Supplementary Material: Paint, Colour, and Style: The Contribution of Minerals to the Palette of the Descent from the Cross, Attributed to the Portuguese Painter Francisco João (act. 1558–1595)

Helena P. Melo [1,2], António João Cruz [1,3,*], Jana Sanyova [4], Sara Valadas [1,2] and Ana Margarida Cardoso [1,2]

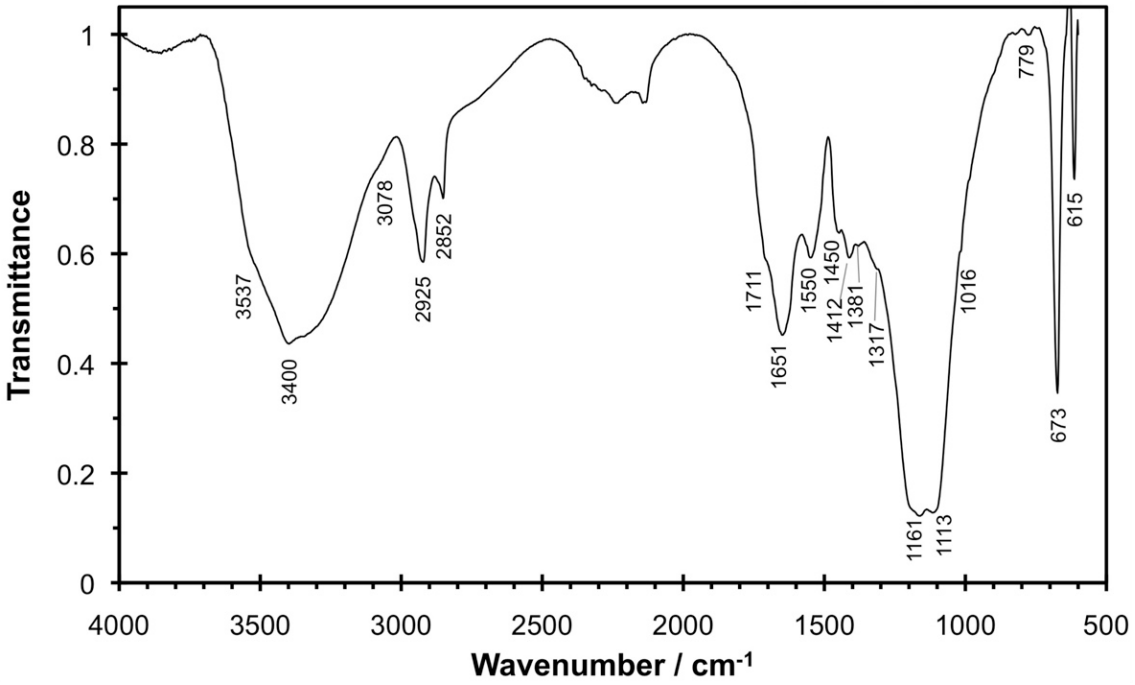


Figure S1. FTIR spectrum of the ground layer of sample #13: sulfates (3537–3400, 1161, 1113, 1016, 673, 615 cm^{-1}), oxalates (1317, 779 cm^{-1}), proteins (3078, 1651, 1550, 1450 cm^{-1}), lipids (2925, 2852, 1711 cm^{-1}). The lipids most probably result from absorption of the *imprimitura* binder applied on top of the ground.

