PRELIMINARY EVALUATION OF NANO-SILICA-BASED CHROMATIC REINTEGRATIONS ON FRESCOES

Daniel Jiménez-Desmond[1], J. Santiago Pozo-Antonio[1] and Anna Arizzi[2]
1) CINTECX, GESSMin group, School of Mining and Energy Engineering, University of Vigo, 36310 Vigo, Spain
2) Dpto. of Mineralogy and Petrology, Faculty of Science, University of Granada, 18071 Granada, Spain

INTRODUCTION

In outdoor exposed wall paintings, lacuna is one of the main deterioration forms where chromatic reintegration treatments are required. Nowadays, the most recommended binder for chromatic reintegration related to outdoor wall paintings is silica-based paint, that is a mixture of pigments with a silica binder. The traditional methods are those based on potassium and sodium silicate. However, while it is known that potassium and sodium silicates can lead to the formation of salts, the behaviour of nano-sized silica for chromatic reintegration has been vaguely studied. Therefore, a preliminary study has been carried out to analyse the physical compatibility between fresco paintings and their nano-size silica-based chromatic reintegrations.

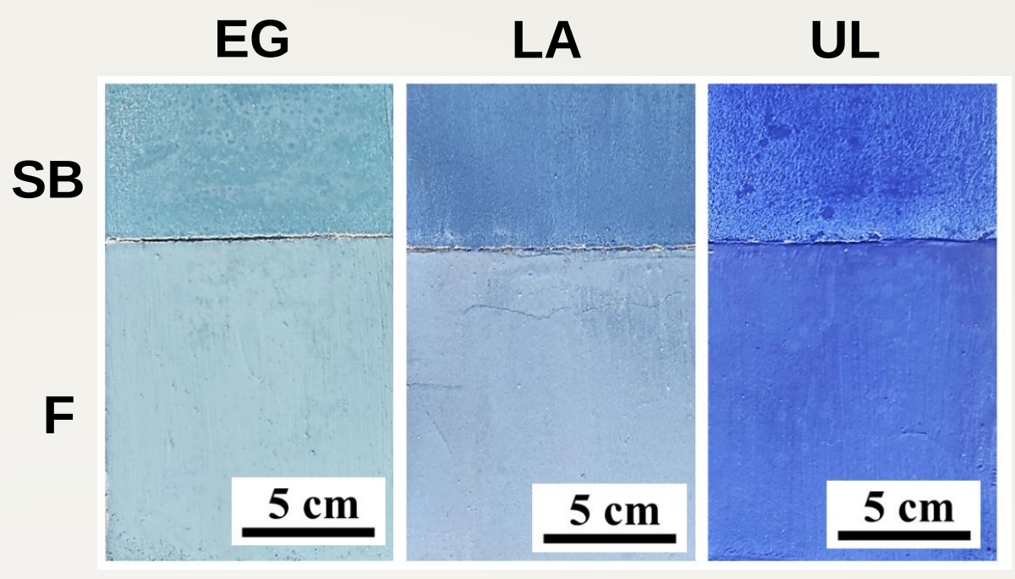
MATERIALS AND METHODS

Fresco paint mock-ups (F) were prepared following traditional recipes while chromatic reintegrations (SB) were carried out with an aqueous colloidal dispersion of nano-sized silica (Nano Estel). The pigment selection criterium was based on colour and historic period of use (Antiquity, Middle Age and 19th century onwards):

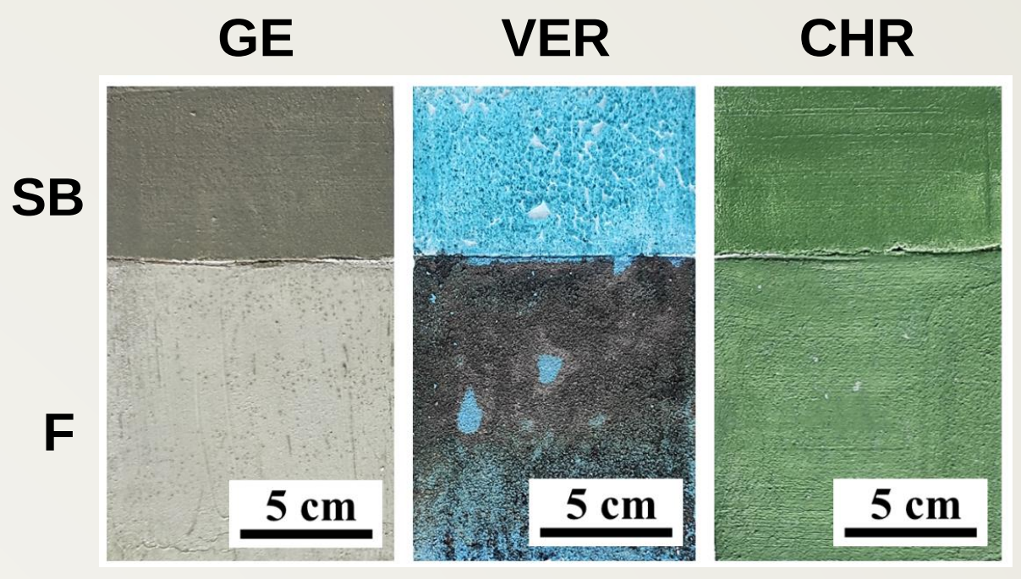
- Blue pigments (B) → egyptian blue (EG), lapis lazuli (LA) and ultramarine blue (UL).
- Green pigments (G) → green earth (GE), verdigris (VER) and chromium green (CHR).
- Red pigments (R) → cinnabar (CIN), vermilion (VER) and mars red (MAR).

This compatibility was studied from a physical point of view: stereomicroscopy (SM), colour spectrophotometry, measurements of gloss, roughness and hydrophobicity. They were also characterized by means of X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM-EDS).

