AN INSIGHT INTO THE GREEN DETERIORATED PAINT LAYERS OF THE MARITIME STATION OF ALCÂNTARA (LISBON): AN ARCHEOMETRIC STUDY

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Abstract

This study reports the first results of the analysis carried out in 2022 on deteriorated green paint layers from the mural paintings made by Almada Negreiros at the Maritime Station of Alcantara, in Lisbon (Portugal). These murals painted in 1945 are one of the most emblematic painting sets done by the modernist artist and exhibit a bright chromatic palette that displays different states of conservation, with the green paint layers particularly damaged, showing severe flaking and powdering in the lightest shades.
To understand the decay phenomenon, in-situ and laboratory analyses were done in an attempt to identify the green chromophores, the painting technique, and the decay agents causing the visible degradation. The analytical setup comprised in-situ technical photography (Vis, Vis-Rak, and UVF), handheld optical microscopy (h-OM), handheld energy dispersive X-ray fluorescence (h-EDXRF), colorimetry, and spectrophotometry in the visible light range. Microsamples of selected paint layers from deteriorated and stable green areas were collected and further analysed in the laboratory by optical microscopy in visible and ultraviolet modes (OM-UV-Vis), variable pressure scanning electron microscopy coupled with energy dispersive spectrometry (VP-SEM-EDS), micro-X-ray diffraction (μ-XRD), micro-Fourier-transform infrared spectroscopy (μ-FT-IR) and micro-Raman spectroscopy.
Results show the presence of both natural and industrial synthetic organic pigments, such as green earths and PG8, used alone or in mixtures with other chromophores (e.g., Fe-based yellow and red pigments, bone and carbon black, ultramarine blue, and the synthetic green PG1 and the yellow PY1). Concerning the decay phenomena, the main hypothesis for the powdering and flaking of the green paint layers is the activity of calcium sulphates (e.g., gypsum), which probably originated from both intrinsic and extrinsic sources and whose presence was found to be widespread in all the microsamples analyzed.

Keywords: Modern Mural Painting; Synthetic Organic Pigments; Gypsum; μ-XRD, micro-Raman spectroscopy

Introduction

Almada Negreiros (1893–1970) was a Portuguese artist who worked as a painter, dancer, choreographer, playwright, writer, and poet [1]. He was also one of the leading figures of the first modern art movement in Portugal [2] and is considered one of the most important Portuguese artists of the 20th century [3].

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Between 1938 and 1956, Almada Negreiros collaborated on the pictorial decoration of the indoors and outdoors of five public buildings designed by Porfirio Pardal Monteiro, a renowned Portuguese architect who worked during the dictatorship regime in Portugal [4, 5]. Among these five buildings is the Maritime Station of Alcântara, inaugurated in 1943 as part of the riverside urbanisation project of Lisbon [5].

The Maritime Station of Alcântara is located in the city of Lisbon, in the parish of Alcântara, near the bank of the Tagus River. For the Maritime Station, Almada Negreiros designed and produced a set of eight monumental mural paintings on the west and east walls of the departure lounge located on the first floor of the building. The murals, at 7.2 m high by 3.8 m wide, date from 1945 and depict myths and historical episodes of the Portuguese culture and working-day life of communities, making them one of the most impressive artworks of Almada Negreiros' career [5, 6].

The mural paintings, classified by the historiography as fresco paintings [5], were made with a bright chromatic palette that today displays different states of conservation [7]. The green paint layers are particularly damaged, showing visible severe flaking and powdering in the lightest shades (Fig. 1). The main goal of this research carried out in 2022 was to understand the decay phenomenon by identifying the green chromophores, the painting technique, and the decay agents. The buildup of the green paint layers from an artistic perspective is beyond the scope of this paper and will be addressed in another study. The results presented in the next sections from the deteriorated green paint layers have allowed for the first time a comprehensive understanding of the current condition and set guidelines for further research on the topic and for the future safeguard of this painting set.
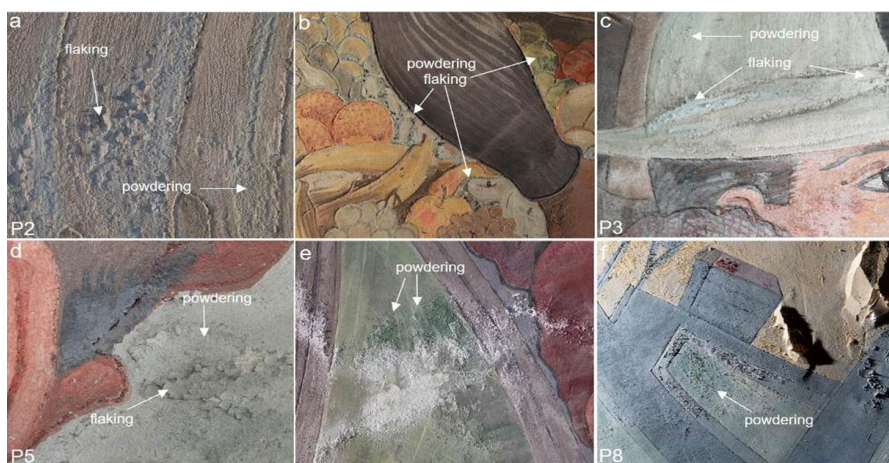

Fig. 1. Details of green deteriorated paint layers in visible (c and d) and in visible raking light (a, b, e, and f). The references P2, P3, P5, and P8 in the bottom right corner of each picture indicate the paintings from which these images come. The location within the paintings is indicated on Fig. 2 (ALMADA2021/22© all rights reserved).

Experimental part

The research on the green paint layers was carried out in two main phases. The first one consisted of an in-situ survey, accompanied by photographic documentation and technical photography in the ultraviolet and visible light ranges (TP-UVF-Vis). Based on the diagnostic survey carried out, the paintings 2, 3, 5, 6, and 8 were found to be representative of the green colour variations observed and of the degree of decay, and they were selected for further research. Figure 2 shows the areas with green paint layers that were studied in-situ. The analytic

setup consisted of handled optical microscopy (h-OM), colorimetry in the visible range, and finally handled energy dispersive X-ray fluorescence (h-EDXRF).

The second phase consisted of laboratory analysis of microsamples collected from deteriorated and more stable green paint layers of the five panels supra mentioned. The analyses performed were optical microscopy in Vis-e UV mode (OM-UV-Vis), micro-X-ray diffraction (µ-XRD), scanning electron microscopy with energy dispersive spectroscopy (VP-SEM-EDS), micro-Raman spectroscopy, and micro-Fourier-transform infrared spectroscopy (µ-FT-IR).

Fig. 2. Panels under study from the Maritime Station of Alcântara.
The rectangle with white dashed lines shows the areas with deteriorated green paint layers
selected for in-situ and laboratory analyses in 2022. The yellow rectangles indicate the location of
the images present in figure 1. Images adapted from Guta de Carvalho, June 2020 © all rights reserved

In-situ non-invasive research

Photo documentation and technical photography

The in-situ survey started with visual inspection and photographic documentation carried out in the visible light range (Vis) for a global overview of the paintings and details of the green paint layers and for the selection of areas for technical photography in the visible and visible raking light (Vis-Vis-Rak) and ultraviolet (UV) for non-invasive analysis in-situ and sampling. The photographic records of Vis, Vis-Rak, and ultraviolet fluorescence induced in the visible range (UVF) were made with a Nikon D3200 digital camera with 24MPX and an objective 18–55mm f/3.5–5.6 GIL.

