Chemical characterization of black stains on mural paintings with granite support from churches of Northern Portugal

Bruno Campos[1], Alexandra Marco[2], Sara Valadas[3], Iuliu Bobos[4], Eduarda Vieira[2], Manuela Pintado[1], Patrícia Moreira[1,2]

1 CBQF Centre for Biotecnology and Fine Chemistry, Universidade Católica Portuguesa
2 CITAR Research Centre for Science and Technology of the Arts, Universidade Católica Portuguesa
3 Laboratory HERCULES, School of Sciences and Technology, University of Évora
4 Institute of Earth Sciences (ICT) – Geology Centre of the University of Porto (CGUP)

CATÓLICA SCHOOL OF ARTS PORTO

Introduction

Mural paintings are art elements inseparable from the architectural monument which aids to define the cultural identity of a country and contribute to the economic development of their implantation regions[1,2].

The main problems associated to mural paintings, inside churches, are intrinsically inherent to the deterioration phenomena, namely, biocolonisation and physical-chemical weathering leading to aesthetical alterations and weakening the mechanical properties of materials[3].

During recent surveys, black stains were detected in 15th-16th centuries mural paintings and respective granite support in several Romanic churches in the north of Portugal.

The present poster intends to elucidate the chemical composition of black stains on the granite support in order to establish the hypothetical relation between the black stains on mural painting and their support.

Goals & Methods

This research work is part of *Bio4mural,* a project aiming at the development of innovative solutions for cleanings and preventive conservation of mural paintings. In order to develop cleaning and preventive solutions, chemical characterization of pigmentation on the granite support and its relationship with the mural painting is a crucial task. The fulfillment of this task has required the selection of cases studies, sample collecting protocols and application of characterization techniques *in situ* and in laboratory. The used methods are briefly described below:

- **Cases studies:** Church of Vila Marim and Church of Folhadela (district of Vila Real);
- **Samples collecting:** scrapping with scalpel;
- ***In situ*:** Digital Microscopy (Dino-lite Pro-X); Colorimetry (Visible spectrometer Datacolor Mercury 3000) and EDXRF (Bruker Tracer III/IV SD);
- **Laboratory:** FT-IR (Bruker Tensor 27 spectrometer).

Results & Discussion

Framework

The two cases studies selected were the Church of Vila Marim or Sta. Marinha (Fig. 1a) and the Church of Folhadela or St. Tiago (Fig 1b). The criteria was based on the blackening of chromatic layer and granite and the geographical proximity (district of Vila Real). The two Romanic churches are made of coarse-grained granite, probably built between 13th-14th century. The interior walls are partially covered with mural paintings with several campaigns and dated from the 15th century, being attributed to the painter Arnão.

Fig. 1 Pictures of the selected case studies. (a.) On the left the church of Vila Marim and (b.) on the right the church of Folhadela. The expanded pictures represent the areas of sampling and analysis on granite. Wall A = left wall; Wall C = right wall.

Digital Microscopy & Colorimetry

The typology of pigmentation found in the expanded pictures of Fig. 1 can be designated by stains (Vila Marim and wall A of Folhadela) and by dots (wall C of Folhadela). The colour observed varies from brown (Fig. 2a) to a bright black-purple (Fig. 2b) and images taken by a digital microscope showed the presence of hyphae (Fig. 2c) in some samples, revealing the possible influence of fungi in the formation of the pigmentation[4].

Fig. 2 Digital microscopy images (435x magnification) of a brown (a) and a black-purple stain (b) of wall A and a brown dot with hyphae found in wall C (c).

The CIELAB parameters (Table 1), obtained by colorimetry, and the calculated ΔE^*_{ab} ($\Delta E^*_{ab} = [(\Delta L^2) + (\Delta a^2) + (\Delta b^2)]^{1/2}$) for black-purple (9,05) and brown (15,23) pigmentation shows some similarity between the pigmentation of Vila Marim (VM) and Folhadela (F).

Pigmentation	L	a	b	ΔL	Δa	Δb	ΔE^*_{ab}
Black-Purple (VM)	17,10	0,52	1,91	8,57	1,90	2,18	9,05
Black-Purple (F)	25,67	2,42	4,09				
Brown (VM)	22,20	0,68	3,08	8,23	6,09	11,29	15,23
Brown (F)	30,43	6,77	14,37				

Table 1. CIELAB colour coordinates for Vila Marim and Folhadela samples. L = lightness; a = red/green value and b = yellow/blue value.

