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The Characterisation of the Organic Binders

Paints are always made up of the same fundamental components: a pigment, which is most typically a fine powder of inorganic or organic coloured material, and, with the exception of frescoes, a fluid binder, which enables the pigment to be dispersed and applied with a brush. Historically, the binder could have been a proteinaceous material such as egg or casein, a vegetable gum, a drying oil, a natural wax or a synthetic polymer. After drying or curing, a solid paint film is produced. The surface on which the paint is applied generally needs to be prepared with a ground layer. Painters were not only artists but also "material scientists", since they had to able to select the best paint materials, process them and apply them in order to suit their needs and achieve the desired aesthetical results. They experimented with a wide range of natural materials[138] and used many layers of paint to produce particular effects. To our eyes the appearance of a painting is thus the final result of the interaction of this complex, highly heterogeneous, multi-material and multi-layered structure with light.

The chemical characterisation of organic components is of great interest because the different organic paint materials used help us to differentiate between the various painting techniques, and because the organic component of the paint layer is particularly subject to degradation. An analysis of organic paint materials is essential for their long-term preservation, to assess the best conservation conditions, to prevent and slow down the decay processes, and to plan the best kind of restoration. Macroscopic degradation phenomena, such as the loss of cohesion in the paint layers, are in most cases related to the chemical alterations of the organic media, such as depolymerisation, oxidation, hydrolysis, cross-linking, and biological attack. Chemical reactions between organic materials and pigments lead to discoloration or colour alteration.

For a complete understanding of the composition of paint layers, several techniques need to be used, including SEM-EDX, XRD, micro-FTIR, micro-Raman, SIMS and many others[139]. Nevertheless, at present, the coupling of gas chromatography with mass spectrometry (GC-MS) is the preferred analytical approach to characterise organic paint materials such as binders or varnishes. The versatility of GC in the investigation of a very broad set of natural organic materials that can be found in artworks was pioneered by Mills and White and confirmed by a number of successful applications and case studies.[140,141.] The choice of GC is driven by the fact that natural organic substances are complex mixtures of many chemical species, which are very similar to each other: the resolution and determination of the molecular profile is essential in order to identify the materials present and the ageing pathways. Consequently, in this specific field, the coupling of GC with mass spectrometry is necessary due to the high number of compounds with similar retention times. In addition, because the most significant compounds are not available as commercial standards, identification cannot be based only on retention times, but requires the confirmation of mass spectra[142].

Experimental

GC-MS analytical procedure to characterise organic binders

The sample is subjected to ammonia extraction in an ultrasonic bath two times to extract proteinaceous binders. The sample is centrifuged, the supernatant ammonia solution is separated, and the extracted ammonia solutions are joined together. The residue containing insoluble organic (i.e. lipid and resinous materials) and inorganic species is kept apart. The extracted ammonia solution is evaporated to dryness, redissolved in trifluoroacetic acid solution, and subjected to extraction with diethyl ether (three times) to extract free acids (monocarboxylic, dicarboxylic and terpenoid) solubilised in the ammonia solution. The ethereal extracts are combined with the residue of the ammonia extraction. The residue of the ether extraction is subjected to purification on OMIX C4 tip. The purified solution, containing proteins and polypeptides, is evaporated to dryness and subjected to acidic hydrolysis assisted by microwave. The residue of the purification is discarded. After the hydrolysis, bidistilled water is added to the acidic hydrolysate constituting the *amino acid fraction*. An aliquot of the amino acid fraction is then analysed with GC-MS after derivatisation with *N*-methyl-*N*-(*tert*-butyldimethylsilyl)trifluoroacetamide) (MTBSTFA), using norleucine and hexadecane as internal standards, pyridine as solvent, and triethylamine as catalyst. The residue of the ammonia extraction, combined with the ethereal extract of the protein and polypeptide solution prior the OMIX C4 tip purification, is subjected to saponification / salification assisted by microwave with KOH in ethanol. After saponification, the alcoholic solution is diluted in bidistilled water, acidified with trifluoroacetic acid, and extracted with *n*-hexane (three times) and diethyl ether (three times). The organic extracts (containing fatty acids, dicarboxylic acids,

Table 1 Sample description

sample	provenance	layer	(built-up) description	sub-sample (analysed)	note
KBL 497*	Eastern Buddha	3	greyish blue	KBL 497	
		2	ochre		
		1	clay		
GBL 246*	Western Buddha			A 1+2	sample flake, containing all paint layers
				A 1	red layer, scraped by scalpel
				A 2	pink layer, scraped by scalpel
GBL 2400+*	Western Buddha			Bt	sample flake, containing all paint layers
				B 1	superficial whitish layer
				B 3	brown paint layer (probably two paint layers are contained
				B 2	yellow layer, probably clay
GBL Einzelstück (ID 172a)*	Western Buddha			Ct	sample flake, conatining all paint layers
				C 1	superficial whitish layer
				C 2	brown layer
				C 3	red layer, containing some clay from underneath
ID 277	Eastern Buddha	fragment	arriccio	277	fragment
ID 97	Western Buddha	7	red hard layer	97 – 7	scraped material, contains a bit of layer 6 as well
		6	grey hard layer	97 – 6	scraped material, might contain a bit of layer 7
		5	black powdery layer	97 – 5	scraped material, contains a bit of layer 6
		4	orange powdery layer	97 – 4	scraped material
		3	pink powdery layer	97 – 3	
		2	plaster	97 – 2	scraped material, might contain a bit of arriccio
		1	arriccio	analyses not required	
ID 172 (172b)	Western Buddha	4	brownish layer, semi-transparent	172	
		3	thin red layer (few residues)	analyses not required	
		2	plaster		
		1	arriccio		
ID 68	Western Buddha	4	residues of pigmented layers	analyses not required	
		3	transparent preparation layer	168 – 3	scraped material
		2	plaster	168 – 2	scraped material
		1	arriccio	analyses not required	
ID 188	Eastern Buddha	5	white layer (few residues)	analyses not required	
		4	yellow ochre layer	188 – 4	scraped material, containing some more of layer 4 than of layer 3
		3	white gypsum layer	188 – 3	sample flakes, containing more of layer 3 than 4
		2	plaster	analyses not required	
		1	arriccio		
ID 214	Eastern Buddha		brown material (restoration)	214 int	contains a bit of blue layer underneath
		6	blue layer	214 – 6	material scraped with scalpel
		5	black layer	214 – 5	material scraped with scalpel
		4	blue layer	214 – 4	material scraped with scalpel
		3	black layer	214 – 3	material scraped with scalpel
		2	plaster	analyses not required	
		1	arriccio		

* Saccharide materials have not been characterised in samples KBL and GBL

Table 1 Sample description (continuing)

sample	provenance	layer	(built-up) description	sub-sample (analysed)	note
ID 14	Western Buddha	8	Indian restoration (only one point)	analyses not required	
		7	grey layer	14 – 7 (5 – 4)	scraped material, containing also layers 5 and 4
		6	red layer (only one point)	14 – 6	scraped material
		5	orange layer	14 – 5	scraped material
		4	white layer	14 – 4	scraped material
		3	transparent layer	14 – 3	scraped material
		2	plaster	analyses not required	
		1	arriccio		
ID 108	Western Buddha	5	few residues of the Indian restoration		analyses not required
		4	glossy brown layer	108 – 4	
		3	glossy brown layer	108 – 3	
		2	plaster	analyses not required	
		1	arriccio		

Table 2 Amino acid relative percentage content of sample KBL

sample	**Ala**	**Gly**	**Val**	**Leu**	**Ile**	**Ser**	**Pro**	**Phe**	**Asp**	**Glu**	**Hyp**
KBL	4.0	4.5	7.3	10.2	5.0	3.5	12.4	6.5	16.4	30.2	0.0

terpenoid acids, alcohols, phenols, hydrocarbons and other neutral and acidic substances arising form lipid and resinous fraction of the sample) constitute the *lipid-resinous fraction*. An aliquot of the lipid-resinous fraction is analysed with GC-MS after derivatisation with *N*,*O*-bistrimethylsilyltrifluoroacetamide (BSTFA), using tridecanoic acid (C13) and hexadecane as internal standards, and isooctane as solvent. Experimental details are published elsewhere.[143]

GC-MS analytical procedure for the determination of saccharide materials

The sample is subjected to microwave assisted hydrolysis to free sugars from polysaccharide materials with high efficiency and reproducibility. Afterwards the hydrolysed solution is purified through a double-exchange resin to remove analytical interferences of inorganic cofactors. The resulting sugars are analysed by GC-MS after derivatisation. The derivatisation procedure is based on mercaptalation followed by silylation, in order to transform the aldoses and uronic acids into the corresponding diethyl-dithioacetals and diethyl-dithioacetal lactones. Using this method only one chromatographic peak for each analyte is obtained, providing simple and highly reproducible chromatograms. Experimental details are published elsewhere.[144]

Samples

In table 1, a description of the samples analysed is summarised. Samples, by means of a scalpel, have been eventually sub-sampled under the binocular microscope.