Halogen lamps (1000W–230V) were used for Vis and Vis-RAK. Raking light at 10-15° from the painting surface was used to observe and record deterioration features (e.g., flaking and powdering) and other painting characteristics such as textures, types of incisions, tool marks, and mortar joints.

UVF photography was used in an attempt to ascertain the presence of organic matter associated with the original painting materials and past intervention products used to fix the flaking paint layers over the years. It is known that the murals were restored at least three times and that paint layers were fixed and retouched, but the exact location of the treatments carried out is unknown. UVF photography was performed using a Labino® MPXL UV PS135 light (35W PS135UV 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 5–15s.

h-OM

Handheld OM enabled the in-situ study of technical and material details such as the type of brushstrokes, pigment mixtures, and deterioration features including microfissures, erosion, stains, and salt formation. Handheld OM was carried out by two digital microscopes, DinoLite PROAM13T-FVW and DinoLite Premier AD3713TB, to document the paint layers with 20× and 435× magnification, respectively.

Colorimetry

Colorimetry and spectrophotometry were employed to characterise the current green painting palette. The green hues cover 3.4 to 26.5% of the total painted surface in the five paintings under study. The selection of the 47 colour measurements considered the differences found visually in the light, medium, and darker tones. Most of them show similar hues, particularly in the lightest shades, which are in poor condition, and this factor restrained the number of measurements taken. Three analyses were made in P2, nineteen in P3, ten in P5, five in P6 and ten in P8.

The equipment used was a Data Colour Check Plus II (Lawrenceville, NJ), with an integrating sphere and the following parameters: diffuse illumination 8 viewing (following the CIE standard No. 15.2. Colorimetry), SCE, and Standard Illuminant/Observer D65/10. The aperture size was USAV (Ø5mm). The results were obtained in the CIE L*a*b colour space and are the average of three measurements taken on each paint surface. The chromatic coordinates measured were a* and +b*, which stand respectively for the red/green and the yellows (0–100); L*, which represents lightness (0–100).

h-EDXRF

Handheld EDXRF was employed to conduct an exploratory analysis of the bulk elemental composition of the 47 green paint layers first characterized by colorimetry. A Bruker™ Tracer III SD® handheld X-ray fluorescence spectrometer (Bruker, Germany), equipped with a rhodium target delivering a polychromatic X-ray beam of 3×3mm and a silicon drift detector (XFlash®). The spectra were obtained using a voltage and a current intensity of 40kV and 30μA, respectively, with an acquisition real time of 30 s. All spectra were recorded using S1PXRF software (Bruker™) and processed using Artax (Bruker™) software to obtain semi-quantitative data. The generated net areas of the fluorescence lines were normalized to the counts of the Rh Kα lines.

Sampling

Sampling of green paint layers was the final phase of the in-situ campaign, and it was carried out on the areas previously analysed by h-OM, colorimetry, and EDXRF to deepen the material and technical characterization. This paper reports the study done on fifteen paint layers representative of the variations found in trichromatic coordinates (L*a*b*) on the elemental composition and degree of decay. Eleven samples are from flaking and powdering paint layers (P2A_2, P2A_3; P2A_5, P3A_8, P3A_12, P3C_6a, P3A_15, P5B_17a/b, P6A_14, P8A_35 and P8A_31a), and four are from paint layers in better condition (P3D_2, P3C_22, P5B_10 and P8A_27). The microsamples range in size $\leq$ 1mm^2. The sampling location is shown in Appendix A.

Laboratory Research
OM-UV-Vis

Optical microscopy in Vis was carried out in two steps. The first consisted of an overview of the micro-fragments without any previous treatment to record the topography of the paint surface, the pigment particles, salt formations, and deterioration features (flaking and powdering). 3D magnified images of the micro-fragments were acquired with an HRX-01 HIROX Digital Microscope equipped with a 5MP sensor to suit 4K resolution and motorised HR lenses. The HR-5000E lens was used to observe the object at magnifications of 140×, 200×, 400×, 800× and 2000×.

The second step was the preparation of cross-sections to study the stratigraphy (number and thickness of paint layers), pigment size, morphology, and distribution within the paint layer, and finally, to ascertain the type of binder used (inorganic or organic). OM was carried out in the visible light range and UV mode with a Leica DM2500M reflected light optical microscope in dark field illumination mode at 100×, 200× and 500× magnification; the photographs were acquired with the Leica MC 170HD digital camera equipped with the corresponding Leica software. For the UV photos, 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, were used.

μ-XRD

A Bruker D8 Discover® diffractometer with a Cu Kα radiation and a 0.3mm collimator was used to ascertain the main phases of original materials and salts formations present in 10 paint layer microsamples. The micro-fragments were mounted on a zero-background sample holder. The diffractograms were collected using an angular range of 3–75°. The step time was adjusted for each sample, considering their small size and complexity, in order to guarantee the identification of the crystalline phases. The DIFFRAC.SUITE EVA® software and the International Centre for Diffraction Data PDF-2 database were used for identification. The diffractograms of the 10 samples can be found in Appendix B.

VP-SEM-EDS

VP-SEM-EDS was applied to image the decay phenomena (e.g., powdering of pigments, microcracks, salts formations, and bio-colonization) and to perform point/area analysis and elemental map distribution of the pigments' particles and matrices. The paint layers were analysed as fragments and/or as cross sections. The microsamples were set in carbon tape and analysed with a variable pressure scanning electron microscope (Hitachi S-3700N) coupled to a Bruker™ XFlash 630M SDD EDS Detector®. The analyses were carried out in backscattering mode (BSE) at low vacuum (40Pa) using an accelerating voltage of 20 kV. The use of variable pressure equipment allowed the analysis of samples without coating.

Micro-Raman spectroscopy

Micro-Raman spectroscopy was also used to ascertain the chemical composition of the green pigments present in seven microsamples considered to be representative of the variations found in trichromatic coordinates (L*a*b*) and by h-EDXRF in the five murals. The samples were analysed using a confocal Raman Spectrometer Senterra R200-L, equipped with a red diode laser (785nm) and a green Nd-YAG laser (532nm), coupled with an Olympus microscope and a thermo-electrically cooled CCD spectrometer. The measuring time, laser power, and number of accumulations were set to obtain a good signal-to-noise ratio while avoiding thermal damage.

