

Supplementary Materials for Publication

Synthesis and Fading of Eighteenth-century Prussian Blue Pigments: a Combined Study by Spectroscopic and Diffractive Techniques using Laboratory and Synchrotron Radiation Sources

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14 This supplementary material includes full texts of the eighteenth-century recipes for the synthesis of
15 Prussian blue, general considerations about how measurements may affect the fading of Prussian blue,
16 background information and application of the Williamson-Hall method, a brief description of various
17 structural models for Prussian blue, results of pair distribution refinements of Prussian blue pigments,
18 uv-visible reflectance spectra of paint layers, scanning electron micrograph of a cross section of an
19 eighteenth-century paint fragment.

20

1 2. Experimental

2 2.1. Sample preparation

3 The original eighteenth-century recipes that were used as far as possible in the preparation of the
4 samples studied in this work follow:

5 **Dossie, 1758** [from Dossie, R. *The Handmaid for the Arts*, Nourse, J., London, 78-80 (1758).]

6 “The Prussian blue may be prepared in perfection by the following process. Take of blood any
7 quantity; and evaporate it to perfect dryness. Of this dry blood, powdered, take six pounds, and of the
8 best pearl-ashes two pounds: mix them well together in a glass or stone mortar; and then put the mixt
9 matter into large crucibles or earthen-pots; and calcine it in the furnace described, p.22; the top of the
10 crucible or pot being covered with a tile, or other such convenient thing, but no luted. The calcination
11 should be continued, so long as any flame appears to issue from the matter; or rather till it become
12 very slender and blue; for if the fire be very strong, a small flame would arise for a very long time.
13 When the matter has been sufficiently calcined, take the vessels which contain it out of the fire; and,
14 as quickly as possible, throw it into two or three gallons of water; and, as it soaks there, break it with a
15 wooden spatula, that no lumps may remain. Put it then in a proper tin-vessel, and boil it for the space
16 of three quarters of an hour or more; and filter it while hot through paper in the tin cullenders
17 described, p.27; and pass some water through the filter when it is run dry, to wash out the remainder
18 of the lixivium of the blood and pearl-ashes; the earth remaining in the filter may be then thrown
19 away. In the mean time, dissolve of clean alum four pounds, and of green vitriol or copperas two
20 pounds, in three gallons of water. Add this solution gradually to the filtered lixivium, so long as any
21 effervescence appear to arise on the mixture; but, when no ebullition or ferment follows the
22 admixture, cease to put in more. Let the mixture then stand at rest, and a green powder will be
23 precipitated: from which, when it has thoroughly subsided, the clear part of the fluid must be poured
24 off, and fresh water put in its place, and stirred well about with the green powder: and, after a proper
25 time of settling, poured off like the first. Take then of spirit of salt double the weight of the green
26 vitriol which was contained in the quantity of solution of vitriol and alum added to the lixivium,
27 which will soon turn the green matter to a blue colour; and, after some time, add a proper quantity of
28 water, and wash the colour in the same manner, as has been directed for lake; and when properly
29 washed, proceed in the same manner to dry it in lumps of convenient size.”

30 **Le Pilleur d’Apligny, 1779** [from Le Pilleur d’Apligny, M., *Traité des couleurs matérielles et de la*
31 *manière de colorer relativement aux différents arts et métiers*, Saugrain and Lamy, Paris, France, 36-
32 38 (1779).]

33 « Le bleu de Prusse est une couleur animale, qui a néanmoins le fer pour base. Voici la manière de
34 faire cette couleur. On prend une livre de potasse bien sèche, qu’on mêle à autant de sang de bœuf
35 desséché et pulvérisé : on met ce mélange dans un creuset, et on le fait calciner doucement. Il faut

