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Supplementary Materials for

Sulfur K-edge micro- and full-field XANES identify marker for preparation method of ultramarine pigment from lapis lazuli in historical paints

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Supplementary Materials and Methods

Historical samples – embedding and imaging details

The sample (Rijksmuseum) from Jan Brueghel (II)'s *Still Life with Flowers in a Glass*, c. 1625 – c. 1630 (Rijksmuseum) was prepared using the same protocol as that for the loose pigments described in the main text. The sample was then imaged with a Zeiss Axio Imager.A2m light under ultraviolet (LED 365 light source) light with a Zeiss AxioCam MRc5 digital camera.

The sample (Mauritshuis) from Jan Steen's *The Life of Man*, c. 1665 (Mauritshuis) was embedded in Technovit® 2000 LC (in 2013) and imaged with a Leica DM2500M under ultraviolet light with a Leica DFC490 digital camera.

The samples (C2RMF) from Johan Maelwael's *Pieta with the Holy Trinity*, c. 1400 (Louvre) and Henri Bellechose's *The Last Communion and Martyrdom of Saint Denis*, 1416 (Louvre) were embedded in polyester resin 'Sody 33' and imaged with a NIKON Eclipse LV100ND with UV-2A fluorescence filter.

The sample (RKD - Netherlands Institute for Art History, archive of Prof. Dr. J.R.J. van Asperen de Boer) from Rogier van der Weyden's *The Lamentation of Christ*, c. 1460 – 1464 (Mauritshuis) was embedded in 'Poly-Pol PS 230' (in 1986) and imaged with a Leica DM2500M under ultraviolet light with a Zeiss AxioCam 512 color digital camera.

Photo-radiation damage in focused microbeam XRF mode

For the study of lazurite in historical samples, limits of the FF-XANES were reached: the low concentration of lazurite pigment particles sometimes within a highly absorbing lead-based matrix made FF-XANES less effective than µXANES in XRF mode with a focused beam for the measurement of XANES spectra. The latter approach allows for pointing to individual particles-of-interest, even in complex mixtures, and with high sensitivity. However, while unlikely for the unfocused beam, X-rays in a focused microbeam mode can introduce artifacts into the spectra. In particular, photo-radiation damage (*7*, *29*, *55*) induced by the beam is a concern.

The influence of photo-radiation on lazurite was investigated comparing exposures of lazurite to either a focused (flux of 3.7×10^9 photon s^{-1}, spotsize of 0.6×1.0 μm^2) or an attenuated focused (flux of 4.3×10^8 photon s^{-1}, spotsize of 0.6×1.0 μm^2, 6 µm Al filter) X-ray microbeam. It was observed that the microbeam has an immediate effect on the spectral response of lazurite, particularly in the pre-edge energy range. Upon initial exposure to the focused beam, the intensity of peaks at 2471.2 and c. 2478 eV – attributed to reduced sulfur species and sulfite, respectively – are more intense relative to those under the attenuated beam on the same sample, while the intensity of the sulfate peak is decreased. Such peak variations indicate that the X-ray microbeam induces photoreduction (e.g. from sulfate) and is consistent with other reports on µXANES.(*7*, *29*, *55*) With each irradiation thereafter with the focused beam at the same position on the sample, subtle further changes are observed (Fig. S7) with the peak at 2471.2 and c. 2478 eV stabilizing and continuing to grow, respectively.

To minimize the risks and effects of radiation damage with analysis of particles-of-interest, XANES spectra were therefore acquired using an attenuated focused microbeam. In this mode, to obtain sufficient signal-to-noise ratios but also avoid repeating acquisitions on the same spot, several µXANES spectra were acquired on multiple particles and/or spots within a particle of lazurite.

Data Files

Raw, pre-processed, and processed data: *doi:10.15151/ESRF-DC-186933507*
GitHub repository: https://github.com/alessaan/rhapsody-in-blue

