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Electronic Supplementary Information

Development of a multi-method analytical approach based on the combination of synchrotron radiation X-ray micro-analytical techniques and vibrational micro-spectroscopy methods to unveil the causes and mechanism of darkening of “fake-gilded” decorations in a Cimabue painting

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Content

S1. Evaluation of the alteration state of the "fake-gilded" decorations in the *Maestà*

S1.1 SR μ-XRD patterns

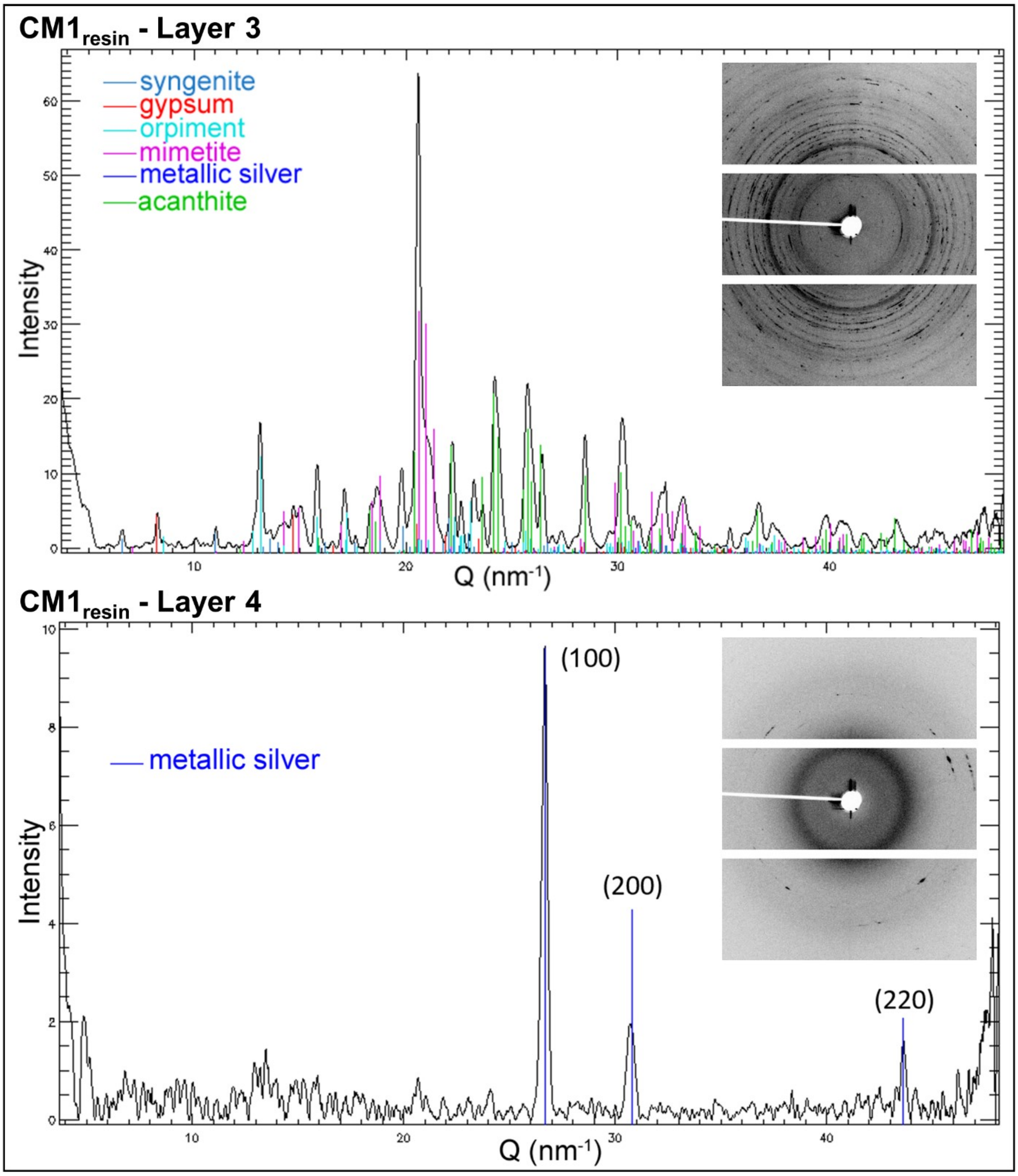

Figure S1. SR μ-XRD patterns obtained from (top) layer 3 and (bottom) layer 4 of cross-section $CM1_{resin}$ [see Figure 1e-g (main paper) for the corresponding μ-XRD maps].