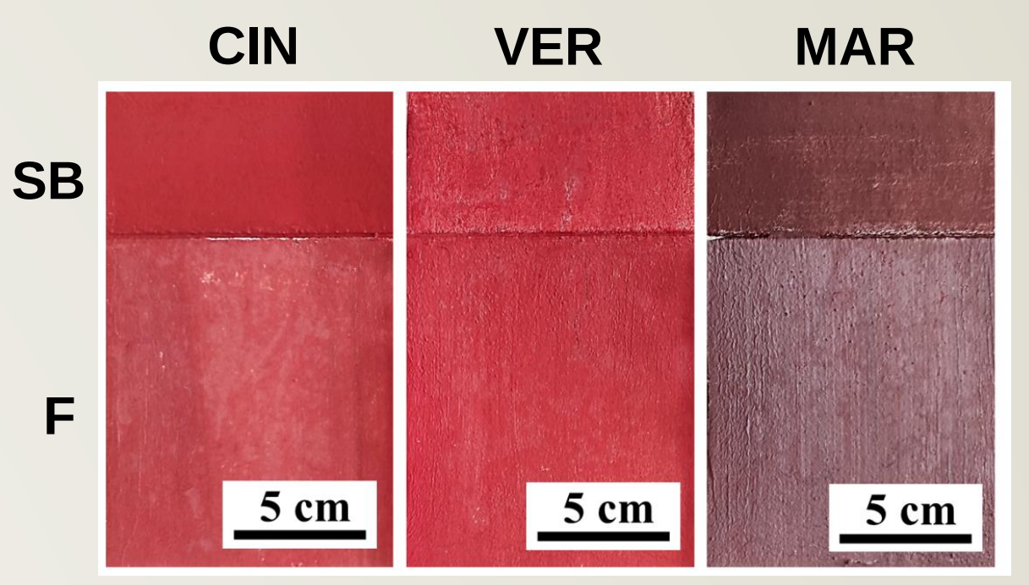
BLUE PAINTINGS (B)



GREEN PAINTINGS (G)



RED PAINTINGS (R)



RESULTS AND DISCUSSION

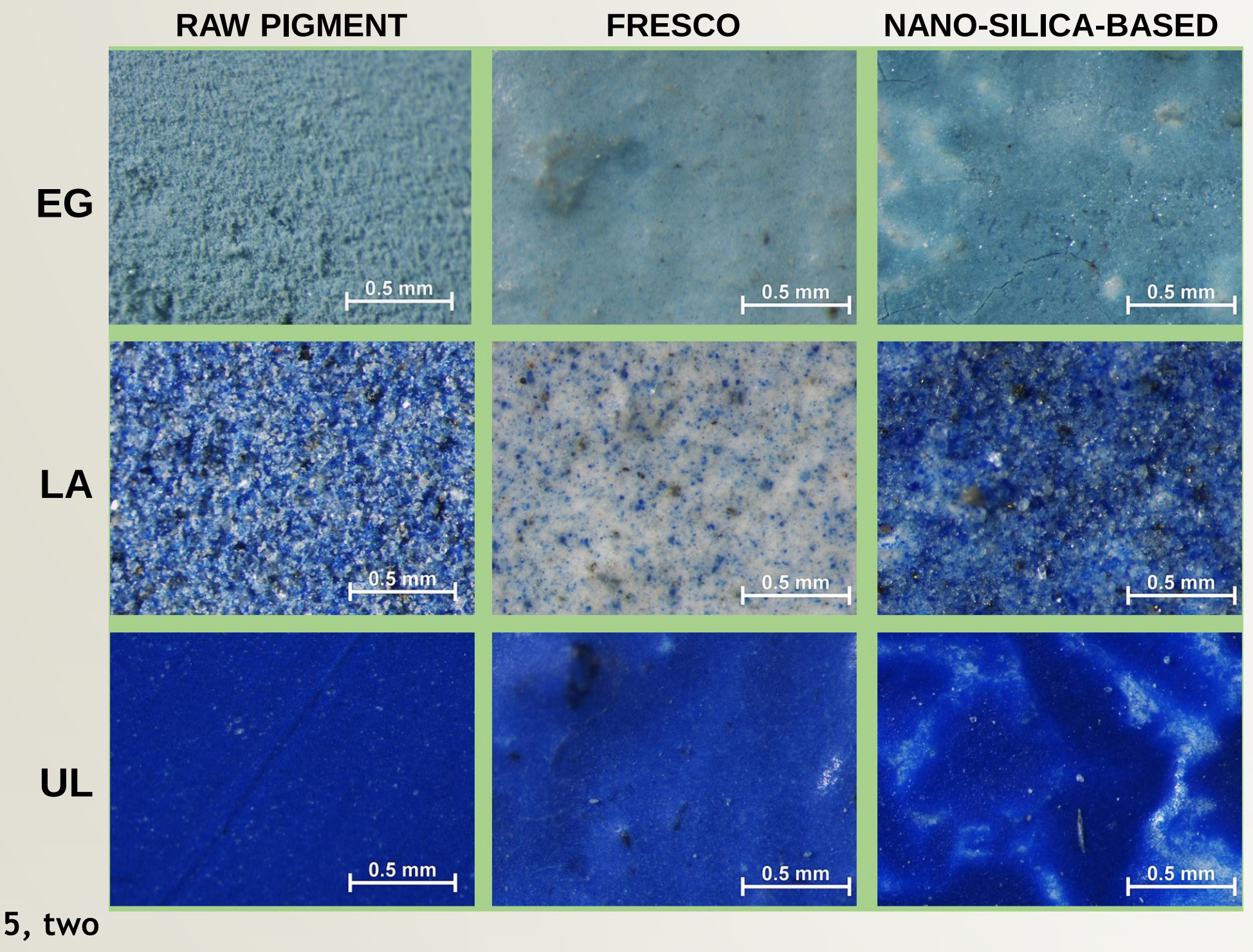
PREVIOUS CHARACTERIZATION OF THE RAW PIGMENTS