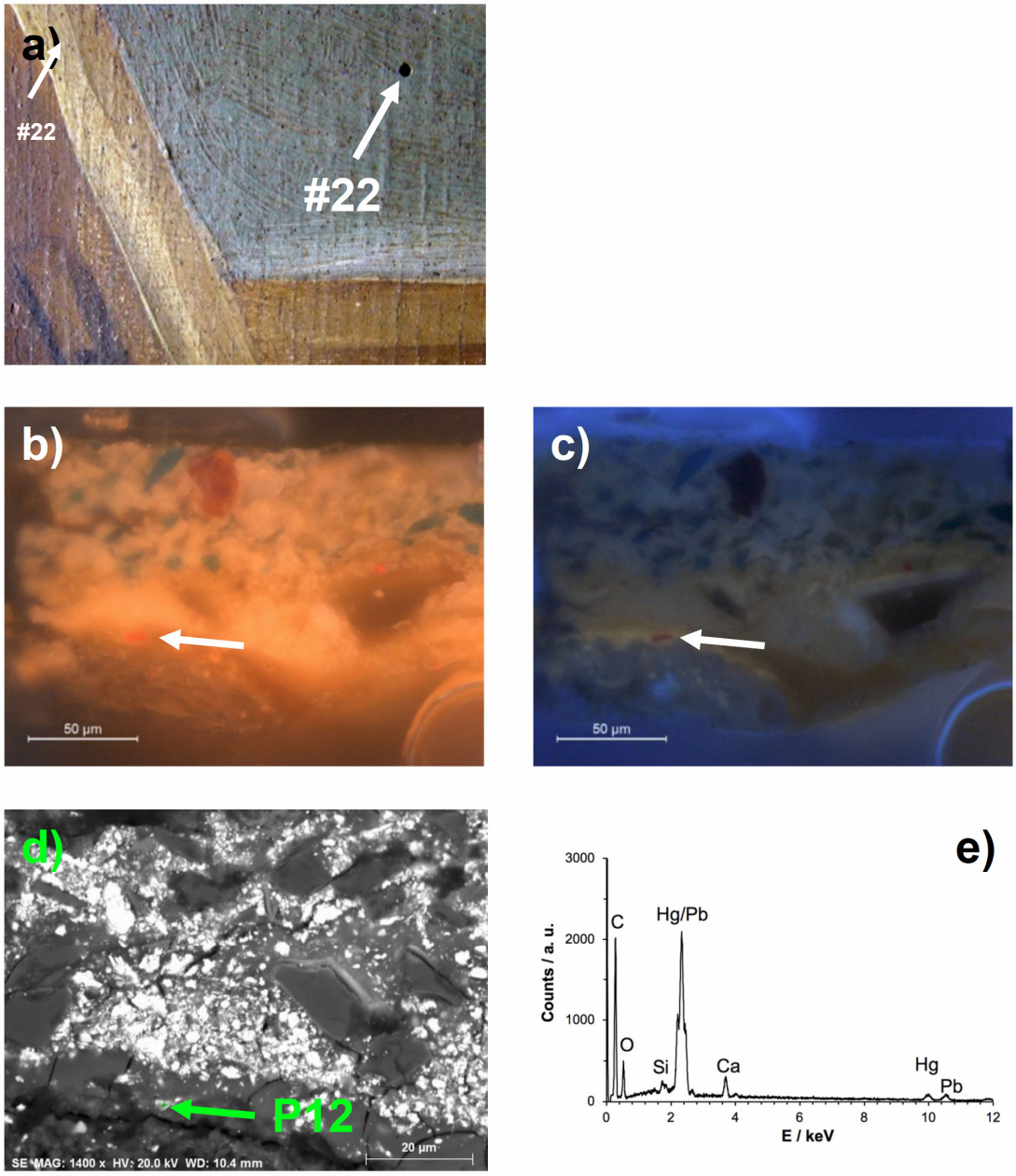


Figure S2. Detail of the area of the sky with location of sample #22 (**a**); cross-section of sample #22 under OM-Vis (**b**); cross-section of sample #22 under OM-UV (**c**); SEM-BSE image of detail from b) and c) (**d**); and SEM-EDX spectrum of P12 (**e**). The arrow in b), c) and d) indicates the particle P12, of vermillion. The medium-rich *imprimitura* containing the vermilion particle exhibits a yellow fluorescence under OM-UV (c).

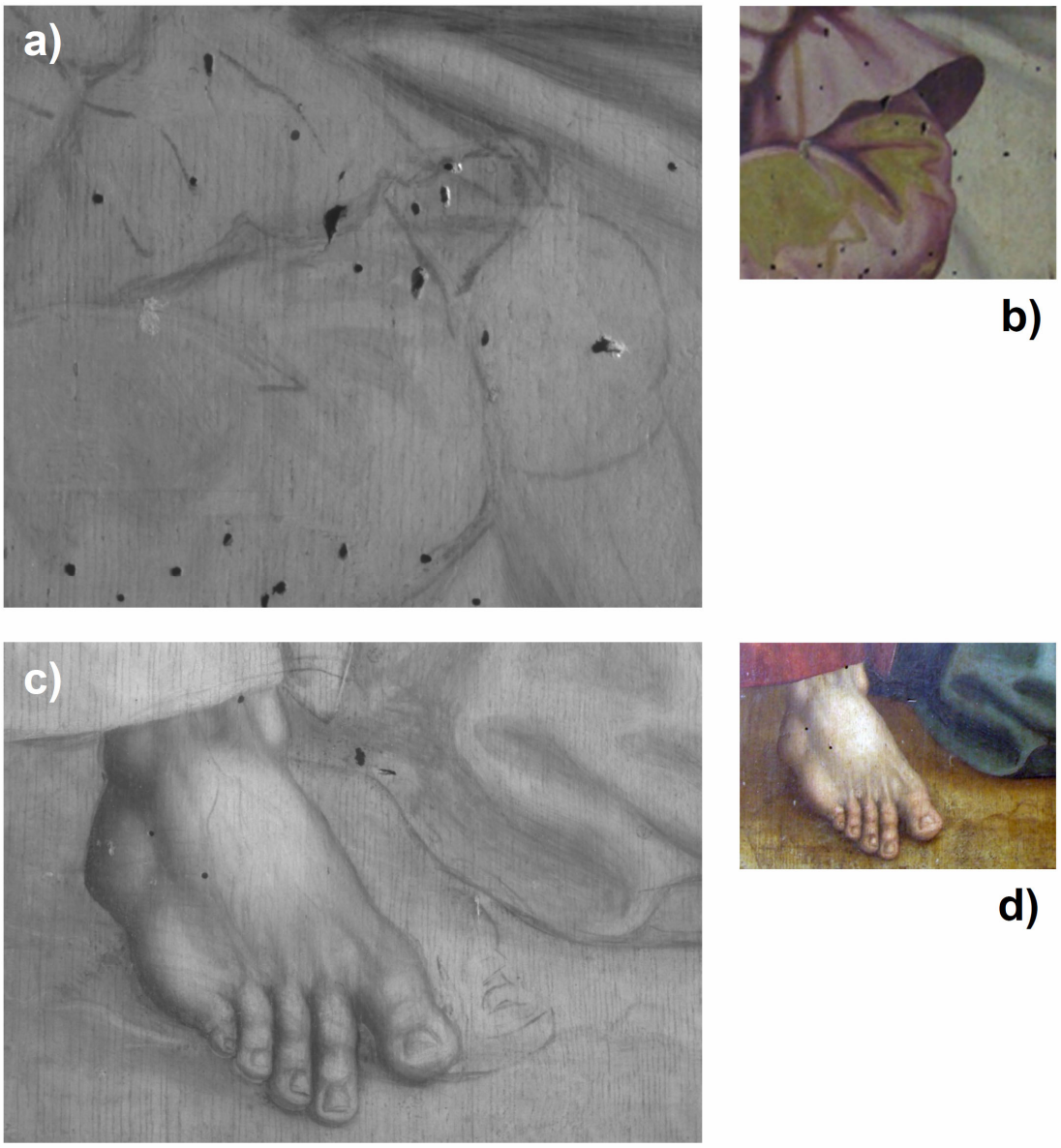


Figure S3. Details under IRR (**a**, **c**) and, under visible radiation (**b**, **d**).