1 avoir attention que le creuset ne soit plein qu'aux deux tiers, afin que la matière qui se gonfle ne se
2 répande pas. Dans les commencemens [*sic*], il s'élève beaucoup de fumée et de flamme; lorsque la
3 flamme cesse, on augmente le feu, pour faire rougir la matière et pour qu'en cet état elle ne laisse plus
4 paroître qu'une flamme légère et bleuâtre. On ôte alors le creuset du feu, et on le laisse refroidir. On
5 ramasse avec une cuiller de fer la pâte rouge qu'il contient, et on jette dans six pintes d'eau bouillante:
6 on filtre la lessive qui en provient, et l'on repasse de l'eau chaude sur le marc, pour achever de le
7 dessaler, et ensuite on réunit les lessives, qu'on fait réduire sur le feu, si l'on veut donner plus
8 d'activité. D'un autre côté, on fait dissoudre ensemble dans une suffisante quantité d'eau chaude six
9 onces de vitriol de Mars et huit onces d'alun de roche et l'on verse dans cette dissolution la lessive
10 susdite chaude. Après une vive effervescence, il se précipite une fécule verdâtre : on remue le
11 mélange et on le verse sur une toile serrée ; la liqueur passe au travers et le précipité reste sur le linge :
12 on l'enlève avec une cuiller, pour le mettre dans une terrine de grès, l'on verse par dessus huit onces
13 d'acide marin, qui lui fait prendre aussitôt une belle couleur bleue ; mais ce précipité reste toujours
14 chargé d'une colle tenace qui lui ôte sa vivacité : on l'en débarrasse par des lotions répétées. L'usage
15 a appris que l'eau de puits, ou toute eau dure avait pour cela plus d'efficacité que l'eau de rivière. Ce
16 lavage exige de la patience ; car il faut trois à quatre semaines, en changeant d'eau ce bleu deux fois
17 par jour : au bout de ce temps, on le passe au travers d'un linge serré ; on le laisse égoutter, et on en
18 forme des gâteaux ou tablettes, qu'on fait sécher à l'ombre et à l'abri de la poussière. »

19 **Le Pilleur d'Apligny, 1779.** A literal translation from French to English of the above preparation
20 follows.

21 Prussian blue is an animal color, that has nevertheless iron as a base. Here is the way to prepare this
22 color. One takes one pound (1 livre = 489.5 g) of very dry potassium carbonate or hydroxide (The
23 French is not clear, "potasse" is a mineral mixture of potassium carbonate and potassium chloride.)
24 and mixes it with one pound of dry powdered cattle blood. One places this mixture in a crucible and
25 calcines slowly the content. One must be careful that the crucible must only be two-thirds full so that
26 the material that swells does not overflow. At the beginning, much smoke and flames come out; when
27 the flames stop, one increases the temperature to redden the material and only a light blue flame
28 appears. One removes the crucible from the heat source and let it cool down. One scoops with an iron
29 spoon the red paste contained in the crucible and throws it in six pints (1 pint = 952.146 mL) of
30 boiling water: one filters the brew that is formed and one washes the grounds with hot water to
31 remove all salts and then one remixes the brews that one reduces on the fire if one wishes more
32 activity. Separately, one dissolves together in enough hot water six ounces (1 ounce = 30.594 g) of
33 iron(II) sulfate, FeSO_4 , (vitriol de Mars) and eight ounces of alum (alum = $\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$) and
34 one pours in this solution the above hot brew. After strong bubbling, a green powder precipitates, one
35 stirs this mixture and filters it on a fine-mesh cloth; the liquor goes through and the precipitate
36 remains on the cloth: one removes it with a spoon to put it in a pottery jar, one pours on top eight

1 ounces of hydrochloric acid, that gives the precipitate a beautiful blue color; but this precipitate still
 2 remains loaded with a strong glue that removes its vivacity: one removes the glue by repeated
 3 washings. Experience has taught that well water, or any hard water, was more efficient than river
 4 water. This washing requires patience; because it takes three to four weeks, changing the water of this
 5 blue powder twice a day: after this time, one filters it through a fine-mesh cloth; one lets the water
 6 drip and forms cakes or tablets, that one dries in the shade and sheltered from dust.

7 **2.2. Fading Experiments**

8 In order to study the fading of a pigment, a special care must be taken to not induce any further fading
 9 or color change when measuring the sample. Because of both the short measurement time relative to
 10 the time needed to induce a fading in Prussian blue and the weak interactions between the radiation
 11 and the sample, hard X-rays, Raman illumination, Mössbauer 14 to 120 keV sources, are not expected
 12 to affect the fading of Prussian blue.