Results and Discussions

Sample KBL 497

The analysis of the proteinaceous content revealed the presence of proteins. The relative amino acid content is reported in table 2. In figure 1 the principal component analysis score plot is reported. The sample is perfectly located in the casein cluster, indicating that it (or milk) was the binder used to disperse the pigments.

The analysis of the acidic fraction revealed the occurrence of monocarboxyilic acid, palmitic being the most abundant, and small amounts of dicarboxylic acids, azelaic being the most abundant. The occurrence of fatty acids at a level higher than the quantitation limit, in addition to the occurrence of dicarboxylic acids, suggests that an oxidised lipid material is present. The profile is not in disagreement with that of milk fats. The proteinaceous content, together with the lipid profile might suggest that the binder is milk and not casein.

Since this sample is characterised by a superficial layer not adherent and, underneath, a quite compact layer, these two layers were sampled separately and analysed. In particular the following samples were collected: a sample from the superficial not adherent layer (KBL 1), one from the compact layer underneath (KBL 2) and another sample containing all layers (KBL 3). Sample KBL 1 showed an amino acid content at the blank level, while both samples KBL 2 and 3 showed a proteinaceous content above the quantitation limit level and the relative amino acid content

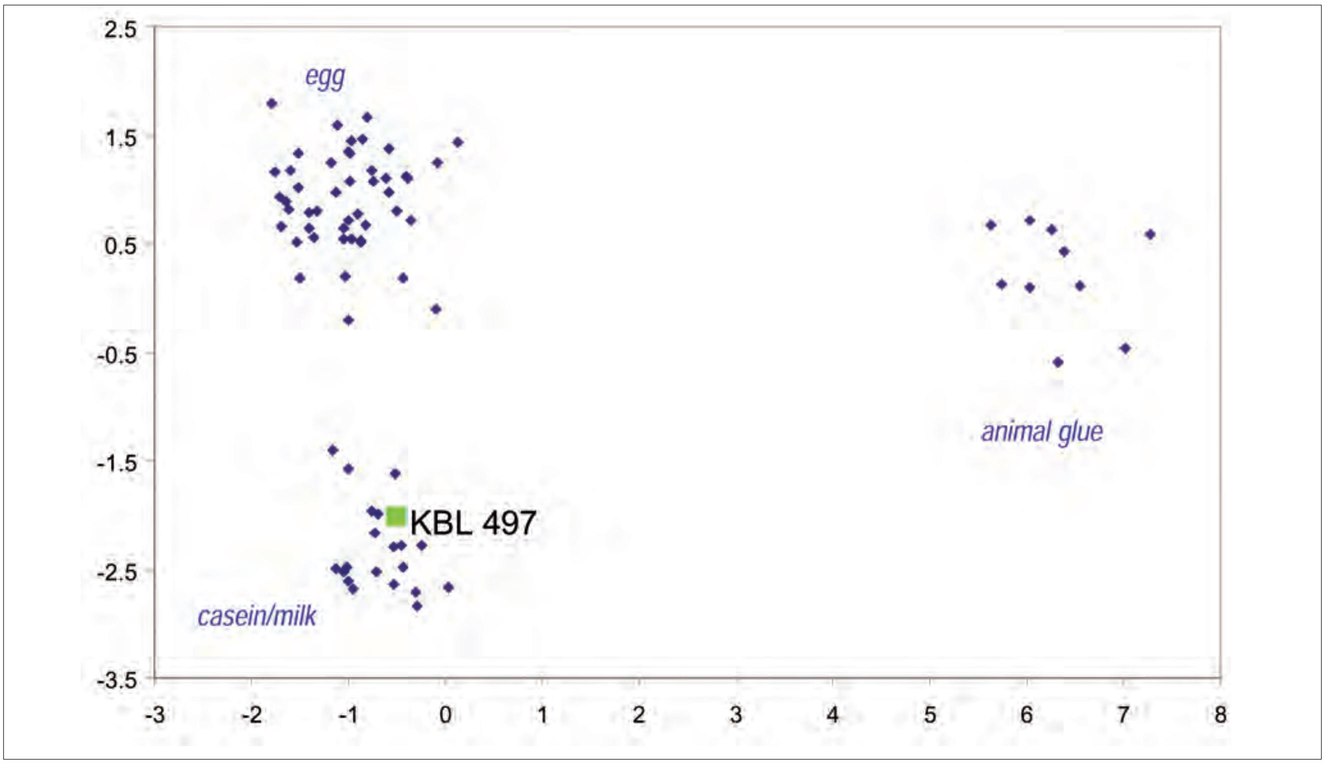
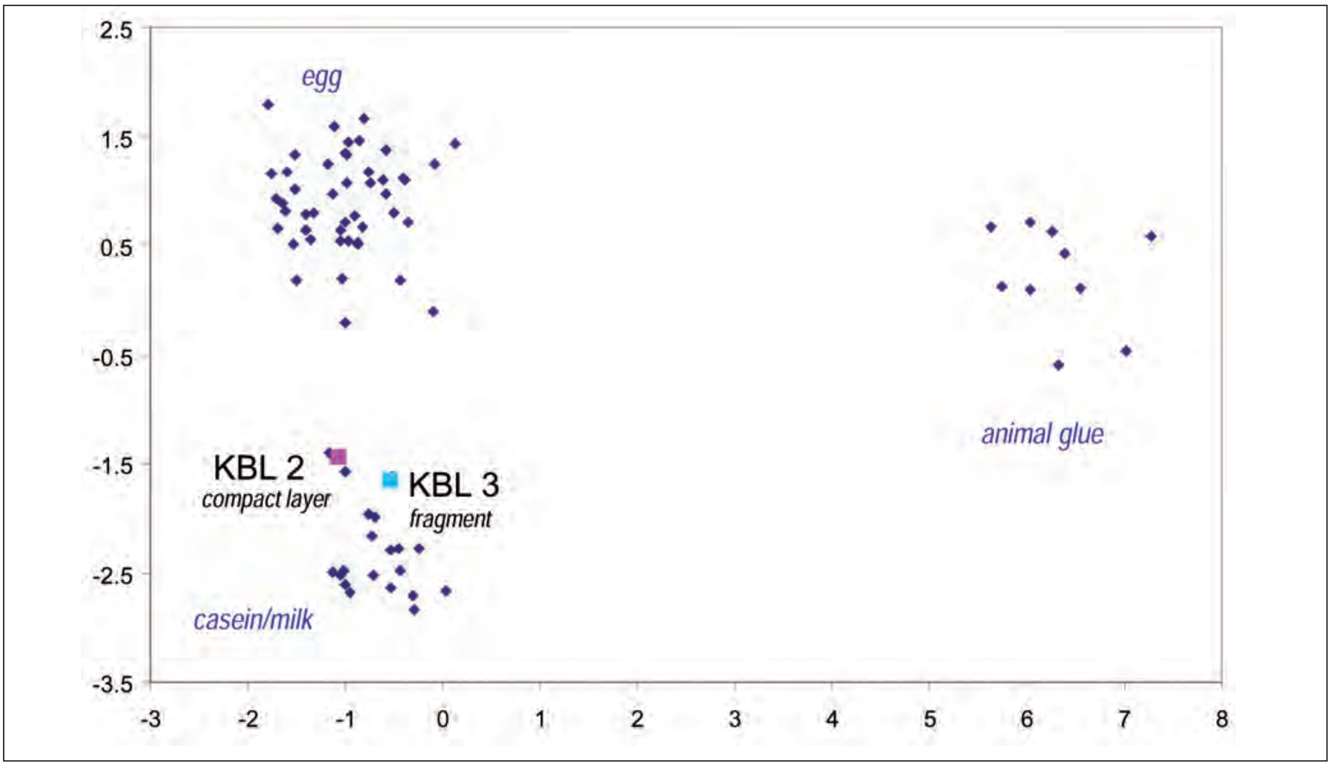


Fig. 1. PCA score plot of KBL497

Table 3 Amino acid relative percentage content of samples analysed

sample	Ala	Gly	Val	Leu	Ile	Ser	Pro	Phe	Asp	Glu	Hyp
KBL 2	5.4	8.0	12.2	14.9	8.0	5.9	7.7	4.8	10.8	22.4	0.0
KBL 3	5.5	7.2	10.5	11.9	6.5	5.3	9.7	5.8	12.1	25.5	0.0

Fig. 2. PCA score plot KBL497



is reported in table 3. The samples were submitted to the PC analysis and the resulting score plot is reported in figure 2. Both samples are located in the casein cluster. Since the sample of the superficial non adherent layer showed a proteinaceous content at the blank level, it can be hypothesised that it has been realised using a binder, which was neither proteinaceous nor lipidic.

Samples GBL 246, GBL 2400+ and GBL Einzelstück (ID 172a)

All samples, with the exception of C1 showed the occurrence of proteinaceous material higher than the blank level. In table 4 the relative amino acid percentage content is reported together with the amount of proteinaceous material found (calculated as the sum of the eleven quantified amino acids).

