

PRELIMINARY DIAGNOSTIC SURVEY OF DETERIORATED PAINT LAYERS AT THE MARITIME STATION OF ROCHA DO CONDE DE ÓBIDOS, LISBON: A MULTIANALYTICAL RESEARCH

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Abstract

This paper reports the preliminary diagnostic survey of the six controversial mural paintings painted in 1946–49 at the Maritime Station of Rocha do Conde de Óbidos in Lisbon, considered the artistic epitome of Almada Negreiros mural painting art. Four research questions drove this research: a) What are the main decay phenomena present and their sources? b) Which are the paint layers most affected, and are they linked to a particular pigment? c) Is there any relation between the painting technique used and the deterioration or stability of the paint layers and pigments? And finally, d) Are there differences in the decay phenomena present in both maritime stations of Alcântara? The analytical setup comprised in-situ and laboratory analysis by way of technical photography documentation (TP), handled optical microscopy (h-OM), handheld X-Ray Fluorescence (XRF), complemented by optical microscopy of microfragments and cross sections (OM-Vis-UV), X-Ray Diffraction (XRD), and Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS). The first results indicate flaking of the paint layers as the main and most severe deterioration feature present in most of the murals. The yellow ochres, browns, blacks, and light greens are the colours most affected, showing different degrees of loss. The pictorial technique used, the presence and action of soluble salts in the structure, and even the products used as adhesives during past interventions might be the root of this phenomenon.

Keywords: Modern Art; Mural Painting; Diagnosti; XRF; SEM-EDS

Introduction

Context and aims of the research

Almada Negreiros (1893–1970) is a key Portuguese artist from the first half of the twentieth century under Salazar's dictatorship in Portugal [1]. This study focuses on four of the six mural paintings in Almada, dated 1946–1949. The paintings at the Maritime Station of Rocha do Conde de Óbidos are located on the first floor of the building, where passengers were welcomed or bid farewell. This was Almada's third painting assignment, and it was so highly contested after its completion—by its modernity and the subject depicted—that the paintings were even at risk of being destroyed [2]. The six murals painted on the east and west walls show signs of deterioration, requiring a diagnostic survey prior to future restoration works. The aim

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was to identify and map the main deterioration features and determine underlying decay phenomena. The diagnostic survey comprised the analysis of the materials and painting techniques used by the artist, along with a characterization of the degradation products with the aim of evaluating their effects on the paint components. The research also included a comparison with the previous study on the 1945 painting set also made by Almada Negreiros in the nearby Maritime Station of Alcântara, which had similar aims [3].

This paper reports the first results from the analytical campaign held on-site and in a laboratory context between March and December 2022. This work implemented an integrated multidisciplinary approach by combining *in-situ* and laboratory analysis by means of technical photography documentation (TP), handheld optical microscopy (h-OM), handheld X-Ray Fluorescence (XRF), complemented by optical microscopy of microfragments and cross sections (OM-Vis-UV), X-Ray Diffraction (XRD), and Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS).

Location and painting description

The mural paintings of the Maritime Station of Rocha do Conde de Óbidos, with dimensions of 720×380cm, consist of six murals, three on opposing sides of the room facing each other, both sets depicting riverfront scenes. The three paintings on the west wall (P1 to P3) are entitled *Sunday outing on the Tagus; Fishwives, and fishermen; jugglers and acrobats at the docks*. The other three on the east wall (P4 to P6) form a triptych commonly known as *Departure of the emigrants* [2, 4]. All are classified as frescos by art historians and have been extensively discussed considering their iconography and importance in modern art history, but no data was found concerning their materiality or painting techniques [2, 4–7]. The research undertaken focuses on the mural paintings referred to as P1, P2, P3, and P4, selected as representative of the entire set after a first visual inspection carried out in January 2021 (Fig. 1).

The building housing these murals is located on the Lisbon riverside near a thoroughfare (N6) that moves traffic as well as public buses, and additionally, the train line that runs from Cais do Sodré to Cascais. This building, as well as the Maritime Station of Alcântara, which is just 1.5 km away, were meant to be the main ports of the city, so naturally both stations are on the riverfront next to the Port of Lisbon and the Marina of Alcântara. Its proximity to water (river or sea) and different sources of air pollution provide an externally aggressive environment, which may have influenced over time the painting's condition.

Experimental part

In-situ Analysis

Photo documentation and technical photography (TP)

Photographs in the visible light range (Vis), visible raking (Vis-RAK), and ultraviolet radiation (UV) were acquired with a Nikon D3200 digital camera with 24Mpx, and an objective Nikkor 18–55mm f/3.5–5.6 GII. Photos in raking light were carried out at a 15–20° angle from the painting surface, from three different directions. UV-induced fluorescence in the visible range (UVF) images were made to ascertain the presence of organic materials that may have been used originally and/or in past interventions. The radiation source in this case was Labino® MPXL UV PS135 light (35W PS135 UV Midlight 230V), with a UV filter included (310–400nm and a peak at 365nm), a midlight distribution angle of 20°, and a start-up time of full power after 5–15 sec. In addition, Vis photographic documentation of painting details and of deterioration features was also carried out with a Canon 80D camera with 24Mpx, and an objective Canon EF-S 18-55mm f/3.5-5.6 IS STM.

Handheld optical microscopy (h-OM)

Handheld OM on the paint layers was performed with two digital microscopes, DinoLite ProX AM 4000 and DinoLite Premier AD3713TB, with 20× and 435× magnification, respectively. The images were taken to document deterioration features, pigment mixtures, and details of the painting technique.



