

Research



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Virtuous colours for Mary. Identification of lapis lazuli, smalt and cochineal in the Andean colonial image of Our Lady of Copacabana (Bolivia)

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The image of Our Lady of Copacabana, a gilded polychrome sculpture carved in maguay wood in 1583, is one of the most important devotions in the Americas. In former research, we have identified the use of gypsum, Armenian bole, cerussite and atacamite in its polychromy. In this study, a red sample taken from the Virgin's tunic and a blue sample extracted from the cloak have been analysed with the aim to identify both pigments and offer

insights into the painting technique. Analysis by micro-Raman spectroscopy complemented with scanning electron microscopy–energy dispersive spectroscopy and high-performance liquid chromatography allowed the identification of carmine lake in the red sample. Analysis by micro-Raman spectroscopy of the surface of the blue sample and its cross section showed the presence of smalt—the blue-glass pigment—over a cerussite layer, bathed by a very thin ultramarine layer—from a probable native origin—following a pictorial tradition that would last even until the eighteenth century. This is the first time that lapis lazuli has been scientifically identified in a Spanish American colonial painted layer.

This article is part of the themed issue ‘Raman spectroscopy in art and archaeology’.

1. Introduction

In 1621, Antonio de Ramos Gavilán, an Augustian friar, published in Lima (Peru) the *Historia del Santuario de Nuestra Señora de Copacabana*, in which he would present the story of the rise of one of the most important devotions in the Americas, that is Our Lady of Copacabana, in the territories of the Viceroyalty of Peru. This gilded polychrome sculpture, carved in maguey wood, had been created by the Andean native Francisco Tito Yupanqui in 1583. Ramos Gavilán explained in his chronicle how Tito Yupanqui would travel from Potosi to La Paz to learn how to make and paint the image, and how he would arrive to the village of Copacabana, on the shores of Lake Titicaca, where the sacred image finally settled down. He also described how this region was identified as the place where a ‘blue stone colorful idol’ which ‘had no more than the figure of a human face without hands and feet’ had been adored [1]. Hence, he would say that the image of the Virgin—‘a precious stone’—would come to substitute the domains of ‘Satan’s court’. In 1641, Father Fernando de Valverde, another Augustinian, published in Lima the bucolic poem *Santuario de Nuestra Señora de Copacabana en el Peru. Poema Sacro* [2]. Using metaphors and a most ornate Gongora’s style, he would exalt the divine and virtuous pigments of the miraculous image, as a symbolic way of counteracting the ancestral idolatric powers. These written sources—together with the testimonies given by the reports of the ‘idolatry visitors and extirpators’ of the region during the seventeenth century that showed how pigments such as azurite, orpiment and vermilion were used in native religious practices—reveal how important the study of the material dimension of this image is.

In former research, we have identified the use of gypsum, Armenian bole, cerussite and atacamite in the sculpture’s polychromy. The stratigraphic structure of the materials in the cross section of the microsample containing atacamite as the green pigment confirmed our hypothesis that the polychromy on the veil had never suffered any kind of intervention [3]. The same can be said about the areas of the image where we took the samples for this research. Although the manipulation of the sacred sculpture has produced, through centuries, some damages on the pictorial layers on the back of the image, we can confirm that our samples belong to an original layer, owing to optical and conservation examination.

In this opportunity, we have focused on the blue and red colours present in the Virgin’s tunic and cloak. Both parts show the use of the ‘esgrafiado’—a technique mainly used in Spain between the fifteenth and eighteenth centuries that involves the use of pigments painted over a golden layer and then scraped to design different decorative patterns (either lines or floral decorations) [4]. The blue and red microsamples were studied by micro-Raman spectroscopy in order to identify the pigments and offer insights into the painting technique. Complementary information was obtained by optical microscopy (OM), scanning electron microscopy–energy dispersive spectroscopy (SEM–EDS) and high-performance liquid chromatography (HPLC). The use of a multianalytical approach to investigate the materials in the polychromy of the sculpture allowed a satisfactory interpretation of the results, particularly regarding the characterization of the mordant of the red lake and in the assessment of the mineral origin of the blue pigment in the cloak.

