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Supplementary Materials

An insight into Gandharan Art: Materials and Techniques of Polychrome Decoration

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S1. Archaeological Description of the Samples

We have considered a group of sample coming from some archaeological sites of the Swatt Valley:

1. Barikot, an important urban site, a fortified agricultural colony in existence between the middle of the 1st millennium BCE and the 4th century CE [1,2];
2. the sacred area of Amluk-dara, about 5 km SE of Barikot [3];
3. Gumbat/Balo Kale, an important sacred area about 5 km SW of Barikot [3,4].

Sample B8 (Figure 3, main manuscript) was taken from the collapses related to the chapel [1123/1023] of Barikot [1]. The building, a rectangular sacellum on a high podium open to the south and located in a courtyard housing other cult buildings, contained a miniature stupa. The sample refers to a portion of the building's top cornice characterised by a row of brackets (S-shaped or cyma reversa-type) made of stone with a calcite-based stucco coating [3]. The dating of the collapse places it in Macrophase 5 of the site sequence (c. 250-300 CE) [3,5], before the great destructive earthquake of the late 3rd-early 4th century CE, which determined the end of the ancient settlement, rebuilt in the following centuries at the slopes of the acropolis.

Sample BKG 1123 (15) (Figure S1), comes from the same site and it refers to a façade decorative covering of the shrine (1123–1023); it is dated to Macrophase 5a (middle-end 2nd century CE).

Figure S1. Sample BKG 1123, 16B: polychrome stucco architectural decoration of building with traces of red colour from Barikot (© ICR, photo Edoardo Loliva).

Sample C 11 (Figure 3, main manuscript) was taken in Amluk-dara from the N (front) side of the podium of the stupa [61], the second building in chronological order after the Great Stupa with whose foundation the history of this sacred area begins. Although founded in the early years of the 2nd century CE, stupa 61, as well as the Great Stupa, underwent a phase of renovation following the collapses caused by the earthquake of the late 3rd-early 4th century CE. In these phases, the traditional bluish schist decoration was replaced by the cheaper and newer stucco production, which had already been successfully experimented, but on a smaller scale, in Buddhist monuments in nearby Barikot. In this sense, sample C 11 is chronologically slightly later than sample B8 from Barikot, briefly discussed above.

A separate discussion should be made of sample A3 from the site of Gumbat/Balo Kale. The sample (Figure 3, main manuscript) was collected from a wall fragment found in the fill of a pit [114] of clandestine excavators and is therefore without direct context. The analysis of the materials compared to the visible architecture allows us to attribute the fragment to the upper drum of the Great Shrine (double dome with vaulted ambulatory and square cell) whose construction is dated to the beginning of the 2nd century CE [4]. It should be added that Pit 114 was excavated immediately behind the N side of the podium of the Great Shrine. If this hypothesis is correct, sample A3 could be considered the oldest of the three analysed in this study.

Furthermore, another sample from the same site of Gumbat/Balo Kale, GBK (18). Figure S2 is a part of the Great Stupa [9] covering, attributed to Period II (end 2nd century–early 3rd century CE).

Figure S2. Sample GBK (18), stucco architectural decoration of building from Gumbat/Balo Kale, photo of cross section (Dinolite, 20x): the white ground layer is visible.

Sample GBK (17) (Figure S3) refers to the Little Stupa covering [17] and its dating is Period II (end 2nd century—early 3rd century CE).

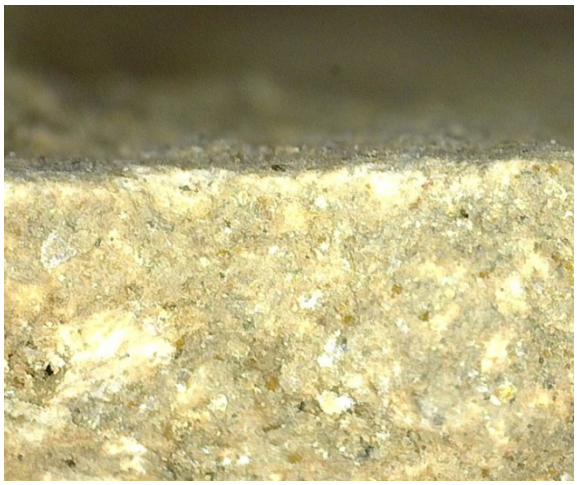

Figure S3. Sample GBK (17), stucco architectural decoration of building from Gumbat/Balo Kale, photo of cross section (Dinolite, 20x): the white ground layer is visible.