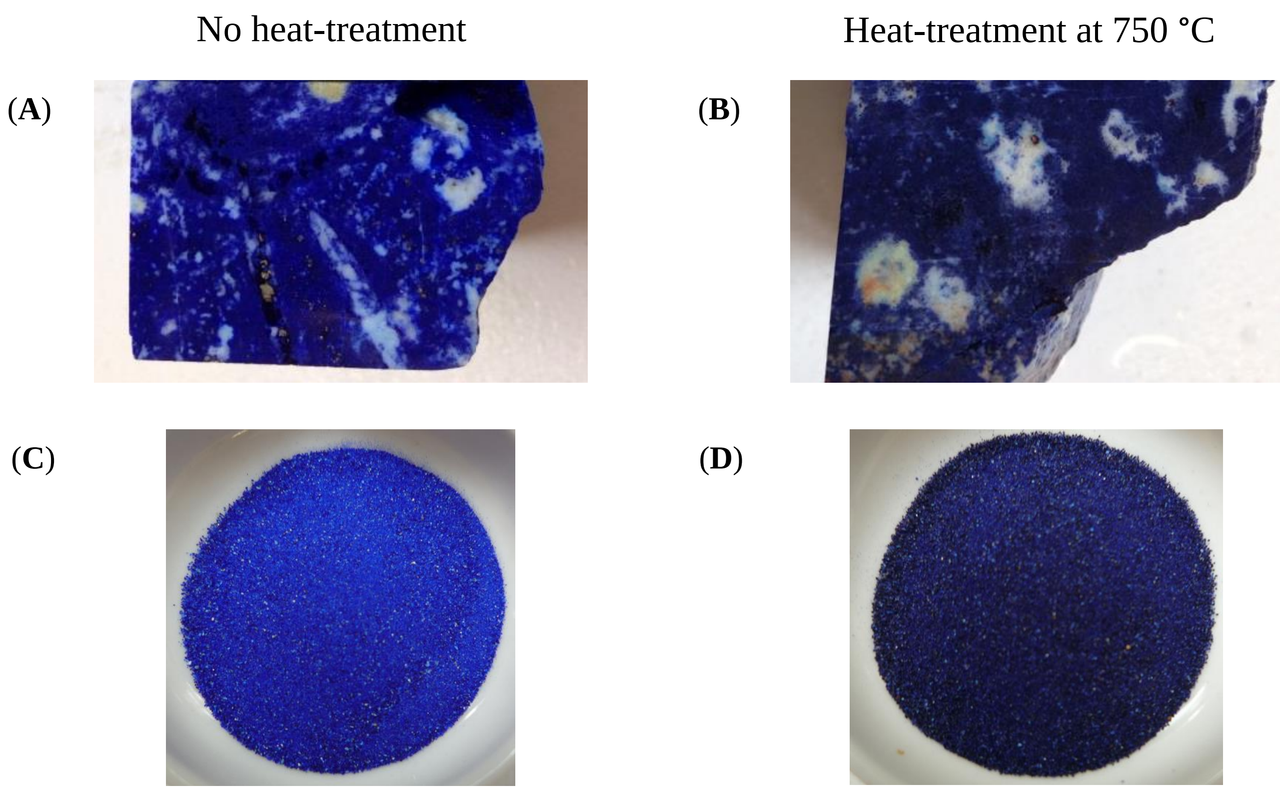
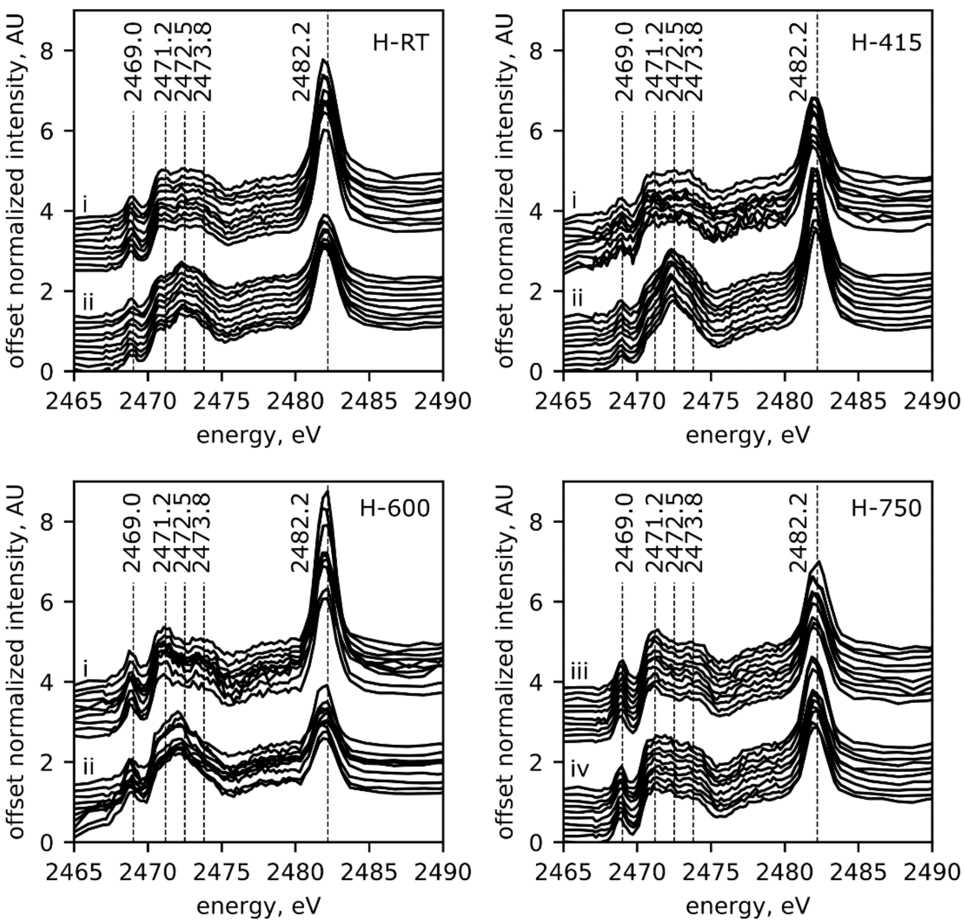


Fig. S1. Lazurite color change with heat-treatment. Visible light images of lapis lazuli following (**A**) no heat-treatment or (**B**) heat-treatment at 750 °C; lazurite pigments H-RT and H-750 (**C** and **D**, respectively) extracted via the *heavy-liquid* method from such rocks (coarsely ground, sieved fraction 30 – 120 µm).

