysis also allowed the detection of metallic particles which reveals atmospheric pollution. The fact that San Pablo's church is located in an area with a busy road helps to explain the presence of black crusts overlapping the patinas [1] in ornamental elements sheltered from washout [13, 23]. Due to gypsum aggressiveness, patinas were altered because it crystallises and penetrates into microfissures contributing to the scaling of the patina.

Raman spectroscopic study

Preliminary Raman studies were attempted using a Raman microscope with excitation at 514 and 785 nm. However, the extremely strong fluorescence background hindered the recording of spectra containing useful features. The fluorescence was significantly reduced by employing a Fourier transform spectrometer with excitation at 1,064 nm. Typical Raman spectra are shown in Fig. 8. All the samples

showed a sharp band at $1,085\text{ cm}^{-1}$ together with weaker bands at 712 and 282 cm^{-1} , which are characteristic of calcite. Other minerals like dolomite and quartz were frequently detected (see Table 2). The characteristic gypsum band at $1,008\text{ cm}^{-1}$ was found in several samples, frequently associated with two broad bands around $1,290$ and $1,590\text{ cm}^{-1}$ that can be attributed to carbonaceous particles (soot) [28]. In some samples from mortars and ashlar, the presence of a band at 962 cm^{-1} can be assigned to the PO_4^{3-} symmetric stretching (ν_1) of apatite [29]. This band was always accompanied by a broad band centred around 770 cm^{-1} (see Fig. 8b), which masked other phosphate normal modes, and corresponds to a characteristic luminescence emission that has been observed for hydroxyapatite and related minerals in spite of near-infrared excitation [30]. The presence of phosphates in the patina could be attributed either to biological activity or degradation of organic additives from ancient treatments, like casein or milk. [12, 31–33]

Calcium oxalates were also clearly identified. This Raman spectroscopy technique can easily distinguish between whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), with the characteristic C=O stretching doublet at $1,462$ and $1,490\text{ cm}^{-1}$ and weddellite ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) with a single band located at $1,476\text{ cm}^{-1}$ (see inset in Fig. 8) [34, 35]. Whewellite was the most common form encountered.

Infrared spectroscopic study

Infrared spectra were obtained in attenuated total reflection (ATR) mode. The short penetration of the radiation when using the ATR technique is an advantage for the study of patinas because the underlying substrate does not interfere in the recorded spectra. The application of high pressure was necessary to achieve an intimate contact between the sample and the ATR element due to the hardness and the irregular surface of the samples. This was only possible using a single-reflection diamond crystal. Typical ATR-FTIR spectra of unaltered Franca substrate and patinas are shown in Fig. 9. The spectrum of the substrate is dominated

