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Stucco decoration of Stupa 61 (Period II) (photo by L. M. Olivieri; courtesy ISMEO).

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Indice

An introduction: the Swat Valley and Florence

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Simona Pannuzi
MIBAC, Istituto Superiore per la Conservazione ed il Restauro

opposite page
Fig. 1
Amluk-dara (Swat), main Stupa. Photo By Luca M. Olivieri

It was Roberto Sabelli who conceived — exactly three years ago — the idea of publishing in the Florentine journal «Restauro Archeologico» the various contributions produced by the second ISCR project on Gandhara directed by Simona Pannuzi (the report on the first ISCR project was published in Pannuzi (ed.) 2015).

I liked the idea, also to acknowledge the contributions that teams from Florence (see also Di Giulio et al. 2018) and Florence University have been giving to the research of the Italian Archaeological Mission in the Swat valley. On the other side, the Mission, that had just contributed to the first issue of «Restauro Archeologico» (Olivieri 2014), have had already collaborated twenty years earlier with Luigi Marino and *Restauro Architettonico* (Olivieri 1996), and with the Cooperativa Archeologia of Florence.

Roberto Sabelli and his team (with his wife Rita Galanti, Anna Mannari, and other members of the Cooperativa) started working in Swat in 1992. In that year, all together, we carried out the topographical and archaeological survey of the area of the ancient city of Barikot (Olivieri 2003) and the first fieldwork on fortified structures and settlements of late ancient and early-Medieval Swat (c. 7th-10th century CE) (published in Olivieri 1996).

In the following three years, Roberto and his team continued working at a steady pace in Swat in a project directed by Domenico Faccenna (the unforgettable 'Direttore' of the Mission) focusing on the survey and documentation of the major Buddhist monuments (stupas and viharas/shrines) of the valley. These majestic structures, true architectural landmarks of the region, are all dated to the golden age of Gandharan art and architecture, i.e. the first four centuries of the current era (with the exception of Butkara I, whose Main Stupa was founded c. 250 BCE). The work was eventually published by Domenico Faccenna in a posthumous monography (Faccenna and Spagnesi 2014).

In 1993 literally Roberto 'fell in love' with the Main Stupa of one Buddhist sanctuary, 5 Km from Barikot: Amluk-dara. In following years we talked at lenght about that site and its problematics. Therefore, in 2012 — I was busy

Fig. 2
A view of the Swat valley (view from SW). In the centre the Barikot hill. Photo by Luca M. Olivieri.

in the excavation of Amluk-dara — I asked him to join me in Swat. A specific Memorandum of Understanding was draft and signed by our Mission and Roberto's Department at the University of Florence. On that year we studied together a possible conservation project for the site. Meanwhile he helped us to find the right methodological approach for the conservation of another stupa at Saidu Sharif I, and other sites in Swat, including the restoration of the missing volumes at the colossal rock-carving of the Buddha of Jahanabad (see Olivieri 2014). Eventually, the conservation project at Amluk-dara became the topic of a thesis entrusted by Roberto Sabelli to Gaia Di Pierro (Conservazione e valorizzazione dell'architettura devozionale del Buddismo nella Valle dello Swat (Pakistan): una proposta progettuale).

One issue particularly attracted both of us. The topic was production and processing of the so-called 'stucco' (calcite-based), and its association to

kanjur (an organogenic limestone) which are both extensively utilized in the late (post-3rd century AD) decoration of the Buddhist stupas in Swat, including Amluk-dara. The results of our discussion and studies should have been elaborated — on the basis of the results of the petrographic and chimical analysis — in a joint contribution for this issue of «Restauro Archeologico». Unfortunately our study was not completed in time.

We were both intrigued by the presence of these new materials in a region where schist is widely available, and where the latter was the only material utilized for sculpture and decoration especially in the first two centuries AD (when stucco was randomly used only for the finishing).

Kanjur, or *kankar*, is not local in Swat, and it is quarried and imported from the South-eastern regions of Taxila, Swabi, and Salt Range, closer to the wide alluvial plateau of the Indus basin. This soft stone, that can be easily cut and carved, totally replaced schist, and was largely utilized for archi-

tectural parts (e.g. false brackets, capitals, pillars and semi-columns, modillons, mouldings, friezes, etc.) notwithstanding its texture does not allow the carving to catch the accuracy and finesse standards that Gandharan artists were used to.
Actually, the *kanjur* elements were just the 'skeleton' of the decoration, as they were completed by heavy layers of stucco plasters, which were adding to them volumes, details, and polichromy.
Not only lime based stucco is the natural complement of *kanjur*, but it is also the best one for its cost-effectiveness. J. Marshall, Director General of the Archaeological Survey of India, described carefully the local production system of lime in contemporary British India.

> For making lime, stone or kankar is burned in kilns [and then] slaked (Marshall 1923: 48).

In fact, not only lime-based stucco can be obtained from *kanjur*, but, it might have been even the natural by-product of *kanjur* stone quarrying, cutting and carving. It was evident to Roberto and me — we were together in 2012 at the dig — that what Marshall had pointed out for contemporary lime production might have been tested for ancient times at Amluk-dara.
In 2012 I had managed to obtain from the Pakistani archaeological authorities the permit for the export of several samples for destructive analysis. Therefore, Roberto carried out on that year a series of dedicated samplings, especially at Amluk-dara. Othere samples were taken at Barikot and other sites. Once the samples were exported, they were handed-over to various Institutions, including the University of Florence, ISCR, and the University of Pisa. The reports on some of these analysis are presented in the following pages (Rosa, Theye, Pannuzi; Bonaduce, et al.).
(LMO)

While these analysis and studies were in progress, Roberto Sabelli (then the Chief Editor of *RA*) proposed the idea to publish together all the reports in a issue of *Restauro Archeologico*. The idea was immediately accepted with enthusiasm at our Institute (ISCR). ISCR had already started an important research on Gandharan scultures, focusing on polichromy and technology (both on schist sculpture and stucco architectonical decoration) (Pannuzi (ed.) 2015).
Gandharan art has been so far considered, with important exceptions of course, especially from the point of view of fine arts and religious studies. Its intrinsic elements of interest can be instead various and unexpected. They can also capture the appeal of the general public especially for their links and their implications, which are reflected in a crucial historical period (the first half of the 1st millennium) from the Mediterranean to East Asia.
To to all of us the possibility of sharing and exchanging ideas with Roberto's team appeared stimulating since the beginning. While we were carrying out together several meetings aimed at creating a suitable table of

contents for the volume, we were aware that we were potentially laying the path for a future development of the study. The field — up to a certain extent — is new, as demonstrated by the attention dedicated to our preliminary results in International Conferences and Workshops.
Roberto's idea is now real, but we hope that such collaboration will not end up with the publication of this issue. We hope that all the specialists involved in this research will have the possibility to keep on collaborating, and contributing on a new phase of the research: from the study of the materials, possibly to restoration projects.

(SP)

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Geological overwiew of Gandharan sites and petrographical analysis on Gandharan stucco and clay artefacts

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Sigea Lazio, Istituto Italiano di Paleontologia Umana

Thomas Theye
University of Stuttgart

Simona Pannuzi
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Sample BKG 1123 15C: architectonical polycrome decoration from Barikot, Pakistan: the arrow indicates the traces of red colour (photo E. Loliva © ISCR).

Abstract

The Gandharan archaeological sites are mostly located in the Indus Suture Zone and in the lower Swat. In a recent past, scholars observed the use of local different type of schists to build buildings and sacred artworks. In this new research we highlighted the use of limestone for stucco artefacts and architectural decorations. This limestone is not a local rock in Swat but its main, extended and closer outcrops are located in the mountains northwest of Islamabad. Indeed, through specific analyses carried out by our team, the compatibility of these outcrops with the rocks used for stucco artefacts and stucco decorations of buildings was observed. This stucco was made by a mixture of different kinds of local crushed rocks (i.e. schists and granites).

Keywords
Limestone, clay artefacts, stucco decorations, Gandharan artefacts, Swat geology, petrographic analysis.

Geological introduction

The formation of the Himalaya mountain range is due to the collision between Eurasia and the north-western side of the Indian Plate, moving from the south, since the Mesozoic Era and up to the present days[1]. The northern termination of the Indian Plate is defined by the Indus-Tsangpo suture zone[2]. This suture zone continues westwards to the Swat area of Pakistan, where it is called "Main Mantle Thrust" – henceforth MMT [3] –. The MMT separates the metamorphic Kohistan island arc sequence north, from the metamorphic continental basement of the Indian plate in the south. The Suture Zone itself consists of a mélange of klippen of various rock types (Fig.1). The Swat valley is located between the Indian Plate and the Kohistan island arc sequences and the Swat River flows in part inside the tectonic lineament called MMT, a zone intensively fractured and erodible[4].

In northern Pakistan the geological succession from south to the north is formed by the following rock formations (Fig. 3):

1. Indian plate continental crust – lower Swat

The lower Swat sequence occurring in the lowermost tectonic position (Manglaur Formation) consists of a high-grade metamorphic augen

[1] Yin, Harrison 2000; Ding et al. 2005: the scholars dated the start of collision to Cenozoic (65-60 My).

[2] Gansser 1980.

[3] Jan, Tahirkheli 1969; Tahirkheli 1979a and 1979b; Tahirkheli 1980.

[4] Faccenna et al. 1993, pp.257-161.

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Fig. 1
Map of Northern Pakistan: shaded area represents pre-Quaternary rock (from Dipietro et al. 1991, fig.1).

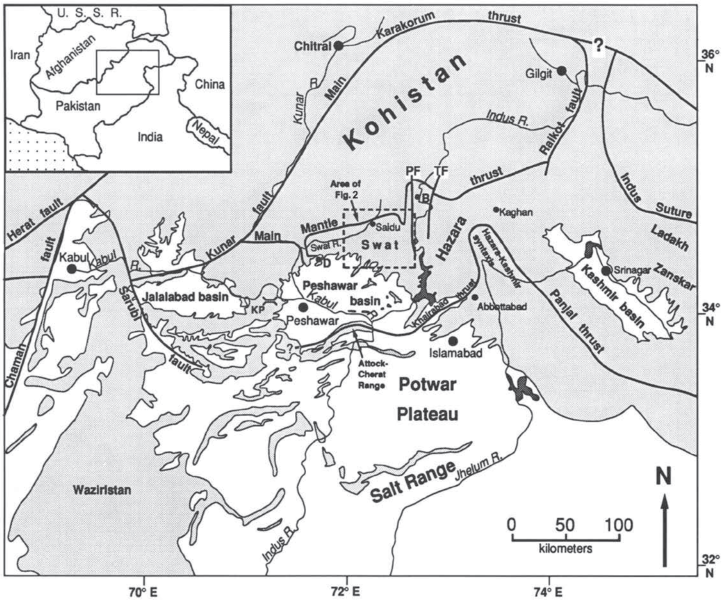
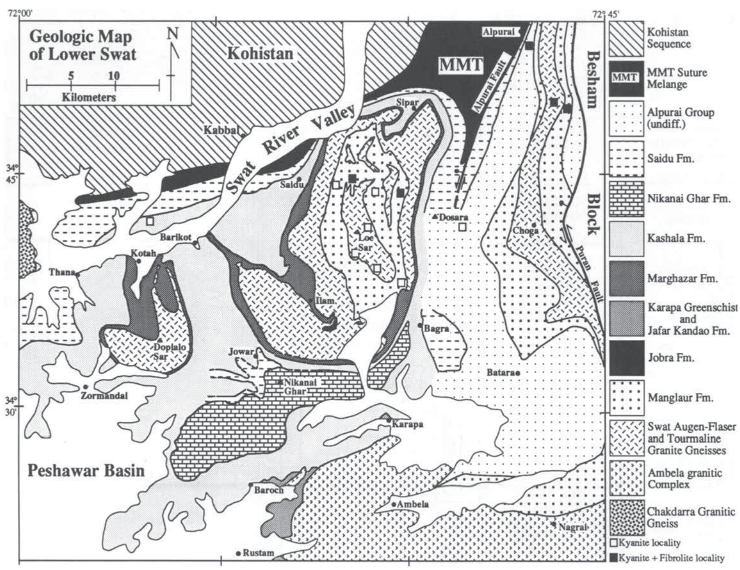


Fig. 2
Geological map of Lower Pakistan (from Dipietro et al. 1991, fig.3).



gneiss, of a tourmaline-bearing granite gneiss and associated metasediments. The metasediments include garnet-bearing micaschists, with parts of kyanite, quartzite, amphibolites, and tremolite marble[5]. This lower Swat sequence is overlaied by subcontinental, low to intermediate grade metamorphic rocks (Alpurai group, Saidu schists). Major rock types in the Alpurai groups are amphibolite schists, mica schists (partly with garnet), calcareous schists, graphitic phyllites, and calc-silicate marbles. Undeformed tourmaline-bearing granite is also attested (Fig. 2).

[5] Dipietro, Lawrence 1991.

2. Indus Suture Zone – separating 1 and 3 zones

The rock types in the suture zone itself includes blocks of low-grade metavolcanics, ultramafic rocks, sheared greenschists, serpentinite, talc-dolomite schists and blueschists[6]. For detailed description of all rock formations and their stratigraphical relationships, the paper of Kazmi et al. in 1984 was a milestone in the geological research of this area[7]. Noteworthy is the occurrence of emerald, close to Mingora[8]. Considered as a whole, the rock assemblage represents a typical, metamorphosed and sheared, ophiolitic mélange association found at convergent plate boundaries (Fig.1).

3. Kohistan island arc association in the north

Major rock types in this unit are calc-alkaline volcanics and intrusives rocks of various metamorphic grade (greenschists, amphibolites, granulites, non-metamorphic) and metasediments (Fig. 3).

Alluvial deposits cover the basement in the Swat river valley. Because of the NE-SW trend of the valley, it is expected that the deposits are fed both from the north and the south. It is important to note the complete absence of limestone outcrops in the Swat valley and surrounding areas (Fig. 3), where the main Gandharan sites are located. In these sites the presence of structures built with limestone and stucco is widespread. The nearest limestone outcrops are located in the north-western area of Islamabad (Fig. 4)[9].

Indeed, a geological overview of the Gandharan settlement in Afghanistan, in northern and southern areas of Kabul, shows the presence of different

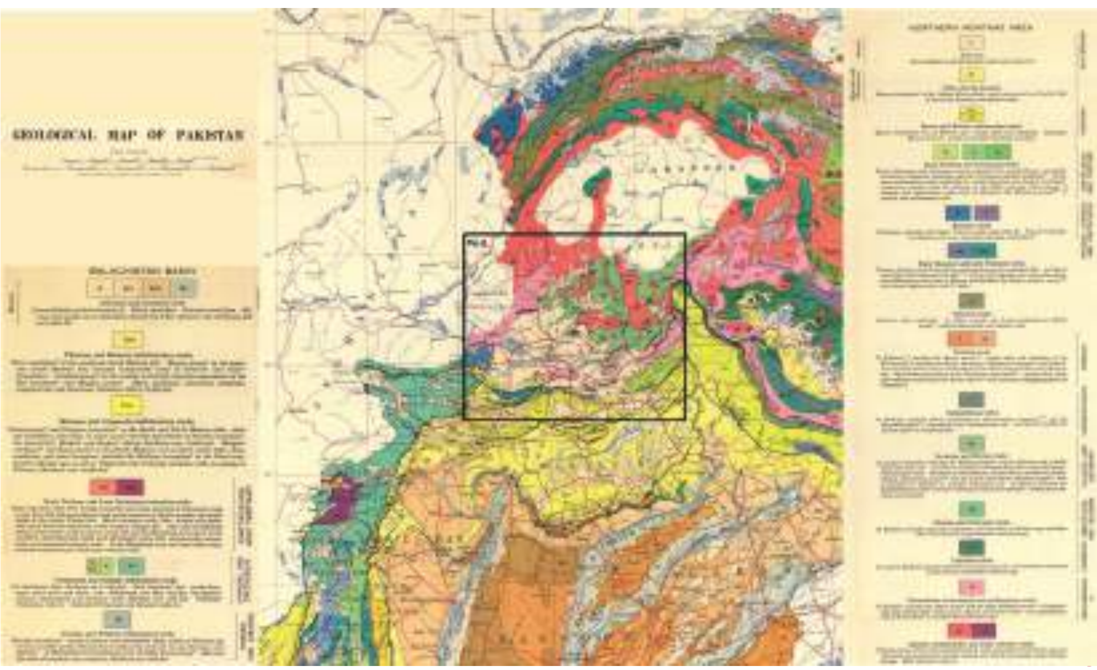


Fig. 3
Geological map of Pakistan by Geological Survey of Pakistan and U.S. Geological Survey 1964 (detail).

[6] Tahirkheli et al., 1979a; Kazmi et al., 1984.

[7] Kazmi et al., 1984.

[8] Kazmi et al., 1986.

[9] Williams et al., 1988-90.

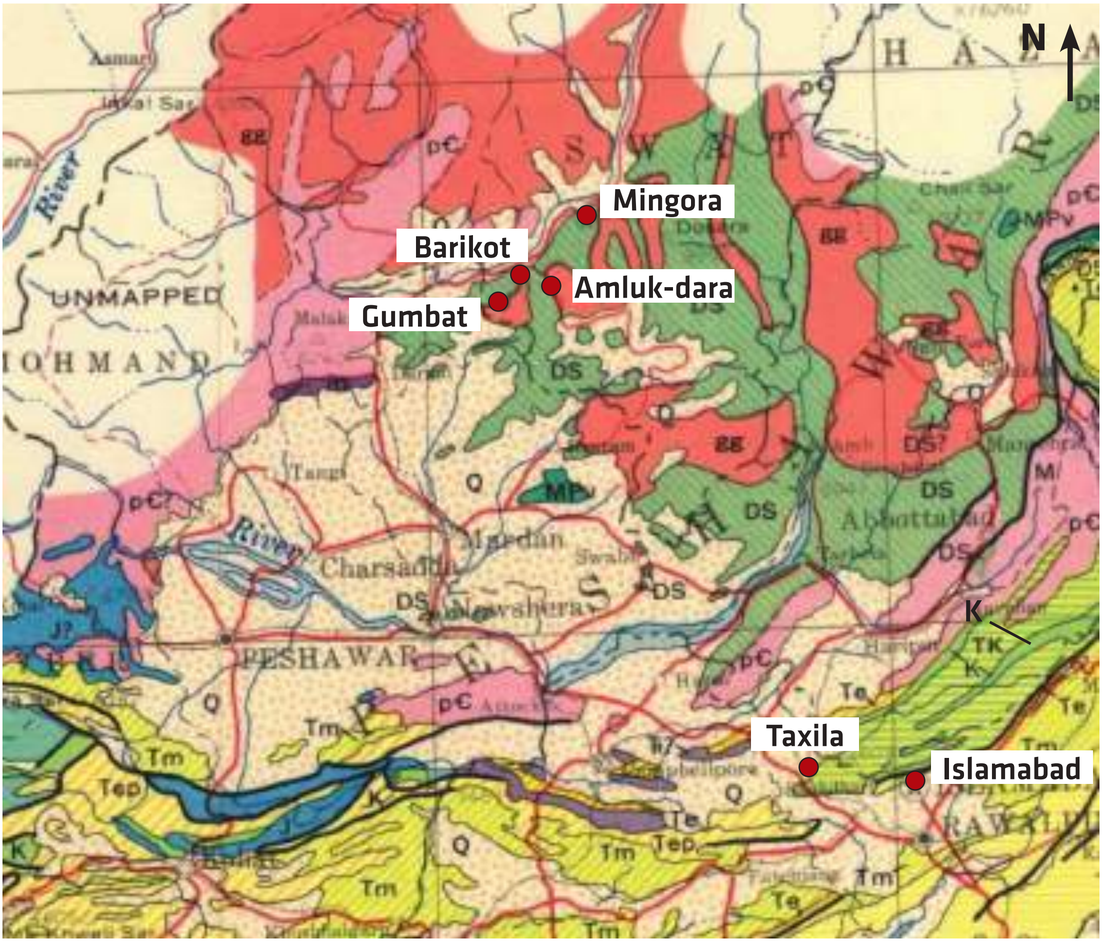


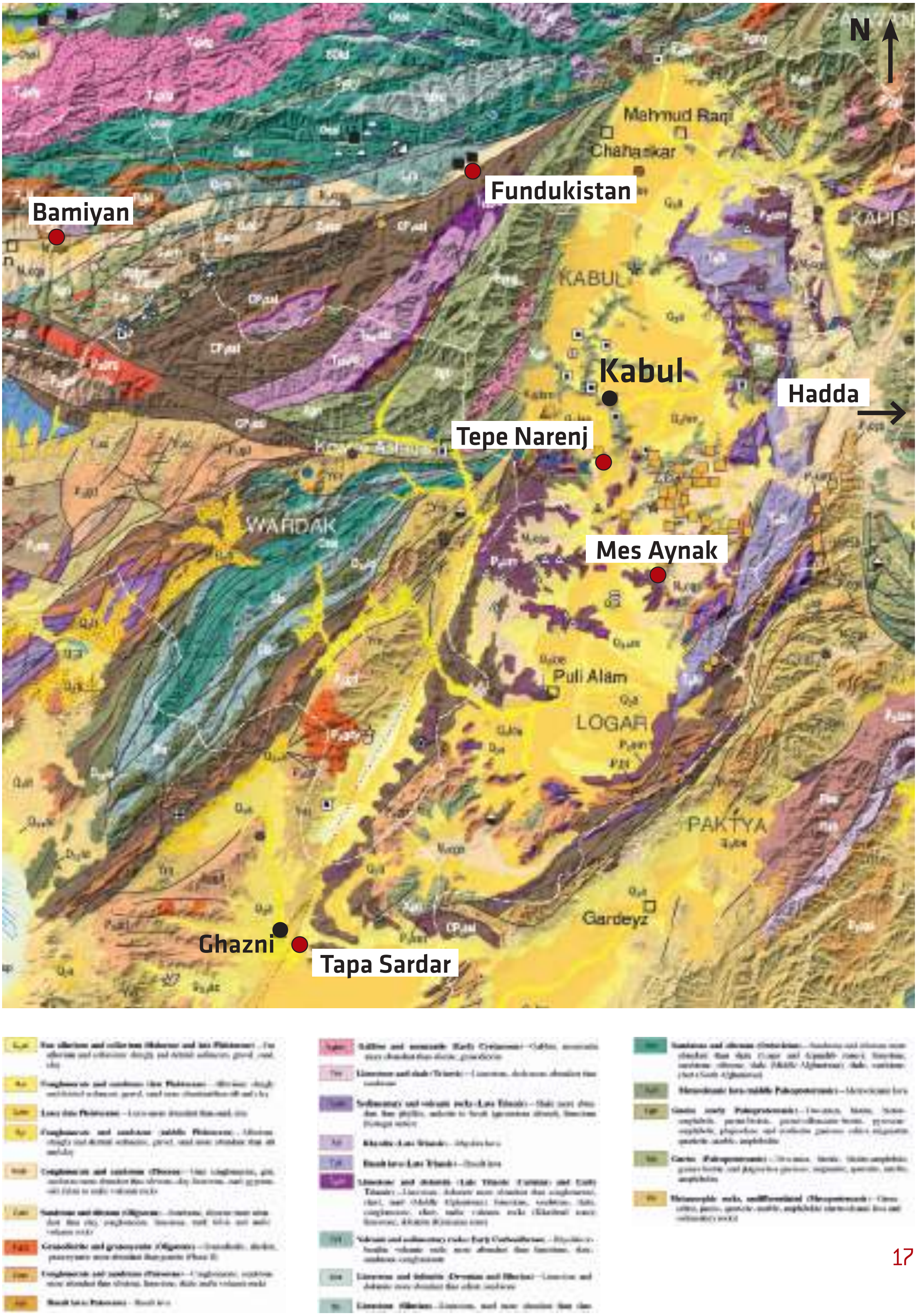
Fig. 4
Islamabad area in Geological Map of Pakistan (Detail of Fig.3) (TK = mostly Eocene nummulitic limestone, Cretaceous limestone and mostly Giumal sandstone; K = mostly limestone and Giumal sandstone).

opposite page
Fig. 5
Geologic and Mineral Resource Map of Afghanistan by U.S. Geological Survey 2006 (detail).

geological formations (Fig. 5). In particular, in the area of Ghazni (where Tapa Sardar is situated), we note the presence of Pleistocenic continental deposits, composed by alluvium and colluvium, loess deposits, conglomerate, and Triassic sandstone and siltstone.

In the Fundukistan area, north of Kabul, we note the presence of: grey schist and phyllite of the Neoproterozoic age; sandstone and siltstone of the Carboniferous-Permian age; limestone and dolomite of Late Triassic and Early Triassic; Miocenic conglomerate and sandstone; gray conglomerate and sandstone more abundant in siltstone, clay and limestone from Pliocene.

The southern area of Kabul (where Mes Aynak, Hadda and Tepe Narenj are located), shows the presence of gneiss (Paleoproterozoic), marble and quartzite Cambrian and Neoproterozoic, limestone and dolomite Middle and Early Triassic, sandstone and siltstone Late and Middle Triassic, ultramafic intrusions (dunite, peridotite and serpentinite of Eocene), Pliocenic conglomerate and sandstone, alluvial conglomerate and sandstone of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Bamiyan
Fundukistan
Mahmud Raqi
Chaharikar
KABUL
Kabul
Hadda
Tepe Narenj
WARDAK
Mes Aynak
Puli Alam
LOGAR
PAKTYA
Gardeyz
Ghazni
Tapa Sardar

Fig. 6
Cross section of sample AKD 2 from Amluk-dara, Pakistan (image is 37 mm across).

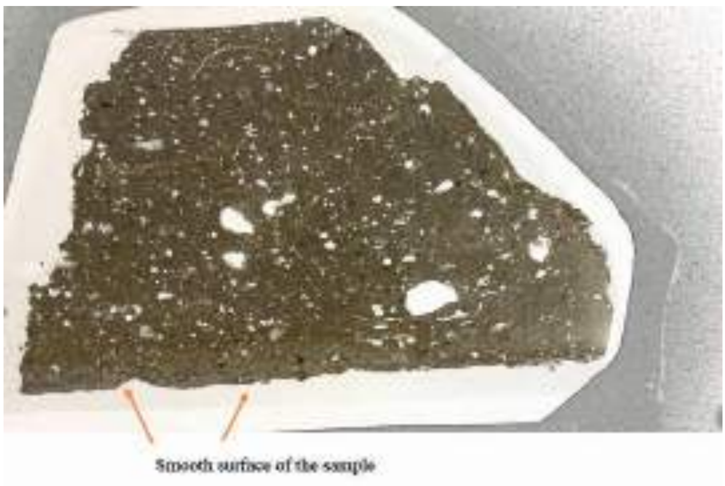


Fig. 7
Cross section of sample AKD 4 from Amluk-dara, Pakistan (image is 37 mm across).

the Middle and Late Pleistocene, alluvial and colluvial fan (Late Pleistocene and Holocene).
(C.R., S.P.)