(A)


H-RT
H-415
H-600
H-750
2469.0
2471.2
2472.5
2473.8
2482.2
i
ii
iii
iv
offset normalized intensity, AU
energy, eV
0
2
4
6
8
2465
2470
2475
2480
2485
2490

(**B**)

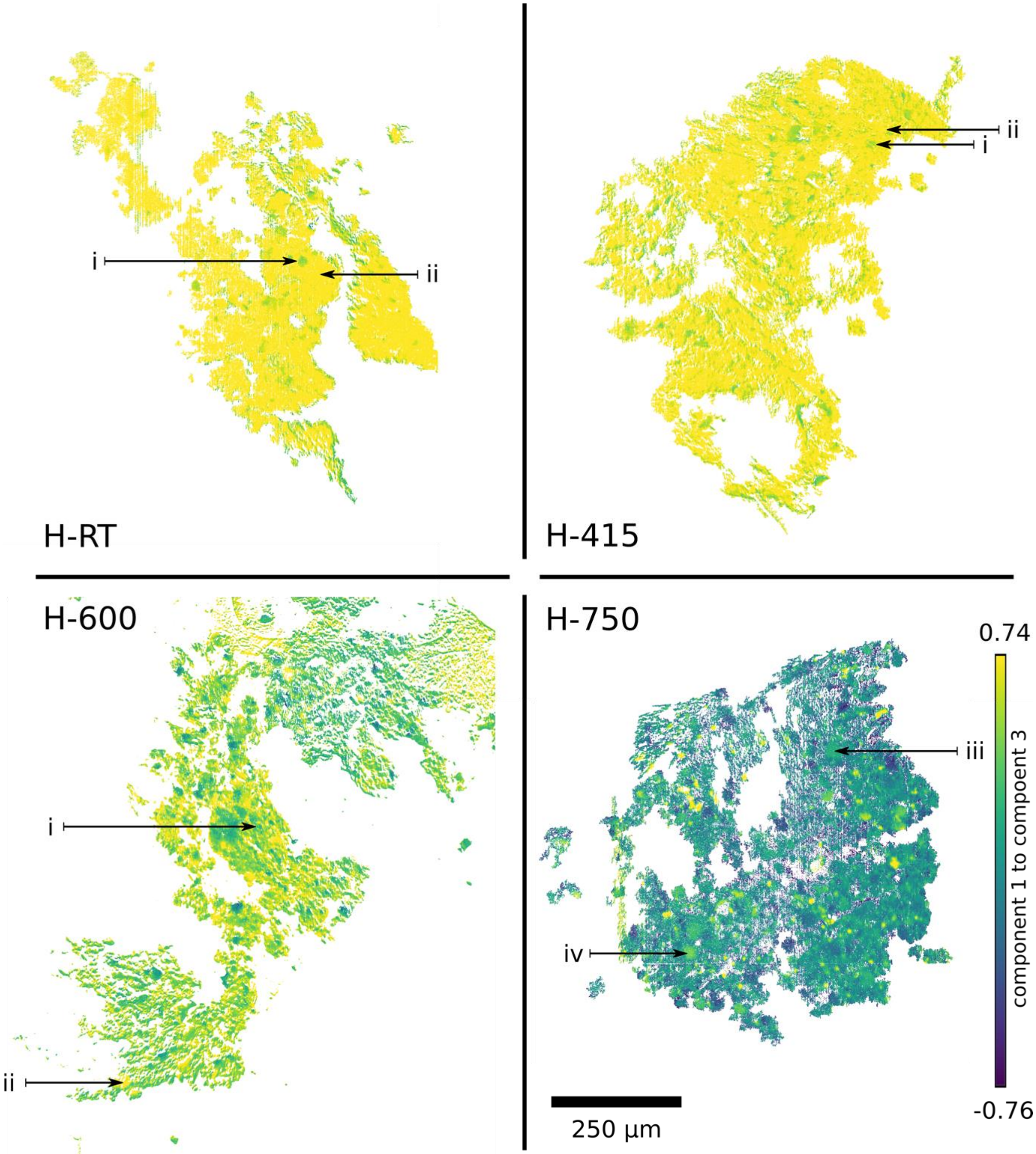


Fig. S2. Heterogeneity in prepared-pigment observed with FF-XANES. (**A**) Offset single-pixel normalized FF-XANES spectra stepping pixel-by-pixel across two different particles (i and ii) in H-RT, H-415, and H-600, and two further different particles (iii and iv) in H-750 noted in the images of (**B**). Dashed lines are at the same energies as in the figures of the main text. (**B**) Corresponding particles (marked with arrows) for spectra of (**A**) in false-colored FF-XANES images (same as Fig. 2) of H-RT, H-415, H-600, and H-750 where each pixel corresponds to the difference between the NMF-derived coefficients for components 3 and 1 of Fig. 2.