Fig. 1. From left to right, overview of the mural paintings 1, 2, 3, and 4 with approx. 720×380cm. The ten of paint layers analyzed by the analytical setup are indicated by the white squares (photos by CML-José Vicente 2013)

Handheld X-ray Fluorescence (XRF)

The first elemental analysis of the paint layers was made with a handheld X-ray fluorescence analyzer, the Bruker Tracer III SD, equipped with an X-ray tube with a rhodium target and a silicon drift detector. This paper reports the results of the analysis carried out on the paint layers most attained by deterioration in the areas selected from the four paintings mentioned (Fig. 1). The analyses were carried out in the areas of flaking (when possible) or in nearby layers of analogous colours that were more stable to avoid causing more damage. In total, 68 measurements were made on the yellows and browns, 49 on the greens, and 36 on the greys and blacks. The spectra were recorded using a voltage and a current intensity of 40kV and 30 μ A, respectively, during a 30s real-time count. The instrument was controlled using the S1PXRF software (BrukerTM). The spectra were later processed using the Artax (BrukerTM) software to obtain semi-quantitative data. The generated net areas of the fluorescence lines were normalised to the counts of the Rh K α lines.

Laboratory Analysis

Laboratorial analyses were carried out on microsamples collected from deteriorated and more stable paint layers on the four paintings under study. The aim was to run a more in-depth characterization of the painting's materials used by Almada, laid down as adhesives, and decay mechanisms causing flaking and powdering.

Optical Microscopy (OM-Vis-UV)

The microsamples were analysed as microfragments and as cross sections. Recordings of the microfragments were made in Vis with a stereomicroscope HRX-01 HIROX Digital Microscope equipped with a 5 MP sensor to suit 4 K resolution and motorised HR lenses at 140 \times , 200 \times , and 600 \times magnifications. The cross sections embedded in epoxy fix resin were studied with a Leica DM2500M reflected light optical microscope in dark field illumination mode. Observations were carried out at 100 \times , 200 \times and 500 \times magnifications. Photographs of cross sections were obtained with a Leica MC 170HD digital camera. OM-UV mode was used to spot the presence of organic materials using a high-pressure burner 103W/2 UV lamp with an excitation filter BP 340–380, a 400 dichromatic mirror, and a suppression filter Lp425, size K.

X-ray Diffraction (XRD)

A Bruker AXS-D8 Advance diffractometer with Cu K α radiation was used to ascertain the main salt phases. The microfragments were mounted on a zero-background sample holder. A step of 0.02 $^\circ$ /s. and a time per step of 1s. were used for collecting 2–70 $^\circ$ 2 θ diffractograms. The DIFFRAC.SUITE EVA $^\circ$ software and the International Centre for Diffraction Data PDF-2 database were used for the identification of the crystalline phases.

Scanning Electron Microscopy with Energy Dispersive Spectroscopy (VP-SEM- EDS)

A Scanning Electron Microscope (SEM) coupled with an Energy Dispersive Spectrometer (EDS) was used to image the deterioration features of the paint layers (e.g., flaking and powdering) and to identify the painting materials and the technique used by Almada. This analysis was carried out on the microfragments and on cross sections. High-resolution pictures of the samples were obtained in 70 \times -2.50 K magnification mode. A Variable pressure Scanning Electron Microscope HITACHI S-3700N operator was used, with an accelerating voltage of 20kV and chamber pressure of 40Pa. The SEM was coupled with a Bruker XFlash 5010 Silicon Drift Detector (SDD) with a resolution of 129eV at Mn K α . Elemental distribution maps were acquired for areas of interest on samples, and EDS spectra were obtained from punctual and area microanalysis with ESPIRIT Compact Software. SEM images were captured in backscattering electron (BSE) mode.

Results and discussion

The main deterioration feature noticed in the four paintings under study by Vis and Vis-Rak is the flaking of paint layers, in several degrees of severity, which has contributed to paint

loss over the years. Powdering of paint layers was also noticed, but to a lesser extent and often associated with flaking. The colours most affected are the yellows and browns, the blacks, and the light greens in all murals. The flaking is particularly severe in P2 and 3 of the west walls, showing large areas of decay, as illustrated in figure 2. Three hypotheses were raised regarding the causes of decay: (a) the painting materials and painting techniques used by the artist; (b) the presence and activity of salts; and (c) past intervention products. The following sections address each of these hypotheses individually, although they can all be interconnected and act simultaneously.

