

# Supplementary material for the article in EPJ Plus: Efficiency of combined MA-XRF and CXRF to give non-destructive insights about changes of a historical painting

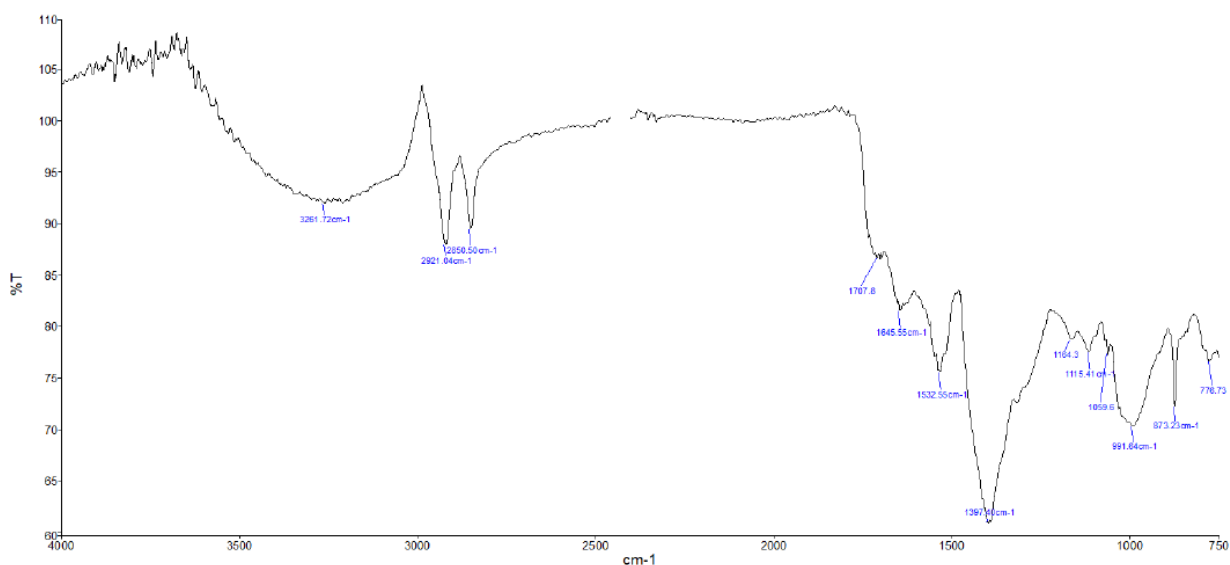
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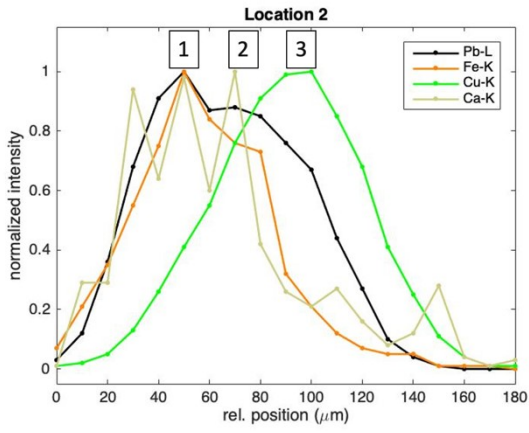
## Comparison between OM and SEM-EDX scans of cross-sections and CXRF depth and lateral scans (z, y) of different paintings studied with the Loux<sup>3D</sup>

**Table A.** Number of layers detected by CXRF lateral and depth scans compared to the layers detected by OM and SEM-EDX.

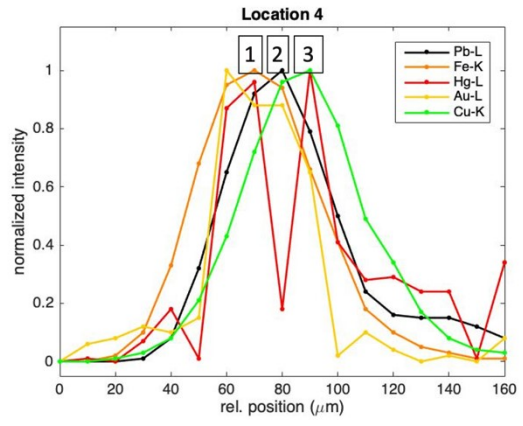
Painting, year of analysis	Cross-section	Number of layers detected by OM and SEM-EDX	Number of layers detected by CXRF lateral scan (y) of the cross-section	Number of layers detected by CXRF depth scan (z) in an adjacent location
<i>Virgin and Child surrounded by saints and a donor</i> , 2022	<b>A</b>	9	4	2/6 (the third coat of arms had been removed prior to the CXRF depth scan)
	<b>B</b>	8	4	5
	<b>C</b>	7	4	3
<i>L'Homme blessé</i> (Gustave Courbet), 2015 [7], [21]	<b>1089</b>	7	4	3
	<b>1087/1088</b>	9	8	3
	<b>1090</b>	8	7	
<i>The Rest on the Flight into Egypt</i> (G. F. Caroto), 2015 [4] <i>Famous men</i> , 2012 [1]	<b>A</b>	3		(Point 4) 2
	<b>5375</b>	4	3	2
	<b>4122</b>	4	3	3
	<b>5378</b>	3	2	1