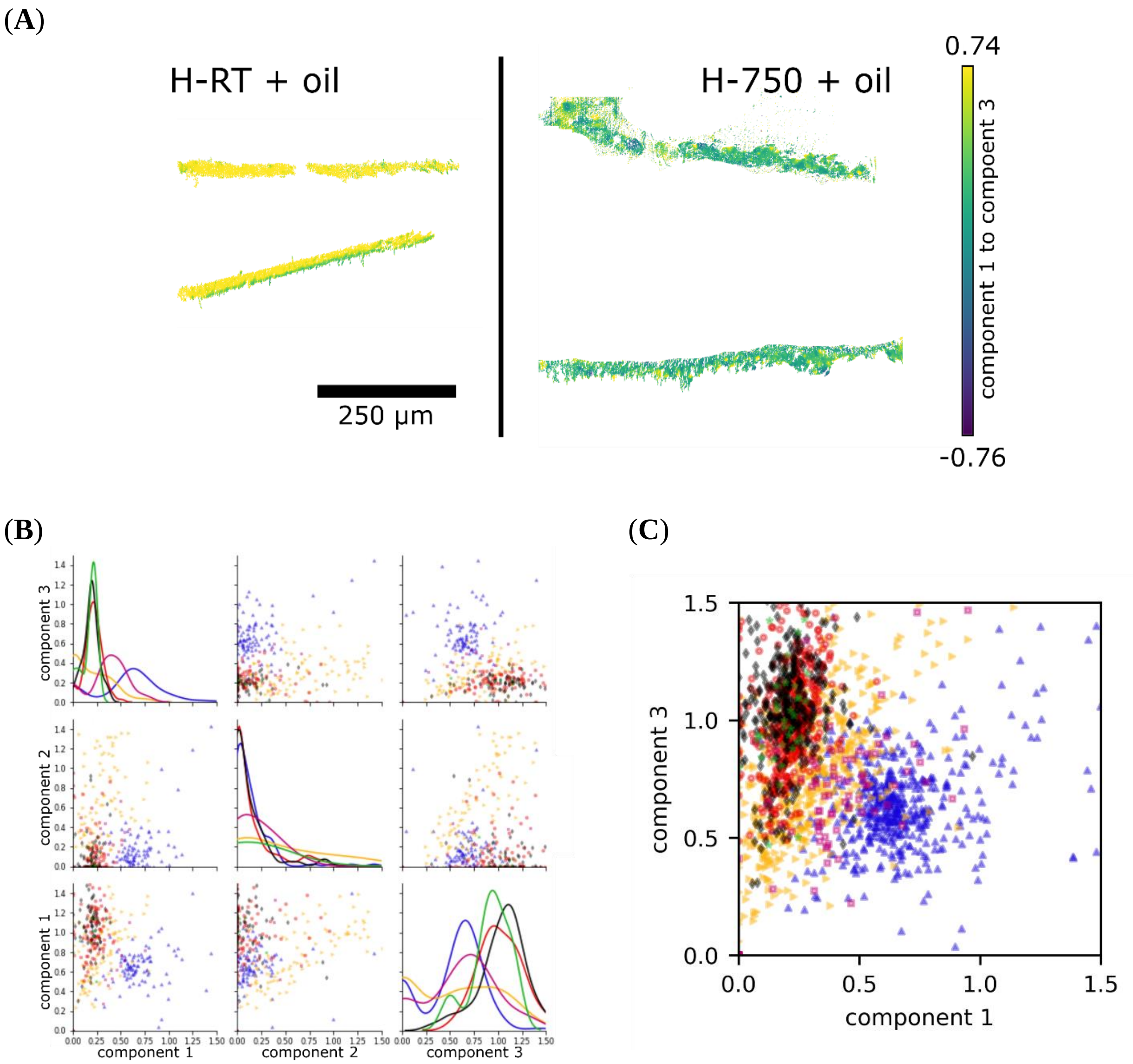
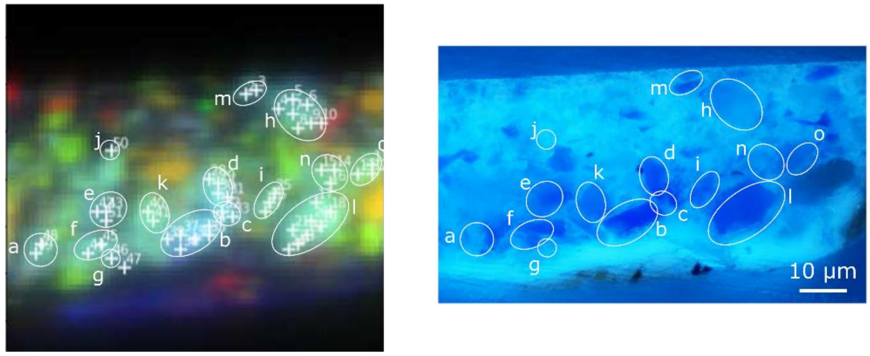


Fig. S3. Influence of aging oil on sulfur chemistry in prepared-pigments. (**A**) False-colored FF-XANES images of H-RT+oil and H-750+oil where each pixel corresponds to the difference between the NMF-derived coefficients for components 3 and 1. (**B**) Pair-plots of NMF-derived coefficients for every pair of components for normalized FF-XANES spectra of H-RT (black diamonds), H-415 (red circles), H-600 (yellow right-facing triangles), H-750 (blue top-facing triangles) particles as well as H-RT+oil (green stars) and H-750+oil (magenta squares); each point represents every 1000th spectrum. Diagonal elements show gaussian kernel density estimates for respective components. (**C**) Enlarged pair-plot of NMF-derived coefficients for component 3 vs. component 1 from (**B**).