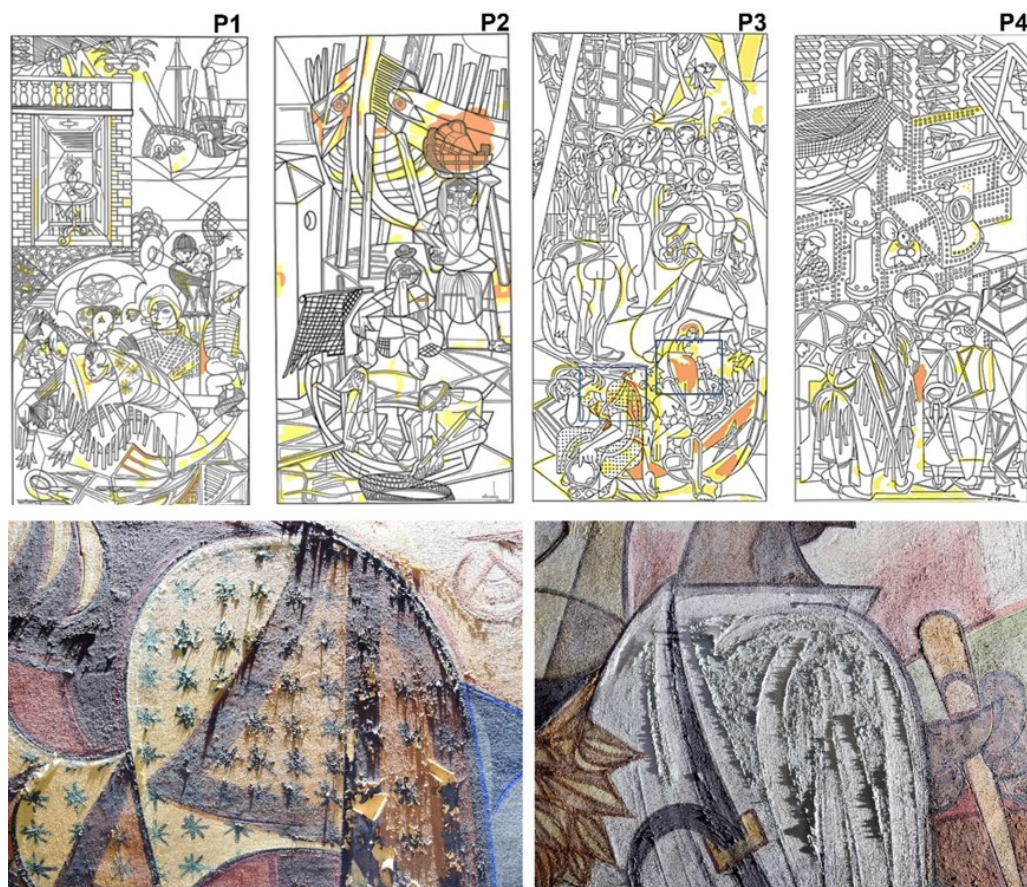


Fig. 2. On the top, graphic map of deteriorated paint layers on P1, P2, P3, and P4, with the indication of the levels of decay observed in April 2022 (light to moderate in yellow and severe in orange). On the bottom, two details in Vis-Rak of paint layers on P3 with severe flaking and imminent risk of paint loss. Powdering is also observed in the same areas. (Graphic documentation by K. Rix and photos by M. Ribeiro 2022)

Painting Materials and painting techniques

Painting Materials. The first approach to the pigment's elemental composition was made on-site with XRF. The following text presents the preliminary results obtained on the paint layers most affected by flaking and powdering. The goal was to have a first identification of the types of pigments used by the artist and to find out whether they could have had an influence on the decay phenomena observed.

On the yellow and brown paint layers, iron (Fe) was the main chromophore found, along with smaller amounts of manganese (Mn) (Fig. 3a). The Fe and Fe-Mn-based pigments are likely

yellow ochres and brown earth pigments, with the brownish shades tending to have more manganese oxide (MnO_2) in the composition (ex. P2B_21 and P3B_11 of Fig. 3a).

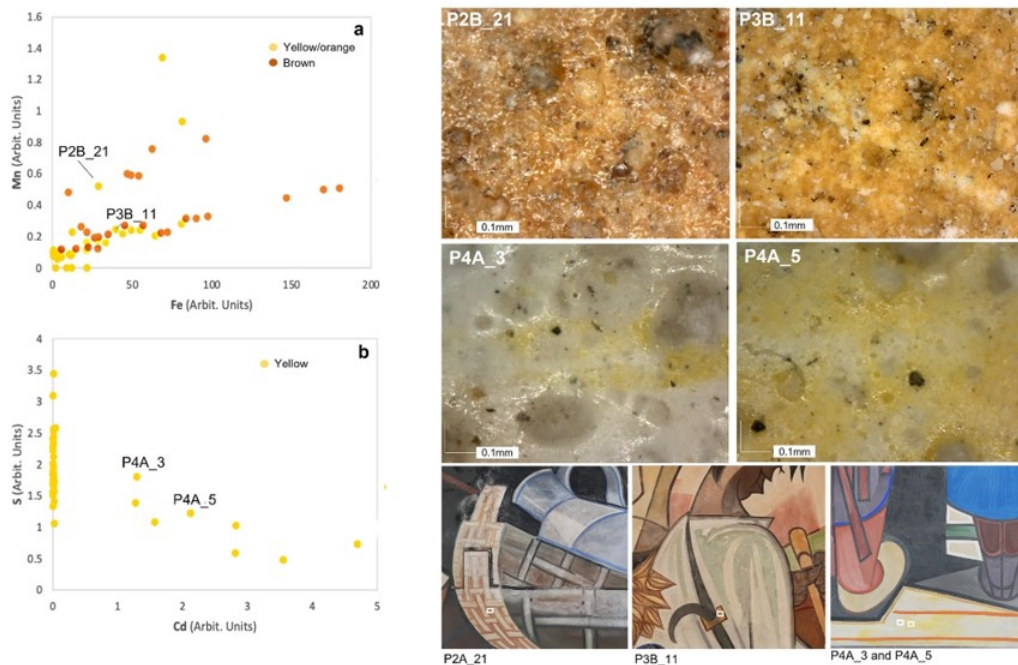


Fig. 3. On the left, an XRF Mn-Fe and S-Cd biplot; on the right, h-OM image details at 435x of yellow and brownish paint layers from P2, P3, and P4, in which the analyses P2B_21, P3B_11, P4A_3, and P4A_5 were carried out

In ochres, Fe oxides and hydroxides, such as hematite (Fe_2O_3) and goethite ($\text{FeO}(\text{OH})$), are known to be responsible for the yellow and red hues [8]. The use of ochres and brown earth pigments in Almada's palette has already been reported in the 1945 murals at the nearby Alcântara maritime station [3]. Similar to that study, the current research has identified by XRF a variable input of elements in most of the yellow and brown paint layers that may be correlated with a natural pigment source, including potassium (K), silicon (Si), sulphur (S), titanium (Ti), aluminium (Al), and arsenic (As) [9, 10]. In figure 4, VP-SEM-EDS analysis of yellow particles in a paint cross section also shows the association of Al and Si with Fe, which is consistent with the composition of a yellow ochre (phyllosilicates with an iron hydroxide).

