



Unveiling the mural painting art of Almada Negreiros at the Maritime Stations of Alcântara (Lisbon): diagnosis research of paint layers as a guide for its future conservation

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Abstract: This paper reports the diagnostic research of deteriorated paint layers from three mural panels made by Almada Negreiros found in the Alcântara Maritime Station in Lisbon. The aim was to understand the main decay phenomena to aid future conservation works. The methodology comprised in-situ analyses by technical photography in Vis, Vis-RaK and UVF, p-OM and h-EDXRF; micro sampling; OM, SEM-EDS, μ -XRD, μ -Raman, μ -FT-IR and Py-GC/MS. Preliminary results show that all the paint layers analyzed are affected by salts (alkali sulphates) that over time have caused flaking, lack of cohesion, erosion, and lacunae. The light greenish/greenish bluish paint layers in all three panels are the most affected. No organic binders were identified, only the presence of vinyl polymer in glossy paint surfaces.

Keywords: Almada Negreiros, mural paintings, diagnostic research, SEM-EDS, μ -XRD, μ -FT-IR, Py-GC/MS

Presentación del arte de la pintura mural de Almada Negreiros en las Estaciones Marítimas de Alcântara (Lisboa): investigación diagnóstica de capas de pintura como guía para su futura conservación

Resumen: Este artículo informa de la investigación de diagnóstico de capas de pintura deterioradas de tres paneles murales realizados por Almada Negreiros en la estación marítima de Alcântara en Lisboa. El objetivo era comprender los principales fenómenos de descomposición para ayudar a futuros trabajos de conservación. La metodología comprendió análisis in situ mediante fotografía técnica en Vis, Vis-RaK y UVF, p-OM y h-EDXRF; micro muestreo; OM, SEM-EDS, μ -XRD, μ -Raman, μ -FT-IR y Py-GC/MS. Los primeros resultados muestran que todas las capas de pintura analizadas están afectadas por sales (sulfatos) que a lo largo del tiempo han provocado escamas, falta de cohesión, erosión y lagunas. Las capas de pintura de color verde claro/verde claro azulado en los tres paneles son las más logradas. No se encontraron aglutinantes orgánicos, solo la presencia de polímero de vinilo en superficies de pintura brillante.

Palabras clave: Almada Negreiros, pinturas murales, diagnóstico, SEM-EDS, μ -XRD, μ -FT-IR, Py-GC/MS

Desvendar a arte da pintura mural de Almada Negreiros nas estações marítimas de Alcântara (Lisboa): Diagnóstico de camadas cromáticas como guia para sua conservação futura

Resumo: Este artigo relata uma pesquisa de diagnóstico de camadas cromáticas deterioradas em três pinturas murais pintadas por Almada na Estação Marítima de Alcântara, em Lisboa. O objetivo foi o entendimento dos principais fenómenos de deterioração como apoio a futuros trabalhos de conservação. A configuração analítica foi composta por afotografia técnica no Vis, Vis-Ras e UVF, p-OM e h-EDXRF; micro-amostragem; OM, SEM-EDS, μ -XRD, μ -Raman, FT-IR e Py-GC/MS. Os primeiros resultados mostram que todas as camadas cromáticas analisadas estão afectadas por sais (sulfatos) que ao longo do tempo tem causado perdas de adesão e de coesão, erosão e lacunas. As camadas cromáticas verdes-claras/verde-claras azuladas presente em todos os painéis são as mais atingidas. Aglutinantes não foram identificados, mas somente a presença de polímeros vinílicos nas superfícies pintadas com brilho.

Palavras-chave: Almada Negreiros, pinturas murais, diagnóstico, SEM-EDS, μ -XRD, μ -FT-IR, Py-GC/MS

Introduction

Almada Negreiros was born on the 7th of April 1893 in São Tomé e Príncipe, Africa. As a key artist from the Portuguese Modern art, he would be recognized as painter, as sculptor and as writer (França 2004, 2014). His versatile background made him one of the most famous artists of the 20th century. He died in Lisbon on the 15th of June 1970 and left behind a rich opus (França 2004). In the period between 1943 and 1949, he decorated the walls of the two Maritime Stations in Lisbon with remarkable murals, eight of them in Alcântara and six in Rocha de Conde de Óbidos (Lobo 2014; Monteiro 2012). The two Maritime Stations stretch for 1.5 km along the Tejo riverside and represent the main port in Portugal, connecting the city of Lisbon with the Atlantic Ocean. These stations are in Alcântara, close to one of the most important traffic arteriae of Lisbon (highways N6 and E1), and to railway and subway stations (Alcântara and Cais do Sodré, respectively).

The diagnostic research undertaken focuses on a collection of three murals painted between 1943 and 1945 at the main hall of Alcântara Maritime Station. In total, eight mural panels with 7.20 x 3.80 meters are presented on the east and west walls: two triptychs and two individual paintings. This research is constrained to the mural panels, referred to as P2, P3 and P6, that depict scenes of everyday life and the mythological history of *nau catrineta* [Figure 1].

Three research questions were posed:

1. Which paint layers are more deteriorated and is this deterioration linked to a specific pigment?
2. Which are the main decay phenomena and what are their dynamics?

3. What is the role of the painting techniques when it comes to stability and deterioration of the pigments?

This paper reports the first results from the analytical campaign held *in situ* and in a laboratory context between May and September 2020. The survey was made on the framework of a wider project entitled *Unveiling the mural art of Almada Negreiros* (PTDC/ART-HIS/1370/2020) that aims to study the painting techniques and pigments used by the artist and its implications in the deterioration processes encountered by Conservators-Restorers in the past 30 years.

Experimental

Diagnostic survey included *in situ* non-invasive analysis which were complemented by laboratory micro-analytical analysis of micro-samples collected from deteriorated and stable paint layers, as well as salt efflorescence.

— *Photo Documentation and Technical Photography in situ (TP)*

Photographs were acquired in visible (Vis), visible raking (Vis-RAK) and ultraviolet light (UVF), and taken with a Nikon D3200 camera, with 24Mpx, and objective Nikkor 18-55mm f:3.5-5.6 GII. They were obtained under the angle of 15-20° from the painting surface, from three different sides. UV induced fluorescence in visible (UVF) photography was used to discover previous interventions or presence of organic binders. UVF photograph was taken with Nikon D3200 camera and Labino® MPXL UV



Figure 1.- Murals P2, P3 and P6 with the location of the deteriorated paint layers analyzed in 2020 (white squares) (photos by Guta Carvalho 2020 © all rights reserved).