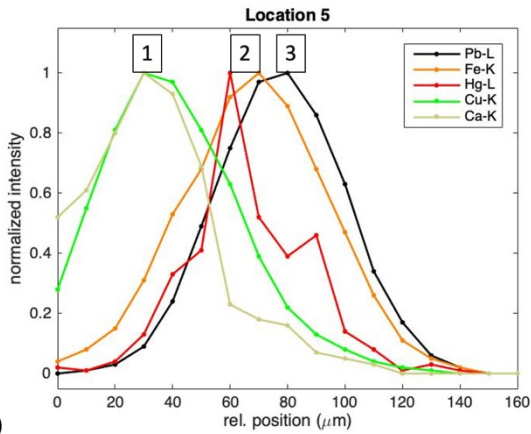
**Fig 1.** FT-IR spectrum of the varnish layer evidenced by the presence of resins in the cross-section A corresponding to the coats of arms obtained with a FT-IR microscope (Perkin-Elmer Spotlight 400/Spectrum Image).



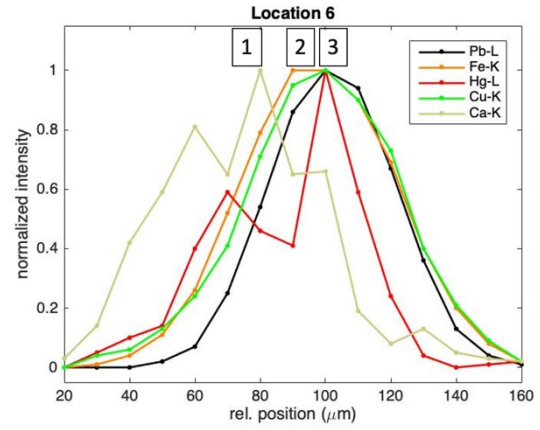
a)



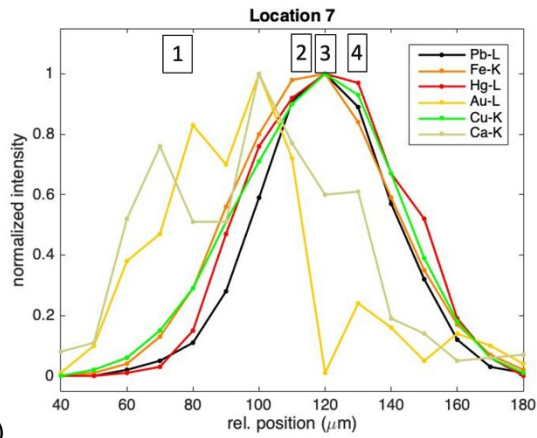
b)



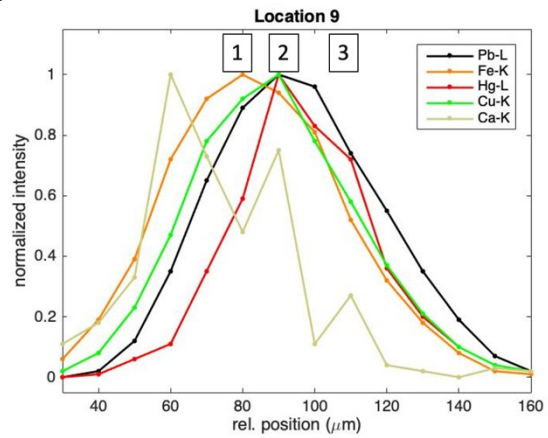
c)



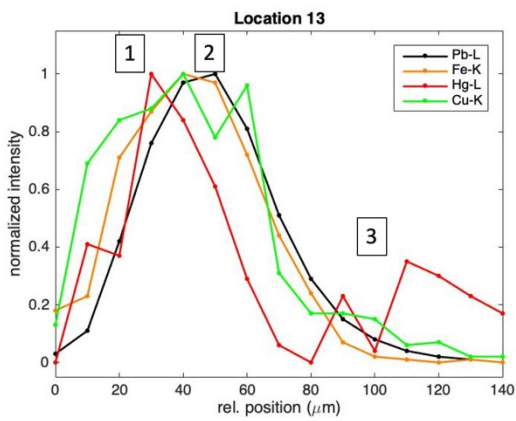
d)



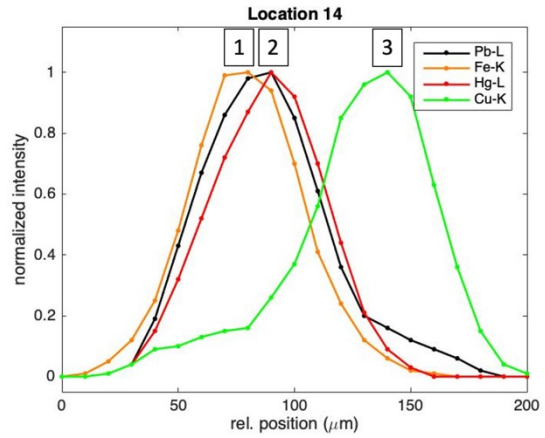
e)