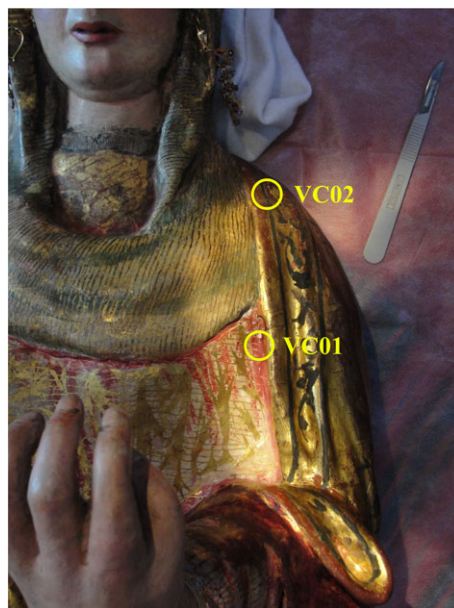


Figure 1. Indication of the location of the red (VC01) and blue (VC02) samples.

2. Material and methods

(a) Samples

Two microsamples (less than $1\text{ mm} \times 1.5\text{ mm}$ area) were extracted with a scalpel from the red area of the tunic decoration (VC01) and the blue area of the flower motif of the cloak (VC02) of the sculpture (figure 1). Polished cross sections were prepared by embedding the fragments in an acrylic transparent resin (Subiton, Laboratories SA, Argentina) according to traditional techniques.

(b) Experimental

Information on the surface of the samples and elemental chemical analyses of the layers of the cross-sections was obtained by using a field environmental scanning electron microscope (FESEM) Zeiss Supra 40 coupled with an energy dispersive X-ray spectrometer INCA X Sight (Oxford Instruments). Semi-quantitative analyses were performed on the surface and selected areas or certain grains of each layer of the samples. OM images were taken with a Leica MZ6 stereomicroscope and a Leica DM 750 microscope equipped with a Cannon Powershot S50 digital camera and a mercury vapour lamp (254 nm). Raman spectroscopy measurements were recorded using a LabRAM HR Raman system (Horiba Jobin Yvon) equipped with two monochromators and a 1024×258 -pixel charge-coupled device detector. A grating of 1800 grooves per mm and a hole of $100\ \mu\text{m}$ resulted in a spectral resolution of 1.5 cm^{-1} (in wavelength). The spectrograph was coupled to an imaging microscope with $10\times$, $50\times$ and $100\times$ objectives. Two different laser excitation sources were used (λ_0): 514.5 nm (Ar^+) and 632.8 nm (He–Ne). Each sample was analysed using the most suitable laser. Several measurements were performed, adjusting the laser power (0.2 – 0.5 mW) in order to ensure that the heating produced by the laser was minimized, and the sample was not altered. Nine Raman spectra were collected from each layer of the sample to obtain representative spectra. Spectra are presented without baseline corrections.

Analytical HPLC–diode array detection (HPLC–DAD) was carried out with a Gilson 506C HPLC system using a Phenomenex Gemini $5\ \mu$ column ($25\text{ cm} \times 4.6\text{ mm}$ internal

