Supporting Information

The Degradation Process of Lead Chromate in paintings by Vincent van Gogh studied by means of Spectromicroscopic methods. Part IV: Artificial aging of model samples of co-precipitates of lead chromate and lead sulfate

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1. EXPERIMENTAL SECTION

1.1 Irradiation with different wavelength bands of the UV-visible light

The emission spectrum of the Cermax xenon lamp (Excelitas Technologies) and the UV-visible transmission spectra of the filters used to perform the irradiation with different wavelength bands of the UV-visible light are reported in Figure S-1A.

The filters show the following percentage values in correspondence of their maximum transmittance energy range: "UVA-Vis": *ca.* 87% transmittance above 370 nm; "UV": 76% transmittance at 341 nm; "blue": 65% transmittance at 421 nm; "red": *ca.* 90% transmittance above 620 nm.

Figure S-1B shows the unsaturated spectrum of unaged powder S^{*}_{3D}, employed to select wavelength ranges of the UV-visible spectrum for aging several coupons of S_{3D} paints.

An intense absorption band between 350 and 560 nm is observable. This is distinctive for the chromate-species and it is ascribable to a charge transfer ($t_1 \rightarrow e$) from the oxygen nonbonding to unoccupied chromium antibonding d-orbitals.[1,2,3,4]