In addition to Fe-based pigments, XRF also allowed the identification of cadmium (Cd) and sulphur (S)-based pigments in the bright yellow paint layers of P3 and P4 (Fig. 3b). These showed slight pigment powdering, and in two cases, it is suspected that they have undergone a chromatic alteration (ex. the variations found on P4A_3 and P4A_5 analysis and h-OM from the same paint area). Cadmium pigments are modern synthetic pigments that began to be produced on a wide scale in the mid-19th century [11]. The use of yellow cadmium pigments in the early 20th century, as opposed to earth pigments, was controversial for fresco painting since the alkaline environment could cause colour fading [11]. According to Fiedler (1986), this effect was due to the presence of cadmium oxalate and carbonate, as well as free sulphur, in a cadmium sulphide composition [11]. The use of CdS pigments in mural paintings by Almada Negreiros has already been reported, but so far, no evidence of fading has been noticed. This is the first time that this hypothesis has been raised [3, 12].

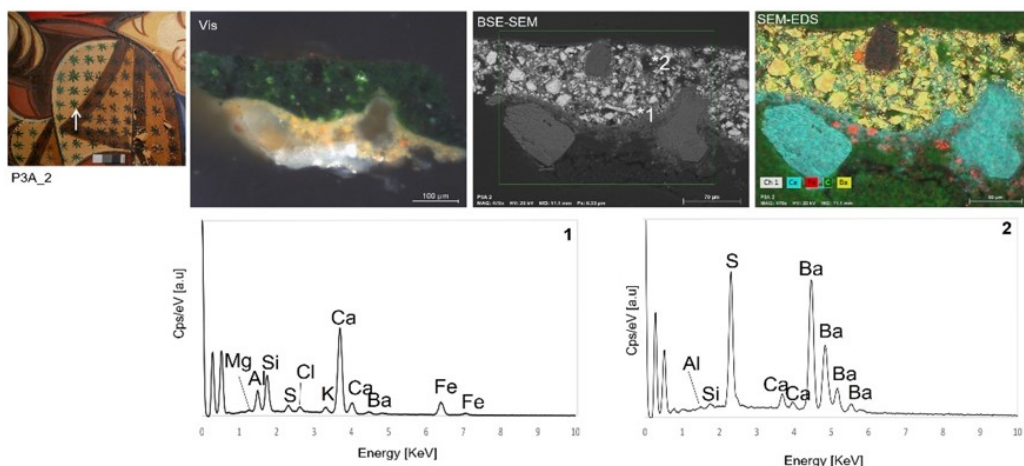


Fig. 4. On the top, from left to right, are the sampling location of sample P3A_2; OM-Vis of the P3A_2 cross section; SEM-BSE image, and the SEM-EDS elemental distribution map of calcium (blue), iron (red), carbon (green), and barium (yellow). On the bottom are the EDS spectra of a yellow particle (1) and of the green matrix (2)

In the green paint layers analysed by h-EDRFXF, the main element identified as a chromophore is also Fe (Fig. 5a). Barium (Ba) and sulphur (S) were also detected in significant amounts in most paint layers, but their presence is most likely related to barium sulphate added as filler to the green pigments, as shown by the SEM-EDS of the coarse grains of Ba on the dark green paint layer in figure 5. The presence of barite (BaSO_4) was also confirmed by μ -XRD on another microsample collected from a bright green background of P2 (P2A_2 from Table 1).

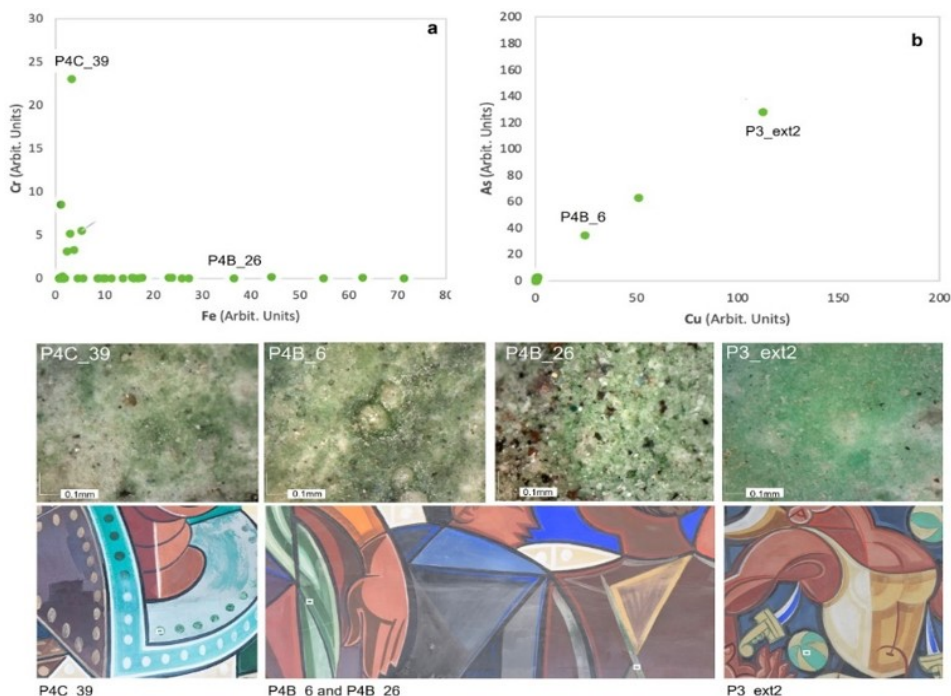


Fig. 5. On the top, the XRF Cr-Fe and As-Cu biplot; on the bottom, the location of the analysis carried out (white squares) and h-OM image details at 435x of green paint layers P4C_39, P4B_26, P4B_6, and P3_ext2 from P4C, B, and P3. On all the paint surfaces, not only the green as the top layer is perceived but also the underlayers of white, brown, and yellowish hues

Table 1. Summary of the μ -XRD mineralogical phases identified. The colours refer to paint layers on which the microsamples of salts formation (salt veils/efflorescence) were collected. Legend: **b**-back of the sample