S1.2 Ag speciation analysis and μ-XRF mapping

In agreement with the SR μ-XRD mapping results [Figure 1 (main paper)], Ag L_3-edge μ-XANES measurements performed at selected spots of the Ag/S-rich darkened layer reveal that α-Ag_2S is the dominant component (Figure S2a,b). To determine the nature and the relative concentration percentage of various Ag species, we described each Ag L_3-edge μ-XANES spectrum as a linear combination of two Ag reference compounds. The best linear combination fitting (LCF) was obtained by including in the model the spectra of α-Ag_2S (~70%) and either silver sulfate (Ag_2SO_4) or silver acetate (CH_3COOAg).

SR μ-XRF mapping results shows the widespread presence of Cl and Pb across the paint stratigraphy (Figure S2c), thus supporting the identification of mimetite [$Pb_5(AsO_4)_3Cl$] by SR μ-XRD [Figure 1f (main paper)].

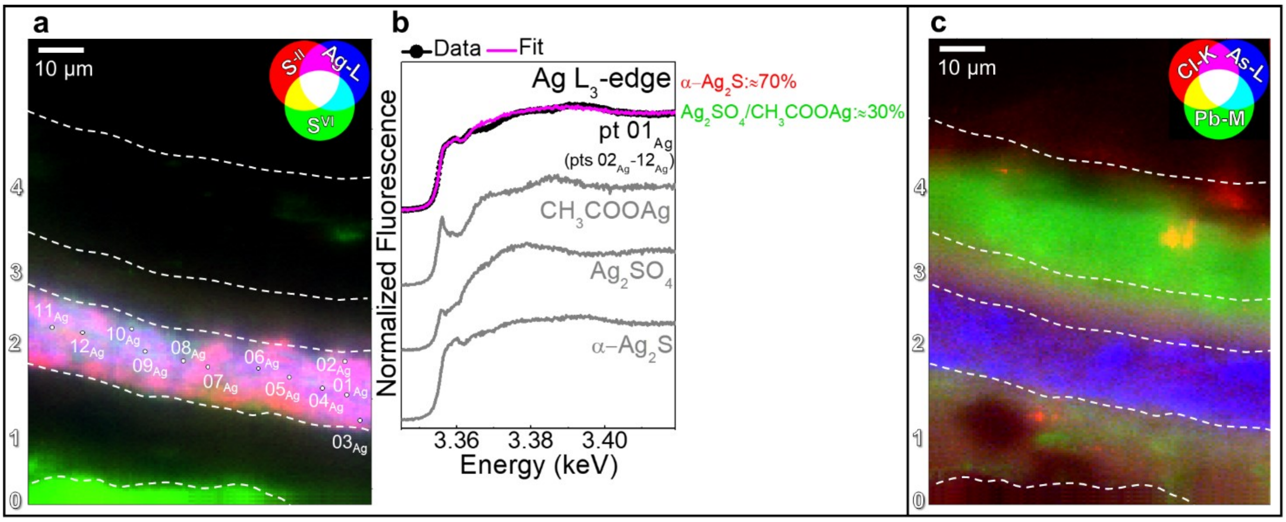

Figure S2. RGB composite SR μ-XRF images of a) S^{-II}/S^{VI}/Ag-L and c) Cl-K/Pb-M/As-L recorded from the area shown in Figure 1c (main paper) [map size (v×h): 99.5.8×74.2 μm^2; step size (v×h): 0.5×0.7 μm^2; exp. time: 100 ms/pixel]. b) Selection of the Ag L_3-edge μ-XANES spectra (black) recorded from the spots shown in a) and LCF results of different Ag-based reference compounds. In grey, the profiles of selected Ag-reference compounds are reported for comparison [see Figures 1-3 (main paper) for further results].