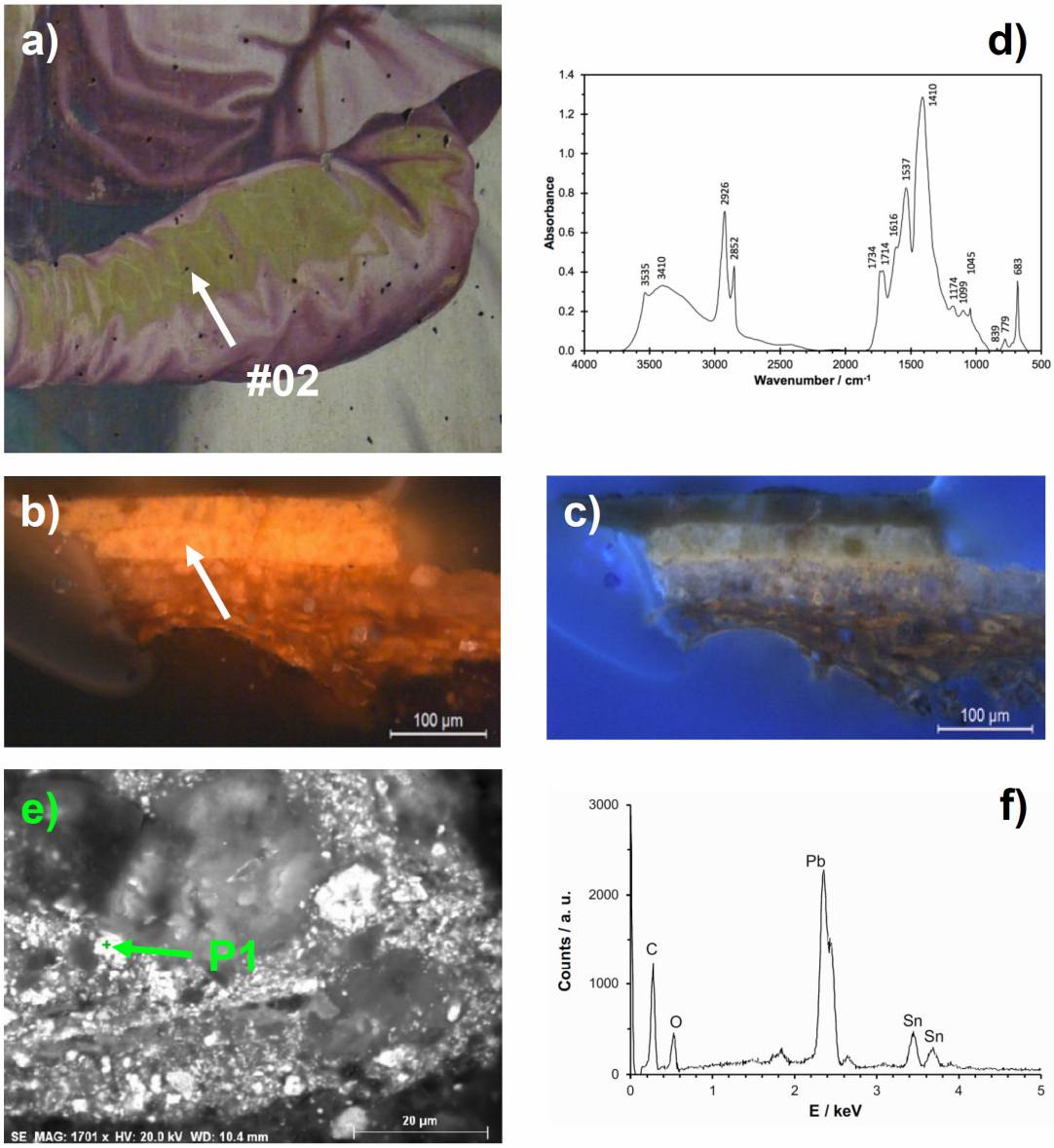


Figure S4. Detail of the drapery in Saint Magdalene's arm with location of sample #02 (**a**); cross-section of sample #02 under OM-Vis (**b**); cross-section of sample #02 under OM-UV (**c**); and FTIR spectrum of yellow layer marked in b) with an arrow (**d**). According to the SEM-EDX results, this layer is rich in lead white and lead-tin yellow: SEM-BSE image of detail of cross-section from sample #02 with location with an arrow of the particle P1 analysed (**e**); and respective SEM-EDX spectrum (**f**). On the FTIR spectrum, lead white is detected due to the presence of carbonate bands at 1410, 1045, and 683 cm^{-1}, along with a ν(OH) distension at 3535 cm^{-1} for hydrocerussite and the characteristic strong 839 cm^{-1} stretching band for cerussite. Lead soaps present as can be seen by the strong ν_a(COO-) band at 1537 cm^{-1}. The carbonyl ν(C=O) bands at 1734, 1714 cm^{-1} along with two sharp bands at 2926 cm^{-1} and 2852 cm^{-1}, due respectively to stretching CH_3 and CH_2 vibrations, identify an aged oil. The broad band centered at 3410 cm^{-1} can be assigned to alcohol and/or hydroperoxide vibrations formed during the ageing of oil.