S2. GC/MS Quantitative Analyses

The quantitative determination of amino acids, aliphatic mono- and dicarboxylic acids was performed by using standard solutions, building calibration curves, and evaluating daily recoveries.

The calibration curves were built using the following solutions:

(i) solution of fatty and dicarboxylic acids in acetone, containing lauric acid (0.24 mg/g), suberic acid (0.27 mg/g of Su), azelaic acid (0.28 mg/g of A), myristic acid (0.25 mg/g of My), sebacic acid (0.3 mg/g of Se), palmitic acid (0.25 mg/g of P), oleic acid (0.51 mg/g of O), stearic acid (0.51 mg/g of S); all acids (purity 99%) were purchased from Sigma–Aldrich (Milan, Italy)

(ii) standard solution of amino acid was in an acid solution 0.1 M HCl, purchased from Sigma-Aldrich containing 12.5 μmol/mL of proline (Pro) and hydroxyproline (Hyp) and 2.5 μmol/mL of aspartic acid (Asp), glutamic acid (Glu), alanine (Ala), arginine, cysteine, phenylalanine (Phe), glycine (Gly), hydroxylysine, isoleucine (Ile), histidine, leucine (Leu), lysine (Lys), methionine (Met), proline (Pro), serine (Ser), tyrosine (Tyr), threonine, and valine (Val).

(iii) solution of monosaccharides and uronic acids in bidistilled water containing a d-(+)-galactose (0.1 mg/g), l-(−)-fucose (0.1 mg/g), l-(+)-arabinose (0.1 mg/g), l-(−)-ramnose (0.1 mg/g), l-(−)-mannose (0.1 mg/g), d-(+)-xylose (0.1 mg/g), d-(+)-glucose (0.1 mg/g), d-glucuronic acid (0.1 mg/g), d-galacturonic acid(0.1 mg/g) monohydrate. All monosaccharides and uronic acids (purity 99%) were purchased from Sigma–Aldrich (Milan, Italy).

The storing conditions of the standars solutions were 4ºC.

The SIM mode was used for the quantitative determination of fatty and dicarboxylic acids, amino acids, monosaccharides and uronic acids.

S3. GC/MS limits of Detection and Quantitation

The detection limit (LOD) and the quantitation limit (LOQ) of amino acids, aldoses, uronic acids, and fatty and dicarboxylic acids were calculated. LOD was calculated as LOD=(ā+tσ)/S and LOQ=3LOD, being: ā the mean value obtained for each compound in the blanks analyzed, σ the standard deviation of the response, t the value of t Student's distribution taken at a statistical significance level of 0.05 and (n−1) degrees of freedom and S the slope of the calibration curve. At a statistical significance level of 0.05, the LODs and LOQs obtained of the proteinaceous, glycerolipids and saccharide materials were as follows:

Proteinaceous material: LOD 0,22μg; LOQ 0,38μg

Glycerolipids: LOD 0.35μg; LOQ 0.50μg

Saccharide material: LOD 0,07μg; LOQ 0,15 μg.

S4. Binder Analysis of Samples from Gandharan Polychromies

Samples from archaeological sites are named following the site name. Samples from museum collections are named after the museum: ex Museo Nazionale di Arte Orientale (ex MNAO), now merged in Museo delle Civiltà in Rome (Italy), Museum Guimet (MG) in Paris (France) and Museo Civico Archeologico di Milano (MCAM) in Milano (Italy). Results from these 19 samples have been already presented in previous studies [6–10]. Sample B8 is the only sample in the whole collection that does not present a preparation layer between the painting layer and the support.

