Supplementary materials:

Figure S.1. Microphotograph (PPL) of cross-section of white sample S2. From the outer to inner: paint layer 1 white lead; ground: raw Sienna. The dotted lines indicate the area examined in SECM experiments.

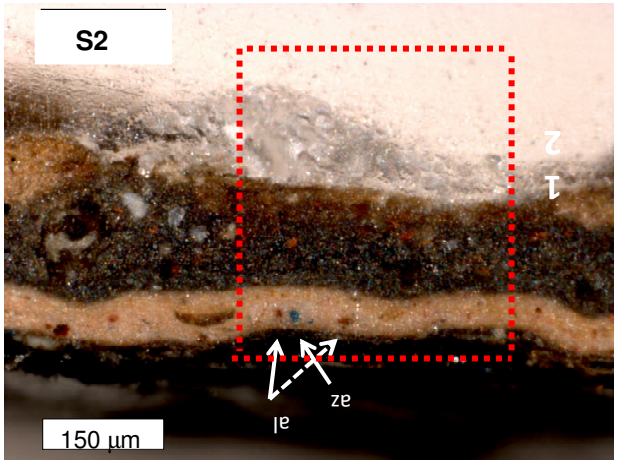

Figure S.2. Microphotograph (PPL) of cross-section of flesh sample S3. From the outer to inner: paint layer 1 azurite and madder grains dispersed in white lead layer; ground: raw Sienna.

