SEARCHING FOR A SUITABLE CHROMATIC REINTEGRATION TECHNIQUE FOR OUTDOOR EXPOSED WALL PAINTINGS

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INTRODUCTION

The appearance of *lacunae* (i.e. paint loss) is a recurrent deterioration form in historical wall paintings, especially when they are partially or completely outdoor-exposed as they are subjected to environmental factors (temperature, relative humidity, solar radiation, rain, etc.). To aesthetically solve this issue, professionals in the conservation of Cultural Heritage field carry out chromatic reintegrations, i.e. the application of a new layer of paint (pigment + binder) where there is paint loss. However, not much is known regarding the materials that are currently being used in this kind of restoration intervention in terms of chemical compatibility and long-term durability [1].

In view of the scarce scientific knowledge in this field, it is appropriate to appoint this matter. In this regard, the use of silica-based techniques has regained popularity in Mediterranean countries, though no study has evaluated this procedure as a chromatic reintegration technique. Thus, an aqueous dispersion of nano-silica was evaluated due to its apparent inalterability and high resistance properties.

MATERIALS AND METHODS

MOCK-UP PREPARATION

Mock-ups (15x10cm) were prepared following traditional wall painting techniques: a lime-based mortar composed of two layers (*arriccio*-inner layer + *intonaco*-outermost layer). After two months carbonation, chromatic reintegrations were applied.

Three silicate pigments were selected: egyptian blue (EG), lapis lazuli (LA) and ultramarine blue (UL). Pigments were mixed with an aqueous dispersion of nano-silica (Nano Estel®) as binder in a 1:1 volumen.

Digital photographs of painted surfaces before outdoor natural exposure: a) Egyptian blue (EG), b) lapis lazuli (LA) and c) ultramarine blue (UL).

NATURAL EXPOSURE

Spain physical map indicating the cities of Vigo and Granada.

Vigo (NW Spain)
Moderate temperature, high relative humidity, high rainfall and marine influence.

Granada (SE Spain)
Extreme temperatures, dry environment and highly contaminated.

ANALYTICAL TECHNIQUES

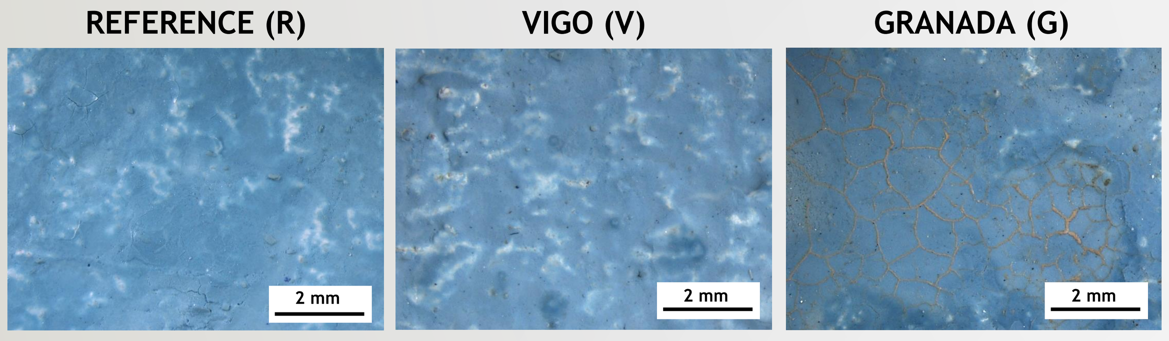
- Physical evaluation: stereomicroscopy, colour spectrophotometry and gloss measurements. Monitorization of colour was carried out every 50 days and the total colour change (ΔE^*_{ab}) was calculated.
- Mineralogical characterization: micro X-ray diffraction.
- Molecular characterization: Fourier-transform infrared spectroscopy (FTIR) in diamond crystal attenuated total reflection (ATR) mode.
- Textural and morphological characterization: scanning electron microscopy (SEM-EDS).