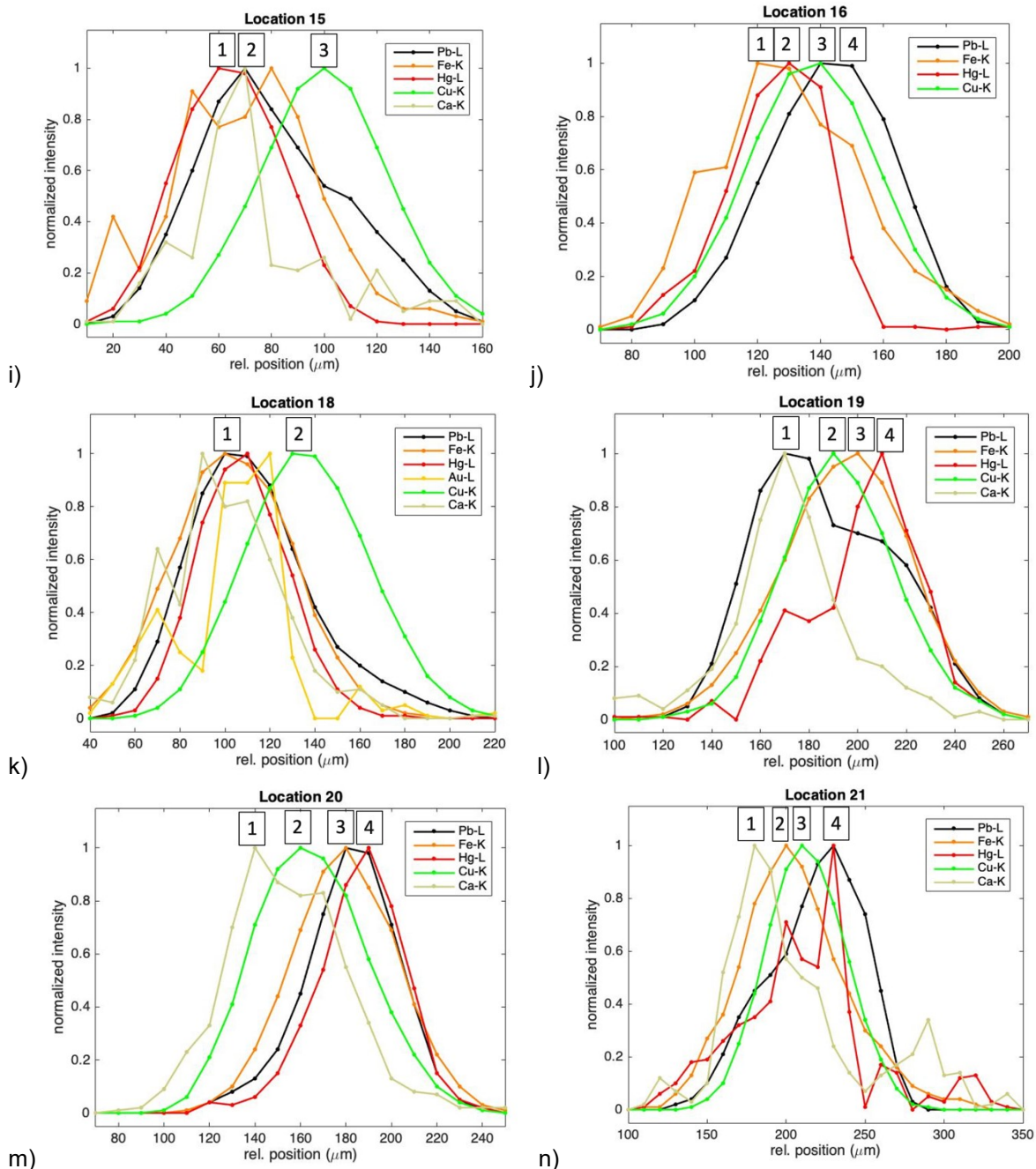
f)



g)



h)



**Fig II.** Results of the CXRF depth profiling. Like before, and contrary to the layer numbering convention, the left side of the depth profiles represents the painting surface. The identified paint layers are indicated with numbers on the depth profiles. Normalized elemental depth profiles for:

- a)** analysis location 2 (the intensity maxima of the Ca K $\alpha$ , Fe K $\alpha$ , Cu K $\alpha$  and Pb L $\alpha$  fluorescence lines are 22, 448, 14528 and 10939, respectively)
- b)** analysis location 4 (the intensity maxima of the Fe K $\alpha$ , Cu K $\alpha$ , Au L $\alpha$ , Hg L $\alpha$  and Pb L $\alpha$  fluorescence lines are 1713, 1027, 52, 152 and 35835, respectively)
- c)** analysis location 5 (the intensity maxima of the Ca K $\alpha$ , Fe K $\alpha$ , Cu K $\alpha$ , Hg L $\alpha$  and Pb L $\alpha$  fluorescence lines are 65, 2208, 4193, 192 and 30522, respectively)
- d)** analysis location 6 (the intensity maxima of the Ca K $\alpha$ , Fe K $\alpha$ , Cu K $\alpha$ , Au L $\alpha$ , Hg L $\alpha$  and Pb L $\alpha$  fluorescence lines are 46, 2074, 452, 124, 131 and 30219, respectively)
- e)** analysis location 7 (the intensity maxima of the Ca K $\alpha$ , Fe K $\alpha$ , Cu K $\alpha$ , Au L $\alpha$ , Hg L $\alpha$  and Pb L $\alpha$  fluorescence lines are 71, 15554, 9294, 48, 566 and 9181, respectively)
- f)** analysis location 9 (the intensity maxima of the Ca K $\alpha$ , Fe K $\alpha$ , Cu K $\alpha$ , Hg L $\alpha$  and Pb L $\alpha$  fluorescence lines are 45, 2132, 1148, 915 and 25341, respectively)
- g)** analysis location 13 (the intensity maxima of the Fe K $\alpha$ , Cu K $\alpha$ , Hg L $\alpha$  and Pb L $\alpha$  fluorescence lines are 785, 46, 105 and 39497, respectively)
- h)** analysis location 14 (the intensity maxima of the Fe K $\alpha$ , Cu K $\alpha$ , Hg L $\alpha$  and Pb L $\alpha$  fluorescence lines are 4560, 1415, 26239 and 1791, respectively)
- i)** analysis location 15 (the intensity maxima of the Ca K $\alpha$ , Fe K $\alpha$ , Cu K $\alpha$ , Hg L $\alpha$  and Pb L $\alpha$  fluorescence lines are 9, 71, 8898, 32030 and 3650, respectively)

j) analysis location 16 (the intensity maxima of the Fe K $\alpha$ , Cu K $\alpha$ , Hg L $\alpha$  and Pb L $\alpha$  fluorescence lines are 278, 68309, 139 and 5549, respectively)

k) analysis location 18 (the intensity maxima of the Ca K $\alpha$ , Fe K $\alpha$ , Cu K $\alpha$ , Au L $\alpha$ , Hg L $\alpha$  and Pb L $\alpha$  fluorescence lines are 79, 2903, 31626, 65, 1687 and 15713, respectively)

l) analysis location 19 (the intensity maxima of the Ca K $\alpha$ , Fe K $\alpha$ , Cu K $\alpha$ , Hg L $\alpha$  and Pb L $\alpha$  fluorescence lines are 26, 4301, 2467, 235 and 16127, respectively)

m) analysis location 20 (the intensity maxima of the Ca K $\alpha$ , Fe K $\alpha$ , Cu K $\alpha$ , Hg L $\alpha$  and Pb L $\alpha$  fluorescence lines are 145, 10855, 3298, 636 and 13215, respectively)

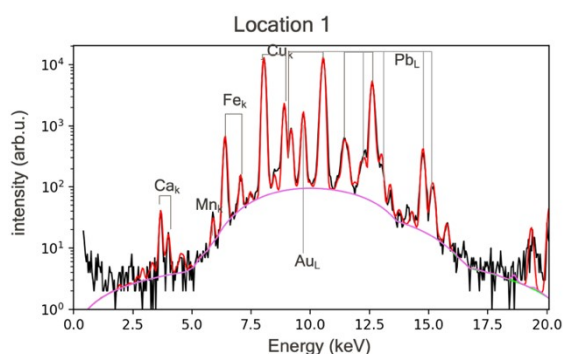
n) analysis location 21 (the intensity maxima of the Ca K $\alpha$ , Fe K $\alpha$ , Cu K $\alpha$ , Hg L $\alpha$  and Pb L $\alpha$  fluorescence lines are 41, 520, 23818, 37 and 2031, respectively)

## CXRF results for 22 locations (depth profiles)

Below are the analysis profiles of the three areas of interest, as well as the triangles on the floor. Locations 1, 2, 3, 10, 19 and 21 correspond to the monk's tunic, locations 11 to 16 and 18 to the coat of arms, locations 4, 8, 9 and 22 to the cross, and for the triangles locations 5, 6, 7 and 20 in addition to locations 4, 8, 19 and 21 presented in the garment and the cross. The identified paint layers are indicated by numbers on the CXRF profiles (Fig. II).

### Monk's tunic

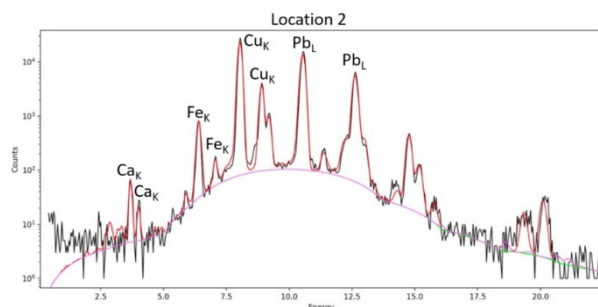
#### Location 1



**Fig III:** Sum spectrum of the CXRF depth scan of location 1 (see Fig. 4c in main article)

Number on the profile	CXRF detected elements	Interpretation	
3	Cu	Bishop's green dress 30 $\mu$ m separation: varnish	Bishop's dress
2	Au	Gold leaf	
1 surface	Pb, Fe	Visible white and beige tunic	Golden detail
			Monk