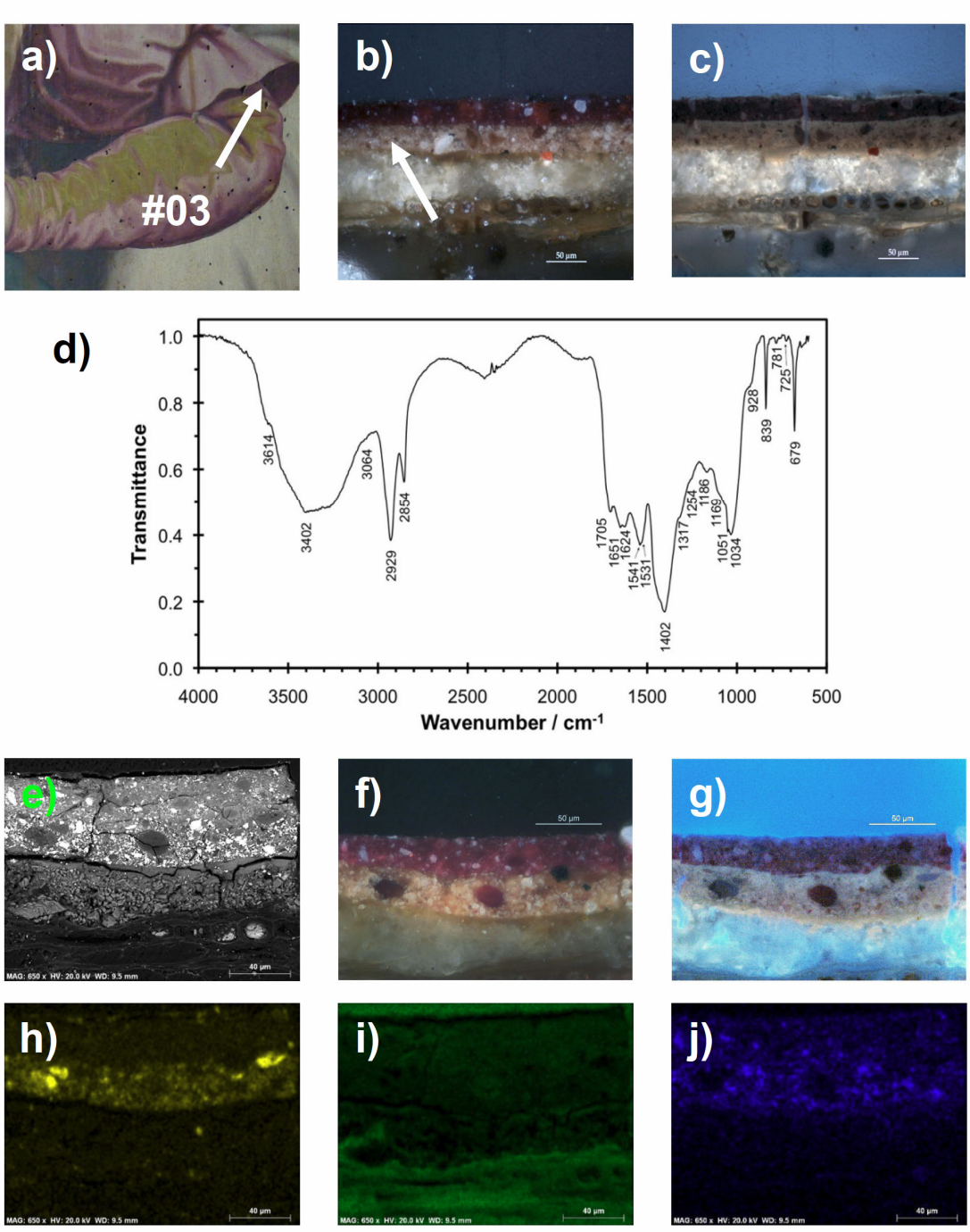


Figure S5. Detail of the tunic of Saint Magdalene with location of sample #03 (**a**); cross-section of sample #03 under OM-Vis (**b**); cross-section of sample #03 under OM-UV (**c**); and FTIR spectrum of pink-ochre paint marked in b) with an arrow (**d**). A red particle of vermilion can be seen in the *imprimitura* layer (b and c). According to the SEM-EDX results, the layer is rich in lead white and a red lake: SEM-BSE image of detail of cross-section of sample #03 (**e**); same detail under OM-Vis (**f**) and under OM-UV (**g**); SEM-EDX maps of Al (**h**), C (**i**), and Pb (**j**). On the FTIR spectrum, lead white is detected due to the presence of carbonate bands at 1402, 1051, and 679 cm^{-1}, along with the characteristic strong 839 cm^{-1} stretching band for cerussite. The ν(OH) distension at 3535 cm^{-1} for hydrocerussite appears as a shoulder in the 3402 cm^{-1} band. Lead soaps are identified by the strong ν_a(COO-) band at 1541 cm^{-1}. The glazes contained ground glass particles: ν_a(Si-O-Si) bands at 1053–1049 cm^{-1} with a shoulder at 1097–1088 cm^{-1}, and a smaller ν_s (Si-O-Si) band at 781 cm^{-1} can be ascribed to glass, and the band at 928 cm^{-1} can to network modifiers in the glass. The carbonyl ν(C=O) bands at 1705 cm^{-1} along with two sharp bands at 2929 cm^{-1} and 2854 cm^{-1}, due respectively

to stretching CH_3 and CH_2 vibrations, identify an aged oil. The broad band centered at 3402 cm^{-1} can be assigned to alcohol and/or hydroperoxide vibrations formed during the ageing of oil. Oxalates resulting from degradation of the organic binding medium can be seen due to the bands at 1317 cm^{-1} ν_a(C-O) and 781 cm^{-1} δ(O-C=O), with a broad band centred at 1651 cm^{-1} ν_s(C=O).

