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Non-invasive and Micro-invasive Investigations on Wall Paintings from a XIII century Temple in Bagan Valley (Myanmar)

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Abstract **- On August 24, 2016, a magnitude 6.8 earthquake struck central Myanmar, seriously damaging and partially destroying more than 300 structures in Bagan Archaeological Zone.**
Department of Archaeology, UNESCO Bangkok Office and Japan International Cooperation Agency collected information about the damage to the cultural heritage caused by the earthquake.
In February and July 2017, a scientific survey concerning XIII centuries wall paintings of temple Me-taw-ya, located in the south of Myinkaba village in Bagan site, carried out. It was supported by Tokyo National Research Institute for Cultural Properties (TNRICP).
As a part of a previous project, preliminary investigations were carried out to acquire information on constitutive materials and construction technology of wall paintings.
The conservation state of wall paintings and the presence of non-original materials were also investigated.
The goal of the present study is to obtain appropriate technical scientific information to draw up a "practical code" to be adopted in wall paintings restoration.

I. INTRODUCTION

The ancient city of Bagan (formerly called Pagan), placed in Myanmar Mandalay Region, was the capital as well as the political, economic and cultural nerve centre of the Pagan Empire from 1044 to 1287. Nowadays the remains of 2200 temples still survive in an area of 104 square kilometres in Bagan plains, being a part of the over 10,000 pagodas, temples and monasteries built during the kingdom [1].

Fig. 1. Temple No. 1205a Me-taw-ya from Bagan Archaeological Area

Fig. 2. Wall paintings in temple Me-ta w-ya

The earthquake that occurred in July 1975 destroyed a lot of monuments [2] and since the 1970s various experts from foreign countries focused on the conservation of Bagan wall paintings according to the authority of international cooperation organizations such as UNESCO and ICCROM.

After the earthquake, which occurred in August 2016, most of the temples were seriously damaged. Department of Archaeology (DoA) and UNESCO Bangkok Office collaborate to plan a risk and damage assessment and property conservation actions for Bagan temples and pagodas protection.

Furthermore, Japan International Cooperation Agency (JICA) and Tokyo National Research Institute for Cultural Properties (TNRICP) carried out a post-earthquake damage assessment survey carried out in order to investigate the state of conservation of Bagan religious buildings [3].

As a part of the same project, scientific surveys were carried out on *Me-taw-ya* Temple (No. 1205) with the aim of investigate wall paintings constitutive materials and construction techniques.

Moreover, the state of conservation of the wall paintings was checked to plan a proper restoration project of the temples [4].

The temple, dating XIII century, belongs to Bagan Dynasty and it is located in the middle of the Bagan Chauk Road, which connects Old Bagan and New Bagan, in the south of Myinkaba village in Bagan site (Fig. 1). The temple constituting materials are fired bricks and mortars, while whitish stucco partially covered the temple facades.

Wall paintings with geometric designs, vegetal, circular and diamonds patterns decorate the plasters of interior wall.

According the historical sources, the plaster executive techniques have been different throughout the times: in XI and XII century a mixture of mud, sand and organic binder (probably molasses) was used while since XII century lime and sand were applied on the wall. Plant-derived binder was used as medium to mixed the pigments.

The mural paintings decay was mainly caused by rainwater infiltrations because the roof was seriously damaged. Nests, insects, animal excrements as well as, flaking, graffiti, tarnishing of adhesives from previous restorations were found too.

The wall paintings colours are mostly whitish or yellowish with dark black, grey and red purple tones (Fig. 2). Probably a pigments discoloration was gone on and the original painting layers were bright-coloured but the decay changed them inexorably.

Therefore, the original pigments used in the mural paintings *palette* were colourful as yellow ochre, orpiment and As-based pigments, vermilion and charcoal.

II. SAMPLING

Me-Taw-Ya temple wall paintings were firstly submitted to non-invasive analysis, performed with ED-XRF spectrometer. Subsequently, representative plasters and paint layers samples (table 1) were collected and properly prepared. The samples were analyzed using micro invasive investigative techniques.

