Supplementary Materials: Microscopic-Scale Examination of the Black and Orange–Yellow Colors of Architectural Glazes from Aššur, Khorsabad and Babylon in Ancient Mesopotamia

Fanny Alloteau , Odile Majérus , Floriane Gerony , Anne Bouquillon , Christel Doublet , Helen Gries , Anja Fügert , Ariane Thomas and Gilles Wallez

Colour palette and main colouring agents

The colour palette and the related main colouring agents of the Aššur, Babylon and Khorsabad corpuses conserved in the VAM or in the musée du Louvre are given in Table S1. These data have been gathered from macroscopical and microscopical observations and from chemical analyses by XRF, SEM-EDX and μ-Raman. The 2D XRF mappings for Khorsabad were performed with a XRF scanner designed and built at the C2RMF, equipped with a molybdenum (Mo) X-ray tube [1]. The spot size was about 1 mm. The map step (distance between two measuring spots) was set at 0.7 mm. Each spot measurement was collected using the following setup: 50 kV, 500 μA current, 0.2 s, in air. Evaluation of the XRF data was carried out using the PYMCA 5.6.7 software [2]. The details of the operating conditions for the other instruments are described in this article.

For Babylon bricks, seven colours representative of the corpus as a whole have been unambiguously identified: yellow, white, black, green, turquoise, dark blue, blue. Note that on brick B-VA17282 the reddish hue of the glaze at the bottom right of its photograph in Figure 3 is limited to its surface and was associated to weathering products of a turquoise glaze by SEM-EDX investigation of a cross-section (results not shown).

For Khorsabad bricks five colours have been unambiguously identified for the corpus as a whole: orange, white, black, and two shades of turquoise: turquoise–blue and turquoise–green.

For Aššur bricks instead, the designation of a colour that would represent the original colour of the glaze has often been ambiguous due to the phenomena of fading or colour change caused by weathering. We used macroscopic and microscopic observations and XRF analysis results on a large selection of more than fifty bricks to define this colour palette, which is intended to be close to the original colours. At least 7 different colours are proposed for the glazes of Aššur: orange, yellow, pale yellow with greenish accent, white, light green, black and one or several colours in the turquoise–blue–green range.

Regarding the black glazes and the group of orange–yellow glazes, their colouring agents and the similarities between the three different corpuses have already been thoroughly described in detail in the present article.

Regarding the whites, for the 3 corpuses, they were found to be opacified by calcium antimonates (this is pointed out in Figure S1 and Figure S2 for instance: the white glazes appear enriched in Ca and Sb on these 2D XRF mappings). Note that for Aššur, we refer to the white flat decors but not to the glazed contour lines used to separate adjacent coloured glazes, that can appear totally white for the bricks dated to the 8th–7th cent. BC (brick fragment A-812093 showed in Figure 2 for instance). No colouring agents could have been identified for these lines and, as already stated in this article, we strongly assume that they were originally black but have become completely discoloured due to weathering.

Regarding the green and turquoise glazes of the 3 corpuses, they are all coloured by copper ions dissolved in the glassy matrix, possibly in combination with other colouring agents: with lead antimonate opacifiers for the green of Babylon ; with calcium antimonates for the turquoise-blue of Babylon and of Khorsabad (Figure S1) and for the light green of Aššur (Figure S2); with manganese ions for the turquoise-green for Khorsabad (Figure S1).

For the group green / turquoise-green / turquoise–blue glazes of Aššur, no discrimination could be made by elemental analysis: they are Cu-coloured without opacifying agents. We never identify both a turquoise and a green glaze on a same brick as for Khorsabad. Generally, the glazes described as green displayed a powdery appearance and appeared somewhat more faded than the ones described as turquoise. A colour change from blue / turquoise to green as a result of the weathering of glass (and to white in extreme cases) may be suspected as it has been mentioned in the literature (for Cu^{2+}-based coloured glasses) [3–6]. Thus, it is not clear if the variety of turquoise-blue-green shades for these glazes is solely the result of irregular deterioration of the same colour or if it reflects an initial variety of colours (whether entailing different colouring agents or various concentrations of these colouring agents). Note that for the light green glazes from Aššur, lower levels of copper than for the green / turquoise–green / turquoise-blue glazes were detected by XRF. It is almost impossible to know whether the copper was originally present in a higher amount but was partially leached during weathering, so that the greenish (or turquoise) accent could have been more pronounced.

Regarding the characteristic dark blue of Babylon, it was obtained by a mix of cobalt and copper ions at low concentration dissolved in the glass matrix [7–9]. These two colouring ions have also been used in association with calcium antimonate-based opacifiers, giving a lighter blue colour identified as "blue".