Sample Ref.	Sampling Location (colour)	Calcite	Barite	Goethite	Gypsum	Kaolinite	Quartz	Whewellite	Weddelite
P2A_2 (b)	Background (green)	◇	◇						
P2B_2	Fish woman basket (whitish translucent film with yellow paint layer attached)	◇		◇	◇				
P2B_2 (b)		◇		◇	◇	◇			
P2B_3	Fish woman basket (black)	◇			◇			◇	◇
P2B_3 (b)		◇			◇			◇	
P2B_7	Fish woman basket (white)	◇			◇		◇		
P2B_9	Fish woman container (bluish white)				◇				
P2B_9 (b)					◇				
P2B_11	Fish woman container (whitish translucent film with blue paint layer attached)	◇			◇				
P2B_11 (b)		◇			◇				

Iron is found in most paint layers with other elements in small or trace amounts, such as K, Al, Cl, Mn, Mg, and Si. The high Fe input can be related to: a) Fe-based green pigments, such as green earths [13], or potentially to Fe-organic synthetic modern pigments such as PG8, or PG1, recently identified at the Maritime station of Alcântara [3]; b) other Fe-brown, red chromophores in mixtures with the greens, or from paint underlayers, as found by SEM-EDS in the cross section of figure 6 or by h-OM in the paint surfaces of figure 4.

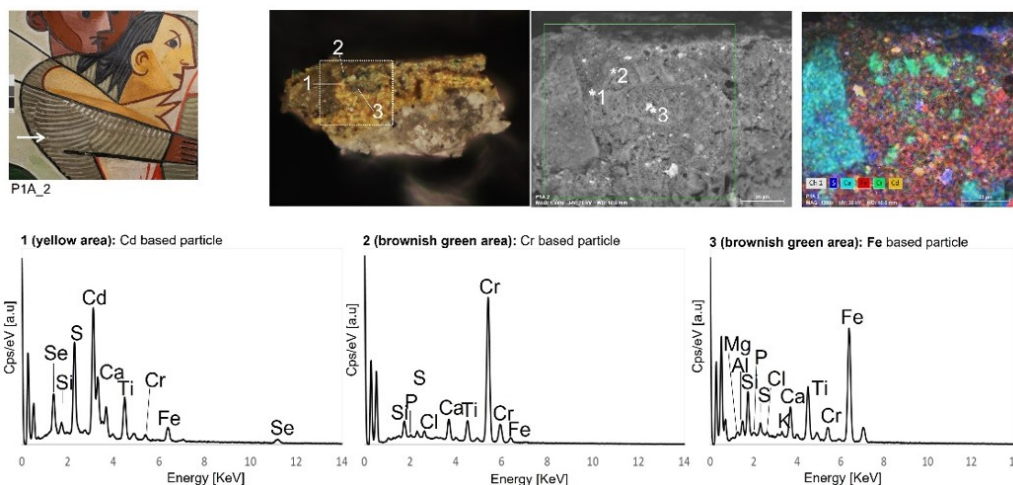


Fig. 6. On the top, sampling location of the brownish green paint layer P1A_2; OM-VIS light of P1A 2 cross section; BSE-SEM image and SEM-EDS sulfur (dark blue), calcium (light blue), iron (red), chromium (green), Cadmium (yellow) elemental maps. On the bottom, EDS spectra of Cd, Cr and Fe based pigments particles

In figure 5a, the high amount of chromium (Cr) in six green paint layers suggests the presence of another green chromophore. Cr is identified in higher amounts in bright green particles such as the ones in P1A_2 of figure 6, and it is likely related to synthetic chromium oxide (Cr_2O_3) or hydrated chromium oxide ($Cr_2O_3 \cdot 2H_2O$) which have been available as artist pigments since the 19th century [14]. In addition to Fig. 5b, it was also found by XRF that high

amounts of Cu and As were present in three paint layers exhibiting a bright green hue, which may imply the presence of emerald green pigment, a copper acetoarsenite of formula $3\text{Cu}(\text{AsO}_2)_2 \cdot \text{Cu}(\text{CH}_3\text{COO})_2$ [15].

Finally, regarding the black paint layers, Fe is also the main element found so far as a chromophore by XRF. Most layers of black paint with severe flaking were the last to be applied, which makes it difficult to interpret the data due to the interference of the coloured materials used in the underlying layers. Further research on microsamples must be conducted to reach conclusions. The painting materials found so far in this research do not seem to be contributing to the flaking of paint layers. These are traditional pigments commonly used in mural painting (e.g., earth pigments), or they are modern pigments (e.g., Cr-based pigments, Cd-based pigments, emerald green), whose deterioration expected on the walls would be colour alteration (fading/darkening) [11, 14, 15].

Painting Technique. During the on-site examination, it was noted that the most deteriorated paint layers exhibited a glossy surface, as shown in figure 7. Traditionally, mural paintings rendered in a fresco technique are matte, and all the paintings at the maritime station of Rocha do Conde de Óbidos are classified as such [1].

The gloss is clearly perceived by h-OM in areas of flaking but also in paint layers of the same color around it, in better condition. It is known that most of the paintings have been restored in the past and that adhesives were applied. Could this glossiness be related to past intervention products, or is it somewhat related to the painting technique (or to paint coatings) used originally by Almada?



Fig. 7. Detail of flaking paint layers with gloss on P3 (photo by M. Gil 2022. Project Almada)

In order to understand whether the glow was restricted to the paint surface or if it was within the paint layer itself, cross sections of some of the microsamples collected from these areas were prepared and visualized by OM in the visible range (Vis) and by ultraviolet radiation (UV). One example collected from a black glossy paint layer on P3 is shown in figure 8. On the cross section obtained, four layers are perceived in the visible range. The first, a white inner layer, corresponds to the mortar used as pictorial support; the 2nd and 3rd are two overlaid paint layers of grey and black hues, respectively; and the 4th is a translucent layer on the surface (Fig. 8). This

layer, which is approximately 152 μm thick, displays a whitish fluorescence in UV mode. This layer is confined to the surface; the two paint underlayers do not exhibit a UV response.