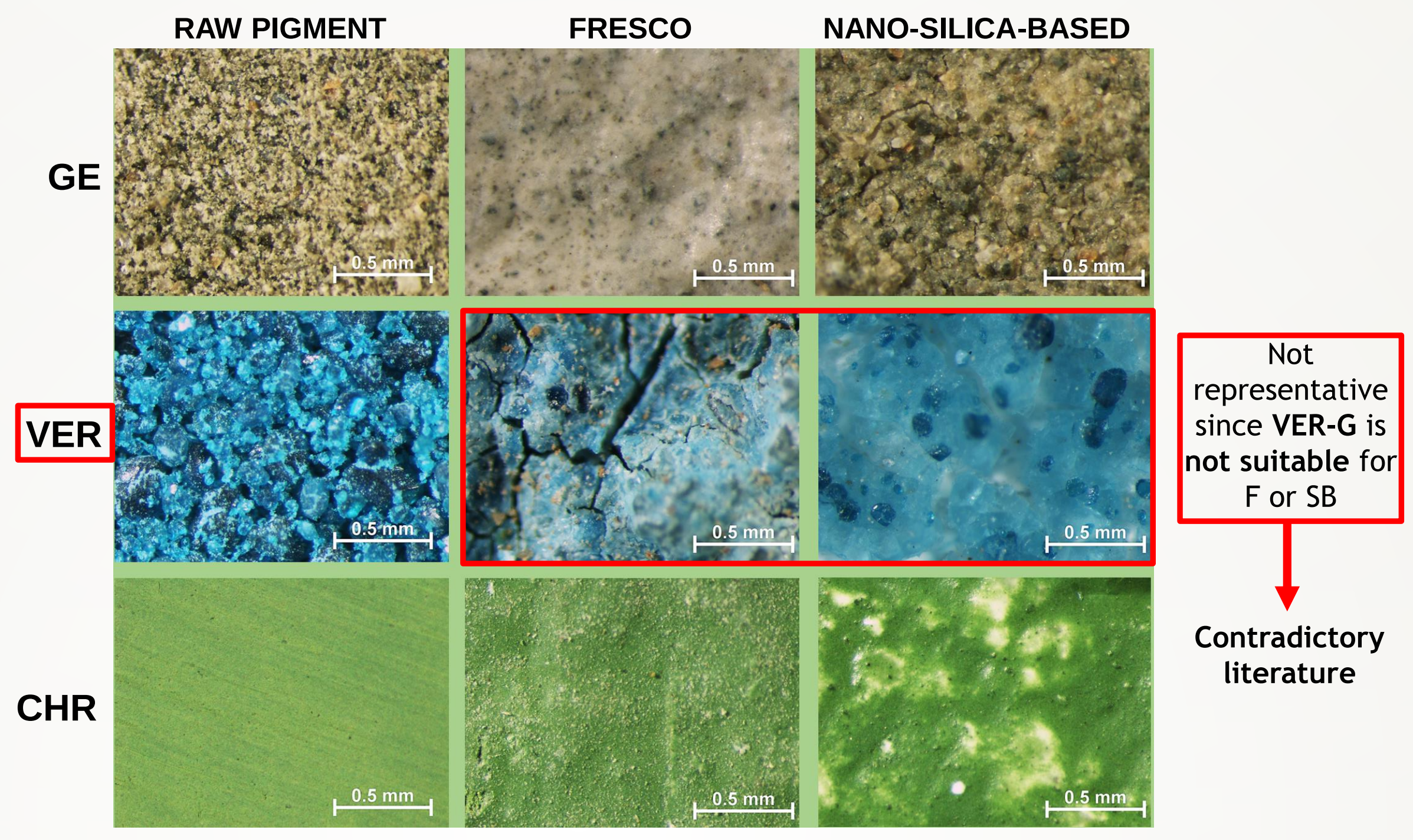
Supplier pigment code	Ref. 100601 Egyptian blue	Ref. 10510 Lapis lazuli	Ref. 45010 Ultramarine blue
Supplier pigment size (μm)	<10	Not supplied	2.50
Supplier pigment composition	Copper silicate from the mineral	Sodium calcium aluminium silicate	Sodium aluminium sulphur silicate
Authors' pigment size (μm)	0.25 – 55	0.3 – 100	0.7 – 35
Authors' pigment mineralogical composition	**Cuprorivaite** ($CaCuSi_4O_{10}$); **Quartz** (SiO_2)	**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** ($Na_8Al_6Si_6O_{24}Cl_2$); **Nepheline** ($NaAlSiO_4$); **Kaolinite** ($Al_2Si_2O_5(OH)_4$)

Supplier pigment code	Ref. 11010 Verona green earth	Ref. 44450 Verdigris	Ref. 44200 Chromium green
Supplier pigment size (μm)	0-80	Not supplied	0.3
Supplier pigment composition	Celadonite ($K(Mg,Fe)Fe^{3+}Si_4O_{10}(OH)_2$)	Copper (II)-acetate-1-hydrate ($C_4H_6CuO_4 \cdot H_2O$)	Chrome oxide (Cr_2O_3)
Authors' pigment size (μm)	0.3 – 125	0.3 – 550	0.15 – 30
Authors' pigment mineralogical composition	**Glauconite** ($(K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$); **Celadonite** ($K(Mg,Fe)Fe^{3+}Si_4O_{10}(OH)_2$); **Muscovite** ($KAl_2(AlSi_3O_{10})(OH)_2$); **Calcite** ($CaCO_3$); **Clinochlore** ($(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$); **Albite** ($NaAlSi_3O_8$); **Anorthite** ($CaAl_2Si_2O_8$); **Kaolinite** ($Al_2Si_2O_5(OH)_4$); **Montmorillonite** ($(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2 \bullet n(H_2O)$)	**Hoganite** ($Cu(CH_3COO)_2 \cdot H_2O$)	**Eskolaite** (Cr_2O_3)

Supplier pigment code	Ref. 10624 Chien t´ou Cinnabar	Ref. 42000 Vermilion	Ref. 48289 Red iron oxide
Supplier pigment size (μm)	<20	Not supplied	0.97
Supplier pigment composition	Cinnabar (HgS)	Mercuric sulfide (HgS)	Synthetic iron oxide (αFe_2O_3)
Authors' pigment size (μm)	0.15 – 35	0.15 – 40	0.15 – 40
Authors' pigment mineralogical composition	**Cinnabar** (HgS)	**Vermilion** (HgS)	**Hematite** (Fe_2O_3)