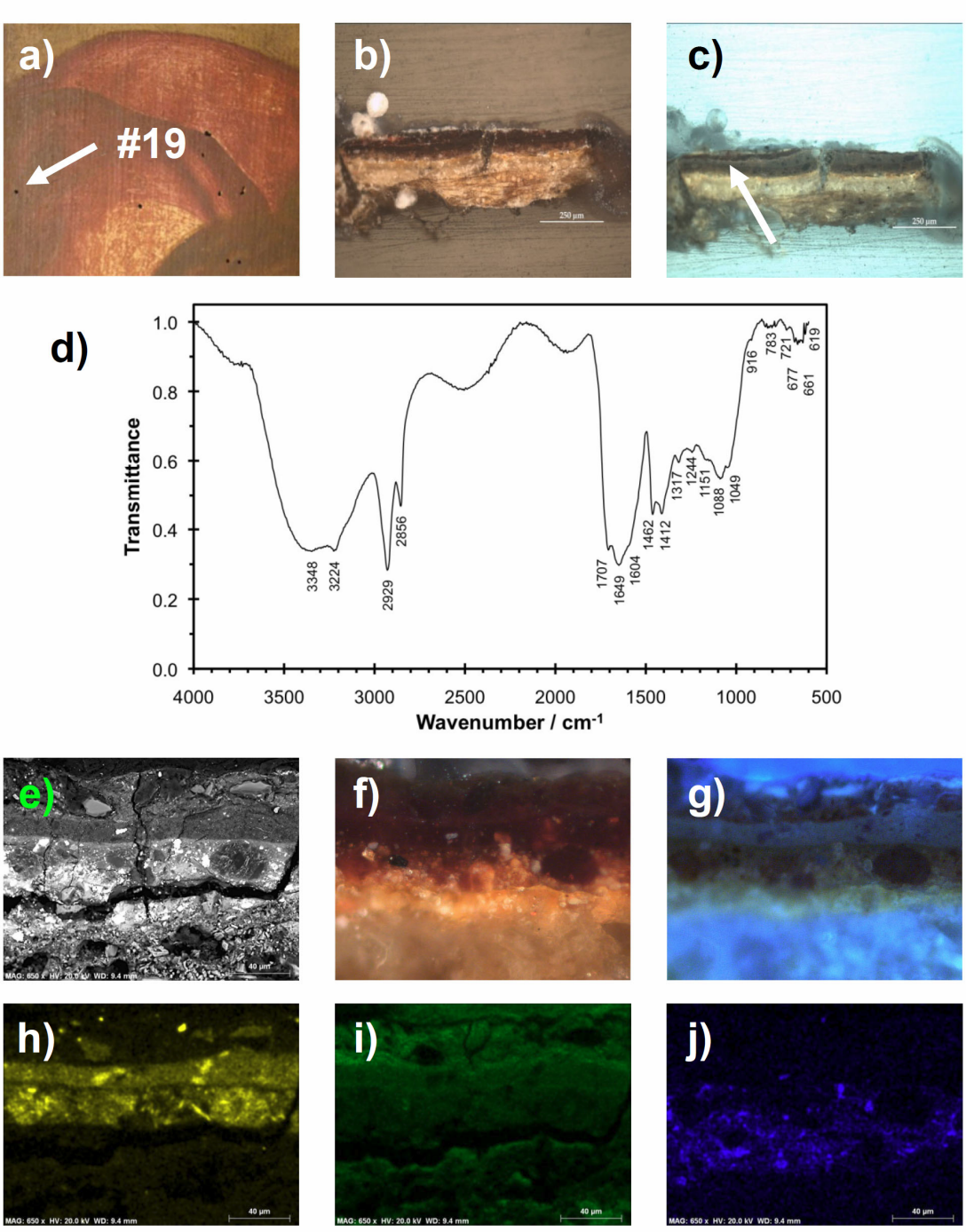


Figure S6. Detail of the cloak of Saint John with location of sample #19 (**a**); cross-section of sample #19 under OM-Vis (**b**); cross-section of sample #19 under OM-UV (**c**); and FTIR spectrum of the red glaze marked in c) with an arrow (**d**). The composition of the layer shown by the SEM-EDX spectrum is characteristic of a lake: SEM-BSE image of detail of cross-section of sample #19 (**e**); same detail under OM-Vis (**f**) and under OM-UV (**g**); SEM-EDS maps of Al (**h**), C (**i**), and Pb (**j**). On the FTIR

spectrum, the glazes contained ground glass particles that can be identified by the ν_a(Si-O-Si) bands at 1049 cm^{-1} and 1088 cm^{-1}, and a smaller ν_s (Si-O-Si) band at 783 cm^{-1}. The band at 916 cm^{-1} can to network modifiers in the glass. The carbonyl ν(C=O) bands at 1707 cm^{-1} along with two sharp bands at 2929 cm^{-1} and 2856 cm^{-1}, due respectively to stretching CH_3 and CH_2 vibrations, identify an aged oil. The broad band centered at 3348 cm^{-1} can be assigned to alcohol and/or hydroperoxide vibrations formed during the ageing of oil. Oxalates resulting from degradation of the organic binding medium can be seen due to the bands at 1317 cm^{-1} ν_a(C-O) and 783 cm^{-1} δ(O-C=O), with a broad band centred at 1649 cm^{-1} ν_s(C=O).