μ-FT-IR

Select microsamples were also analysed in a Thermo Nicolet Nexus 670 FTIR spectrometer coupled to a Continuum IR microscope to ascertain the presence of organic materials. FTIR spectra were collected in transmission mode using the compression diamond Spectra-TechSample Plan cell. Each FTIR spectrum is the average of 254 scans collected at $4cm^{-1}$ resolution in the region from 4000 to $650cm^{-1}$. No spectral processing other than the removal of the carbon dioxide bands was performed. The identification of the chemical compounds was made through the comparison of the samples' spectra with reference FTIR

spectra from the Thermo Scientific spectral libraries Coatings Technology, Industrial Coatings, and Hummel Polymer and Additives.
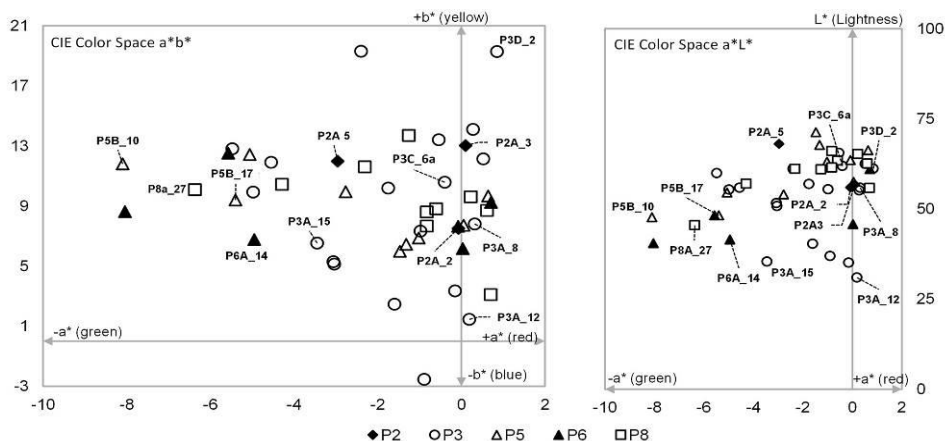

Fig. 3. 2D projection of colorimetric coordinates in the CIE a*b* and CIE a*L* colour spaces with the indication of 12 of the fifteen paint layers that were sampled for further analysis and that are mentioned in the results discussion. The missing three are stated on Table I and come from paint layers that were difficult to access (P3C_22) or presented a high degree of visible decay (P8A_31a and P8A_35)

Results and discussion

Green painting palette and pigment identification

An overview of the current green colour palette projected in the CIE a*b* and CIE a*L* colour spaces is shown in figure 3. The 47 green hues measured in the five mural paintings span from -0.07 to -8.1 in the -a* axis (green) and from 1.45 to 19.30 in the +b* axis (yellow). The L* parameter ranges from 30 to 71, with 35 paint layers exhibiting light hues (L* > 50). The yellow shades indicated by the +b values in figure 3 are due to the presence of yellow, brown, and red pigment particles within, under, and on top of the paint layers analysed, as can be seen in the h-OM of figure 4 and in the paint cross sections of figure 5. The same accounts for the layers showing 0 and +a* values, such as P2A_3, P3A_8 and P3A_12.

The results reveal a restricted range of green hues on the backgrounds for shading and highlighting areas. In figures 4 and 5, some examples of the green hue variations found are shown, revealing the green pigments were laid down in a single or in two layers, the latter tending to be more fluid, darker, and saturated in colour (e.g., P5B10, P5B_17, P8A_27 and P3A_15). The opaque and lighter greenish hues were mainly found as background tones, and, in some cases, they are what is left as the top layers of paint have disappeared (e.g., P2A_3, P3A_8 and P3A_12 of figure 4).

The elemental composition of the 47 green paint layers was first studied in-situ by h-EDXRF (Table I and Fig. 6). The main elements identified in all samples, as shown in Table I, were calcium (Ca), iron (Fe), barium (Ba), and sulphur (S), chromium (Cr), potassium (K), titanium (Ti), strontium (Sr), and silicon (Si) were also occasionally detected in significant amounts. h-EDXRF also enabled the detection of other elements in minor or trace amounts, such as chlorine (Cl), manganese (Mn), and zinc (Zn).
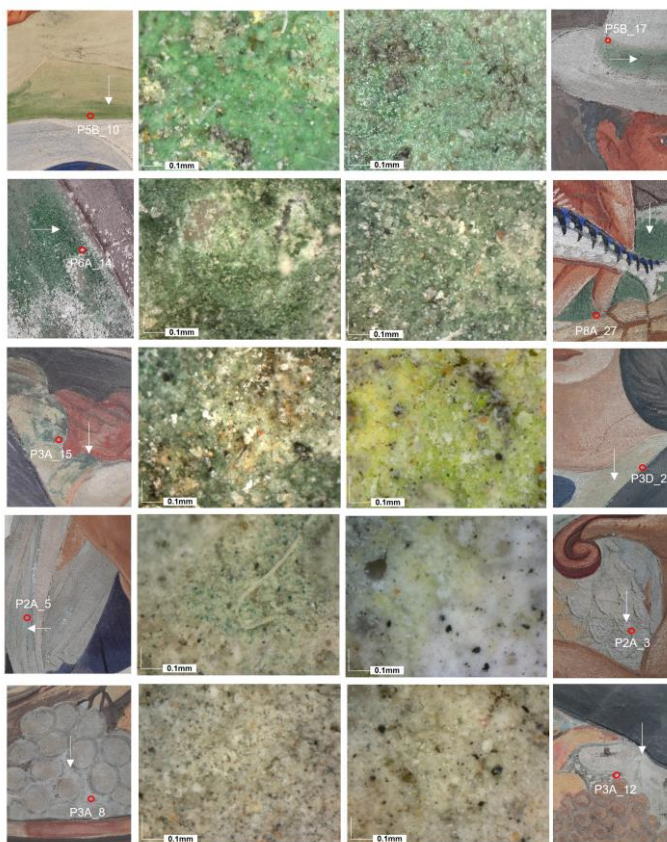
Fig. 4. Examples of the green hue variations found in the trichromatic coordinates (L*a*b*)
in the green paint layers. On the inside, the OM-Vis images at 430× and, on the outside,
the location of the colorimetric measurement taken (white arrow)
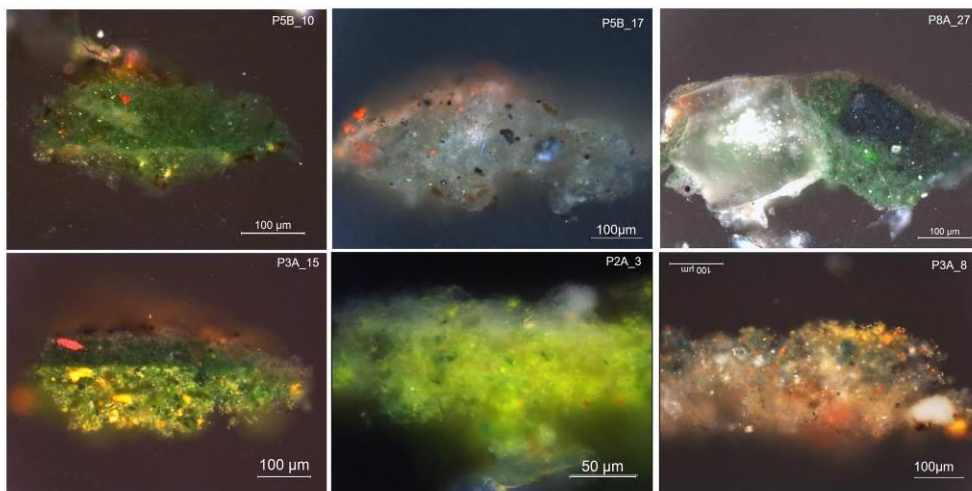and of the sampling place (red circle)