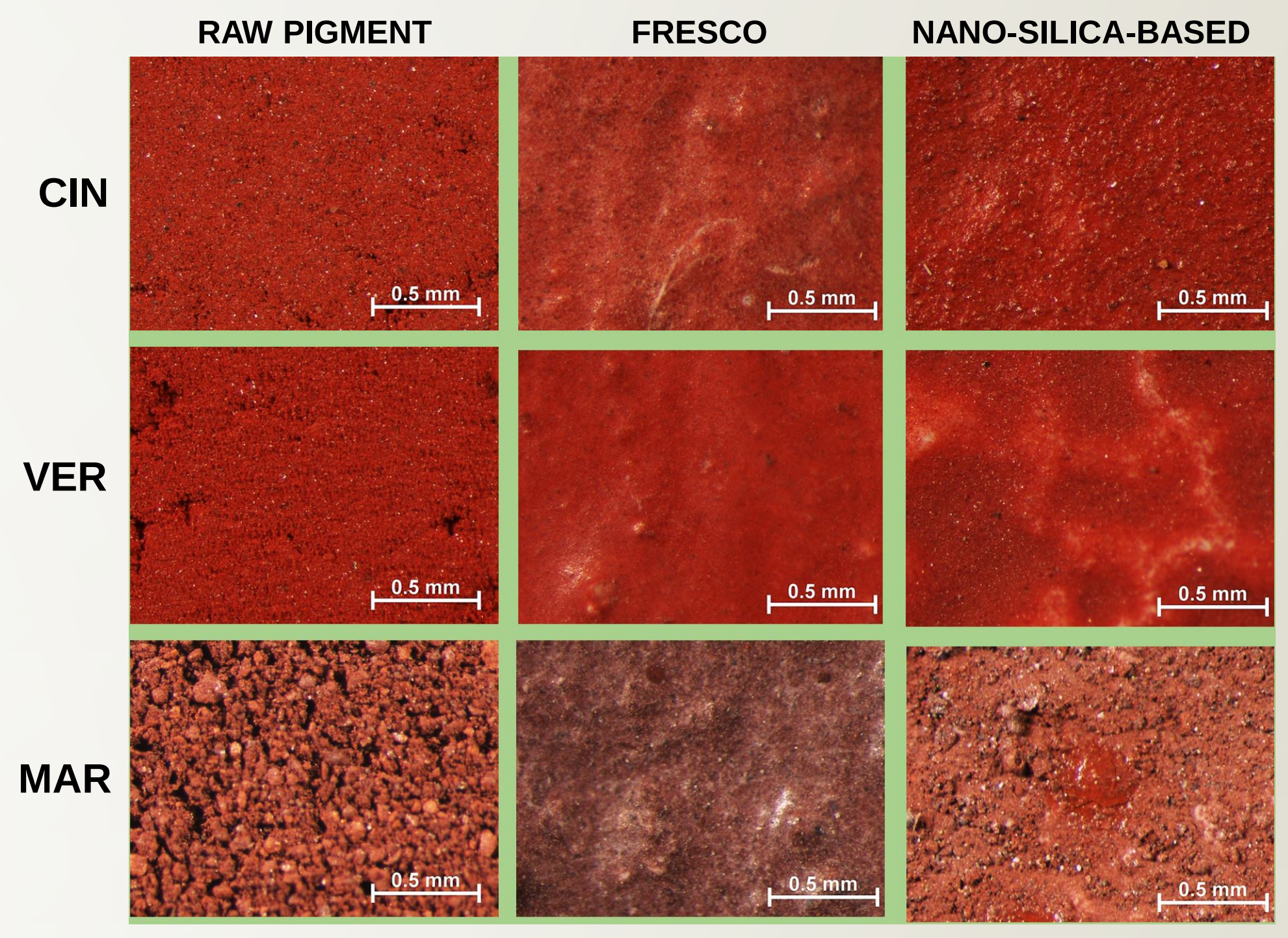
PHYSICAL COMPATIBILITY





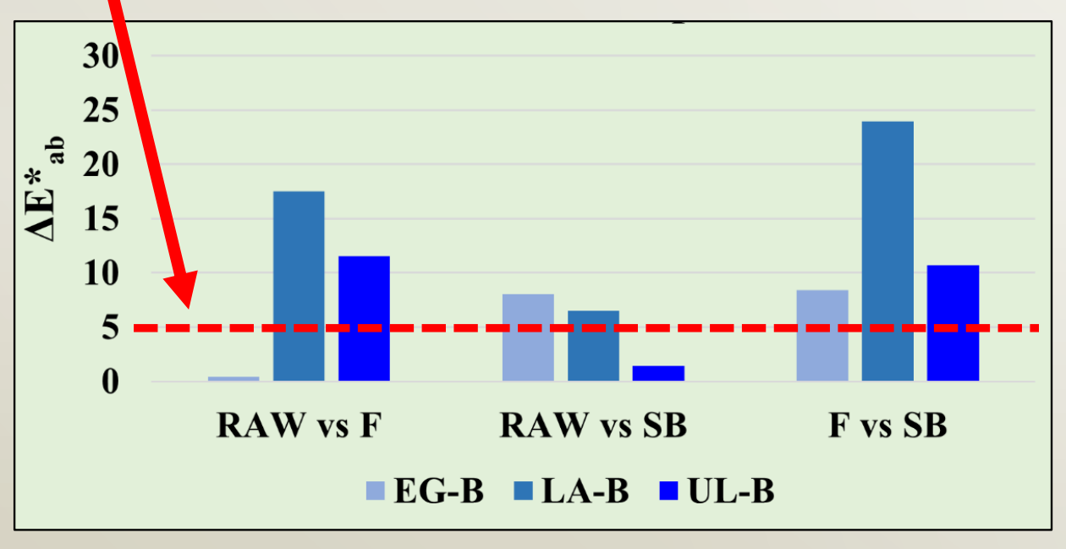
Not representative since **VER-G** is **not suitable** for F or SB