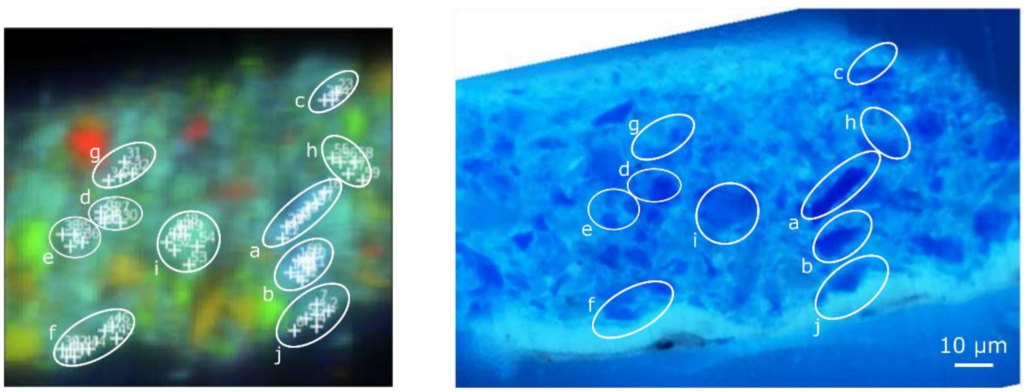
Artist	Painting name	Year	Sample number	Sample location	Support, medium, dimensions	Collection
Johan Maelwael	*Pieta with the Holy Trinity*	c. 1400	18500	Blue on verso	Panel, mixed binder (oil and proteins), 64.5 cm diameter	Louvre
Henri Bellechose	*The Last Communion and Martyrdom of Saint Denis*	1416	18506	A blue garment	Panel, mixed binder (oil and proteins), 162×211 cm^2	Louvre
Rogier van der Weyden	*The Lamentation of Christ*	c. 1460 – 1464?	MH-0264x07b	Mary's blue robe	Panel, oil, 80.6×130.1 cm^2	Mauritshuis
Jan Brueghel (II)	*Still Life with Flowers in a Glass*	c. 1625 – c. 1630	SK-A-2102_8	Blue hyacinth on the right	Copper, oil, 24.5×19 cm^2	Rijksmuseum
Jan Steen	*The Life of Man*	c. 1665	MH-0170_5	Blue garment of right-most figure	Canvas, oil, 68.5×81.6 cm^2	Mauritshuis

Fig. S4. Details about historical paintings. Details about the five historical paintings from which samples were measured.

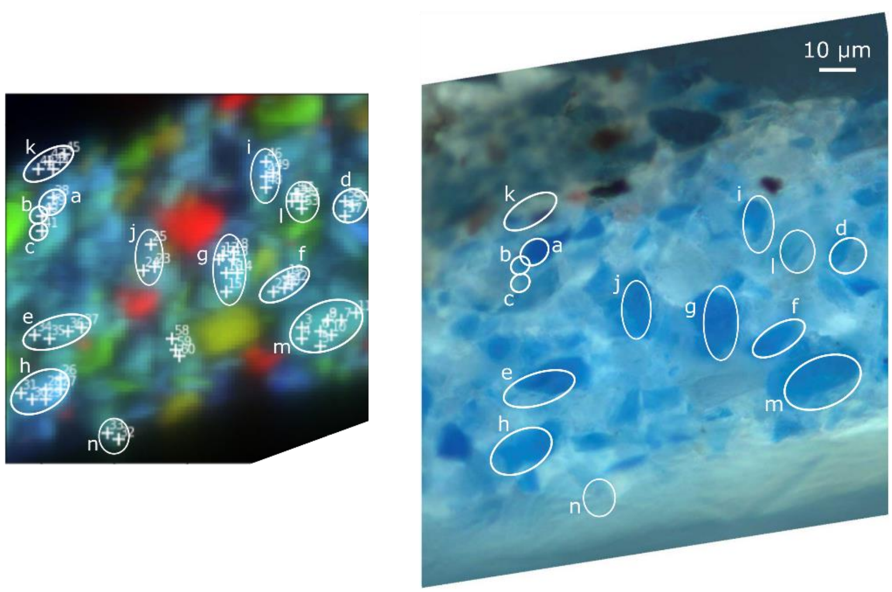
(**A**)