Petrographic analysis of Gandharan stucco samples from Pakistan

Sample AKD 2

This sample was taken from a stucco architectonical decoration of a building in Amluk-dara archeological site.

Through a petrographic microscope analysis we noted that the large white grains are angular fragments of quartzite, whereas grey colored grains are mainly fragments of single crystals of calcite, probably originating from coarse marble (Fig. 6). The fine-grained binder matrix consists of calcite appears brownish (note the smooth surface at the bottom of the image). Fragments of a smooth surface layer are preserved. This is mainly composed by fine-grained sheet silicates and some larger mica flakes. Small quartz grains are also present.

As the microscopic study shows, the surface layer derives from a smoothing, because the original one was rough, owing to the presence of coarse-grained components in the stucco, such as quartzite or calcite grains. It can also be expected that the original surface was somehow shiny, due to the presence of coarser mica flakes.

Sample AKD 4

This sample was taken from a stucco architectonical decoration of a building in Amluk-dara archeological site.

Through a petrographic microscope analysis we noted that intermediate size white grains are angular fragments of quartzite; the grey colored grains are mainly fragments of single crystals of calcite probably originating from coarse marble. The fine-grained binder matrix, mainly consisting of calcite, appears brownish (Fig. 7).

Fragments of a smooth surface layer are also preserved. This is mainly composed by fine-grained sheet silicates ('clay') and of some larger mica flakes. Small quartz and tourmaline grains are also present. Interesting results also came from microprobe analysis, about the presence and the amount of calcite (Fig. 8).

On the surface we observed three layers: a very thin (c. 2 μm) red brownish layer is covered by a fine-grained ochre layer, covered by a dirty layer rich of sheet silicates, mica flakes and quartz grains (and tourmaline) (Fig. 9).

Sample AKD 5

This sample was taken from a stucco architectonical decoration of a building in Amluk-dara archeological site.

Through petrographic microscope analysis we noted that the sample contains centimetric angular fragments of quartzite, granite, gneiss, garnet, and marble. In addition, mica flakes are present. The fine-grained binder matrix, mainly consisting of calcite, appears brownish (Fig. 10).

The surface layer is composed of fine-grained sheet silicates ('clay') and some larger mica flakes. Small quartz grains are also present.

This layer is separated from the stucco by a 20 μm thick sheet of fibrous calcite with fiber axis perpendicular to the surface. This layer could represent the product of a water-lime suspension painted into the stucco surface.

Sample AKD 14C

This sample was taken from a stucco architectonical polychrome decoration of a building in Amluk-dara archeological site.

Through a petrographic microscope analysis we noted that the stucco in this sample has been made using a lime mortar. The added rock fragments

Fig. 8 a, b, c
Sample AKD 4 from Amluk-dara, Pakistan (back-scattered electron image). The surface layer consists of mica flakes that are aligned parallel to the surface. Quartz and titanite grains are present as well. Spots 2 to 5 are mainly composed of calcite with smaller amount of Al and Si (see spectra 2 to 5) probably resulting from a small portion of clay minerals.

mainly consist of angular rock compounds, up to 2 mm in size. The grain size spectrum is continuous (Fig.11).

The stucco contains mm-sized angular fragments of quartzite, granite, gneiss, garnet, and marble. In addition, mica flakes are present in the fine-grained matrix. The fine-grained binder matrix, mainly consisting of calcite, appears brownish (Fig. 12).

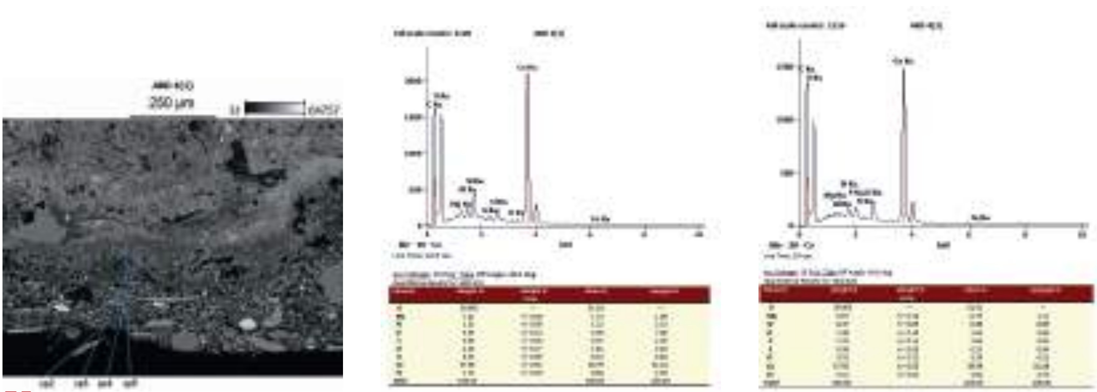
Fragments of a smooth surface layer are preserved. The layer rested on a smooth surface of the stucco material. The layer itself is composed by two sublayers: an inner one is a thin reddish layer (0.01 mm thick). This inner layer is covered by an outer layer that contains a large amount of fine-grained material (binder ?) and some larger mica flakes. The red colour results hematite (c. 2 µm) by Raman analysis (Figg. 13, 14). Partly, the surface of the sample is covered by a layer of dirt rich in fine grained sheet silicates and calcite.

Sample AKD 13C

This sample was taken from a stucco architectonical polychrome decoration of a building in Amluk-dara archeological site.

This sample is a fragment of an architectural decoration in stucco, made using lime mortar (fig. 15). Petrographic microscope analysis and Electron Microprobe analyses highlighted that the matrix contains a great amount of calcite (Figg. 16, 17, 18).

The added rock fragments mainly consist of angular rock compounds up to 7 mm in size. The grain size spectrum is continuous. Rock fragments comprise high-grade metamorphic rocks, plutonic rocks and marble. The region of provenance is probably an heterogeneous basement area. Some rock fragments of garnet micaschist are composed of a large, mm sized garnet, with attached mica rich country rock. Such aggregates are unstable in the sedimentary process. It is therefore evident that the rocks were artificially crushed to produce the lime mortar.



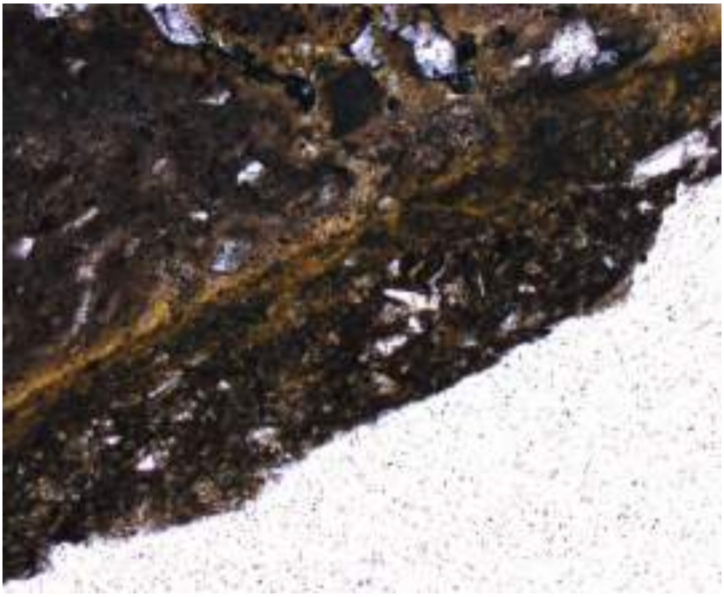


Fig. 9
Sample AKD 4 from Amluk-dara, Pakistan (image is 1.8 mm across).

Fig. 10
Cross section of sample AKD 5 from Amluk-dara, Pakistan (image is 37 mm across). Note the smooth surface at the bottom of the image.

XRD analyses on sample AKD 14C and AKD 13C show a similar chemical composition of the stucco material, with a high presence of calcite (Fig. 19).

Sample BKG 1123 16C

This sample was taken from a stucco architectonical polychrome decoration of a building in Barikot archeological site.

The sample BKG 1123 16C consists in stucco produced from a lime mortar. The added rock fragments mainly consist of angular rock compounds up to 1 mm in size. The grain size spectrum is continuous (Fig. 20).

opposite page

Fig. 11
Sample AKD 14C of architectonical polycrome decoration from Amluk-dara, Pakistan (photo E. Loliva ©ISCR).

Fig. 12
Cross section of sample AKD 14C from Amluk-dara, Pakistan (image is 37 mm across). Note the original smooth surface on the right side of the image. Remnants of reddish color are visible there.

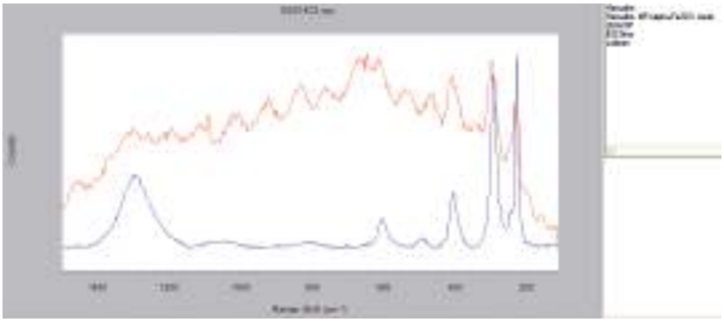
Fig. 13
Sample AKD 14C from Amluk-dara, Pakistan (petrograpich microscope image is 1.8 mm across-1 polar). Detail of the partly preserved smooth surface layer.

The added rock and mineral fragments mainly indicate a sedimentary origin (limestones). Only a few fragments come from some relatively high metamorphic or igneous rocks. Angular fragments mainly consist of quartz and limestone. The grain size distribution is serial with a few fragments of more than 1 mm in size. Fragments are embedded in a brownish, fine-grained matrix representing the former lime mortar. The grain size distribution of added fragments is mainly in sand fraction or finer (Fig. 21). Enlarged view of the mortar matrix mainly composed of tiny calcite crystals (Fig. 22).
The EDS analyses reveal that the mortar attached to the rock fragments mainly contains Ca, as due to the calcite content. Additional elements found in the rock fragments contain Na, K, Ca, Mg, Fe, Al, and Si. These elements can be related to various minerals such as plagioclase, K-feldspar, muscovite, biotite, and garnet (Figg. 23, 24). On the surface of the sample we recognise a few traces of very pale, faint and dilute red colour that it was not possible to analyze in this research.

Sample BKG 1123 15C

This sample was taken from a stucco architectonical polychrome decoration of a building in Barikot archeological site.
Sample BKG 1123 15C is a stucco, made using a lime mortar. The added rock fragments mainly consist of angular rock compounds up to 6 mm in size. The grain size spectrum is serial continuous. Added rock and mineral fragments mainly indicate a relatively high metamorphic origin (Fig. 25). By means of a petrographic microscope we note some irregular pore spaces (shrinking cracks ?) in the fine grained brownish matrix (Fig. 26). The sample contains rock fragments of a relatively high-grade metamorphic rock, containing minerals such as feldspar, muscovite, biotite, margarite, tourmaline, and garnet. These minerals are embedded in a fine-grained binder mainly composed of calcite.
EDS analyses of the binder indicate that, in addition to calcite, elements such as Si, Al, K and S are present. This could point to a certain fraction of clay added to the binder of the stucco mixture.

Fig. 14
Sample AKD 14C from Amluk-dara, Pakistan. Raman spectrum of the thin red layer (red) compared with a pure hematite spectrum (blue).



On the surface of the sample a few traces of very pale, faint and diluted red color were observed, though it was not possible to analyze them, we hope to do it in next future.

Sample GBK 17A

This sample was taken from a stucco architectonical polychrome decoration of a building in Gumbat archeological site.

By petrography analysis we highlighted that the sample GBK 17A is a stucco made using lime mortar. The added rock fragments mainly consist of limestones up to 1 mm in size and, to a lesser extent, of quartz grains. The grain size spectrum is serial continuous. The added rock and mineral fragments mainly indicate a sedimentary origin (limestones). Only a few fragments come from relatively high metamorphic or igneous rocks. A surface layer has a different composition if compared to the bulk sample. The surface layer contains a higher fraction of mica flakes (Fig. 27).

In addition, irregular pores are visible (possibly partly artificially created during preparation). The origin of a thin, curved pore is not clear (Fig. 28), fibre-like pore structures have an unknown origin (Fig. 29). The surface layer of the sample is composed by much finer grained material. The surface layer is about 0.6 mm thick (Fig. 30). By Electron microprobe analyses the bulk sample is mainly composed by fragments of limestone with a few fragments of relatively high-grade metamorphic rock (Fig. 31).

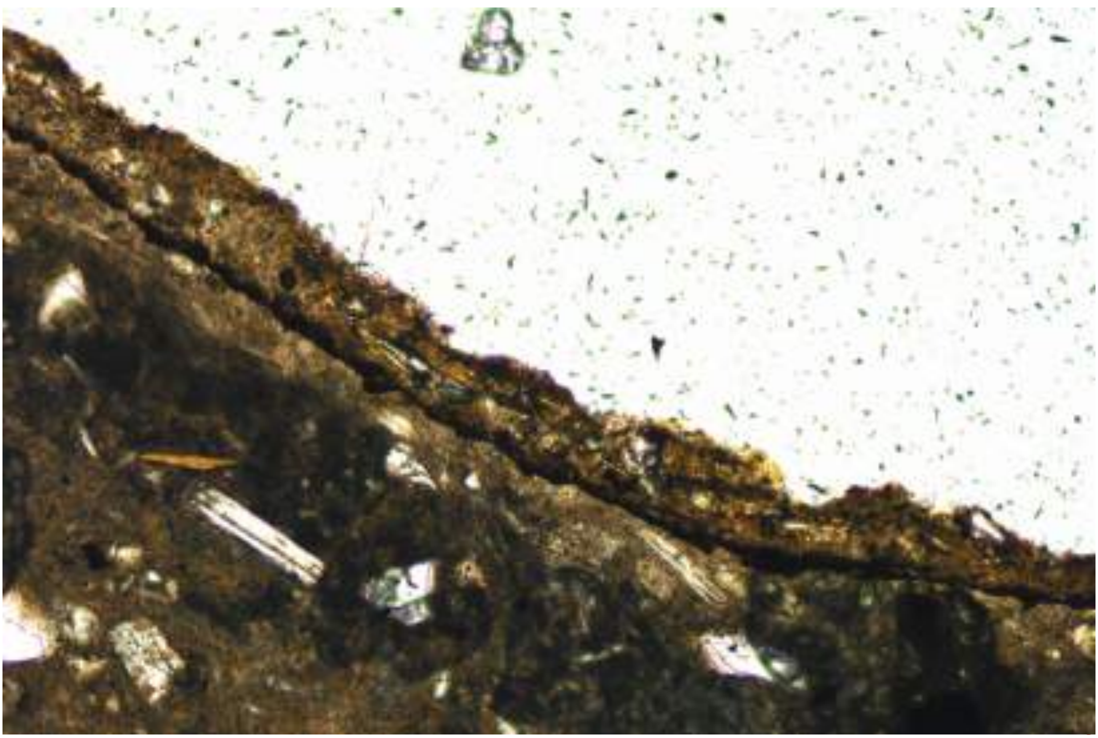


Fig.15
Sample AKD 13C of architectonical decoration from Amluk-dara, Pakistan (photo E. Loliva ©ISCR).

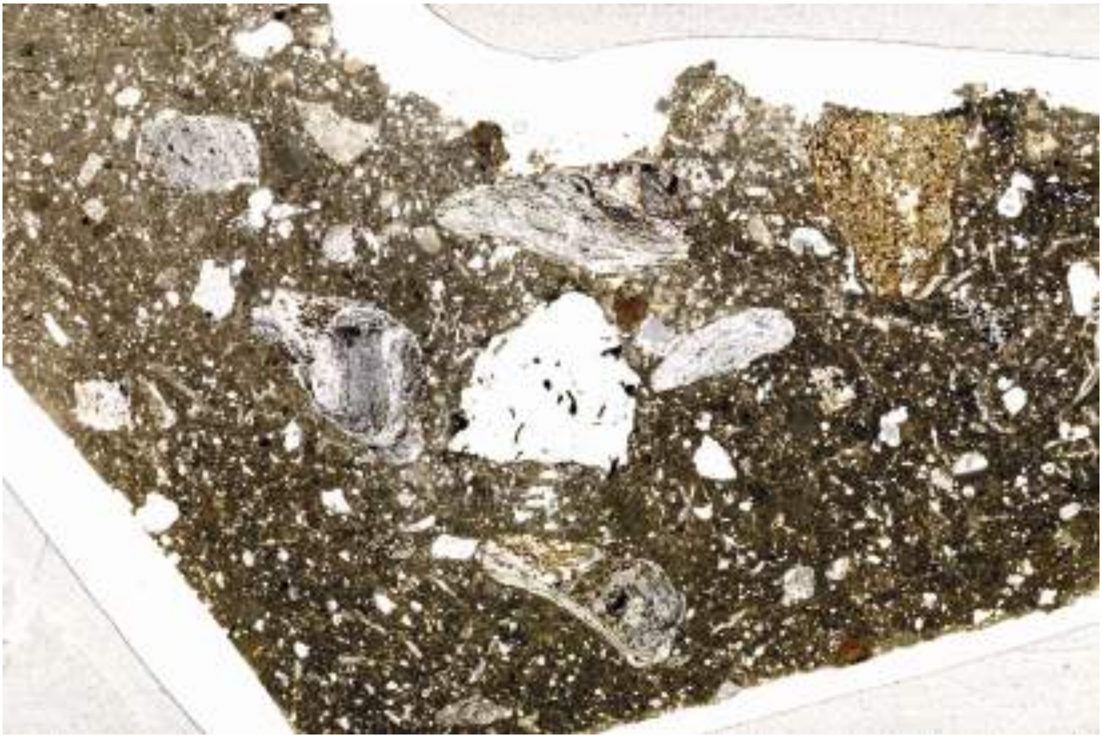
Fig.16
Thin section of sample AKD 13C from Amluk-dara, Pakistan (image is 37 mm across). Large rock fragments partly consist of micaschists that contain mm-sized garnet crystals.

These minerals are embedded in a fine-grained binder, mainly composed of calcite. EDS analyses of the binder indicate that, in addition to the calcite, elements such as Si, Al, K and S are present. This element could point to a certain fraction of clay added to the binder. A surface layer has a different composition: it contains a high fraction of metamorphic minerals such as feldspar, muscovite, garnet, and chloritoid. Furthermore, XRD analysis pointed out that the surface layer contains much more feldspar, mica, and calcite than the bulk sample.

Sample of 'Kanjur'

This fragment of 'kanjur' rock is a sample of building material taken in an archaeological excavation in Amluk-dara site (Swat) (Fig. 32). Petrographical analysis higlighted that this sample is an organogenic limestone, mainly composed of calcite. A prominent feature of this rock is a porous microstructure (Fig. 33). Furthermore, spherical structures and pagoda-like structures characterized by a central void (marked by arrows) are visible. The rock was probably originate by a colony of calcareous porifera or calcareous algae in a marine environment (ancient Tethis sea). Such a rock may be classified as a biocalcarenite. The rock can easily be cut and shaped. In addition, the rough surface of the porous rock is decorative and may be used for ornamental purposes.

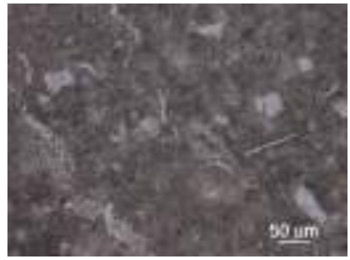
By an analysis of the microstructure of the rock we noted a cone-like structure of calcite sheets with a central channel (Fig. 34). Moreover, relatively closely packed structure of spheroidal shape are present (Fig. 35).



Then, back scattered electron images are used to document the microstructure of the samples. Compared to transmitted light images, the resolution is higher because only the polished surface of the samples is displayed (Figg. 36, 37).
For the phase analysis, X-ray diffraction techniques were also applied. It can be confirmed that calcite is the main phase of this sample of stone. No other mineral can be detected (Fig. 38).
(T. T)

Petrographic analysis on the Gandharan clay samples from Afghanistan

Sample 1 from Tapa Sardar, Afghanistan
Sample 1 is a fragment of a relatively hard and solid fired clay artefact (Fig. 39). By a petrographic microscope analysis we noted that the color is red, with 0.5 to 1 mm sized, bright sand components, visible to the naked eye (Fig. 40). It contains sand fragments that are angular shaped minerals (feldspar, quartz) and rock fragments (phyllite, limestone, quartzite) (Fig. 41). A natural clay served as a binder. Chemical analyses of sheet silicates show that particularly biotite was oxidized during the burning process. Remnants of clay minerals are characterized by low totals and also oxidized during the burning process. The rock and mineral fragments can derive from sedimentary rocks (limestone) or from crystalline rocks (hornblende, K-feldspar, garnet). The compositions of the latter ones conform to a medium to high grade metamorphic basement.
In addition to the petrographic microscope, the microstructure of this sample was analyzed with an electron microprobe. The chemical composition of the minerals is measured with the same machine, employing wavelength dispersive techniques.



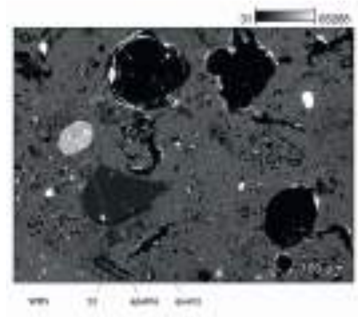


Fig.17
Sample AKD 13C from Amluk-dara, Pakistan (petrographic microscope image: 1 polar). The fine-grained brownish matrix is composed of µm-sized calcite crystals.

Fig. 18
Sample AKD 13C from Amluk-dara, Pakistan. Back-scattered electron image, 13 calcite: fine-grained matrix with mica flake and pore space (black).

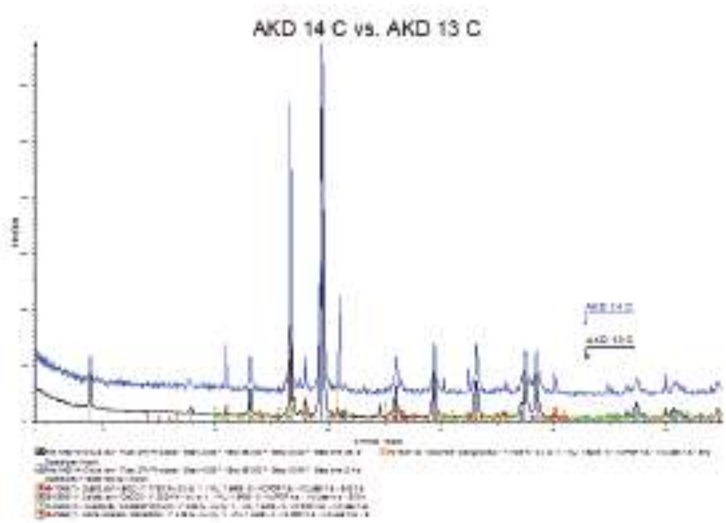
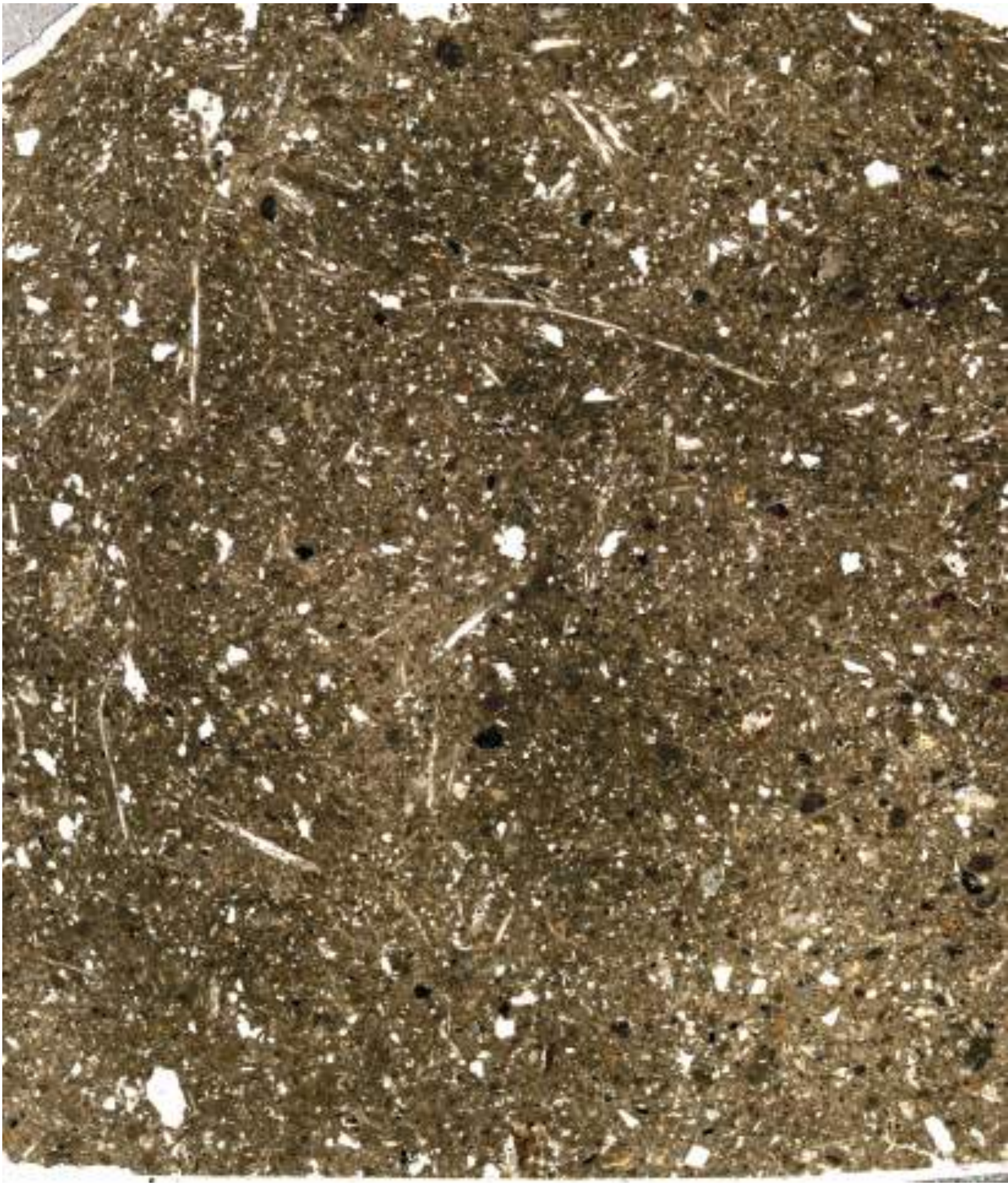


Fig. 19
X-ray diffraction (XRD) analyses on samples AKD 14C and AKD 13C from Amluk-dara, Pakistan.