Contradictory literature

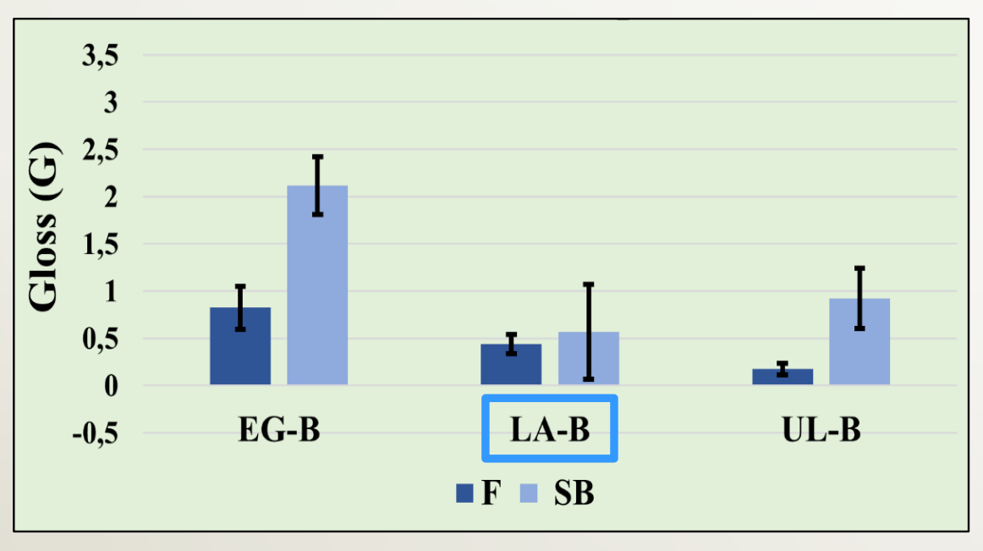


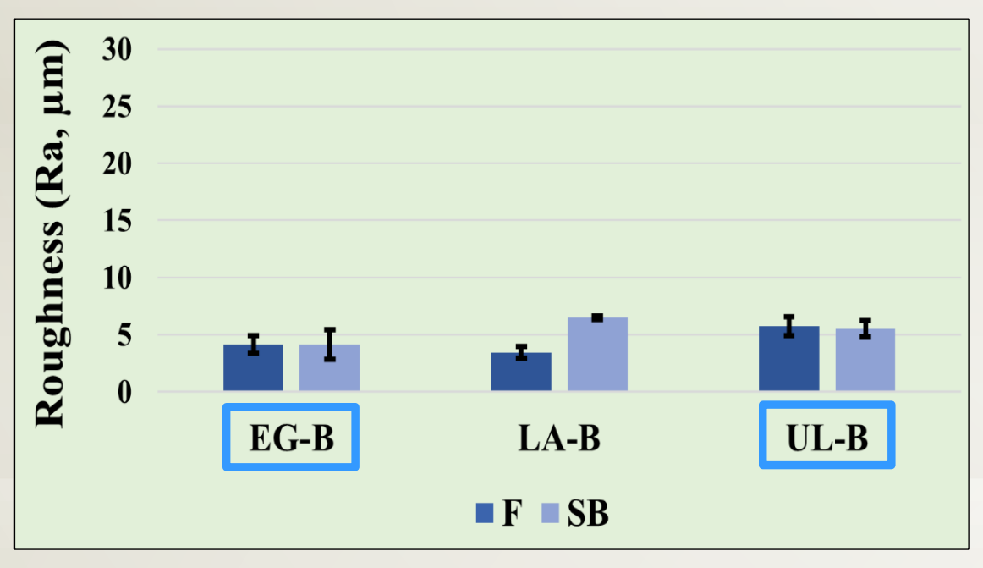
SM: differences in colour and in texture, specially in LA-B, GE-G, CHR-G and MAR-R mock-ups. Also, SB paints were more similar to the raw pigments in terms of colour than the F analogues.

ΔE^*_{ab}>5, two different colours[1]

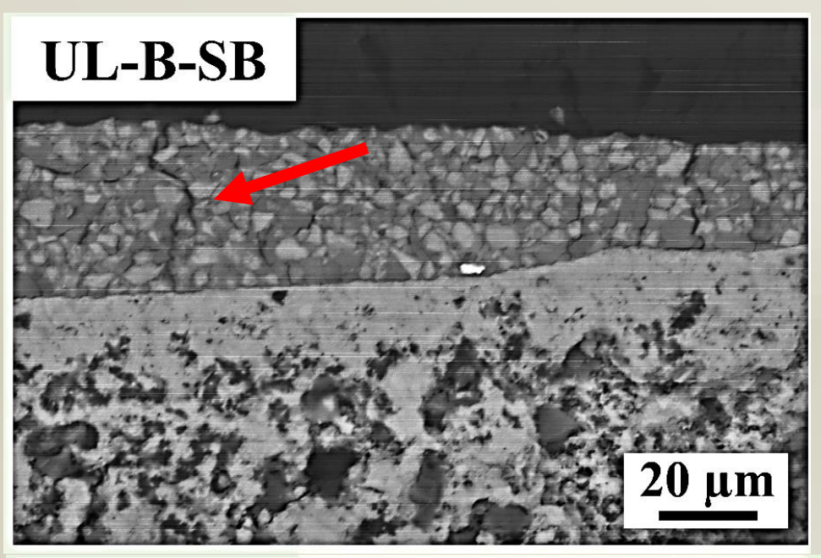


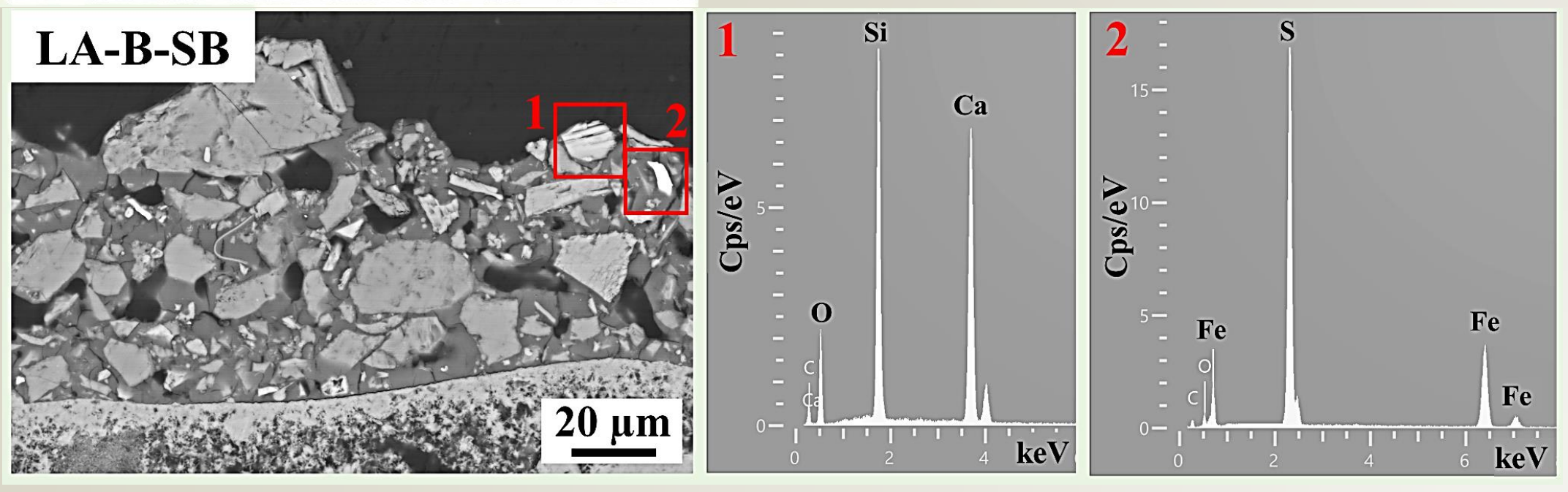
Major **ΔE^*_{ab}** between F and SB mock-ups, specially in LA-B.
Minor differences between UL-B-SB and the raw pigment.



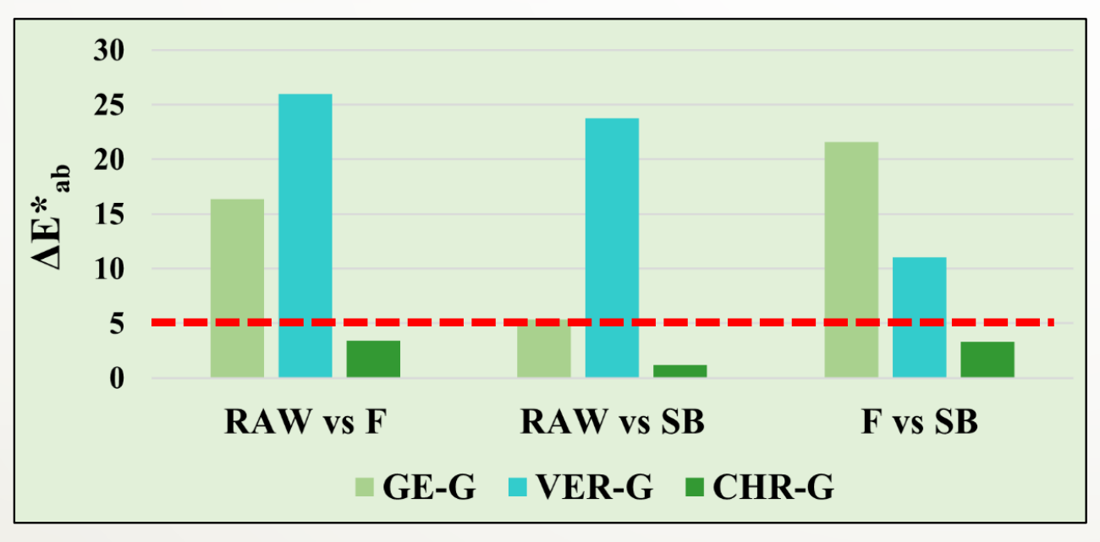


LA-B showed similar **G** values between F and SB, but higher **Ra** variations.
EG-B and UL-B similar values of **Ra**.