PS135 light (35W PS135 UV Midlight 230V) with UV filter included (310-400mm and a peak at 365nm), a midlight distribution angle of 20° and a start-up time full power after 5-15sec.

— *Portable optical microscopy (p-OM)*

Two portable microscopes Dinolite PRO AM13T-FVW and DinoLite Premier AD3713TB were used with 20 and 434x magnifications to record details of the deterioration features and pigment particles.

— *Handled X-ray Fluorescence (h-EDXRF)*

Handled X-ray fluorescence allowed a preliminary in situ and non-invasive identification of the elemental composition of the painting materials. A handheld X-ray fluorescence analyzer Bruker Tracer III SD was used, equipped with an X-ray tube with rhodium target and a silicon drift detector. A total of 83 paint areas covering the entire palette's color range were analyzed. Spectra were recorded using a voltage and a current intensity of 40 kV and 30 μ A, respectively, during a 30 s real-time count. The instrument was controlled using the S1PXRF software (Bruker™). The spectra were later processed using the Artax (Bruker™) software to obtain semi-quantitative data.

— *Optical microscopy (OM)*

First step in laboratory analysis was optical microscopic documentation of micro fragments, collected from different paint layers. Cross sections were embedded in epoxy fix resin and studied using a Leica DM2500M reflected light optical microscope in dark field illumination mode. Observations were carried out under 100x, 200x and 500x magnification. Photographs of cross sections were obtained with a Leica MC 170HD digital camera Leica software. UV mode was used to spot the presence of organic materials. A Leica M205C stereomicroscope was also used to obtain images of both powder samples and cross sections in magnifications 7.8x - 160x. The stereomicroscope used is equipped with a Leica DFC295 digital camera and external illumination.

— *micro-X-ray Diffraction (μ -XRD)*

A Bruker D8 Discover® diffractometer using Cu K α radiation was employed to identify the main mineralogical phases in the salt efflorescence. The samples were mounted as powder on a zero-background specimen holder. An angular range of 3–75° 2 θ , step size of 0.05 °/s and step time of 2 s was used for collecting the diffractograms. Identification of crystalline phases was performed using the DIFFRAC.SUITE EVA® software and the ICDD PDF-2 database.

— *Scanning Electron Microscopy – Energy Dispersive Spectroscopy (SEM-EDS)*

Scanning electron microscope (SEM) coupled with an energy dispersive spectrometer (EDS) enabled the obtention of high resolution images and elemental analysis of the micro samples. Backscattering mode (BSE) was used to document micro-morphology of the paint layers and salt efflorescence. This analysis was carried out with a variable pressure SEM HITACHI S-3700N operator with an accelerating voltage of 20 kV and at 40 Pa. SEM was coupled with Bruker XFlash 5010 Silicon Drift Detector (SDD) with resolution of 129 eV at Mn K α .

— *micro – Fourier Transform Infrared Spectroscopy (μ -FT-IR)*

For the detection of organic compounds, Fourier transformed infrared spectroscopy was carried out. Samples were collected from the panels by gently scratching the paint surface. Powder samples were analyzed using a Bruker Tensor 27 Mid-IR (MIR) spectrometer, coupled with HYPERION 3000 microscope, and controlled by OPUS 7.2 software with corresponding OPUS library (copyright© 2012 Bruker Optics and Microanalysis GmbH, Berlin, Germany). A MCT (Mercury Cadmium Telluride) detector was used, cooled with liquid nitrogen. Analyses were done in transmission mode using a 15x objective and an EX'Press 1.6 mm diamond compression microcell, STJ-0169. Spectra were plotted in region of 4000-600 cm^{-1} , with 64 scans and 4 cm^{-1} resolution.

— *micro – Raman Spectroscopy*

Powder samples of green pigment layers were analyzed using a HORIBA XPlora Raman spectrometer, equipped with a 785 nm red diode laser, and coupled with an Olympus™ microscope. The system uses a thermo-electrically cooled charge-coupled device detector (CCD). The calibration of the instrument was performed with the Raman band of a silicon crystal at 520 cm^{-1} . Raman spectra were acquired in the 100-2000 cm^{-1} region. The measuring time, laser power, and number of accumulations were set to obtain a good signal-to-noise ratio while avoiding thermal damage. The 50x objective was used for all the samples. The instrument itself was controlled using the LabSpec software. The collected Raman spectra were further processed in GRAMS (ThermoFisher Scientific™).

— *Pyrolysis Gas Chromatography coupled with Mass Spectrometry (Py-GC/MS)*

For identification of organic components, pyrolysis-gas chromatography coupled with mass spectrometry was