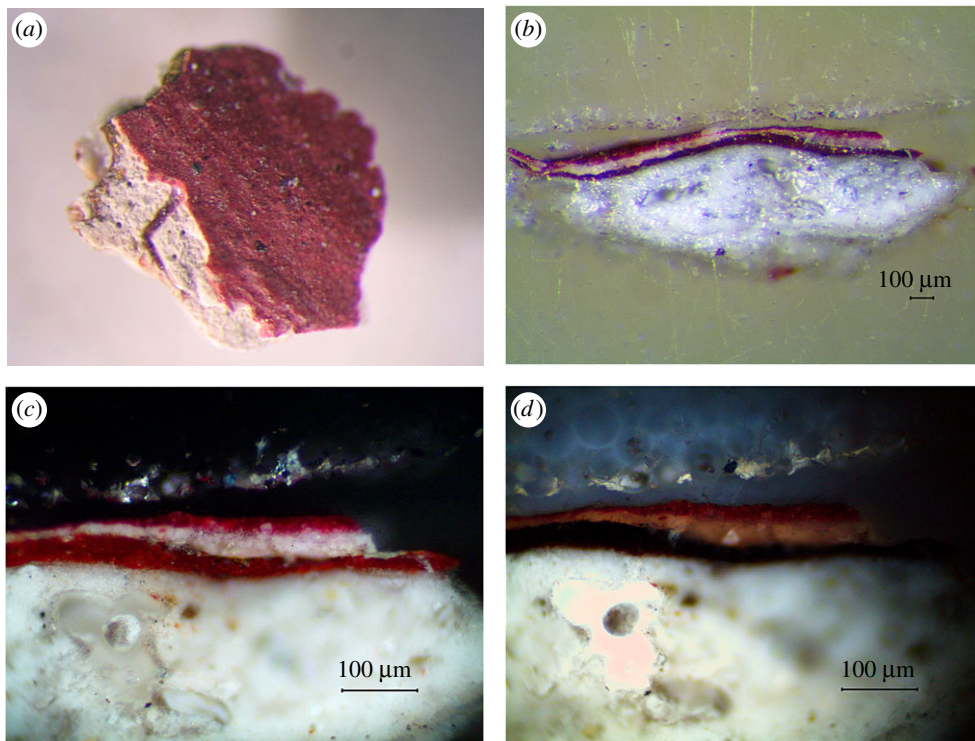


Figure 2. (a) Optical image of the red microsample VC01; (b) cross section of the red sample under polarized light ($10\times$); (c) detail of the cross section under polarized light ($50\times$); (d) detail of the cross section under UV (254 nm) light ($50\times$).

diameter). Gradient elution was performed, using mixtures of MeOH and 1% (v/v) aqueous orthophosphoric acid as solvents. The gradient started with 36% MeOH during 5 min and was raised to 90% MeOH within 10 min, followed by 20 min at this condition. Solvents used in HPLC were filtered through a $0.2\ \mu\text{l}$ filter prior to use. The flow rate was $0.8\ \text{ml}\ \text{min}^{-1}$, and the detection wavelength was 540 nm. The reference sample of carmine lake (Carmine Naccarat 42100) was supplied by Kremer Pigmente.

3. Results and discussion

(a) Red sample

Light microscopy examination of the red microsample (figure 2a) showed a gold layer, a white priming layer and the red pigment layer. More information on the stratigraphic structure of the sample was revealed by OM observation of the cross section under polarized light (figure 2b,c). Observation of a white preparation layer covered by a red layer of bole onto which the gold leaf was applied is characteristic of the *water gilding* technique, traditionally used for wood surfaces [4].

Analysis by micro-Raman spectroscopy of the white priming layer (figure 3a) consisted of a carbonate stretching band at $1055\ \text{cm}^{-1}$ characteristic of cerussite (PbCO_3) [5]. This neutral lead carbonate can be easily distinguished from the basic lead carbonate hydrocerussite ($2\text{PbCO}_3\cdot\text{Pb}(\text{OH})_2$) by the presence of two strong bands at $1049\text{--}1055\ \text{cm}^{-1}$ in the Raman spectrum [6]. Normally, the term lead white referred to the synthetic basic lead carbonate, which was produced from lead and vinegar since early historic times. On the other hand, cerussite is

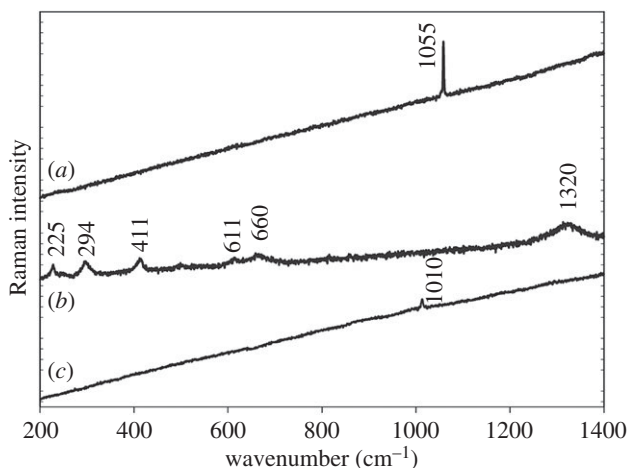


Figure 3. Raman spectra of (a) cerussite layer; (b) red bole layer; and (c) gypsum layer (λ_0 : 514.5 nm).