The black colour on the surface of this sample was so far not found to have a chemical characterisation (Fig. 42).
Moreover, by an X-ray diffractogram analysis of this sample the following phases were recognized: quartz, plagioclase (albite), K-feldspar, hornblende, and muscovite (Fig. 43).

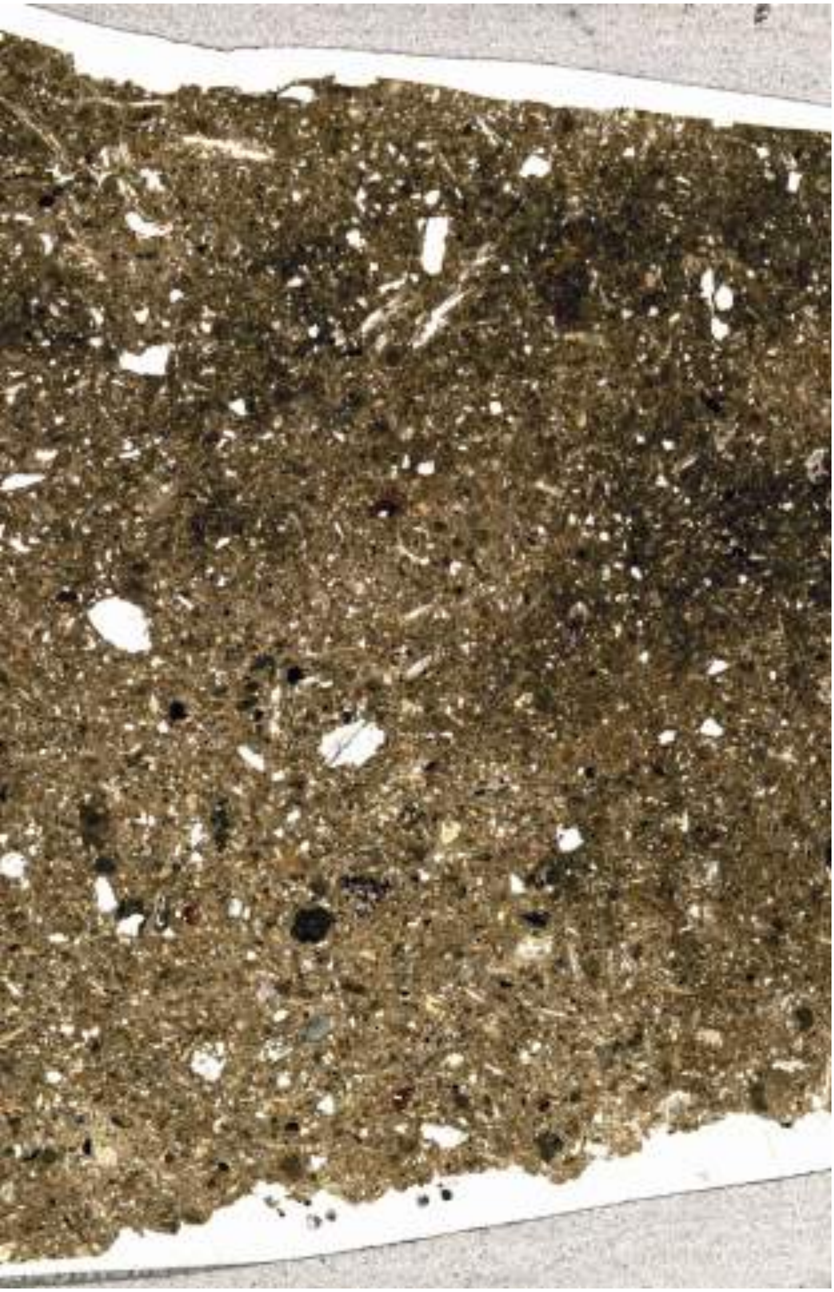
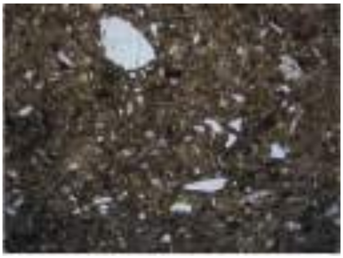


Fig. 20
Thin section of sample BKG 1123 16C from Barikot, Pakistan (image is 37 mm across).

Fig. 21
Sample BKG 1123 16C from Barikot, Pakistan (petrographic microscope image: image is 7 mm across - 1 polar).

Fig.22
Sample BKG 1123 16C from Barikot, Pakistan (petrographic microscope image: image is 0.45mm across - 1 polar).



Sample 2 from Tepe Narenj, Afghanistan

Sample 2 is a fragment of a relatively soft fired clay artefact (Fig. 44), which tends to disintegrate during the handling. The color is red with 0.5 to 1 mm size, bright sand components are visible to the naked eye. By petrographic microscope analysis we highlighted that it contains sand fragments consisting in angular shaped minerals (feldspar, quartz) and rock fragments

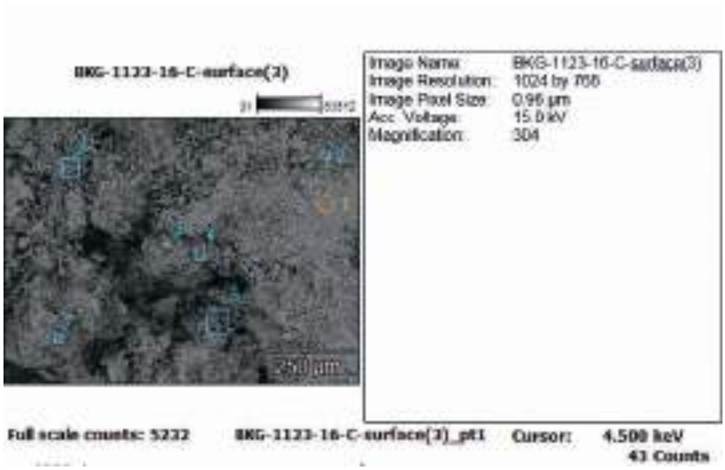


Fig. 23
Sample BKG 1123 16C from Barikot, Pakistan. Electron Microprobe analyses (WDS): surface of the sample.

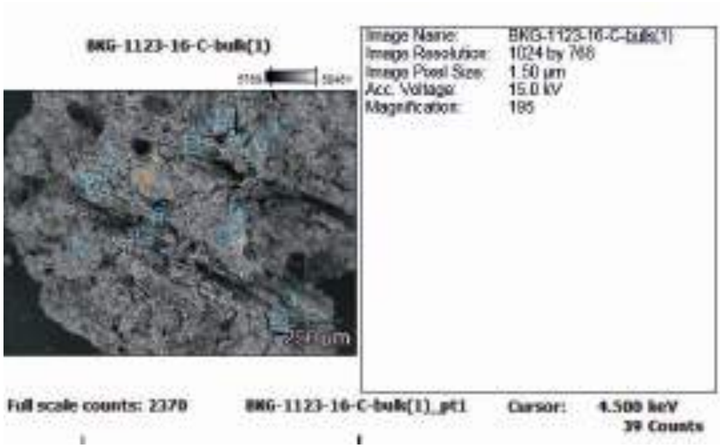


Fig. 24
Sample BKG 1123 16C from Barikot, Pakistan. Electron Microprobe analyses (WDS): bulk of the sample.

Fig. 25
Thin section of sample BKG 1123 15C from Barikot, Pakistan. Petrographic microscope image: image is 37 mm across.

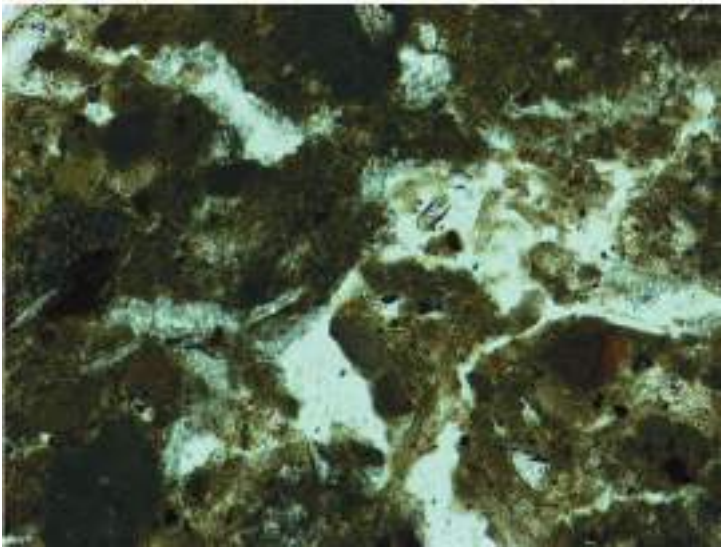


Fig. 26
Sample BKG 1123 15C from Barikot, Pakistan (image is 0.9 mm across - 1 polar). Petrographic microscope image: view of irregular pore space (shrinking cracks ?) in the fine grained brownish matrix.

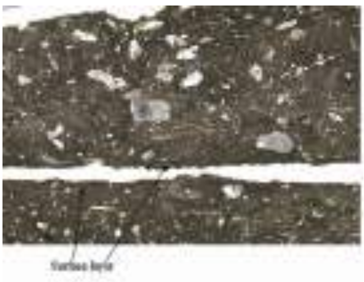


Fig. 27
Thin section of sample GBK 17A from Gumbat, Pakistan (image is 37 mm across).

Fig. 28
Sample GBK 17A from Gumbat, Pakistan (image is 7 mm across - 1 polar). Petrographic microscope image: an overview of the sample shows angular rock fragments in a fine grained matrix.

Fig. 29
Sample GBK 17A from Gumbat, Pakistan (image is 0.9 mm across -1 polar). Petrographic microscope image: a fibre-like pore structure of unknown origin and, at the bottom of the image, a fragment of limestone embedded in a matrix of fine grained calcite is visible.

Fig. 30
Sample GBK 17A from Gumbat, Pakistan (image is 1.8 mm across -1 polar). Petrographic microscope image: the surface layer (facing down) is composed by much finer grained material compared to the bulk sample.

(phyllite, limestone, quartzite). A natural clay and fine-grained calcite served as binders (Fig. 45).

The peculiarity of the sample is that relatively large single crystals of gypsum are in the sand fraction. Because gypsum is thermally not stable during a normal, high temperature burning process, it can be concluded that this mineral is either the result of a secondary process or the temperature of the burning process was very low (Fig. 46).

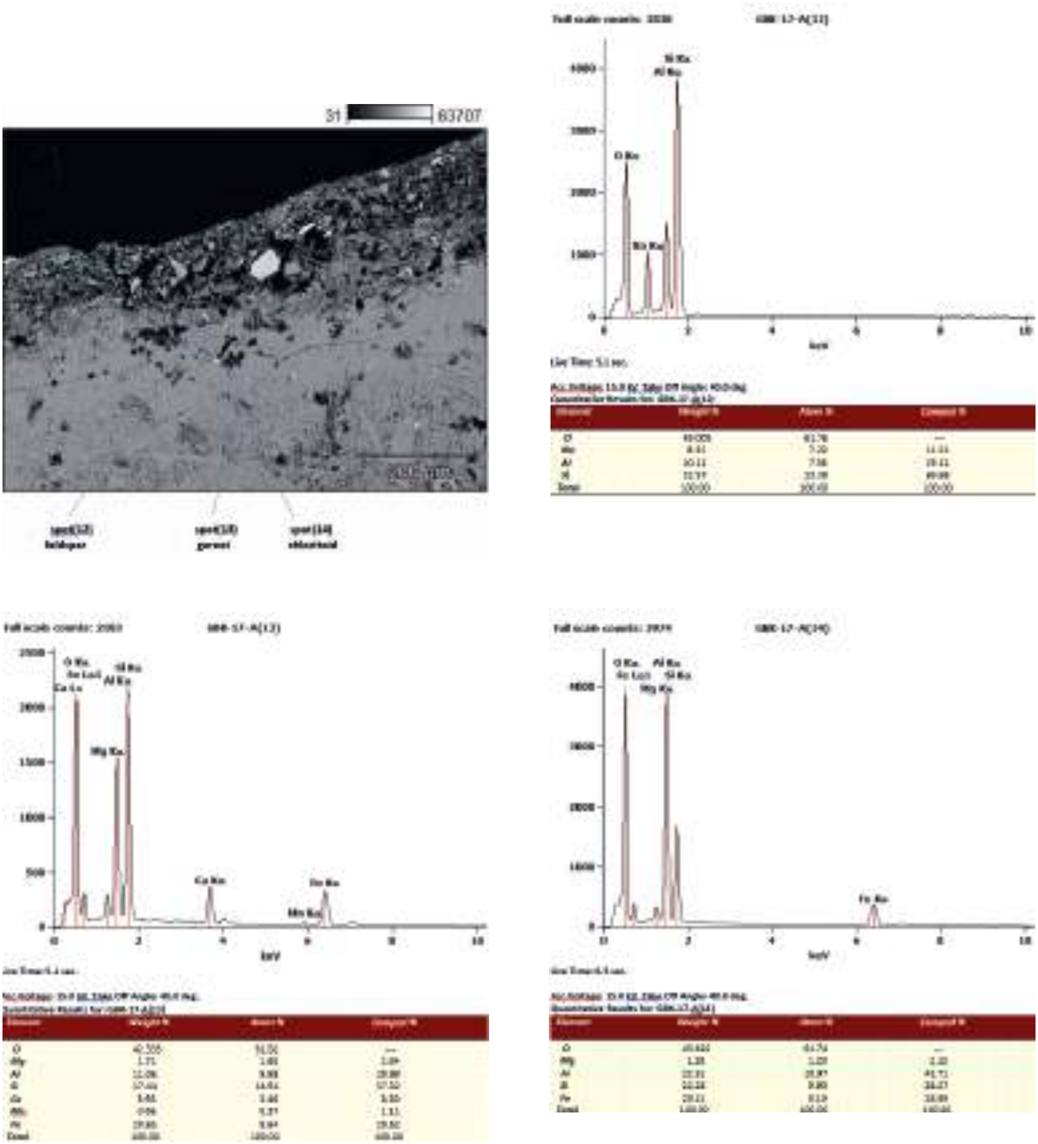


Fig. 31 a, b, c, d

Sample GBK 17A from Gumbat, Pakistan. Electron Microprobe analyses (WDS): detail of fine-grained minerals in the surface layer. Note the presence of mica, feldspar, and garnet. Spot 12, 13 and 14: EDS analysis of the fine-grained matrix.

Chemical analyses of sheet silicates show that most of them were altered during the burning process. The analyzed compositions are particularly rich in Ca, in contrast with the naturally occurring ones. The rock and mineral fragments could derive from sedimentary rocks (limestone) or from crystalline rocks (hornblende, K-feldspar, garnet). The composition of the latter ones, conform to a medium to high grade metamorphic basement (Fig. 47). The composition of hornblende in this sample is different from the one in the sample from Tapa Sardar, indicating a different region of provenance of the sand.

Fig. 32
Sample of 'kanjur' rock (photo T. Theye).

By an X-ray diffractogram analysis the following phases can be recognized: quartz, plagioclase (albite), K-feldspar, hornblende, muscovite, calcite, and gypsum (Fig. 48)
(T.T., C.R.)

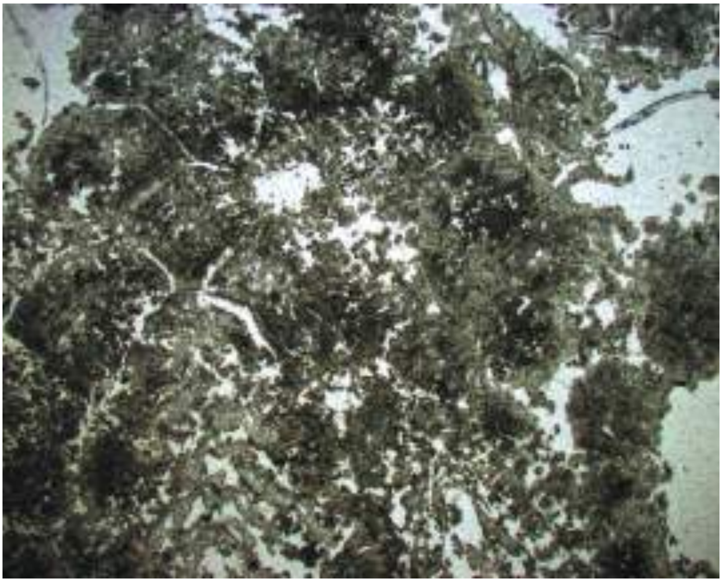
Conclusions

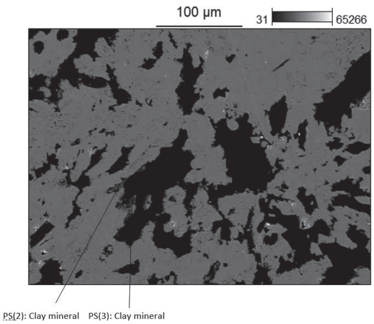
The Gandharan archaeological sites are mostly located in the Indus Suture Zone (see above, n.2) and in the lower Swat (see above n.1). In a recent past, scholars observed the use of local different type of schists to build buildings and sacred artworks[10]. In this new research we highlighted the use of limestone for stucco artefacts and architectural decorations. This limestone is not a local rock in Swat (see above) but its main, extended and closer outcrops are located in the mountains northwest of Islamabad. Indeed, through specific analyses carried out by our team, the compatibility of these outcrops with the rocks used for stucco artefacts and stucco decorations of buildings was observed[11]. This stucco was made by a mixture of different kinds of local crushed rocks (i.e. schists and granites).

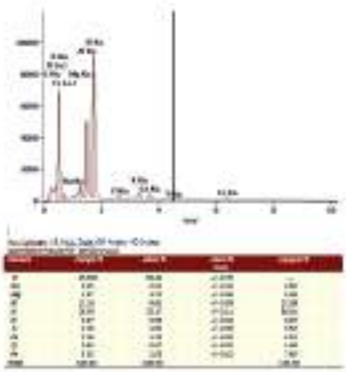
Fig. 33
Polished thin section of 'kanjur' rock, overview: a prominent feature of this rock is a porous microstructure (white areas in the image) (image is 3.5 cm across).

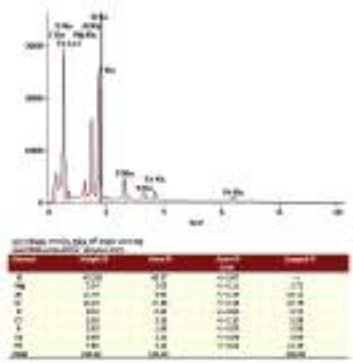
Fig. 34
Sample of 'kanjur' rock, analysis of the microstructure: cone-like structure of calcite sheets with a central channel. Petrographic microscope image: left image: 1 polar; right image + polars (images are 6.8 mm across).

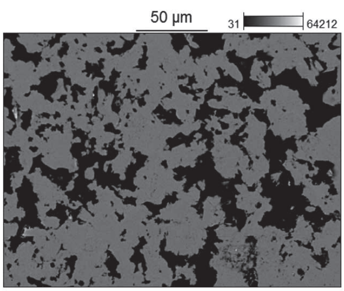
Fig. 35
Sample of 'kanjur' rock, analysis of the microstructure: relatively closely packed structure of spheroidal shapes (petrographic microscope image is 6.8 mm across – 1 polar).











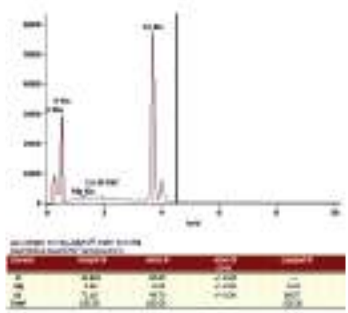


Fig. 36 a, b, c
Sample of 'kanjur' rock. Back-scattered electron image. Impurities in the calcite structure consisting of tiny particles of clay mineralswhich appears darker than calcite. EDS spectrum and elemental composition of clay fragments. Chlorine may be contributed by the resin (araldite).

Fig. 37 a, b
Sample of 'kanjur' rock. Back-scattered electron image. Detail of the core of the spheroidal particle: most of the calcite shows euhedral crystal faces. EDS spectrum and elemental composition of calcite: note the presence of small amount of Mg in calcite.

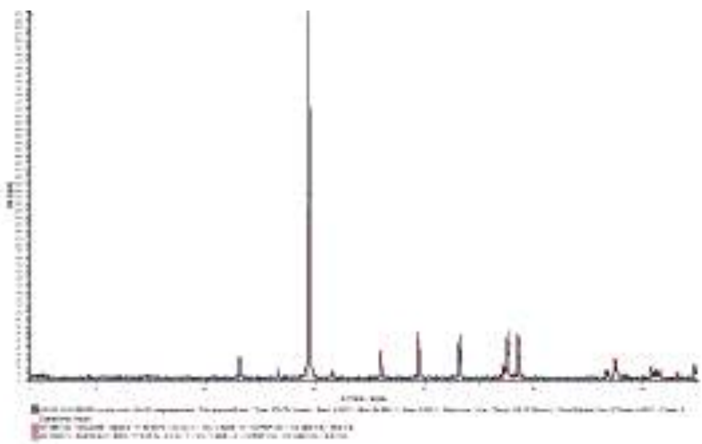


Fig. 38
Sample of 'kanjur' rock. X-ray diffraction (XRD) analysis.

Fig. 39
Sample 1 of clay artefact from Tapa Sardar, Afghanistan. Close-up of sample. Bright, mm sized sand fragments embedded in a reddish matrix are visible (photo T. Theye).

We therefore suppose that the limestone was transported from these sites to Swat mainly by road paths and perhaps through water ways.
The study of the geological outcrops shows a great difference between the area of Gandharan sites in Pakistan and the Afghanistan ones. In Pakistan we mainly note the presence of metamorphic rocks, whereas in Afghanistan, of limestone, sandstone and siltstone, attributed to different ages, are the most abundant geological formation. In the latter Gandharan sites in Afghanistan stucco and clay artworks are frequently found, as these materials are easily available on site.
(C.R., S.P.)

[10] Di Florio et al. 1993, pp. 357-372; Faccenna et al. 1993, pp. 257-270; Olivieri 2006, pp. 137-156.

[11] See Olivieri, in this issue.

Fig. 40
Sample 1 of clay artefact from Tapa Sardar, Afghanistan. Thin section of sample: the glass slide is 48 mm across, and the fragment is 10 mm across.

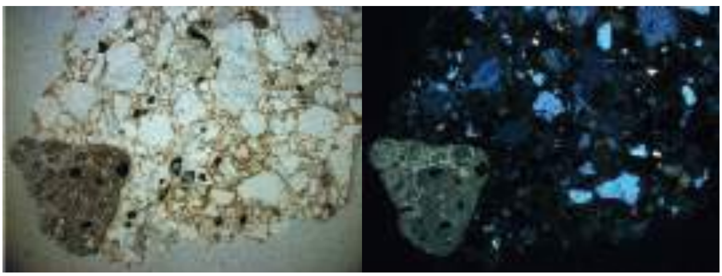


Fig. 41
Sample 1 of clay artefact from Tapa Sardar, Afghanistan. Microscopic overview of the sample. The colorless grains are quartz and feldspar. The large fragment in the lower left is a biogenic limestone. Note the reddish/brownish pigments on the grain boundaries of the sand components. These pigments, responsible for the macroscopic red color, consist of oxidized iron bearing clay particles (petrographic microscope image: left image: 1 polar; right images + polars; image is 6.8 mm across).

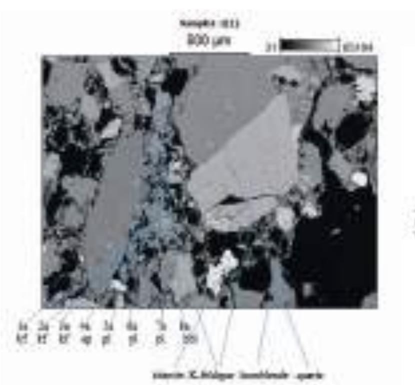


Fig. 42
Sample 1 of clay artefact from Tapa Sardar, Afghanistan. Electron Microprobe analyses.

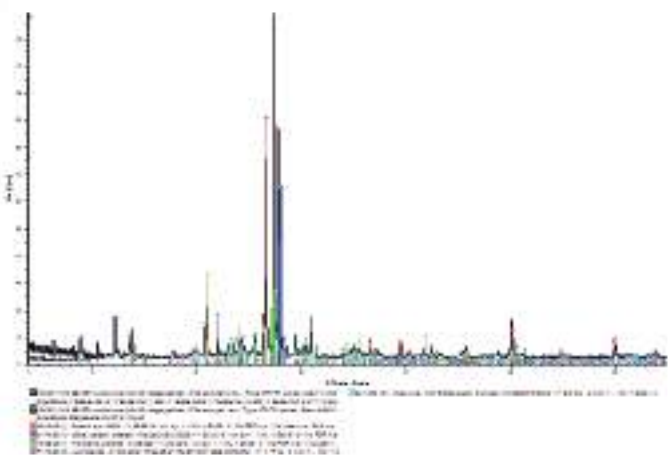


Fig. 43
Sample 1 of clay artefact from Tapa Sardar, Afghanistan. X-ray diffraction (XRD) analysis.

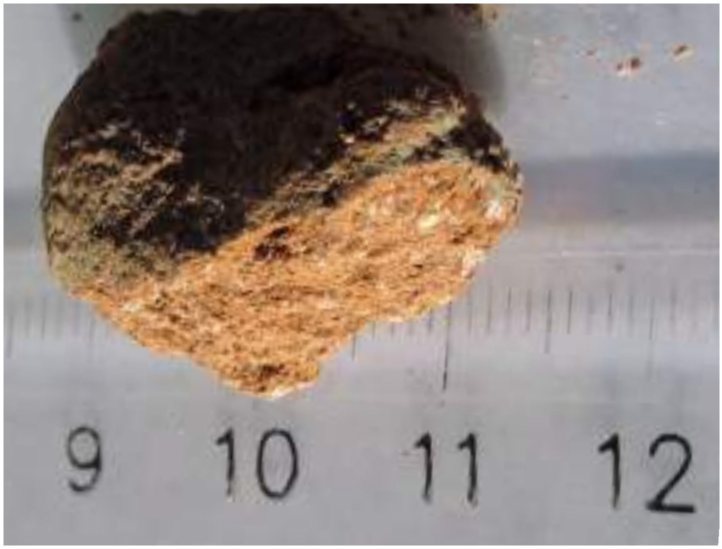


Fig. 44
Sample 2 of clay artefact from Tepe Narenj, Afghanistan. This sample is characterized by a sand fraction in which the grains are poorly attached to each other. Loose sand just from normal handling (photo T. Theye).