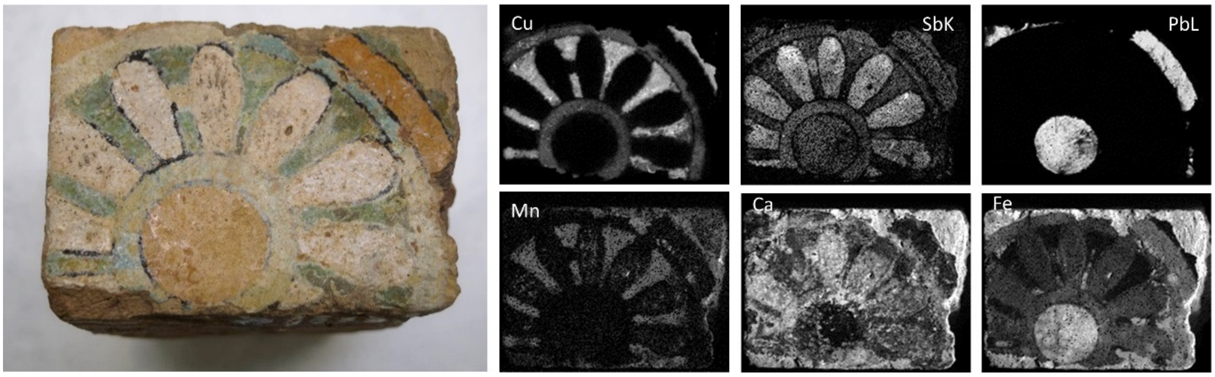

Figure S1. XRF Cartography of the K-N8123 brick from Khorsabad. This brick remarkably bears the five colours found in Khorsabad and referred to as Orange, White, Black, Turquoise-blue (two circles surrounding the flower yellow heart and the flower white petals) and Turquoise-green (between the white petals of the flower).

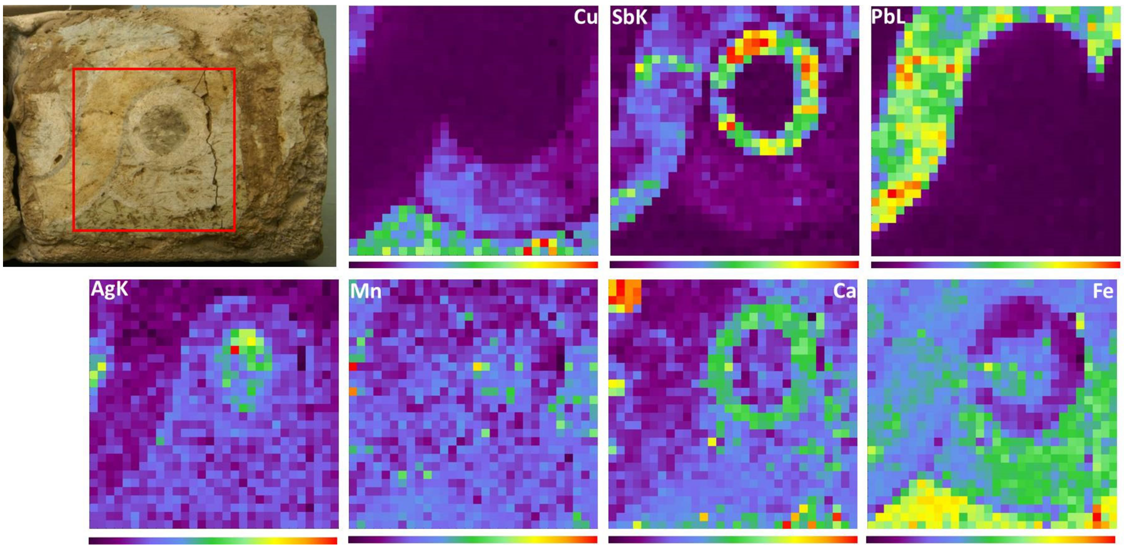

Figure S2. XRF Cartography of a glazed area of the A-810791 brick from Aššur (area marked with a red rectangle on the top left image). Five glaze colours referred to as Yellow (Pb- and Sb-rich top ribbon), Light green (Cu and Sb-rich bottom ribbon), Green (Cu-rich background at the bottom), White (Ca- and Sb-rich outer circle) and Black (contour line and inner circle) are identified on this area.