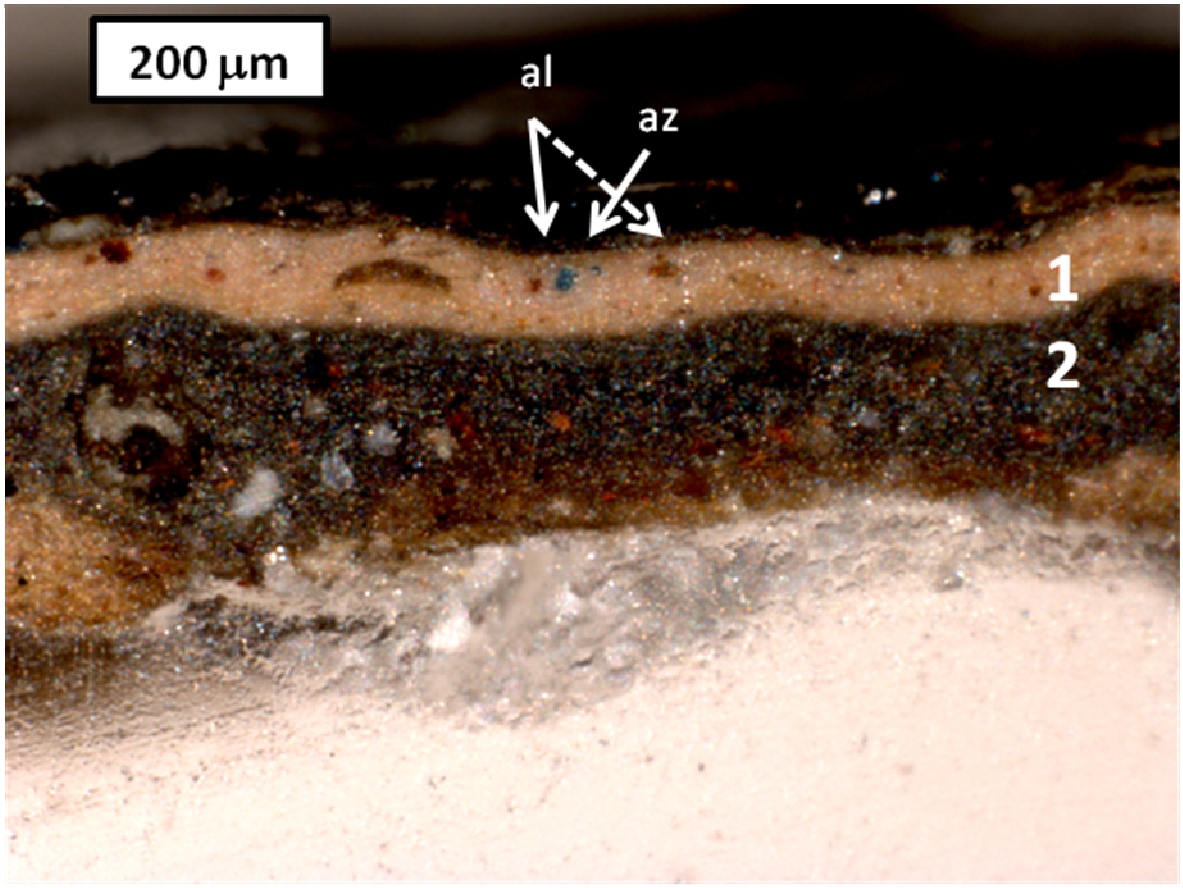

Figure S3 shows SECM images of a microparticulate deposit of lead white ($2PbCO_3.Pb(OH)_2$) on Pt substrate before and after application of a prolonged reductive step to the pigment. As can be seen on comparing Figs. 3a and 3b, the peaked features corresponding to the lead white grains decreased progressively and became entirely replaced by a growing feature in an adjacent position, attributable to the formation of a Pb grain.

Figure S.3. SECM topographic images of a microparticulate deposit of Lead white (K46002 Kremer pigmente) on Pt substrate immersed into air-saturated 0.25 M HAc/NaAc, pH 4.75. a) E_T = –0.45 V; E_S = 0.00 V; b) E_T = –0.45 V; E_S = –0.70 V; c) E_T = +0.30 V; E_S = –0.70 V after application of a potential of –0.70 V to the substrate during 10 min. Continuous arrows mark the feature corresponding to the emerging Pb while dotted arrows mark the decreasing lead white grains.

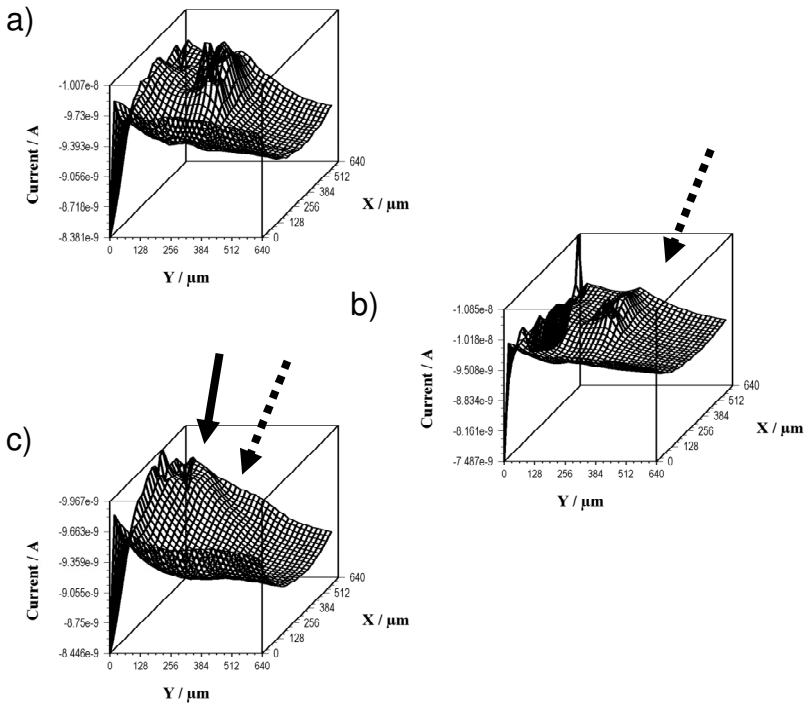

Table S.1. Changes in height and roughness of samples in Figures 5 and 6.