The relative percentage amino acid contents were subjected to the principal component analysis (PCA) together with 104 reference samples containing egg, animal glue and casein (or milk) and the resulting score plots are shown in figure 3 (A, B, C).

The lipidic component has been analysed as well. All samples contained monocarboxylic acids with an even number of carbons, palmitic and stearic acid being the most abundant, and small amounts of dicarboxylic acids and monocarboxylic acids with an odd number of carbons. Cholesterol was identified in samples but sample A1+2. Beeswax was identified in small amounts in sample Bt and Ct.

GBL 246. All three sub-samples contain casein, as it can be inferred from the PCA score plot reported in Figure 1-A. The lipid fraction shows a fatty acid profile that is not ascribable to a drying oil in none of the sub-samples analysed. Moreover the high amount of stearic acid, together with the occurrence of cholesterol, odd number of carbon fatty acids and dicarboxylic acids ranging from eptandioic to hexadecandioic acid, point to the occurrence of a fat of animal origin (not egg lipids, since palmitic and stearic acid are in similar amounts). These results suggest that milk could have been used as painting medium for both paint layers.

GBL 2400+. The interpretation of the composition of this sample seems more complex and more investigation seems necessary to clarify the binding media composition layer by layer.

The lipid composition again point to the occurrence of a fat of animal origin, although not egg lipids, since palmitic and stearic acid are in similar amounts. Moreover very small amounts of beeswax have been identified in the sample flake: it might be ascribable to a restoration material, which was not identified in the B1 sub-sample because this was too small.

The sample flake (Bt) contains proteinaceous material, or, due o the position in the score plot, a mixture of proteinaceous materials. Animal glue is present due to the presence of hydroxyproline, its marker. Sample B1 contains both casein and animal glue. Sub-sample B3, representing the paint layers, and though in contact with B1 contain casein. Sub-sample B2, representing the clay in contact with the paint layer contains what seems a mixture of egg and animal glue. Since no fats were not present in the lipid fractions egg white must be hypothesised. Thus a possible interpretation of the sub-sample composition can be as follows: the superficial whitish layer (which is a restoration layer) was performed with animal glue; the brown paint layers have been applied with casein (probably milk, due to the occurrence of fats); and finally the clay was prepared with a mixture of egg white and animal glue.

GBL Einzelstück (ID 172a). The structure of this sample seems similar to the one from GBL 2400+. In fact the lipid fraction contains animal fats (not egg fats) as well as very small amounts of beeswax. The proteinaceous content reveals the occurrence of egg and animal glue in the sample flake, and the red sub-sample, containing some clay seems a mixture of the three paint proteinaceous binders. The brown paint layer seems to contain just casein. Thus also in this case it can be hypothesised that the paint has been applied with casein and the clay has been previously prepared with animal glue and egg white.

Samples ID 277, 97, 172, 168, 188, 214, 14, and 108

In all samples but sample ID 14 (sub-samples 14-3, 14-4/5/6 and 14-4/5/7) non drying fats, most likely from animal origin, were observed, being characterised by the presence of:

Table 4 Amino acid relative percentage content of samples analysed and amount of proteinaceus material found (μg)

sample	Ala	Gly	Val	Leu	Ile	Ser	Pro	Phe	Asp	Glu	Hyp	Proteinaceus material found
A 1+2	4.2	3.3	5.7	8.1	5.1	5.5	11.8	4.9	14.2	37.1	0.0	6.7
A 1	3.7	2.3	6.4	9.8	4.9	4.2	10.7	3.3	14.1	40.7	0.0	12.6
A 2	5.5	6.4	6.0	9.5	5.3	5.0	13.5	5.6	13.1	30.0	0.0	4.7
Bt	5.5	7.0	6.1	8.4	5.0	5.4	4.8	8.5	21.5	27.5	0.4	10.2
B 1	5.4	9.8	5.5	5.4	3.5	5.5	10.1	5.7	21.8	26.6	0.7	2.6
B 2	14.1	6.3	6.1	9.7	4.2	4.1	10.6	1.3	15.2	27.9	0.5	2.0
B 3	6.4	6.7	7.3	11.8	12.0	7.2	8.3	3.5	13.0	23.3	0.5	9.6
Ct	11.7	7.8	5.3	6.5	3.8	11.7	11.5	6.0	12.4	23.3	0.0	2.0
C 2	5.3	5.7	7.9	11.0	6.7	9.9	8.9	4.7	12.7	27.4	0.0	2.5
C 3	11.3	7.7	7.7	10.1	4.6	10.9	8.0	2.9	10.2	27.5	0.5	0.9

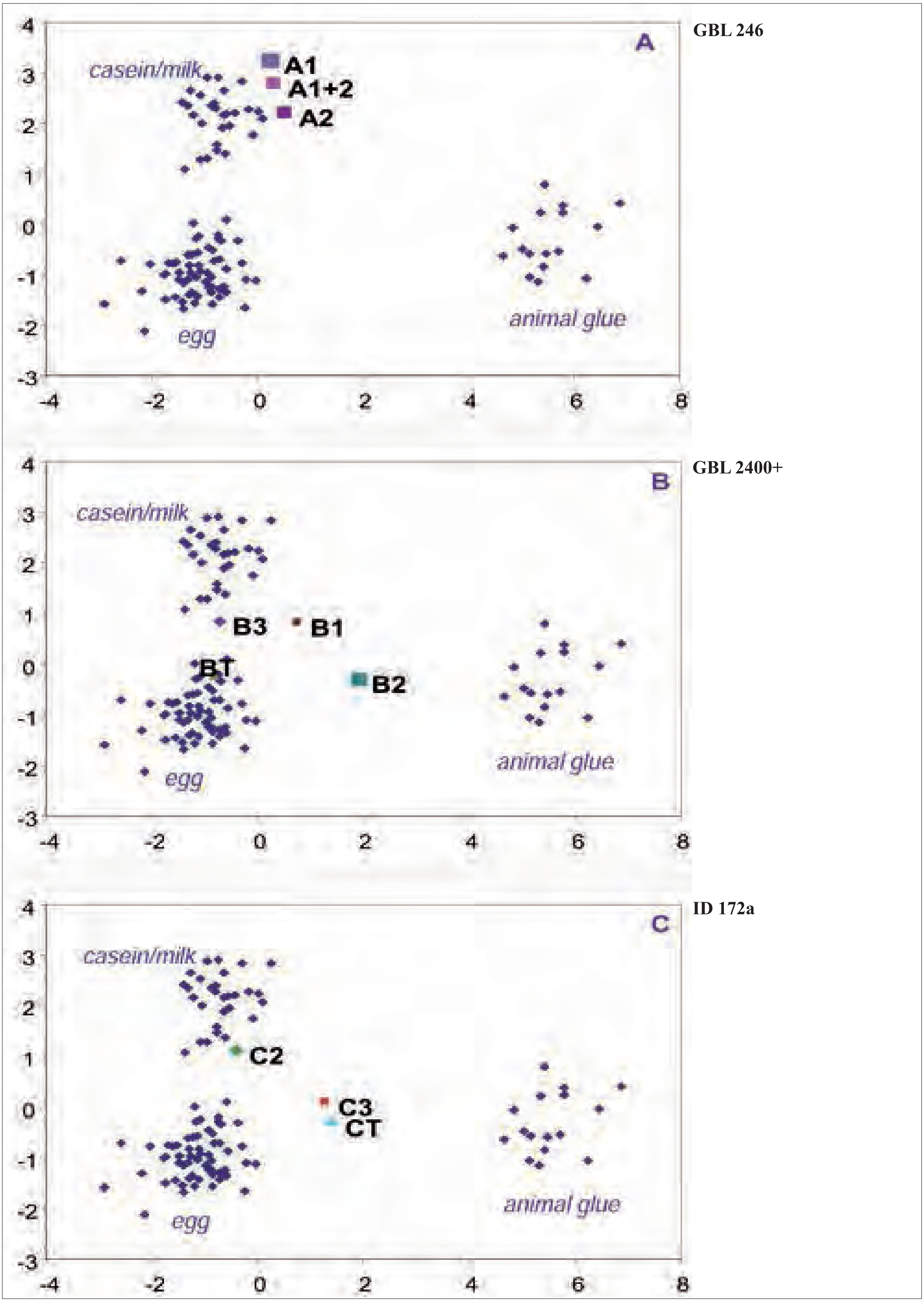


Fig. 3. PCA score plots (A, B, C) of GBL 246, GBL 2400+ and ID 172a

- monocarboxylic acids with even number of carbons (palmitic being the most abundant);
- small amounts of dicarboxylic acids (azelaic being the most abundant);
- small amounts of monocarboxylic acids with an odd number of carbons.

All samples showed the occurrence of proteinaceous material higher than the blank level, with the exception of the sub-sample 168-3, whose amino acidic content was between the detection and quantitation limit levels. In table 5 the relative amino acid content of the samples is reported together with the protein content, calculated as the sum of the eleven quantified amino acids. Any of the samples presented hydroxyproline in their composition indicating the absence of animal glue.