Fig. 5. OM-Vis of paint layer cross sections collected from the dark mid and light hues of figure 3.
The green pigments were laid down in one or two layers, and were used alone or in mixtures with black,
yellow, red, brown, and white chromophores. Only in P3A_8 can a brownish underlayer be seen.
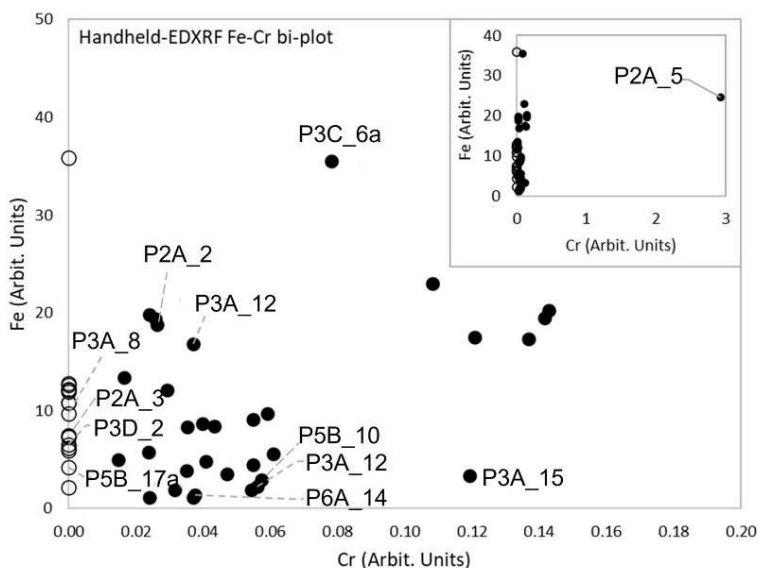
Fig. 6. Handheld-EDXRF Fe-Cr bi-plot of the 47 green paint layers revealing the presence of two main groups: one in which Fe is exclusively detected (empty circles) and another with Fe and variable amounts of Cr (black circles)

The widespread presence of Ca as a main element and the detection of calcite by XRD are associated with lime-based painting techniques and lime-based mortars used by Almada and have already been reported in a previous study [7]. On the other hand, the presence of S in all samples is correlated with the identification of barium and calcium sulphates (Tables I and II). Barite ($BaSO_4$) and gypsum ($CaSO_4.2H_2O$) were identified by XRD in deteriorated paint layers and in paint layers in better condition, raising the hypothesis that both materials may have been originally used as fillers or extenders (Table 1). Unlike barite, the occurrence of gypsum as a neoformation salt is also considered given the high level of disruption of paint layers observed in-situ, especially in the lighter green hues (Fig. 1).

In turn, the high amount of Fe found in most of the paint layers is related to green chromophores but also to other Fe-based chromophores within, under, and above the paint layers (Figs. 4 and 5). The presence of Mn, Sr, Ti, and Cr may also be linked to the composition of Fe-based pigments, but it may also be indicative of the occurrence of other green pigments originally used by Almada or, in some cases, might have been added in the past by mimetic reintegration (hypothesis raised for microsample P2A_5 that was collected near a retouched lacuna). Finally, the significant amounts of K and Si detected in samples P3A_12 and P3C_6a, on the other hand, are likely related to the use of earth pigments

Further analyses were carried out on microsamples with μ-XRD and micro-Raman spectroscopy in an attempt to identify the green chromophores used by Almada Negreiros (Figs. 7 and 8). Table 1 summarises the in-situ and laboratory analysis results obtained.

Micro-XRD analyses enabled the identification of the mineral phases that may impart green hues in only two samples: P3C_6a and P3A_12 (Fig. 7, Table 1). In both cases, the identification of clinochlore, an aluminosilicate of Fe and Mg, suggests the use of a green earth pigment. The amounts of silicon and potassium identified by h-EDXRF as well as the identification of Fe, Al, Mg, and K in microsample P3C_6a by VP-SEM-EDS also corroborate this hypothesis (Fig. 7).

Table 1. Summary of the analysis carried out on 15 paint layers reported in the results discussion obtained by colorimetry, h-EDXRF, μ-XRD and micro-Raman spectroscopy (legend: PY 1- Pigment yellow 1, PG 8- Pigment green 8, PG 1-Pigment green)

Sample ID	State of conservation	CIELAB chromatic coordinates			h-EDXRF (in bold main elements)	μ-XRD*	micro-Raman Spectroscopy	μ-FT-IR
		L	*a	*b				
P2A_3	Powdering	56.70	0.10	13.00	**Ba**, **Ca**, **Fe**, K, Mn, **S**, Si, Sr	_	PY 1, PG 8, baryte, gypsum	_
P2A_2	Powdering /Flaking	55.89	-0.07	7.51	**Ba**, **Ca**, Cr, **Fe**, K, Mn, **S**, Si, Sr, Ti, Zn	_	_	Gypsum, animal black, oxalates
P2A_5	Flaking/ Powdering **	67.99	-2.96	11.97	**Ba**, **Ca**, **Cr**, **Fe**, K, Mn, Pb, **S**, Si, **Sr**, **Ti**, Zn	_	_	_
P3A_8	Powdering	55.9	0.32	7.80	**Ba**, **Ca**, Cl, Cr, **Fe**, K, Mn, Pb, **S**, Si, Sr, Ti	Gypsum, quartz	PG 1, carbon black, hematite, gypsum	Gypsum, oxalates, calcium carbonate, vinyl polymer, silicates?
P3A_12	Powdering	31.00	0.19	1.45	Ba, **Ca**, Cl, Cr, **Fe**, K, Mn, Pb, **S**, **Si**, Sr, Ti, Zn	Quartz, gypsum, calcite, clinochlore, plagioclase, sepiolite	_	Gypsum, oxalates, calcium carbonate, vinyl polymer, silicates?
P3A_15	Powdering **	35.40	-3.45	6.53	**Ba**, **Ca**, Cr, **Fe**, K, Pb, **S**, Si, **Sr**, Zn	Baryte, gypsum, calcite	PG 8, hematite, baryte	_
P3C_6a	Powdering	61.90	-0.40	10.6	Ba, **Ca**, Cl, Cr, **Fe**, **K**, **S**, **Si**, Sr, Ti	Gypsum, quartz, rutile, clinochlore, calcite, baryte	_	Gypsum, oxalates, calcium carbonate, vynil polymer, silicates?
P3C_22**	Stable	_	_	_	_	Baryte, gypsum, calcite	_	_
P3D_2	Stable	61.12	0.85	19.28	**Ba**, **Ca**, **Fe**, K, Mn, **S**, Si, **Sr**, Zn	_	_	_
P5B_10	Stable	47.64	-8.1	11.8	**Ba**, **Ca**, Cr, **Fe**, **S**, Si, **Sr**, Zn	_	PG 8, baryte	_
P5B_17	Powdering	48.20	-5.40	9.39	**Ba**, **Ca**, Cl, **Fe**, Mn, **S**, Si, Sr	Gypsum, calcite, baryte	PG 8, carbon black, gypsum	Baryte, gypsum, calcium carbonate, oxalates, vinyl polymer
P6A_14	Powdering **	41.50	-4.95	6.76	**Ba**, **Ca**, Cl, Cr, **Fe**, K, **S**, Si, Sr	Gypsum, calcite, baryte	PG 8	
P8A_31a*	Powdering	-	-	-	-	Baryte	PG 8, ultramarine blue, calcite, gypsum	

| P8A_27 | Stable | 45.46 | -4.29 | 10.44 | **Ba**, **Ca**, Cr, Cu, **Fe, S,** Si, Sr, Zn | _ | _ | _ |
| P8A_35 *** | Flaking | _ | _ | _ | _ | Gypsum, quartz | _ | Gypsum, oxalates, silicates, vinyl polymer, calcium carbonate, siccative oil? |