S1.3 ATR mode μ-FTIR spectra

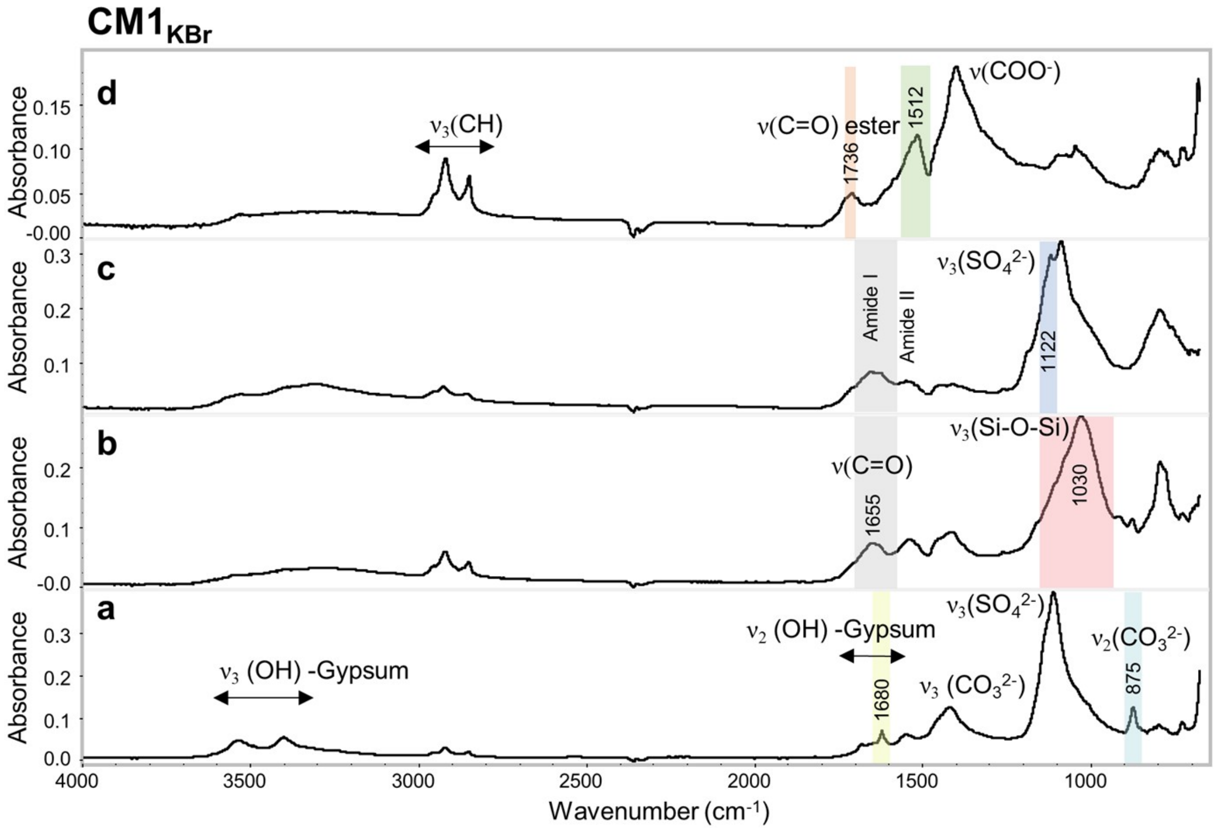

Figure S3. Selection of ATR mode μ-FTIR spectra extracted from the maps of Figure 3 (main paper) with rectangles showing the ROIs used to map the different compounds. a) Spectrum of the ground layer with selected bands of gypsum (1680 cm^{-1}) and calcite (875 cm^{-1}); b) spectrum extracted from layer 1 with highlighted the band of silicates and proteinaceous material [v(C=O) Amide I]; c) spectrum obtained from layer 3 with the band of sulfates; d) spectrum extracted from layer 4 with bands selected for mapping the lipidic material [v(C=O)ester] and lead carboxylates [v(COO)$^-$].

S2. Orpiment-based paint mock-ups

S2.1 Unaged paints

SR μ-XRD mapping (Figure S4a,b) in combination with SR μ-XRF/μ-XANES measurements at S K-edge (Figure S4c,d) show that the unaged Orp mock-up is only composed of α-As_2S_3. No evidence of the presence of oxidized S-species was revealed by μ-XANES spectroscopy.