The quantitative percentage content of amino acids of the sub-samples determined from the amino acid fraction was subjected to a multivariate statistical analysis together to a data-set of 121 reference samples of animal glue, egg and casein, using the principal components analysis (PCA) method. Resulting score plots for each of the analysed samples are presented in figure 4.

Results indicate the use of egg in almost all sub-samples except for 97-5 and 97-2 (Western Buddha), where milk is the binding medium identified. The presence of non drying fats from animal origin identified in the lipid-resinous fraction (see above) indicated the use of egg yolk or whole egg. In sample 14 (sub-samples 14-6-5-4, 14-7-5-4 and 14-3) the absence of lipid materials suggests the use of the egg albumen (Western Buddha).

As far as the saccharide fraction is concerned, the glycoside profiles of the sub-samples are presented in table 6.

Three different kinds of sub-samples can be distinguished on the base of their polysaccharide content:

- polysaccharide content at the blank level of the procedure (97-7, 97-6, 97-5, 97-3-4, 168-3, 14-6-5-4, 14-3)
- polysaccharide content between the detection and quantitation limits (97-2, 168-2, 188-3, 14-7-6-5-4
- polysaccharide content higher than the quantitation limit (277, 172, 188-4, 214 int, 214-6-5, 214-4-3, 108-4, 108-3). Sample 188-4 contains also fructose.

The polysaccharide material could not be identified as one of the known plant gums, that is Arabic, tragacanth and fruit three gum. The presence of all sugars in samples 188-4, 172, 214-6-5, 108-4 and 108-3 suggests the use of a mixture of saccharide materials.

The sugar profiles observed are quite complex and the following remarks may be drawn:

- Sub-samples from the Western Buddha with a glycoside profile higher than the quantitation limit correspond to superficial layers and plaster ones.
- Sub-samples corresponding to plaster layers (97-2, 168-2) present a similar glycoside profile (xylose, arabinose and galactose). Galactose could be considered the result of the contribution of the saccharide content of the proteinaceous binder present in the samples.
- Sample 108-4, 108-3 and 172 consist in brownish layers on top of the sample build-up. However, quantitative profiles present some differences among them: all monosaccharides are present in sample 108 while in sample 172 glucose is absent and galacturonic acid

Table 5 Amino acid relative percentage content of samples 277, 97, 172, 168, 188, 214, 14, and 108

sample	**Ala**	**Gly**	**Val**	**Leu**	**Ile**	**Ser**	**Pro**	**Phe**	**Asp**	**Glu**	**Hyp**	**Protein content [μg]**
277	8.6	13.4	8.9	12.0	7.0	7.3	6.5	6.9	16.6	12.8	0.0	2.0
97 – 7	9.1	24.7	9.3	16.7	8.9	3.8	5.4	4.6	6.8	10.7	0.0	0.4
97 – 6	11.6	18.2	11.1	16.8	9.1	3.5	6.4	4.0	5.6	13.7	0.0	0.5
97 – 5	5.7	7.9	11.1	16.9	8.4	4.8	9.7	6.8	11.6	17.2	0.0	1.0
97 – 4 – 3	4.7	5.4	9.5	13.6	7.2	8.5	2.2	7.1	15.3	26.4	0.0	2.3
97 – 2	4.4	4.9	8.9	12.1	6.4	10.9	7.9	6.3	13.4	24.8	0.0	4.3
172	8.6	19.6	8.3	15.3	8.3	2.9	7.3	6.2	9.2	14.3	0.0	0.2
168 – 3	13.0	14.5	10.3	15.9	9.0	5.5	4.0	3.9	6.8	17.0	0.0	0.1
168 – 2	8.5	10.3	12.1	19.6	9.4	5.8	6.2	6.9	9.3	11.9	0.0	0.4
188 – 4	6.7	7.7	8.4	12.0	5.3	19.7	3.3	5.4	11.5	19.9	0.0	3.1
188 – 3	9.6	12.4	13.3	20.8	11.5	1.4	11.8	5.6	4.7	8.9	0.0	0.3
214 int	7.3	8.5	10.9	12.9	8.2	11.2	4.1	6.5	18.4	12.2	0.0	2.5
214 – 6 – 5	5.5	6.4	9.6	11.4	7.2	11.6	5.0	5.7	17.6	20.0	0.0	3.5
214 – 4 – 3	7.4	6.9	14.4	19.0	10.7	12.2	3.6	7.1	11.7	7.1	0.0	3.8
14 – 6 – 5 – 4	7.4	10.3	12.5	19.1	10.3	5.9	5.3	7.5	13.6	8.1	0.0	0.8
14 – 7 – 5 – 4	8.8	10.8	15.0	22.9	11.3	4.4	5.5	7.1	7.6	6.7	0.0	0.5
14 – 3	16.0	15.5	18.6	23.7	13.7	1.5	0.1	2.4	4.9	3.6	0.0	0.6
108 – 4	12.4	15.7	13.4	14.9	9.4	5.3	5.2	5.4	10.3	8.0	0.0	0.3
108 – 3	14.9	16.5	14.6	21.0	11.6	4.2	1.1	1.6	3.4	11.2	0.0	0.2

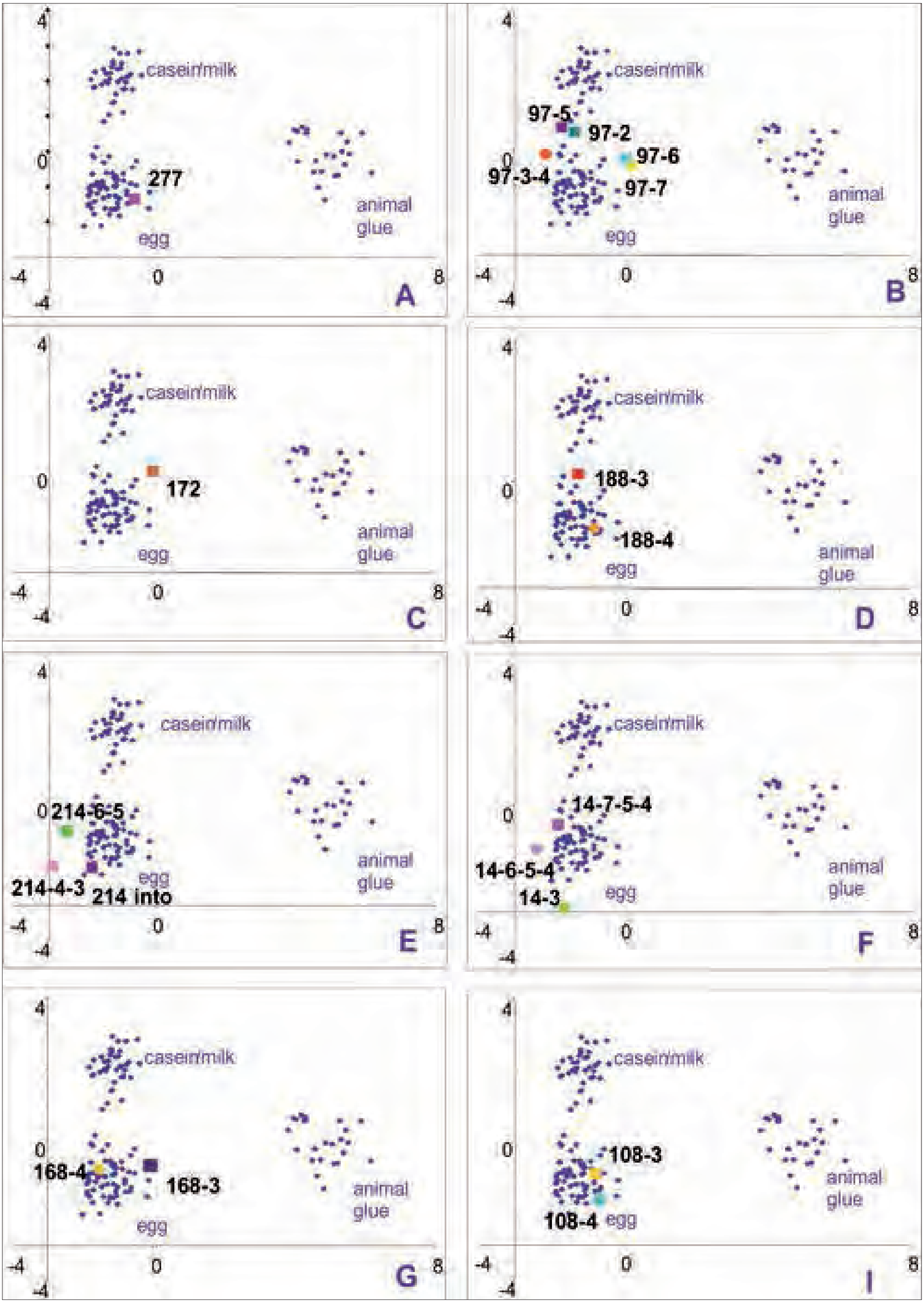


Fig. 4. PCA score plot of samples A) ID 277; B) ID 97; C) ID 172a; D) ID 188; E) ID 214; F) ID 14; G) ID 168; H) ID 108

content is higher than in sample 108. Sample 14-7-5–4 shows also a glycoside profile with all sugars but galacturonic acid.