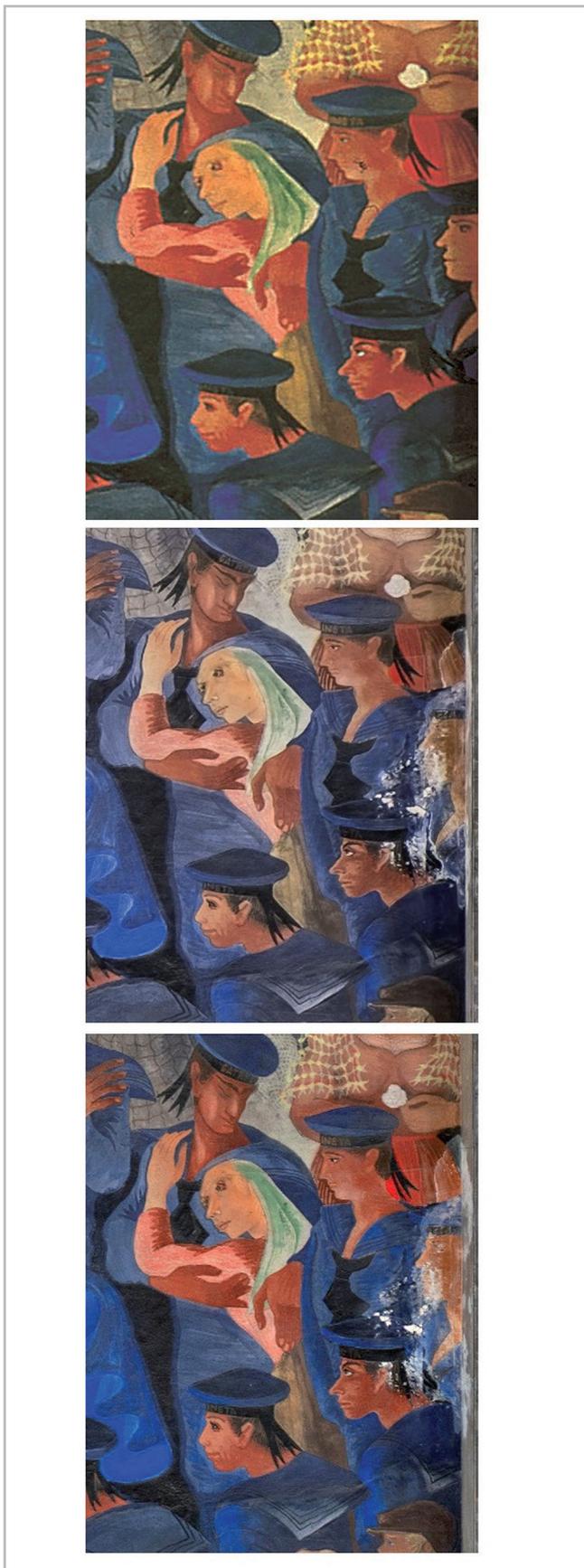


Figure 2.- Three images of a detail of P3. From top to bottom, APL Archival (late 1990s), CML-José Vicente (July 2013), Guta Carvalho (June 2020). Salt veils and efflorescence's are visible on the right border of the panel (photo credits © all rights reserved).

selected. A Frontier Lab PY-3030D double-shot pyrolyser coupled to a Shimadzu GC2010 gas chromatographer and a Shimadzu GCMS-QP2010 Plus mass spectrometer were used. Pyrolysis interface was maintained at a temperature of 280 °C. A capillary column Phenomenex Zebron-ZB-5HT was used for separation, with helium as carrier gas, adjusted to a flow rate of 1.5 ml min⁻¹. The mass spectrometer was programmed to acquire data between 40 and 1090 m/z. The sample (<200 µg) was previously derivatized with 3 µL of tetramethylammonium hydroxide (2.5% in methanol, v/v) in a 50-µL Eco-cup capsule and pyrolysed at 500 °C. Compound identification was performed using AMDIS software integrated with NIST-Wiley database.

Results and discussion

The main deterioration features noticed in the three mural panels by visible and raking light were flaking lack of cohesion, erosion, and lacunae of paint layers. Particularly affected by severe flaking is a light greenish/greenish blue paint layer identified in the Angel's garment of P2 and in the other two panels in the background and in some decorative motifs [Figure 1 to Figure 3].

Salt veils, salt concretions and salt efflorescence are clearly seen with the naked eye in P3 and P6 [Figure 2 and Figure 3]. The decay that the salts have induced over the past twenty years in P3 is shown in Figure 2. From detailed observation of the three sets of photographs from the late 1990s, 2013 and 2020 it is possible to conclude that this phenomenon is still ongoing. The occurrence of salts could have been trigger by water infiltration and condensation due to old and damaged installations and leaking pipes (Hanafi *et al.* 2018; Young 2008). It must be noted that within the main hall, the mural panels span over two stories high, which positions the floor joint in the middle of the paintings as illustrated in Figure 4. The most deteriorated areas of the mural panels are aligned with this junction favoring the occurrence of thermal bridges (Jedidi & Benjeddou 2018; Zedan *et al.* 2016). A thermal bridge can be explained as the movement of heat across an object that is more conductive than the surrounding materials leading to heat loss. Thermal bridges in buildings, besides having an impact on thermal resistance, can cause water condensation within the architectural elements. This may be one of the reasons for the current state of conservation of the paint layers in panels P3 and P6.

In terms of deterioration, P6 presents the most complex case due to the extent and degree of the paint layers affected [Figure 1]. The main decay phenomena in this panel follows the pattern of the two previous ones: salts induced stress and subsequent flaking, lack of cohesion, erosion and lacunae of paint layers as shown in Figure 3 in Vis e Vis-Rak.

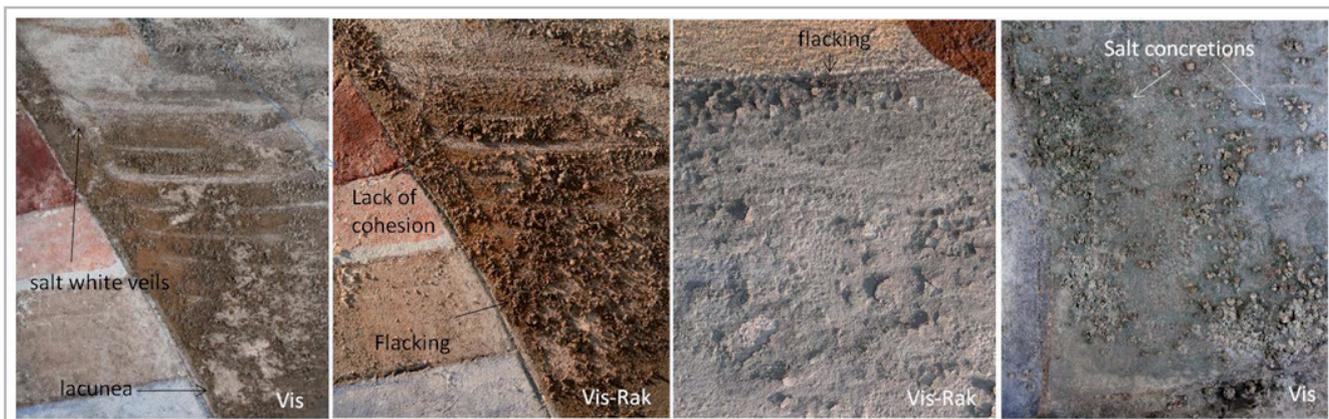


Figure 3.-Details in Vis and Vis-Rak of deterioration features in P6: flaking, lack of cohesion, lacunae, salt veils, concretions, and efflorescence.