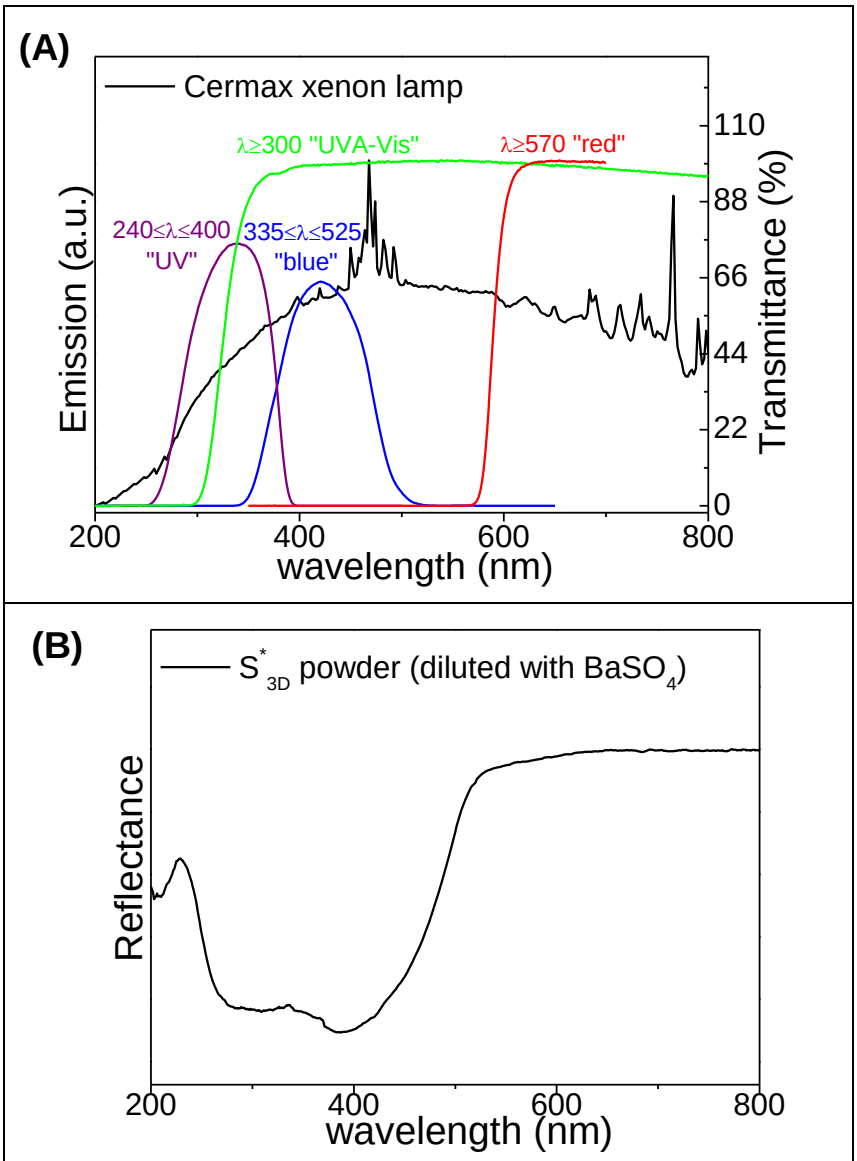

Figure S-1 (A) Spectral irradiance of the (black) Cermax xenon lamp and UV-visible transmission spectra of the filters used to perform the aging treatment in the (purple) "UV", (blue) "blue", (green) "UVA-Vis", and (red) "red" region of the UV-visible light. (B) UV-visible diffuse reflectance spectrum of a S^*_{3D} pellet. In (A) the emission spectrum of the Cermax xenon lamp was provided by the manufacturer (Excelitas Technologies).

2. RESULTS AND DISCUSSION

2.1 Colorimetric analysis of paint model S_{3D} and historic sample A

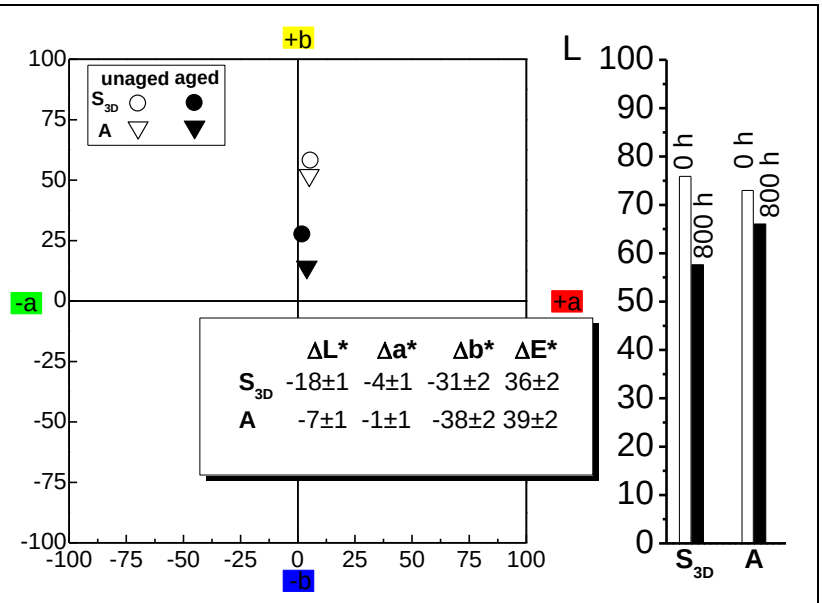

Figure S-2. Colorimetric analysis of samples S_{3D} and A [(open symbol) unaged and (filled symbol) aged (UVA-visible light, Solarbox, 800 h); (triangle) sample A and (circle) S_{3D}].