- Samples from Eastern Buddha presenting a saccharide content higher than the quantitation limit correspond to the arricio (277) and to pigmented layers (188, 214). In particular:
- Sample 188-4 presents all the sugars and 5 peaks of fructose. The main sources of fructose are fruit, vegetable and honey.
- Sample 188-3 presents xylose, arabinose, glucose and galactose that are also present in higher amounts in sub-sample 188-4 suggesting a contamination from this layer.
- Sub-sample 214-int, corresponding to a restoration layer and 214-6-5 present a similar profile (though xylose relative amounts are very different). A penetration of the restoration material can be suggested by the data.
- The presence of all sugars in sample 277 suggests the use of a mixture of saccharide materials.

On the basis of the results obtained from the analysis of the polysaccharide, lipid and proteinaceous fractions it is possible to draw some conclusions on the sample and sub-sample compositions. In table 7 the organic materials identified in each sub-sample are reported.

On these bases it is possible to draw the conclusions summarised in table 8.

Interpretation and conclusions

The discussion of the painting technique is quite complex, and requires the support of conservators, to better understand the aesthetical effect of each paint layer, and their originality. Moreover, it can be assumed from the analysed materials that partly the binders of overpaintings have penetrated the lower layers, resulting in the presence of several materials inside a single layer. It is necessary to analyse more samples to assure the results, but it is possible to draw some conclusions as preliminary interpretation:

The *arriccio,* which is the undercoat underneath the finish clay coat, contains a saccharide material and small amounts of egg (sample ID 277). The addition of saccharide materials are known to have been used in Asian clay plasters to increase the viscosity and adhesiveness of (straw) mud modelling pastes: In China, water from cooking sticky rice (i.e. starch) or an extract of the *luo han guo* fruit have been used.

In the surface of the clay, egg has been found. Sample ID 168 contains egg, ID 14 egg white, ID 172a and GBL 2400+ a mixture of egg white and animal glue. It can be assumed that these materials have been used as isolation of the clay surface before applying the paint layers. In one sample (ID 97) milk was found in the surface of the clay. This can be interpreted as the traces of a lost priming layer although this can not be ascertained yet. All examined samples come from the Western Buddha. For a further interpretation more analyses are required.

Table 6 Glycoside profiles of ID 277, 97, 172a, 168, 188, 214, 14, and 108

sample	sugars									Saccharide content [µg]
	xylose	arabinose	ramnose	fucose	galacturonic acid	glucuroni acid	glucose	mannose	galactose	
277	44.5	22.9	2.3	1.0	0.0	1.4	17.6	3.1	7.0	129.0
97 – 7										-
97 – 6										-
97 – 5										-
97 – 4 – 3										-
97 – 2	y	y	-	-	-	-	-	-	y	-
172a	44.1	8.8	2.3	1.7	6.7	2.2	0.0	20.0	14.3	1.8
168 – 3										-
168 – 2	y	y	-	-	-	-	-	-	y	-
188 – 4	7.8	13.6	0.5	0.8	0.6	2.1	50.8	4.0	19.8	3.6
188 – 3	y	y					y		y	-
214 int	10.9	3.3	1.3	1.0	0.0	0.6	46.4	13.2	23.3	2.8
214 – 6 – 5	7.3	4.9	1.9	1.4	0.7	1.3	34.2	15.5	32.8	5.1
214 – 4 – 3	47.2	12.1	2.0	1.1	0.0	0.0	0.0	0.0	37.5	0.6
14 – 6 – 5 – 4	y	y	y	y	-	y	y	y	y	-
14 – 7 – 5 – 4										-
14 – 3										-
108 – 4	8.3	13.5	1.6	2.0	1.1	3.3	25.8	10.5	34.1	7.9
108 – 3	11.7	12.8	0.8	1.8	0.5	0.9	31.1	7.1	33.3	1.7

Table 7 Results of analyses of sub-samples

sub-sample	proteinaceous fraction	saccharide fraction	layer composition
277	egg	mixture of saccharide materials	saccharide materials (main component) and egg (whole-yolk)
97 – 7	egg	-	egg (whole-yolk)
97 – 6	egg	-	egg (whole-yolk)
97 – 5	milk	-	milk
97 – 3 – 4	egg	-	egg (whole-yolk)
97 – 2	milk	milk contribution	milk
172	egg	mixture of saccharide materials	saccharide materials (main component) and egg (whole-yolk)
168 – 3	egg	-	egg (whole-yolk)
168 – 2	egg	egg sugars	egg (whole-yolk)
188 – 4	egg	mixture of saccharide materials fructose detected	saccharide materials (including fruit juice of honey) and egg (whole-yolk)
188 – 3	milk	possible contamination from other layers	milk
214 int	egg	mixture of saccharide materials	saccharide materials and egg (whole-yolk)
214 – 6 – 5	egg	mixture of saccharide materials	saccharide materials and egg (whole-yolk)
214 – 4 – 3	egg	possible contamination from other layers	unidentified saccharide material and egg (whole-yolk)
14 – 7 – 5 – 4	egg	mixture of saccharide materials, possible contamination from the superficial layer	saccharide materials with egg white
14 – 6 – 5 – 4	egg	-	egg white
14 – 3	egg	-	egg white
108 – 4	egg	mixture of saccharide materials	saccharide materials (main component) and egg (whole-yolk)
108 – 3	egg	mixture of saccharide materials	saccharide materials (main component) and egg (whole-yolk)

Table 8 Sample composition, layer by layer

provenance	sample ID	layer	(built-up) description	organic material characterised
Eastern Buddha	277	-	arriccio (preparation layer underneath the plaster)	saccharide binder, with little egg (whole or yolk)
Western Buddha	97	7	red hard layer	egg
		6	grey hard layer	egg
		5	black powdery layer	milk
		4	orange powdery layer	egg
		3	pink powdery layer	egg
		2	plaster	milk
		1	arriccio	n.a.
Western Buddha	172	4	brownish layer, semi-transparent	saccharide binder and egg
		3	thin red layer (few residues)	n.a.
		2	plaster	n.a.
		1	arriccio	n.a.
Western Buddha	168	4	residues of pigmented layer	n.a.
		3	transparent preparation layer	egg (whole-yolk)
		2	plaster	egg
		1	arriccio	n.a.
Eastern Buddha	188	5	white layer (few residues)	n.a.
		4	yellow ochre layer	saccharide materials (including fruit juice or honey) and egg
		3	white gypsum layer	milk
		2	plaster	n.a.
		1	arriccio	n.a.
Eastern Buddha	214	7	brown material (restoration)	saccharide binder and egg
		6	blue layer	saccharide binder and egg
		5	black layer	saccharide binder and egg
		4	blue layer	egg
		3	black layer	egg
		2	plaster	n.a.
		1	arriccio	n.a.
Western Buddha	14	8	Indian restoration (only one point)	n.a.
		7	grey layer	saccharide material and egg
		6	red layer (only one point)	egg
		5	orange layer	egg
		4	white layer	egg
		3	transparent layer	egg
		2	plaster	white
		1	arriccio	n.a.
Western Buddha	108	5	Indian restoration residues	n.a.
		4	glossy brown layer	saccharide material and egg
		3	glossy brown layer	saccharide material and egg
		2	plaster	n.a.
		1	arriccio	n.a.

In samples from groups 1 and 2, i.e. the red parts of the *sangati*, all paint layers contain mainly egg. Milk was found in the orange layer of sample GBL 246 and the black layer of discoloured orange in sample ID 97. The use of milk or casein for this layer could also explain the massive discoloration of the minium as an aqueous binder would provide less protection for the pigment than an egg binder. In the preliminary interpretation we assume that the pink layer (= first preserved paint layer) was bound with egg, the overpainting with minium with milk or casein and the last overpainting with the white lead containing layer and, on the Western Buddha, iron oxide red, with egg.

The clay suspension from the Indo-Afghan restoration always contains polysaccharides. Traces of beeswax might be a contamination.

Blue layers (group 5) could not be interpreted satisfyingly yet. While in a sample from the Western Buddha (ID 214) both blue layers and their black underpaintings contain egg and polysaccharides, a sample from the Eastern Buddha (KBL 497) contains milk or casein. It is planned to do further analyses on other blue samples.

The brown overpainting layers (groups 3 and 4) provide a similar problem: while two samples (GBL 2400+ (group 3) and ID 172a (group 4) contain casein, two others (ID 108 (group 3) and ID 172b (group 4) contain egg and polysaccharides. While the polysaccharides may be interpreted as binder of the Indo-Afghan clay suspension, casein or egg should be the main components of the brown layers. As samples ID 172a and b in fact are two halves of the same fragment, they should contain the same binders. While on ID 172a the brown layers have been sampled, on ID 172b only a thin glossy layer on top of the brown was analysed.

This could mean that casein is the binder of the brown layer which possesses a thin coating containing egg and traces of the Indo-Afghan clay containing polysaccharides.