To ascertain the painting technique used by Almada, further analysis was carried out on this microsample by VP-SEM-EDS. By EDS, the high amount of carbon (C) and its widespread distribution on the surface confirmed the organic nature of the glossy layer, whereas the presence of calcium (Ca) and its elemental map distribution suggest a lime-based painting technique on the underneath black and grey paint layers (Fig. 8). On the SEM-BSE image, the absence of a Ca-carbonation line at the interface of the mortar and the grey paint layer reveals a fresco execution. Yet, its presence at the interface of the two paint layers may indicate that Almada has laid down the black paint when the previous one has already dried (Fig. 8). The application of additional paint layers at a later stage may imply the use of *secco* painting techniques with pigments mixed with lime (lime painting) or with an organic material. The presence of Ca in the matrix of both paint layers in figure 8 suggests that lime was a binder in both cases. However, the additional use of organic binders in this sample and in the others collected from deteriorated paint layers cannot be completely excluded and should be further explored by other analytical techniques.

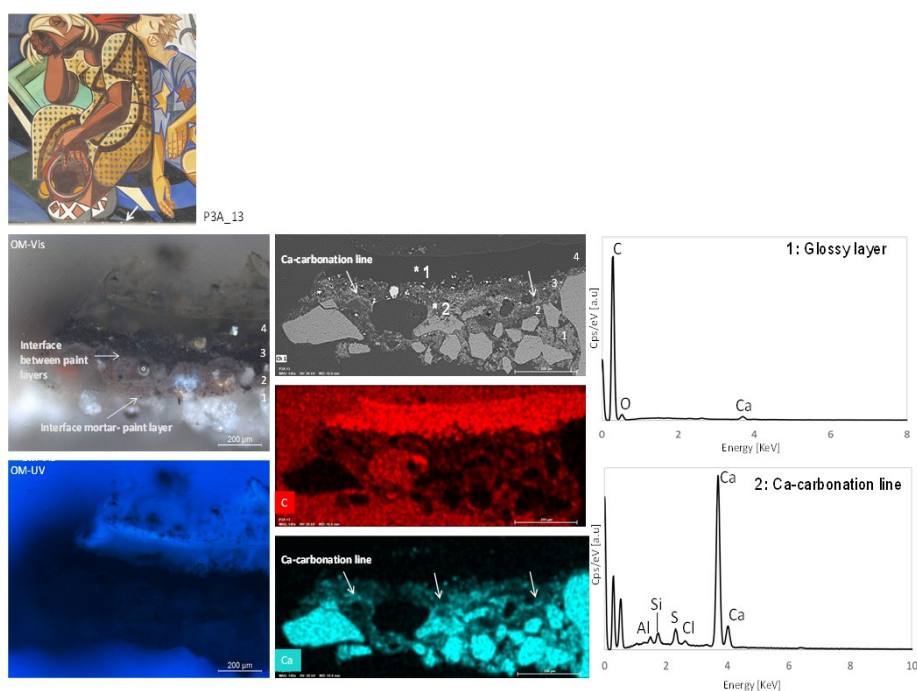


Fig.8. On the left, the sampling location of P3A_13; OM-Vis-UV of P3A_13 cross section with the indication of the 4 layers found. On the middle and right, VP-SEM-EDS analysis with the location of the thin carbonation layer at the interface between layer 2 and 3

Presence and activity of salts

Painting 2, on the west wall, seems to have been particularly affected by water infiltrations, with two active moisture stains with white salt formations clearly visible from the ground (Figs. 1 and 2). Six micro-samples of the most deteriorated paint layers with salt veils and salt efflorescence were collected from the green background and the fish woman basket standing up and analysed by μ -XRD. The goal was to ascertain the main phases present and to compare with the salts already identified in the nearby maritime station of Alcântara. Table 1 reports the phases

identified on the front and back of the microsamples. These were: calcite (CaCO_3), barite (CaSO_4), quartz (SiO_2), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), gypsum ($\text{Ca}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$), and calcium oxalates, whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and weddellite ($\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$). The first three minerals are associated with painting materials used as pigments, binders, and fillers; the last two are associated with the decay phenomena observed.

Gypsum, a hydrated calcium sulphate, was found in most of the analyses carried out (Table 1, Fig. 9). No other sulphates were identified from the list already reported in 2021 by *M. Gil et al.* [3]. The salts in the Alcântara murals include thenardite (Na_2SO_4), 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), in addition to calcite and gypsum. These salts were not identified at Rocha do Conde de Óbidos, possibly due to the amount sampled being below the limit of detection of the μ -XRD.