2.2 Cr pre-edge peak region of XANES spectra collected from unembedded samples (unfocused X-ray beam mode)

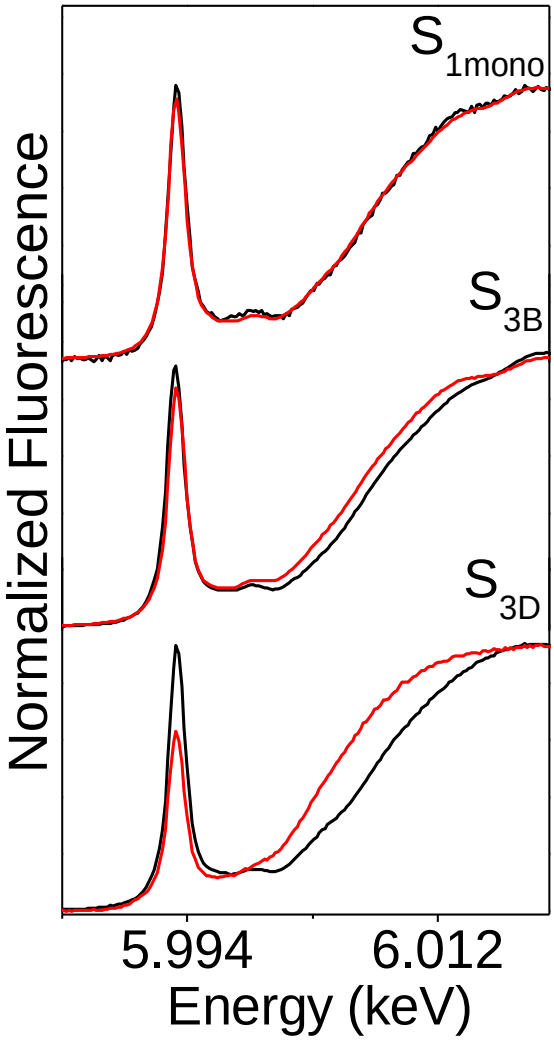

Figure S-3. Pre-edge peak energy range of the Cr XANES spectra recorded from the not embedded model paint S_{1mono}, S_{3B}, and S_{3D}. (black) before; (red) after aging.