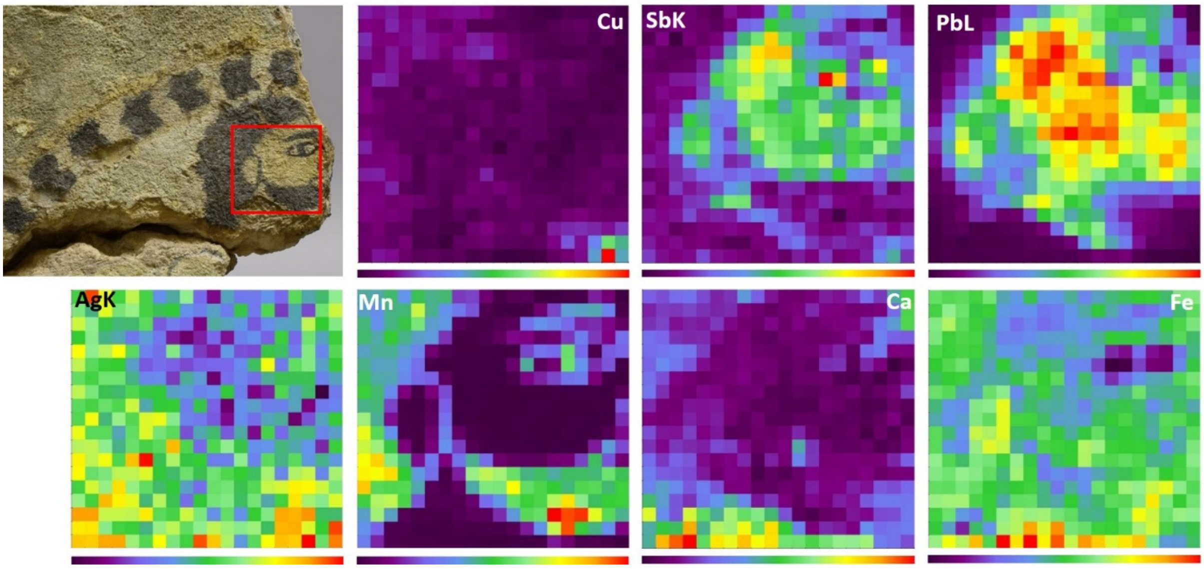

Figure S3. XRF Cartography of a glazed area of the A-810373 brick from Aššur (area marked with a red rectangle on the top left image). Two glaze colours referred to as Yellow (Pb- and Sb-rich) and Black (Mn-rich) are identified on this area.

Table S1. Colour palette and colouring agents identified for the three different corpuses of glazed bricks: Khorsabad, Aššur and Babylon as given by visual examination and XRF analyses. The general information gained by SEM-EDX analysis of the orange-yellow and black colours has been included. * These minor antimonates are very likely products of reaction of the Pb-antimonate with the glass. **Suspected but to be confirmed by other samples.

Brick	Colour	Main colouring or opacifying agent	Secondary colouring or opacifying agent
Khorsabad	Orange	Pb-antimonates bearing Fe and Ca	Hematite (Fe_2O_3) Ca-antimonates* Fe-antimonates*
Khorsabad	White	Ca antimonates (by XRF on N8123)	Not investigated
Khorsabad	Black	Copper sulphide nanoparticles, bearing variable amounts of Pb, Fe and Sb	
Khorsabad K-N8123 (two circles surrounding the flower yellow heart and the flower white petals)	Turquoise-blue	Cu in the glass, Ca-antimonates, and traces of Fe	Not investigated
Khorsabad, K-N8123 (between the white petals of the flower)	Turquoise-green	Cu and traces of Mn in the glass	Not investigated
Aššur A-811251 (border of the arcade patterns) A-811452 A-810750 (animal figure)	Orange	Pb-antimonates bearing Fe and Ca	Hematite (Fe_2O_3)**
Aššur A-810373 (character's face and outline of the pattern line) A-812093 A-810791 (one out of two ribbon)	Yellow	Pb-antimonates bearing Fe and Ca	Hematite (Fe_2O_3)
Aššur A-811251 (inner part of the arcades) A-811452 (inner part of the circles, and one out of two glazes of the alternating band pattern on right)	Pale yellow (with greenish accent)	Pb-antimonates bearing Fe and Ca	Cu in the glass
Aššur	White (not the contour lines)	Ca antimonates	
Aššur A-810791 (one out of two ribbon)	Light green	Ca antimonates	Cu in the glass
Aššur	Black	Mn oxides	