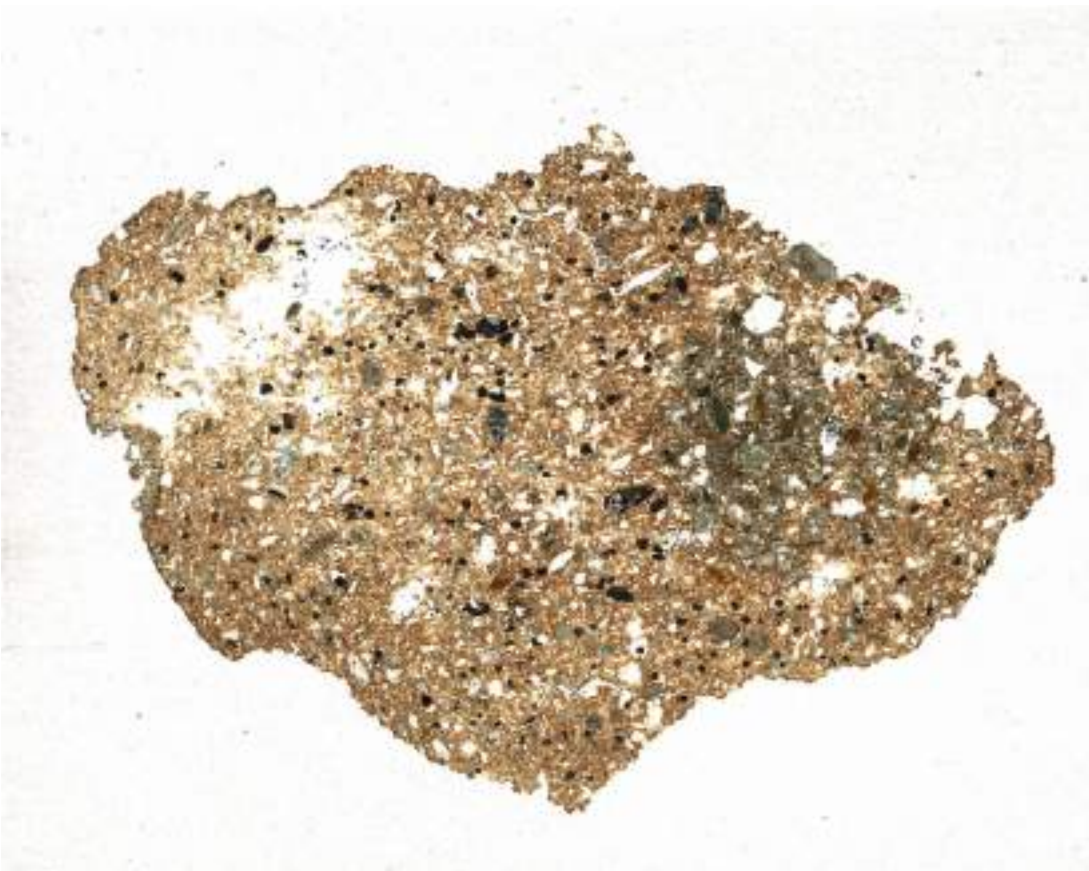


Fig. 45
Sample 2 of clay artefact from Tepe Narenj, Afghanistan: thin section of sample. The width of the image is 48 mm. A brownish component forms the majority of the brick. Note the presence of sand grains embedded in a fine-grained reddish matrix. Small grains of white matter is also present consisting of gypsum, as verified by Raman spectroscopy and electron microprobe.

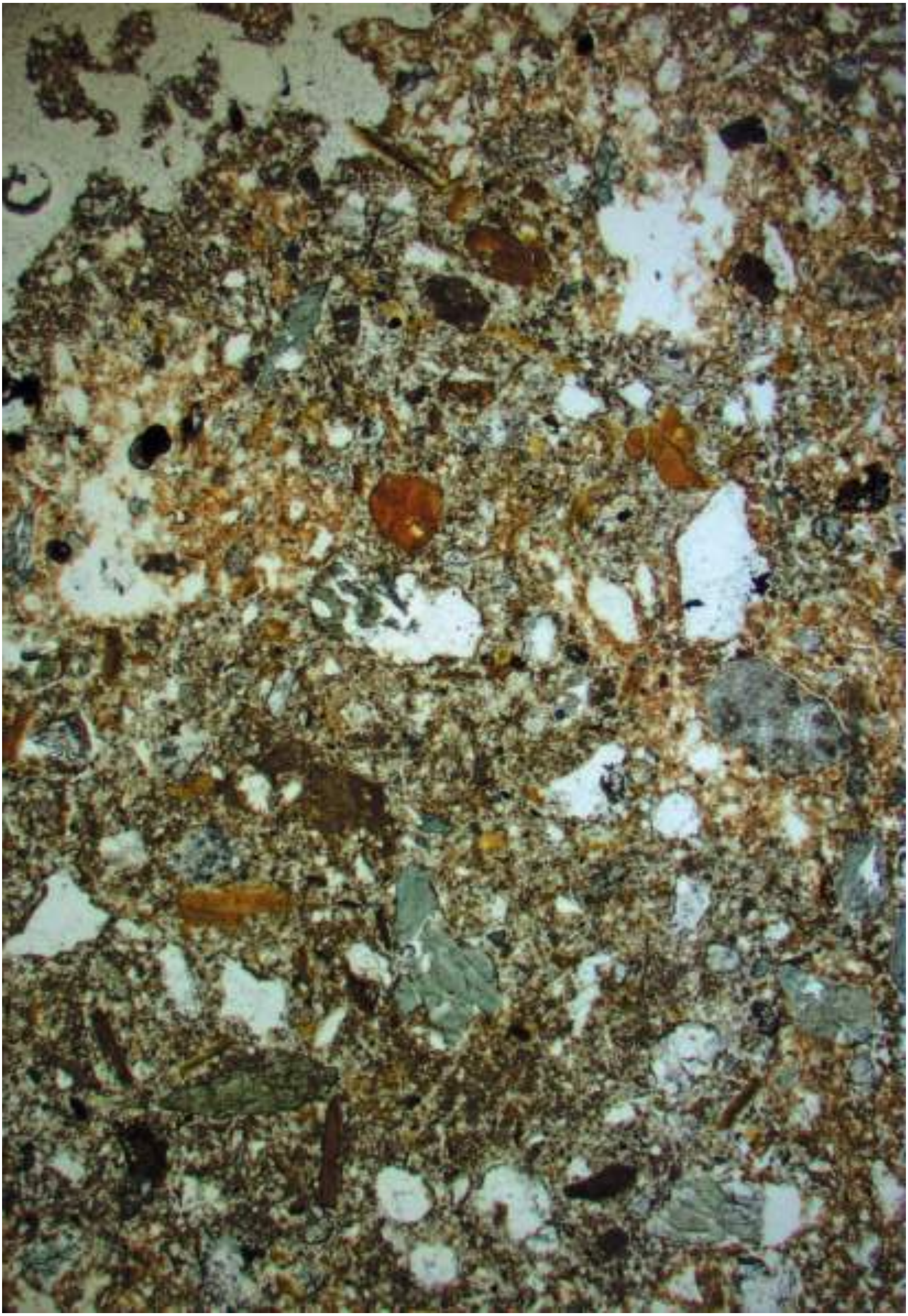


Fig. 47 a, b
Sample 2 of clay artefact from Tepe Narenj, Afghanistan: back-scattered electron image, detail of the microstructure of sample. Pores appear in black. The chemical composition of the binding clay fraction is shown in spectrum no. AAA(3) that shows higher concentrations of the elements O, Si, Al, Mg, Fe, Ca, and K typical for clay minerals. Chlorine is a component of the resin.

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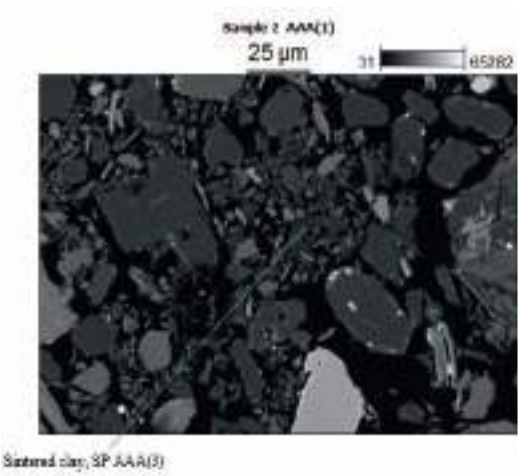

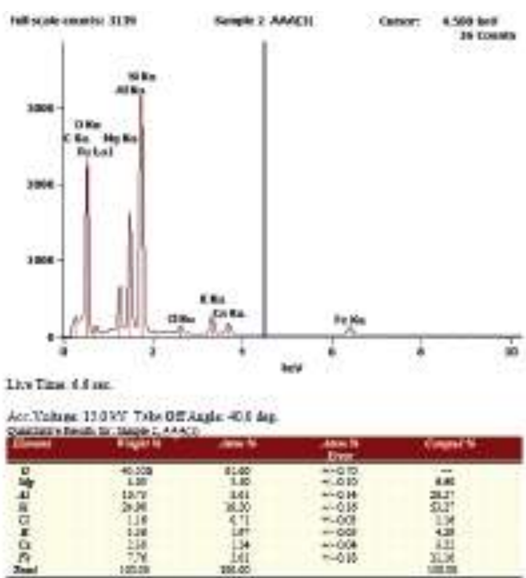

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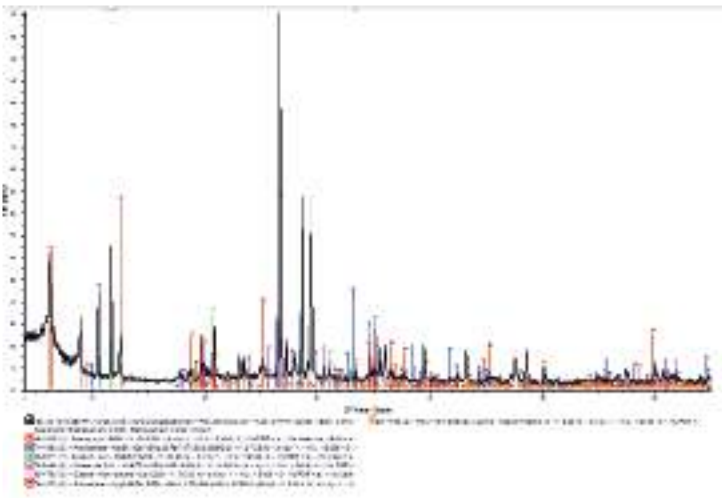

Fig. 48
Sample 2 of clay artefact from Tepe Narenj, Afghanistan: X-ray diffractogram of sample. The following phases can be recognized: quartz, plagioclase (albite), K-feldspar, hornblende, muscovite, calcite, and gypsum.

Polychromy and gilding in the Gandharan sculptures from Pakistan and Afghanistan: samplings from Museum Guimet in Paris, Civic Archaeological Museum of Milan and Museum of Oriental Art of Turin

Simona Pannuzi, Fabio Talarico, Giuseppe Guida

MIBAC, Istituto Superiore per la Conservazione ed il Restauro

Carlo Rosa

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opposite page

Stucco Buddha head from Milan Museum (A 987.03.1, sample 32): the red colour is clearly visible (photo S.Pannuzi).

Abstract

This paper will discuss the scientific results of a recent sampling of the polychrome and gilded stone, stucco and clay sculptures of Gandharan art not yet published. Four years ago, we had the opportunity to begin an articulated research project focused on the Gandharan polychrome stone and stucco sculptures, and in the last two years, thanks to a very limited grant, offered by the Italian Government to the Istituto Superiore per la Conservazione ed il Restauro (ISCR), we had the opportunity to develop a new research. This allowed us to investigate some important artefacts displayed in these Museums: the Archaeological Museum of Milan, the Museum of Oriental Art of Turin, the Museum Guimet in Paris. Moreover, we had the opportunity to take some archaeological samples from the new excavations of the Italian Archaeological Mission in Pakistan and the Italian Archaeological Mission in Afghanistan.

In this new research we analysed the artistic technique of painting and gilding on sculptures of Gandharan art made in different materials (stone, stucco and clay).

The results discussed in this paper comes from a notable number of chemical analyses (optical stero-microscope, SEM-EDS, micro-FTIR, micro-XRD and micro-Raman).

Keywords
polychromy, gilding, stucco arteworks, stone arteworks, clay arteworks, chemical analyses, Gandharan art.

Materials, polychromies and gildings of the Gandhara sculptures and the results of recent scientific investigations

This paper will discuss the scientific results of a recent sampling of the polychrome and gilded stone, stucco and clay sculptures of Gandharan art not yet published. Four years ago, we had the opportunity to begin an articulated research project focused on the Gandharan polychrome stone and stucco sculptures, in collaboration with the Museum of Oriental Art "Giuseppe Tucci" of Rome (ex MNAO, now merged into the *Museo delle Civiltà*) and the Italian Archaeological Mission in Pakistan (MAI), now led by Luca M. Olivieri. In the last two years, thanks to a very limited grant offered by the Italian Government to the Istituto Superiore per la Conservazione ed il Restauro (ISCR), we had the opportunity to develop this research. Our study aimed to clarify some issues, already highlighted in the preliminary

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Fig. 1a, 1b
Elephant schist statue from Museum Guimet. SEM image of cross section of sample 1 with a thick ground layer on the surface.

research. We had the chance to cooperate with several European Museums of Oriental Art: the Museum Guimet in Paris, the Civic Archaeological Museum of Milan (Oriental Art Collection) and the Museum of Oriental Art of Turin (MAO).

This new research allowed to investigate on some important artefacts displayed in these Museums: the Archaeological Museum of Milan has an interesting collection acquired on antique market and the Museum of Oriental Art of Turin exhibits a part of the artefacts discovered during the excavations by Domenico Faccenna, chief of the Italian Archaeological Mission in Pakistan from the Fifties to the Nineties.

Moreover, we had the opportunity to take some samples from the famous statues with polychromy and gilding from the Gandharan sites in Pakisthan and Afghanistan preserved in Museum Guimet in Paris.

Thanks to this funding, we kept cooperating with the Italian Archaeological Mission in Pakistan and we increased the number of samples of different materials, including a series of plaster samples, some of which with polychromy, found in the recent archaeological excavations of the Italian Mission (2014-15)[1].

Recently, we have also begun to cooperate with Italian Archaeological Mission in Afghanistan, led by Anna Filigenzi, and we had the possibility to analyze some samples from Tapa Sardar, near Gazhni, and Tepe Narenj, near Kabul, two important Buddhist sites of the Gandharan culture.

In the frame of these studies, it has been fundamental to cooperate for the scientific investigations, especially about the binders, with Ilaria Bonaduce and Anna Lluveras Tenorio of Chemical Department team of Pisa University, led by M. Perla Colombini.

The first phase of our study (2014-2015) was focused on technological and conservative issues, concerning, in particular, the polychrome stone sculptures of the Rome Museum collection (ex MNAO)[2]. Only a few petrographic studies were carried in the past on the Gandharan stone and stucco sculptures and on the composition of the stucco; the polychromy and the gilding layers on these artworks were not analysed[3].

In the past geological studies on Gandharan metamorphic schists were scarcely supported by specialized geological mappings[4]. Lithological-petrographic studies were carried out in order to find out if the use of different stones was owed to the proximity of the caves or to political-economic reasons, that changed according to different periods, as in the site of Taxila in Pakistan[5]; but simply, the use of different stones could be depended on the different types and employment of the artefacts.

In our first research, carried out in ISCR in cooperation with Roma 3 University on the samples taken from Rome Museum (ex MNAO), information on the lithotypes on record was considered in the perspective of the local outcrops and the general archaeological and cultural contexts[6].

Petrographic and mineralogical analyses of the samples [carried out with Scanning Electronic Microscope/Energy Dispersive X-Ray Analysis (SEM-EDS) and with X-rays diffraction (XRD)] verified that the main lithotype of

[1] The samples were allowed by MAI in Pakistan/ACT-Field School Project (Cooperazione Italiana allo Sviluppo, UTL Pakistan) with export licence of Directorate of Archaeology and Museums Government of Khyber Pakhtunkhwa/Department of Archaeology and Museums Government of Pakistan. We thank L.M.Olivieri for this.

[2] Pannuzi 2015; Talarico 2015; Pannuzi, Talarico 2018.

[3] About bibliography on this theme, see: Pannuzi 2015, pp.10 and 14, footnotes 8-10). In the latter researches, little attention was given to the polchromy and the gilding of the artworks, although Alexander Cunningham and Alfred Foucher, famous explorers of the late nineteenth century, had already commented on the presence of gilded and polychrome sculptures (Foucher, 1918; Faccenna, 1980, pp. 719-720, note 6).

[4] See for these themes: Rosa, Theye, Pannuzi in this issue.

[5] A search for the schists caves and the technology of architectural stone carving was organized in 1990 by Domenico Faccenna, together with Peter Rockwell (Rockwell, 2006, pp.157-159) and the University of Bari (see e.g.: Di Florio et al., 1993, pp. 357-372; Faccenna et al., 1993, pp. 257-270; Olivieri, 2006, pp. 137-156.
As regards the use of lithotypes in different historical periods in Taxila site: Marshall, 1951, pp. 476-481 and 671-699.

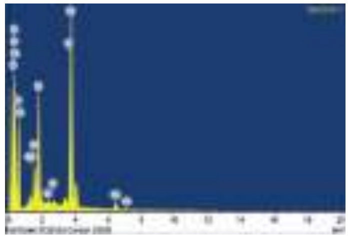
Swat is not a schist, as previously stated, but *serpentinite*. Other less common lithotypes were found such as *talcoschist* and *serpentinoschist*[7]. In the future we hope to implement geochemical studies: we will compare these samples with a stone sampling to be carried out in Swat schist mines. Our aim will be to identify — if possible — the provenance of the stone used for the sculptures in the Gandharan region of Pakistan and whether some stones were preferred because of the vicinity of the quarry to the religious sites or because of the different carving methods.

We are planning to carry on this research about the stone of the Gandharan artefacts, adding other samples taken from reliefs of the Milan Museum, that were acquired through the antique trade. In this latter case, the comparison with already acquired results, could help to establish a geological origin of these stones. Through this comparison we might also understand if an artefact is original or not.

During our new research we decided to extend our investigations also to stucco and clay polychrome and gilded artworks. The selection of samples, from Paris, Milan and Turin Museums[8], was based on the characteristics of the raw materials (stone, stucco and clay) and the polychromy covering with gilding or pigments. In these phase, as well as in the past, micro samples were taken from the back of artefacts preserved in the museums, or in spots where the surface films were already detached.

Moreover, our interest was devoted to the stucco architectural decorations of the religious monuments of Buddhist sites in Swat (Amluk-dara, Barikot and Gumbat), discovered during the recent archaeological excavations[9]. These stucco samples come from the walls of some collapsed buildings, decorated with coloured patterns on the stucco coatings and on the polychrome stucco architectural and figurative elements; the coloured surfaces of the walls were damaged by weathering. These samples are very important for their precise dating elements, deriving from the stratigraphic contexts, even though they are not fine artefacts as the sculptures kept in the Museums. We developed a growing interest in detecting the precise composition of stucco artefacts from archaeological excavations and from Museums, the kind of pigments and the binders used on the stucco artefacts. Moreover, it was interesting to compare the various type of stucco used to made artworks, come from different sites of Gandhara. These new scientific data could be compared with the few others highlighted in the past about stucco in Gandharan art[10].

By scientific investigations (optical microscope, FTIR, SEM-EDS analyses) on artworks kept in the Museums, we noted the presence of calcite, gypsum and clay in the plaster of Head of Salabhanjika from Hadda (near Jalalabd) preserved in Museum Guimet (samples 6, 7)[11]. Indeed, also in the plaster of an important artwork of Milan Museum, the painted monk statue (sample 22), we detected the high presence of the gypsum in the plaster, while another stucco Bodhisattva statue of Milan Museum reveals a calcium carbonate matrix with heterogeneous grains (iron, potassium, sodium, silicon-aluminate) (sample 23).



[6] Petrographic studies followed the standards of stone identification of the International Union of Geological Sciences (IUGS): see Guida et al., 2015.

[7] Guida G. et al. 2015.

[8] About the Gandhara sculptures of these Museums see e.g.: Verardi, 1991; Provenzali,2005 and in this periodical; Bartoux, 1933; Hackin, 1940; Cambon, 2004, 2010, 2013 and in this periodical.

[9] About this theme see e.g.: Faccenna, 1980; Faccenna, 1995; Callieri et al., 1992; Callieri et al., 2000, pp. 191-226; Faccenna, 2002a; Faccenna, 2002b; Faccenna and Spagnesi, 2015; Olivieri, 2015; Olivieri and Filigenzi, 2018.

[10] Barthoux, 1933, pp.45-47; Faccenna, 1980, pp.703-718; Varma, 1987, pp.13-16: the scholar precisely identified two type of stucco used in Gandhara art, a mixture of quick-lime and sand and a "gypsum compound"; Middleton and Gill, 1996; Ohlídalová et al., 2016, pp.124-131. About sculptures of North India see also: Kumar, 1984.

[11] Barthoux had already noted the presence of gypsum in the stucco statues discovered in his Hadda excavations: Barthoux, 1933, p. 46

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Fig. 2a, 2b
Schist statue of Maitreya from Museum Guimet. SEM image of cross section of sample 5: thick ground layer on the surface.

By petrographic microscope, SEM-EDS, XRD analyses, the fragments of stucco architectonic decoration from the archaeological excavations in Swat show mostly a plaster with calcite, and sometimes fragments of quartzite, granite, gneiss, garnet, marble and mica flakes, produced from limestone with a certain fraction of clay added, in which the gypsum is always absent.

The use of stucco decoration in the Swat valley is certainly notable but the "kanjur" stone – the limestone probably used for realised stucco artefacts, considering that the petrographic analyses have shown a chemical compatibility, belongs to another geological areas of Pakistan. The area of Taxila, other important Gandharan site, is one of the nearest (others are e.g. Buner, Swabi). Based on this we suppose that the Swat sites imported limestone from an external area, in order to build and to create stucco architectonic decoration and sculptures[12]. This import is a considerable change for the economy of Swat sites at the end of the 3th century A.D. In the future, the new historical and archaeological research about Gandharan culture will have to check why this stone was used in those times instead of the schist rock[13].

Instead, the artefacts from Hadda in Afghanistan were surely made with a local conglomerate and sandstone rocks, that it can easily find in that region, as also gypsum that in some cases was used in the plaster.

Then, we compared the pigments and their possible ground layers on stucco artefacts, both from excavations and Museums, with the polychromy of stone sculpture already analysed in the past to verify if the same polychrome technique was used for different materials or if in the Gandharan area two different methods were used to produce painted stone and stucco objects.

White ground layer for painting polychrome decoration is clearly visible on the schist artworks and it is sometimes very evident and thick as a base for painting over the raw stone surface of statues and reliefs (1, 3, 5 samples from Museum Guimet and 25-26, 27-28-29, 30-31 samples from Milan Museum)[14]. By SEM-EDS and FTIR analyses on the schist samples, the composition of this white ground layer shows a high amount of calcium carbonate and aluminum-silicate; in some cases, we also observed inclusions of iron, titanium, zirconium and gypsum[15].

Instead, this white ground layer is not usually visible on all stucco artefacts, probably because is not usually necessary for this material: on these artefacts we noted only a smoothing white surface and over the polychrome layer. We verified this lack of a real ground layer both on the stucco statues from different Museums[16] and on the fragments of the painted architectural decorations. Instead, in a stucco cornice from Butkara I stored in Rome Museum (ex MNAO) (n.1240), by Scanning Electron Microscopy (SEM-EDS) we verified the presence of four different ground layers for overlapping red pigment, containing calcium: in this case we suppose that these ground layers were the trace of successive ancient restorations of polychromy[17]. Therefore, it is possible to hypothesize that for par-

[12] See Rosa, Theye, Pannuzi, in this issue.

[13] This argument was examine by L.M.Olivieri during the last Conference at Courtauld Institute of Art in London (Spring 2016). Also see about it: Olivieri and Filigenzi, 2018, pp. 81-85.

[14] This ground layer was preserved when the incorrect restorations or the times did not destroy it.

[15] Moreover, we also noted the high presence of calcium, sometimes combined with coloured layers, on the surface of the limestone artefacts (e.g. sample 11 from Museum Guimet), a fair but permeable stone.

[16] It was very interesting the analysis of the cross section of a stucco artwork from Milan Museum (sample 22): it showed the lack of the ground layer and the absorption of red colour into the surface of stucco, as still not solidified.

ticular purposes, e.g. for restorations, even the stucco artefacts could have had a background under the colour layers.

Recently, for an exhibition in National Museum of Prague, Czech équipe analysed Afghanistan stucco artworks with a clay core: they noted that on the artworks made in lime stucco the thick polychrome layers are directly applied on the plaster, as in the cases that we studied[18].

Then, also on painted clay artworks we verified the possible presence of the ground layer.

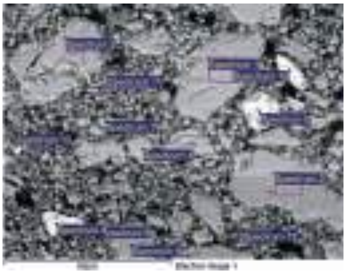
On some samples (15, 17 and 20, Two Naga Kings and Seated Buddha) from Museum Guimet, SEM-EDS analysis of the cross sections showed a lower red orange layer, characterised as red lead (minium) for the high presence of lead, under the blue (lapis lazuli), yellow (orpiment) and red (vermillion) pigments. Instead, on another artwork of the same Museum (samples 18 and 19, statue of Bodhisattva) under the blue ultramarine pigment we noted a red ground constituted by a red ochre mixed with calcite. On artwork from Milan Museum (sample 33, Brahma Head) yellow pigment (an ochre) was lied on a red layer achieved with a red ochre.

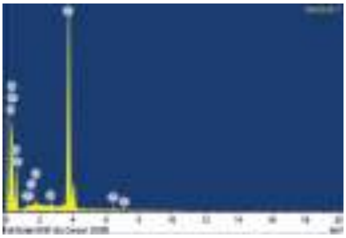
So, it would seem that also the clay artefacts had a kind of ground layer for the polychromy: above the red clay it was made with another coloured layer, always red, not white like that of stone artworks. Probably, we suppose that this red covering was laid on whole surface of clay artefacts also to make uniform those parts that should not have been painted later. We think that this is more a coloured surface finish than a real ground layer for the polychromy. It needs to verify this hypothesis in the future with other analyses.

Therefore, we always verified the need of a ground layer or a surface finish for painting on the Gandharan sculptures. The artists used these ground layers as a base with a uniform colour, on which they could then paint. Thus, these ground layers were made in different ways on different raw materials.

Moreover, we noted a various use of colours for painting the stone, stucco and clay artworks: red, with various hue, yellow, white, blue, with various hue, black. Thanks to scientific investigations we highlighted that the Gandharan artists used many pigments: ochre, red lead (minium), vermillion, orpiment, lead white, blue ultramarine, bone black. We also highlighted in some cases the particular techniques to stratify different pigments on the surface and to mix different chemical elements probably to obtain a colour with particular shades. Furthermore, it seems that red ochre from hematite (iron oxide) is the most used pigment for the polychrome decoration on stone and stucco artefacts, usually upon a white ground layer on the schist artworks[19], as we highlighted in our previous sampling in Rome Museum (ex MNAO)[20].