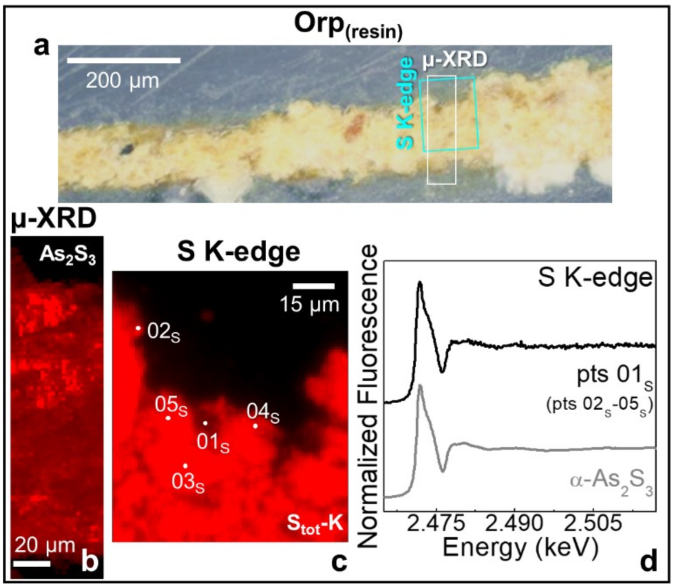

Figure S4. a) Photomicrograph of unaged Orp$_{(resin)}$ cross-section and b) corresponding SR μ-XRD image of α-As_2S_3 [map size (v×h): 189.5×50 μm²; step size (v×h): 1.5×2 μm²; exp. time: 1s/pixel; energy: 21 keV]. c) SR μ-XRF image of S_{total} [map size (v×h): 84×97 μm²; step size (v×h): 1×1 μm^2; exp. time: 100 ms/pixel; energy: 3.4 keV] and d) S K-edge μ-XANES spectrum (black) recorded from the area shown in c), compared to that of α-As_2S_3 reference compound (gray). In a), rectangles show the areas where maps of b,c) were recorded. In d), numbers in brackets indicate the spectra showing similar features to that reported.

For Orp-Ag (Figure S5a), the presence of α-As_2S_3 and Ag^0-crystals occurs along with that of few grains of α-Ag_2S (green) (Figure S5b-f). Small abundances of sulfate-compounds are also detected at a single spot by S K-edge XANES (Figure S5d: pt 04_S).