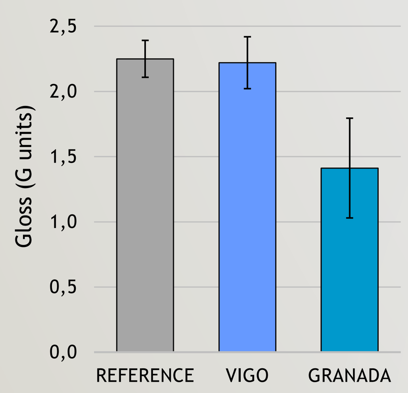
RESULTS AND DISCUSSION

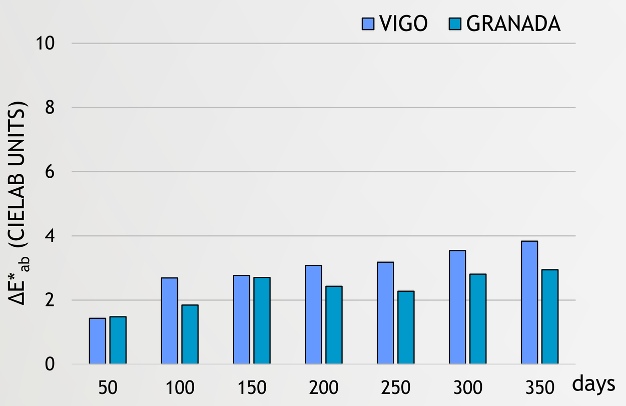
EGYPTIAN BLUE (EG)

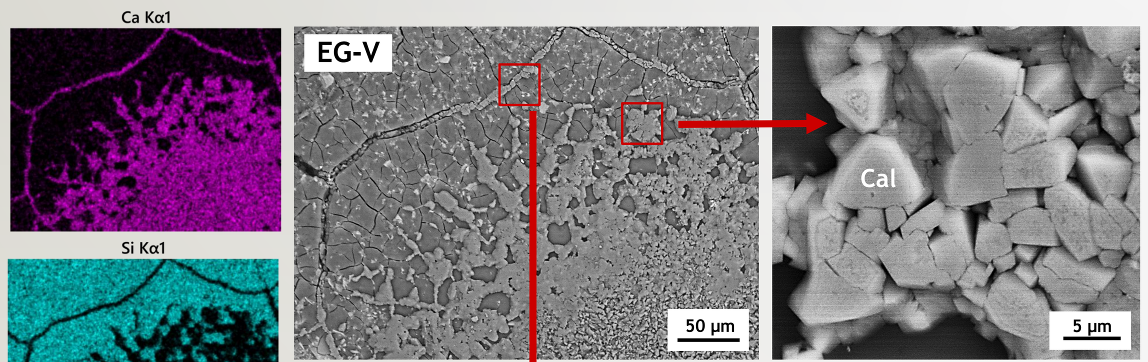
Ref. 100601 Egyptian blue	Raw pigment	Reference paint	After 1 year exposition in Vigo	After 1 year exposition in Granada
Mineralogical characterization by µXRD	**Cuprorivaite** ($CaCuSi_4O_{10}$); **Quartz** (SiO_2)	**Cuprorivaite** ($CaCuSi_4O_{10}$); **Calcite** ($CaCO_3$)	**Cuprorivaite** ($CaCuSi_4O_{10}$); **Calcite** ($CaCO_3$); **Gypsum** ($CaSO_4$)	**Cuprorivaite** ($CaCuSi_4O_{10}$); **Calcite** ($CaCO_3$); **Gypsum** ($CaSO_4$)

REFERENCE (R) VIGO (V) GRANADA (G)