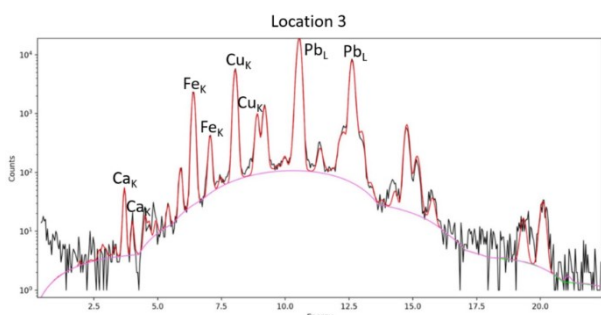
#### Location 2



**Fig IV:** Sum spectrum of the CXRF depth scan of location 2 (see Fig. IIa)

Number on the profile	CXRF detected elements	Interpretation	
3	Cu	Bishop's green dress 25 $\mu$ m separation: varnish	Bishop's dress
2	Pb, Fe	30 $\mu$ m separation	Monk
1 surface	Pb, Fe	Visible white and beige tunic	

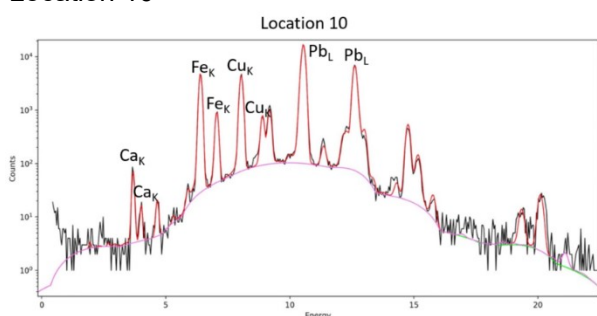
### Location 3



**Fig V:** Sum spectrum of the CXRF depth scan of location 3 (see Fig. 6a in main article)

Number on the profile	CXRF detected elements	Interpretation	
2	Cu	Donator's short dress 55 $\mu\text{m}$ separation: varnish	Donator
1 surface	Pb, Fe, Ca	Visible long white tunic	Monk

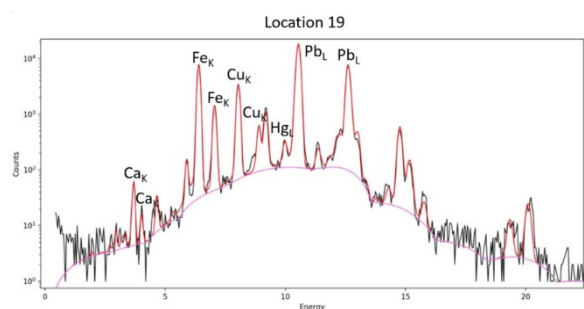
### Location 10



**Fig VI:** Sum spectrum of the CXRF depth scan of location 10 (see Fig. 6b in main article)

Number on the profile	CXRF detected elements	Interpretation	
3	Cu, Hg, Fe	Donator's legs 10 $\mu\text{m}$ separation	Donator
2	Pb, Fe (Ca)	Monk's white-brown tunic	Monk
1 surface	Ca	Probable varnish on the surface	

### Location 19

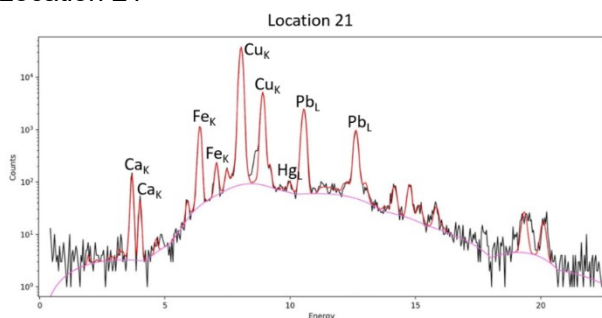


**Fig VII:** Sum spectrum of the CXRF depth scan of location 19 (see Fig. IIL)

Number on the profile	CXRF detected elements	Interpretation	
4	Hg, Pb	Beige floor 10 $\mu\text{m}$ separation	Floor
3	Fe, Pb	Sol beige 10 $\mu\text{m}$ separation: varnish?	
2	Cu	Triangle on the floor 20 $\mu\text{m}$ separation	Triangle
1 surface	Pb, Hg, Ca	Brown border of the garment	Monk



## Location 21

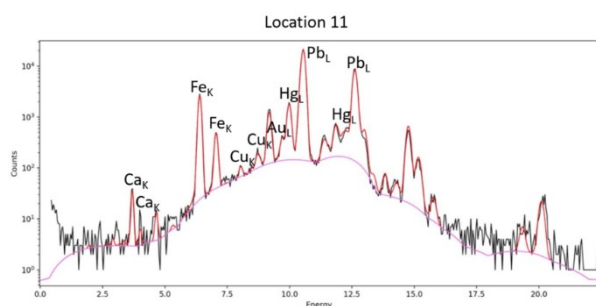


**Fig VIII:** Sum spectrum of the CXRF depth scan of location 21 (see Fig. II n)

Number on the profile	CXRF detected elements	Interpretation	
4	Pb, Hg	Beige floor	Floor
3	Cu	10 $\mu$ m separation: varnish?	Trianale
2	Fe	Brown border of the garment	Monk
1 surface	Ca	15 $\mu$ m separation Varnish?	