a natural lead carbonate mineral worldwide distributed, whereas the mineral hydrocerussite is extremely rare and therefore rarely used as a pigment source [7]. In the Andean region, the Jesuit Father Bernabé Cobo reported in 1653 on the occurrence of lead carbonate mines in Juli and Azángaro in the Viceroyalty of Peru [8]. These facts suggest a mineral source for the cerussite identified in the priming layer of the sample. The Raman spectrum of the red bole layer (figure 3b) showed the characteristic bands of haematite (α -Fe₂O₃) at 225, 294, 411, 611 and 1320 cm⁻¹, together with a weak band at 660 cm⁻¹ that has been reported for disordered structures in natural haematite [9,10]. The band at 1010 cm⁻¹ in the Raman spectrum of the preparation layer (figure 3c) is characteristic of gypsum [11]. These results and SEM–EDS analysis of each layer are in accordance with those previously reported for the stratigraphic analysis of a green sample from the veil of the sculpture of the Virgin of Copacabana [3].

The Raman spectrum of the red pigment layer (figure 4) showed bands at 469, 570, 1110, 1256, 1315, 1485 and 1645 cm⁻¹, consistent with those reported for carmine, a red lake pigment prepared from carminic acid, the principal component of the organic dyestuff obtained from the insect *Dactylopius coccus* Costa [12]. Bands at 674, 785, 970 and 1010 cm⁻¹ in the Raman spectrum may be assigned to silicates and aluminosilicates, such as pyroxenes and clays [13–15], presumably present in the substrate used to prepare the lake. SEM–EDS analysis of the surface of the red layer indicated sulfur, aluminium and potassium, characteristic of alum as the mordant, together with silicon, calcium and iron that may be ascribed to clays. According to Kirby *et al.* [16], the composition of red lakes depends on the source and method of extraction of the natural dyestuff as well as on the recipe and method of manufacture of the substrate. In European historical recipes, the most common mordant used in lake preparation was aluminium, but other supporting substrates used were calcium salts, more frequently calcium carbonate. Therefore, the identification of pyroxenes and clays in the red lake layer of sample VC02 is unusual and deserves new studies on the composition of substrates in red lakes used in Andean colonial paintings. The presence of carmine was further confirmed by HPLC–DAD analysis of the acid hydrolysed red microsample. The UV spectrum of the peak in the chromatogram at 14.25 min (figure 5) showed bands at 275, 311, 495 and 531 nm in accordance with those of the carminic acid standard and reported data [17].

Observation of the cross section under UV polarized light showed fluorescence in the priming layer containing cerussite (figure 2d), which could indicate the presence of an organic binder [18]. This result is in accordance with the detection of protein by selective staining with fuchsin in the priming layer of a green microsample taken from the veil of the sculpture [3].

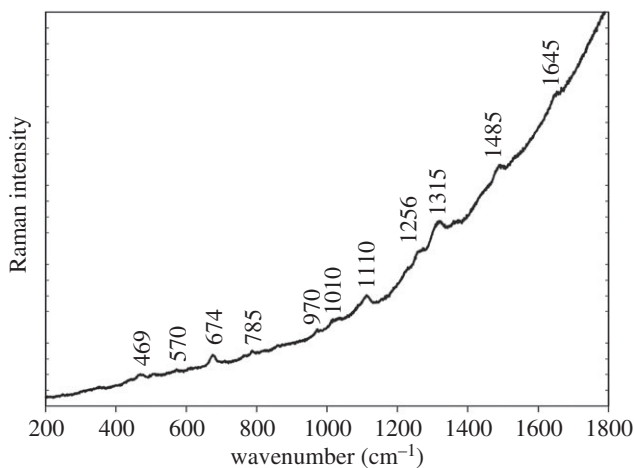


Figure 4. Raman spectrum of cochineal lake layer (λ_0 : 514.5 nm).

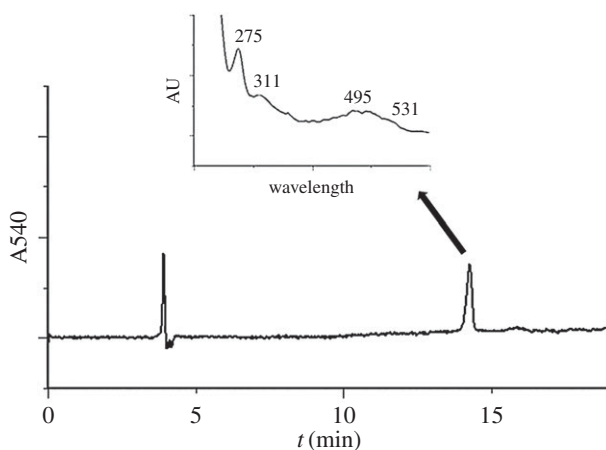


Figure 5. HPLC chromatogram of hydrolysed sample VC01 at 540 nm with UV spectrum of the peak at 14.25 min.