EDXRF

The EDXRF analysis made *in situ* on brown and black-purple pigmentation and granite revealed the presence of some typical inorganic elements, such as Al, Ca, Fe, K and Si (Table 2). For brown pigmentation the higher percentage can be attributed to Fe (28%-77%) and for black-purple to Mn (8%-51%). The possible formation of pigmentation can be assigned to the efflorescence of Fe (probably from biotite) and Mn soluble ions through the granite, forming at the surface Fe and Mn oxides. Some authors ascribed the oxidation of Mn (II into III/IV) to the presence of a microbial community[5] and Mn and Fe are also found in Fungal peroxidases (heme plus cofactor). The element K (2%-14%) and Ca (1%-23%) are also elements with representativity, mainly for granite, probably, due to the presence of the potassic- and calcic-feldspars minerals and the calcium carbonate of the lime mortar.

		Relative Abundance (%)																	
Church	Pigmentation	Al	Ar	Ca	Cl	Cu	Fe	K	Mn	Ni	P	Pb	Pd	Rh	S	Si	Sr	Ti	Zn
Vila Marim	Brown	0,20	5,15	7,83	0,48	2,33	28,97	6,16	21,14	6,00	0,05	0,71	4,23	10,03	0,12	2,41	1,21	2,33	0,66
	Black-Purple	0,14	3,75	9,41	0,33	1,15	22,88	2,82	39,90	4,52	0,04	0,33	3,18	7,17	0,10	1,39	0,92	1,43	0,54
	Granite	0,21	7,14	21,10	0,39	2,26	30,46	5,84	0,76	7,28	0,00	1,90	4,71	13,03	0,01	1,54	0,83	2,37	0,17
Folhadela	Brown (wall A)	0,18	3,59	21,05	1,12	1,14	28,56	9,71	11,06	6,43	0,05	0,41	3,74	3,66	4,78	0,05	2,65	0,36	1,47
	Black-Purple (wall A)	0,07	2,52	5,25	0,52	0,90	21,86	3,70	50,65	3,43	0,03	0,42	2,50	2,12	3,24	0,04	1,03	0,38	1,32
	Brown (wall C)	0,04	2,61	1,41	0,30	1,12	76,69	6,59	0,92	1,96	0,02	1,05	1,45	1,21	3,08	0,06	0,28	0,44	0,76
	Black-Purple (wall C)	0,33	5,13	5,98	1,57	2,12	28,83	13,19	8,93	7,83	0,06	0,77	5,79	5,39	6,53	0,08	5,29	0,55	1,62
	Granite	0,41	3,87	22,82	1,17	1,53	29,01	11,82	1,73	6,85	0,02	0,33	4,48	4,70	5,45	0,11	4,02	0,33	1,36

Table 2. Relative abundance (%) of atomic elements present in brown and black-purple pigmentation and granite.

FT-IR

The pigmentation analysed by FT-IR (Fig. 3) was collected by scrapping and thoroughly selected by optical microscope. The presence of carbonaceous compounds is indicated at 2924 and 2851 cm^{-1} (νCH3/νCH2) and the νOH at 3433 cm^{-1}. A sharp stronger band at 1385 cm^{-1} is related to the ν3 stretching mode of NO_3^-. The weak bands at 1150 and 1100 cm^{-1} are typical of gypsum bands. The range of bands between 1034 and 690 cm^{-1} may be ascribed to the νSi-O of different minerals, probably Kaolinite (1034 cm^{-1}), Quartz (783, 721 and 690 cm^{-1}) and Orthoclase (640 cm^{-1}). The bands at 582 and 532 cm^{-1} suggest the presence of νFe-O, probably Magnetite and Hematite, respectively. In the literature[6] was also found a reference to a Mn oxide mineral at 532 cm^{-1}.