13 In the Mössbauer experiment, the 120 keV gamma rays go through the absorber without absorption.
 14 The 14.4 keV gamma rays either go through the absorber without absorption or are resonantly
 15 absorbed by the iron-57 nuclei, that deexcite by re-emitting 14.4 keV photons that go through the
 16 absorber. Hence, it is not expected that the Mössbauer radiations would cause any fading.

17 Similarly the hard X-rays also go through the sample or are diffracted and then go through. The
 18 exposure time to hard X-rays is very short and hence there is no need to worry about any fading
 19 effect. Regarding Raman spectroscopy a weak laser power of 50 μ W and a relatively short integration
 20 time of 20 seconds were used in order to avoid any decomposition of the Prussian blue.

21 **3. Characterization of Eighteenth-century Prussian Blue Pigments**

22 **3.4. Crystal structure**

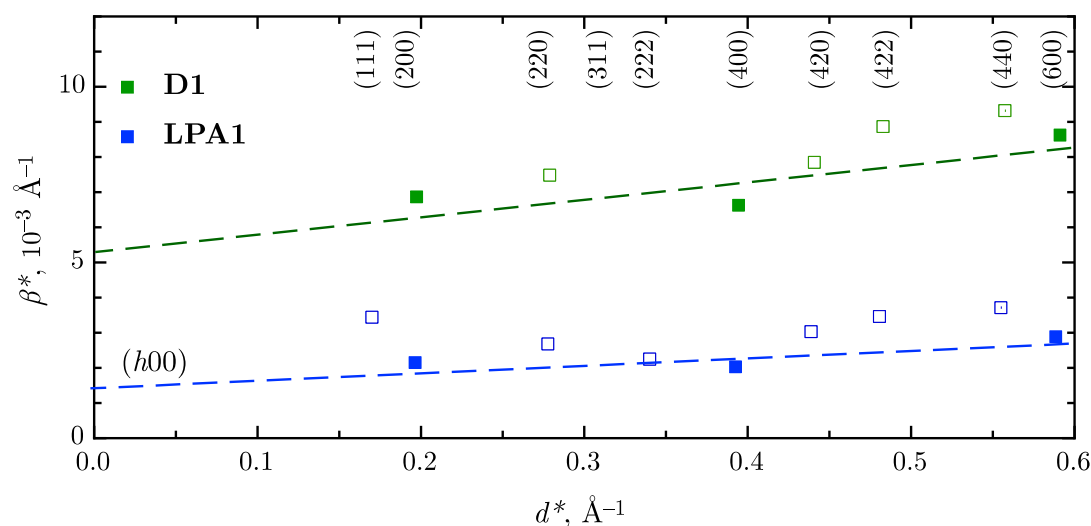
23 In x-ray powder diffraction, the Williamson-Hall method (Williamson & Hall, 1953) is used to extract
 24 the average crystallite size and the strain present in a sample from the analysis of the peak broadening.
 25 If both the contribution due to the particle size, β^S , and that due to the strain, β^D , can be described by a
 26 Lorentzian function, the total broadening, β , is also a Lorentzian function,

$$\begin{aligned}
 & b = b^S + b^D \\
 27 \quad & b = \frac{l}{L \cos q} + h \tan q, \quad (\text{eq. S1 - 3}) \\
 & \frac{b \cos q}{l} = \frac{1}{L} + h \frac{\sin q}{l}
 \end{aligned}$$

1 where L is the average size, defined in one particular crystallographic direction, λ is the wavelength of
 2 the radiation, θ is the scattering angle, and η is the strain, as defined by Stokes and Wilson (Stokes &
 3 Wilson, 1942).

4 Equation S3 corresponds to a linear relationship, $y = ax + b$, where y is $\beta = \beta \cos \theta / \lambda$ and x
 5 is $\frac{1}{d^2} = \frac{1}{L^2} + 2 \sin^2 \theta / \lambda^2$. The intercept of the straight line is the inverse of the crystal size, L , and the slope is the
 6 strain, η .