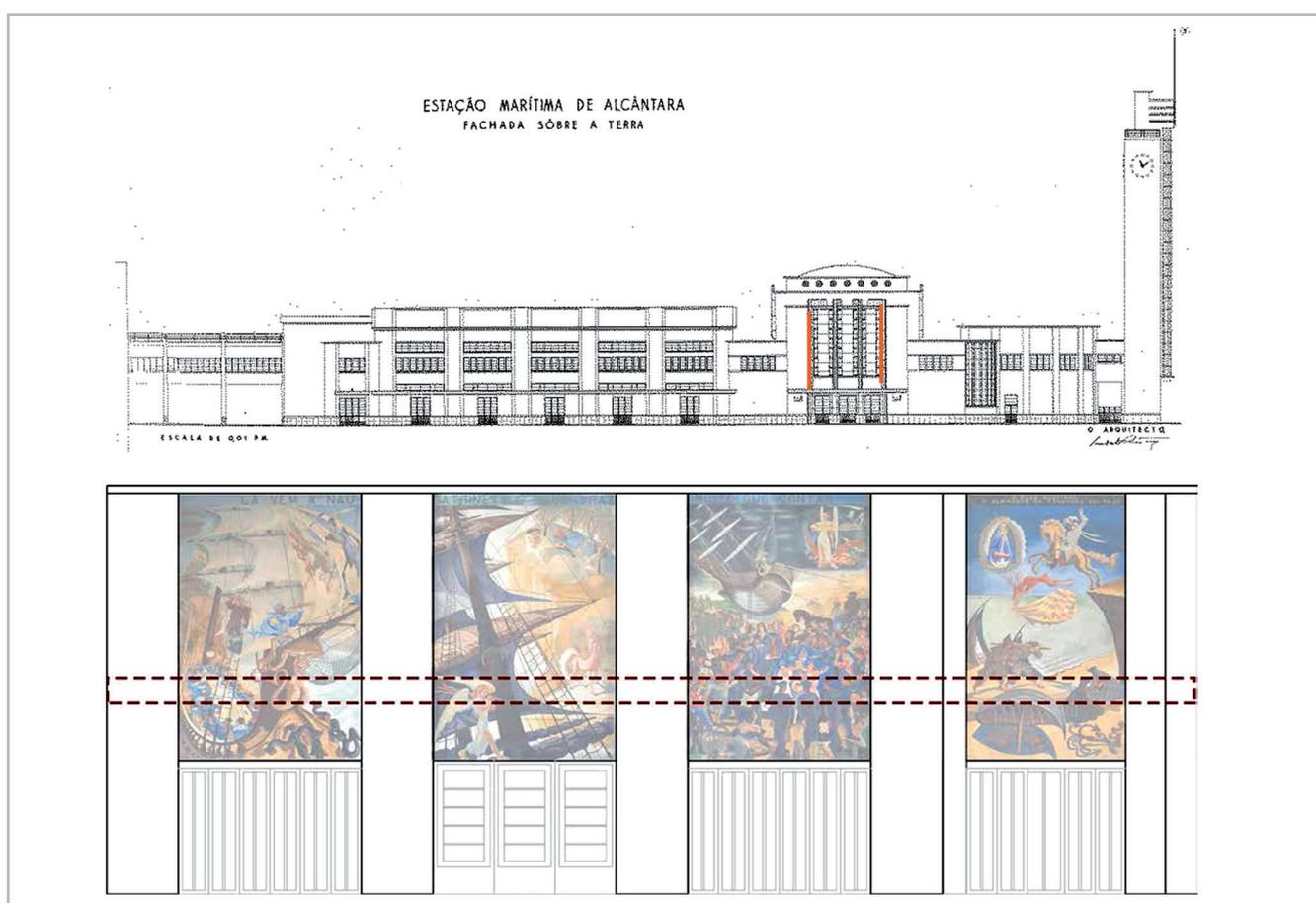


Figure 4.- On top, cross section of Alcântara station with marked positions of the murals. Source of the section (Monteiro 2012); on the bottom, scheme of the west wall with the display of the murals and indicated position of thermal bridge that corresponds with construction joint between two floors. Drawing by Mila Cvetković 2020.

— *Identification and characterization of salts*

Five powdered samples of salt efflorescence collected from P3 and P6 were analyzed by μ -XRD, for mineralogical phase identification [Table 1, Figure 5]. The results obtained revealed that sulphates were the main phases found in all five samples: thenardite (Na_2SO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), syngenite ($\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$), apthitalite ($\text{K}_3\text{Na}(\text{SO}_4)_2$)

and anhydrite (CaSO_4) [Table1]. Calcite (CaCO_3) and barite (BaSO_4) were also found in most samples [Table1]. Gypsum was also identified in the eight deteriorated paint layers analyzed by μ -FT-IR showing that this salt is widespread in the paint surfaces [Table 2].

Alkaline and alkaline earth sulfates are among the most common degradation agents in wall paintings (Salvadori et

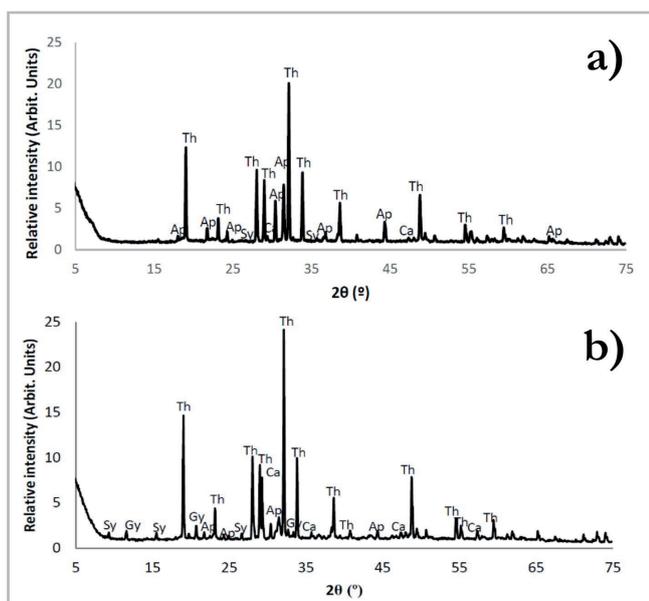


Figure 5.- XRD diffractograms of samples P3B_5 a) and P3B_6 b) showing identified mineralogical phases (Ca – Calcite, Th – Thenardite, Sy – Syngenite, Ap – Aphthitalite, Gy – Gypsum).

al. 2003). Their formation is generally associated to the dry and wet acid deposition of SO_x and the infiltration of water (Madariaga *et al.* 2014). In fact, the presence of water in buildings, even at a micrometric level, causes the leaching and migration of dissolved ions which are essential for the formation of efflorescence crystals (Madariaga *et al.* 2014). The composition of the building materials used is also an important factor in the type of salt efflorescence formed.