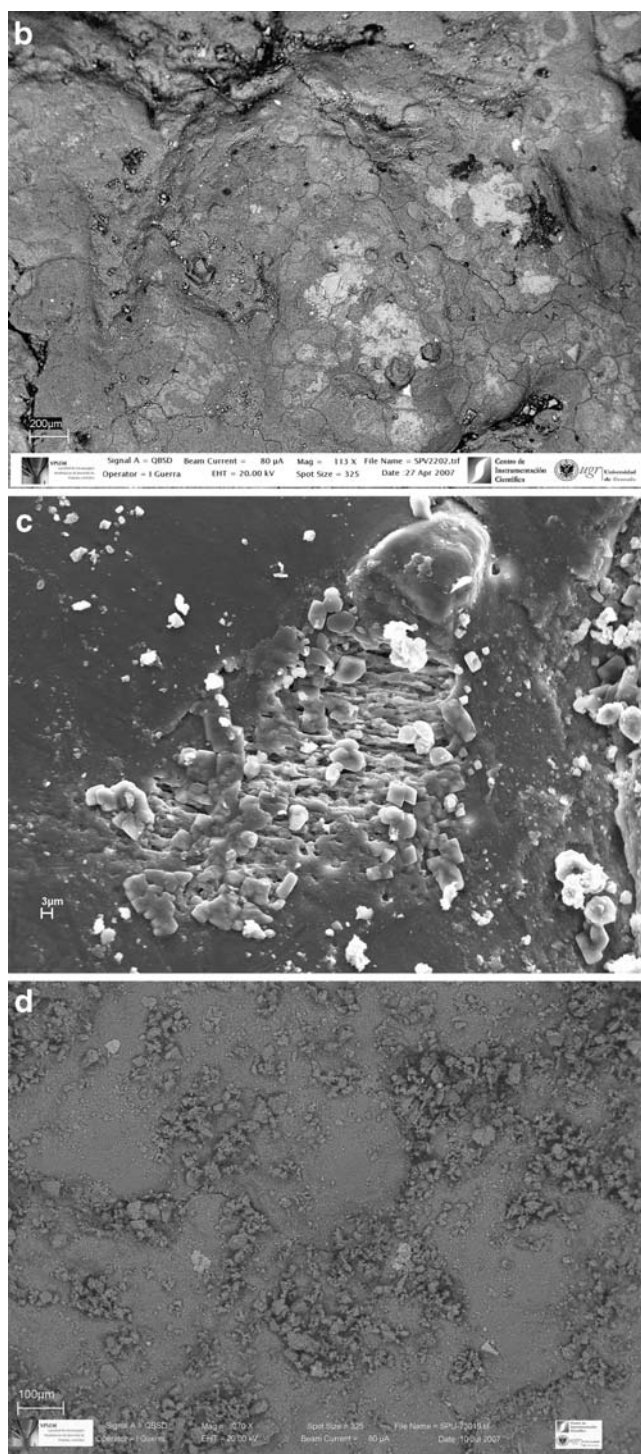


Fig. 6 (continued)

by typical bands of calcarenite: two broad absorption bands centred at about 1,400 and 1,000 cm^{-1} due to carbonates and silicates, respectively, and two sharp spectral features located at 872 and 712 cm^{-1} due to calcite.

Infrared spectra of the patinas revealed the presence of different amounts of calcium oxalates and calcite in all the samples studied (Fig. 9). The distinction between the two

forms of calcium oxalate using IR is more difficult than using Raman spectroscopy, because it is based on the slightly shifted symmetric O–C–O stretching vibrations of whewellite, and weddellite, located at 1,317 and 1,324 cm^{-1} , respectively [13, 36]. Thus, although the characteristic absorption peak of whewellite was mainly detected, slight shifts of the band can indicate the presence of weddellite. The identification of other compounds is more complicated due to the overlapping of broad spectral features in the region 900–1,200 cm^{-1} . However, the use of the second derivative allowed discrimination between overlapping bands [13]. In this way, gypsum with an antisymmetric stretching band of SO_4^{2-} at 1,111 cm^{-1} [37] and apatite with PO_4^{3-} antisymmetric stretching at 1,029 cm^{-1} [29] could be identified in some samples.

Different analytical techniques: critical discussion

The different analytical techniques employed in the study of patinas have provided complementary information. The observation of the patina, substrate and the interface between them by optical and electronic microscopy afforded useful information about the homogeneity and morphology of the patina. Furthermore, microscopic techniques allowed the estimation of the thickness of the layer. However, optical microscopy provided little success in identifying the minerals present in the cryptocrystalline aggregates. The elemental composition provided by EDX could not achieve the unambiguous identification of a typical patina component like calcium oxalate as it is composed of the same elements as calcium carbonate.