7 The integral width, β , in equations S1 to S3 is the *pure* integral width, *i.e.*, the integral width due to
 8 the sample itself, without any instrumental contribution. The pure profile is extracted by
 9 deconvolution from the experimental profile, by assuming an *a priori* knowledge of the profile shape
 10 function. Herein this profile shape function was taken as a *pseudo-Voigt* profile, *i.e.*, an approximation
 11 of the normalized Voigt profile, which is the convolution product of a Lorentzian function and a
 12 Gaussian function. The instrument resolution profile for the PANalytical diffractometer was
 13 determined from the $\text{Na}_2\text{Ca}_3\text{Al}_2\text{F}_{14}$ standard by Rietveld refinement. The deconvolution of the x-ray
 14 powder diffraction patterns with a pseudo-Voigt profile function was carried out with the *Peakoc*
 15 software developed by Masson (Masson, 1998). The adjustments were optimized with the Levenberg-
 16 Marquardt algorithm. Individual adjustment of each peak is suitable for the Prussian blues because the
 17 x-ray diffraction lines do not overlap. The Williamson-Hall method was finally applied to extract
 18 from the line broadening the average crystallite size and the strain. Figure S1 shows the Williamson-
 19 Hall plot for the two crystallized eighteenth-century Prussian blue powders.



20
 21 **Figure S1** Williamson-Hall plot obtained from x-ray powder diffraction data of two eighteenth-
 22 century Prussian blues shown in Figure 5. The dashed lines correspond to a linear best fit for the three
 23 (h00) reflections, in solid symbols.

1 No errors bars have been estimated on the absolute values reported in the Williamson-Hall plot
2 because the method is rather more qualitative than quantitative. The main assumption of the method,
3 *i.e.*, that the size and strain effects induce a line broadening that can be fully described by Lorentzian
4 functions, is usually not realistic. However, the Williamson-Hall plot might reveal trends in crystallite
5 size and strain, trends that in turn can be related to the microstructure of the product.

6 **3.5. Pair Distribution Refinement**

7 **Structural Model for Prussian Blue**

8 The crystal structure of Prussian blue is notoriously complex because of the colloidal character of the
9 precipitate upon formation and the presence of vacancies in the lattice. The structure of insoluble
10 Prussian blue is best approximated by the *Fm3m* space group, in which a quarter of the $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$
11 sites are vacant and replaced by water molecules (Herren *et al.*, 1980). Additional water molecules
12 can either occupy zeolitic positions or be bound by hydrogen bonds to coordinated water. Accordingly
13 the chemical stoichiometry is $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$ where x typically ranges from 14 to 16, *i.e.*, six
14 coordinated water molecules and eight to ten water molecules that are either hydrogen bonded to the
15 coordinated water or are interstitial.

16 The *Fm3m* space group implies a statistically random distribution of the vacancies. In contrast, in
17 single crystals the $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ vacancies are not randomly distributed. In this particular case the
18 structure corresponds to the lower symmetry *Pm3m* space group [5]. In this cubic primitive model
19 Buser *et al.* (Buser *et al.*, 1977) introduced an occupancy parameter, p , which is the probability that
20 the $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ anionic site at the center of the unit cell is occupied. When p is zero the structure is
21 completely ordered and all occupancies are integers. In contrast, a p value of 3/4 indicates that 1/4 of
22 the $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ sites are vacant; this situation corresponds to the cubic face-centered *Fm3m* model
23 previously described (Buser *et al.*, 1977).

24 The structural model proposed by Buser *et al.* (Buser *et al.*, 1977) is suitable for describing the
25 average structure as seen by diffraction but fails to describe the local order on a length-scale shorter
26 than or comparable to the lattice parameter of Prussian blue, *i.e.*, up to $a = 10.2 \text{ \AA}$. As Herren *et al.*
27 (Herren *et al.*, 1980) proposed, the structure of insoluble Prussian blue can be considered as a sum of
28 ordered substructures containing zero to four $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ anion vacancies (Herren *et al.*, 1980).