*The diffractograms can found in appendix B

**The sample was collected from or near areas suspected of having been restored in the past.

***On these paint layers, it was only possible to carry the sampling due to the location and/or degree of decay.

Clinochlore $(Mg, Fe, Al)_6(Si Al_4)O_{10}(OH)_8$ is a mineral belonging to the chlorite group [8–10]. It is one of the most abundant phyllosilicates in nature [10], commonly displaying pale green to dark green hues [11]. Studies have shown that iron content has a significant influence on the colour of clinochlore and that chromium can be incorporated into the structure of this phyllosilicate [12]. Clinochlore is also one of the minerals associated with the pigment green earth [13], although the clay minerals glauconite and celadonite are the most frequently mentioned mineral phases when describing this pigment [8]. In mural paintings, clinochlore has been reported, for instance, in the greenish hues of the Roman wall paintings of Alcazaba (Mérida, Spain) [13], in the preparatory layers and green paint layers from the 17th century wall paintings from the Petros and Paulos Church, Ethiopia [14], and in the green light painting palettes from the pharaonic town of Amara West [15].
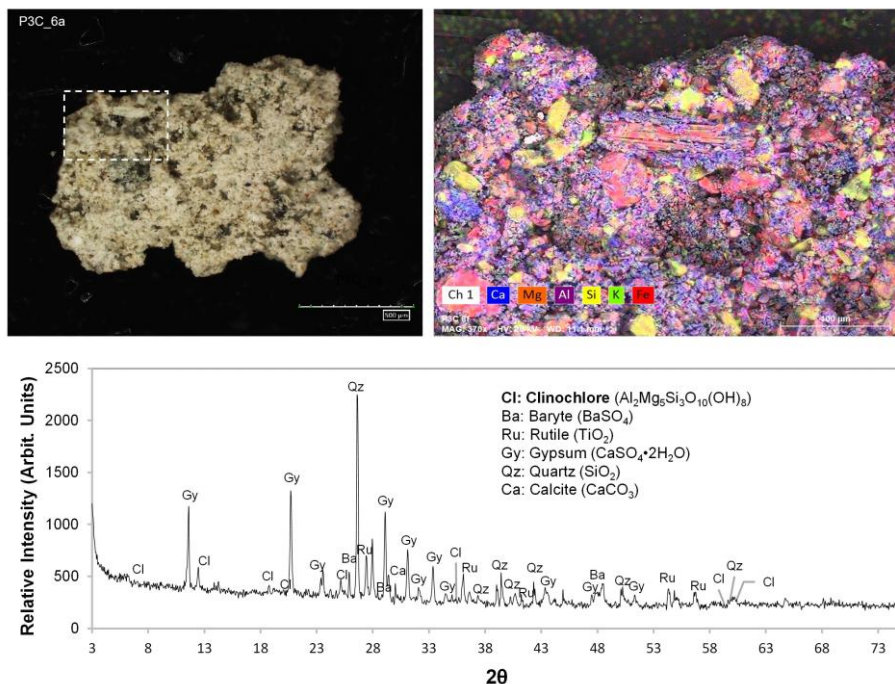

Fig. 7. On top: OM-Vis of the paint surface of P3C 6a at 140× magnification, and corresponding VP-SEM-EDS elemental map distribution of Ca (in blue), Mg (in light red), Al (in pink), Si (in yellow), K (in green) and Fe (in red). On the bottom: μ-XRD diffractogram, showing the presence of clinochlore likely associated to the presence of green earth pigments
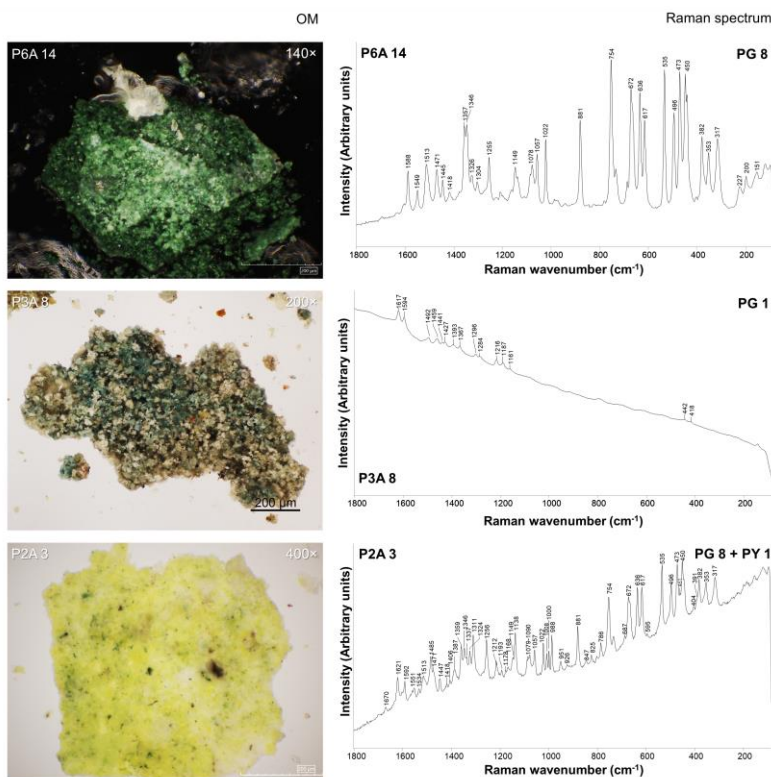
Fig. 8. On the right, OM-Vis of the paint surface of microsamples P6A_14, P3A_8, and P2A_3. On the left, Raman spectra of samples P6A_14, P3A_8, and P2A_3. The bands were attributed to the synthetic organic pigments PG8, PG 1, and PY1

Micro-Raman spectroscopy, on the other hand, enabled the identification of synthetic organic pigments in seven microsamples: P2A_3, P3A_8, P3A_15, P5B_10, P5B_17, P6A_14, and P8A_31a. With the exception of P3A_8, all the aforementioned samples contain an Fe-based modern synthetic organic pigment known as Pigment Green 8, or PG8, identified by the characteristic Raman bands at 151, 200, 227, 317, 353, 382, 450, 473, 496, 535, 617, 636, 672, 754, 881, 1022, 1057, 1078, 1149, 1255, 1304, 1326, 1346-1357, 1418, 1445, 1471, 1513, 1549-1551 and 1588-1592cm^{-1} (Fig. 8) [16]. The likely presence of pigment PG8 had already been reported in one microsample on the first survey of the paint layers from the Maritime Station of Alcântara in 2020 [7]. In the current research, PG8 was identified in the green samples from the five panels under study, which makes this discovery by itself a case study to be further explored in the future considering that, as far as the authors know, this colourant has never been reported before in modern mural paintings.