(b) Blue sample

Examination of the blue microsample under the stereomicroscope indicated a dark blue colour. OM observation of the cross section of the sample under polarized light (figure 6a) revealed four different layers: a gold layer (I), a white priming layer (II), a layer containing blue-glass crystals (10–30 μm length) (III) and an outer thin layer with very small blue crystals (IV). The gypsum preparation layer and the red bole layer were detached when the microsample was extracted with the scalpel.

SEM–EDS analysis of the surface of the blue sample indicated the presence of silicon, aluminium, sulfur, sodium, potassium and iron as the major elements, together with minor amounts of calcium (table 1). This elemental composition suggested the presence of ultramarine blue, a complex sulfur-containing sodium aluminium silicate [19]. Natural ultramarine was traditionally obtained from the mineral lapis lazuli, following a complex method of selective extraction of the blue particles. Lapis lazuli is a rock mineral rich in lazurite ($(\text{Na,Ca})_8(\text{Al,SiO}_4)_6(\text{SO}_4,\text{S,Cl})_2$), responsible for its intense blue, that may be accompanied by some natural impurities, such as diopside ($\text{CaMgSi}_2\text{O}_6$), forsterite (Mg_2SiO_4), wollastonite (CaSiO_3), calcite

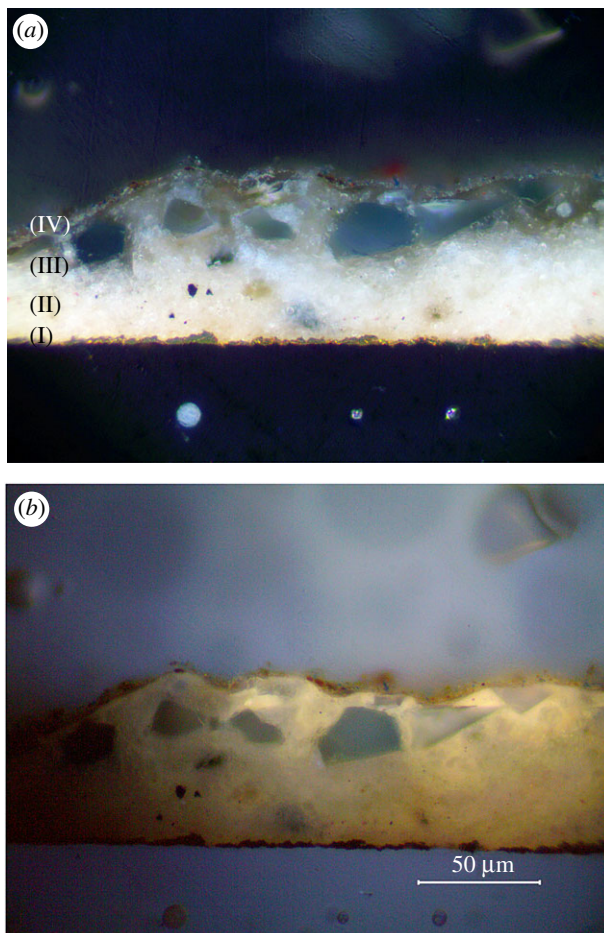


Figure 6. (a) Detail of the cross section of the blue microsample VC02 under polarized light ($50\times$). I: gold layer; II: cerussite layer; III: smalt layer; IV: lapis lazuli layer. (b) Detail of the cross section under UV (254 nm) light ($50\times$).

(CaCO_3) and pyrite (FeS_2) [19,20]. In 1828, an artificial ultramarine was synthesized by Jean-Baptiste Guimet and rapidly adopted by European painters owing to its lower price in comparison with natural ultramarine.

The Raman spectrum (figure 7a) of the outer blue layer of sample VC02 (figure 6, layer IV) showed characteristic bands of lazurite at 545 , 586 , 807 and 1092 cm^{-1} [21], together with minor bands at 626 and 967 cm^{-1} attributed to wollastonite. The symmetric stretching vibration of S_3^- radical anion at 545 cm^{-1} is appreciable in the spectra of natural and artificial ultramarine but the presence of bands of wollastonite is indicative of a natural pigment [20]. This fact together with the presence of iron and magnesium in the SEM-EDS analysis of the surface blue layer of the sample, attributable to pyrite and forsterite or diopside, suggests the use of a natural ultramarine blue in the glazing of sample VC02.