29 A random distribution of these ordered substructures can be calculated as a binomial distribution. In
30 principle, the pair distribution function of Prussian blue at short distances of the order of the unit cell
31 must be described by a weighed sum of the pair distribution functions from each of these
32 substructures according to their proportions in the sample. For **LPA2**, because Prussian blue is a
33 minor phase, its pair distribution function was described only by the substructure with the highest

1 probability, *i.e.*, the ordered structure that counts only one $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ anionic vacancy per cell. The
2 atomic occupancies were constrained to unity for all occupied sites.

3 Results of the pair distribution refinements for **LPA2**, **LPA3** and **D2** are given in Tables S1 and S2.
4 One should note that the refinements performed herein were obtained on impure and nanometric
5 phases and are therefore used to confirm the identification and relative proportion of the present
6 phases rather than to obtain accurate structural parameters. Taking into account the quality of the pair
7 distribution functions shown in Figure 6, the refined lattice parameters and atomic positions obtained
8 herein and given in Table S1 are nevertheless reasonably comparable to those previously reported in
9 the literature (Buser *et al.*, 1977; Michel *et al.*, 2007).

10 For the pair distribution refinement for **LPA2** the isotropic atomic displacement parameters in the
11 minor Prussian blue phase were constrained to the same value of 0.01 \AA^2 . The pair distribution
12 refinement for **LPA3** revealed an occupancy parameter for Al of 1.17(1). This value higher than one
13 could be explained by a substitution of some aluminum ions by iron ions because ferrihydrite,
14 $\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$, and alumina hydrate, $\text{Al}_{10}\text{O}_{14}(\text{OH})_2$, are isostructural.

15 **Table S1** Refined Lattice Parameters, Spherical Nanoparticle Diameter, Agreement Factor and Phase
16 Content

| Parameter | LPA2 | | LPA3 | D2 |
|---------------------------------------|------------------------|-----------------|----------------------------------------------------------------|---------------------------------------------------------------|
| | <i>Fh</i> ^a | PB ^b | Alumina hydrate, $\text{Al}_{10}\text{O}_{14}(\text{OH})_2$ | Alumina hydrate $\text{Al}_{10}\text{O}_{14}(\text{OH})_2$ |
| <i>a</i> , Å | 6.08(2) | 10.17(4) | 5.96(2) | 5.77(4) |
| <i>c</i> , Å | 8.47(3) | – | 8.64(3) | 8.62(8) |
| <i>d</i> , Å | 12.550(1) | – | 15.435(1) | 10(1) |
| <i>R_w</i> , % | 29.5 | | 21.8 | 31.8 |
| Phase content, % mass ^c | 87(1) | 13(1) | 100 | 100 |

17 ^a*Fh* stands for ferrihydrite. ^bPB stands for Prussian blue. ^cThe relative phase content is determined by
18 considering both the scale factor and the atomic content of the unit cell, because each contribution in the pair
19 distribution function is weighed according to the product of the scattering factor of the atoms.