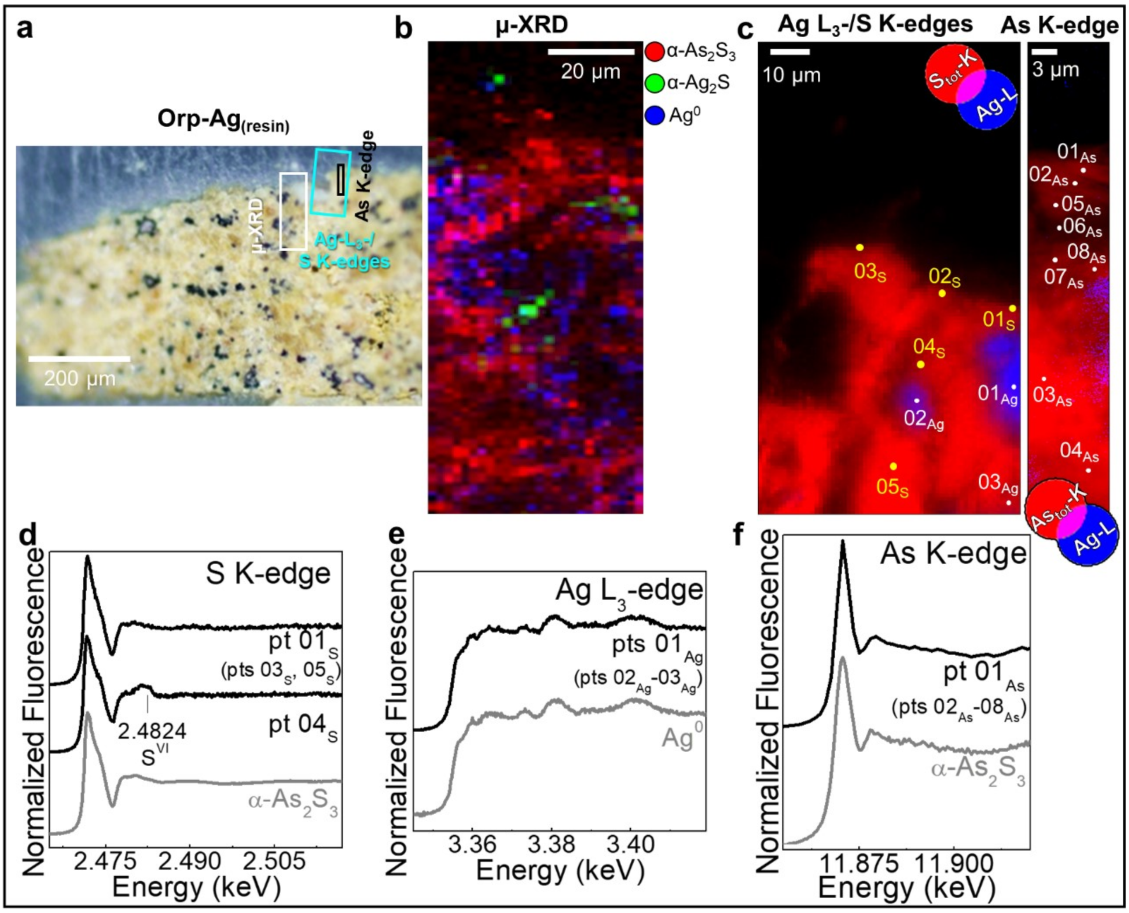

Figure S5. a) Photomicrograph of unaged Orp-$Ag_{(resin)}$ cross-section and b) corresponding composite SR μ-XRD maps of α-As_2S_3 (red), α-Ag_2S (green) and Ag^0 (blue) [map size (v×h): 150×50 μm²; step size (v×h): 1.5×2 μm²; exp. time: 1s/pixel; energy: 21 keV]. c) RB composite SR μ-XRF images of (left) S_{total}/Ag-L [map size (v×h): 117×65 μm²; step size (v×h): 0.86×1 $μm^2$; exp. time: 100 ms/pixel; energy: 3.4 keV]] and (right) As_{total} /Ag-L [map size (v×h): 56.9×9.9 μm²; step size (v×h): 0.1×0.15 $μm^2$; exp. time: 100 ms/pixel; energy: 12 keV]. Selection of the μ-XANES spectra (black) recorded at d) S K-edge, e) Ag L_3-edge and f) As K-edge from the spots shown in c) and compared to those of selected reference compounds. Numbers in brackets refer to the spectra showing similar features to those reported.

Single point μ-Raman investigations (Figure S6a,b) corroborate the SR μ-XRD mapping results (Figure S5b), revealing the possible presence of a Ag_2S-based phase (broad band at *ca.* 220 cm^{-1} and signal below 150 cm^{-1})[1] in selected darker grains of the α-As_2S_3/Ag^0-based paint matrix. In addition, As_2O_3 was locally identified by μ-FTIR mapping measurements (band at 796 cm^{-1}) (Figure S6c-e).[2,3]

Such results provide evidence that an *in-situ* degradation process of the paint has already occurred before artificial aging in the areas where α-As_2S_3 and Ag^0 are in contact.