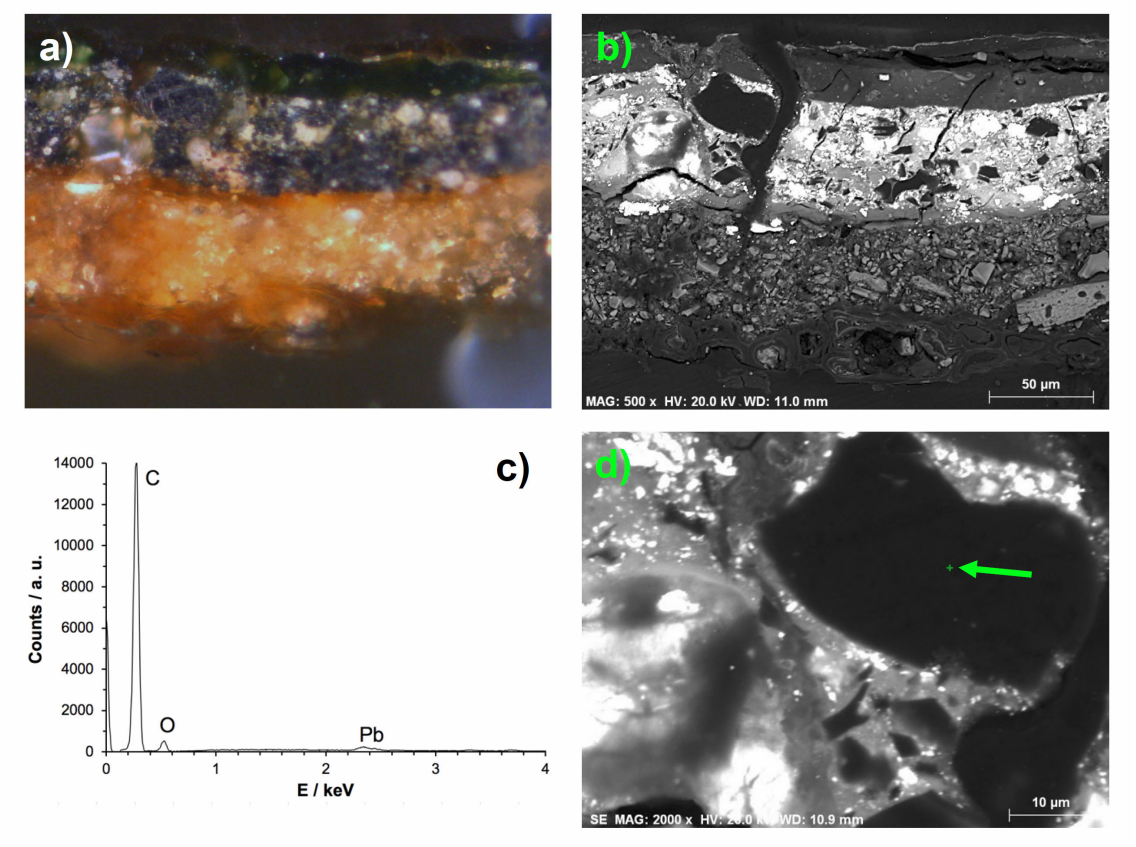


Figure S7. Cross-section of sample #11, corresponding to a green drapery, under OM-Vis (**a**); cross-section of sample #11 under SEM-BSE (**b**); SEM-EDX spectrum of charcoal particle (**c**) viewed in the SEM-BSE image (**d**).