The formation of thenardite and aphthitalite, for example, can be associated to underground water and air pollution (El-Gohary 2011), or connected to the use of building materials such as cement which have significant amounts of alkalis in their composition (Pavía 2008). Moreover, previous researches have shown that syngenite can develop from Portland cement (Charola & Bläuer 2015). In fact, in general, the period between 19th and 20th century can be perceived as a transitional period between the use of lime-based binders and the general use of the modern Portland cement. This is also valid for Portugal (Figueiredo *et al.* 2019). As such, although there are no records of the use of Portland cement during the

construction of the Maritime Stations, this possibility cannot be excluded.

Sodium sulphates, in general, can form efflorescence and sub-efflorescence causing, over time, the flaking of paint layers (El-Gohary 2011, 2008). Aphthitalite, with its complex crystallization behavior, can also be extremely damaging to building materials (Pavía 2008; Marszałek *et al.* 2020).

Gypsum is considered the most common salt efflorescence found in carbonated wall paintings (Salvadori *et al.* 2003). This calcium sulfate can also be found in construction materials such as cement (Azimi & Papanagelakis 2011). The transformation of gypsum to anhydrite generally occurs at elevated temperatures (Azimi & Papanagelakis 2011). However, the presence of sulfuric acid, as well as NaCl, promotes and accelerates this transformation even at lower temperatures (Azimi & Papanagelakis 2011). In this case, environmental factors can explain the presence of both sulfuric acid and sodium chloride, given that the first is the main constituent of acid rain, and the second is the primary component of sea spray.

Calcite detected in the salt efflorescence collected is most likely the result of minor amount of Ca-based paint layers and their underlying support being accidentally sampled. This is consistent with the lack of paint layer cohesion previously mentioned. On the other hand, the presence of barium sulphate, identified in the samples P3B_5 and P6A_15, can likely be associated to the pigments themselves, as this compound was frequently added as a filler by pigment manufacturers (Lähteenmäki 2009; Driel *et al.* 2016).

— *Characterisation of painting materials*

• Pigment identification

Table 2 reports the summary results of h-EDXRF obtained in eleven deteriorated paint layers and SEM-EDS and μ-FT-IR analysis of the corresponding micro-samples.

The analytical setup reveals the presence of Fe-based pigments in samples P6A_17, P6A_20, and P6C_2. The high

Samples	Mineralogical phases identified						
	Thenardite	Gypsum	Syngenite	Aphthitalite	Anhydrite	Calcite	Barite
P3B_5	◊	◊	◊	◊		◊	◊
P3B_6	◊		◊	◊		◊	
P6A_2	◊	◊	◊		◊		
P6A_15	◊	◊	◊			◊	◊
P6A_18	◊	◊				◊	

Table 1.- Main mineralogical phases identified by μ-XRD analysis in five salt efflorescence samples collected from paint layers of P3 and P6.

Fe content found and the variable input of terrigenous elements such as Al, K and Si in h-EDXRF strongly suggest that Almada Negreiros used ochre pigments to build up the warm hues. Characteristic bands of aluminosilicates – at 3696, 3668, 3652, 3619, 1114, 1036, 1011, 914, 798, 781 cm^{-1} – were also identified by μ -FT-IR in sample P6C_2.

Ochres are natural earth colorants and have been used since pre-historic times as pigments. Their color, ranging from yellow to red, comes mainly from iron oxides and hydroxides such as hematite ($\alpha\text{-Fe}_2\text{O}_3$) and goethite ($\text{FeO}(\text{OH})$) (Gil *et al.* 2007). Manganese oxides are usually associated to brown shades and justified the Mn content found in P6C_2 [Table 2].

Almada Negreiros used ochres alone and, occasionally, in a mixture with small amounts of yellow/orange and red Cd-based pigments as detected by h-EDXRF [Table 2] in samples P6A_20 and in P6C_2 by SEM-EDS point analysis [Table 2, Figure 7a]. Cadmium pigments, unlike ochres, are synthetic and started to be produced and commercialized in a wide scale in the mid-1840s. Cadmium yellow is essentially cadmium sulfide (CdS) but as Fedler & Bayard (1986) states, over the years several chemical and physical modifications have been developed to produce shades ranging from very light lemon yellow to light orange. An enrichment in Se is expected from deep oranges to reds [$\text{Cd}(\text{S},\text{Se})$]. It must also be noted that different red, orange, or yellow hues can be obtained by partial substitution of Cd with Zn, or S with Se, within the crystal lattice of Cd pigments (Fedler&Bayard 1986).

It is known that Almada Negreiros applied both kinds of Cd-based pigments in another mural painting set in Lisbon (DN building), and they have also been found in power form in his studio.

These findings are rare because in the past the use of Cd pigments in mural paintings, especially with fresco technique, was controversial. The stability of the pigments relied on their chemical composition and manufacture process. According to Feller (1986), cadmium yellow light hues were not advised since they could contain cadmium oxalate or carbonate, or even free sulfur, which would trigger reactions in the alkaline medium leading to a fast fading of the color. Maybe this can be the reason why Almada Negreiros limited the use of these pigments in these murals, but further research is needed to reach firm conclusions. However, it is important to note that in the two Cd-containing paint layers analyzed by OM there is no evidence of pigment discoloration [Figure 6a]

In turn, h-EDXRF and SEM-EDS analyses of samples P3B_2 and P6A_7 collected from blue paint layers revealed the presence of Na, Al, Si, S and Cl indicating the use of ultramarine blue pigment, a complex sulfur-containing sodium aluminum silicate of formula $(\text{Na},\text{Ca})_8(\text{AlSiO}_4)_6(\text{SO}_4,\text{S},\text{Cl})_2$ (Plaster1996). The synthetic deep opaque blue particles can be seen by OM reflected