On stucco artifacts more colours are used perhaps than on those in stone. Domenico Faccenna noted in Butkara site (Swat Valley, Pakistan) the use of various pigment to paint on stucco works, both ornamental and figured, and on schist sculptures[21]: red, with different shade (red ochre), yellow (yel-





[17] Talarico 2015, pp.55-5 and 59.

[18] Ohlídalová et al., 2016, pp.127-128. This équipe studied a different type of stucco artefacts with inside a clay core: lime stucco (statues) and gypsum stucco artworks (heads of Buddha with a gilded covering of the whitish gypsum stucco, in the latter case). Some details of these heads, e.g. the eyes, are painted, but in the Czech work it is not explained the stratigraphic relationship between coloured layers, gilding and stucco surface.
In our research we didn't analysed stucco artefacts with inside a clay core, a more elaborated technical and decoration, that Varma well described (Varma, 1987, pp.41 and 63-75). Therefore, in the next future we would also examine in depth this type of artworks and compare the use of pigment and gilding with the stucco alone artefacts.

[19] By new sampling only one a schist sample from Milan Museum (simple 30) preserved the traces of red polychromy (probably hematite) upon a white ground layer.

[20] Talarico, 2015, pp.55, 56, 59. The prevalence of the use of the red colour was also highlighted on coloured patterns of paintings from ancient sites of Central Asia (Lapierre, 1990, pp.33-34), in Indian sculptures and reliefs (Giuliano, 2015, p. 22, 24) and also in Greek and Roman wall paintings and coloured architectures and sculptures. Certainly, this colour, when made with red ochre, shows a great stability over time.

low ochre), blue (lapis lazuli) and black (ivory black), and also green, though these pigments were identified by microscopic preliminary analysis without more precise scientific investigations[22].

In his important research about Gandhara stuccos K. M. Varma examined the mode of colouring stucco artworks and listed the colour used in order of frequency of employment: red, red-brown, black, grey black, crimson and blue. The scholar did not chemically analyse the pigment but only related the colour vision verified on many artefacts. Thus, he supposed the use of some pigments (e.g. vermillion, lac, lampblack), some of which we've not found in our analyses about Gandhara stucco artworks[23].

Successively, some studies were carry out on polychromy of stucco sculptures of British Museum but it seems without specific analyses, only using binocular microscope: they noted that "many of piece present very smooth, well-finished surfaces (...) achieved by the application of a thin layer of fine plaster, termed slip", with a similar composition of the body of the stucco[24]. Sometimes this slip was pale bluff or yellow due to the presence of ochre. In this paper is not clear if we have to consider this slip as a finish of the stucco surface or a real polychromy.

However, the scholars noted that the "polychrome decoration" (generally with the use of black, red-brown, blue and also gilding) was limited only on some part of the sculptures examined (e.g. hairs, eyes, lips and dresses)[25].

By some scientific investigations (optical microscopy, SEM-EDS, XRD, Raman spectroscopy, FTIR, XRF) Czech équipe highlighted on lime stucco artefacts the presence of hematite, sometimes perhaps in combination with gypsum and a red dye to achieve a pink colour; to made black they suppose a mixture of bone, carbon black, gypsum and plant fibres. They verified on the gypsum stucco artworks the use of lampblack and of orpiment in grains under the gilding[26]; they also found cinnabar on the red painted lips of the Buddha head[27].

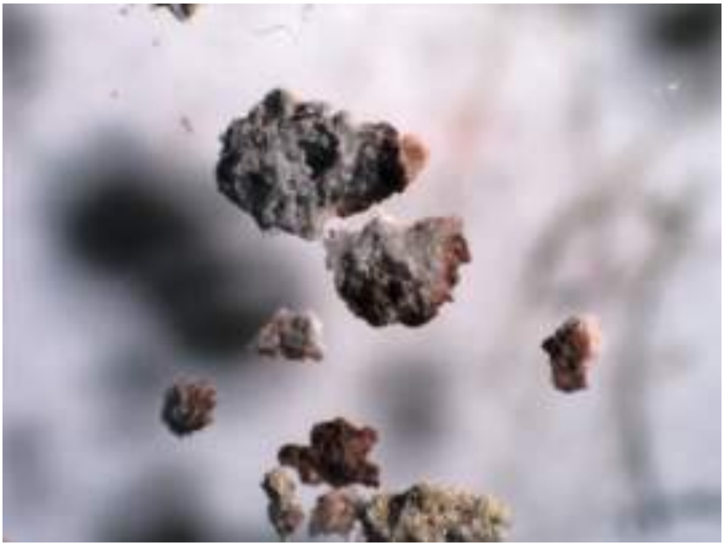


Fig. 3
Hadda's head from Museum Guimet, sample from headgear: microphotography of sample 6 (red layer and stucco mixture) (25x).

[21] Faccenna, 1980, pp.719-721. During the restorations, by microscopic preliminary analysis the restorer Franca Callori di Vignale, verified the use of tempera and fresco techniques to paint in successive times the Buddhist buildings: Faccenna, 1980, pp.704, 707. They noted that the pigments were applied directly on the surface of the stone artefacts or "laid on a red bole" (for gildings), not better specified (Faccenna, 1980, p. 720).

[22] It has already been highlighted that the green colour was rarely preserved, and probably used, in wall paintings found in ancient settlements of Central Asia (Bactria, Sogdiana and Parthia) and in Indian art. Probably its absence, or limited presence, was due to the discolouring of the green colour (also Varma noted that this colour was not employed in Indo-Afghan stuccos: Varma, 1987, pp.122-123); according to some scholars, this scarce use of the green colour was perhaps due to its lack in the palette of five main colours mentioned in some Sanskrit texts (Lapierre, 1990, pp.34, 37. Giuliano reports its presence in some of more ancient texts: Giuliano, 2012, pp. 58, 62; Giuliano, 2013, p.96). However, these texts were written in more recent time than the Gandharan period, but they show the ancient artistic tradition; about the relationship between these texts and the real artistic practise: Giuliano, 2013, pp. 108-113.

Fig. 4
Stucco Buddha head with traces of colour from the Civic Archaeological Museum of Milan (A.987.03.1) (photo S.Pannuzi).

About the palette of the colours used interesting comparisons can be verify with the ancient Central Asia and Indian paintings and sculptures[28].
By SEM-EDS analyses we examined the traces of red ochre, (samples 22, 23 and 32) and yellow ochre from samples of Milan Museum (samples 32, 33). The cross section of the sample from Hadda Head of Museum Guimet (sample 7) shows over the stucco a red layer of ochre and then another layer of red lead (minium): in this case we suppose that, perhaps, this overlapping was an ancient restoration of the polychromy or a refined way to achieve a pinkish colour. Moreover, we analysed another sample from a limestone Hadda relief with a particular polychrome covering: the blue ultramarine, made by lapis lazuli, was mixed to a few grains of red pigment (hematite) and lead white to get a pale blue colour (sample 10 from Museum Guimet). Certainly, this latter polychrome covering reveals a high artistic level and a great experience to use the different pigments.
We verified that the Gandharan artists usually spread the colours on the surface when the stucco plaster was solidified, but in one case (sample 22 from Milan Museum) our analyses showed that the red colour was

It needs to rectify that the colour visible on the stucco artifact of the ex MNAO (inv.1240) was not green but a blackish colour not identified in that research (Talarico, 2015, p. 53; Giuliano, 2015, p. 22).

[23] Varma 1987, pp. 113-126. Thus far, e.g., we never found lac, although this pigment was use in ancient Indian art: see e.g. Giuliano, 2012, p. 59.

[24] Middleton and Gill, 1996, p. 367. The research on the stucco sculptures of the British Museum highlighted a different compositions and modelling tools and the use of polychromy and gilding (Middleton and Gill, 1996, pp. 363-368).

[25] Middleton and Gill, 1996, pp.363-368.

[26] Yellow colour under the gilding was also noted on clay arteworks from Nisa: Bollati 2008, p. 180.

[27] Ohlídalová et al., 2016, pp. 128-131.

[28] About these themes see e.g.: Varma, 1970, pp.106-108; Kumar, 1984, pp. 199,203; Lapierre, 1990; Bollati, 2008; Appolonia et al., 2008; Capanna et al., 2012; Giuliano, 2012 (in particular for the use of lead white and orpiment in Ajaṇṭā painting: pp. 61, 63); Capanna, 2013; Giuliano, 2013; Giovagnoli et al.,2013; Iole, Giovagnoli, Mariottini, 2013; Iole, Giovagnoli, Artioli, 2013.

Fig. 5
Hadda's head from Museum Guimet, sample from cheek: micro-photography of sample 7 (100x).

Fig.6
Hadda's head from Museum Guimet, sample from cheek: SEM image of sample 7.

opposite page

Fig. 7
Sampling of Hadda's relief from Museum Guimet (sample 10) (photo S.Pannuzi).

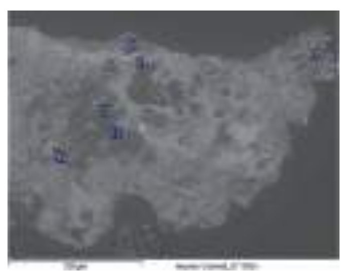
Fig. 8
Hadda's relief from Museum Guimet: micro-photography of sample 10.

absorbed into the surface of stucco: we can suppose that the plaster was heterogeneous and the pigment was fluid or, most probably, that the stucco mixture was not still solidified. Thus, we can reasonably hypothesize not a hastily work to make this artefact, but on the contrary, the aim to achieve on purpose a better duration of the painted covering, through an integration between colour and stucco similar to a fresco technique.

On the surface of some samples from stucco architectural decorations form Swat, we noted a few traces of very pale, faint and dilute red colour: by preliminary investigations (Raman analysis) we verified the use of the red ochre (hematite)[29]. We hope in next future to analyse thoroughly.

Concerning the clay artworks of Gandharan art, found in Afghan sites, their loamy composition and the type of pigments used for the polychromy we have little bibliographic informations[30]. Unbaked polychrome clay sculptures, mostly Buddhas and Bodhisattvas, were recently found in Mes Aynak excavations: the colours preserved are red, black, blue, white and gilding on the Buddha heads[31]. In comparison with these our investigations we analysed the data about clay polychrome sculptures from Nisa excavations in Turkmenistan[32]. There it was used cinnabar and red ochre for red colour, red ochre with kaolin for pale pink, lac for pink, yellow ochre for yellow colour, blue Egyptian and lapis lazuli for blue colour, lampblack for black colour and kaolin and gypsum for white ground layer for painting[33]. In that site it was noted a very developed processing techniques to make pigments.

The results obtained in our research on clay sculptures will need further analyses regarding the production of the clay mixture, always unbaked but in some cases baked at low temperatures, as we are checking with our analyses[34]. On clay artworks we highlighted the presence of different pigment for polychromy, also with a stratification: by SEM-EDS analyses on the cross section of sample taken from Two Naga Kings statue of the Museum Guimet (from hair) we found on the clay surface a red orange layer with lead (minium) (sample 15) with overlapping lapis lazuli layer (blue ultramarine); in another sample taken from the same artworks (sample 17) (from ear) under the yellow colour (orpiment) the analysis showed a lower red orange layer (minium), already found in the first sample. Moreover, on the surface of clay statue of Bodhisattva from Fundukistan (from hair) we found a red layer with iron (red ochre) with an overlapping blue ultramarine layer, that visually turned to a black colour (sample 18); instead on



[29] See Rosa, Theye, Pannuzi in this issue.

[30] A few hints about this theme in: Fussman, Le Berre, 1976, p.78; Verardi, 1983, pp.479-502; Tarzi, 1990, pp.57-93. About the Gandharan art in Afghanistan settlements see e.g.: Taddei and Verardi,1978, pp.33-135; Taddei and Verardi, 1981, Taddei, 1993, pp.118-122; Filigenzi, 2008.

[31] The clay sculptures were compared to the artworks from Kabul area (IV-IX century A.D.). In Mes Aynak excavations the archaeologists also found stone and plaster sculptures (AA.VV., 2011, p. 32).

[32] Bollati, 2008, pp. 188-189; Appolonia et al., 2008, pp. 197-209.

[33] As indicated before, on clay sculptures analysed from Paris and Milan Museum we found under the polychromy a red layer, not white as on Nisa clay sculptures.

[34] By polarized optical microscope, preliminary analysis on Tapa Sardar sample indicated that this clay mixture baked with low temperatures, because calcite, still well-formed, indicates surely temperatures below 600°C. I thank Anna Lluveras Tenorio for this important information. See also Rosa, Theye, Pannuzi in this issue.

the garland of this same statue (sample 19) we found a complex stratification: a layer with lead compound mixed with calcium silicate and lapis lazuli covered a layer with lead white (cerussite/hydrocerussite) mixed with bone black (calcium phosphate) spread on red ochre layer visible on the clay surface. On clay seated Buddha from Museum Guimet (sample 20) we saw two different red layers overlapping: with lead the lower one and with cinnabar (vermillion pigment) the upper one. Then, a clay Brahma Head from Milan Museum (sample 33) showed the presence of two different coloured layers, red below and yellow above, together made with ochres.
By this overlapping of colour layers, always with the red below, we suppose that this is more a clay surface finish than a real ground layer for the polychromy (see above). We suppose that on the clay artworks this red layer, with red lead (minium) or red ochre, was used as a ground layer, spread on the artwork surface to paint over with other different colours (see above).
Moreover, very interesting results are issued by analyses on schist sculptures with visible and now invisible traces of gilding. The investigated gildings were always constituted of a gold leaf made with a high percentage of gold and little copper and silver (indicatively by our analyses, the amount of gold is between 93.04% and 97.26%, copper between 1.27% and 5.14%, silver between 0.78% and 2.26%.). In all cases the gildings were put on different ground layers: a bolus composed by hematite, gypsum and clay, similar to the typical technique for gildings in Mediterranean area (sample 13 from Museum Guimet and sample from Saidu Sharif excavation[35]); a red layer composed by calcium and lead (probably minium) (sample 14 from Museum Guimet); a ground layer was composed by a whitish mixture of clay, red ochre and mainly with the presence of calcium (standing Buddha from Milan Museum, sample 21); a mixture of silicon, aluminum and calcium (samples 34,35 from Turin Museum).
On sample 12 from a very famous statue of Buddha from Paitava monastery in Afghanistan, kept in Museum Guimet, SEM-EDS analysis showed a different chemical composition in different fragments of the leaf: one of these had less gold and more copper percent, while the silver was a similar percentage to other fragments. We supposed that this part of the gilding could have been restored in ancient time, as we already noted for other Gandharan artworks[36]. These data clarify the presence of continuous maintenances, carried out by artists to preserve the beauty of the sacred images.
Finally, by FTIR analysis, GC-MS and MS proteomics analysis[37] we thoroughly examined the type of binders used for stucco and clay polychrome artworks and the technique used to achieve gilded stone artworks. These investigations clearly showed different types of binders for polychromy and gildings, especially proteinaceous materials: only animal glue[38] [sample 21 (gilding), sample 22 (polychrome stucco) and sample 25 (polychrome clay) from Milan Museum]; animal glue, milk[39] and eggs together (samples 15-17 and 18-19 from Museum Guimet); a protein binder, probably eggs[40] (samples 12-13 from Museum Guimet)[41]. On one clay fragment from Tapa

[35] See the results discussed in Zaminga et al., in this issue.
In Butkara site Domenico Faccenna already highlighted the presence of typical bolus under the gildings; in other cases the gilding was laid directly on the surface of the stucco artefacts (Faccenna, 1980, p.720).
[36] Pannuzi, 2015, p.12; Talarico et al., 2015, p.59; Zaminga et al., in this issue.
[37] The proteomics analysis is one of the most promising analytical approaches to identify proteins, introduced in the field of cultural heritage about eleven years ago See the results of GC-MS and proteomics analysys discussed in Bonaduce et al., in this issue.
[38] Animal glue is obtained by boiling bones, hide or other cartilaginous parts of animals; it is made of, collagen partially hydrolysed.

opposite page
Table 1
Sample 1, SEM-EDS spot analysis by the cross section. All results in weight %.
Table 2
Sample 5, SEM-EDS spot analysis by the cross section.
Table 3
Sample 9, SEM-EDS spot analysis by the cross section.

Sardar in Afghanistan it is very interesting the identification of tragacanth gum as the polysaccharide binder used in the clay mixture and a proteinaceous binder in painted layer[42]. Vegetable gum was noted also by analyses recently achieved on stucco artworks by Czech équipe[43] and on painted layers of clay samples from the lost Giant Buddhas of Bāmiyān in Afghanistan (6th-7th century AD)[44].
By GC-MS analysis on samples of architectural decoration from Swat excavations (Amlukdara, Gumbat and Barikot) traces of proteinaceous material have been highlighted as binder in the red painted layers (not animal glue, perhaps egg)[45]. Very interesting was the analyses on a sample collected from a polychrome decoration on plaster coming from Amlukdara in Pakistan (sample AKD14C): on ground layer of colour GC- MS analysis showed the presence of proteins, most likely milk or egg white. By proteomics analysis on the painted layer the identification of 26 peptides ascribable to collagen allows us to ascertain the presence of animal glue in the sample. Moreover, a comparison of the peptide sequences with the available databases allowed us also to identify the specific biological source of the collagen: bovine[46]. In next future, we would understand if different binders have been purposely used on different raw materials or if the choice of the binder was connected to the costs and to the natural resources available to the artists in different sites.
In conclusion, in Gandharan sculptures we highlight the use of different ground layers, pigments and gildings with various, refined and expensive technology to paint and to gild the artworks. Indeed, although lapis lazuli[47], lead, iron, gold[48], silver and copper are present in large amount in the Afghan and in Pakistani regions, we have to consider the costs of the different productions of the pigments, the gildings and especially the binders with eggs and milks. Thus, in the future, we will try to understand if these different artistic modalities to work were due to different and not local traditions, come to the Gandharan sites through trades or invasions of foreign people, or if these various artistic technologies were specific creations of Gandhara artists in different times[49] and sites, linked with the local different resources.
(S. P.)

Gandharan artworks from Guimet Museum in Paris: chemical analyses on polychromies (see Sampling List)

Sample 1

By SEM-EDS spot analysis by the cross section of the sample, taken from an Elephant schist sculpture, the spectra 1, 8, 9 show the presence of a high amount of calcium carbonate (figg.1A and 1B, tab. 1), to be referred to a white substance applied over the schist stone and used for a polychrome decoration that is now lost. Considering the geo-archaeological origin of the land in the Ghandara area, there is no reason to presume that this layer has a natural origin due to the presence of water, rich in carbonates, in the earth where the objects were found.

[39] Milk is a water emulsion of proteins and lipids.

[40] Eggs can be used whole, or using only one of its components: yolk or glair.

[41] It is very interesting the presence of saccharidic and proteinaceous materials in subsequent painted layers of the lost Giant Buddhas of Bāmiyān, Afghanistan, (6th-7th century AD) (Lluveras Tenorio et al., 2017).

[42] See the results about clay of sample 1 from Afghanistan: Rosa, Theye, Pannuzi, in this issue.

[43] Ohlídalová et al., 2016, pp. 128-130. Moreover, on gilded gypsum stucco artwork the Czech équipe noted the presence of a binder probably based on polysaccharides (p.131). The presence of this type of binder (polysaccharides) has also been identified on polychrome clay artefacts from Nisa excavations (Bollati, 2008, p.188, n.134).

[44] The tragacanth gum was found in the clay modelling of the sculptures and in the following restorations of the painted covering (with egg) (Lluveras Tenorio et al., 2017, pp.8, 12-13). Instead milk and egg were found as binder of original polychromy and of first historical restorations.
On Central Asian paintings the binder with vegetable origin, probably a gum, was discovered (Lapierre, 1990, p.35). The use of gum was report by Sanskrit texts (Giuliano, 2012, pp.59-60; Giuliano, 2013, pp.101-104).

[45] Report of Pisa University (20-10-2015) to ISCR.

[46] See Bonaduce et al. in this issue.

[47] About lapis lazuli quarries see, e.g.: Varma, 1970, p.165 note 76.

[48] Chinese pilgrims reported that the Gandharan monasteries in Swat possessed mines of gold and iron (Tucci, 1958, pp-280-281).

Table 1

Spectrum	Na	Mg	Al	Si	S	Cl	K	Ca	Mn	Fe	Total
Spectrum 1	0,00	2,06	7,29	20,37	0,60	0,90	1,89	61,19	0,00	5,70	100
Spectrum 2	0,00	0,00	4,88	84,05	0,00	0,72	0,58	5,94	0,00	3,82	100
Spectrum 3	0,00	0,76	4,85	82,36	0,00	0,76	0,81	5,56	0,00	4,90	100
Spectrum 4	0,90	0,00	13,81	64,61	0,00	1,20	3,55	10,81	0,09	4,55	99,54
Spectrum 5	0,00	2,1	31,9	29,3	0,00	0,79	0,88	2,56	0,35	31,16	99,05
Spectrum 6	0,68	1,4	29,02	32,31	0,00	0,81	0,54	4,24	0,00	31,00	100
Spectrum 7	0,00	1,65	29,84	26,53	0,00	1,00	0,87	7,26	0,28	31,62	99,06
Spectrum 8	1,14	1,43	7,45	23,74	0,59	1,14	3,45	56,4	0,00	4,67	100
Spectrum 9	0,00	1,66	5,19	15,98	0,00	1,14	1,01	71,85	0,00	3,16	100

Table 2

Spectrum	Mg	Al	Si	Cl	K	Ca	Fe	Total
Spectrum 1	0,37	0,54	1,27	1,27	0,00	93,27	3,28	100,00
Spectrum 2	0,74	0,68	1,05	0,85	0,00	94,45	2,23	100,00
Spectrum 3	0,00	0,58	1,09	0,96	0,00	95,39	1,98	100,00
Spectrum 4	0,48	0,62	1,49	0,73	0,00	94,61	2,07	100,00
Spectrum 5	0,00	0,00	1,65	1,10	0,00	95,42	1,83	100,00
Spectrum 6	0,00	0,00	1,26	0,98	0,00	94,88	2,88	100,00
Spectrum 7	0,40	0,97	1,66	1,26	0,00	91,63	4,08	100,00
Spectrum 8	0,00	2,38	3,97	0,74	0,00	36,12	56,79	100,00
Spectrum 9	0,00	1,83	3,03	1,20	0,67	38,53	54,74	100,00
Spectrum 10	0,89	2,49	3,45	0,89	0,78	36,32	55,18	100,00
Spectrum 11	0,00	1,04	1,96	1,61	0,00	91,86	3,53	100,00
Spectrum 12	0,00	0,98	3,24	1,72	0,00	90,80	3,28	100,00
Spectrum 13	0,00	1,18	2,24	3,38	0,00	89,62	3,58	100,00

Table 3

Processing option: All elements analysed (Normalised)

Spectrum	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	As	Pb	Total
Spectrum 1	1,25	0,00	1,37	4,04	4,04	0,00	4,77	1,31	13,72	0,00	9,20	60,30	100
Spectrum 2	0,00	0,00	0,00	6,50	5,26	0,00	4,85	1,20	21,88	0,00	8,88	51,43	100
Spectrum 3	0,00	0,00	1,39	4,20	4,68	0,00	5,55	1,32	23,34	0,00	9,62	49,90	100
Spectrum 4	2,49	11,92	4,21	36,80	1,13	1,67	2,53	1,79	28,70	1,17	0,51	7,09	100
Spectrum 5	4,49	6,71	8,13	31,29	0,00	4,67	3,78	2,67	27,29	0,00	2,09	8,89	100
Spectrum 6	1,97	4,27	8,37	16,32	3,04	3,68	6,51	4,05	14,03	5,39	3,41	28,96	100
Spectrum 7	0,83	3,42	1,68	7,12	0,73	0,86	1,68	1,35	5,01	67,99	1,01	8,32	100

In the lower layer of the cross section, the presence of Ce, Nd, and Th (group of Lantanidi) is common in the schist stone, as well as the presence of Ti, often combined with iron.

Sample 2

This sample was taken to an Elephant schist sculpture (see sample 1). SEM EDS analysis is only referring to the schist stone. Zr is contained in the sam-

[49] We hope that it will be possible to clarify the chronology of the various Gandharan artefacts (see Ingholt, 1960), especially with the help of new historical and archaeological researches.

opposite page
Table 4
Sample 11, SEM-EDS spot analysis by the cross section.
Table 5
EDS analyses of gilding from sample 12. Elements are expressed as atomic percent.
Table 6
EDS analyses of gilding from sample 14. Elements are expressed as atomic percent.
All results in weight%.

ple, as commonly in the schist stones. Inclusions of Ti combined with iron are observed.

Sample 3
By SEM EDS analysis the sample, taken from a white layer on the surface of Pakistani schist relief from Buner Valley, shows the presence of a high amount of calcium. Inclusions of iron and Ti are observed too. This layer has to be referred to a white substance applied over the stone and used for a polychrome decoration that is now lost. The analyses do not include the schist.

Sample 4
SEM EDS analyses achieved on sample from Pakistani relief see above (see sample 3) are only referring to the schist stone (with a silico-alluminate matrix). Inclusions of Ti combined with iron are observed too. Thanks to the thin section, despite the small amount of material, it is possible in next future to deepen the petrographic investigation aiming at the definition of the lithotipe.

Sample 5
The sample was taken from a white surface, preserved on the right foot, of the schist statue of Bodhisattva Maitreya from Pakistan. SEM-EDS analyses of highlighted the presence in the spectra of an abundant amount of calcium, probably in combination with calcium carbonate, owed to a white preparation layer, put on the surface of the stone and used for a polychrome decoration that it has now been lost (figg.2A and 2B, tab. 2).
(G. G., C. R.)

Sample 6
This sample was taken from the headgear of stucco head of Salabhanjika from Hadda (Afghanistan). Micro-FTIR analyses on the powders identified calcite and gypsum in the plaster (fig. 3). As known FTIR technique is unable to detect oxides (e.g. hematite, a red oxide). Micro-XRD analysis detected quartz, calcite and albite ($NaAlSi_3O_8$ – plagioclase feldspar mineral) as main components of plaster.