20

1 **Table S2** Refined Positional, Occupancies, and Displacement Parameters

| Phase | Atom or ion | Wyckoff position | <i>x</i> | <i>y</i> | <i>z</i> | Occ. | <i>U</i> , Å ² |
|-------------------------------------------------------------------------------------------------------|-------------|------------------|----------|----------|----------|---------|---------------------------|
| LPA2 | | | | | | | |
| <i>Fh</i> ^a | Fe1 | 6c | 0.167(1) | 0.833(2) | 0.627(3) | | |
| Fe ₁₀ O ₁₄ (OH) ₂ | Fe2 | 2b | 1/3 | 2/3 | 0.295(1) | 0.68(6) | 0.0272(2) |
| | Fe3 | 2b | 1/3 | 2/3 | 0.976(1) | | |
| | O1 | 2a | 0 | 0 | 0.068(1) | | |
| | O2 | 2b | 1/3 | 2/3 | 0.743(1) | | |
| | O3 | 6c | 0.135(3) | 0.864(3) | 0.261(1) | | |
| | O4 | 6c | 0.548(3) | 0.451(3) | 0.973(1) | | |
| | | | | | | | |
| PB ^a | | | | | | | |
| Fe ^{III} ₄ [Fe ^{II} (CN) ₆] ₃ ·14H ₂ O | Fe1 | 1a | 0 | 0 | 0 | | |
| | Fe2 | 3c | 0 | 1/2 | 1/2 | | |
| | Fe3 | 3d | 1/2 | 0 | 0 | | |
| | C1 | 6e | 0.315(9) | 0 | 0 | | |
| | C2 | 12h | 0.197(6) | 1/2 | 0 | 1 | 0.01 |
| | N1 | 6e | 0.171(6) | 0 | 0 | | |
| | N2 | 12e | 0.317(8) | 1/2 | 0 | | |
| | O2 | 6f | 0.272(2) | 1/2 | 1/2 | | |
| | O4 | 8g | 0.217(2) | 0.217(2) | 0.217(2) | | |
| LPA3 | | | | | | | |
| Alumina hydrate | Al1 | 6c | 0.167(2) | 0.833(2) | 0.644(1) | | |
| Al ₁₀ O ₁₄ (OH) ₂ | Al2 | 2b | 1/3 | 2/3 | 0.314(1) | 1.17(6) | 0.0154(1) |
| | Al3 | 2b | 1/3 | 2/3 | 0.986(1) | | |
| | O1 | 2a | 0 | 0 | 0.032(1) | | |
| | O2 | 2b | 1/3 | 2/3 | 0.780(1) | | |
| | O3 | 6c | 0.157(3) | 0.843(3) | 0.241(1) | | |
| | O4 | 6c | 0.534(3) | 0.466(3) | 0.980(1) | | |
| | | | | | | | |
| D2 | | | | | | | |
| Alumina hydrate | Al1 | 6c | 0.163(5) | 0.837(5) | 0.639(1) | | |
| Al ₁₀ O ₁₄ (OH) ₂ | Al2 | 2b | 1/3 | 2/3 | 0.320(1) | 0.87(6) | 0.014(3) |
| | Al3 | 2b | 1/3 | 2/3 | 0.014(1) | | |
| | O1 | 2a | 0 | 0 | 0.010(1) | | |
| | O2 | 2b | 1/3 | 2/3 | 0.761(1) | | |
| | O3 | 6c | 0.159(6) | 0.841(6) | 0.238(1) | | |
| | O4 | 6c | 0.531(5) | 0.468(5) | 0.982(1) | | |
| | | | | | | | |

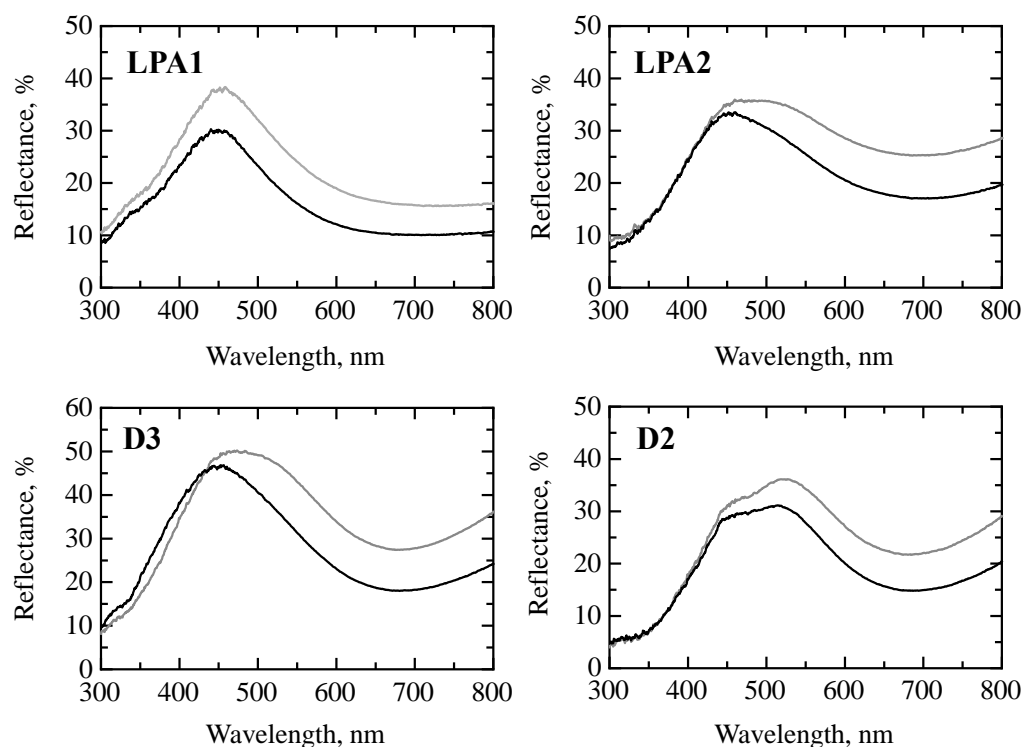
2 ^aThe scale factor for the ferrihydrite, Fh, phase and the Prussian blue, PB, phase is 0.0309(8) and 0.0032(4),
3 respectively.