	Height (nm)				
	initial		final		shift
	mean value	desv st	mean value	desv st	
haematite	1420	0.06	180	3	1240
morin	680	3	450	20	230

	Roughness (nm)					
	Initial		Final		Shift	
	Ra	Rq	Ra	Rq	Ra	Rq
haematite	12	16	32	37	20	21
morin	47	60	72	86	25	26

Figure S.4. SEM/EDX spectra recorded in different spots in sample S1 corresponding, respectively, to lead white and azurite accompanied by traces of $CaCO_3$ and aluminosilicate clays.

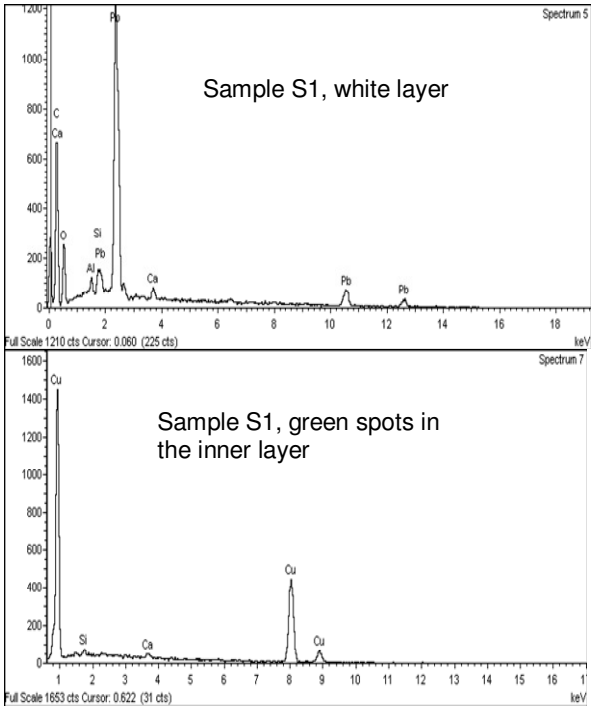

Figure S.5. SEM/EDX spectra recorded in different spots in sample S1 corresponding, respectively, to iron earth accompanied by traces of $CaCO_3$ and aluminosilicate clays and lead white.

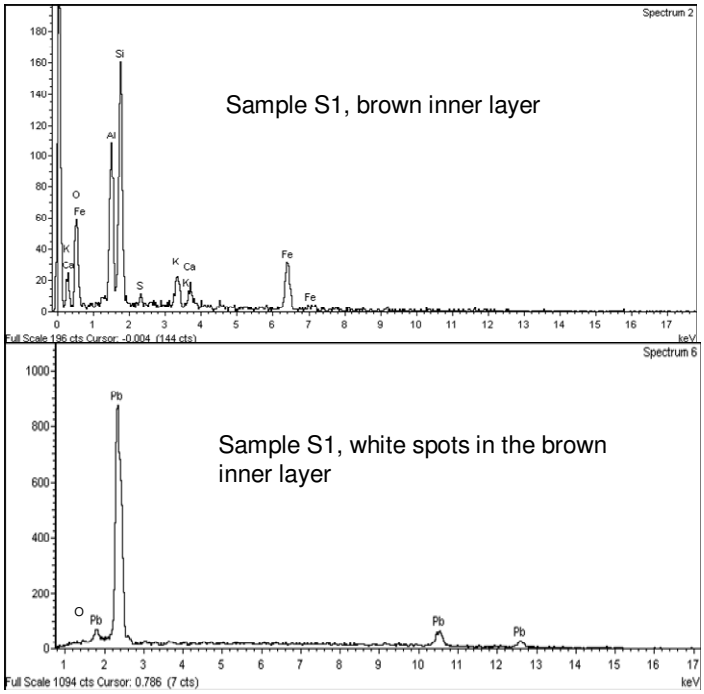

Figure S.6. SECM topographic images of paint sample S2 in parallel arrangement (Figure 1 b) on Pt substrate immersed into 2.0 mM $K_4Fe(CN)_6$ plus 0.25 M HAc/NaAc, pH 4.75. a) E_T = +0.30 V; E_S = 0.00 V. Here grain pigments appear as negative feedback features but large differences in the tip-sample distance results in smoothed background.