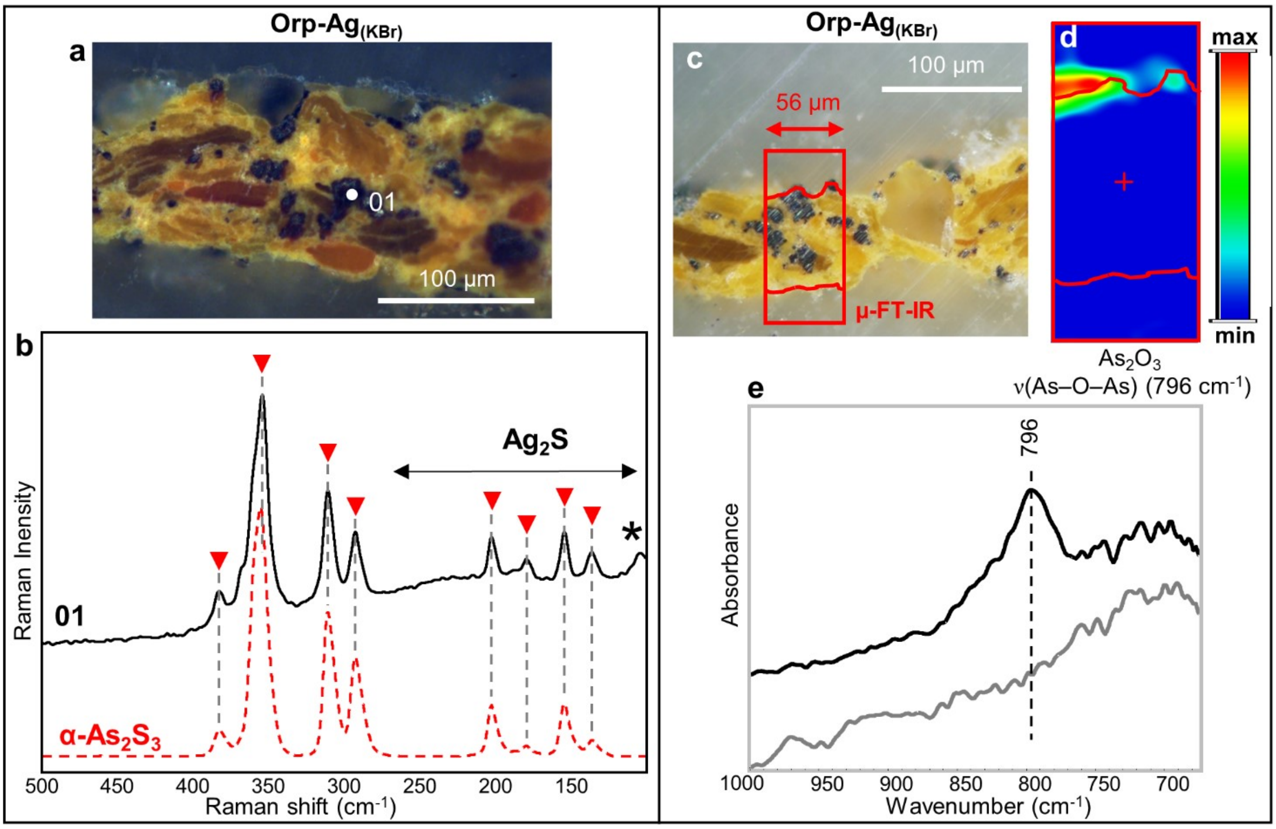

Figure S6. a,c) Photomicrographs and corresponding b) single-point μ-Raman (black) and d) ATR mode μ-FTIR mapping results obtained from unaged Orp-$Ag_{(KBr)}$ cross-section. e) FTIR spectra extracted from the As_2O_3-free region (grey) and As_2O_3-rich area (black) of the map shown in d). In b) one Raman spectrum is reported as example. The asterisk indicates Ag lattice vibrational modes of Ag_2S. [1]

S2.2 Orp-Ag$_{UVA-vis}$ paint: μ-Raman, Ag/As speciation investigations and SR μ-XRD patterns

In line with the SR μ-XRD and μ-FTIR mapping results [Figure 5 (main paper)], single point μ-Raman analysis (Figure S7a,b) and Ag L_3-edge/As K-edge μ-XANES investigations (Figure S7c-g: pts 01_{Ag}-03_{Ag}, pts 01_{As}-04_{As}) reveal that α-Ag_2S and As_2O_3 are localized in the uppermost darkened areas of the Orp-Ag$_{UVA-vis}$ paint stratigraphy. Ag^0 and As_2S_3 remain instead the main components of the innermost side of the paint (Figure S7f,g: pt 04_{Ag}; pts. 05_{As}-11_{As}).