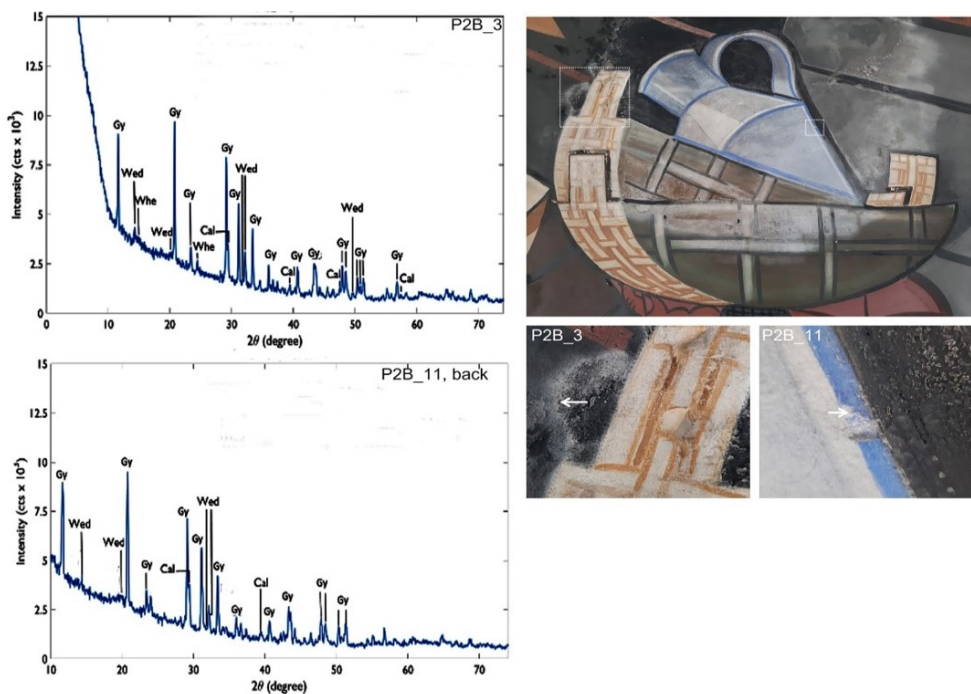


Fig. 9. On the right, the sampling locations of microsamples P2_B3 and P2B_11, back collected from P2, are most affected by water infiltration. On the left, the corresponding μ -XRD diffractograms show identified mineralogical phases (Gy – Gypsum, Cal – Calcite, Whe – Whewellite, Wed – Weddellite)

It is known that hydrated calcium sulphate is one of the main and most common salts encountered on carbonated mural paintings [16, 17]. Sulphates are usually found in soils, polluted atmospheres, and sea spray [18–22]. In a building, the formation of sulphates is typically spurred by the wet and dry acid deposition of SO_x in conjunction with water infiltration, which prompts the leaching and migration of dissolved ions into the architectural structure [21]. In this research, the presence of gypsum could be anticipated considering that both stations were a) built with the same building materials (which include reinforced cement [7]) and b) only 1.5km apart, and as such, the paintings were exposed over the years to the same weathering environment (proximity of thoroughfare and the river or sea). The activity of soluble salts, such as gypsum, is one of the main causes of flaking (and powdering) of the paint layers due to the gradually disruptive cycles of crystallisation and dissolution within a porous material.

In addition to gypsum, only two other minerals have been identified by μ -XRD that may be actively contributing to the deterioration of paint layers. These are the whewellite and weddellite calcium oxalates found on the front and back of samples P2B_3 and P2B_11 (Fig. 10, Table 1). The origin of these minerals in the paintings may be related to the deterioration of organic binding media, biological activity and metabolism products, or the oxidation of organic materials applied in past interventions [23]. In figure 10, the presence of bioactivity on the paint surface over the glossy carbon-based layer may suggest a combination of the last two hypotheses.

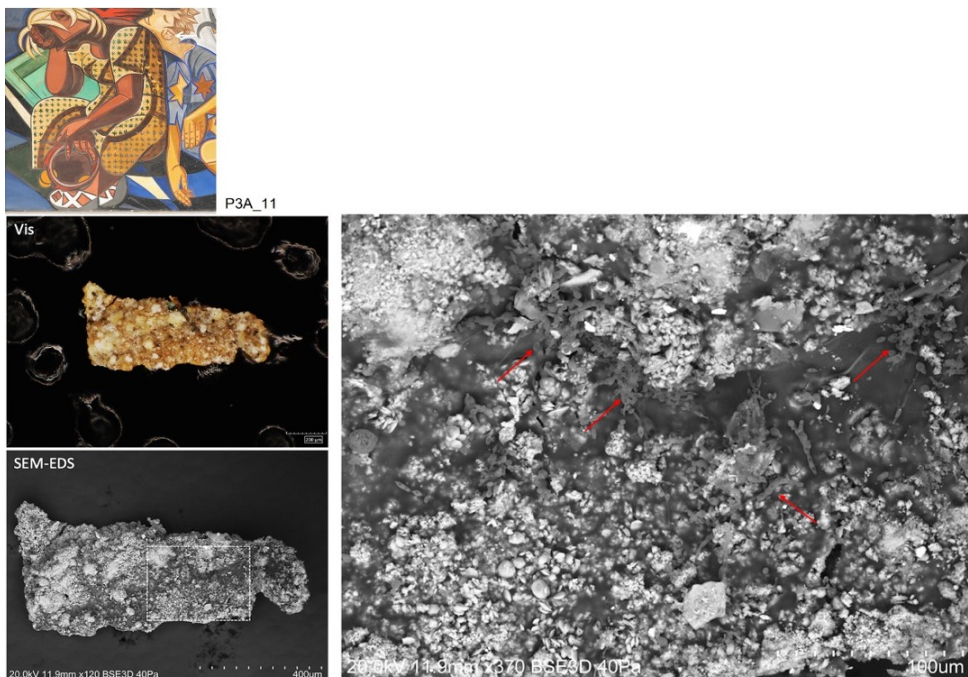


Fig. 10. On the left, OM-VIS (top) and SEM-BSE (below) images of sample P3A_11 collected from a brownish paint layer on P3. On the right, detail of BSE-SEM image of the paint layer surface, indicating biological colonization over a carbon-based layer (red arrows)

Calcium oxalates are considered to be one of the most common and harmful salt contaminants, leading to powdering of the mortar and flaking of the paint layers [24]. According to *T. Rosado et al.* [24], typically microorganism activity on the surface of a mural painting, like fungi, bacteria, lichen, and algae, can serve as a biological substrate, resulting in the development of calcium oxalates [24]. The metabolism of these microorganisms produces oxalic acid ($H_2C_2O_4$) that reacts with calcite on lime-based murals to form calcium oxalate (CaC_2O_4) [23, 24]. In the deteriorated paint layers analysed that exhibit a glossy layer at the surface, the presence of microbial activity may be related to the original coatings used by Almada or to adhesives applied to past interventions. The colonisation of microorganisms is known to be supported by organic and inorganic nutrient sources, and a carbon-based layer can act as such [25].