SEM-EDS analysis (table 1) of a blue crystal (figure 8a) in the blue-crystal layer (figure 6, layer III) of sample VC02 revealed the presence of silicon, potassium and cobalt, characteristic of smalt, a potassium glass of blue colour owing to the addition of variable amounts of cobalt. Its composition is variable and it may contain other elements such as barium, calcium, sodium, arsenic, magnesium, iron, nickel, copper and manganese [22]. Arsenic is often present at levels equal to or considerably greater than cobalt, depending on the cobalt ore used and the degree to which it was roasted. Further analysis by SEM-EDS of the blue-crystal layer (figure 8b) indicated

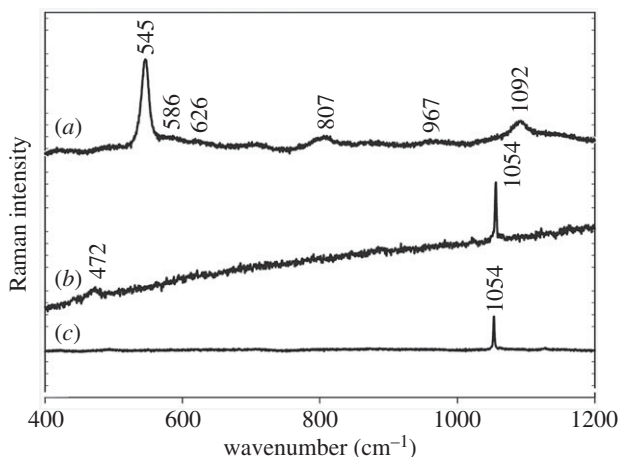


Figure 7. Raman spectra of (a) blue glazing layer (λ_0 : 632.8 nm); (b) smalt layer (λ_0 : 514.5 nm); (c) cerussite layer (λ_0 : 632.8 nm).

Table 1. Results from elemental microanalysis (FESEM–EDS) of blue sample VC02. Values are expressed in atomic %; (a), (b) and (c) refer to the areas shown in the cross section of sample VC02 in figure 8.

element	blue surface layer	blue crystal (a)	blue crystals layer (b)	white priming layer (c)
C		5.5	69.1	66.0
O	71.1	63.3	24.3	28.0
Si	11.4	22.3	4.5	
Al	4.2		0.1	
Ca	0.8	0.6	0.3	
S	1.6			
Pb	0.7		0.6	5.7
Fe	1.8	0.5	0.1	
Cl		0.2	0.1	
Co		0.7		
As		1.1	0.1	
Na	3.9	0.8		
K	2.5	5.1	0.8	
Cu				0.2
Mg	1.4			
Ti	0.5			

the characteristic elements for smalt, together with the presence of lead. The Raman spectrum of the blue layer (figure 7b) showed a broad and weak band centred at 472 cm^{-1} attributed to altered smalt [23] together with a band at 1054 cm^{-1} of cerussite. The Raman spectrum of the priming layer showed the characteristic band of cerussite at 1054 cm^{-1} as described for the red sample (figure 7c).

We have previously identified smalt in 17 paintings done in the Andes region during the colonial period (1610–1780). In most of the paintings, smalt was applied as a sole blue pigment