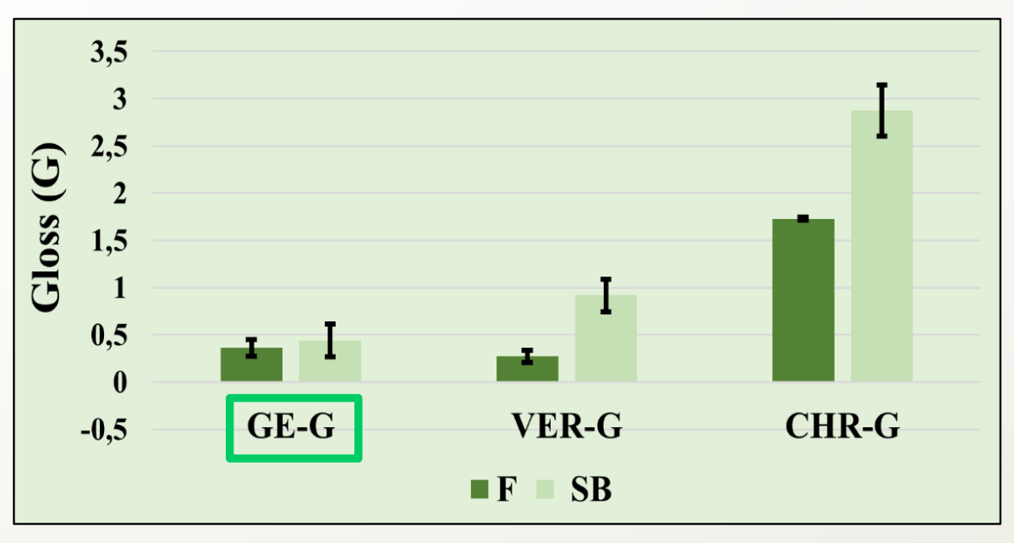


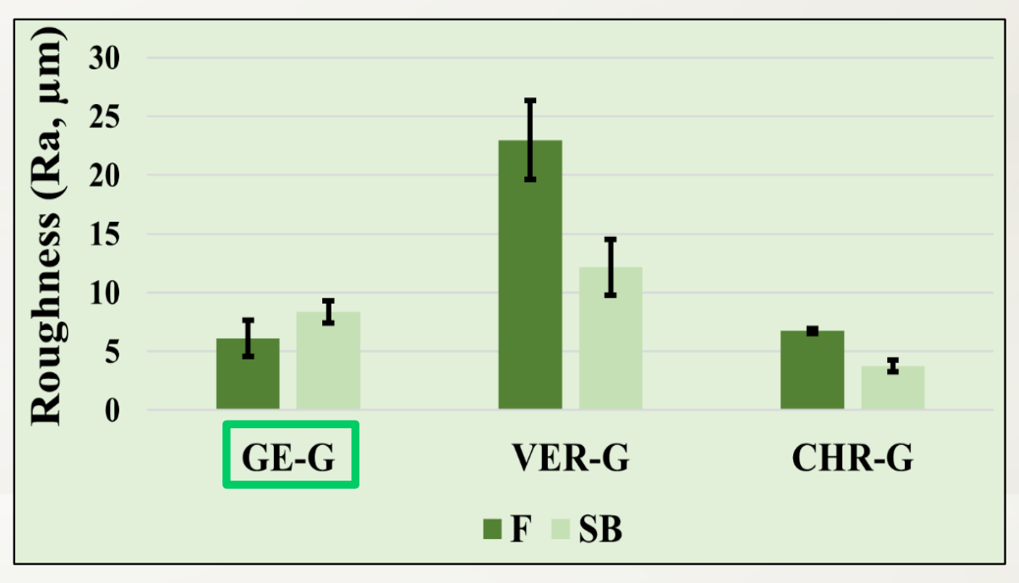


All SB mock-ups: cracked surface and a painted layer bonded to the mortar surface (*intonaco*).
LA-B-SB: irregular surface (impurities of Si/Ca and S/Fe).
UL-B-SB: smooth surface.