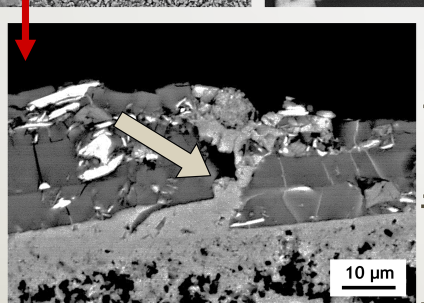




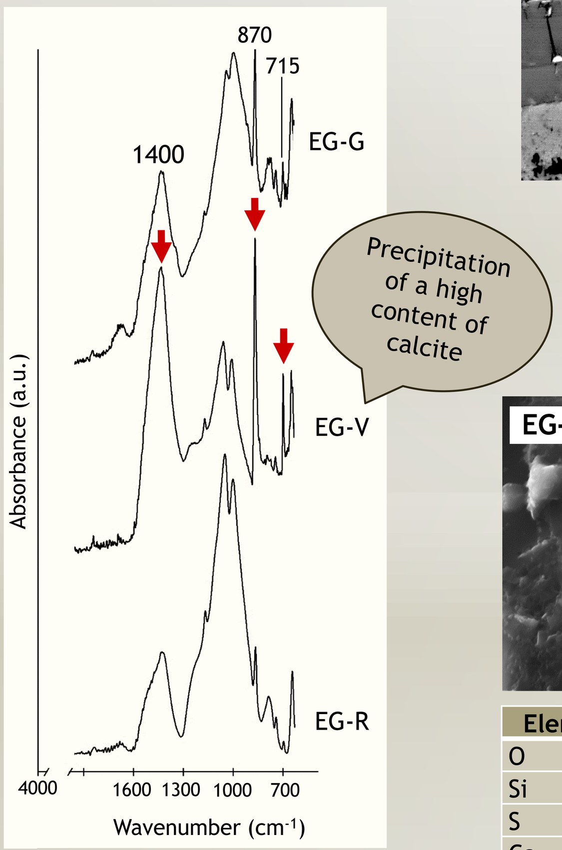




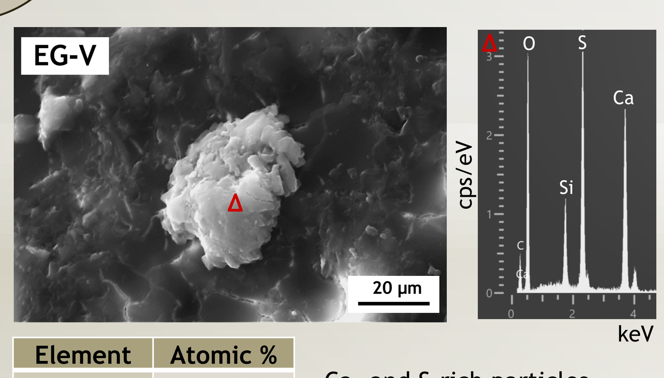
Ca-rich deposits were observed by SEM-EDS.



Does calcite come from the lime mortar and deposit on the surface?



1400, 870 and 715 cm^{-1} are related to CO_3^{2-} bonds (stretching, and asymmetrical and symmetrical bending) assigned to calcite.



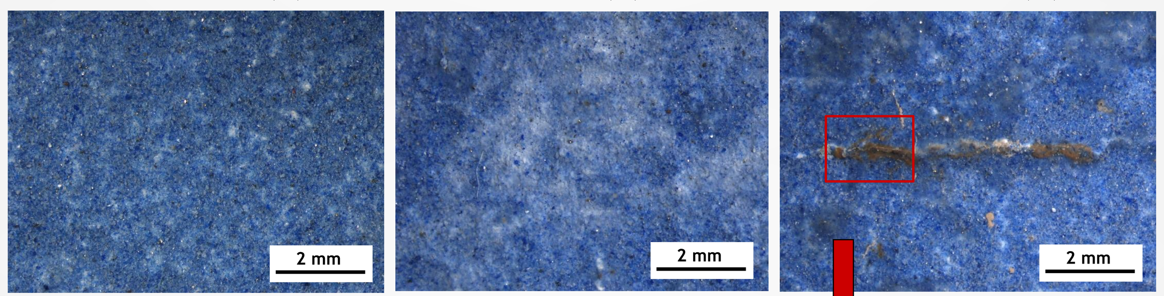
Element	Atomic %
O	63.92
Si	2.14
S	6.48
Ca	6.07
C	21.38
Total	100.00

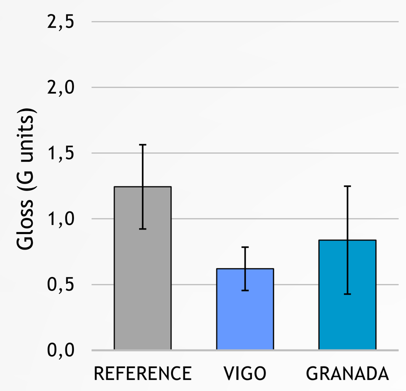
Ca- and S-rich particles on the surface with different habit (acicular or tabular).