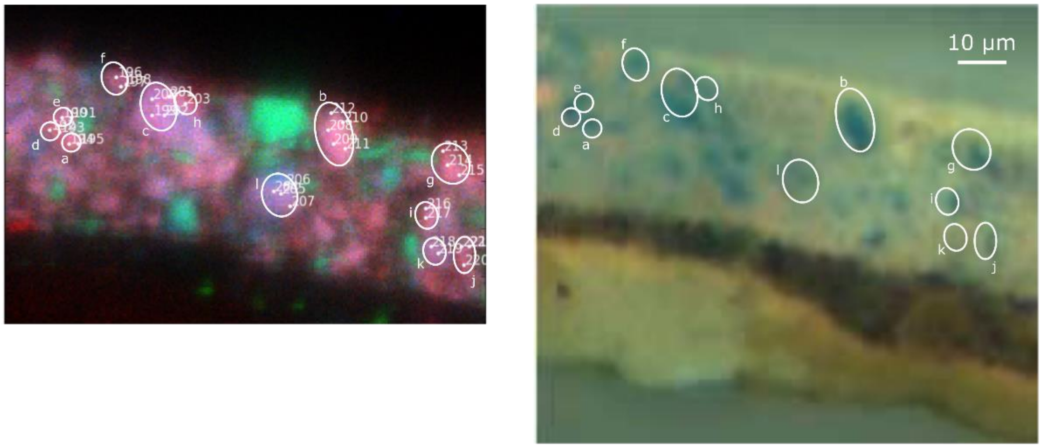
(**B**)



(**C**)



(**D**)



(**E**)

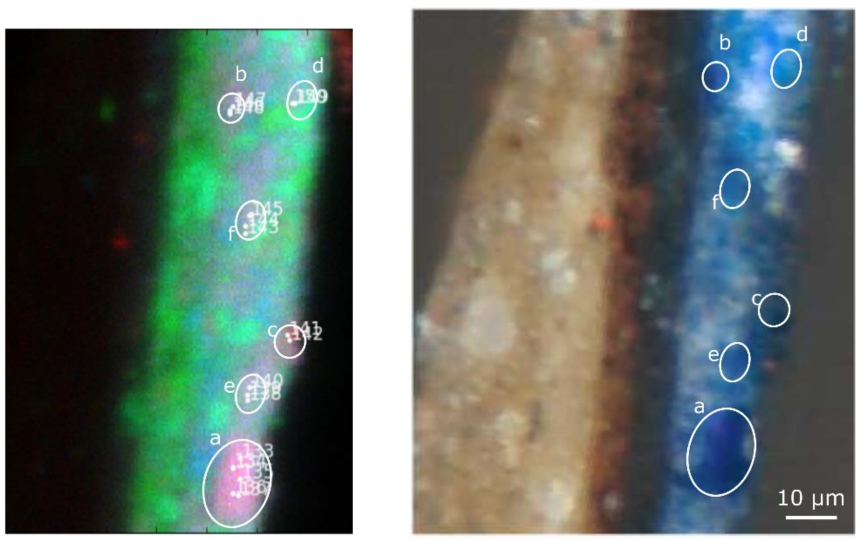


Fig. S5. µXRF maps and microscope images of historical paint cross-sections. From (**A**) Johan Maelwael's *Pieta with the Holy Trinity*, c. 1400 (Louvre); (**B**) Henri Bellechose's *The Last Communion and Martyrdom of Saint Denis*, 1416 (Louvre); (**C**) Rogier van der Weyden's *The Lamentation of Christ*, c. 1460 – 1464 (Mauritshuis); (**D**) Jan Brueghel (II)'s *Still Life with Flowers in a Glass*, c. 1625 – c. 1630 (Rijksmuseum); and (**E**) Jan Steen's *The Life of Man*, c. 1665 (Mauritshuis), µXRF map (left) and light microscope image (right, under UV illumination) of paint cross-section used to select lazurite particles for µXANES (attenuated) spectral acquisition, with the following photo credits for the latter: (**A**, **B**) ©C2RMF, Paris/Myriam Eveno; (**C**) ©RKD, The Hague/Prof. dr. Dr. J.R.J. van Asperen de Boer; (**D**) ©Rijksmuseum, Amsterdam/Nouchka de Keyser; and (**E**) ©Mauritshuis, The Hague/Sabrina Meloni. The µXRF maps are false-colored (**A**, **B**, **C**) red, green, and blue and (**D**, **E**) green, blue, and red for silicon, aluminum, and sulfur intensities, respectively. Numbers refer to the spectral scan, and the corresponding µXANES spectra averaged over such scans per particle are shown in (**A**) Fig. 5 and (**B** – **D**) Fig. S6.