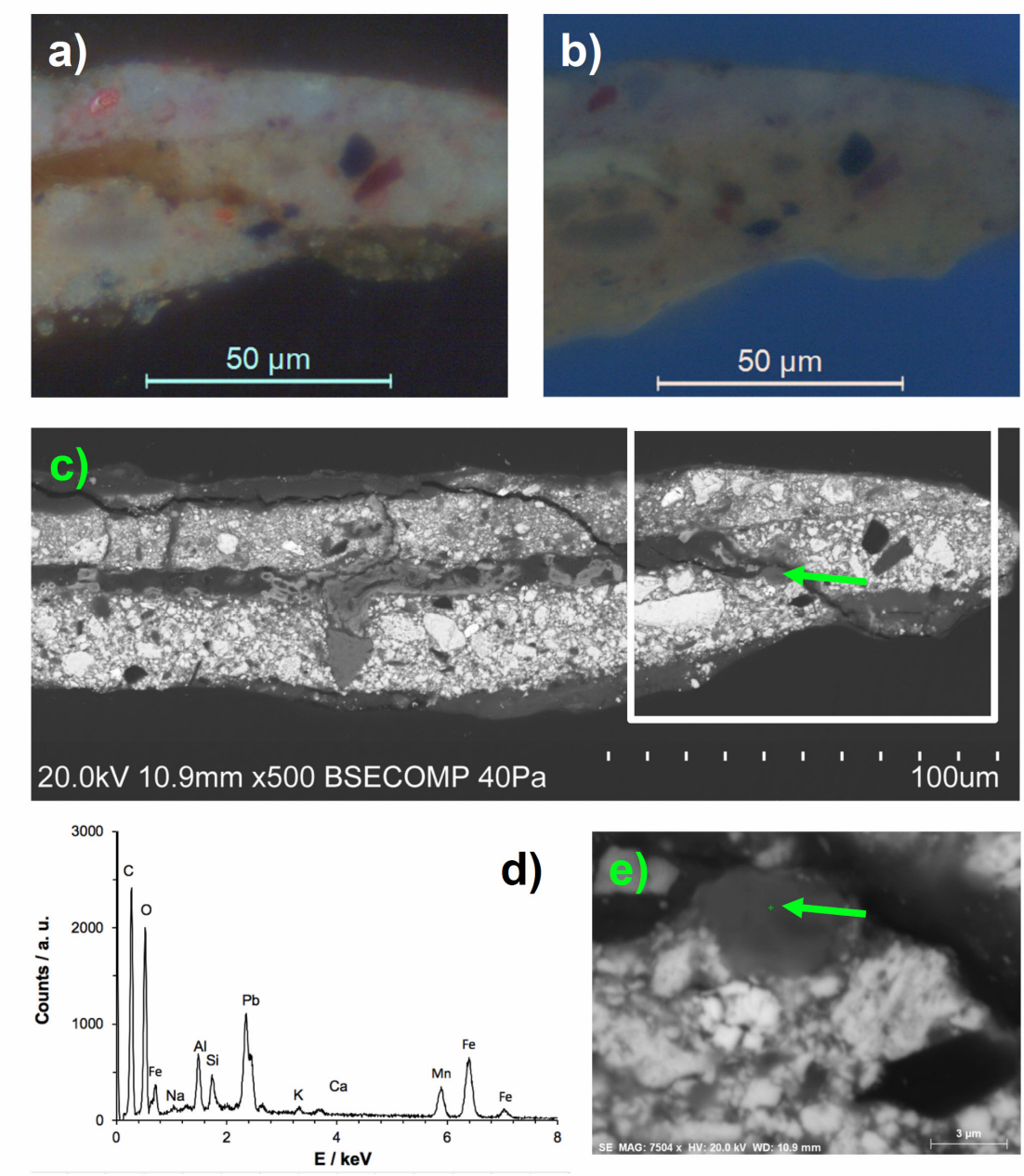


Figure S8. Detail of cross-section of sample #04, corresponding to the flesh of Saint Magdalene's face, under OM-Vis (**a**); detail of cross-section of sample #04 under OM-UV (**b**); SEM-BSE image of cross section of sample #04 with the location of the detail shown in a) and b) (**c**); SEM-EDX spectrum of umber particle (**d**) viewed in the SEM-BSE image (**e**).

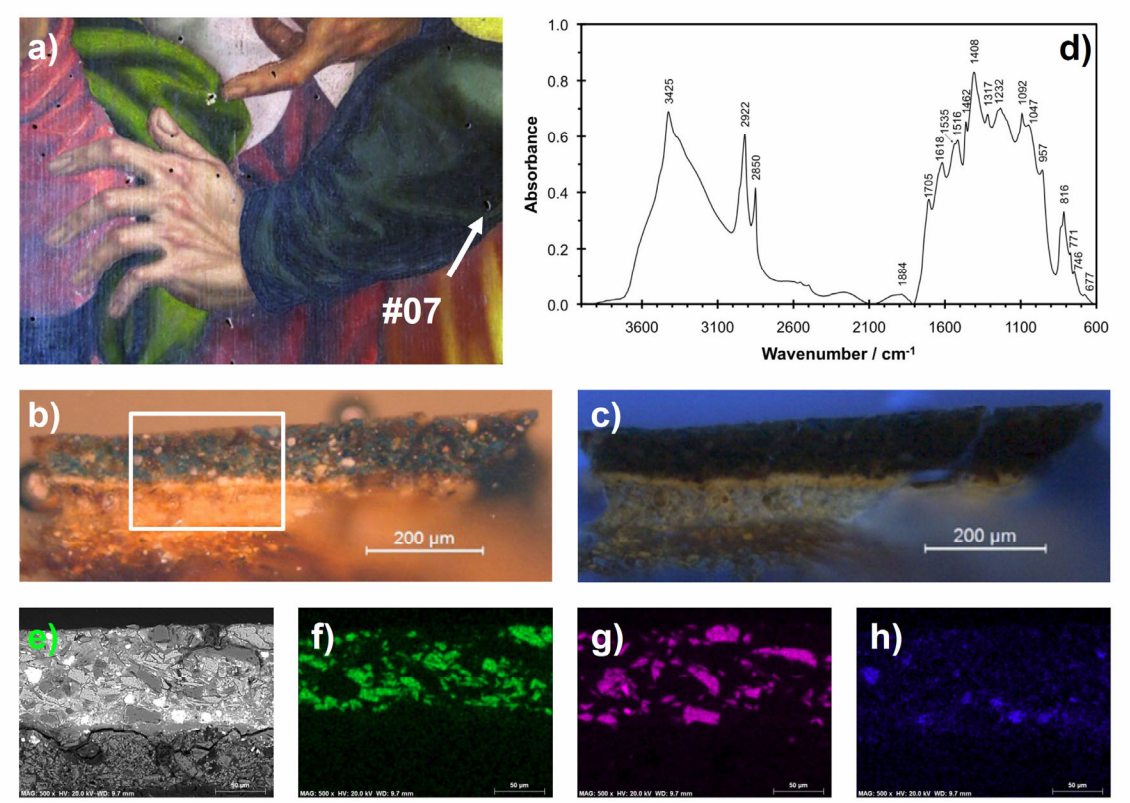
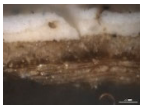
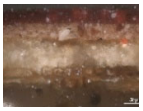
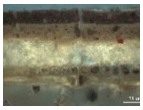
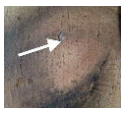
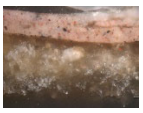
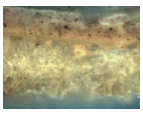
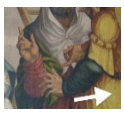
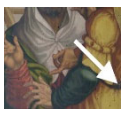
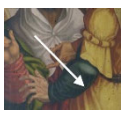
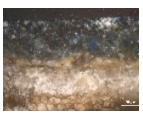
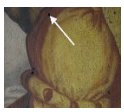
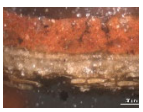
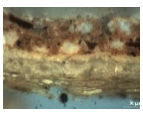
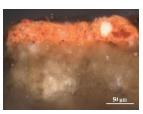
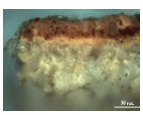
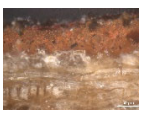
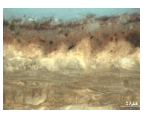
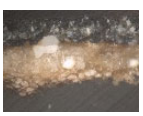
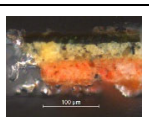
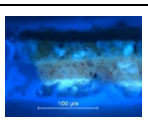
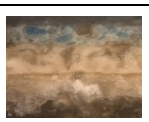
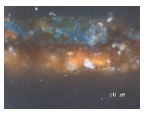
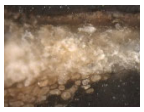
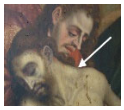
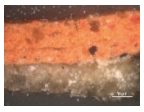
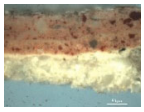
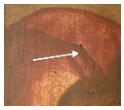
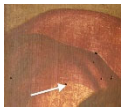
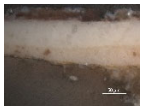
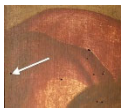
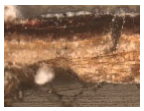
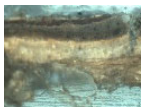
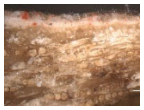
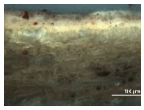
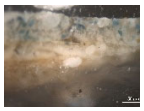
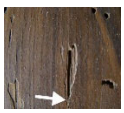
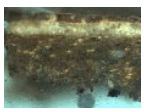
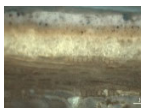