2.3 Linear combination fitting results of Cr K-edge XANES spectra of aged sample S_{3D}

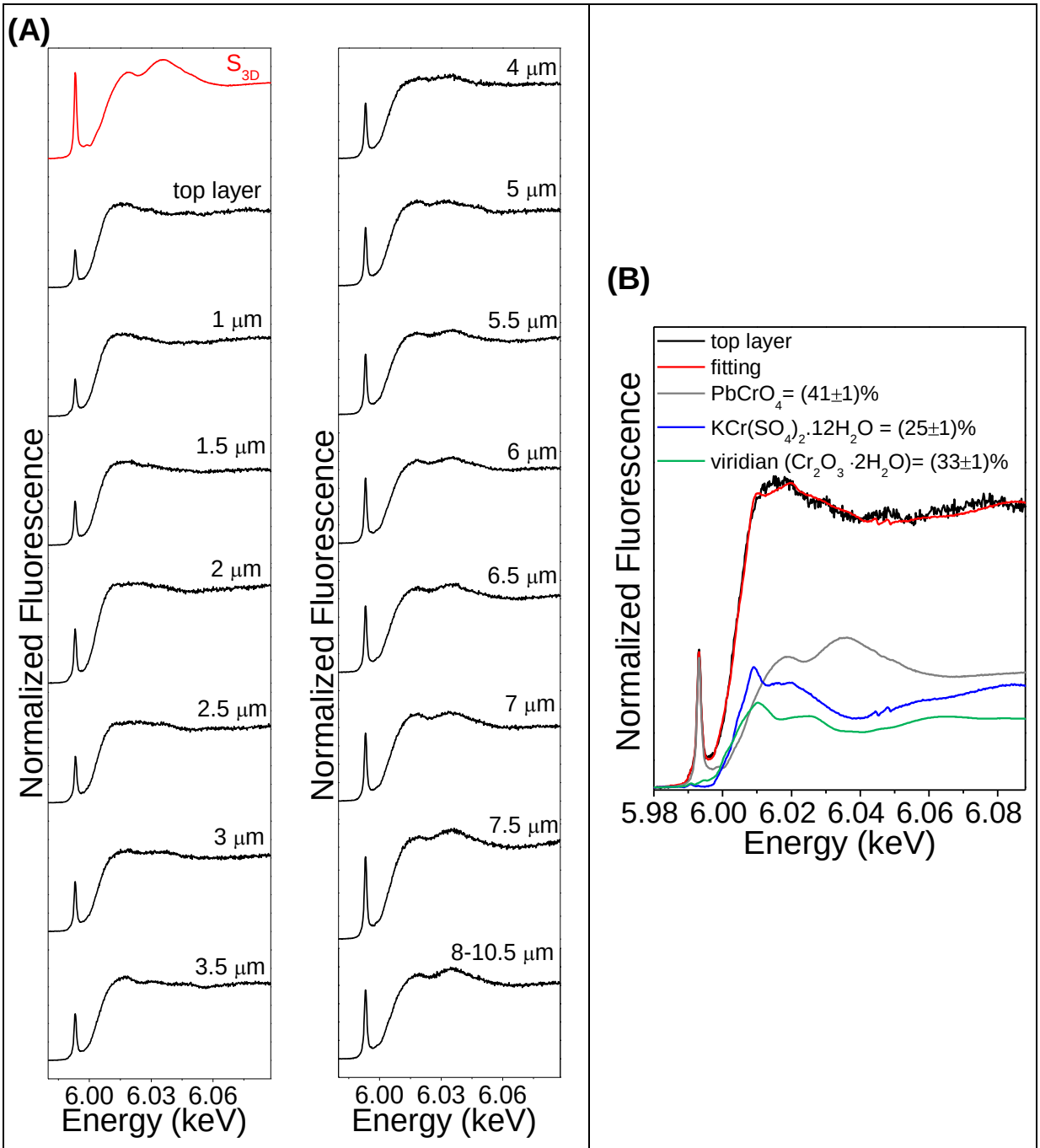

Figure S-4. (A) Cr K-edge XANES spectra recorded from embedded paint model S_{3D}: (red) before and (black) after UVA-visible light exposure (Solarbox). (B) Quantitative estimation of the Cr species in the aged sample S_{3D}: (red) Fit of the (black) spectral data as a linear combination of (gray) $PbCrO_4$, (green) $Cr_2O_3 \cdot 2H_2O$, and (blue) $KCr(SO_4)_3 \cdot 12H_2O$ reference spectra and estimation of their relative abundances.

Table S-1. Data from series of Cr K-edge XANES spectra collected from embedded aged paint models composed of different sulfate amount: wavelenght bands and system used for samples aging, aging time, total depth and step size of XANES spectra line, quantitative estimation of Cr species, expressed as [Cr(VI)]/[Cr_{total}] versus depth**.**

Sample	wavelength bands and system for aging treatment	Aging time (hours)	depth Cr K-edge XANES spectra line (µm)	Step size (µm)	Linear combination fitting results			
					3 components		2 components	
					Total depth (µm)	[Cr(VI)]/[Cr_{total}] (%)	Total depth (µm)	[Cr(VI)]/[Cr_{total}] (%)
S_{1mono}	UVA-visible, Solarbox	800	3	0.5	-	-	3	80
S_{1ortho}	UVA-visible, Cermax xenon lamp	98	3; 2 point measurements, depth: 4 and 11.5 µm	0.5	-	-	-	80-90
S_{3B}	UVA-visible, Solarbox	800	3	0.5	-	-	3	70-80
D_1	UVA-visible, Solarbox	800	3	0.5	-	-	3	80-85
S_{3C}	UVA-visible, Solarbox	800	6.5	0.5	2	55-60	From 2.5 to 6	60-70
S_{3D}	UVA-visible, Solarbox	800	10.5	0.5	3.5	40-50	From 4 to 10.5	60-80
S_{3D}	"UVA-Vis", Cermax xenon lamp	98	8	first 4 µm: 1µm; every 2 µm for the spectra at greater depth	2	40	From 3 to 8	60-80
S_{3D}	"UV", Cermax xenon lamp	98	7	1	3	50-55	From 3 to 7	60-75
S_{3D}	"Blue", Cermax xenon lamp	98	3 point measurements, depth: 0,2 and 9 µm	-	-	-	-	65-80

References

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