Chemically, PG8 is an iron complex of 1-nitroso-2-naphtol, reported for the first time in a paper by Otto Hoffmann in 1885 and commercialised by the company BASF in 1921 [17]. PG 8 was mainly used for wallpaper manufacturers, rubber coloration, and the textile industry until the early 1950s, when its use declined and it was gradually substituted by copper phthalocyanine green pigment (PG7) [17, 18]. In terms of its application as an artist's pigment, very few records can be found of its use. One case is reported by Saverwyns (2010), which identifies PG 8 in a copy of an oil painting dated 1915 and attributed to Liubov Popova, a renowned Russian painter from the avant-garde artistic trend [18]. Another interesting study from *C. Defeyt, et al.* (2016) on twenty-eight paintings made on canvas, paper, and masonite by

the U.S.A painter named Sam Francis has also found this green colourant in two polyvinyl acetate (PVA)-based samples collected from art works dated from 1963–1965 and from 1970 [19].

In addition to the PG8, Pigment Green 1 (PG1), a pigment from the triaryl carbonium pigment class, was also identified in sample P3A 8 due to the characteristic Raman bands at 418, 442, 1161, 1187, 1216, 1284, 1296, 1367, 1393, 1427, 1441, 1459, 1492, 1594 and 1617cm^{-1} [20, 21]. According to *S. Simon, et al.* (2019), PG1 was introduced in the 1920s, but its cationic dye had already been known since 1879 [22].

Besides the green pigments described, other chromophores were also identified in the paint layers by micro-Raman spectroscopy (Table 1, Fig.8):

a) Hansa yellow (PY1) mixed with PG 8 was detected in microsample P2A_3 (Fig. 8). PY1, a yellow synthetic organic pigment with a generic chemical formula $C_{17}H_{16}N_4O_4$, was identified based on the characteristic Raman bands at 391, 461, 595, 687, 786, 825, 846, 926, 951, 988, 1000, 1138, 168, 1178, 1193, 1212, 1256, 1311, 1337, 1359, 1387, 1406, 1447, 1485, 1534, 1621 and 1670cm^{-1} [23, 24]. PY1 was the first pigment of Hansa Yellows synthesised in 1909 and led to the synthesis of other possible combinations from 1910 onward [17].

b) Hematite (Fe_2O_3) was found in microsamples P3A_8 and P3A_15 due to the characteristic Raman bands at 498, 408, 290 and 224cm^{-1} [25]. Hematite is the main chromophore of red Fe-based pigments of natural and synthetic origin (e.g., ochres and Mars colours) [26]. Both kinds of pigments were found at Almada's studio in powder from the manufacturer Le Franc-Paris and may have been used by the artist in this painting set, mixed with the greens to enrich the chromatic palette used [27].

c) Carbon black and ultramarine blue were also identified in microsamples P3A_8, P5B_17, and P8A_31a, based on the characteristic Raman bands at 1576 and 1332cm^{-1} [20]; and 584cm^{-1} (sh), 550 and 256cm^{-1} [25], respectively.

Considering the dimensions of the mural paintings as well as the fact that Almada Negreiros executed the paint work alone, doubts remain as to the use of the fresco technique in all paint layers. In a previous diagnostic study, *M. Gil et al*. [7] identified the fresco technique in red, brownish, and blue paint layers. In the greens, the authors did not reach conclusions due to the poor conditions of the microsamples collected [7]. The same difficulty was also felt in the current research. Figure 9 shows BSE-SEM images and VP-SEM-EDS of calcium elemental distribution on the paint cross sections of samples P2A_3, P3A_15, P8A_27, and P3C_22. In a fresco painting, the pigment particles should be embedded in a calcium matrix, which does not occur in the paint layers analyzed. On the VP-SEM-EDS elemental map distribution, Ca is mainly found as aggregates in P8A_27 and P3C_22. As a binder, Ca is only clearly perceived on the mortar of P3C_22 and on a white brushstroke over the yellow green in P2A_3 (Fig. 9).

Painting technique

As stated in the introduction, the mural paintings in the Maritime Station of Alcântara are classified as frescoes [5]. This painting technique consists of painting over a layer of fresh lime-based plaster, the pigment particles being fixed by the carbonation reaction of the calcium hydroxide arising from the mortar with carbon dioxide from the atmosphere [28].

BSE-SEM images of all cross sections show a highly disruptive stratigraphy with loose particles of Ba, Si, and Fe. The same deterioration feature was also noticed in the microsamples analysed as micro-fragments, as shown in figures 10 and 11. No additional information about the painting technique was provided by UV observations onsite or by the OM-UV images of paint cross sections. In figure 9, only a thin layer on top of P3A_15 shows a whitish fluorescence in UV, which can be attributed to vinyl polymers applied as adhesives in past interventions to fix the paint layers. So far, these are the only organic materials found by μ-FT-IR (Table 1).
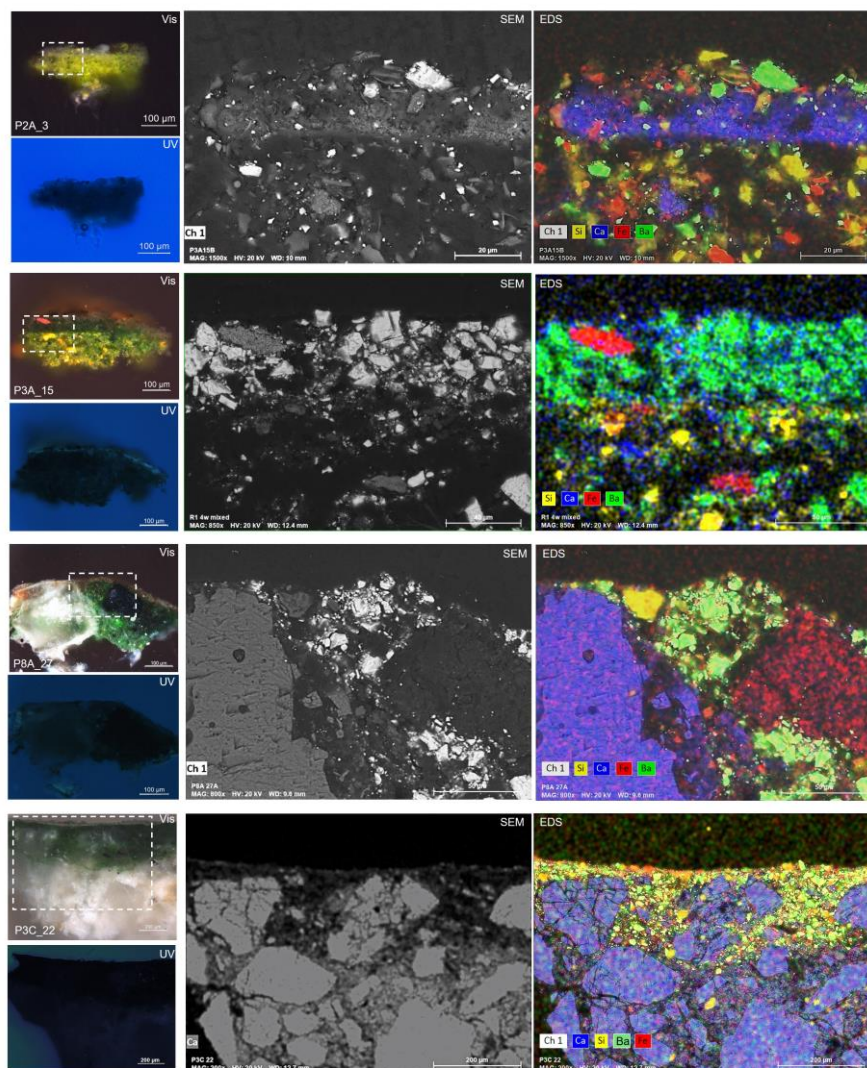
Fig. 9. From left to right: OM-Vis-UV of paint layers cross sections P2A 3, P3A 15, P8A 27 and P3C_22 with 200× magnification; BSE-SEM image and VP-SEM-EDS elemental map distribution of Ca (in blue), Si (in yellow), Ba (in green) and Fe (in red)

Decay agents

Based on the results of the analyses carried out by VP-SEM-EDS, micro-Raman spectroscopy, μ-DRX and μ-FT-IR, the main hypothesis raised for the powdering and flaking of the green paint layers is the disruptive activity of calcium sulphates. Gypsum ($CaSO_4.2H_2O$) was found in all the microsamples analysed from the dark, mid, and lighter green hues collected from deteriorated and stable paint layers (Table I). Fig. 10 shows two examples of the surface appearance of powdering paint layers from P3 and P6, the last being collected from an area severely affected by salt efflorescence's. VP-BSE-SEM image reveals that most particles on the paint surface are exposed to the environment.