9th cent. BC A-810273 A-810738			
Aššur 8th-7th cent. BC A-812641 A-810791	Black	No particular colouring oxide – AgS nanoparticles for A-810791	
Aššur	Green / Turquoise-blue / Turquoise-green	Cu in the glass	
Babylon	Yellow	Pb-antimonates bearing Fe and Ca	Hematite (Fe_2O_3)
Babylon	White	Ca antimonates	
Babylon	Black	Copper sulphide nanoparticles bearing variable amounts of Pb	
Babylon	Green	Cu in the glass and Pb-Sb,Fe antimonates	
Babylon	Turquoise-blue	Cu in the glass and Ca antimonates	
Babylon B-VA17274	Dark blue	Co and Cu in the glass	Not investigated
Babylon	Blue	Co and Cu in the glass Ca antimonates	

XRD diagram and Rietveld analysis of the lead antimonate reference compounds

The XRD patterns of the mock-up samples were recorded on a Bruker D8 Endeavor diffractometer in Bragg-Brentano configuration, using the CoKα1-2 radiation. The 10-140 ° 2θ range, step 0.02 ° was scanned during 1 hour. The Rietveld analysis of the XRD patterns was carried out with the FullProf suite [10] . Concerning the pyrochlore solid solution, a site occupation scheme corresponding to the $Pb_2(Sb_{1-x},Fe_x)_2O_{7-2x}$ formula was implemented and the x value was refined for the 0.8 Fe sample (x = 0.8 in the synthesis mixture), assuming that Fe^{III} rather substitutes for Sb^{V} than for Pb^{II}, owing to their ionic radii. The two samples revealed significant differences:

The refinement of the 0 Fe sample (x = 0 in the synthesis mixture) was made difficult by the presence of one, maybe two secondary unidentified phases, which peaks somewhat overlapped those of the main phase. The latter was identified as a pyrochlore-type compound with cell parameter a = 10.415(2) Å, presumably $Pb_2Sb_2O_7$ (also known as oxyplumboromeite, a = 10.3783(6) Å [11]).

Conversely, the 0.8 Fe sample appeared almost single-phased, with only few and faint unidentified impurity peaks (Figure S4). The cell parameter of the pyrochlore phase was a = 10.4800 (9) Å and the site occupancy factors accounted for a $Pb_2(Sb_{0.88},Fe_{0.12})_2O_{6.76}$ composition, instead of the expected $Pb_2(Sb_{0.60},Fe_{0.40})_2O_{6.20}$. Although the phase was obviously depleted in iron, the present measurement must be seen with caution. Based on the peaks broadening compared to the instrumental function calibrated with a LaB_6 standard, the average crystallites' size was estimated at 100 nm.

It is worth to note that a pyrochlore phase with almost the same cell parameter as in 0.8 Fe was observed in an intermediate 0.4 Fe sample (x = 0.4 in the synthesis mixture), also studied in the frame of this work, which suggests that both phases are saturated in iron. This phase was found to be associated to a rhombohedral phase (space group R-3m, a = 3.702(1), c = 9.615(3) Å). The resolution of the crystal structure of the latter revealed a distorted fluorite-type array. Owing to the strong tendency of the pyrochlore compounds to disorder into a more simple structure at high temperature and/or when departing from stoichiometry, the present phase can be modeled as $(Pb_{2+x},Sb_{2-x})(O_{7-1.5x},\ _{1+1.5x})$, where corresponds to a vacancy. Due to the high electron density contrast between the cation and anion sites, we did not succeed in refining the Pb/Sb ratio, nor the phases relative amounts.