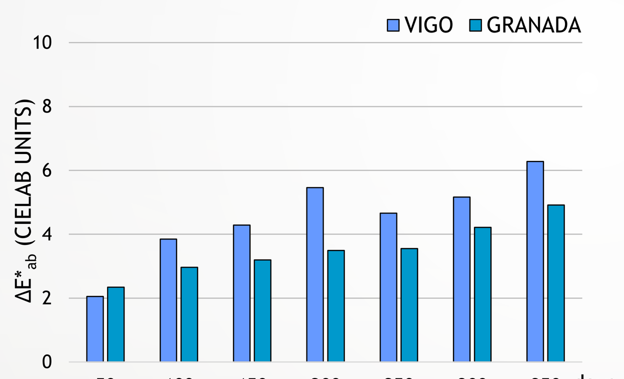
LAPIS LAZULI (LA)

Ref. 10510 Lapis lazuli	Raw pigment	Reference paint	After 1 year exposition in Vigo	After 1 year exposition in Granada
Mineralogical characterization by µXRD	**Lazurite** ($Na_3Ca(Al_3Si_3O_{12})S$); **Sodalite** ($Na_8Al_6Si_6O_{24}Cl_2$); **Calcite** ($CaCO_3$); **Diopside** ($CaMgSi_2O_6$); **Pyrite** (FeS_2); **Albite** ($(Na,Ca)(Si,Al)_4O_8$); **Muscovite** ($KAl_2Si_3AlO_{10}(OH)_2$); **Wollastonite** ($CaSiO_3$)	**Lazurite** ($Na_3Ca(Al_3Si_3O_{12})S$); **Sodalite** ($Na_8Al_6Si_6O_{24}Cl_2$); **Calcite** ($CaCO_3$); **Diopside** ($CaMgSi_2O_6$); **Pyrite** (FeS_2); **Muscovite** ($KAl_2Si_3AlO_{10}(OH)_2$)	**Lazurite** ($Na_3Ca(Al_3Si_3O_{12})S$); **Sodalite** ($Na_8Al_6Si_6O_{24}Cl_2$); **Calcite** ($CaCO_3$); **Diopside** ($CaMgSi_2O_6$); **Muscovite** ($KAl_2Si_3AlO_{10}(OH)_2$)	**Lazurite** ($Na_3Ca(Al_3Si_3O_{12})S$); **Sodalite** ($Na_8Al_6Si_6O_{24}Cl_2$); **Calcite** ($CaCO_3$); **Diopside** ($CaMgSi_2O_6$); **Muscovite** ($KAl_2Si_3AlO_{10}(OH)_2$)

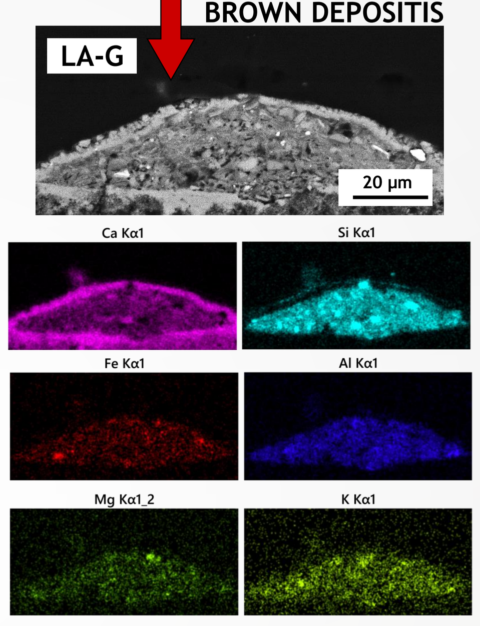
REFERENCE (R) VIGO (V) GRANADA (G)