1 5. Color Change in Painted Layers of Eighteenth-century Prussian Blues Pigments

2 Uv-visible reflectance spectroscopy

3 The accelerated fading experiments have shown that the samples that contain a fraction of
4 ferrihydrite, such as LPA2, or an extender, such as D2 and D3, are more strongly degraded than pure
5 Prussian blue, such as LPA1 and D1. Furthermore, LPA2, D2, and D3 show a tendency to turn green,
6 as is evidenced by the reflectance spectra obtained by uv-visible spectroscopy, see Figure S2. The
7 maximum in the reflectance for the LPA2, D2, and D3 samples is clearly shifted upon light exposure
8 towards longer wavelengths, a shift that results in a greenish appearance of the exposed paint layers.
9 In contrast, LPA1 does not exhibit such a shift but, rather exhibits a slightly higher reflectance after
10 light exposure, see Figure S2a. The tendency of Prussian blue to turn green and the importance of the
11 preparative method have already been reported in eighteenth- and nineteenth-century books.

12



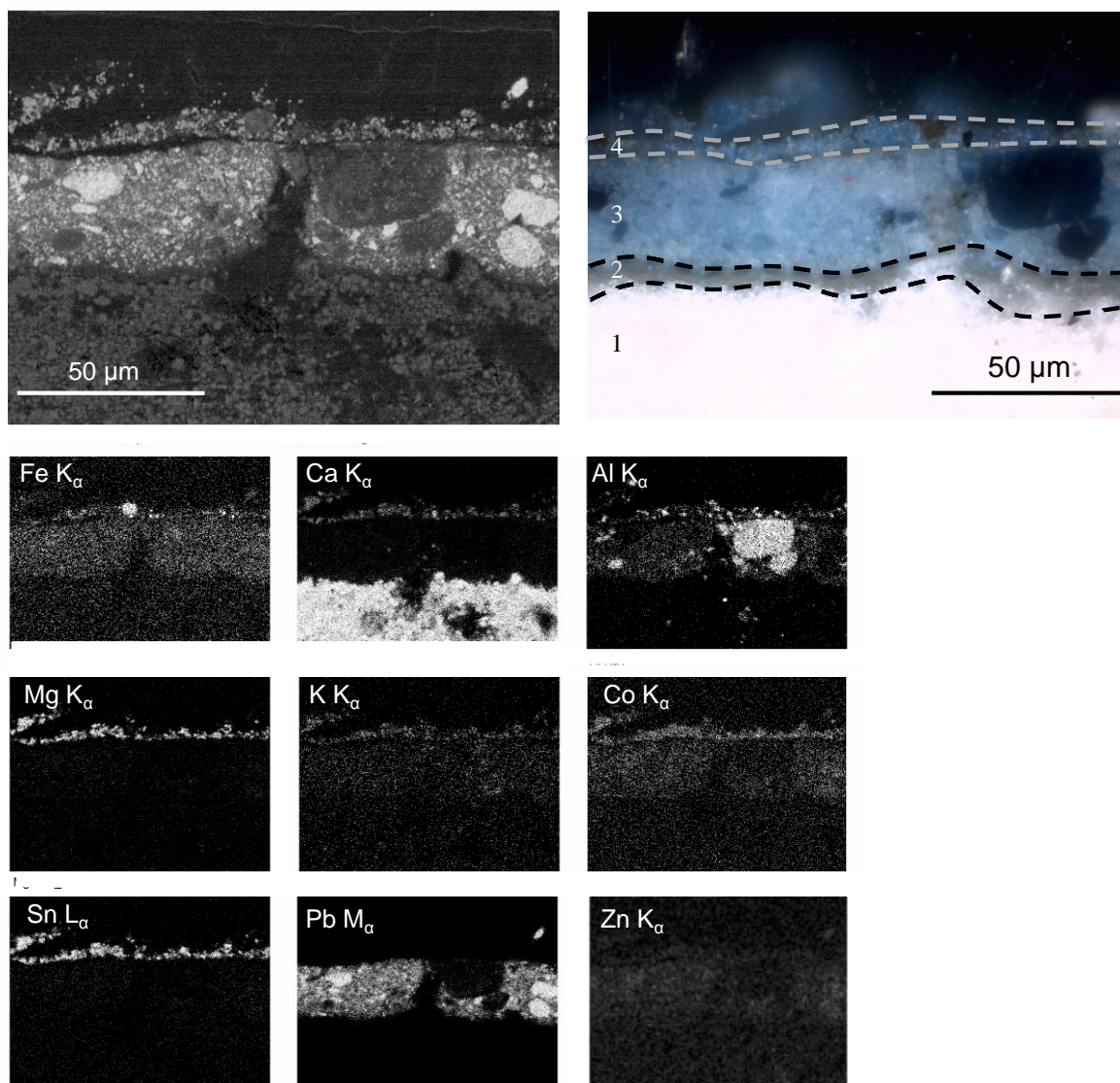
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14 **Figure S2** Reflectance uv-visible spectra of eighteenth-century Prussian blues mixed with gum
15 arabic and painted in a light shade on watercolor paper. The gray curves correspond to the exposed
16 portion of the paint layer.

17 6. Analysis of a Genuine Paint Fragment

18 Scanning Electron Microscopy. The analysis of a paint cross-section, prepared from a millimeter-size