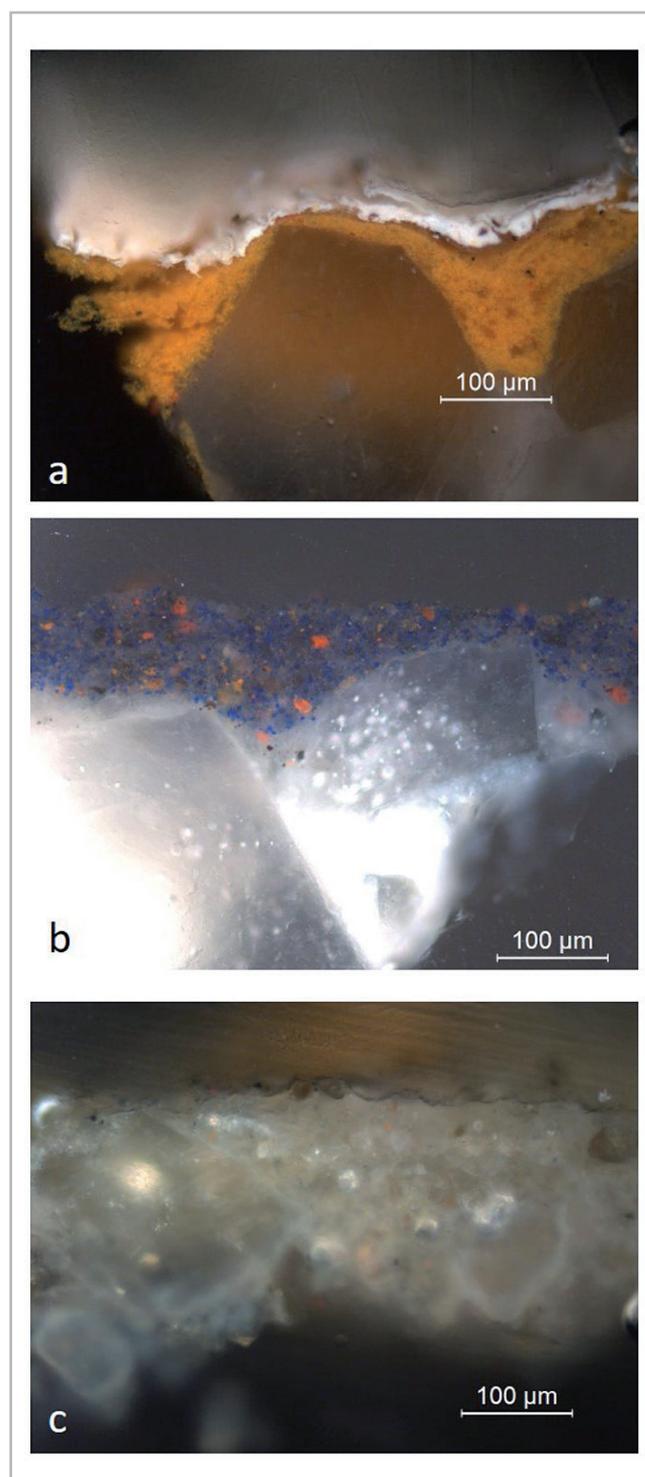


Figure 6.- OM-Vis of paint layers cross sections P6C_2(a), P3B_2(b) and P6C_5 at 200x magnification.

light as granules of uniform rounded shape and of size $\leq 4 \mu\text{m}$ [Table 2, Figure 6b].

The identification of iron and phosphorous in the darker blue shade of sample P3B_2 suggests a combined use of ultramarine with ochres and bone black. Bone black has also been identified in an inner black paint layer in sample P6A_17 by μ -FT-IR, due to the characteristic phosphate group band at 2013 cm^{-1} .

In what concerns the greens, h-EDXRF and SEM-EDS analyses of samples P2_4, P6A_3, P6A_23, and P6C_5 collected from the light greenish and greenish blue paint layers severely affected by flaking revealed the presence of Fe, Al, K, Mg, Na and Si, which might imply the use of green earths [Table 2, Figure6c]. Green earths are natural pigments containing as chromophores the clay minerals glauconite (K, Na) $(\text{Fe}^{3+}, \text{Al}, \text{Mg})_2(\text{Si}, \text{Al})_4\text{O}_{10}(\text{OH})_2$ and celadonite $\text{K}(\text{Mg}, \text{Fe}_2^+) (\text{Fe}^{3+}, \text{Al})[\text{Si}_4\text{O}_{10}](\text{OH})_2$ (Eastaugh *et al.* 2004).

Micro-samples P2_4 and P6A_3 also display high Ti content within the paint layers showing the use of TiO_2 as a white pigment instead of calcium carbonate as it was expected in a fresco technique.

The identity of the chromophore remains unclear for samples P6A_14 and P6A_16 [Figure 7] collected from the bright and darker greens paint layers of the fishing boat in P6 [Figure 1]. Elemental analysis revealed an enrichment in Fe, Al, K, Cu, As, Sr, Mg, Si, Ca, Na, and Cl, which could indicate different kinds of pigments combined with salts. Micro-FT-IR on P6A_14 and P6A_16 suggests the presence of emerald green pigment, a copper(II) acetoarsenite of formula $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$ based on the characteristic bands at 1556 and 1455cm^{-1} (Cortea *et al.* 2020; Fiedler&Bayeard 1997), but this assignment is still uncertain due to the absence of As in h-EDXRF [Table 2]. On the other hand, the Raman spectra of both green micro-samples reveal the following bands at 154, 196, 221, 314, 353, 381, 449, 472, 497, 537, 618, 636, 670, 754, 883, 1025, 1077, 1150, 1225, 1303, 1353, 1447, 1471, 1513, 1552 and 1590cm^{-1} , which could be tentatively assigned as the synthetic organic pigment PG 8 (Coccatto *et al.* 2016).

• Painting technique

The painting technique was identified as fresco in sample cross-sections P3B_2, P6A_17, P6A_20, and P6C_2 collected from red, brownish, and blue paint layers. Painting at fresco implies the use of a fresh mortar to laid



Figure 7.- OM-Vis of sample P6A_16 at 100x magnification.

down the colors. Stratigraphically this technical feature can be ascertained by SEM-EDS in the interface mortar-paint layer by the absence versus the presence of a Ca-crust layer of carbonation. Its presence would suggest that the mortar surface was already dried when the painter started to paint. This was not the case of the paint layers analyzed. The absence of a Ca-rich crust is confirmed in the interface mortar-paint layer in SEM-EDS BSE images as seen in Fig.8. Furthermore, in most paint layers analyzed the pigment particles are embedded in a Ca matrix that can range up to $104\ \mu\text{m}$ thickness – a strong indication that the pigments were not mixed only with water (as in the case of buon fresco) but with a thicker solution of calcium hydroxide (e.g., lime milk) before being laid down on the fresh mortar (lime fresco technique).