Sample 7
This sample was taken from the pinkish cheek of Hadda's stucco head (see sample 6). Micro-FTIR analyses on the powders identified calcite and gypsum in the plaster (fig. 4). The result of the analyses about the pigments used on this artwork to achieve a pinkish colour is very difficult to understand. Optical microscope images of the cross-section matched with SEM-EDS analyses seems to show a very thin, discontinuous red layer of ochre; a second red orange layer, slightly more thick, is over imposed to the previous one. Its chemical composition reveals the presence of lead, probably minium. This evidence may be explained as an ancient inter-

Table 4

Processing option: All elements analysed (Normalised)

Spectrum	Na	Mg	Al	Si	P	S	Cl	K	Ca	Fe	As	Pb	Total
Spectrum 1	1,25	0,00	1,37	4,04	4,04	0,00	4,77	1,31	13,72	0,00	9,20	60,30	100,00
Spectrum 2	0,00	0,00	0,00	6,50	5,26	0,00	4,85	1,20	21,88	0,00	8,88	51,43	100,00
Spectrum 3	0,00	0,00	1,39	4,20	4,68	0,00	5,55	1,32	23,34	0,00	9,62	49,90	100,00
Spectrum 4	2,49	11,92	4,21	36,80	1,13	1,67	2,53	1,79	28,70	1,17	0,51	7,09	100,00
Spectrum 5	4,49	6,71	8,13	31,29	0,00	4,67	3,78	2,67	27,29	0,00	2,09	8,89	100,00
Spectrum 6	1,97	4,27	8,37	16,32	3,04	3,68	6,51	4,05	14,03	5,39	3,41	28,96	100,00
Spectrum 7	0,83	3,42	1,68	7,12	0,73	0,86	1,68	1,35	5,01	67,99	1,01	8,32	100,00

Table 5

Spectrum Label	1	2	3	4	5	6	7	8	9	10
Cu	4.58	4.74	3.87	5.14	42.14	29.02	2.74	3.25	1.27	4.86
Ag	1.52	2.22	0.78	1.47	0	5.31	0	1.26	2.26	1.63
Au	93.9	93.04	95.36	93.39	57.86	65.67	97.26	95.5	96.47	93.51
Total	100	100	100	100	100	100	100	100	100	100

Table 6

Processing option: All elements analysed (Normalised)

Spectrum	Mg	Al	Si	P	S	Cl	K	Ca	Fe	As	Au	Pb	Total
Spectrum 1	0,00	2,45	9,93	8,48	2,74	5,32	1,58	14,67	13,92	0,00	0,00	40,90	100,00
Spectrum 2	0,00	1,47	5,99	9,88	0,00	5,55	1,36	19,98	2,79	0,00	0,00	52,99	100,00
Spectrum 3	1,44	3,75	8,62	6,92	0,00	4,84	1,73	14,16	5,03	0,00	0,00	53,52	100,00
Spectrum 4	0,00	0,85	2,43	5,78	0,00	5,44	0,00	11,61	1,53	3,50	0,00	68,85	100,00
Spectrum 5	1,03	3,38	9,87	7,78	0,00	5,66	2,01	15,57	6,19	0,00	0,00	48,52	100,00
Spectrum 6	0,00	0,00	0,00	0,00	0,00	0,00	0,75	5,94	2,63	0,00	90,68	0,00	100,00

vention on the artifact, required to regain the chromatic integrity, or as a device to obtain a pinkish colour (figg. 5, 6). The chemical composition of the greater part of the cross-section is mainly silicon, aluminium, calcium and potassium. The most of calcium is present as carbonate, only a little part is gypsum, thus confirming FTIR analyses. Silicon, aluminum and potassium confirm the presence of clays in the stucco mixture. Spare grains of silica were identified too. EDS map shows iron grains, to refer to red and yellow ochres.

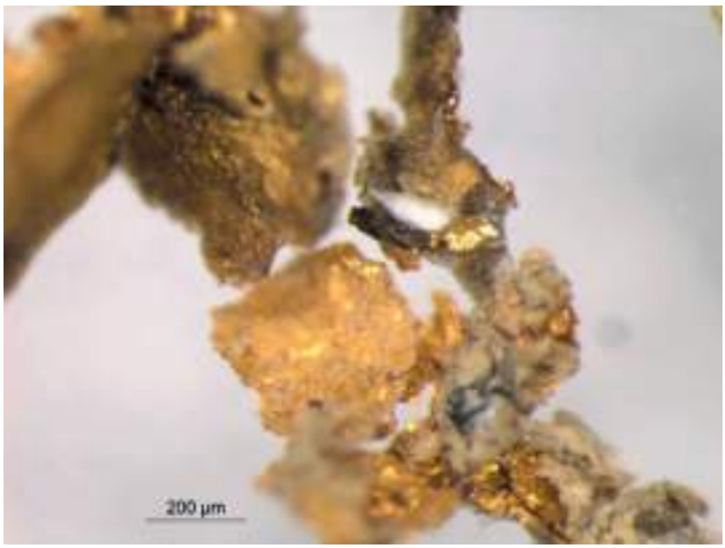
Sample 8 (n. 9 sampling)

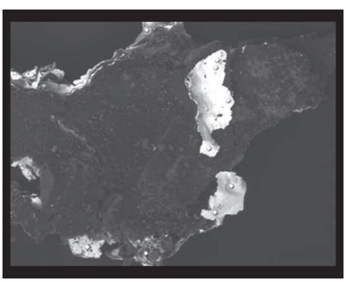
This sample, taken from a figure of red painted limestone relief from Hadda, Tapa-i-Kafariha monastery (Afghanistan), was examined only by micro-FTIR. The main evidences of limestone are the presence of calcium carbonate and silicates. We noted also the presence of calcium oxalate: a

Fig. 9
Buddha statue of Paitava from Museum Guimet (sample 13): micro-photography. You can see the bolus.

Fig. 10
Buddha statue of Paitava from Museum Guimet (sample 12), gilding micro-photography. You can see the gilding.

Fig. 11
Buddha statue of Paitava from Museum Guimet (sample 12): SEM image of sample.





by-product of the deterioration of organic materials. As known, this technique is unable to detect oxide compounds, we cannot therefore say more about the red pigment. Micro-XRD analysis confirmed the presence of calcite and quartz raw material of the artefact.
(F. T.)

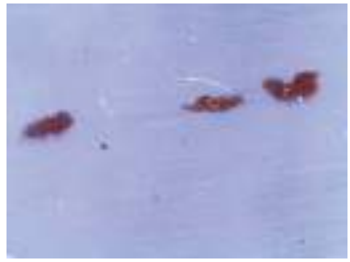
Sample 9 (n.10 sampling)
The SEM-EDS analyses are referring to the limestone of the same relief of Hadda (see sample 8). Spectra 1, 2, 3, carried out on the surface, highlight a high amount of Pb (probably minium) owed to a surface painting of the

artefact. The spectrum 7 indicates a high amount of iron (probably hematite): it must be referred to the composition of the raw material (with a silicon-aluminate matrix) of the relief (tab. 3).
(G.G., C.R.)

Sample 10 (n.11 sampling)
The sample was a greyish blue pigment taken from the same relief of Hadda see above (samples 8 and 9) (fig.7). We realized SEM-EDS analyses. Blue grains are made of lapis lazuli, characterized by a very good relation among the elemental maps of silicon, aluminum, sodium and sulphur, thus confirmed by spot analyses. A greyish component is associated to silicon-aluminates of magnesium; calcium carbonate is diffused on the whole sample, probably as a component of the raw material of the artefact. White grains contain mainly lead, probably as carbonate (lead white, i.e. cerussite / hydrocerussite). Note that arsenic is associated to lead, but at the moment a satisfying explanation for this cannot be given. Observing the micro-photo of this sample, we can suppose that lead white was mixed to the lapis lazuli, in order to obtain a pale blue colour (fig.8).
Phosphorus was detected in spot EDS analyses corresponding to lead. Some hypothesis may be proposed: it could be associated to the mineral composition or it could be a marker of a casein glue, but it is necessary to deepen this problem through specific analyses.
Few grains of red pigment are mixed to the ultramarine blue; EDS elemental maps and spot analyses report only iron, with no other chemical element, we can therefore suppose the presence of hematite (Fe_2O_3).
(F. T.)

Sample 11 (n.12 sampling)
The sample is only representative of the surface of the artefact, a limestone relief from Hadda, Chakhil-i-Ghoundi monastery, stairway of stupa C1 (Afghanistan). The SEM-EDS analysis shows a high amount of calcium, perhaps owed to the ground layer of a polychrome decoration or a raw material of the artefact (tab. 4). Other analyses will carry out to investigate this issue.
(G. G., C. R.)

Samples 12 and 13 [n.13 sampling (gilding and bolus on schist) and n.14 (bolus and schist)]
Some analyses were carried out on some samples of gilding and on an evident underlying bolus of a famous gilded statue in schist of *Buddha* in the *Miracle of Sravasti*, from Paitava monastery (Afghanistan). The results are very interesting, because micro-FTIR analyses detected a protein, probably egg, in the bolus. The red bolus, analysed by micro-Raman technique, is mainly composed by hematite (Fe_2O_3), with some gypsum ($CaSO_4 \cdot 2H_2O$) and clay as silicon-aluminate (fig.9). This result reminds the typical technique for gilding sculptures and paintings in the Mediterranean area.



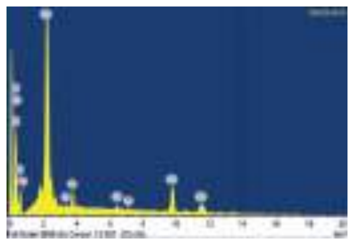


Fig. 12
Shotorak relief from Museum Guimet (sample 14): microphotography of gilded sample.

Fig. 13a
Shotorak relief from Museum Guimet (sample 14): SEM image of some fragments.

Fig. 13b
Shotorak relief from Museum Guimet (sample 14): EDS analysis of Spectrum 6 (see Fig.13a).

Fig. 14
Sampling of Statue of two Naga Kings (from hair) from Museum Guimet (sample 15) (photo S.Pannuzi).

Fig. 15
Statue of two Naga Kings statue (from hair) from Museum Guimet (sample 15): micro-photography of cross section (100x).

FTIR analyses carried out on several spots of the same sample shows the probable presence of egg glue as binder of the red colour. In some of the analyzed points we found a synthetic vinyl acetate based adhesive, certainly related to a recent intervention.

Analyses were performed after selecting one fragment of gilding, directly on the sample without any process to embed the sample in a cross section (fig.10). All analysed gildings are constituted of a gold leaf. SEM image clearly highlights the presence of three fragments of gilding on the *bolus* (fig.11). EDS analyses show a different chemical composition: two fragments have a very similar composition (see tab. 5, measurement nn. 1, 2, 3, 4, 7, 8, 9, 10): the amount of gold is between 93.04% and 97.26%, copper between 1.27% and 5.14%, silver between 0.78% and 2.26%. The third one, unlike the previous ones, has a very different chemical composition (measurements nn. 5 and 6): it was poor in gold (57.86% and 65.87%), rich in copper (29.2% and 42.14%,); silver varied from 0% to 5.31%. The great difference in chemical composition in this part of gilding suggests a probable ancient restauration.

It is interesting to highlight the heterogeneous chemical composition in the same gold alloy; we suppose that this evidence could be related to the technique of purification and production of the gold leaf. Observing under microscope the gilded fragments we often note some roughness of the surface.

(F. T.)

Sample 14 (n.15 sampling)

The sample has been taken from a schist relief from Shotorak monastery (Afghanistan) with visible traces of a red colour. By optical microscope a golden guilding, not visible to the naked eye, has been detected (fig. 12). By SEM EDS analysis the presence of Pb might be referred to the red colour (minium ?). The presence of calcium (in varying amounts) might be owed to a preparation layer of gilding (figg.13A and 13B, tab. 6).

(G. G., C. R.)

Sample 15 (n.16 sampling)

A sample of blue color was taken from the hair of one of two clay figures of the two Naga Kings sculptures from Fundukistan (Afghanistan) (fig.14). Observing under a microscope the cross-section obtained from the sample, a very interesting sequence of layers of paint appeared (fig.15). In the lower part of the cross-section an orange coloured heterogeneous layer, with various thickness, is characterized by the presence of lead; by SEM-

Fig. 16
Sampling of two Naga Kings statue (from arm) from Museum Guimet (sample 16) (photo S.Pannuzi).

Fig. 17
Statue of two Naga Kings statue (from arm) from Museum Guimet (sample 16): SEM image of cross section.

Fig. 18
Sampling of two Naga Kings statue (from hear) from Museum Guimet (sample 17) (photo S.Pannuzi).

EDS analysis we assume that it was minium. In the middle of the cross section elemental maps of silicon, aluminum and magnesium show a very good overlapping. A discontinuous white layer was observed on the left of the cross section, under the blue pigment. Blue ultramarine was used in the upper layer.

Sample 16 (n.17 sampling)

This sample was taken from the arm of one of two clay figures of the two Naga Kings sculptures from Fundukistan (Afghanistan) (fig.16). By SEM-EDS analysis the maps of elements of this cross-section show the overlapping of cobalt and tin (fig.17). The only possible explanation for this is the presence of stannous cobalt, a modern pigment synthesized in the second half of the 19th century. So its presence is due to a modern restoration. On the upper layer of the cross-section Cobalt is not related to tin, (point 12) so we suppose that the pigment cobalt blue has been used ($CoAl_2O_4$). Spot analyses on point 12 show a good connection between calcium and phosphorus, probably due to the presence of calcium phosphate, typical of bone black.

The lower part of the cross-section reveals the presence of silicon, aluminum and iron, related to the clay material of the statue.

Sample 17 (n.18 sampling)

The sample has been taken from one ear of one of Naga kings (see samples 15 and 16) (fig.18). The cross-section has a complex stratigraphy, at least four layers have been detected. The most interesting layers show, under visible light, a well-defined yellow pigment, applied on a red-orange layer (fig.19). The red-orange layer, indeed, when observed under UV light, is almost split into two layers not well defined (fig.20). Indeed, the lower red-orange layer of the cross-section appears heterogeneous and incoherent.

Fig. 19
Statue of two Naga Kings (sample from hear) from Museum Guimet: microphotography of cross section of sample 18 (visible light).

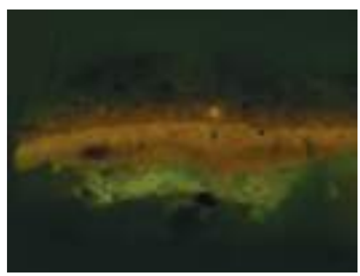


Fig. 20
Statue of two Naga Kings (sample from hear) from Museum Guimet: microphotography of cross section of sample 18 (UV light).

Fig. 21a, b, c
Statue of two Naga Kings (sample from hear) from Museum Guimet: EDS elemental maps of Sulphur, Arsenic and Lead on cross section of sample 18.

Fig. 22
Sampling of Statue of Bodhisattva (from hair) from Museum Guimet (sample 18) (photo S. Pannuzi).

Fig. 23
Statue of Bodhisattva (from hair) from Museum Guimet: microphotography of sample 18 (25x).

Fig. 24
Sampling of Statue of Bodhisattva (from garland) from Museum Guimet (sampling 19) (photo S. Pannuzi).

Another superficial and incoherent layer, over the yellow layer, was chemically characterized by silicon, aluminum, calcium and potassium and may be explained as dirt or as a restoration ground layer.

A more complex description is necessary to describe the red-orange and the yellow layers. These layers, as seen above, are clearly visible under UV light. Both layers, however, do not have a different chemical composition: both maps and spot analyses reveal the presence of lead as main element. No silicon, nor aluminum or iron have been detected in these layers, we therefore exclude the presence of a clay and we can attribute them to two painted layers. Lead is the most plentiful chemical element, both in the red-orange layer than in the upper yellow layer.

The presence of lead may be owed to the presence of different pigments, according to their color: in the lower layer, the red-orange colour, may be related to the pigment minium.

SEM-EDS elemental maps and spot analyses of the upper yellow layer show a very good fit between arsenic and sulphur, related to the pigment orpiment (fig.21). Moreover, the presence of lead in this layer, may be inferred to the use of massicot/litharge pigment, mixed with the orpiment pigment.

Micro-FTIR analyses highlighted the presence of an animal glue as binder of the pigments.

Table 7
EDS analyses of gilding from sample 19. Elements are expressed as atomic percent.

Table 8
EDS analyses from sample 20. Elements are expressed as atomic percent.

Samples 18 (n.19 sampling)

This sample was taken from the hair of clay Bodhisattwa statue from Fundukistan monastery (Afghanistan) (figg. 22, 23). It was constituted of a powder and it was analyzed by micro-FTIR. The FTIR spectrum of the black-blueish pigment well fits with the pigment ultramarine blue. The underlying red ground was constituted by red ochre mixed with calcite. At the moment we are not able to state if this red layer comes from to the clay material or it is a ground for the blue pigment; we are presently working on this issue and hope to be able to answer soon.

opposite page

Fig. 25
Statue of Bodhisattva (from garland) from Museum Guimet: micro-photography of cross section of sample 19 (100x).

Fig. 26
Statue of Bodhisattva (from garland) from Museum Guimet: SEM image of cross section of sample 19.

Sample 19 (n. 20 sampling)

This sample was got from the garland of the same clay Bodhisattva statue (see sample 18) (fig.24). The cross-section highlights two different layers made by a blue-greyish colour and a red colour. The cross-section was analyzed by SEM-EDS. Note that the photo is upside down, so the red color is the inner layer, while the blue-greyish is the upper one (fig.25).
The upper blue-greyish layer was obtained by mixing a blue pigment and a greyish one. Elemental maps highlight a lead compound mixed with calcium silicate (see maps of lead, silicon and calcium). Spot analyses on blue

Table 7

Spectrum	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Br	Pb	
1	3,07	5,14	10,79	45,06	0,00	0,00	2,59	2,28	28,34	0,00	0,00	0,00	2,72	100
2	0,00	7,89	4,82	48,93	0,00	0,00	0,00	1,35	35,46	0,00	0,00	0,00	1,55	100
3	6,32	1,43	21,22	43,82	0,00	0,00	3,62	3,65	16,14	0,00	0,00	0,00	3,81	100
4	0,00	0,77	0,95	92,36	0,00	0,00	0,00	1,16	2,84	0,00	0,00	0,00	1,92	100
5	0,00	14,32	9,70	43,36	0,00	0,00	1,41	22,64	4,23	1,97	0,00	0,00	2,38	100
6	0,00	1,69	21,04	46,57	0,00	0,00	2,34	14,56	4,74	1,23	5,51	0,00	2,31	100
7	0,00	0,00	4,33	15,79	0,00	0,00	0,00	1,55	2,65	0,00	74,19	0,00	1,49	100
8	0,00	0,00	0,00	24,30	0,00	0,00	1,32	1,02	4,12	0,00	59,50	8,04	1,70	100
9	0,00	1,63	8,18	29,78	0,00	0,00	2,60	1,34	5,00	0,00	49,91	0,00	1,57	100
10	0,00	1,74	14,87	47,94	0,00	0,00	3,03	4,92	10,00	0,00	13,84	0,00	3,66	100
11	0,00	3,09	3,28	14,63	0,00	0,00	0,00	1,12	4,77	0,00	73,11	0,00	0,00	100
12	0,00	3,63	5,02	27,93	0,00	0,00	0,00	2,75	20,57	0,00	0,00	0,00	40,11	100
13	0,00	3,58	3,96	17,71	0,00	0,00	0,00	0,00	11,01	0,00	0,00	0,00	63,74	100
14	0,00	8,30	3,79	47,11	0,00	0,00	0,00	0,83	38,14	0,00	0,00	0,00	1,84	100
15	0,00	3,24	0,00	31,27	5,46	0,00	7,91	5,25	18,18	0,00	3,61	4,86	20,23	100
16	0,00	2,55	6,85	24,70	8,69	0,00	10,00	5,07	19,40	0,00	3,03	0,00	19,71	100
17	0,00	0,00	3,69	22,53	9,27	0,00	9,74	0,00	22,60	0,00	3,06	0,00	29,11	100
18	0,00	2,02	4,45	18,35	11,12	0,00	9,63	0,00	25,17	0,00	4,14	0,00	25,11	100
19	0,00	2,23	3,55	14,17	0,00	0,00	1,20	1,53	4,25	12,39	59,07	0,00	1,61	100
20	0,00	8,62	1,86	47,15	0,00	1,51	0,00	1,03	38,46	0,00	0,00	0,00	1,38	100

grains (see fig. 26 and tab. 7, point 3: silicon, aluminum, sodium) and related elemental maps are congruent with ultramarine blue (fig.27). The greyish grains were analyzed by SEM-EDS too, in order to determine if the grey color was originated from the discoloration of the ultramarine blue pigment. As known, this pigment, in acidic conditions, may decay in a discoloured greyish pigment. This event was not confirmed, because the chemical composition of the greyish grains differs from the blue grains one. Lead could be formerly related to the lead white pigment; if this hypothesis is confirmed, we might suppose a chemical deterioration to lead oxide (plattnerite).

Under the blue-blackish layer, a white thin area in SEM image is related to the presence of lead. It is interesting to notice that in the thin white layer a good correspondence was among lead, calcium and phosphorous; we suppose that lead white (cerussite/hydrocerussite) was used, mixed with bone black (calcium phosphate), and applied directly on the red material.

The red material is characterized by a very good overlapping among the elemental maps of iron, silicon and aluminum, corresponding probably to a red ochre; some granules of silica were observed. It seems to be a "painted" red layer above the clay material of the statue.

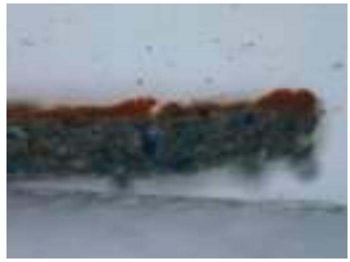


Table 8

Spectrum	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Br	Pb
1	3,07	5,14	10,79	45,06	0,00	0,00	2,59	2,28	28,34	0,00	0,00	0,00	2,72
2	0,00	7,9	4,83	48,98	0,00	0,00	0,00	1,35	35,5	0,00	0,00	0,00	1,55
3	6,32	1,43	21,22	43,82	0,00	0,00	3,62	3,65	16,14	0,00	0,00	0,00	3,81
4	0,00	0,77	0,95	92,36	0,00	0,00	0,00	1,16	2,84	0,00	0,00	0,00	1,92
5	0,00	14,37	9,73	43,5	0,00	0,00	1,41	22,71	4,24	1,98	0,00	0,00	2,39
6	0,00	1,69	21,04	46,57	0,00	0,00	2,34	14,56	4,74	1,23	5,51	0,00	2,31
7	0,00	0,00	4,33	15,79	0,00	0,00	0,00	1,55	2,65	0,00	74,19	0,00	1,49
8	0,00	0,00	0,00	24,3	0,00	0,00	1,32	1,02	4,12	0,00	59,5	8,04	1,7
9	0,00	1,63	8,18	29,78	0,00	0,00	2,6	1,34	5	0,00	49,91	0,00	1,57
10	0,00	1,74	14,88	47,97	0,00	0,00	3,03	4,92	10,01	0,00	13,85	0,00	3,66
11	0,00	3,09	3,28	14,63	0,00	0,00	0,00	1,12	4,77	0,00	73,11	0,00	0,00
12	0,00	3,63	5,02	27,93	0,00	0,00	0,00	2,75	20,57	0,00	0,00	0,00	40,11
13	0,00	3,58	3,96	17,71	0,00	0,00	0,00	0,00	11,01	0,00	0,00	0,00	63,74
14	0,00	8,3	3,79	47,11	0,00	0,00	0,00	0,83	38,14	0,00	0,00	0,00	1,84
15	0,00	3,24		31,27	5,46	0,00	7,91	5,25	18,18	0,00	3,61	4,86	20,23
16	0,00	2,55	6,85	24,7	8,69	0,00	10	5,07	19,4	0,00	3,03	0,00	19,71
17	0,00	0,00	3,69	22,53	9,27	0,00	9,74	0,00	22,6	0,00	3,06	0,00	29,11
18	0,00	2,02	4,45	18,35	11,12	0,00	9,63	0,00	25,17	0,00	4,14	0,00	25,11
19	0,00	2,23	3,55	14,17	0,00	0,00	1,2	1,53	4,25	12,39	59,06	0,00	1,61
20	0,00	8,62	1,86	47,15	0,00	1,51	0,00	1,03	38,46	0,00	0,00	0,00	1,38

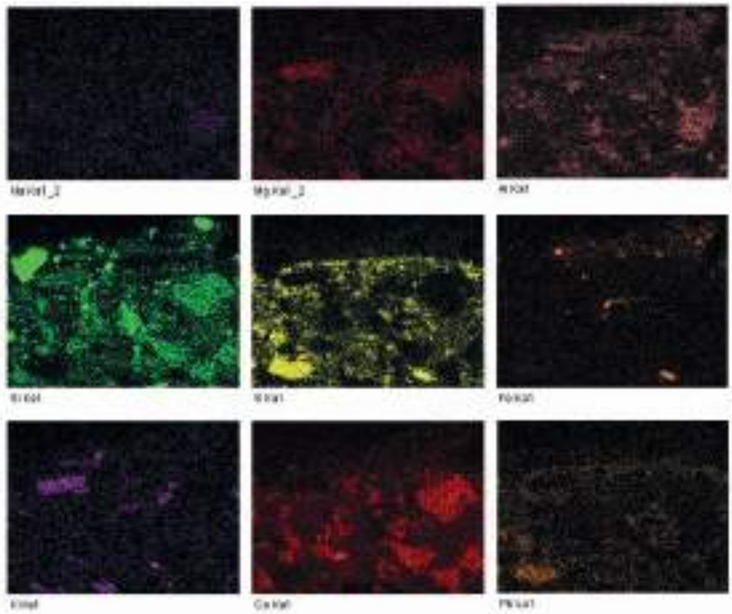


Fig. 27
Statue of Bodhisattva (from garland) from Museum Guimet (sample 19): EDS elemental maps of Sodium, Magnesium, Aluminium, Silicon, Sulphur, Iron, Potassium, Calcium and Lead.

opposite page

Table 9
EDS analyses of gilding from sample 21. Elements are expressed as atomic percent.

Table 10
EDS analyses of gilding from sample 21, *versus*: ground layer under the gilding. Elements are expressed as atomic percent.

Table 9

Spectrum Label	1	2	3	4	5	6	7	8
Cu	1,68	3,01	2,14	2,14	2,20	1,23	2,82	2,29
Ag	5,23	4,65	5,06	5,57	5,05	5,84	4,36	4,69
Au	93,09	92,34	92,80	92,29	92,75	92,93	92,81	93,03
Total	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

Table 10

Spectrum Label	18	19	20	21	22	24
Mg	0,77	0,74	0,00	0,00	0,00	0,00
Al	2,41	2,63	1,76	3,12	1,89	2,32
Si	2,90	3,28	2,22	4,47	1,51	2,95
S	0,93	1,16	1,54	1,58	0,00	1,00
K	0,00	0,00	0,00	0,69	0,00	0,00
Ca	87,05	85,37	90,79	85,21	88,60	88,59
Fe	0,00	0,96	0,00	1,20	0,82	0,59
Au	5,95	5,85	3,68	3,73	7,19	4,55
Total	100,00	100,00	100,00	100,00	100,00	100,00

Sample 20 (n. 21 sampling)
This sample was picked up from the clay statue of seated Buddha (fig. 28). The micro-photo of the powder shows a sequence of four different painted layers: a brown-greysh layer, two different red painted layers (figg.29A and

29B). The cross-section obtained from one of the fragments clearly shows the sequence of layers (fig.30). SEM-EDS analyses of red layers show in the lower layer mainly lead probably as minium, a lead oxide (Pb_3O_4), and a little of chlorine. In the upper red layer mercury and sulphur are related to cinnabar (or vermillion); vermillion is mixed in the upper layer to red lead (see Pb vs. Cl and Hg vs. S elemental maps (figg. 31 A and 31 B, tab. 8).