19 paint fragment obtained from the right sandal of the guardian angel of La Gleize, by scanning electron

1 microscopy coupled with energy-dispersive x-ray spectroscopy was first carried out in 1994. In order
2 to update and eventually to complete the results obtained in 1994 the analyses were repeated.
3 The elemental composition mapping shown in Figure S3 indicates the composition of each layer of
4 the paint cross-section. Prussian blue is located in the third layer. The big dark blue particles also
5 contain aluminum, suggesting the presence of alumina hydrate used as an extender in the Prussian
6 blue.



7
8 **Figure S3** Scanning electron micrograph obtained at 15 keV with backscattered electrons,
9 optical photomicrograph obtained in reflected visible light with dark field illumination, and the
10 elemental composition mapping performed by energy-dispersive x-ray spectroscopy of the cross-
11 section of a blue fragment from the guardian angel of La Gleize.

12
13

1 References

- 2 Buser, H., Schwarzenbach, D., Petter, W. & Ludi, A. (1977) *Inorg. Chem.* **16**, 2704–2710.
- 3 Herren, F., Fischer, P., Ludi, A. & Haelg, W. (1980) *Inorg. Chem.* **19**, 956–959.
- 4 Masson, O. (1998) Ph.D. Thesis, Université de Limoges
- 5 Michel, F. M., Ehm, L., Antao, S. M., Lee, P. L., Chupas, P. J., Liu, G., Strongin, D. R., Schoonen,
6 M. A. A., Phillips, B. L., Parise, J. B. (2007) *Science* **316**, 1726–1729
- 7 Stokes, A. R. & Wilson, A. J. C. (1942) *Proc. Camb. Phil. Soc.* **38**, 313–322.
- 8 Williamson, G. K. & Hall, W. H. (1953) *Acta Metallurgica* **1**, 22–31
- 9