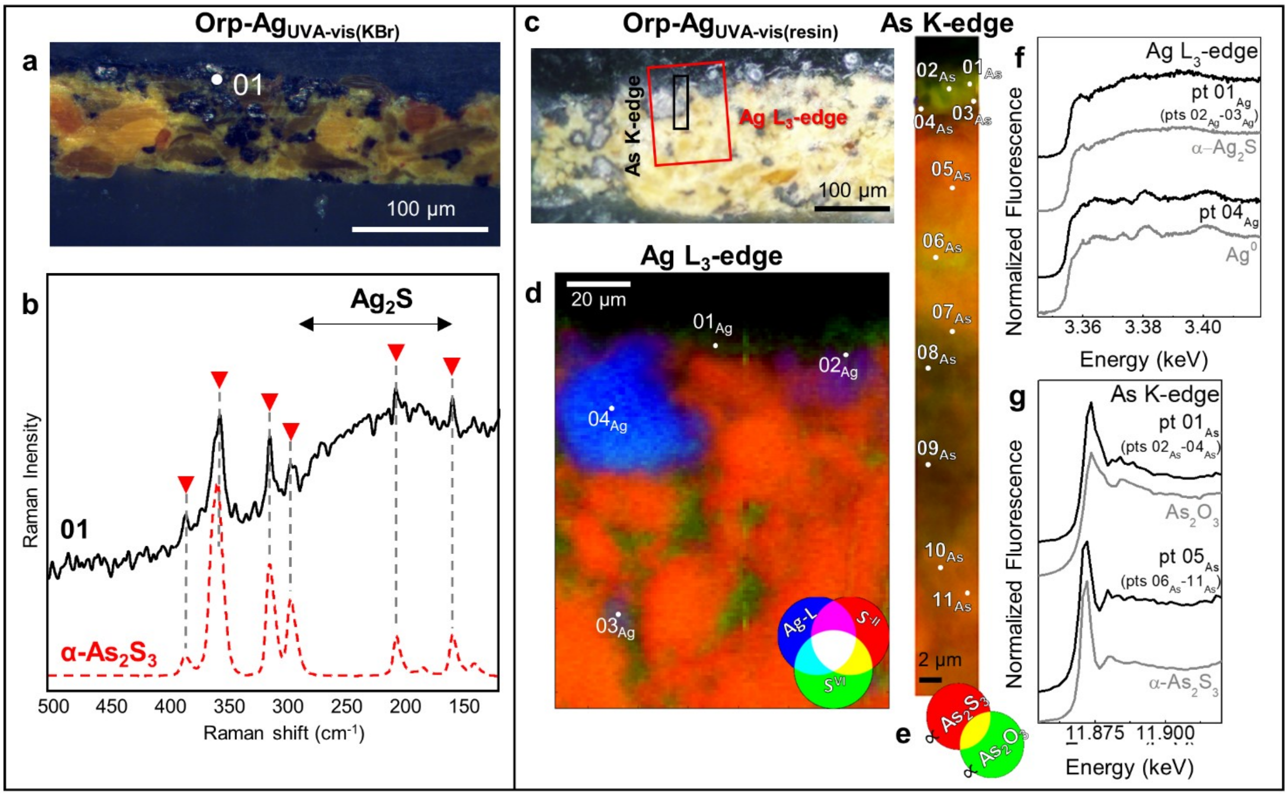

Figure S7. Photomicrographs of a) Orp-Ag$_{UVA-vis\ (KBr)}$ and c) Orp-Ag$_{UVA-vis\ (resin)}$ cross-sections. b) μ-Raman spectrum (black) recorded from the spot shown in a) and compared to that of α-As_2S_3 reference compound (red). d) RGB composite SR μ-XRF images of d) S^{-II}/S^{VI}/Ag-L [map size (v×h): 130×100 μm²; step size (v×h): 0.97×1.1 μm^2; exp. time: 100 ms/pixel; ; energy (S^{-II})= 2.473 keV, energy (S^{VI})= 2.482 keV] and e) As^{III} (∝α-As_2S_3) / As^{III} (∝α-As_2O_3) [map size (v×h): 58.1×5.4 μm²; step size (v×h): 0.1×0.1 μm^2; exp. time: 100 ms/pixel; energy (As^{III}, ∝α-As_2S_3)= 11.870 keV, energy (As^{III}, ∝α-As_2O_3)= 11.8754 keV] recorded from the areas reported in c). μ-XANES spectra (black) recorded at the f) Ag L_3-edge and g) As K-edge obtained from the spots shown in d,e) and compared to those of a set of Ag/As reference compounds (gray). In f,g), numbers in brackets refer to the spectra showing similar features to those reported.