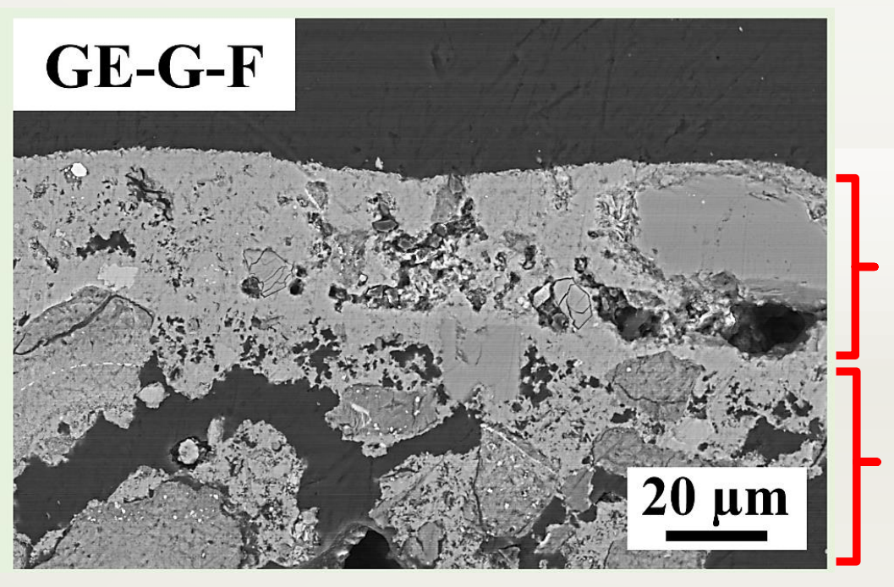


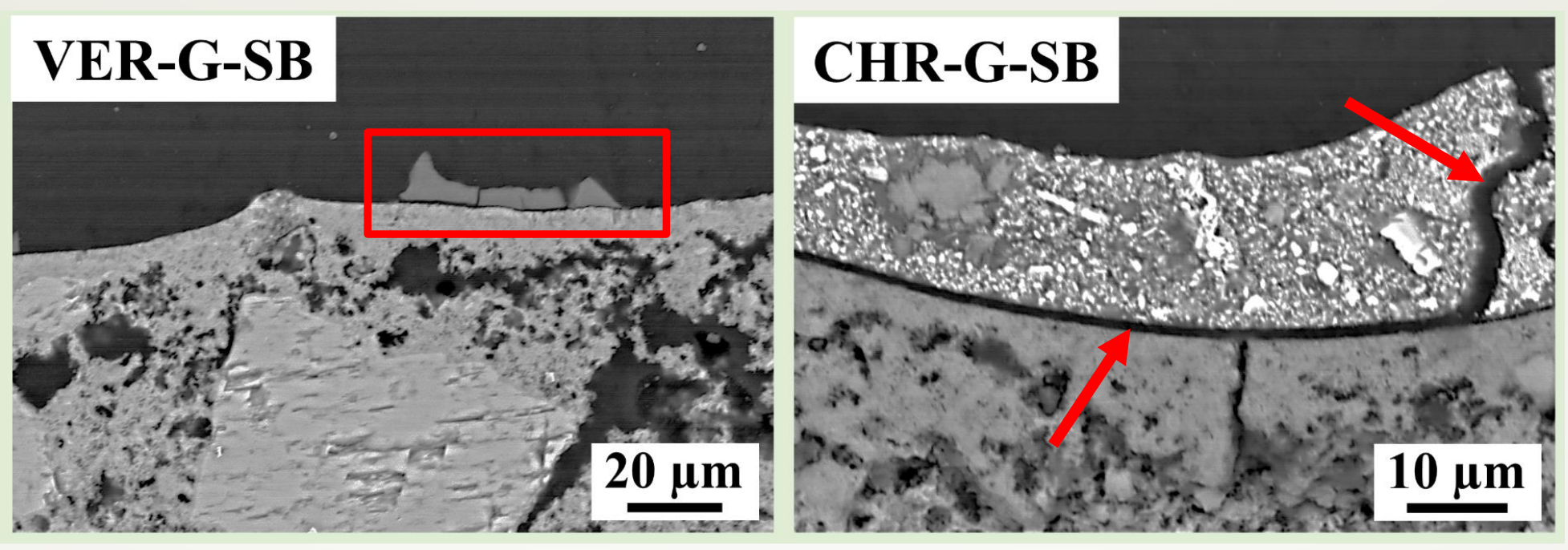
Major **ΔE^*_{ab}** between F and SB mock-ups in GE-G and less in CHR-G.
Minor differences between CHR-G-SB and GE-G-SB and the raw pigment.



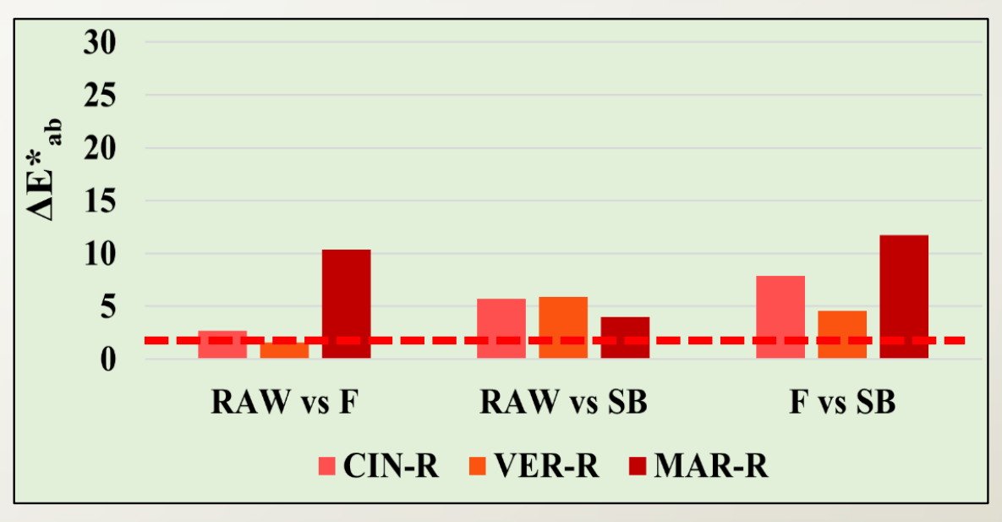


GE-G mock-ups showed similar **G** and **Ra** values between F and SB.

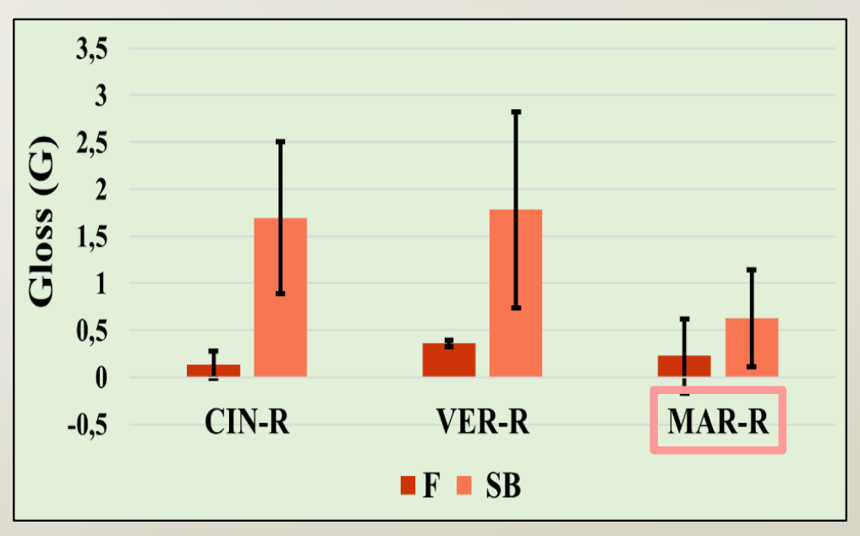


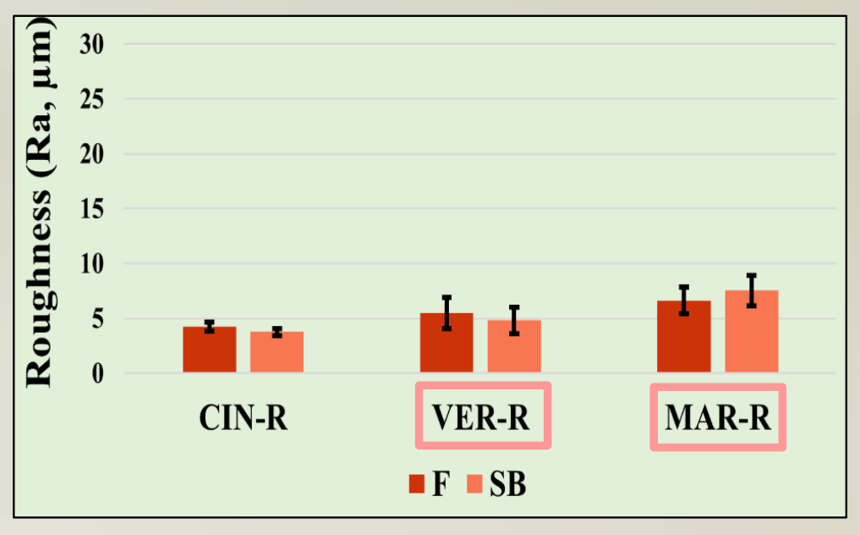


GE-G-F: uniform and unified paint layer.
VER-G: cannot be used neither in F nor in SB techniques.
CHR-G-SB and GE-G-SB: cracked and puntually detached painted layer.