The lower brown layer is characterized by a very good overlapping of the elemental maps of silicon, aluminum and potassium. Minor elements detected are iron, calcium and magnesium, not directly related to the main elements (K, Si, Al), probably as oxide (i.e. Fe_2O_3, hematite) or carbonates ($CaCO_3$, $MgCO_3$).

The chemical analyses may be explained as a clay (characterized by the main elements K, Al, Si) well mixed with iron oxides and calcium/magnesium carbonates, because the elemental maps of the main elements are not related to the minor elements (Fe, Ca, Mg).

Inside the clay ground some red-orange and black stripes on a red orange grain may be observed. The chemical spot analyses highlights iron, silicon, aluminum and potassium.

(F. T.)

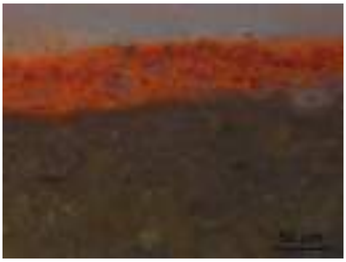


Fig. 28
Sampling of Statue of Seated Buddha from Museum Guimet: detail of the dress (sampling 20) (photo S.Pannuzi).

Fig. 29
Statue of Seated Buddha from Museum Guimet: micro-photography of sample 20 (12.5x).

Fig. 30
Statue of Seated Buddha from Museum Guimet: micro-photography of cross section of sample 20.

Gandharan artworks from Civic Archaeological Museum in Milan: chemical analyses on polychromies

Sample 21 (n. 4 sampling)

This sample has been taken from a gilded stone statue representing Budda, one of most important statues of the Milan Archaeological Museum (fig.32). The statue was made in shale and covered with a gilding; now only some spare traces of gold are preserved. This sample was representative of a gilding applied on its ground. The sample was analyzed by SEM-EDS on the *recto* (gilding) and *verso* (ground) (figg. 33, 34).

SEM-EDS analyses allowed us to understand the chemical composition of the gold leaf. Seven analyses were performed on the gold sample (see tab. 9). Gold (Au), Silver (Ag) and Copper (Cu) were found. The average (as atomic percentage) and the standard deviation (s.d.) were: Au 92.75% (s.d. = 0.3), Ag 5.06% (s.d. = 0.49), Cu 2.19% (s.d. = 2.19). The black material, partially covering the gilding, seems to be a superficial sediment, probably due to residues of excavation soil or atmospheric pollution. Its chemical composition (tab.: main elements, expressed as atomic percent) is Si (41,46%), Al (26,14%), Ca (16,58%), Fe (5,97%), K (5,78%).

The ground, *verso* side, representing the layers under the gilding the analyses revealed the presence mainly of calcium (Ca); minor elements were potassium (K), aluminium (Al), silicon (Si), iron (Fe), magnesium (Mg), sulphur (S) (tab. 10). The high content of calcium is due to calcium carbonate; gypsum, considering to the low amount of sulphur, is absent. Similar results were obtained on the EDS analyses, performed on *recto*. The high content of calcium highlights the absence of schist on this sample. Calcium carbonate has probably the function of the bolus: meant to make the gild-

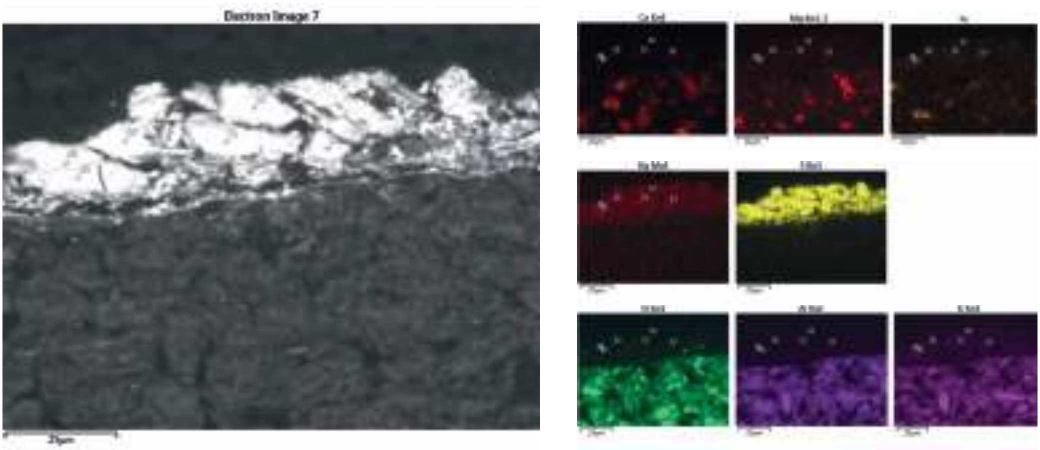


Fig. 31 a, b
Statue of Seated Buddha from Museum Guimet (sample 20).
31 a: SEM image of the cross section of the sample.
31 b: EDS elemental maps of Calcium, Magnesium, Iron, Mercury, Sulphur, Silicon, Aluminium, Potassium.

ing adhere to the schist surface of the statue. FTIR analyses confirmed the presence of a clay, perhaps a red ochre, along with calcite and dolomite.

Sample 22 (n. 5 sampling)
Sample 5 was taken from a lateral point of a painted stucco statue representing a Monk wearing a red dress (Fig. 35). Now it seems that the face and the hands of the monk were not covered with by red pigment.
The sample was analyzed by micro-FTIR and no relevant information was obtained. SEM-EDS analysis of the cross section gave more interesting results. Iron (Fe) was found in the upper part of the cross-section; Iron maps are superimposed to aluminum and silica maps. According to these result the red pigment is a red ochre. An interesting goal was observed. The cross section in visible light highlights that beneath the surface (the exterior red painted layer measures 40-50 μm) the iron concentration gradually diminished, till 400-500 μm (fig.36). This evidence may be explained relating this to the ancient painting technique of Gandharan art. The colour

Table 11
EDS analyses from sample 22. Elements are expressed as atomic percent.

Table 11

Spectrum Label	7	1	2	3	4	5	6
Na	1.86	2.97	1.32	0,00	1.31	0,00	1.53
Mg	2.06	2.65	0.94	2.93	1.76	1.57	1.61
Al	9.53	12.79	5.01	7.14	8.13	4.51	8.18
Si	19.65	25.01	9.12	10.68	14.61	8.65	15.80
S	0,00	1.43	1.05	0.54	0.87	0,00	0.91
K	1.53	2.08	0.85	0.92	0.97	0,00	1.22
Ca	60.71	48.99	79.31	73.97	68.00	83.69	66.04
Ti	0,00	0.66	0,00	0,00	0.84	0,00	0,00
Fe	3.94	3.44	2.41	3.83	3.50	1.59	4.72
Mo	0.72	0,00	0,00	0,00	0,00	0,00	0,00
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 12

Spectrum Label	1	2	3	4	5	6	7	8	9
Na	1,76	1,52	1,42	1,18	1,56	2,65		1,44	
Mg	4,07	4,25	3,85	6,67	3,03	11,56	2,00	5,57	2,21
Al	7,17	4,29	1,93	9,49	10,51	15,93	0,76	11,50	0,95
Si	14,30	9,57	6,11	22,60	44,12	33,11	3,21	44,06	4,76
P				0,37					
S	1,39	2,66	0,88	0,72	1,25	0,22		0,28	
Cl	2,29	3,08	1,64	1,55	2,48	0,40	0,47	1,26	0,64
K	1,75	0,77	0,48	1,69	2,02	0,58		3,25	
Ca	62,40	69,72	82,47	50,85	32,61	15,32	93,30	28,41	91,04
Ti	0,55	1,47			0,61	4,16		0,36	
Mn						0,22			
Fe	3,85	1,97	1,23	4,89	1,41	15,84	0,27	3,86	0,40
Zn	0,46	0,72							
Mo									
Ba					0,40				
Total	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

Spectrum Label	10	11	12	13	14	15	16	17	18	19
Na		1,70	1,88	2,18		1,80	1,04	1,35		1,44
Mg	2,00	5,28	4,96	3,97	3,52	6,65	4,28	5,26	4,29	3,55
Al	2,73	10,19	3,85	4,25	5,81	3,13	1,71	1,69	2,27	1,84
Si	12,36	40,40	16,38	13,63	58,34	11,25	12,65	8,41	8,56	7,02
P			0,44							
S		0,34	1,67	1,41	1,30	1,40	0,64	0,72	0,55	0,38
Cl	0,70	0,87	2,67	1,78	2,65	2,62	2,41	1,69	1,93	1,06
K	0,59	1,62	1,13	1,09	1,72	0,86	0,51	0,49		
Ca	80,72	34,33	58,93	68,35	24,07	71,43	75,86	78,90	81,59	84,23
Ti		0,75						0,78		
Mn										
Fe	0,67	4,51	7,54	3,35	2,22	0,87	0,91	0,72	0,81	0,49
Zn			0,53		0,37					
Mo	0,24									
Ba										
Total	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

is applied on a fresh layer of ground, so it diffused in the underlying stucco that is the raw material of this statue. The dough was obtained mainly by milled gypsum (more than 40%), mixed with silicates (figg. 37 A and 37 B, tab. 11). A large grain of dolomite [$(MgCaCO_3)_2$, see Ca/Mg maps] was observed. Despite of the refined execution of the statue, a simple technique was revealed by the heterogeneity of the materials and the coarse dough employed on this artifact.

Table 12
EDS analyses from sample (23) (spectra 1-19). Elements are expressed as atomic percent.

Fig. 32 Sampling of schist statue of Buddha from Milan Museum (sample 21) (photo S.Pannuzi).

Fig. 33 Schist statue of Buddha from Milan Museum (sample 21): micro-photography, *recto* (10x).

Fig. 34 Schist statue of Buddha from Milan Museum (sample 21): micro-photography, *verso* (10 x).

Sample 23 (n. 6 sampling)

This sample was taken from a stucco statue representing a Bodhisattva, discontinuous traces of red pigment are visible (Fig. 38). The cross-section of this sample reveals a thin red layer 10-20 μm; its chemical composition shows the presence of red ochre for the presence of Fe, Si, Al in the upper layer of the cross-section (Fig.39). Unlike sample 5, the red pigment has not been found in the underlying layer, it is therefore probable that the pigment was applied over the dried base.

The ground too differs from the sample 5. Observing its cross-section under visible light, we observe the presence of black and red grains that characterize the ground. Grains of iron, potassium and sodium silico-aluminate sprinkled in a calcium carbonate matrix (Figg. 40, 41; tab. 12).

Elemental maps of iron, aluminum and silica are often superimposed, denoting the presence of ochres (Fig.42). We noted a very good relation among silicon, aluminum, strontium and potassium. The diffuse presence of calcium carbonate was confirmed by micro-FTIR analyses on the powder of the sample. The cross-section highlights the presence of large grains of calcium carbonate, approx. 0,2-0,3 mm, mixed inside the stucco.
Micro-XRD analyses were performed on a grounded sample: calcite, dolomite and quartz were detected; the same analysis on *tal quale* sample detected quartz, calcite and gold. This result is very interesting because gilding was not visible to the naked eye and on the cross section analyzed by SEM EDS. In next future other analyses will carry out to understand the presence of gold.

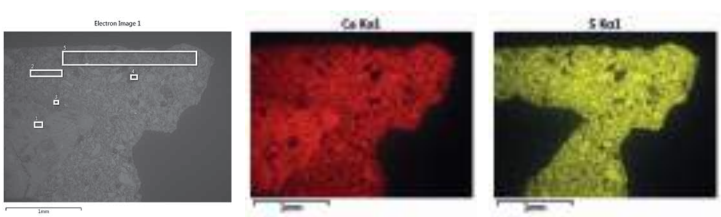
Sample 24 (n.7 sampling)
The sample was a powder picked up from a schist false corbel (*Nagadanta*) (fig.43). Micro FTIR analyses highlights the invasive presence of a synthetic adhesive, belonging to polyamides employed in a previous restoration. The strong signals of the adhesive hide the weak signals due to the original material. Only in a little fragment it was possible to observe weak signals, typical of the bands of silico-aluminate compounds.

Samples 25 and 26 (nn.8 and 9 sampling)
These samples were picked up from a relief in schist with Buddha life scenes, characterized by a superficial white layer (Fig.44). Observing the fragments under microscope and owing to the FTIR results we can assert that the upper white layer is not owed to the excavation soil or to the environment dust, it is something derived from human activity, most likely to be associated to a painting technique (Figg.45, 46).
Micro-FTIR analyses show the presence of Calcium carbonate and aluminum-silicate. Both samples were not suitable to get cross-sections.

Samples 27, 28 and 29 (nn. 10, 11 and 12 sampling)
These samples were taken from a stele, representing a Bodhisattva (Fig.47). The samples seem very similar to the samples 25 and 26, previously described: schist with a superficial white layer (fig.48). On sample 28 only the schist is visible, probably with some traces of the upper layer. Chemical analyses (FTIR) give similar results too: calcium carbonate and alumina-silicate.
(F. T.)

Fig. 35
Sampling of a stucco Monk statue from Milan Museum (sample 22) (photo S.Pannuzi).

Fig. 36
Statue of stucco Monk from Milan Museum: micro-photography of cross section sample 22 (50x).



Fig, 37
Statue of stucco Monk from Milan Museum (sample 22). SEM image of the sample and EDS elemental maps of Calcium and Sulphur.

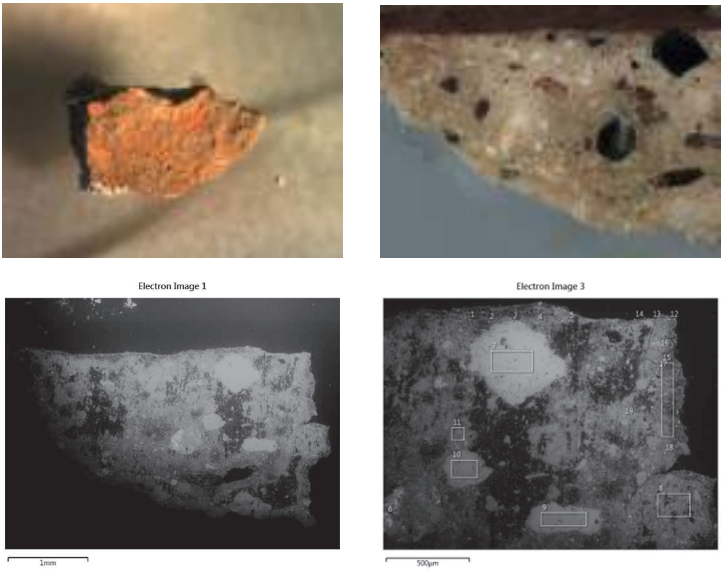


Fig. 38
Stucco statue, Bodhisattva from Milan Museum (sample 23): image of the sample 6 *tal quale* (8x).

Fig. 39
Stucco statue, Bodhisattva from Milan Museum (sample 23): micro-photography of cross section (15x).

Fig. 40
Stucco statue, Bodhisattva from Milan Museum (sample 23): SEM image of cross section.

Fig. 41
Stucco statue, Bodhisattva from Milan Museum (sample 23): SEM blow up image of cross section.

Samples 30 and 31 (nn.14, 15 sampling)

These samples were taken from a schist capital of a lost pilaster (Fig.49). Grey schist and another whitish material are well shown in micro-photograph (fig. 50). The whitish material of sample 30 is analytically characterized by micro-FTIR analysis as calcite, gypsum and silicon-aluminate.
By SEM EDS analysis, in spectum 4, we noted a certain amount of calcium, probably matched to calcium carbonate, owed to a white superficial preparation layer, laid on the schist stone and used for a polychrome decoration that has now disappeared. A high amount of Fe, Ti and Zr were detected in the thin section.
Micro-Raman analyses on a red grain highlighted the presence of hematite, probably traces of ancient polychromy, not visible by naked eye.
(F. T., G. G., C. R.)

Sample 32 (n.17 sampling)

This sample was taken from the stucco Buddha's Head (Figg.51, 52). The cross-section obtained from this sample clearly shows on the right side the presence of a red layer, whereas on the left side the surface is quite orange (Fig. 53). Despite of this evidence, EDS analyses do not denote significant differences in chemical composition of the two colours: the presence of iron, aluminum, silicon as main chemical elements, in similar percent, are due to two chromatically different red colours, but chemically very similar ochres. According to FTIR and SEM-EDS analyses, the ground is mainly a mix of calcium (as carbonate) and silicon (as SiO_2). Note that magnesium was present mainly in red and orange ochres, as we can see in EDS maps of Ca and Mg.

Sample 33 (n.25 sampling)
This sample was taken from the hair of the clay head of Brahma (Fig.54). The cross section clearly highlights the sequences of the layers (Figg.55, 56). The clay plaster seems polished, in order to obtain a smooth surface coved by a thin layer of yellow paint.
Indeed, observing the cross-section at a greater magnification we notice in the upper part two layers of two very thin layers of different pigments over a rough clay plaster: a yellow pigment is applied on an underlying red pigment. EDS analyses show a good overlapping of the elemental maps of iron, magnesium and silicon, respectively due to two different ochres, a yellow and a red one.
The rough plaster was characterized by heterogeneous materials consisting in red, yellow, grey and black grains: a large red granule is observed on the right and greyish components characterize this sample. The chemical composition of the rough plaster was explained by SEM-EDS analyses: Silicon, Aluminium, Iron and Calcium and Magnesium are the main chemical elements found along the cross-section. The greyish component in the clay is composed by a calcium silicate.
(F. T)

Gandharan artworks from Museum of Oriental Art in Turin: chemical analyses on gildings
Samples 34 and 35 (nn.1 and 2 sampling)
Two samples of gilding were taken from two different sides of a schist corbel (MAO n. 4581), in order to analyse the chemical composition of gilding and its ground.
Looking at the micro-photos, the following superimposition of layers has been observed: 1) greenish grey of the schist; 2) a white ground; (3) partially browned in the upper; (4) gold leaf (Fig.57).
Sample 34 represents only the gilding and its underline layer (Fig.58).

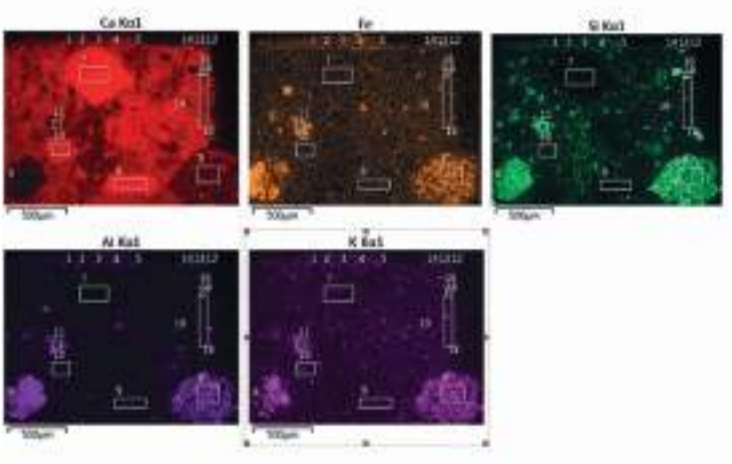


Fig. 42
Stucco statue, Bodhisattva from Milan Museum (sample 23): EDS elemental maps of Calcium, Iron, Silicon, Aluminium, Potassium.

The samples were arranged without any preliminary treatment on the *stub* and analyzed by SEM-EDS (Figg.59, 60). In sample 1 gilding is characterized by gold leaf with a little amount of copper (Au = 97,64%; Cu = 2,36%) (tab. 13). Under the leaf the browned ground is a silicate compound, characterized by variable amounts of silicon, calcium, aluminum, magnesium and iron.

Micro-photo of sample 35 shows the golden leaf with browned ground, similar to the previous one (Fig.61). Micro-photography highlights some traces of manufacturing of the gold leaf, such as the curved lines on the left of the micro-photo. Its chemical composition is very similar to the sample 1 (Au = 96,85%; Cu = 3,15%) (Figg.62, 63, tab. 14).

The only important difference between these two samples of gilding is a not negligible presence of lead (its amount is few less than 10%), only found upon some gilded areas. This occurrence is hard to explain. Observing micro-photos we are led to exclude the presence of red minium or other lead oxides, such as the lead white. A hypothesis might be made: the lead comes from air pollution.

EDS analyses on brownish ground give a good overlapping among the elemental maps of silicon, aluminum, calcium, magnesium, iron. These results are very similar to that obtained for sample 34.

(F. T)

Conclusive comment about the analyses

The results discussed in this new research comes from a notable number of chemical analyses. Micro-photos of sample were collected under opti-

Fig. 43
Schist false corbel from Milan Museum: microphotography of sample 24 (8x).

Table 13

Spectrum Label	1		2		3		4	5	
O	15,24		15,37		14,98		18,97	15,06	
Na			0,31						
Mg	0,59		0,56		0,58		0,95	0,59	
Al	1,23		1,42		1,27		2,76	1,27	
Si	2,48		2,52		2,38		5,36	2,50	
S									
Cl									
K	0,45		0,52		0,45		1,35	0,44	
Ca	2,55		2,29		1,86		2,49	2,26	
Ti									
Fe	0,87		0,87		0,80		1,32	0,77	
Cu	1,87	2,50	1,57	2,11	1,79	2,36		0,74	0,99
Au	74,73	97,5	74,58	97,89	75,91	97,64	66,80	76,37	99,01
Total	100,00		100,00		100,00		100,00	100,00	

Spectrum Label	6	7	8	9	10	11	12
O	25,82	42,55	34,01	40,65	40,42	16,15	37,98
Na	0,55				0,48		
Mg	0,94	3,06	2,74	11,39	1,72	0,77	6,47
Al	2,93	4,83	5,11	9,29	13,15	1,74	5,62
Si	12,49	23,72	9,78	15,21	17,81	3,00	12,10
S		2,18	1,63	1,23	1,18		3,43
Cl		0,42	0,54	0,31	0,22		0,52
K	0,76	1,45	1,37	1,02	5,55	0,63	1,01
Ca	2,63	8,71	27,60	7,32	4,40	3,26	17,55
Ti	0,15				0,38		
Fe	1,48	3,52	3,91	5,67	2,58	1,09	4,45
Cu	0,63		0,38				
Au	51,61	9,56	12,94	7,91	12,11	73,36	10,88
Total	100,00	100,00	100,00	100,00	100,00	100,00	100,00

cal stero-microscope (Leica M125). Cross-sections of greater samples were achieved embedding any sample in polyester resin and observed and photographed under optical microscope (Leica DM-RXP). Samples (as micro-fragment, powder or cross sections) were analysed by SEM-EDS (Evo 60 Zeiss), collecting data as chemical maps and spot chemical analyses. Micro-FTIR analyses were performed after a preliminary study under optical microscope. After this preliminary selection, the samples were housed on a diamond cell and then analysed under micro-FTIR spot by spot. In addition, some micro-XRD and micro-Raman analyses were carried out.

Table 13
EDS analyses from sample 34 (spectra 1-12). Elements are expressed as atomic percent.

Fig. 44
Sampling of schist relief from Milan Museum (sample 25) (photo S.Pannuzi).

Fig. 45
Schist relief, micro-photography of sample 25 from Milan Museum (16x).

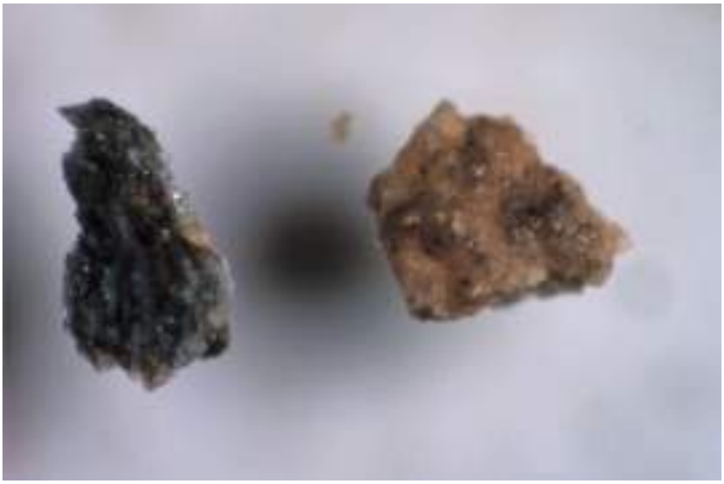


Table 14

Spectrum Label	1	2	3	4	5	6	7
Ca	0,00	1,38	1,34	2,38	2,84	0,55	0,67
Mg	0,00	0,65	0,77	0,59	0,67	0,00	0,33
Al	0,88	1,88	2,11	1,96	1,80	0,00	0,89
Si	1,10	2,83	3,36	2,98	2,85	0,98	1,33
Cl	0,00	0,00	0,00	0,00	0,00	0,00	0,00
K	0,00	0,48	0,58	0,59	0,57	0,16	0,25
Ti	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Fe	0,58	1,24	1,27	1,20	1,46	0,44	0,51
Cu	2,11	2,20	1,73	2,15	2,54	2,09	1,73
Au	85,34	81,36	88,84	81,39	80,50	85,01	85,52
Pb	9,99	7,98	0,00	6,76	6,77	10,77	8,76

Spectrum Label	8	9	10	11	12	13	14
Ca	12,35	6,31	8,39	3,29	13,79	17,71	3,29
Mg	2,01	2,19	3,71	2,08	2,23	4,61	1,66
Al	5,42	6,03	12,72	17,27	13,11	8,49	4,57
Si	8,98	9,08	27,46	23,30	18,07	17,47	7,59
Cl	0,00	0,00	0,00	0,00	0,64	6,80	0,00
K	2,81	2,24	5,52	7,67	5,06	2,65	1,29
Ti	0,52	0,52	0,00	0,46	0,00	0,00	0,00
Fe	14,85	17,52	6,55	3,90	3,39	5,48	2,70
Cu	1,95	2,31	1,25	1,07	0,00	0,00	2,02
Au	51,11	53,79	34,41	40,97	43,72	36,78	76,89
Pb	0,00	0,00	0,00	0,00	0,00	0,00	0,00

Table 14
EDS analyses from sample 35 (spectra 1-14). Elements are expressed as atomic percent.

In this research we analysed the artistic technique of painting on sculptures of Gandharan art made in different materials (stone, stucco and clay). A white layer was observed under the pigment in a lot of the artifacts analyzed, often in little amounts, as a residue of the lacked painting used to decorate the surface of the artworks. This layer in painting plays the role of "ground" for the pigments. Often in the past it was accidentally removed with the soil during the cleaning operations performed in the excavation operations.
As regarding the red pigments studied in this work, we found that ochre was the most frequently employed pigments. Ochre are characterized by the presence of iron oxides and aluminum-silicates; their colour may differ one to the other mainly by the chemical composition, the oxidation number of iron, and different amounts of crystallized water. In red ochre a strict relation among silicon, iron and magnesium was noted. More, a lead red-orange pigment was employed. As only EDS chemical analyses were carried out without mineralogical insights, we believe that minium, a red

Fig. 46
Schist relief, microphotography of sample 26 (16x).