The identification of the saccharide materials cannot be performed since in all cases the sugar composition seems due to unknown saccharide binders. The use of honey or a fruit juice could be proven in one of the samples.

The white priming layer of sample ID 188 contains egg. The yellow ochre paint layer contains egg and polysaccharides, the latter may be a contamination of restoration materials of the Indo-Afghan intervention. ID 188 belongs to the samples of group 6 which cannot be assigned to the Buddha statues without doubt and thus could also show a different painting technique. The use of egg for the pigment layer however is comparable to paint layers which can be definitely assigned to the statues.

The interpretation of the analyses allows drawing a first, tentative conclusion on the painting technique: The undercoat of mud straw contains a saccharide material which probably was added to improve the plastic properties of the layer. The surface of the finished clay modelling was impregnated with a binding medium to obtain a dust-free support with homogenous absorption properties. Egg or egg white have been found in samples of the Western Buddha, in two samples a mixture of egg white and animal and in one sample milk. Further investigations are necessary, also including samples of the Eastern Buddha. Paint layers contain mainly egg, with exemption of the minium layer for which milk or casein seems to have been used. Brown and blue layer require more analyses to assure if egg with saccharides or casein/milk have to be regarded as the main component.

The clay suspension of the Indo-Afghan restoration contains an addition of saccharides which probably should increase the adhesion and the cohesion of the layer.

The analysed samples do not prove general differences between the painting technique of the Eastern and the Western Buddha, but more analyses are necessary to assure this fact.

Notes

1 Bauer-Bornemann et al. 2003, p. 3.
2 Burnes 1834, pp. 185-186.
3 Ritter 1838, p. 48. '*Der Körper ist nicht nackend, sondern mit einer Art Mantel überkleidet, der alle Theile bedeckt, aber aus einem aufgelegten Gypsstucco besteht. Noch bemerkt man viel eingetriebene Holzpflöcke, die unstreitig dazu dienten, diesem Stucco Halt zu geben.*'
4 Eyre 1843, p. 364, in Godard et al. 1928, p. 88.
5 Maitland, P. J.: *Additional note on Bāmiyān*, in Talbot/Simpson 1886, p. 348, cited in: Godard et al. 1928, p. 93.
6 '[...] *il parvint ainsi jusqu'à l'amorce du revêtement de briques recouvrant la pièce de bois qui formait l'ossature de l'avant-bras et supportait la main levée en abahyapāni-mudra (geste qui rassure) (fig. 23). M. Carl découvrit, chemin faisant, des fragments de revêtement, composés d'un melange de terre et de paille hacheé recouvert d'une mince pellicule de mortier de chaux, qui garnissait le grossier épannelage de la statue; nous avouns recueilli des fragments simulant les plis du manteau monastique encore munis de leur armature de cordes et de piquets et revêtus de la couche de painture rouge qui couvrait primitivement le manteau tout entier.*' Hackin/Carl 1933, p. 15. Fig. 23 shows Carl standing on the Western Buddha's right forearm; fig. 24 is a detail of the folds of the *sangati* (black and white).
7 Burnes 1834, pp. 185–186.
8 Tarzi 1997, vol. 2. p. 117.
9 GBL 852: imprint of a peg; GBL 1445: imprint of a rope.
10 For example pegs no. GBL 826, 1367, 1733, 1734, 1737, 1825, 1911, 1923, 1937, 1939, 1950, 2009 and 2119.
11 Sengupta 1984, p. 41.
12 For a detailed description of the ropes see: *Materials made of plant fibres: ropes and textile fragment* in this publication.
13 For example fragment GBL 1651.
14 Few round timber were found as well, e. g. GBL 448l, but it is not clear if they belong to the Buddha statue or if they were parts of its original construction.
15 So far, there was no possibility to measure the depth exactly, because this can only be done on a scaffold.
16 Burnes 1834, pp. 185–186.
17 The *Gypsstucco* (gypsum stucco) mentioned by Ritter 1838 can be regarded as a misinterpretation of the word *plaster* (as plaster of Paris = in German Gips) used by Burnes to whom he explicitly refers.
18 Hackin/Carl 1933, p. 15.
19 Hackin 1939 (German translation of the French book of 1934), p. 38.
20 Gettens 1937–38, p. 168.
21 Sengupta 1984, description on p. 41.
22 Visible for example on the fragments GBL 1025-27, GBL 1070, GBL 1088.
23 The preparation of rock surfaces with animal dung is regarded as a classical method in Indian wall paintings (personal information by Y. Taniguchi).
24 Analysis by XRD by V. Tucic in Nov. 2004, samples GBF 002 (on stone, sample 2) and KBL 073 (on clay, sample 3)) interpreted the results as clay–lime slurry (KBL 073) with a calcite content of 22 m% and about 1 m% of hematite as colouring material. GBF 002 contained 14 m% of gypsum and 8 m% of calcite and this is a gypsum clay or gypsum-lime-clay mixture. A content of 6 m% weddelite was detected. Quartz contents vary between 48-52 m%. – Analysis with PLM by C. Blänsdorf, peg from Western Buddha, no. a, found on July 7, 2007: Iron oxides, calcite, clay minerals, some gypsum and quartz, 1 particle lead oxide. The rather large calcite particles indicate the use ground limestone. Light pink areas contain more calcite than darker ones.
25 Visible for example on fragments GBL 1088 and 1205, both fold ridges of the Western Buddha.
26 In China, for example, clay mortars are traditionally spread on the walls with the hands. Wooden boards only serve to scoop up larger quantities from a bowl.
27 Leather piece in GBL 2026. Textile fragment: without number.
28 GBL 2090.
29 Visible on samples ID 28 and ID 53.
30 GBL 684.
31 Eastern Buddha: KBL 200, below the right arm: reddish undercoat, fine clay layer, greyish coarse layer; Western Buddha: GBL 1288–1292: undercoat, two finish coats.
32 KBL 285 from the Eastern Buddha could be dated by ^{14}C- AMS to the same time as the other clay fragments.
33 The paint layer on these parts is yellowish ochre.
34 National Research Institute for Cultural Properties 2006, p. 121–124.
35 Sengupta 1989, p. 205
36 As they did not have a scaffold at that time, they probably could not reach the statues at all.
37 White filling with brown coating from the Western Buddha, sample 2 of July 2006. Analysis with PLM by C. Blaensdorf: yellowish white matrix calcium sulphate dihydrate and semi-hydrate, some calcite; white clusters: fibrous calcium sulphate semi-hydrate. Transparent particles: quartz (sand). – Sample ID 224, Eastern Buddha, analysis with XRD: anhydrite, dihydrate, amorphous substances, see: Mineralogical investigations on loam plaster fragments of the destroyed Buddha statues at Bāmiyān, Afghanistan, in this publication.
38 Sample ID 84, Western Buddha, analysis with XRD, see *Mineralogical investigations on loam plaster fragments of the destroyed Buddha statues at Bāmiyān, Afghanistan* , in this publication.
39 Western Buddha, sample ID 84.
40 Information by Mr. Ajan who worked in the restoration team. Fragment archive of E. Melzl, GBL 135.
41 Analysis by XRD, V. Tucic, September 2004 on sample GBL 001.
42 KBL 497, analysis with PLM, C. Blänsdorf, and XRD, V. Tucic. KBL 1524, 1, PLM by C. Blänsdorf.
43 Burnes says that the Western Buddha '*is mutilated; both legs having been fractured by cannon; and the countenance above the mouth is destroyed*. […] *The hands* […] *were both broken*'. Burnes 1834, p. 185. - Vincent Eyre 1843 describes the face of the Western Buddha as '*entirely destroyed*'. He also reports that the Eastern Buddha '*is greatly mutilated by cannon shot for which act of religious zeal credit is given to Nadir Shah*'. Godard explains the missing faces as a result of systematic mutilation. Godard et al. 1928, p. 11 (Godard) and p. 88 (Eyre). – Hackin 1939, p. 26, referring to the Eastern Buddha: '*Das Gesicht ist verstümmelt, die Hände fehlen ganz*' (englisch: The face is mutilated, the hands are missing entirely); p. 38,

regarding the Western Buddha: '*Das Gesicht ist eigenartig verstümmelt, vornehmlich Stirn, Augen, Wange, Nase*' (The face is mutilated in a strange way, especially the forehead, the eyes, the cheek, the nose).

44 Sengupta 1989, p. 205: '[…] *various theories were propounded as both of them have vertical cut from the forehead to the lower lip. Close observation, during the execution of restorations, revealed that the faces were modelled with wooden frames. A chase was cut in the depression of the rock behind the lower lip of each face, to receive the basal wooden beam on which were erected vertical posts for support of the horizontal stakes tied to them according to the required shape of the face. The other end of the horizontal stakes was made to rest on the rock for which rows of grooves in the vertical face are still visible. Pieces of charcoal and charred wood of the wooden frame of the face were recovered from the crevices where one could not reach without an elaborate scaffolding as was erected for the restoration work*.'