## Coat of arms

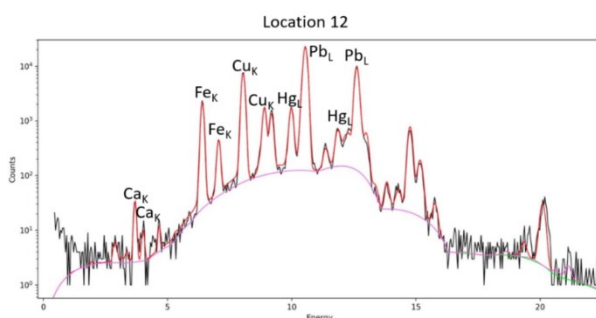
### Location 11



**Fig IX:** Sum spectrum of the CXRF depth scan of location 11 (see Fig. 6d in main article)

Number on the profile	CXRF detected elements	Interpretation	
2	Au	Gold	Coat of arms 1
1 surface	Fe, Pb, Hg (Ca) (Cu)	40 $\mu$ m separation: varnish Beige layer	Coat of arms 2

### Location 12



**Fig X:** Sum spectrum of the CXRF depth scan of location 12 (see Fig. 6c in main article)

Number on the profile	CXRF detected elements	Interpretation	
2	Cu	Copper background of the first coat of arms	Coat of arms 1
1 surface	Pb, Hg, Fe, Ca	40 $\mu$ m separation: varnish Beige layer	Coat of arms 2

Location 13

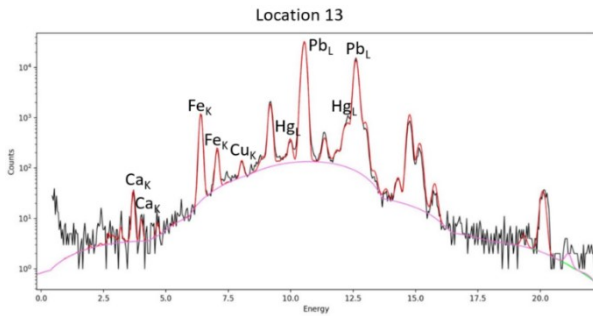


Fig XI: Sum spectrum of the CXRF depth scan of location 13 (see Fig. IIg)

Number on the profile	CXRF detected elements	Interpretation	
2	Pb, Fe	Beige layer	Coat of arms 2
1 surface	Hg, Cu	Beige column	Coat of arms 3

Location 14

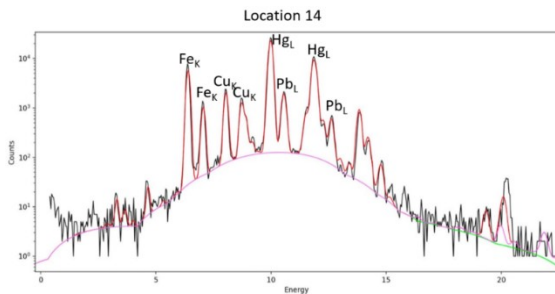


Fig XII: Sum spectrum of the CXRF depth scan of location 14 (see Fig. IIh)

Number on the profile	CXRF detected elements	Interpretation	
3	Cu	Copper background of the first coat of arms 50 µm separation: varnish	Coat of arms 1
2	Pb, Hg	Red layer	Coat of arms 2
1 surface	Fe	Beige-red layer	

Location 15

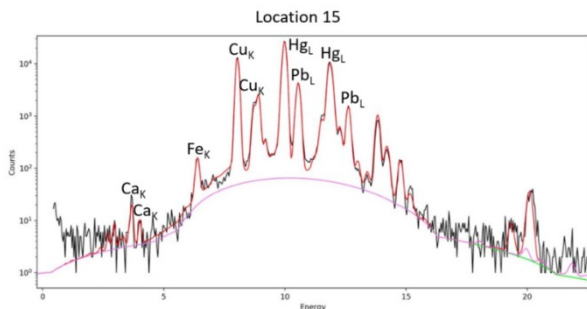
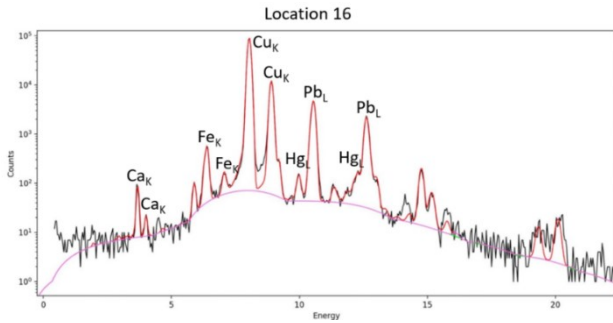


Fig XIII: Sum spectrum of the CXRF depth scan of location 15 (see Fig. IIIi)