Gypsum had already been identified along with other Ca-sulphates (thenardite, syngenite, and aphthitalite) in previous analyses of salt efflorescence's from the mural paintings of the Maritime Station of Alcântara [7]. The powdering and flaking of paint layers can be

caused by crystallization or dissolution cycles of soluble salts within, between, or between the paint layers, or between the paint layer and the mortar. The physical stress produced by the expansion of crystals of gypsum and other sulphates due to hydration or thermal expansion can, gradually and over time, cause both types of decay [29, 30]. The disruptive phenomenon as pointed out by *M. Gil et al.* (2020) could have been triggered by water infiltration occurrences over the years, increased by the particularly aggressive weathering environment of the maritime station on the riverside of Lisbon (e.g., traffic air pollution and aerosols from the nearby Atlantic Ocean) [7].
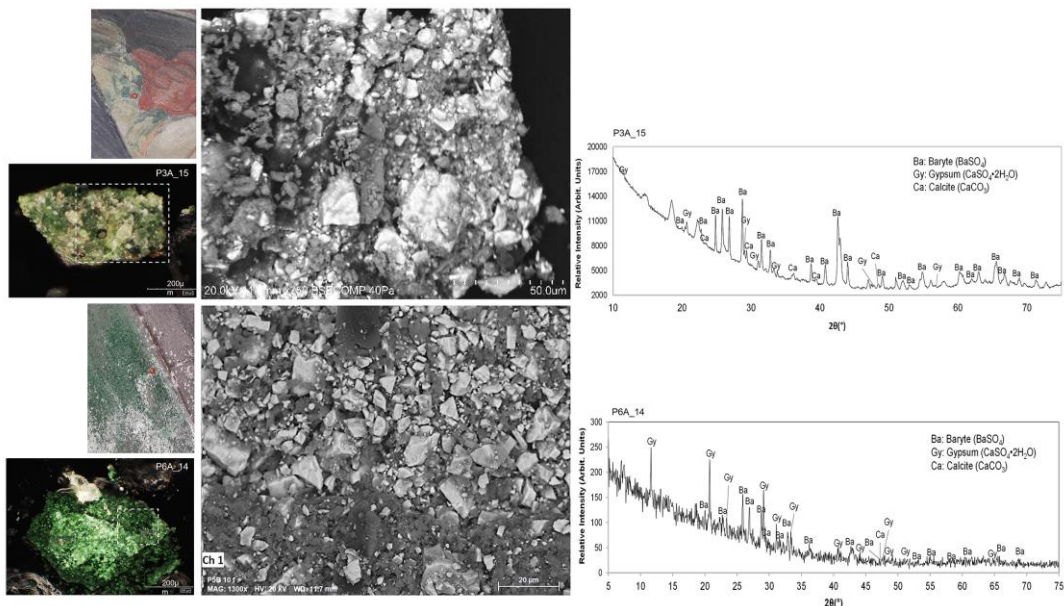
Fig. 10. On the outside, sampling location and OM-Vis of the paint surface of microsample P3A_15 and P6A_14 at 200×. On the center, BSE-SEM image of the paint surface showing particles (pigments and fillers) loose and exposed
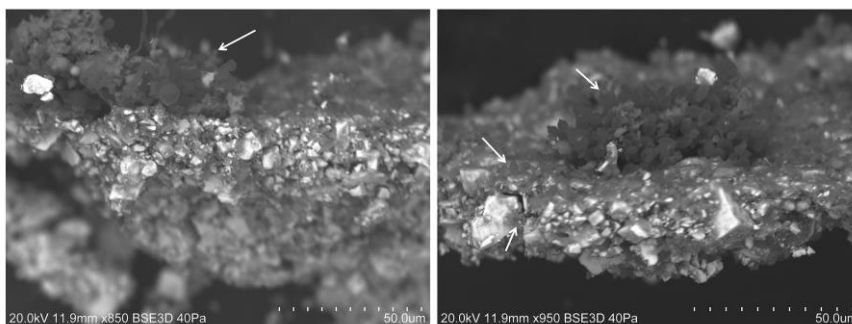

Fig. 11. Detail of microsample P5B_10 in profile by VP-BSE-SEM image showing signs of bio-contamination on the paint surface and near a loose particle (white arrows)

Beyond the presence of salts, it must also be noted that signs of bio-colonisation were observed by VP-BSE-SEM in one paint layer (Fig. 11). High relative humidity, pH, temperature, light, and biodegradable materials are the main factors that can trigger the appearance and growth of microorganisms [31-33]. Although a more in-depth study on the topic could not be carried out at this point, the traces of bio-colonisation may be linked to the past occurrence and permanence of humidity in the paintings [7]. The roughness of the paint

surfaces can also promote the capture of moisture and dirt deposits; rough surfaces are good hosts for microorganisms since they protect them from the wind and light radiation [31-33]. In addition to these factors, one must also add the past interventions of organic products used as adhesives, identified in the current and in a previous survey as vinyl polymers [7], which may have acted as substrates.

Conclusions

The present study offers for the first time an insight into the deteriorated green paint layers of one of the most impressive modern artworks, Almada Negreiros, painted in 1945 on the riverside of Lisbon. Both natural and industrial synthetic pigments were found in a restricted colour palette enriched with mixtures with other chromophores such as Fe-based pigments, calcium carbonates, and carbon black. Clinochlore, a mineral less commonly reported for green earths, was found, as well as the green synthetic organic pigments PG 8 and PG 1. The two latter are totally unconventional for a fresco's traditional chromatic palette, and their presence in mural artworks from the first half of the 20th century is quite exceptional and, to the author's knowledge, reported here for the first time. Both were synthesised in the first half of the 20th century, but further research will be conducted to ascertain their authenticity as paint materials originally used by Almada Negreiros and not as subsequent retouch paint products.

In regard to the decay mechanisms, the main hypothesis raised for the powdering and flaking of the green paint layers is that the disruptive presence of gypsum found in most paint layers probably originated from both intrinsic and extrinsic sources. However, the drawbacks of the painting techniques used and the impact of bioactivity cannot be disregarded at this point, meaning that further research must be undertaken to reach firm conclusions.