X-ray diffraction of powder scratched from patinas has been previously used to identify the different mineral phases [13, 38]. However, in our case, the limited amount of



Fig. 7 SEM-BSE image of the surface of a typical black crust of lenticular gypsum crystals (with dust particles trapped in the network) on the patina SPU-29. Scale bar 10 μm

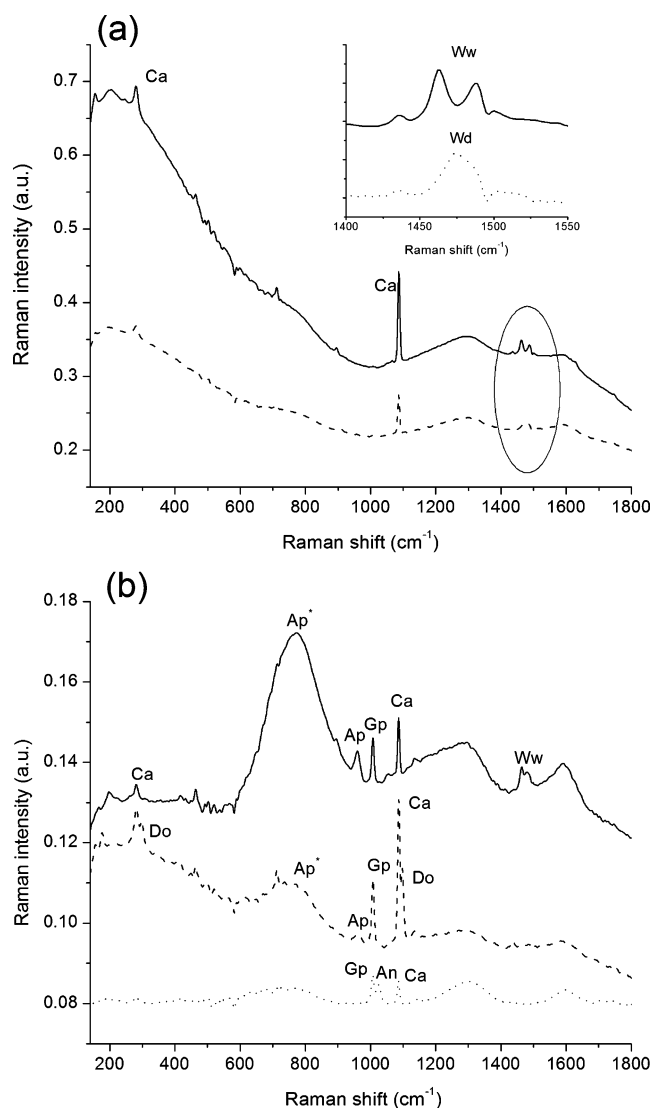


Fig. 8 Recorded Raman spectra of (a) samples from ornamental elements SIU-17 (black) and SPU-31 (red), inset 1,400–1,550 cm^{-1} region showing the oxalate contribution; and (b) samples from supporting elements SPU-55 (black), SPU-61 (red) and SPU-68 (green). *Ca* calcite, *Gp* gypsum, *Do* dolomite, *An* anhydrite, *Ap* apatite (*Ap** luminescence band of apatite), *Wd* weddellite, *Ww* whewellite

sample and the thinness of the patinas found in Úbeda (ca. 50 μm average), did not allow for their complete isolation from the substrate making the analysis extremely difficult. In fact, the signals from oxalates, phosphates and Fe oxides were probably underestimated due to the contribution of the underlying rock; thus, their clear detection was hindered. X-ray microdiffraction (μXRD) could constitute a useful alternative [39].

Vibrational spectroscopic techniques were, in this work, revealed to be very useful for the determination of the composition of the patinas because of the tiny amount of sample required and the absence of sample preparation. Raman spectra were directly recorded on the surface of the

patinas, thus avoiding their destruction by preparing polished sections. The major drawback of this technique was the strong luminescence background, which was observed even with a Fourier transform spectrometer using excitation in the near-infrared region.

For infrared spectroscopy, attenuated total reflectance (ATR) provided a simple and effective alternative to conventional transmission measurements. For ATR, it was not necessary to scratch the patina (being careful to minimize contamination from the calcareous substrate) to obtain a powder for preparing KBr pellets. Samples were placed directly on the ATR crystal and pressed. In this way, the short penetration of the evanescent wave guarantees that the recorded spectra corresponded only to the patina.