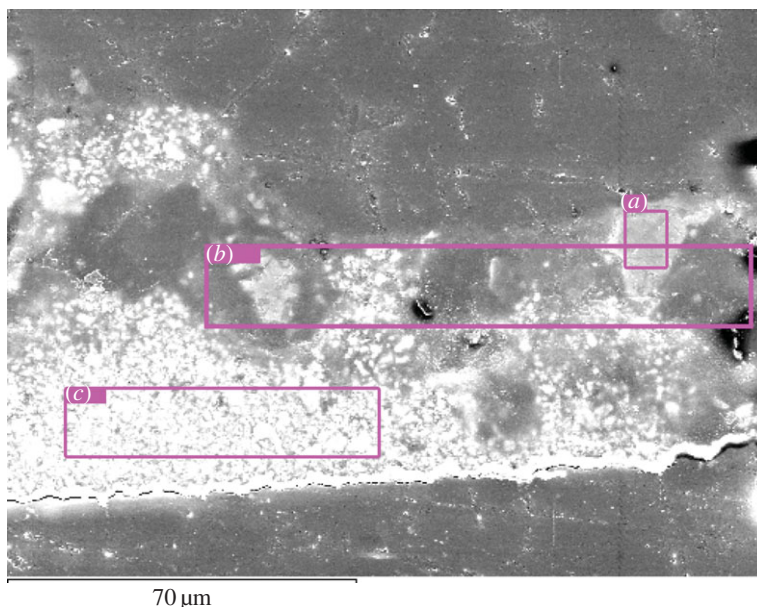


Figure 8. SEM micrograph of the cross section of sample VC02: (a) blue crystal; (b) blue crystals layer; and (c) white priming layer.

layer, but in two of them, it was mixed with azurite (a basic copper carbonate) on the palette or applied with azurite in different layers of paint [24]. Smalt is a synthetic material that was not produced in the Americas before the second half of the nineteenth century [25], so it had to be imported from Europe.

4. Conclusion

In the tunic, the painter applied the ‘esgrafiado’ by using a cochineal lake over the gold, a red colourant obtained from the Viceroyalty of New Spain, processed in Spain, and then commercialized in the Andean markets [26]. Within the red layer, the identification of alum’s use as mordant shows that the Andean painter was aware of the traditional way of treating this colorant, as can be shown in Alexo Piamontes’s *Book of Secrets* when, for making ‘fine grain lake’ he recommended to pour five ounces of rock alum into a pound of fine scarlet ‘tundidura’ [27].

As for the Virgin’s cloak, its decorative patterns show the presence of smalt—the blue-glass pigment whose main element, cobalt, came from Saxony, the only major source of cobalt minerals in Europe until the beginning of the eighteenth century—over a white layer, bathed by a very thin ultramarine layer, following a pictorial tradition that would last even until the eighteenth century. Francisco Pacheco, the famous Spanish painter and treatise writer, suggested that he would not endorse the ‘bathed blues’ unless made with ultramarine, whereas Palomino de Castro would advise that the ultramarine should only be used for glazing or painting over any other blue pigment [27]. This is the technique that can be seen in our sample. In this case, it appears that the ultramarine was applied with a small brush over in a final step.

As for the pigment itself, the elemental composition of the ultramarine layer obtained by SEM-EDS and the identification of wollastonite in the Raman spectrum were helpful in the assignment of the mineral nature of the pigment, which is also in accordance with the fact that the polychromy was manufactured in 1583. Lapis lazuli was a very expensive pigment obtained from lazurite, a mineral whose best ores could be found in Afghanistan [19]. Early-modern Spanish art treatises warned about the scarceness of this rich pigment, whereas commercial documents evidenced

that its trading started diminishing since the fifteenth century within the European milieu [28]. Francisco Pacheco would say that the lapis lazuli ‘was neither used in Spain, nor did the painters have enough to use’, although there are some testimonies of trading practices through the city of Venice [29]. In our sample, the possibility of an Afghan origin of the ultramarine blue is remote, owing to these facts, and makes us consider that it could have a native origin. In fact, by the beginning of the eighteenth century, some lapis lazuli ores were registered in the Chilean Andes [30] and in the middle of the nineteenth century a lapis lazuli deposit was discovered in Chile [31]. Therefore, it should be no surprise that the painter used Andean lapis lazuli, as he also used other native pigments, such as the green atacamite in the Virgin’s veil [3].

It should be stressed that this is the first time that lapis lazuli has been scientifically identified in a Spanish American colonial painted layer.

Authors’ contributions. E.P.T.: OM of microsamples and their cross sections, acquisition and interpretation of SEM–EDS data, analysis and interpretation of Raman data, drafting the article. F.M.: preparation of cross sections, acquisition and interpretation of Raman data. V.P.C.: hydrolysis of the red sample, acquisition, analysis and interpretation of HPLC data of carminic acid. C.R.L.: extraction of microsamples from the polychrome sculpture, discussion and interpretation of results. G.S.: design of the study, drafting the article, discussion and interpretation of results in art history context. M.S.M.: design of the study, drafting the article, discussion and interpretation of the analytical data. All authors gave final approval for publication.

Competing interests. The authors declare that they have no competing interests.

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