Fig. 47
Sampling of schist Bodhisattva (sample 27) from Milan Museum (photo S.Pannuzi).

Fig. 48
Schist Bodhisattva: micro-photography of sample 29.

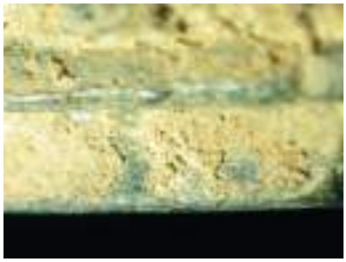


Fig. 49
Sampling of schist capital from Milan Museum (samples 30, 31) (photo S.Pannuzi).

Fig. 50
Schist capital from Milan Museum: micro-photography of sample 30 (16x)

oxide, was used; however, we cannot be completely excluded other lead oxides, such as litharge and massicot.
In next future we will examine this issue. In a few cases, vermillion pigment, a mercury sulfide, was also found.
The technique of applying colours shows some differences in the artifacts studied. An interesting feature was observed on the head of Salabhanjika from Hadda, kept in Museum Guimet (samples 6 and 7), having a high level of manufacturing. Indeed, the cross-section of sample 7 shows red ochre mixed with yellow ochre. In the surface a very thick layer of lead oxide minium was superimposed to the ochre layer, that are not undamaged. This suggests that the head was re-painted with a different pigment, having a red-orange hue.
Ochre pigments were frequently employed in yellow hue too. Lead oxide pigments (massicot/litharge) and orpiment, an arsenic sulphide, were found.
Some blue hue was obtained with ultramarine blue (lapis lazuli). No copper pigments, as azurite and chrysocolla, were found. Some modern synthetic blue pigments containing cobalt and tin were found on an important sculpture (sample 18 from Museum Guimet). We can suppose that this is a trace of a modern restoration[50].
Black pigments were obtained from bone calcinations.
By micro-XRD we analysed the stucco sample form Bodhisattva statue kept in Milan Museum (sample 23): calcite, dolomite and quartz were identified. As calcite is the binder of the stucco, dolomite and quartz are the inert components of the plaster. It is very interesting the presence of dolomite in this stucco sample, that could be used as a marker to identify the source of the stone materials used into the stucco. This information is very important because the origin of this artwork is uncertain as it comes from antique market.

[50] See Cambon in this issue.

Some gildings and their different ground layers were studied. Gold was applied as a leaf. Its purity is around 98%, the remaining was copper, and very little silver.
In the case of the sample from the corbel of the Turin Museum micro-photos well describe the sequence of the overlapped layers: over the schist we observe a whitish layer of ground, partially browned in the upper. Its chemical composition is similar to a clay material: silicon, aluminum, calcium, magnesium, iron characterize this ground. Gold leaf was applied on this ground. The origin of the brownish layer is not clear. Probably it is due to a chemical decay of an organic binder, because we observe this colour even under the leaf gold. We exclude that the browning was originated by air pollution. We would examine this sample by other analyses about the binder (GC-MS and Proteomics analyses).
In the next future, we intend to carry on with other analyses on some of these samples to verify important issue showed by the investigations *supra* highlighted. Furthermore, we also hope to increase the sampling of the Gandharan artworks to verify some hyphoteses suggested in this our research.
(F. T., S. P.)

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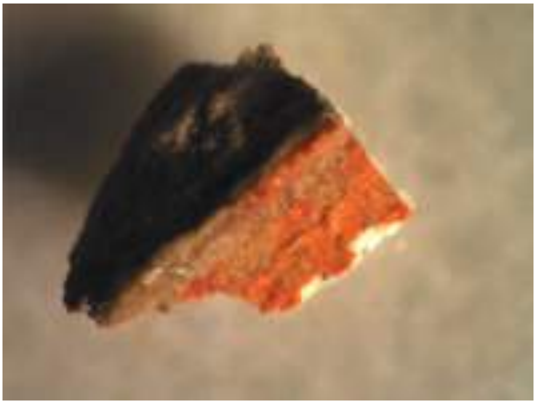
Fig. 51
Sampling of Stucco Buddha head from Milan Museum (sample 32) (photo S.Pannuzi).

Fig. 52
Stucco Buddha head from Milan Museum: micro-photography of sample 32 (16x).

Fig. 53
Stucco Buddha head from Milan Museum (sample 32): micro-photography of cross section (25x).



Sampling list 2015-2016

N.	N. sampling	Museum Inv.	Artwork	Sampling description
			Museum Guimet, Paris	
1	1	MA 6295	Elephant schist statue (M.G.Fremont gift 1996)	White ground layer from back
2	2	MA 6295	Elephant schist statue (M.G.Fremont gift 1996)	Schist from back
3	3	AO 2956	Schist relief from Buner Valley (Pakistan)	Pale yellow ground layer from base
4	4	AO 2956	Schist relief from Buner Valley (Pakistan)	Schist from the left side
5	5	AO 2908	Schist statue of Bodhisattva Maitreya from Pakistan, III-IV century A.D.	White ground layer from foot
6	6	MG 17203	Stucco head of Salabhanjika from Hadda, Tapa- i- Kafariha monastery (Afghanistan), III century A.D.	Red layer from headgear
7	7	MG 17203	Stucco head of Salabhanjika from Hadda, Tapa- i- Kafariha monastery (Afghanistan), III century A.D.	Pinkish layer from cheek
8	9	Barthoux mission (1928) no number	Limestone relief from Hadda, Tapa- i- Kafariha monastery (Afghanistan), II-III century A.D.	Red layer from a figure
9	10	Barthoux mission (1928) no number	Limestone relief from Hadda, Tapa- i- Kafariha monastery (Afghanistan), II-III century A.D.	Red layer from a figure
10	11	Barthoux mission (1928) no number	Limestone relief from Hadda,Tapa- i- Kafariha monastery (Afghanistan), II-III century A.D.	Blue-greyish layer from a hair of a figure
11	12	MG 17191	Limestone relief from Hadda, Chakhil- i- Ghoundi monastery- stairway of stupa C1 (Afghanistan), II-III century A.D.	White ground layer from a figure
12	13	MG 17478	Schist statue of Buddha from Paitava monastery (Afghanistan, Kapiça region), III century A.D.	Gilding with red ground (bolus) from arm
13	14	MG 17478	Schist statue of Buddha from Paitava monastery (Afghanistan, Kapiça region), III century A.D.	Red ground (bolus) from the left side
14	15	MG 22148	Schist relief from Shotorak monastery (Afghanistan), II-III century A.D.	Red ground (bolus) with traces of gilding from base
15	16	MG 18957	Clay statue of two Naga Kings from Fundukistan monastery Ghorband Valley (Afghanistan), VII century A.D.	Blue colour layer from hair
16	17	MG 18597	Clay statue of two Naga Kings from Fundukistan monastery Ghorband Valley (Afghanistan), VII century A.D.	Blue colour layer from arm
17	18	MG 18597	Clay statue of two Naga Kings from Fundukistan monastery Ghorband Valley (Afghanistan), VII century A.D.	Pale yellow layer from ear

N.	N. sampling	Museum Inv.	Artwork	Sampling description
18	19	MG 18959	Clay statue of Bodhisattva from Fundukistan monastery Ghorband Valley (Afghanistan), VII century A.D.	Blue-blackish colour layer from hair
19	20	MG 18959	Clay statue of Bodhisattva from Fundukistan monastery Ghorband Valley (Afghanistan), VII century A.D.	Blackish colour layer from garland
20	21	MG 18970	Clay statue of seated Buddha from Fundukistan monastery Ghorband Valley (Afghanistan), VII century A.D.	Orange layer with ground layer from drapery dress
			Civic Archaeological Museum of Milan	
21	4	A.09.10692	Schist standing Buddha, II-III century A.D.	Gilding with ground layer from drapery dress
22	5	A.988.02.1	Painted stucco Monk, IV-V century A.D.	Red layer and stucco from the right side
23	6	A.990.04.1	Painted stucco Bodhisattva, IV century A.D.	Red layer with ground layer from arm
24	7	A.996.01.3	Figurative schist false corbel (Nagadanta)	Whitish layer from drapery dress
25	8	A.09.21700	Schist relief with Buddha life scenes, I-II century A.D.	Whitish ground layer from architectural motif
26	9	A.09.21700	Schist relief with Buddha life scenes, I-II century A.D.	Whitish ground layer from figure
27	10	A.09.2921	Schist Bodhisattva stele, II-IV century A.D.	White ground layer from drapery dress
28	11	A.09.2921	Schist Bodhisattva stele, II-IV century A.D.	Schist with traces of ground layer from the top
29	12	A.09.2921	Schist Bodhisattva stele, II-IV century A.D.	White ground layer from drapery dress
30	14	A.990.05.1	Figured schist capital of a pillar, I-II century A.D.	Schist with whitish ground layer from base
31	15	A.990.05.1	Figured schist capital of a pillar, I-II century A.D.	Schist with whitish ground layer from base
32	17	A.987.03.1	Stucco Buddha head	Red layer from ear
33	25	A.09.9421	Clay Brahma head	Yellow layer from hair
			Oriental Art Museum of Turin	
34	1	4581	Schist corbel, probably I-II century A.D.	Gilding from bottom
35	2	4581	Schist corbel, probably I-II century A.D.	Gilding from the top

Fig. 54
Sampling of clay Brahma head from Milan Museum (sample 33) (photo S.Pannuzi).

Fig. 55
Clay Brahma head from Milan Museum (sample 33): micro-photography of cross section of the sample.

Fig. 56
Clay Brahma head from Milan Museum, micro-photography: blow up of cross section of the sample.

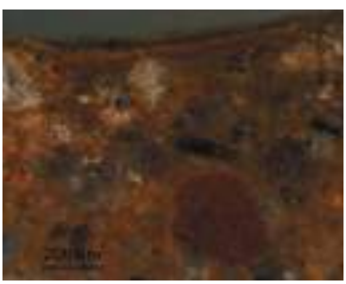


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Fig.57
Schist gilded corbel from MAO of Turin, detail of the sampling (photo S.Pannuzi).

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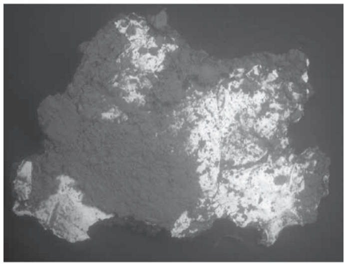
Fig. 58
Schist gilded corbel from MAO of Turin: microphotography of sample 34.

Fig. 59
Schist gilded corbel from MAO of Turin: SEM image of sample 34.

Fig. 60
Schist gilded corbel from MAO of Turin: SEM blow up image of sample 34.



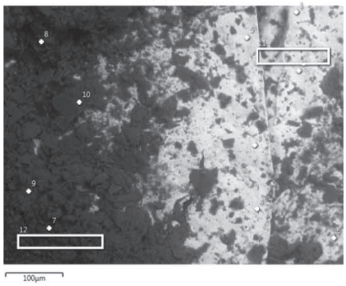


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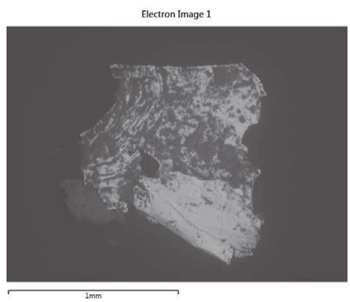
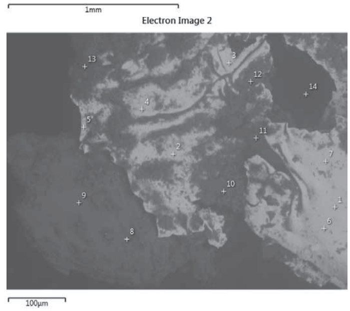
Fig. 61
Schist gilded corbel from MAO of Turin: microphotography of sample 35.

Fig. 62
Schist gilded corbel from MAO of Turin: SEM image of sample 35.

Fig. 63
Schist gilded corbel from MAO of Turin: SEM blow up image of sample 35.





The characterisation of paint binders in the polychromies and gildings of the Gandharan artworks

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Fig. 3
Painted clay Brahma head from Milan Museum (A.09.9421, sample 25) (photo Simona Pannuzi).

Abstract

In a polychrome artefact, coloured paint layers are applied on architectural elements or sculptures. Paint layers are made up of the colour, which is most typically an inorganic pigment and, with the exception of frescos, an organic binder, which enables the pigment to be dispersed and applied with a brush. From an analytical point of view the characterisation of organic paint binders is very challenging: the organic matter represents a very small amount of the total weight of the sample which is very small and aged. In this paper we describe the analytical approach applied for the characterisation of samples collected from a selection Gandhara polychromies. The analytical strategies and techniques employed are described and examples of the results obtained are presented.

Introduction

In a polychrome artefact, coloured paint layers are applied on architectural elements, sculptures, etc (Harris, 1977). Paint layers are always made up of the same fundamental components: the colour, which is most typically an inorganic pigment — a fine powder of inorganic coloured material — and, with the exception of frescos, an organic binder, which enables the pigment to be dispersed and applied with a brush. The organic binder is a fluid material that, upon drying and curing, produces a solid and elastic film, which keeps the pigment particles together, and ensures the adhesion of the coloured layer on the support. In the course of the centuries, artists have always experimented with a variety of organic natural materials to be used as paint binders, alone or in mixture, which are all based on four main classes of natural occurring organic compounds - proteins, lipids, carbohydrates and terpenoids (Mills and White, 2012). In most cases artists used many layers of paint to produce the wanted aesthetical effects, making a polychromy a complex, highly heterogeneous, multi-material and a multi-layered structure.

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The chemical analysis of organic paint binders

From an analytical point of view the characterisation of organic paint binders is very challenging (Colombini et al., 2010). Several organic materials are often simultaneously present in the layered structure, mixed with inorganic materials. In these mixtures, the organic matter represents a very small amount of the total weight of the sample (a few percentage points in the overall weight, or even lower), and the sample is, for obvious reasons, very small (0.1-100 mg). Moreover, non-original compounds, which have formed as a result of curing and ageing, interaction with the environment as well as other materials simultaneously present, or which were introduced during past restoration treatments, are also present.

As a result of all this, analytical approaches must be specifically developed for the characterisation of organic materials in the field of cultural heritage, and much research has been devoted at this task by the scientific community (Colombini et al., 2010; Vinciguerra et al., 2016; Bonaduce et al., 2016; Cartechini et al., 2010; Dallongeville et al. 2015;, Calvano et al., 2016).

Among the paint binders used in ancient polychromies, saccharidic and proteinaceous materials are the most commonly found, from the Far East to the Mediterranean Basin (Bonaduce, Ribechini et al. 2016), as for example the polychromy of the Terracotta Army, Xi'an, China (3rd century BC (Bonaduce et al., 2008)), that of the lost Giant Buddhas of Bāmiyān, Aghanistan, (6th-7th century AD) (Lluveras-Tenorio et al., 2017), and the murals of the Palace of Nestor, Pylos, Greece (13th century BC (Brécoulaki et al., 2012)).

Saccharidic and proteinaceous materials were both identified in the samples collected from a selection Gandhara polychromies, and in the following paragraphs their analysis is discussed and examples are presented.

Saccharide materials

Plant gums are the most commonly used saccharide materials as paint binders. These are naturally occurring polysaccharides, exuded from several species of plants or extracted from the endosperm of some seeds, in-

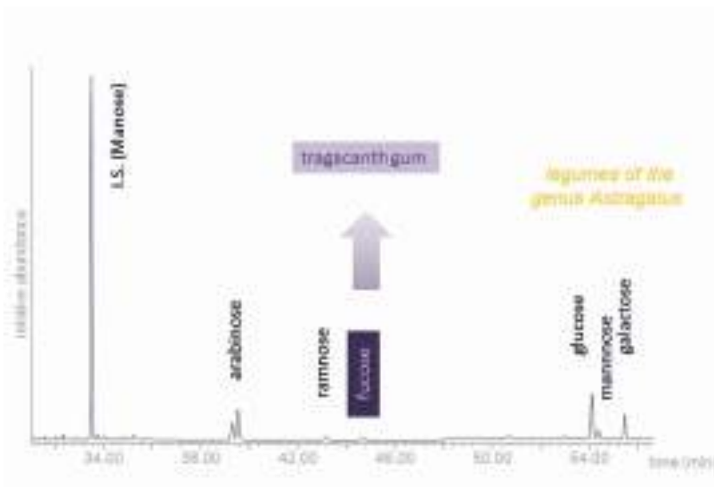

Fig. 1
Chromatogram in the SIM mode relative to the fraction containing the saccharide material of a polychrome sample coming from an excavation site in Afghanistan (Tapa Sardar, bulk sample), and dated to Late Gandharan period. Chromatographic peaks correspond to the different sugars identified. I.S. corresponds to internal standard of derivatisation (mannitol).

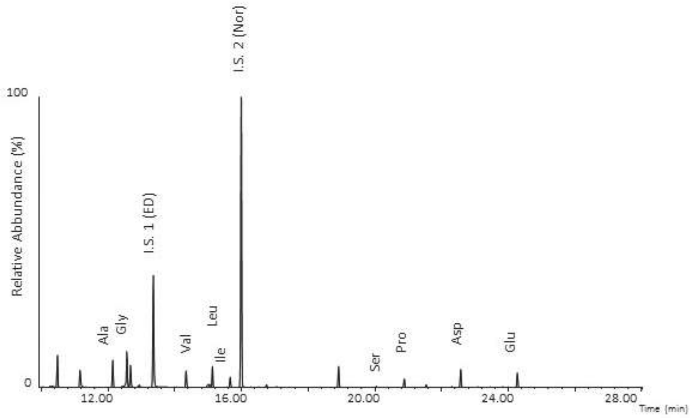

Fig. 2
Chromatogram in the SIM mode relative to the fraction containing the proteinaceous material of a polychrome sample coming from an excavation site in Pakistan, and dating back to the 3rd century AD (sample AKD14C, preparation layer). Chromatographic peaks correspond to: S.I.1 corresponds to internal standard of injection (Hexadecane), S.I.2 corresponds to internal standard of derivatization (norleucine).
Amino acids:
Ala=alanine; Gly=glycine; Val=valine; Leu=leucine; Ile=isoleucine; Prot=proline; Ser =serine; Phe=phenylalanine; Asp=aspartic acid; Glu=glutamic acid.

cluding arabic gum, exuded from *Acacia Senegal* and *Acacia Seyal* plants, tragacanth gum, exuded from *Astragalus genus* plants, and fruit tree gum, obtained mainly from cherry, apricot, peach and plum trees. Honey is also a saccharide material, which has been used as additive to increase the cohesion of paint layers in ancient polychromies (Lluveras-Tenorio et al., 2017). From the chemical point of view, plant gums are made up of aldoses (xylose, arabinose, fucose, rhamnose, mannose, galactose) and uronic acids (glucuronic and galacturonic acids) - polymerised thought the glycoside bond, while honey contains free ketose (fructose) and aldose (glucose). The most common approach for the analysis of saccharide materials aimed at their identification in a paint sample is based on the use of gas chromatography coupled to mass spectrometry (Colombini et al., 2010). The analysis of polysaccharides by gas chromatography requires an initial chemolysis step to free the sugars, that is a chemical reaction to decompose the original polymer into the constituting building blocks: the sugars (Andreotti et al., 2008). The choice of GC is driven by the fact that several sugars are isomers and thus the resolution and determination of the molecular profile is essential in order to identify the source of the saccharide material. The identification of the source of the saccharide material is then based on the evaluation of molecular profiles, and on the comparison between the chromatographic sugar profile of the sample with that of reference gums (Bonaduce et al., 2007). The presence of mixtures of saccharide materials, the effect of ageing, interaction with inorganic materials, biological and environmental contaminations can all affect the sugar profile of a sample from a paint or polychromy, seriously challenging the data interpretation (Lluveras-Tenorio et al., 2012).
A sample scraped from one of the paint layers of a polychrome fragment coming from an excavation site in Afghanistan (Tapa Sardar bulk sample), probably dated to Late Gandharan period, showed the presence of aldoses above the detection limit of the procedure used, indicating that they did not originate from environmental contamination (Lluveras et al., 2009).

The saccharide profile comprised arabinose, rhamnose, fucose, glucose, mannose and galactose (Figure 1). The evaluation of the saccharide profile, its comparison with a database of reference materials (Lluveras-Tenorio et al., 2012), and an evaluation of its level of contamination, suggests the possible identification of tragacanth gum as the polysaccharide binder used in this paint layer materials (Lluveras-Tenorio et al., 2012).

Proteinaceous materials

Among the proteinaceous materials, those that most commonly have been used as paint binders (Mills and White, 2012) are:

animal glue, obtained by boiling bones, hide or other cartilaginous parts of animals. It is made of (partially hydrolysed) collagen;

egg, which can be used whole, or using only one of its components: the yolk or the glair. Dry whole hen's egg contains 45% of proteins, 41% of fats, and 2% of cholesterol. Ovoalbumin (54%), conalbumin (12%), ovomucoid (11%), e lysozyme (3.4%) are the most abundant proteins;

milk. Milk is a water emulsion of proteins and lipids. Dry cow milk contains 26% of proteins (casein, lactalbumin, lactoglobulin), 26% lipids, and sugars.

From the chemical point of view, a protein is made up of amino acids. Twenty are the natural amino acids, which are biosynthesised in cells: alanine - ala; arginine - arg; asparagine - asn; aspartic acid - asp; cysteine - cys; glutamine - gln; glutamic acid - glu; glycine - gly; histidine - his; isoleucine - ile; leucine - leu; lysine - lys; methionine - met; phenylalanine - phe; proline - pro; serine - ser; threonine - thr; tryptophan - trp; tyrosine - tyr; valine - val. In proteins of our interest, another amino acid is very imprortant, hydroxyproline (hyp), which can be found in animal glue, and is produced in a post-translational modification. In a protein, amino acids are bonded one to the other through the peptide bond, constituting natural high molecular weight polymers. From the analytical point of view, several analytical approaches have been proposed, which can be used to identify and characterise proteins in samples from paintings and polychromies (Dallongeville et al., 2015). They can be based on spectroscopic, immunochemical or mass spectrometric approaches. Proteinaceous materials can be analysed by GC-MS after decomposition of the polymer into its constituent building-blocks, the amino acids (Colombini et al., 2010). The sequence of the amino acids (relative abundances and order) determines the characteristics of each protein. For this reason, a way of distinguishing a protein from the other after GC-MS analysis, is to compare relative amino acidic composition of the sample to a database of amino acid profiles of reference materials (Dallongeville et al., 2015).

A sample collected from a polychrome decoration on plaster coming from an excavation site in Pakistan, and dating back to the 3rd century AD (sample AKD14C, preparation layer) showed the presence of amino acids above the limit of detection, indicating that they were not originating from environmental contamination. The chromatogram is show in Figure 2.

Protein name	Matching peptides	Sequence coverage
collagen alpha-1(I)	11	10%
collagen alpha-2(I)	10	12%
collagen alpha-1(III)	5	5%

Table 1
Results of the proteomics analysis of a sample from an excavation site in Pakistan, and dating back to the 3rd century AD (sample AKD14C, paint layer).

Source	Sample codes	Results
Milan Museum (2-3rd A.D.)	A.09.10692	animal glue
Milan Museum (4-5rd A.D.)	A.988.02.1	animal glue
Milan Museum	A.09.9421	animal glue
Paris, Museum Guimet (7rd A.D.)	MG 18957	animal glue, milk, egg
	MG 18959	animal glue, milk, egg
Pakistan, Swat, Barikot (second half of 3rd A.D.)	BKG 1123A BKG 1123B	traces of proteins – source not identified
Afghanistan,Tapa Sardar (probably Late Gandhara)	no code	tragacanth gum traces of proteins – source not identified in the paint layer
Pakistan, Swat, Amluk-dara (late 3rd AD)	AKD14C	animal glue in the paint layer and egg in the preparation

Table 2
Results of all investigation performed so far using both GC-MS and MS proteomics approaches on samples from Gandhāra polychromies.

As amino acids were only present at the trace level (that is below the level of quantitation), quantitative comparisons between the sample amino acid profile, and the databases of profiles of reference materials was thus not possible. The absence of hydroxyproline, though allows us to asses that animal glue is absent, and possibly milk or egg were used.

One of the most promising analytical approaches to identify proteins currently available is that based on proteomics, and most commonly bottom-up proteomics. Proteomic was introduced in the field of cultural heritage about thirteen years ago (Tokarski et al., 2006), and was imported from the clinical and biological research. In a bottom-up proteomic approach, proteins are extracted from the sample and subsequently treated with an enzyme -trypsin in the vast majority of the cases - to obtain specific peptides. These peptides are then analysed by mass spectrometry (Dallongeville et al., 2015). Unlike GC-MS, this approach allows to retain information on the amino acid sequence in the peptide, resulting in the fact that, proteomics enables us to unequivocally identifying a protein, and, in some cases, even the biological source of the protein.

Proteomics was used to analyse also a selection of the polychrome samples from Gandhara (fig.3). As an example, the results of the proteomics analysis of another sample from an excavation site in Pakistan, and dating back to the 3rd century AD (sample AKD14C, paint layer), are reported in Table 1.

The identification of 26 peptides ascribable to collagen allows us to ascertain the presence of animal glue in the sample. Moreover, a comparison of the peptide sequences with the available databases, allowed us also to identify the biological source of the collagen: bovine.
Results of all investigation performed so far using both GC-MS and MS proteomics approaches to determine organic binders in samples from Gandhāra polychromies are summarised in Table 2.

Conclusions

Scientific investigations of organic materials in polychrome objects may help us to unravel the complex, structured mixtures of aged natural materials that constitute paint layers. Identifying the materials present in polychrome objects, organic binders and pigments, is also fundamental to reconstruct the original appearance of the artifact, and can also contribute to the selection of suitable preservation strategies to be put in place in the course of a conservation treatment. Moreover, such knowledge is of great use in improving our understanding of cultural traditions, technical know-how, knowledge circulation of a certain period of time in a specific geographical area, finally helping to recreate a more accurate picture of our past. It has to be kept in mind, though, that each analytical technique gave us information only on a specific chemical aspect of the investigated material; thus, complex problems may be solved by using a wide range of techniques and exploiting the synergy of complimentary data and knowledge. In this context it is important to stress that, when planning an analysis, the questions to be answered are the key in determining the analytical approaches to be used. This entails a detailed discussion of the problematics between the conservator, the archaeologist and the analytical chemist. Also, scientific investigation should take place before conservation treatments are undertaken, in order to avoid the loss and/or contamination of the residual polychromies remaining on the object, irredeemably loosing forever such inestimable traces of our past.

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