45 Dr. Dietger Grosser, Ludwig-Maximilians Universität München. The report was not available.

46 Analysis by Dr. Hans Georg Richter.

47 Prof. Dr. Tillich and Prof. Dr. D. Podlech, Ludwig-Maximilians Universität München, faculty of biology

48 Fragments GBL a, 506, 507, 612, 664, 708, 1139, 1368, 1447, 1773, 1832, 2458.

49 Z-twist, S-ply: GBL 662, 1 rope of GBL 708.

50 Information by Nasir Modabbir. According to Kabir, the plant can be found near the village of Schahidan in direction to Band-I-Amir. Fragment catalogue, GBL 283-288.

51 Analysis by Prof. Dr. Hans-Jürgen Tillich, faculty of biology, Ludwig-Maximilians University, Systematic Botany and Mycology, Munich.

52 Information by Prof. Tillich, also see: Dieterle 1973, p. 13.

53 Dieterle 1973, p.60.

54 Information by Prof. Tillich.

55 Analysis with transmitted light microscopy by C. Blänsdorf.

56 Analysis by Prof. Dr. Hans-Jürgen Tillich, faculty of biology, Ludwig-Maximilians University, Systematic Botany and Mycology, Munich, in December 2006.

57 According to photographs representatives of the species *Capra hircus*, *Ovis aries*, *Bos taurus*, and *Equus asinus.*

58 Wriggins 1966.

59 A comprehensive compilation of dating attempts since the early 20th century can be found in: Akira Miyaji, "The art-historical study on *Bāmiyān* and the radiocarbon dating", in: National Research Institute for Cultural Properties Japan 2006, pp. 133. Although it focuses on the murals, information on the sculptures can be found here as well.

60 National Research Institute for Cultural Properties 2006, p. 133 with reference to: Hackin, Joseph: *L'Œuvre de la Délégation Archéologique Francaise en Afghanistan (1922-1933)*, Tokyo: Maison Franco-Japonaise, p. 19–57 : '*Hackin linked the 'monastery built by a former king' mentioned in the Da Tang Xiyu Ji, to the Kushan King Kanishka. He was of the opinion that this monastery might have been built near the East Giant Buddha and concluded that the date for the beginning of the Bamiyan sites was around the second century A. D. He dated the East Giant Buddha which shows the influence of the Gandharan Buddhas in its weavy hair and the expression of the drapery to around the second and third century. In contrast, the West Giant Buddha, which has schematic, formalized drapery, he dated to around the third to fourth century, and he suggested that it might have influenced the Buddha images of Mathura in the Gupta period*.'

61 National Research Institute for Cultural Properties 2006, p. 134: Itsuji Yoshikawa from the University of Tokyo made researches about Bamiyan in 1939.

62 '*Der Typ der römischen Toga, wie wir sie aus Bildnissen der Kaiserzeit kennen, ist hier in dem Mantel oder 'sang-hati' des* [kleinen] *Buddha wiederzuerkennen. Nach dem noch streng klassischen Stil der Kleidung zu urteilen, könnte diese Statue etwa im 2. oder 3. Jh. entstanden sein* […] *oder daß wir es mit einem Beispiel für das Überleben oder Wiederaufleben des frühen Gandhara-Stils zu tun haben, wie wir es oft zwischen dem 4. und 8. Jh. in östlicher gelegenen Fundstellen Zentralasiens beobachten.*' - '*Die Statue selbst* [Großer Buddha] *ist stilistisch eine gigantische Vergrösserung der typisch indischen Buddha-Figuren aus der Gupta-Periode-Mathuras (ca. 320–600)* […] *eine Datierung zwischen dem 5. und 7. Jh. scheint für den gesamten Komplex des 53 Meter hohen Buddha angemessen.*'

63 National Research Institute for Cultural Properties 2006, p. 136 with reference to: Tarzi 1977.

64 National Research Institute for Cultural Properties 2006, p. 137 with reference to: Kuwayama 1987.

65 National Research Institute for Cultural Properties 2006, p. 137 with reference to: Klimburg-Salter 1989.

66 National Research Institute for Cultural Properties 2006, S. 138 with reference to: Tanabe 2004.

67 National Research Institute for Cultural Properties 2006. 43 samples of chaff and straw from the lower clay layer and one splinter of an anchoring beam for clay sculptures were taken for analysis. The samples come from the caves at Bamiyan, cave Nr. 43 and 44 in Kakrak (2 samples), cave no. 2, 4, 5 and 6 in Fuladi (6 samples), Da'uti caves (2 samples).

68 National Research Institute for Cultural Properties Japan 2006, p. 121 and p. 147.

69 Beal 1884, p. 50.

70 Barbier de Meynard 1861, p. 80: '*Cette ville est petite; mais elle est le cheflieu d´un territoire étendu. Dix jours de marche la séparent de Balkh, et huit de Ghaznah. On y voit un édifice dont le sommet est d´une élévation prodigieuse; il est soutenu par des piliers gigantesques et couvert de peintures représentant tous les oiseaux créés par Dieu. Dans l´intérieur sont deux idoles immenses creusées dans le roc et allant du pied de la montagne au sommet. L´une est appelée l´idole rouge, et l´autre, l´idole blanche. On ne peut rien voir de comparable à ces statues dans le monde entier*.'
Yakut or Yaqut ibn 'Abdallah ar-Rumi or Yakut al Hamawi, 1179–1229, was born in Greece and became a slave of an Arab merchant. The surname ar-rumi (the Roman) refers to his Greek parentage, the name al-Hamawi to his later hometown Hamah. From about 1212 to 1222 he travelled in Persia, Syria, Egypt, and Afghanistan. In 1221, he fled from the invasion of Genghis Khan's troops, settled in Mosul and started to write down a famous and extensive geographical dictionary. He spent his last two years in Aleppo. His dictionary *Mu'jam ul-Bulddn* includes all the places mentioned in Arab literature, listed in alphabetic order, reporting their geographical position, history, government, important monuments, and renowned citizens. A translation of the entries concerning the ancient Persian Empire

was published by Charles Barbier de Meynard in 1861.

71 Burnes reports an anecdote from the 'History of Timourlane by Sherif o deen' according to which the Buddha statues were so tall that no archer could strike their head (BURNES 1834, p. 188). This indicates that as early as in the 14th century (Tamerlane lived from 1336 to 1405) there were no edifices in front of the statues (anymore), because it is difficult to imagine that the archers aimed at their heads through an existing building, even if it was a half-open pavilion-like construction.

72 Sir Francis Wilford (1750 or 1760–1822) on the accounts of Me'yan Asod Shah, in: WILFORD 1801, pp. 464–466. If Me'yan Asod Shah really visited Bāmiyān ten or twelve times, he may have made these travels in the last two decades of the 18th century.

73 Another possibility to explain Me'yan Asod Shah's reference to 'embroidery' could be that he took the ridges of the folds and the partly exposed anchoring holes in the stone surfaces for remnants of decorations.

74 BURNES 1834, pp. 185–186. The description on p. 185 mainly deals with the Western Buddha: '*The figure is covered by a mantle, which hangs over it in all parts, and has been formed of a kind of plaster; the image having been studded with wooden pins in various places, to assist in fixing it*'. About the Eastern Buddha he only says that it is '*more perfect*' […] "*and has been dressed in the same way'*.

75 There are, for example, wrong details of the drapery, and a reduction of the real distance between the sculptures which, however, can be explained as an artistic trick to get both statues into one picture and still show them as very big.

76 Burnes reduced the design, just giving an idea of the paintings, but the text states clearly that he had recognised the figurative decoration: '*The niches of both have been at one time plastered, and ornamented with paintings of human figures, which have now disappeared from all parts but that immediately over the heads of the idols. Here the colours are vivid, and the paintings as distinct, as in the Egyptian tombs.'* BURNES 1834, p. 186.

77 Maitland, P. J.: *Additional note on Bāmiyān*, in TALBOT/SIMPSON 1886, p. 348, cited in GODARD ET AL. 1928, p. 93.

78 '*nous avons recueilli des fragments simulant les plis du manteau monastique encore munis de leur armature de cordes et de piquets et revêtus de la couche de peinture rouge qui couverait primitivement le manteau tout entier.*' HACKIN/CARL 1933, p. 15. Fig. 23 shows J. Carl standing on the Western Buddha's right forearm; fig. 24 is a detail of the folds of the *sangati* (black and white).

79 HACKIN 1939, p. 26.

80 SENGUPTA 1984, p. 41.

81 For example the names are mentioned in the texts by two Iranian travellers, Mohamad b. Ahmad al Biruni (died 1048) and Khwaja Abdallah Ansari (died 1089). MELZL/PETZET 2007, p. 69.

82 The undercoat of the Eastern Buddha is slightly more greyish than the one of the Western Buddha which appears more yellowish ochre.

83 MOMII/SEKI 2006, p. 94: A yellowish transparent organic layer was observed on the murals.

84 White and brownish pink spots: for example on samples ID 38, 53and 74; ochre spots on ID 46.

85 Consolidant on the surface: for example sample ID 118, 135 or 54 (partially). Fibres sticking to the consolidant: ID 77.