Number on the profile	CXRF detected elements	Interpretation	
3	Cu	Copper background of the first coat of arms 30 µm separation: varnish	Coat of arms 1
2	Pb, Fe, Ca	Beige layer	Coat of arms 2
1 surface	Hg	Red layer	

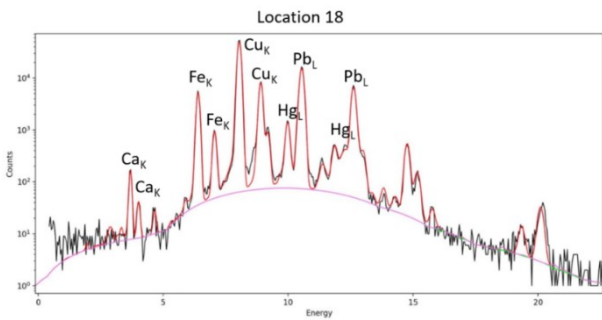
Location 16



**Fig XIV:** Sum spectrum of the CXRF depth scan of location 16 (see Fig. IIj)

Number on the profile	CXRF detected elements	Interpretation	
4	Pb	White / beige? layer	Coat of arms 2
3	Cu	Brown animal figure	
2	Hg	Brown animal figure	
1 surface	Fe	Brown animal figure	

Location 18

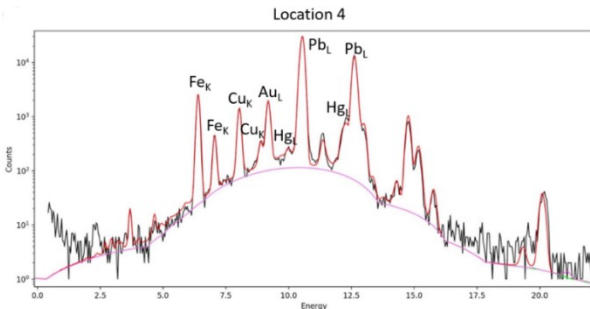


**Fig XV:** Sum spectrum of the CXRF depth scan of location 18 (see Fig. IIh)

Number on the profile	CXRF detected elements	Interpretation	
2	Cu	Copper background of the first coat of arms	Coat of arms 1
1 surface	Pb, Fe, Hg, Ca	30 µm separation: varnish Brown layer on the animal	Coat of arms 2

**Cross**

Location 4

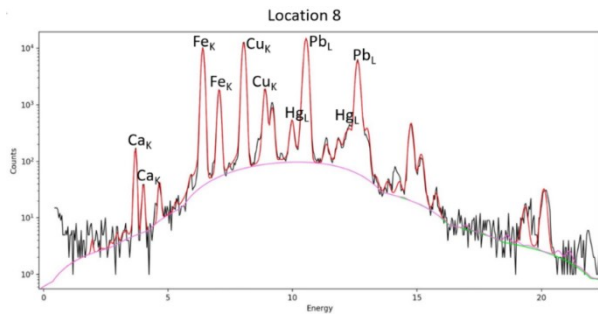


**Fig XVI:** Sum spectrum of the CXRF depth scan of location 4 (Fig. IIb)

Number on the profile	CXRF detected elements	Interpretation	
3	Cu (Hg)	Brown triangle on the floor	Brown triangle
2	Pb, Hg	Dark brown part of the cross under the beige?	Cross
1 surface	Fe, Hg	Cross, beige zone	



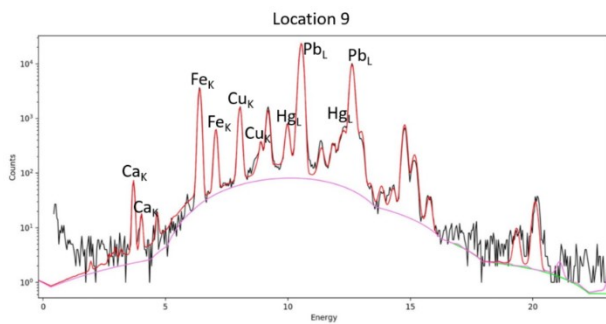
## Location 8



**Fig XVII:** Sum spectrum of the CXRF depth scan of location 8 (see Fig. 6e in main article)

Number on the profile	CXRF detected elements	Interpretation	
5	Pb, Hg	Beige floor	Floor
4	Fe, Pb, Hg	Beige floor 25 $\mu$ m separation: varnish?	
3	Cu	Triangle du sol 15 $\mu$ m separation	Brown triangle
2	Pb (Fe)	Brown cross	
1 surface	Hg, Ca	Brown cross	Cross

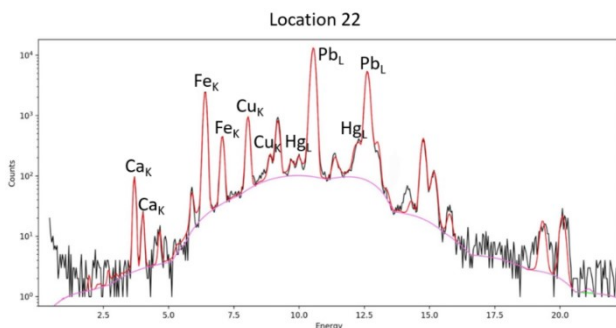
## Location 9



**Fig XVIII:** Sum spectrum of the CXRF depth scan of location 9 (see Fig. II f)

Number on the profile	CXRF detected elements	Interpretation	
3	Pb, Hg	Wrist skin tone	Hand
2	Cu, Hg, Pb	Brown cross 15 $\mu$ m separation	
1 surface	Fe, Ca	Brown cross	Cross