Figure S9. Detail of a blue drapery with location of sample #07 (**a**); cross section of sample #07 under OM-Vis (**b**); cross section of sample #07 under OM-UV (**c**); and FTIR spectrum of blue paint marked in b) with an arrow (**d**). According to the SEM-EDX results, the layer is rich azurite and smalt: SEM-BSE image of detail, marked in b), of cross-section of sample #07 (**e**); SEM-EDS maps of Cu (**f**), Si (**g**), and Pb (**h**). On the FTIR spectrum, azurite, as a basic copper carbonate, had characteristic ν(OH) bands around 3425 cm^{-1}; ν(CO_3) bands at 1408, 1092 cm^{-1}; a ν(CO) band at 957 cm^{-1}, and lastly, δ(OCO) bands at 816, 771, and 746 cm^{-1}. The band at 1462 cm^{-1}, together with the doublet at 1535 and 1516 cm^{-1} indicates the formation of both potassium (from the smalt) and lead soaps. The carbonyl ν(C=O) bands at 1705 cm^{-1} along with two sharp bands at 2922 cm^{-1} and 2850 cm^{-1}, due respectively to stretching CH_3 and CH_2 vibrations, identify an aged oil. The band at 1317 cm^{-1} ν_a(C-O) indicates the presence of oxalates.

Table S1. List of samples collected and analytical methods performed.

Sample number	Colour and location		OM-Vis	OM-UV	SEM-EDX	FTIR	μ-RS	HPLC
#01		White Magdalene's cloak				×		
#02		Yellow-greenish Magdalene's tunic			×	×	×	
#03		Pink, dark Magdalene's tunic			×	×		×
#04		Flesh, mid-tone Magdalene's eyelid			×	×	×	
#05		Yellow Tunic of apostle			×	×		
#06		Purple, dark Belt of apostle			×	×		
#07		Blue, dark Tunic of apostle			×	×		
#08		Orange Tunic of apostle					×	
#09		Red, mid-tone Tunic of apostle			×		×	
#10		Red, dark Tunic of apostle			×	×	×	×
#11		Green, dark Apostle's cloak			×			
#12		Green, light Apostle's cloak						
#13		Blue, light Virgin's cloak			×	×		

Sample number	Colour and location		OM-Vis	OM-UV	SEM-EDX	FTIR	μ-RS	HPLC
#14		Blue, dark Virgin's cloak						
#15		Brown S. John's hair						
#16		Red, mid-tone S. John's tunic			×	×	×	×
#17		Burgundy red, deep S. John's cloak			×	×		×
#18		Burgundy red, light S. John's cloak						
#19		Burgundy red, mid-tone S. John's cloak			×	×	×	×
#20		Pink, light Arquitecture, background				×		
#21		Blue-grey Sky						
#22		Blue, light Sky			×			
#23		Brown Cross						
#24		Blue grey Sky with cross underneath			×			