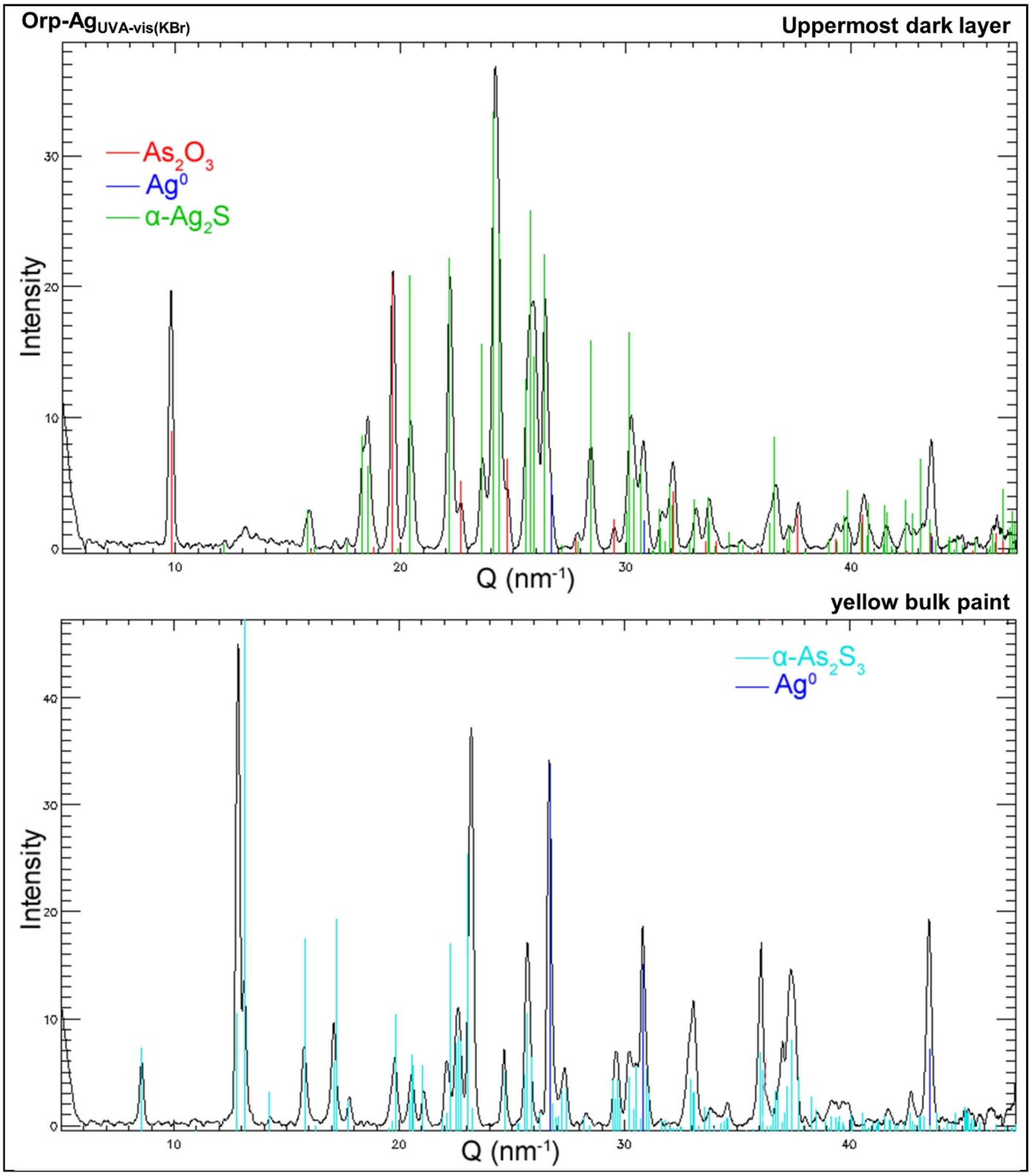

Figure S8. SR μ-XRD patterns obtained from (top) the uppermost dark layer and (bottom) the yellow bulk paint of Orp-Ag$_{\text{UVA-vis (KBr)}}$ (see Figure 5d (main paper) for the corresponding μ-XRD maps].

S3. Ag^0 paint mock-ups

SR μ-XRD mapping acquired from Ag and $Ag_{UVA-vis}$ paint cross-sections (Figure S9) show in both cases the presence of Ag^0 and AgCl (the latter present as impurity of the powder). The fact that the exposure to UVA-visible light did not promote the formation of α-Ag_2S is in line with the smaller total color change of the paint surface [Table 2: ΔE=5±1 (main paper)] with respect to that of the Orp-$Ag_{UVA-vis}$ paint (ΔE=32±2); furthermore, it provides evidence that in Orp-Ag paint mock-ups, the main responsible for the formation of α-Ag_2S are S^{2-} ions arising from the degradation of As_2S_3.

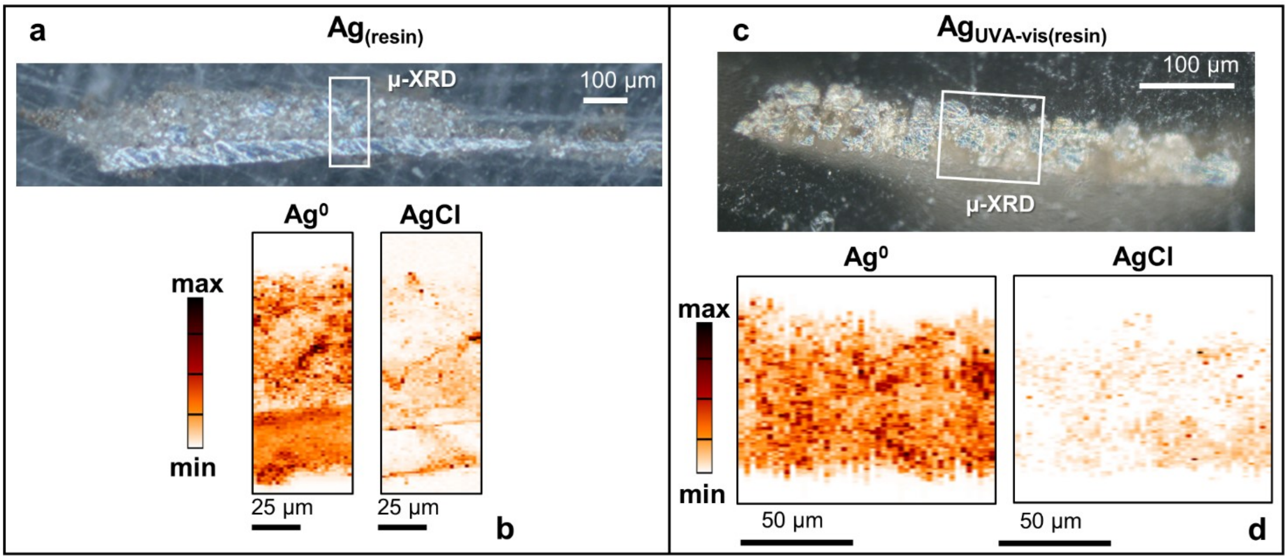

Figure S9. Photomicrographs of a) $Ag_{(resin)}$ and c) $Ag_{UVA-vis(resin)}$ cross-sections and b,d) corresponding SR μ-XRD distribution of Ag^0 and AgCl [Panel b): map size (v×h): 180×50 μm²; step size (v×h): 1.5×2.0 μm^2; exp. time: 1 s/pixel; energy: 21 keV. Panel d): map size (v×h): 105×100 μm²; step size (v×h): 1.0×2.0 μm^2; exp. time: 0.5 s/pixel; energy: 21 keV].

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