## Location 22

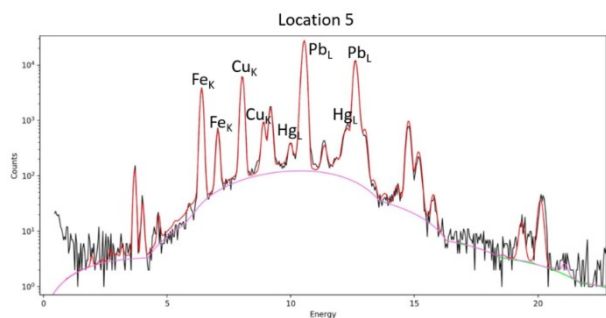


**Fig XIX:** Sum spectrum of the CXRF depth scan of location 22 (see 6f in main article)

Number on the profile	CXRF detected elements	Interpretation	
4	Pb	White layer? (cape)	Red cape
3	Cu	Red cape? 25 $\mu$ m separation: varnish?	
2	Fe, Pb	Brown cross	Cross
1 surface	Hg, Ca (Cu)	Beige cross	

**Triangles** (already shown in locations 19 and 21 in the monk's tunic section, as well as 4 and 8 in the cross section)

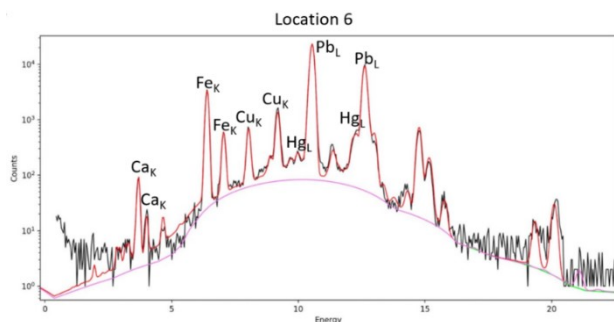
**Location 5**



**Fig XX:** Sum spectrum of the CXRF depth scan of location 5 (see Fig. IIc)

Number on the profile	CXRF detected elements	Interpretation	
3	Pb, Hg	Beige floor	Floor
2	Fe, Hg	Beige floor	
1 surface	Cu, Ca	40 µm separation: varnish? Brown triangle on the floor	Brown triangle

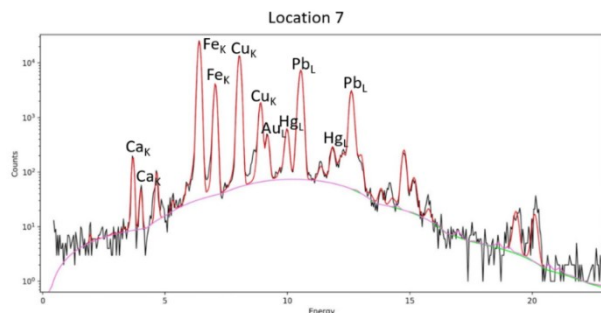
**Location 6**



**Fig XXI:** Sum spectrum of the CXRF depth scan of location 6 (see Fig. II d)

Number on the profile	CXRF detected elements	Interpretation	
3	Pb, Cu	Beige floor	Floor
2	Fe, Hg	Beige floor	
1 surface	Ca	Probable varnish on the surface	

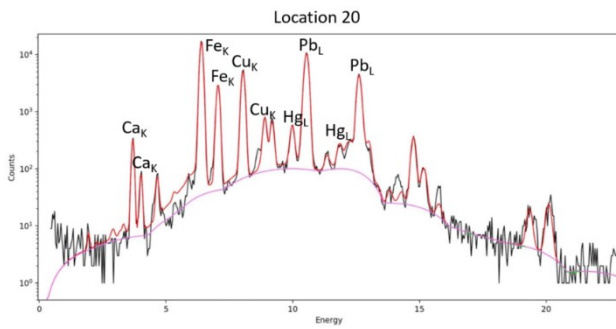
**Location 7**



**Fig XXII:** Sum spectrum of CXRF depth scan of location 7 (see Fig. IIe)

Number on the profile	CXRF detected elements	Interpretation	
3,4	Cu, Pb, Hg	Beige floor	Floor
2	Fe	Beige floor?	
1 surface	Ca	Probable varnish on the surface	

Location 20



**Fig XXIII:** Sum spectrum of the CXRF depth scan of location 20 (see Fig. IIm)

Number on the profile	CXRF detected elements	Interpretation	
4	Hg, Pb	Beige floor	Floor
3	Fe, Pb	Beige floor	
		15 $\mu$ m separation: varnish?	
2	Cu (Ca)	Triangle on the floor	Brown triangle
1 surface	Ca	Probable varnish on the surface	