Raman and infrared spectroscopy allowed for the clear identification of calcium oxalate in the patinas, apart from other minerals already detected by the other techniques. Infrared spectroscopy was found to be more sensitive to the presence of small amounts of this compound, whereas the distinction between monohydrated (*Ww*) and dihydrated (*Wd*) forms was more easily achieved by Raman spectroscopy. Furthermore, the latter technique also allowed for the clear identification of phosphates.

Elucidation of the origin and role of the patinas

The homogeneity of the patinas on the ornamental elements in San Isidoro and San Pablo churches together with their perfect parallel positioning suggest that they were the result of a protective treatment applied in the past. This hypothesis can also be supported by the scarce presence of lichen and fungi and the fact that similar patinas were not identified in the natural stone throughout the areas near the old quarries (nowadays closed) [26]. Protective treatment probably consisted in using lime mortar mixed with organic binders of a still unknown nature. The detected calcium oxalate would be the result of the degradation of these compounds in a calcium-rich environment. The extremely high fluorescence background found in Raman spectra could be attributed to traces of degradation and oxidation products resulting from

Table 2 IR and Raman bands used for the identification of minerals

Mineral	IR wavenumber (cm^{-1})	Raman shift (cm^{-1})
Calcite	1,414; 872; 712	1,085; 713; 283; 156
Dolomite		1,098; 300; 177
Gypsum	1,685; 1,621; 1,144; 1,116	1,007
Apatite	1,029	960
SiO_2	1,082	462
Silicates (kaolinite)	1,098; 1,032; 1,009; 914	
Weddellite	1,324	1,474
Whewellite	1,618; 1,316	1,485; 1,461