GC/MS and proteomics have been used in a complementary way: 6 samples were studied by proteomics while 14 were analysed by GC/MS (Figure S1a). Almost all the samples analysed (80%) by proteomics consisted in the samples from statues preserved as part of museum collections (Figure S1b). The amount of sample at our disposal in those cases was very little. Only one sample collected from a statue at the exMNAO was analysed by GC/MS (ex MNAO 11). However, samples representative of all types of support were analysed by proteomics.

All samples from architectural decorations, both coming from the archaeological site or from pieces preserved in museums, were analysed by GC/MS. Therefore, 90% of the samples analysed by GC/MS were from architectural decorations (Figure S1c) but for sample exMNAO11. Almost all samples analysed by GC/MS are on stucco support but for samples exMNAO 5 and 7 that are polychromies on stone (14% of the samples analysed by GC/MS).

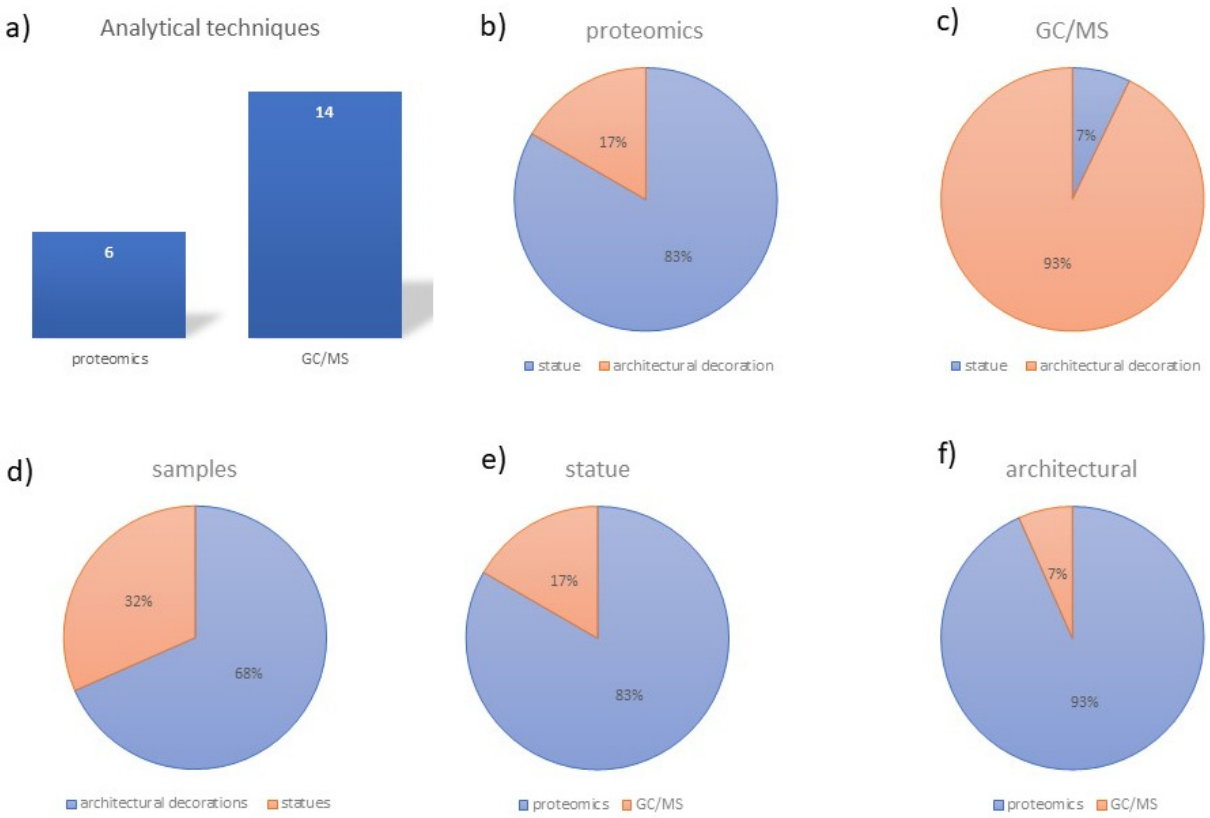

Figure S4. Statistical data related to the samples analysed and the type of analysis performed.