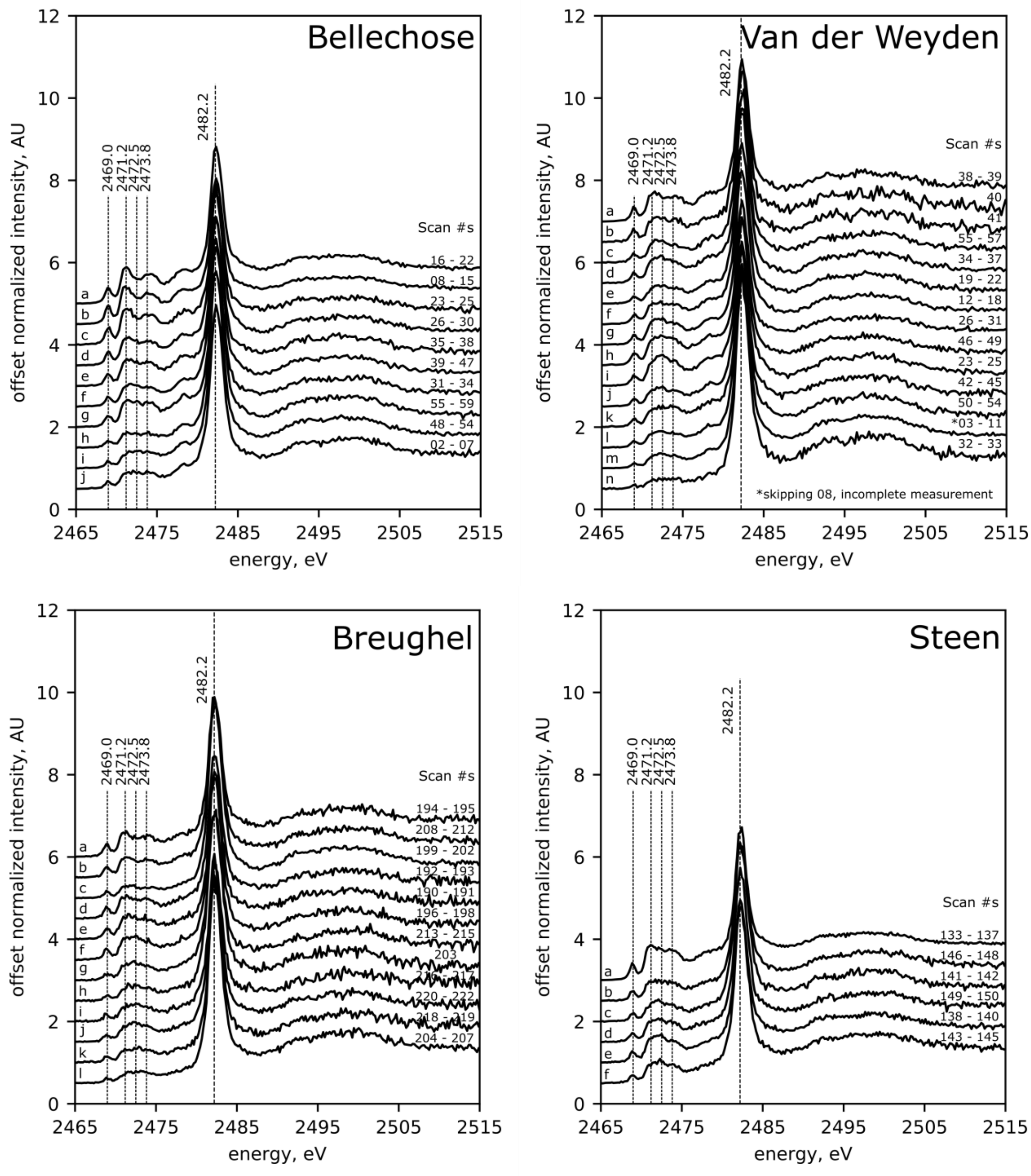


Fig. S6. µXANES spectra from individual lazurite particles within historical paint samples. For corresponding paintings, offset average normalized µXANES (attenuated) spectra per particle as labeled in the paint cross-sections of Fig. S5 (**B** – **D**, right) showing heterogeneity in the lazurite sulfur signals. The scan numbers are those included in each average and correspond to the µXRF maps in Fig. S5 (**B** – **D**, left). For each, spectrum ‘a’ is the same as that shown in Fig. 4.