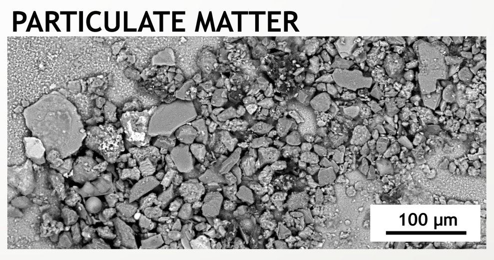




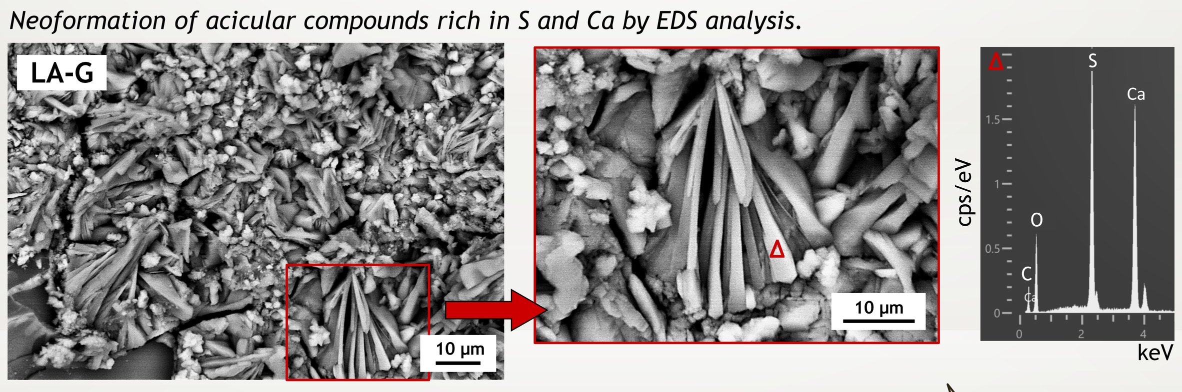
BROWN DEPOSITS

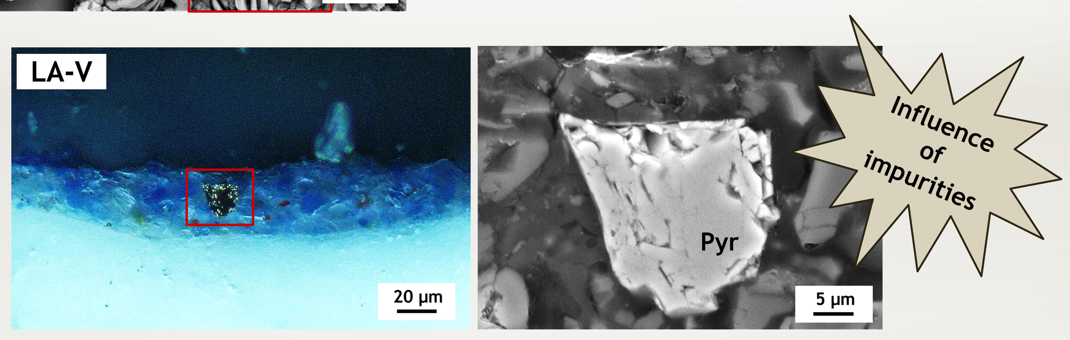


PARTICULATE MATTER



Neoformation of acicular compounds rich in S and Ca by EDS analysis.