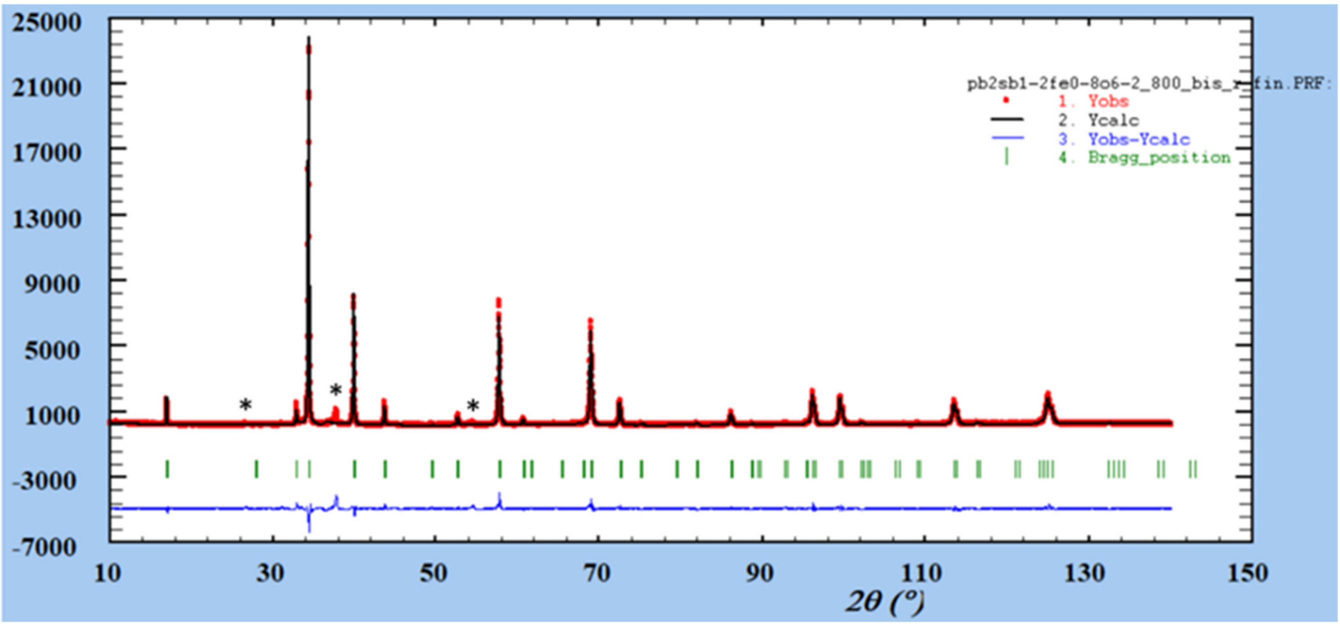

Figure S4. Final Rietveld plot for the 0.8 Fe sample. R_{Bragg} reliability factor of the pyrochlore phase is 0.046. Impurity Bragg peaks are marked with *.

References

1. Ravaud, E., Pichon, L., Laval, E., Gonzalez, V., Eveno, M., Calligaro, T. Development of a versatile XRF scanner for the elemental imaging of paintworks. *Applied Physics A* **2016**, *122*, pp.17-24.
2. Solé, V.A., Papillon, E., Cotte, M., Walter, P., Susini, J. A multiplatform code for the analysis of energy dispersive X-ray fluorescence spectra. *Spectrochimica Acta B* **2007**, 62, pp.63-68.
3. Vandiver, P. Glass technology at the mid-second Millennium BC Hurrian site of Nuzi. *J. Glass Stud.* **1983**, *25*, pp. 239-247.
4. Knight, B. Excavated window glass: a neglected resource? *Stud. Conserv.* **2017**, *41*, pp. 99-104.
5. Shortland, A., Kirk, S. Eremin, K., Degryse, P., Walton, M. The analysis of late Bronze Age Glass from Nuzi and the question of the origin of glass-making. *Archaeometry* **2017**, *60*, pp. 764-783.
6. Starr, R.F.S., Sears Chute, R., Ehrich, R.W., Eliot, H.W., Gettens, R.J. Lacheman, E.R. *Nuzi: report on the excavation at Yorgan Tepa near Kirkuk, Iraq, conducted by Harvard university in conjunction with the American schools of oriental research and the University museum of Philadelphia, 1927-1931*; Harvard University Press: Cambridge, United States, 1939.
7. Fitz, S. Die Farbglasuren spätbabylonischer Wandverkleidungen - The colored glazes of Neo-Babylonian wall facings. *Ceramic forum international / Berichte der Deutschen Keramischen Gesellschaft* **1982**, *59*, pp. 179-185.
8. Matson, F. Glazed brick from Babylon - historical setting and microprobe analyses. In *Technology and Style: Ceramics and Civilization II*; Kingery, W.D., Eds; American Ceramics Society: Columbus, United States, 1986; pp. 133-156.
9. Rodler, A., Klein, S., Artioli, G, Brons, C. Probing the provenance of archaeological glaze colorants: polychrome faunal reliefs of the Ishtar Gate and the processional way of Babylon. *Archaeometry* **2019**, *51*, pp. 837-855.
10. J. Rodriguez-Carvajal, FULLPROF: A Program for Rietveld Refinement and Pattern Matching Analysis, Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, Toulouse, France, 1990, p. 127
11. U. Hålenius, F. Bosi, "Oxyplumboroméite, $Pb_2Sb_2O_7$, a new mineral species of the pyrochlore supergroup from Harstigen mine, Värmland, Sweden", Min. Mag. 77, 2931-2939, 2013