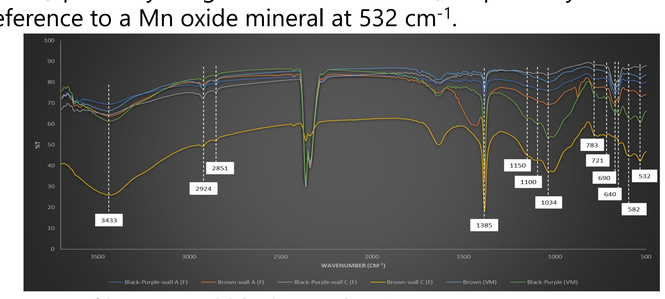

Fig. 3 FT-IR spectrum of brown and black-purple pigmentation.

Conclusions

The blackening of mural paintings and the respective granite support is a peculiar deterioration of the constituent materials. The Church of Vila Marim and the Church of Folhadela are two examples of this phenomenon and have in common the proximity (district of Vila Real) and the building blocks are essentially made of granite. The most abundant type of blackening are stains, pigmentated dots were mostly found in wall C (Folhadela). Moreover, mostly of hyphae images were also found in wall C, suggesting the possible formation of pigmentated dots by microbial influence. The CIELAB colour coordinates show some similarity between brown and black-purple pigmentation of both churches and XRF showed that Fe and Mn are the most abundant elements in brown and black-purple pigmentation, respectively, possibly by efflorescence of their soluble salts and the formation of Fe and Mn oxides at the surface. The FT-IR analysis may support this hypothesis showing a possible presence of Fe and Mn oxides (at 582 and 532 cm^{-1}) and a probable blackening attributed to a microbial community due to the carbonaceous assignments (at 2924 and 2851 cm^{-1}).

References

1. Rosewell, R. (2014). *Medieval wall paintings*. Oxford: Shire Publ.
2. Palmeirão, J. *et al* (2018). The shift of paradigm when religious art works become heritage: The dilemma of material vs. immaterial significance. An overview of Portuguese Reliquaries and Mural Paintings. In: U. Schädler-Saub and B. Szmygin, ed., *CONSERVATION ETHICS TODAY: ARE OUR CONSERVATION-RESTORATION THEORIES AND PRACTICE READY FOR THE 21ST CENTURY?*. Lublin: International Scientific Committee for Theory and Philosophy of Conservation and Restoration ICOMOS, pp.375-379.
3. Costantini, I., Castro, K. and Madariaga, J. (2018). Portable and laboratory analytical instruments for the study of materials, techniques and environmental impacts in mediaeval mural paintings. *Analytical Methods*, 10(40), pp.4854-4870.
4. De la Rosa, J., Martin-Sanchez, P., Sanchez-Cortes, S., Hermosin, B., Knicker, H. and Saiz-Jimenez, C. (2017). Structure of melanins from the fungi Ochroconis lascauxensis and Ochroconis anomala contaminating rock art in the Lascaux Cave. *Scientific Reports*, 7(1).
5. Saiz-Jimenez, C., Miller, A., Martin-Sanchez, P. and Hernandez-Marine, M. (2012). Uncovering the origin of the black stains in Lascaux Cave in France. *Environmental Microbiology*, 14(12), pp.3220-3231.
6. Casanova Municchia, A., Bartoli, F., Bernardini, S., Caneva, G., Della Ventura, G., Ricci, M., Boun Suy, T. and Sodo, A. (2016). Characterization of an unusual black patina on the Neang Khmau temple (archaeological Khmer area, Cambodia): a multidisciplinary approach. *Journal of Raman Spectroscopy*, 47(12), pp.1467-1472.

Acknowledgements

PROGRAMA OPERACIONAL CAPITAL HUMANO POCH · PORTUGAL 2020 · UNIÃO EUROPEIA Fundo Social Europeu · FCT Fundação para a Ciência e a Tecnologia · CATÓLICA PORTO ESCOLA DAS ARTES · CENTRO DE INVESTIGAÇÃO EM CIÊNCIA E TECNOLOGIA DAS ARTES – CITAR · CITAR · CATÓLICA PORTO ESCOLA SUPERIOR DE BIOTECNOLOGIA · CENTRO DE BIOTECNOLOGIA E QUÍMICA FINA – CBQF Laboratório Associado · CBQF · E-RIHS.pt EUROPEAN RESEARCH INFRASTRUCTURE FOR HERITAGE SCIENCE portuguese platform · LABORATORIO HERCULES HERANÇA CULTURAL: ESTUDOS E SALVAGUARDA · UNIVERSIDADE DE ÉVORA