86 Eastern Buddha: No surface: 200, 278, completion: ID 224. No or only traces of paint layer: ID 177, 182 (traces of red), 191 (traces of red), 225, 240, 258. Samples ID 177. Western Buddha: No surface: Samples ID 27, 44, 88, 151, 160; no paint layer: 1, 86 (yellow clay layer); not fitting into the group scheme: 71 (covered by clay slurry), 82 (traces of red); 136 (traces of white?), 174 (red); 63; sample ID 84, 159 filling materials from 1969-78.

87 Fragments blackened by soot: Western Buddha, group 1: ID 81, group 2: ID 63, 122, 131, 136; group 5, ID 103; soot with brown coating: ID 122 and 131.

88 Sample ID 239 and 241.

89 Sample present in Munich: Sample ID 180.

90 PLM: Catharina Blänsdorf, Maximilian Knidlberger, Stephanie Pfeffer, Technische Universität München, Chair of Restoration.

91 Visible for example on samples ID 47, 58, 59, 102 and 112.

92 RAPP 2009, p.2: Analysis of sample ID 166.

93 XRD of fragments ID 165 and ID 166.

94 RIEDERER 1977, p. 369.

95 ZOU ET AL. 1997, pp. 362–368.

96 GETTENS 1937/38, p. 189.

97 RAPP 2009, p.2.

98 Micro XRF with vacuum: Sonngard Hartmann, Roman Germanic Central Museum, Mainz.

99 TANIGUCHI/OTAKE 2008, p. 398, description of the *Laternendecken* with oily bound paint layers.

100 TANIGUCHI/OTAKE 2008, pp. 397–404: oily layers, white: lead white; green: lead white, chrysocolla (?).

101 This result is reported only in: KOSSOLAPOV/KALININA, 2006, p. 90.

102 Some analyses of sculptures from Dunhuang have been performed, but the results are available only in Chinese.

103 BOLLATI 2008, p. 196.

104 For Penjikent and Afrasiab see: KOSSOLAPOV/KALININA 2006, p. 90. Analyses by Kossolapov, A./Viazmenskia, L, in: KOSSOLAPOV/MARSHAK 1999; ABDURAZAKOV/KAMBAROV 1975. Translation and summary of results by Anna Rommel, Technische Universität München, Chair of Restoration, 2008.

105 KOSSOLAPOV/KALININA 2006, p. 90.

106 RIEDERER 1977, vol. 4, p. 353–423, identification of 17 different pigments in murals from Xinjiang ('Eastern Turkistan'), namely Kizil and Kumtura, survey in table on p. 386.

107 The antique oasis of Miran is located on the Southern Route of the Silk Road between Qarqan and Dunhuang in the Autonomous Region of Xinjiang. The paintings evidently show a strong 'Western' influence, characterised by Kakoulli as 'Greco-Buddhism with Asiatic influences'. KAKOULLI 2006, p. 82.

108 WANG/FU 2006, p. 114: compilation of pigment analyses of wall paintings from *c.* 430 to 780.

109 The wall paintings in the Tiantishan grottoes in Liangzhou in Gansu Province date from the Northern Wei to the Ming Dynasty. Examination of paint layers from the Northern Liang (397–439) to the Tang Dynasty (618–906): ZHOU ET AL. 1997, pp. 362–368.

110 KOSSOLAPOV/KALININA 2006, p. 90.

111 SHARMA 2006, p. 102.

112 Interpretation in: GUNASINGHE 1957.

113 KAKOULLI 2006, p. 82.

114 GUNASINGHE 1957, p. 15. Though he writes about quicklime, he

also refers to binders. Smoothing or burnishing of the surface is also mentioned.

115 Gettens 1937/1938, pp. 186–193. – Momii/Seki 2006, p. 94.

116 Kumtura and Kizil: Riederer 1977. – Afrasiab: Abdurazakov/Kambarov 1975. Translation and summary of results by Anna Rommel, Technische Universität München, Chair of Restoration, 2008.

117 Miran: Kakoulli 2006, p. 82. – Mogao: Wang/Fu 2006, p. 117.

118 Underpaintings: Gunasinghe 1957, pp. 57–60. Ajanta is located in the north-eastern part of the Indian state of Maharashtra, 100 km north of the city of Aurangabad. – Black and red contour lines: Sharma 2006, p. 102.

119 Analyses for white: Afrasiab: gypsum, kaolin; Penjikent: calcite, gypsum; Sharistan: gypsum; Kucha: gypsum, calcite (Kossolapov/Kalinina 2006). Kumtura, Kizil: Gypsum (dihydrate), anhydrite (Riederer 1977). Tiantishan: gypsum, anhydrite, chalk and kaolin (Zhou et al. 1997), Mogao: chalk, kaolin, talc, gypsum mica (Wang/Fu. 2006), Ajanta: lime/gypsum/kaolin (Sharma 2006), Indian manuscripts (Gunasinghe 1957, p. 43).

120 Lead white was found in the Bāmiyān caves, Afrasiab, Kucha, Kizil and Kumtura, and the Mogao grottoes.

121 Zhou et al. 1997, pp. 362–368.

122 Orange and Red: Nisa, bright red: cinnabar, brownish red: red ochre, also mixed with kaolin for pale pink (Bollati). Afrasiab: red ochre; vermillion (Abdurazakov/Kambarov 1975). Penjikent, red: ochre, orange: red ochre; Sharistan, red: ochre; Kakrak, orange: minium; Kucha: vermilion, minium (Kossolapov/Kalinina 2006, p. 90). Kizil/Kumtura: minium, cinnabar, red ochre (Riederer 1977). Miran: iron oxides (?; Kakoulli 2006), Mogao: vermilion, red ochre, minium (Wang/Fu. 2006). Tiantishan: cinnabar, on Tang sculptures (?) also minium and cinnabar (Zhou et al. 1997); Ajanta: red ochre (Sharma 2006); *Vìsnudharmottara*: Gunasinghe 1957, p. 45.

123 Yellow: Nisa: yellow ochre (Bollati); Penjikent: litharge, orpiment; Afrasiab: orpiment; Sharistan: litharge; Kucha: orpiment (Kossolapov/Kalinina 2006, p. 90). Kumtura, Kizil: yellow ochre, orpiment (minimally used), massicot (Riederer 1977, p. 386). Miran: impure yellow and brown earths (Kakoulli 2006, p. 83). Mogao: realgar (Wang/Fu 2006). Tiantishan: very few yellow (Zhou et al. 1997). Ajanta: yellow ochres (Sharma 2006). Indian manuscripts: Gunasinghe 1957, p. 44 (*Vìsnudharmottara*, pp. 48–49).

124 Brown: Penjikent magnetite, red; Sharistan: ochre brown; Kakrak: minium + laureonite ochre (Kossolapov/Kalininia 2006, p. 90.

125 Blue: Nisa: Egyptian blue and ultramarine (Bollati). Afrasiab: ultramarine (Abdurazakov/Kambarov 1975; Kossolapov/Kalinina 2006, p. 90). Penjikent: ultramarine; Kakrak: ultramarine; Sharistan: ultramarine; Kucha: ultramarine (Kossolapov/Kalinina 2006, p. 90). Kumtura, Kizil: ultramarine, azurite, indigo (Riederer 1977, p. 386). Mogao: azurite, ultramarine (Wang et al. 2006). Tiantishan: azurite (Zhou et al. 1997). Ajanta: ultramarine (Sharma 2006). Indian manuscripts: Gunasinghe 1957, pp. 47–48 (description does not clearly indicate which pigments are mentioned in the *Vìsnudharmottara*).

126 Next to ultramarine in Bāmiyān caves: Momii / Seki 2006, p. 93–100.

127 Green: Nisa (Bollati 2006); Penjikent: no green; Sharistan: malachite, black: tenorite; Kakrak: paratacamite; Kucha: atacamite (Kossolapov/Kalininia 2006, p. 90). Kumtura and Kizil: chrysocolla (Riederer 1977). Miran: malachite (Kakoulli 2006). Mogao: malachite, verdigris (Wang/Fu 2006). Tiantishan: malachite, in Tang dynasty paint layers: atacamite and paratacamite (Zhou et al. 1997).

128 Ajanta: Sharma 2006.

129 Afrasiab/Penjikent: natural orpiment with indigo. Indian manuscripts: Gunasinghe 1957, pp. 45–46.

130 Black: Nisa: charcoal (Bollati); Kakrak: burnt bone; Kucha: burnt bone, gypsum, (Kossolapov/Kalinina 2006, p. 90). Kumtura, Kizil: soot, carbon black (Riederer 1977, p. 386). Miran: carbon black, from Chinese ink (Kakoulli 2006). Tiantishan: soot (Zhou et al. 1997). Ajanta: lamp black (Sharma 2006).

131 Nisa (Bollati 2006).

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133 Kumtura and Kizil: Riederer 1977, p. 385.

134 Gunasinghe 1957, pp. 53–54.

135 Zhou et al. 1997, pp. 364–365.

136 Taniguchi et al. 2007, pp. 181–188.

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