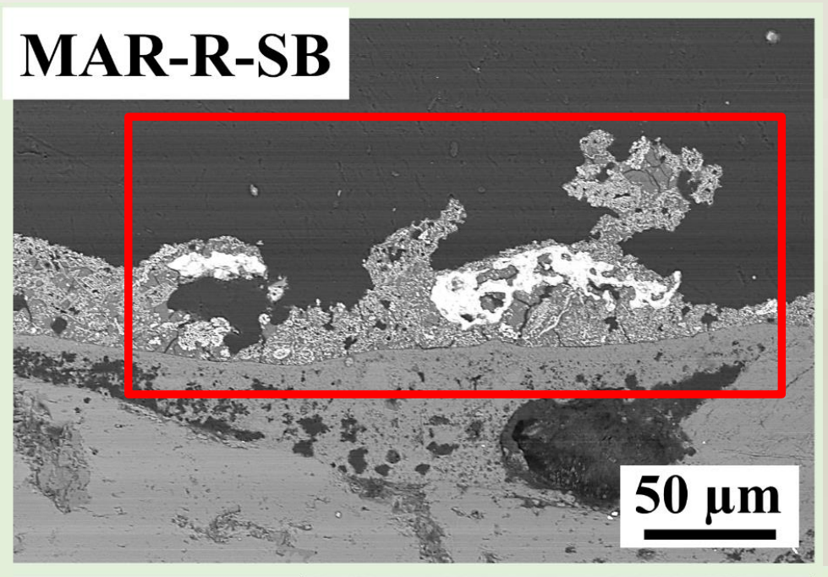


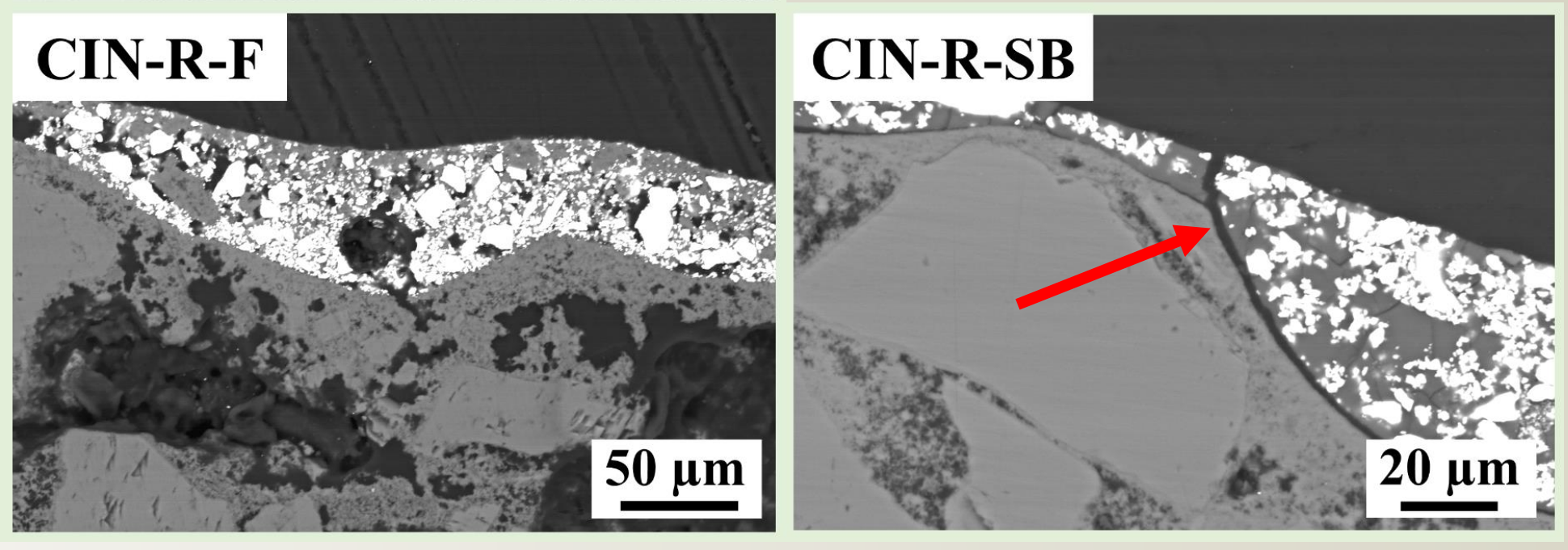
Major **ΔE^*_{ab}** between F and SB, especially CIN-R and MAR-R.
SB mock-ups were similar to the raw pigment.





Major **G** variations between F and SB in CIN-R and VER-R, on the contrary of MAR-R.
Ra values were similar in all red F and SB mock-ups.





MAR-R-SB: irregular surface.
CIN-R-SB: cracked and not well adhered painted layer.

No changes in **hydrophobicity** were detected, since all paintings were hydrophilic (<90°)

XRD and **FTIR**: No mineralogical and chemical changes were detected

CONCLUSIONS

Compatibility regarding the painting techniques:

- All SB mock-ups show higher gloss values and a cracked surface, common when using Nano Estel[2].
- Independent from the nature of the pigment, all paintings were hidrophilic (<90°).
- Verdigris is not suitable for neither of the techniques (due to the copper?).

Compatibility regarding the pigment:

- In general, artificial manufactured pigments show more homogeneus surfaces and less colour variations.
- Only blue pigments are completly bond to the surface.
- All SB mock-ups were similar to the raw pigment in terms of colour, specially artificial manufactured pigments.

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[1] Mokrzycki, M. y Tatol, M. 2011. *Colour difference ΔE - A survey.* Machine Graphic & Vision 20, 4 , 383-411.
[2] Borsoi, G., Veiga, R., & Santos Silva, A. *Effect of nanostructured lime-based and silica-based products on the consolidation of historical renders*. Proceedings of the 3rd Historic Mortars Conference, Glasgow, UK, 11-14 September 2013. University of the West of Scotland.