Acknowledgments

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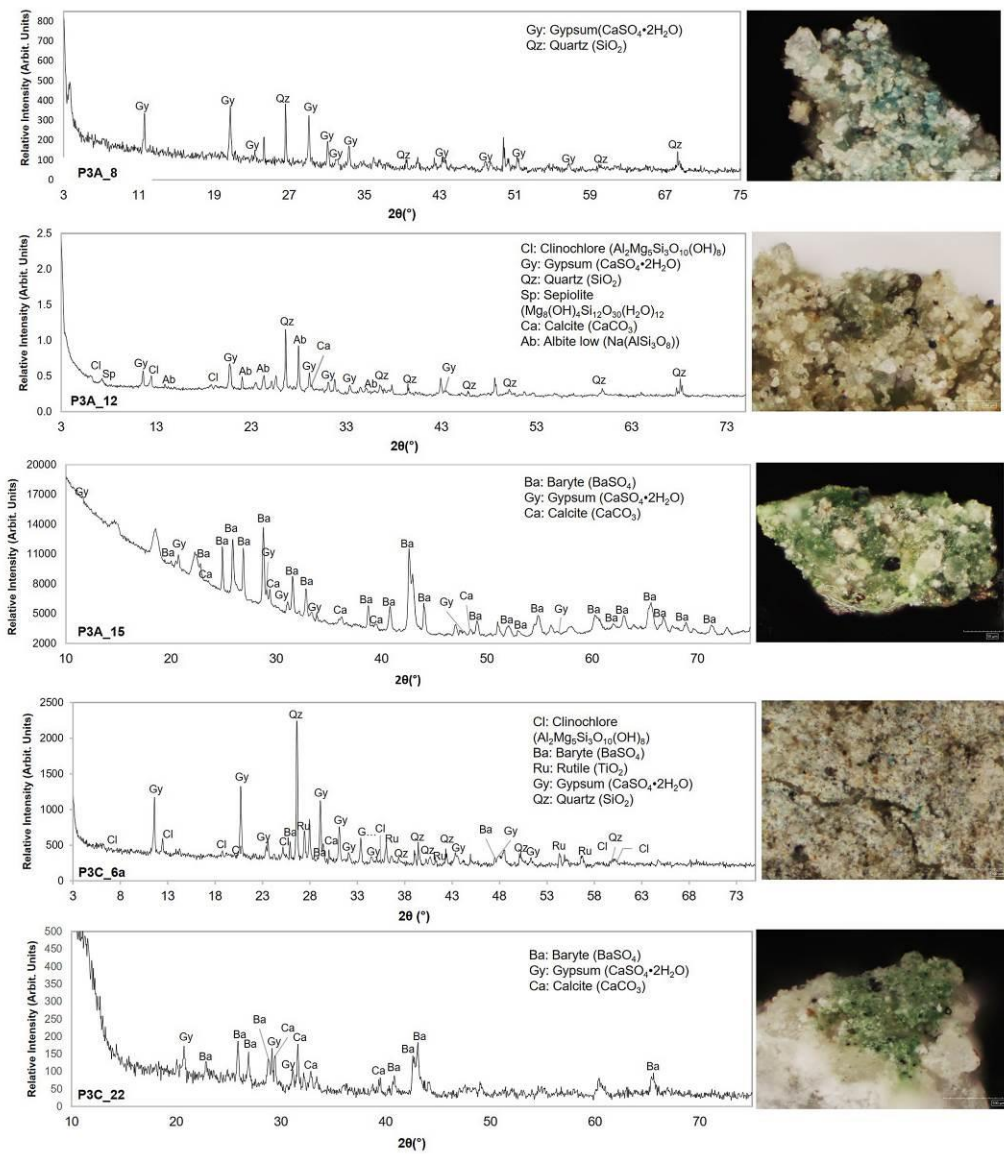
Appendix A. Micro sampling location
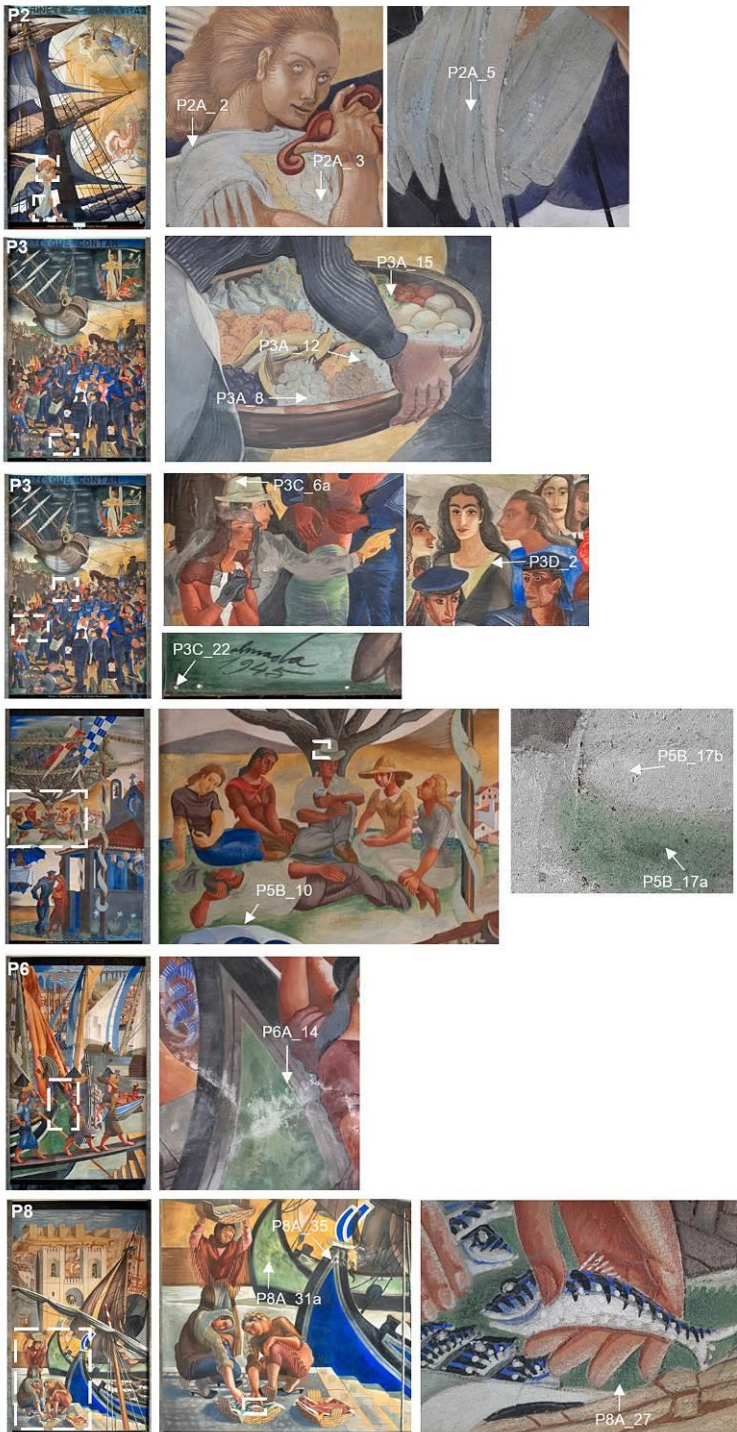
Appendix B. μ-XRD diffractograms of micro samples

Appendix B. μ-XRD diffractograms of micro samples