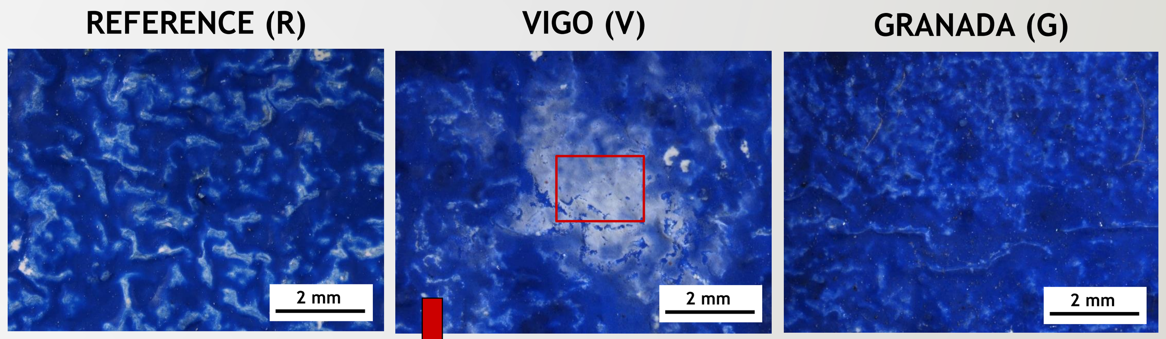


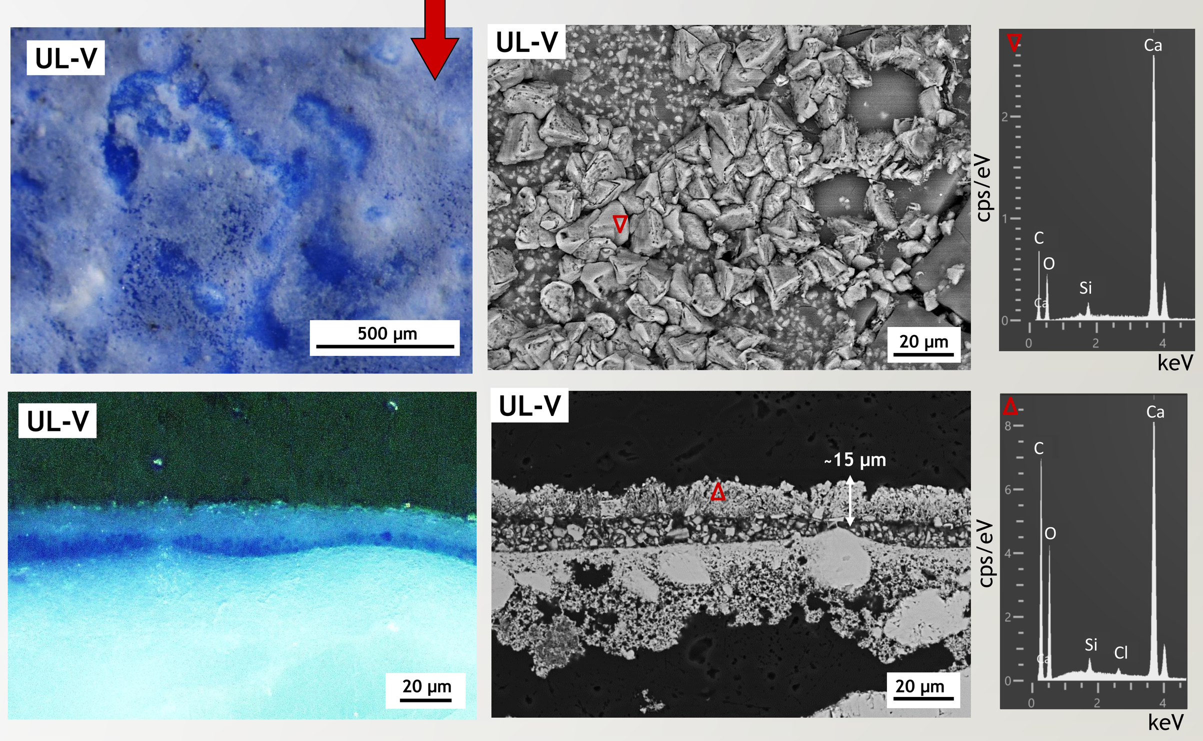
Optical microscopy allowed the observation of black particles within the paint layer. S and Fe were detected by EDS and identified as pyrite (as detected by µXRD).

ULTRAMARINE BLUE (UL)

Ref. 45010 Ultramarine blue	Raw pigment	Reference paint	After 1 year exposition in Vigo	After 1 year exposition in Granada
Mineralogical characterization by µXRD	**Lazurite** ($Na_3Ca(Al_3Si_3O_{12})S$); **Sodalite** ($Na_8Al_6Si_6O_{24}Cl_2$); **Nepheline** ($NaAlSiO_4$); **Kaolinite** ($Al_2Si_2O_5(OH)_4$)	**Lazurite** ($Na_3Ca(Al_3Si_3O_{12})S$); **Kaolinite** ($Al_2Si_2O_5(OH)_4$); **Calcite** ($CaCO_3$); **Portlandite** ($Ca(OH)_2$)	**Lazurite** ($Na_3Ca(Al_3Si_3O_{12})S$); **Nepheline** ($NaAlSiO_4$); **Kaolinite** ($Al_2Si_2O_5(OH)_4$); **Calcite** ($CaCO_3$)	**Lazurite** ($Na_3Ca(Al_3Si_3O_{12})S$); **Nepheline** ($NaAlSiO_4$); **Kaolinite** ($Al_2Si_2O_5(OH)_4$); **Calcite** ($CaCO_3$)