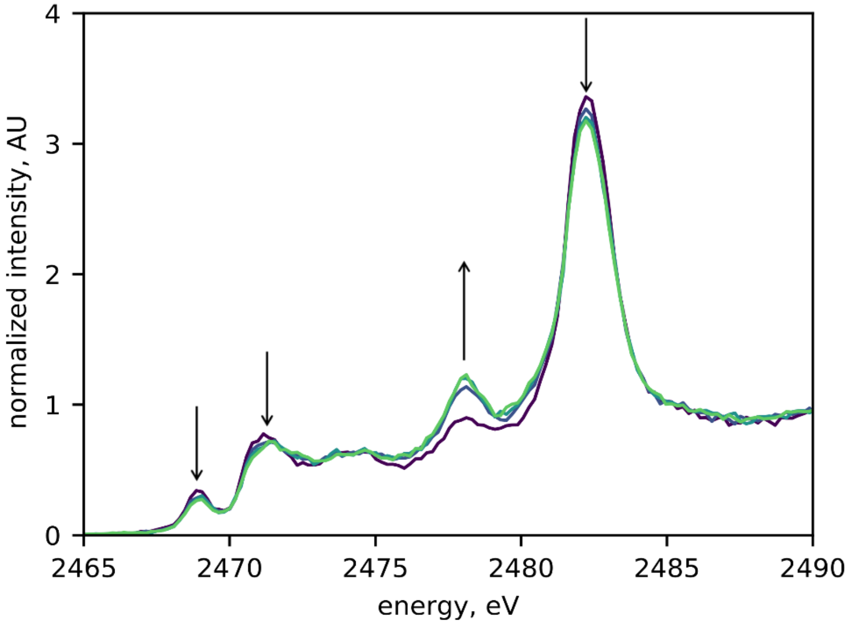


Fig. S7. μXANES spectra demonstrating photo-radiation damage. XANES spectra in XRF microbeam mode of lazurite from a historical sample gathered sequentially for six scans (dark purple to green to pale yellow) focused on one spot demonstrating the influence of beam-damage on the sulfur speciation. Arrows point in the direction of changing intensity with consecutive scans and correspond to energies at 2469.0, 2471.2, c. 2478, and 2482.2 eV.

No heat-treatment | Heat-treatment at 750 °C

(**A**) (**C**)

(**B**) (**D**)

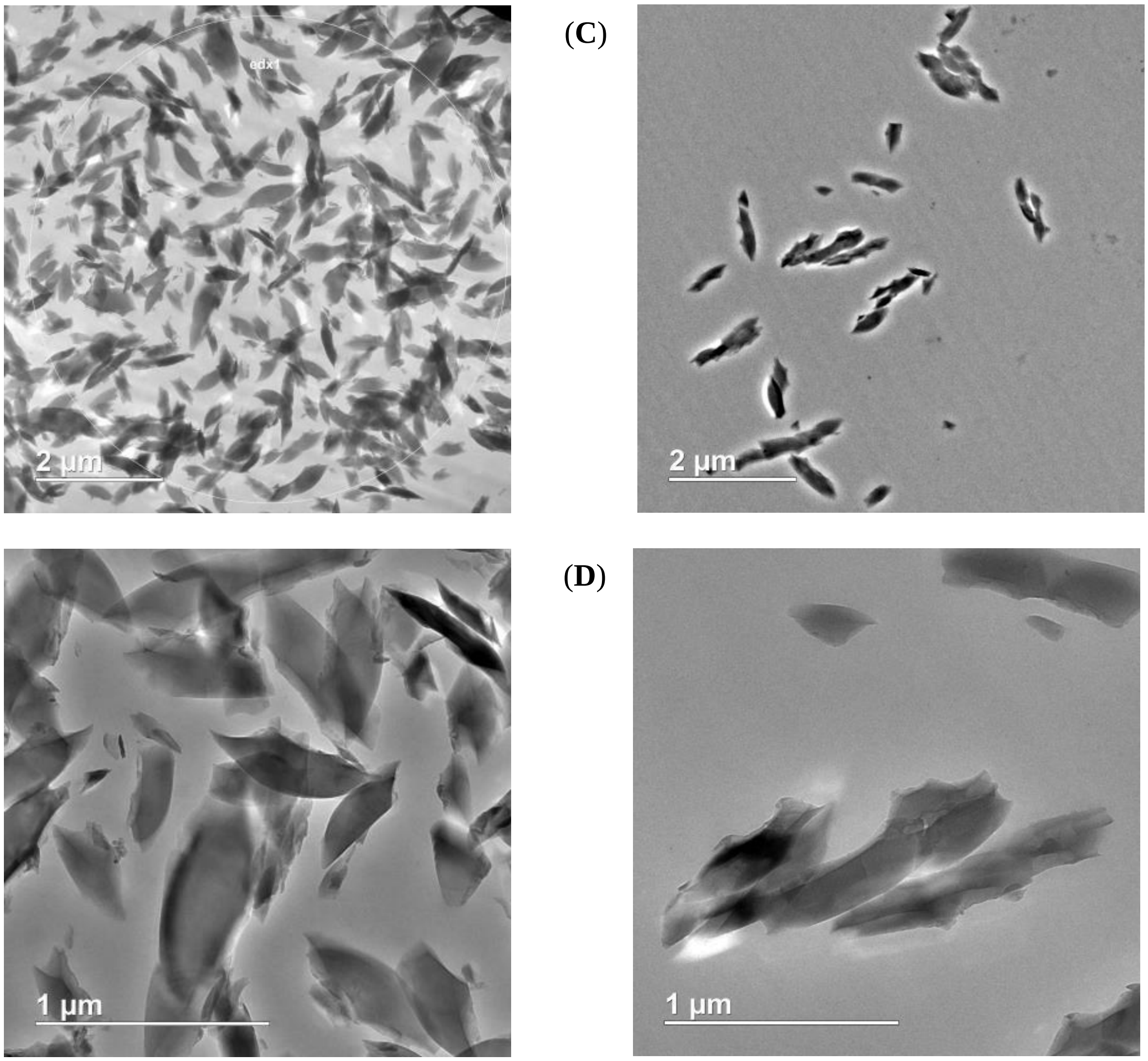


Fig. S8. TEM images of prepared-pigments. TEM images at two magnifications of lazurite pigment extracted via the *heavy-liquid* method from lapis lazuli following (**A**, **B**) no heat-treatment (H-RT) or (**C**, **D**) heat-treatment at 750 °C (H-750) and finely ground.