Two more samples have been analysed presenting particular characteristics: Tapa Sardaar, which is a clay fragment, probably a statue, of unknown origin, and sample exMNAO 8, which consisting in a solidified drop of paint.

Table S1 reports the relative amino acid percentage content of the analyzed samples showing a proteinaceous content above the quantitation limit. Figure S5 shows the PCA score plot of sample exMNAO8. Sample is located in the egg cluster.

Table S1. Relative amino acid percentage content of the samples with an amino acid content above the quantification limit.

Sample	**Sample Weight (mg)**	**Ala**	**Gly**	**Val**	**Leu**	**Ile**	**Ser**	**Pro**	**Phe**	**Asp**	**Glu**	**Hyp**
exMNAO8	2.3	10.2	4.4	10.9	16.2	8.5	3.8	8.7	10.8	9.6	16.8	0.0
C11	4.3	9.5	11.9	10.6	16.0	6.0	3.3	2.7	8.8	8.1	22.2	1.0
B8	5.4	8.0	13.9	5.5	8.5	8.3	12.3	7.6	6.1	8.8	19.2	1.8

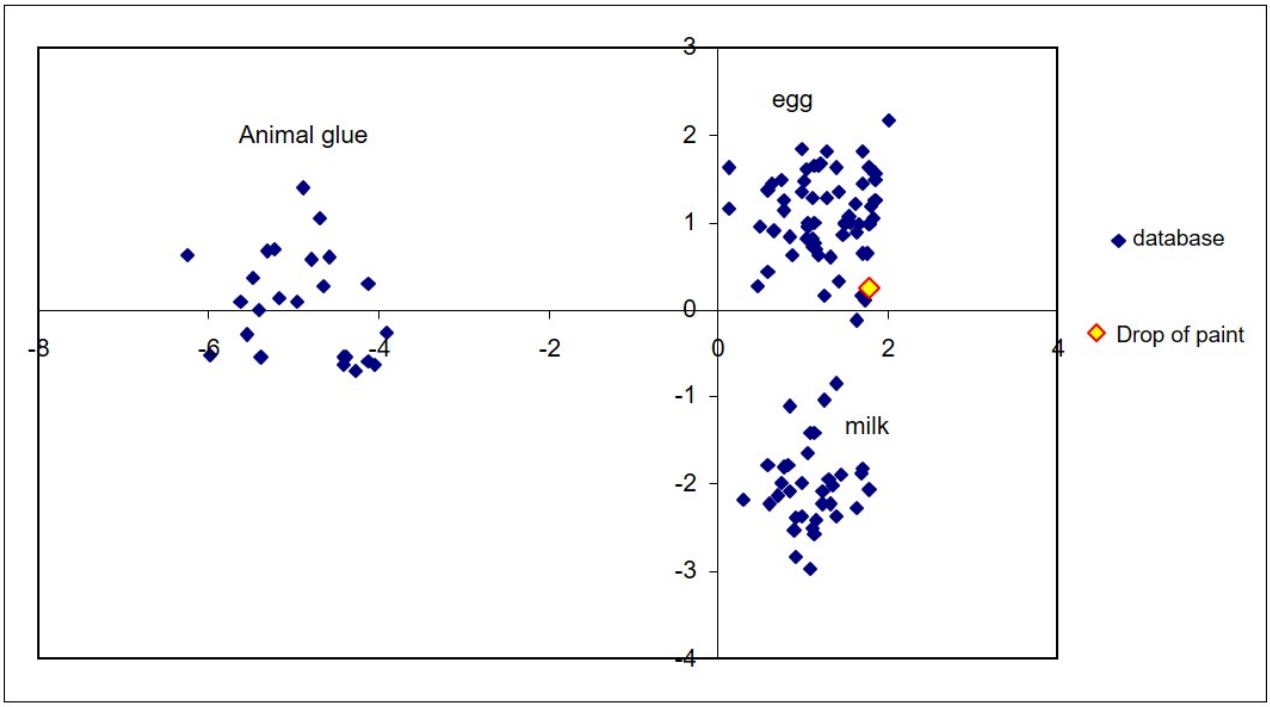

Figure S5. PCA score plot of the sample consisting in a drop of paint.

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