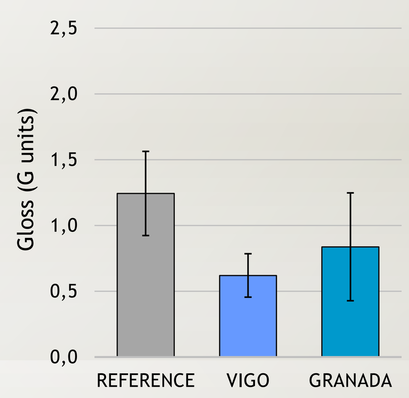
REFERENCE (R) VIGO (V) GRANADA (G)

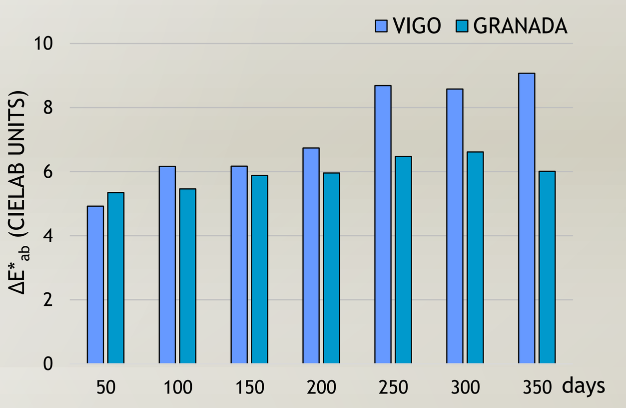


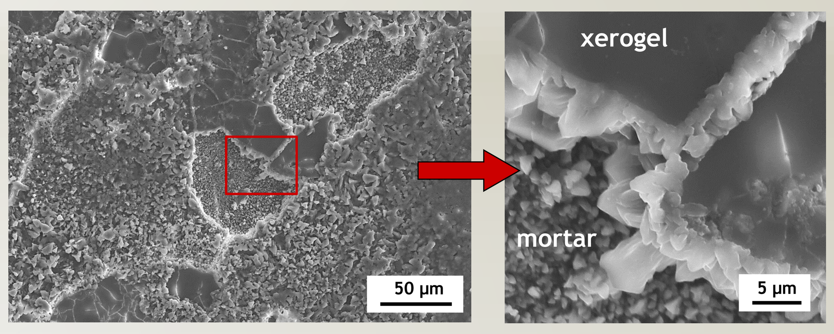


Observations by stereo and optical microscopy of the surface and cross-sections allow the visualisation of a whitish layer of considerable thickness (~15 µm).

SEM-EDS allowed the identification of a calcite layer on the paint layer.







Calcite grains were found on and below the xerogel.

General discussion

Mock-ups exposed in **Vigo** underwent higher colour variations and a slight gloss reduction. This could be due to a higher presence of Ca-rich efflorescences, as observed in the FTIR spectra. Nevertheless, these deposits were observed on all paintings, regardless of the pigment and location. Most probably, calcite originated from the lime mortar.

All the paint mock-ups exposed in **Granada** presented brown deposits and particulate matter on the surface (quartz, calcite, dolomite, phyllosilicates, etc. as reported in [2]). This surely influenced the total colour variation (ΔE^*_{ab}) of paintings in Granada.

Gypsum ($CaSO_4$) was present in all samples regardless of pigment and location. This could trigger decay processes on the historical wall painting.

CONCLUSION

- ❖ In general, calcite deposits were found on the surface of all painting, forming from the lime substrate. Those Vigo-exposed presented more, which undoubtley induced the higher colour change when compared to the samples exposed in Granada.
- ❖ The presence of impurities in lapis lazuli (natural pigment) such as pyrite (FeS_2) could determine future colour variations, endangering the colour of our chromatic reintegration.

[1] Jiménez-Desmond, D., Pozo-Antonio, J. S., Arizzi, A. (2024). *Present and future of chromatic reintegrations of wall paintings.* Journal of Cultural Heritage, 67, 237-247.

[2] Horemans, B., Cardell, C., Bencs, L., Kontozova-Deutsch, V., De Wael, K., & Van Grieken, R. (2011). *Evaluation of airborne particles at the Alhambra monument in Granada, Spain.* Microchemical Journal, 99(2), 429-438.