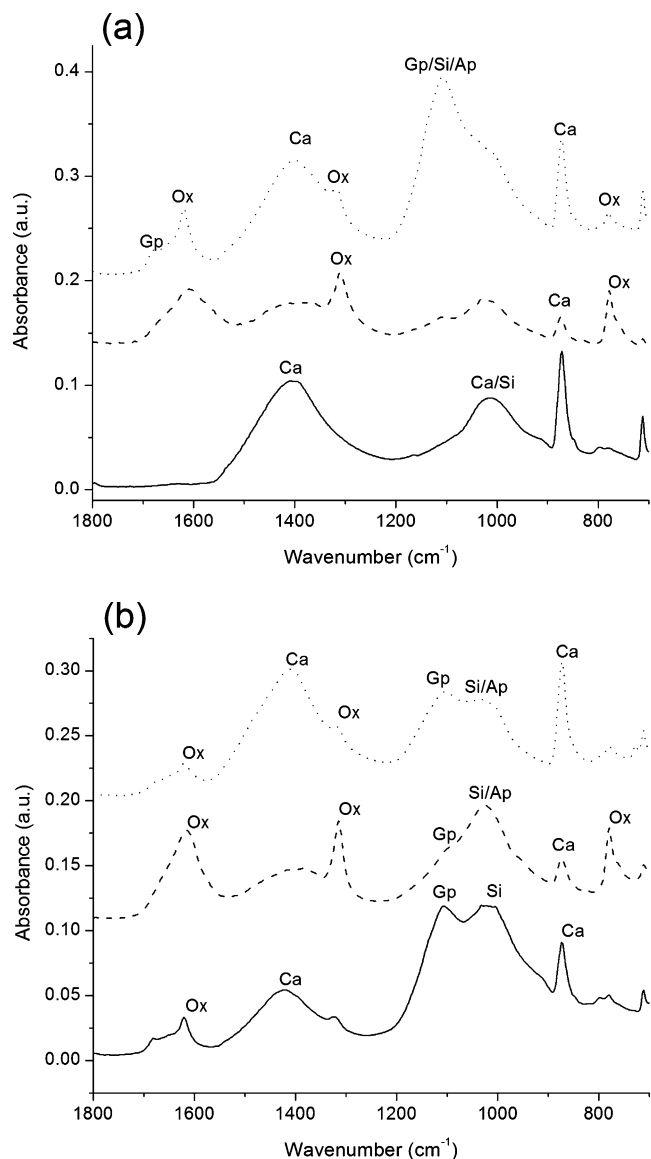


Fig. 9 Recorded Infrared spectra of (a) “Franca substrate” (black) and two samples from ornamental elements SIU-17 (red) and SPU-73 (green); and (b) samples from supporting elements SPU-55 (black), SPU-61 (red) and SPU-68 (green). *Ca* calcite, *Gp* gypsum, *Ap* apatite, *Si* silicate, *Ox* oxalate

the alteration of proteinaceous binders [39]. The absence of phosphates in patinas from ornamental elements discarded the use of caseinate-based or bone-based binders [8, 12].

Taking into account the location of the patinas in the two churches, more considerations can be made. San Isidoro’s church patinas were concentrated in the ornamental elements of the southern façade, whereas they were not detected in adjacent masonry, mortars or northern façade. On the other hand, patinas were found in the three façades, northern, western and southern, of San Pablo’s church. The interface between the patinas of the southern fronts (sixteenth century) and the calcareous substrate in both churches was regular and well defined. However, in the older northern and western

façades (fifteenth and thirteenth, respectively) of San Pablo’s church, the patinas covered a weathered substrate and penetrated inside microfissures or cavities.

Furthermore, the temporal coincidence in the construction of the southern façades in San Pablo and San Isidoro’s churches and the fact that they are the most elaborate fronts suggests that a treatment was applied at the time of the construction to protect the porous and weak ornamental elements made of Franca stone. In contrast, the penetration of the patina inside irregularities of the weathered stone in northern and western fronts in SPU indicates that the protective treatment was applied long after their construction, probably in the Renaissance period when the southern façade was redecorated.

Patinas were also found in sheltered lower and humid ashlar, although more scarcely than in ornamental elements. In those cases apatite was always detected together with oxalates which could indicate the application of a different treatment on already weathered ashlar. Furthermore, the hypothesis of biological origin for the patinas in these elements can also be considered because such protective treatments are not expected in mortars and supporting elements (Viva stone). Additionally, traces of lichens were identified in these sheltered areas.

In summary, the presence of a calcite–oxalate layer as a consequence of the application of organic treatments seems to develop a protective function in ornamental elements of Franca stone (southern façades) because it reduces the high porosity of this litype and preserves the surface, whereas the same patina in a previously altered surface (ornamental elements, in northern and western facades of San Pablo’s church) plays a consolidating role. The appearance of oxalate–apatite layers is possibly the result of biological growth in sheltered and humid ashlar. However, a more detailed study of minerals and especially further work on the analysis of organic constituents would be necessary to confirm this hypothesis.

Conclusions

Ochre-coloured patinas found in the studied churches of Úbeda have different compositions according to their appearance on ornamental elements or ashlar and mortars. All the patinas were composed of calcite and calcium oxalate, but patinas found on supporting elements also contained apatite. These results suggest a double origin for these films. Whereas the application of protective treatments is the more plausible origin for patinas on ornamental elements, a biogenic origin cannot be disregarded for those found on ashlar and mortars.

Furthermore, some considerations about the historical moment when the protective coating was applied can be deduced. Renaissance façades showed homogeneous pati-

nas that adhere perfectly to the underlying calcarenite, indicating that the treatment was applied for protective purposes at the moment of construction. However, in older façades, the surface under the patina is full of cavities and it usually penetrates between the calcarenite grains, suggesting that the patina was applied for the purpose of consolidation when the stone had already been weathered.

These findings are supported by the complementary information provided by the different analytical techniques. Raman and infrared spectroscopy succeed in the identification of calcium oxalate and apatite, while usual petrographic and mineralogical techniques such as OM, XRD and SEM-EDX failed in the unambiguous identification of these compounds due to the thinness of the patinas in Úbeda, the low amount of sample available and the small size of the microcrystals.

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