Samples P2_4, P6A_3, P6A_23, P6C_5 P6A_14 and P6A_16 collected from the green paint layers present the most disruptive stratigraphy with loose material particles hindering the undisputed identification of the painting techniques used in their production.

Further examination was done using μ -FT-IR and Py-GC/MS on the samples that UVF indicated could have organic materials. Micro-FT-IR analyses of the samples P6A_23 and P6C_5 from the greenish paint layers with a glossy appearance showed presence of vinyl polymer identified by characteristic bands at 2942, 2914 and 1376cm^{-1} .

Many acrylic and vinyl compounds were (and still are) used in the art and art conservation field as binding media, paint additives, coatings and consolidants (Schossler *et al.* 2013). In the case of the mural paintings in the Maritime station of Alcântara, it is known that they were restored over the years. The unpublished intervention reports from Conservation Institute José de Figueiredo (IJF) and former conservators-restorers mention adhesion and consolidation treatments with Plextol (methyl methacrylate and ethyl acrylate copolymer) and Calaton (soluble nylon) but it was not possible to confirm the presence of these products. So far only vinyl polymer was found as stated above. The origin of the vinyl polymer used apparently as an adhesive is still uncertain, but its presence was assigned in most of the greenish paint layers with severe flaking.

No biomarkers suggesting the use of organic binders were detected on eight samples analyzed by Py-GC/MS collected from similar green and blue paint layers in P2 and in P6. Some aromatic compounds with fused benzene rings such as indene or naphthalene were identified, but they may originate from the layer of soot covering the paint layer (Song & Peng 2010). Oxalates identified by μ -FT-IR analyses [Table 2], likely calcium oxalates given the Ca-rich matrix, may originate from lichen or algal activity (Peris-Vicente *et al.* 2009), but since no such activity was found on the analyzed samples other possibilities should be considered in further analyses as well, such as the reaction of calcium monoxide from the air with calcium carbonate from the painting surface (Peris-Vicente *et al.* 2009).

Location	Color	h-EDXRF (major elements for pigments identification in bold)	Micro- sampling Ref.	SEM-EDS (at.%)	μ-FT-IR
P2: angel's dress	Light greenish blue	Al , Ba, Ca, Cl, Cu, Fe , K, Mn, Ni, Pb, S, Si, Sr, Zn	P2_4	Na (2.90), Mg (9.52), Al (9.43), Si (23.59), S (14.60), Cl (1.15), K (1.85), Ca (27.14), Ti (3.20), Fe (6.63)	Calcite, Gypsum, Barite, Oxalates
P3: sailor's beret	Blue	Al , Ca, Cl, Cu, Fe, K, Mn, Ni, S, Si , Sr, Ti, Zn	P3B_2	[blue particles] Na (3.96), Al (29.09), Si (25.82), S (3.47), K (2.71), Ca (32.67), Fe (2.27)	-
P6: background	Light greenish	Al , Ba, Ca, Cl, Cu, Fe , K, Mn, Ni, Pb, Rb, S, Si, Sr, Ti, Zn	P6A_3	Na (2.78), Mg (1.87), Al (1.99), Si (2.49), S (1.15), Cl (1.48), K (0.93), Ca (12.51), Ti (71.72), Cr (0.79), Fe (2.28)	-
P6: shoulder sleeve of the first female figure	Blue	Al , Ba, Ca, Cl, Cu, Fe, K , Mn, Ni, S, Si , Sr, Ti, Zn	P6A_7	[blue particles] Na (13.30), Mg (0.68), Al (14.36), Si (16.19), P (0.80), S (26.51), K (1.91), Ca (26.25)	-
P6: boat behind the second female figure	Dark Green	Ba, Ca, Cl, Cu , Fe, K, Mn, Ni, S, Si, Sr, Zn	P6A_14	Na (1.83), Al (2.51), S (36.49), Cl (1.79), K (0.64), Ca (17.35), Fe (3.10), As (2.80), Sr (2.79), Ba (30.68)	Gypsum, Calcite, Calcium Oxalate, Barite, Emerald Green?
P6: boat behind the second female figure	Green	Ba, Ca, Cl, Cu , Fe, K, Mn, Ni, S, Si, Sr, Zn	P6A_16	-	Barite, Emerald Green?
P6: dress sleeve of the second female figure	Dark brownish red layer over a black	Al, Ca, Cl, Cu, Fe , K, Mn, Ni, S, Si, Sr, Ti, Zn	P6A_17	[red particle] Na (5.97), Mg (3.27), Al (2.97), Si (1.49), P (1.25), S (2.36), Cl (1.14), Ca (24.67), Fe (56.90) [black particle] Na (5.57), Mg (1.91), Al (1.10), P (17.80), S (3.10), Cl (0.89), K (1.5), Ca (66.57), Fe (1.56)	Gypsum, calcite, Silicates, bone black
P6: arm of the second female figure	Flesh	Ba, Ca, Cd , Cl, Cu, Fe , Mn, Ni, Pb, S, Si, Sr, Ti, Zn	P6A_20	[reddish particles]: Na (4.73), Mg (2.87), Al (3.95), Si (1.70), S (9.42), Cl (2.87), Ca (64.60), Fe (9.86)	Gypsum, Oxalates, Silicates
P6: background	Light greenish	Al , Ba, Ca, Cl, Cu, Fe , K, Mn, Ni, Pb, Rb, S, Si, Sr, Ti, Zn	P6A_23	Mg (10.24), Al (8.57), Si (16.87), S (5.16), Cl (1.16), K (0.59), Ca (4.95), Fe (50.15), Ba (2.31)	Gypsum, Calcite, Oxalates, Barite, Vinyl Polymer
P6: rope of the boat	White layer over an orange yellow	Al, Ca, Cl, Cu, Fe , Mn, Ni, Pb, S, Si, Sr, Ti , Zn	P6C_2	[top white layer] Na (3.14), Mg (2.18), Al (3.19), Si (3.07), P (0.15), S (2.46), Cl (0.94), Ca (7.95), Ti (71.72), Fe (2.59), Cd (2.00) [inner layer-yellow] Na (3.14), Mg (2.18), Al (3.19), Si (3.07), P (0.75), S (2.46), Cl (0.94), Ca (7.95), Ti (71.72), Fe (2.59), Cd (2.00) [inner layer-orange particle] Na (3.65), Mg (3.27), Al (15.47), Si (27.52), P (1.68), S (4.34), Cl (1.62), Ca (16.83), Fe (20.93), Cd (2.62)	Aluminosilicates, Gypsum, Calcite, Oxalates
P6: water background near the rope (Fig.3d)	Light greenish blue	Ba, Ca, Cl, Cu, Fe , K, Mn, Ni, Pb, S, Si, Sr, Zn	P6C_5	[Brownish green particle] Na (1.66), Mg (22.09), Al (3.49), Si (43.98), S (1.48), Ca (15.63), Fe (11.67)	Gypsum, Calcite, Oxalates, Vinyl Polymer