Past Intervention Products

The mural painting set of Rocha do Conde de Óbidos was already restored at least twice according to the documental survey conducted in 2022 in the archive of the Laboratory *José de Figueiredo* (LJF) at the *Biblioteca de Conservação e Museus*, in Lisbon. The first past intervention was held in 1971, and the second in 1979. Occasional visual inspections also took

place in 1992, 1993, and 1995, and in the last two, photographic records were made of the paintings that show the recurrence of flaking in some of the areas previously consolidated.

The documentation produced in 1971 and 1995 provides a small amount of context to the past treatments undertaken at Rocha do Conde de Óbidos, and which products used at that time may now be degrading and contributing to the flaking of the original paint materials [26, 27]. The report made in 1971 is particularly important since it specifies the tests made with adhesives on P1 [26] and the location of the different experiments done with Paraloid (the type is not referred to, but it is most likely B72 that was the one most used for this purpose) and Gervatol (Fig. 11). Chemically, Paraloid is an ethyl methacrylate-methyl acrylate copolymer, and Gervatol (or gelvatol) a polyvinyl alcohol. Both were tested in different concentrations diluted in xilol and in water and ethanol, respectively. Paraloid was deposited twice, reaching more than 20% in areas B, C, and F, which may be responsible for the glossy areas observed on-site in April 2022 (Figs. 8, 10 and 11). The results of these experiments are not given, nor is the final product selection, but remnants of adhesive layers are clearly identified in P1 and P2 on deteriorated paint layers.

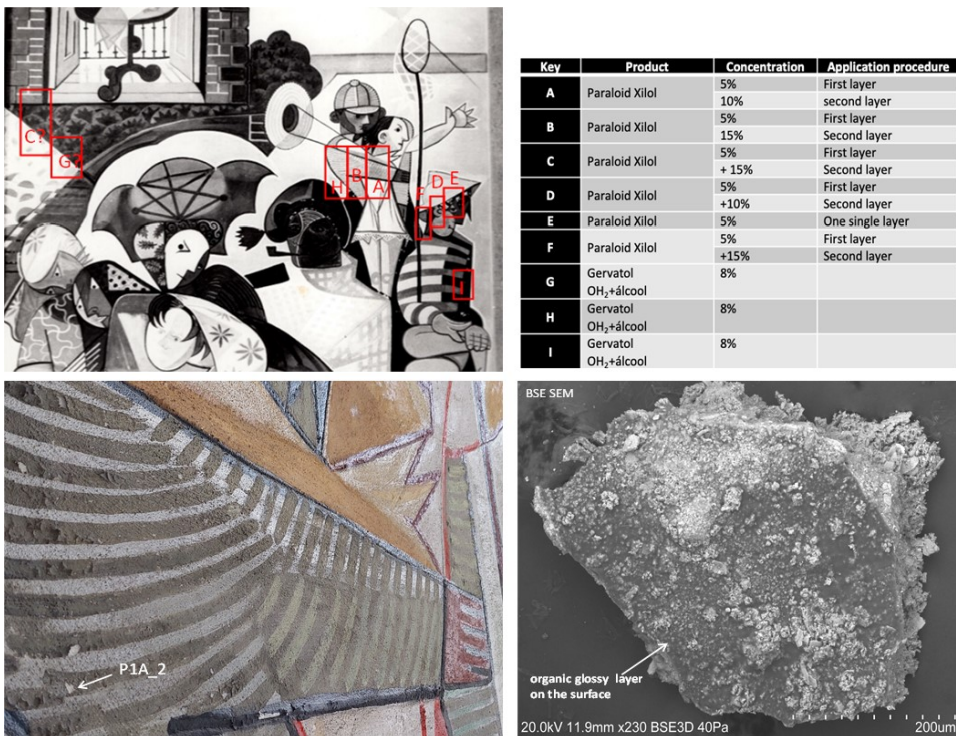


Fig. 11. On top, documentation from 1971 with the indication of adhesive tests carried out on painting 1 (red squares). The letters A to I on the table correspond to the different test locations signaled. Below, on the left, is the location of the microsample collected from a previously consolidated greenish-brown paint layer. On the right, a BSE-SEM image of the surface of the microsample P1A_2 shows a carbon-based layer on top of the paint layer

Paraloids (in particular B72) are among the most well-known acrylic resins widely used as adhesives and protective coatings in the field of cultural heritage [28, 29]. Paraloids are generally appreciated for their relative stability, reversibility, mechanical resistance, and transparency [29]. But despite their popularity, polymer materials are known to age and deteriorate due to light, heat, acid-base environments, and bioactivity [28]. Moreover, when applied in thick layers, they can produce a hydrophobic barrier that may cause further damage to paint layers affected by moisture and soluble salts. This is the case with the severe flaking paint

layers on P2, where gypsum was identified. The past conservation products applied in this area show a brittle appearance and are peeling together with the paint layer.

Conclusions

The research carried out at the Maritime station Rocha Conde de Óbidos enabled us to identify for the first time the flaking of the paint layers as the main and most severe deterioration feature of the yellows, browns, blacks, and light greens paint layers in the four paintings studied in April 2022. The analysis performed on site and in the laboratory has allowed an initial identification of the painting materials most affected and to ascertain the likely sources of their decay. The results show that on the deteriorated paint layers: a) the presence of glossy carbon-based layers on the paint surface; b) the presence of soluble salts such as gypsum and calcium oxalates; and c) the thick, brittle, and peeling layers of past adhesives (e.g., gervatol and paraloid) are mostly responsible for their current poor condition. So far, it has not been possible to determine a correlation between the pigment's composition and the flaking phenomenon. As already stated in the results discussion, the pigments found so far are either earth pigments (e.g., ochres) commonly found in fresco mural paintings or modern pigments (e.g., Cr-based pigments, Cd-based pigments, emerald green), whose deterioration expected on the walls would be colour alteration (fading or darkening). The binder found so far is only lime, but future research on stable paint layers will give a deeper insight into the painting techniques and materials used.

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