Table 2.- Summary of h-EDXRF, SEM-EDS, and μ-FT-IR of eleven paint layers analyzed.

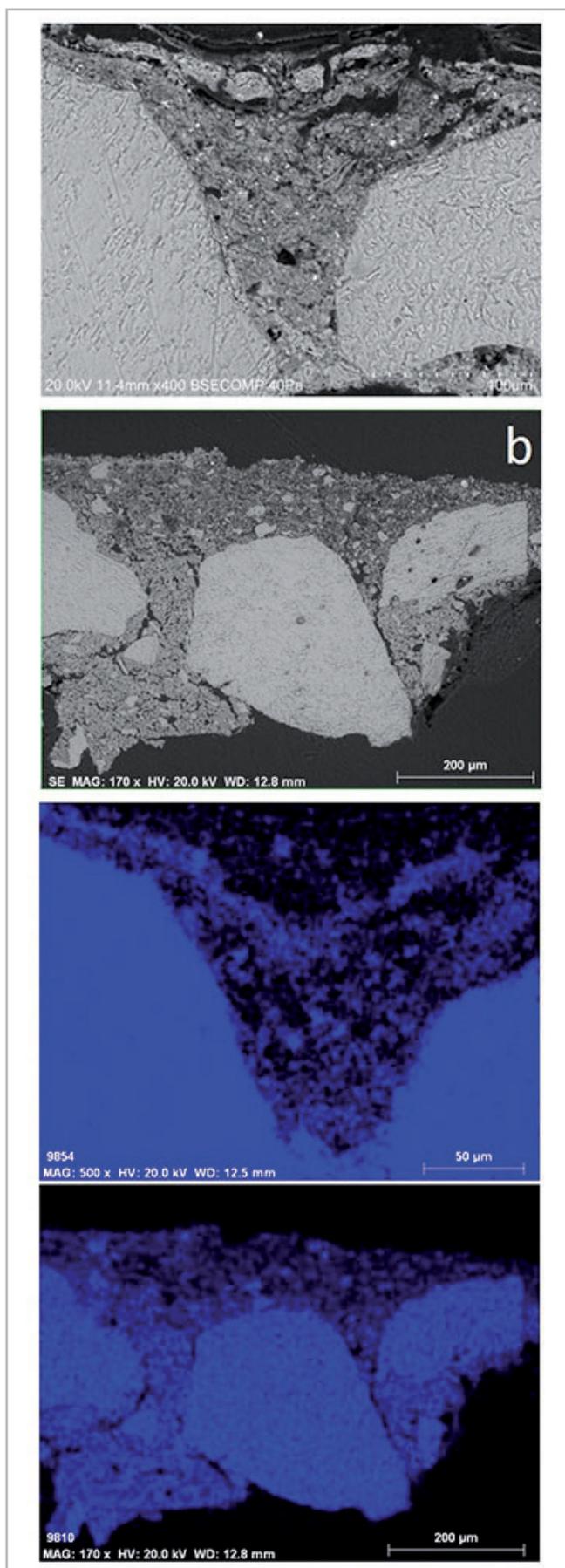


Figure 8.- SEM BSE images paint layers cross sections P6C_2(a), P3B_2(b) and corresponding EDS Ca elemental map distribution (in blue).

Conclusions

This paper reports for the first time a diagnostic research on deteriorated paint layers of Almada Negreiros' mural painting art in the city of Lisbon by in loco non-invasive and laboratory microanalytical techniques. The goal was to answer to the concerns of conservators-restorers stated in the three research questions regarding the state of conservation and decay mechanisms. The work carried out highlights the main deteriorations features noticed in the three murals made by the artist in 1945.

All the paintings analyzed are affected by lack of cohesion, flaking, erosion and lacunae. The light greenish and greenish blue paint layers are particularly affected. First results of in situ and archival survey indicate salts as the main decay phenomenon which is still ongoing. Analysis of salt efflorescence samples and of samples of the affected paint layers revealed the presence of alkali and alkali earth sulphates as the main agents responsible for the current state of conservation of the paintings. The origin of the salts might be related to structural architectural deficiencies, the building materials used (e.g. Portland cement), and to the environmental conditions caused by the proximity to the sea and by the pollution of the city.

The results also show that Almada Negreiros used new synthetic painting materials that go beyond the traditional palette of a fresco painting technique employing these pigments alone or in mixtures (e.g., titanium white, Cd-based pigments). The characterization of the green paint layers was not straightforward, and more research is needed to confirm the hypothesis raised at this point of research for the pigments' identification. Finally, in what concerns the painting technique used by Almada Negreiros, so far only, the fresco technique was identified in the paint layers analyzed but doubts remain in the most disrupted light greenish and greenish blue paint layers affected by flaking. Regardless of the remaining doubts, the analytical campaign enabled a comprehensive picture of the main deterioration features affecting the paint layers and the identification of the materials involved, both original and from previous interventions (e.g. the vinyl polymer). These data are crucial to build a structural review and to project future cleaning and consolidation measures of these paintings. Furthermore, the results will set the baseline for future analytical campaigns in these painting sets and in other mural painting nucleus of Almada Negreiros in the city of Lisbon.

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