Sample Code	Sample description
MY31	Blackish paint layers and plaster
MY32	Brownish paint layers and plaster
MY33	Reddish paint layer and plaster
MY44	Blackish paint layer and plaster
MY45	Plaster
MY45e	Brownish/yellowish paint layer and plaster

Table 1. Sample list

III. METHODS

The wall paintings were investigated with both non-invasive and micro-invasive techniques as follow.

- Energy Dispersive X-ray Fluorescence (ED-XRF) analysis was carried using an Oxford Instruments X-Met 8000 energy dispersive handheld spectrometer, with X-Flash SDD detector and 6 mm diameter spot, with a Rh target X-ray tube operating both at 8 kV, 50 μA and 40 kV, 8 μA. The first operating condition is particularly sensitive to light elements (from about Al), the second to heavier ones including Sn, Sb and Ba K-lines. Measurement time was 100 s: 74 s at 8 kV and 26 s at 40 kV. Data were processed using proper software like Artax.
- Transmitted light optical microscope observations on samples cross sections were performed using reflected polarized and UV light. An OLYMPUS BX51 optical microscope was used directly connected to an Olympus SC50 camera and to Stream Basic software for images acquisition.
- Morphological observations and chemical microanalysis were carried out on the same cross sections by using Hitachi Tabletop TMT3030 Electron Scanning Microscope (SEM) equipped with an energy dispersive X-Ray spectrometer (EDS) and dedicated software Quantax 70. The elemental composition was carried out at acceleration voltage 20 kV with a variable working distance (from 7.3 to 11.4 mm).
- Samples were studied by using infrared spectroscopy

FT-IR/ATR. Infrared spectra were collected with a spectrophotometer Nicolet 380 (Thermo Electron Corporation) equipped with ATR accessory Smart Orbit and interfaced with a microscope FT-IR Nicolet Centaurus. The ATR accessory is equipped with a diamond crystal. FT-IR spectra were acquired in the range 400-4000 cm-1.
Micro-Raman spectra were recorded with a Labram instrument from the Jobin Yvon-Horiba, equipped with a red 633 nm laser, a Peltier-cooled (-70°C), CCD detector with 1024 x 256 pixels, spectral resolution 1 cm-1 and spatial resolution by 1 µm. According to the intrinsic intensity of the recorded spectrum, the scanning time varied from 5 to 20 s and and the number of scans from 5 to 20 with the laser power (5 mW) attenuated to about 1/10. Olympus long-distance objectives with 50 and 100 enlargements were used. Raman analyses were performed on selected cross sections.

IV. RESULTS

ED-XRF non-invasive analyses were carried out on-site to provide preliminary information in the constituting elements of plasters and paint layers.
In the plaster the main detected elements is calcium followed by silicon, potassium and iron. Therefore carbonate binder with silicatic aggregate was probably used. Sulphur was also detected and it could be related to sulphate phase linked to intervention of restoration or/and decay phenomena. Sometimes arsenic (arsenic-based pigments) and traces of chlorine were detected.
Calcium is always the main component revealed in paint layers. In brownish paint layer, high amounts of silicon, potassium, iron, titanium and manganese contents associated to earth pigments were detected.
Arsenic presence is related to As-based pigments and only in few cases it is in association with sulphur as orpiment/realgar. Mercury and sulphur are related to Hg-based pigment (cinnabar) and also zirconium and phosphorous were detected.
In brownish-yellowish paint layers high arsenic amounts were identified with low sulphur, mercury, potassium and chlorine traces.
In blackish tones, arsenic (As-based pigments) with silicon, iron, nickel and manganese traces (earth pigments) were detected. Mercury traces (probably related to altered cinnabar) and phosphorous were found.
In whitish tones, calcium, arsenic (As-based compounds), silicon, potassium, iron, nickel, phosphorous, titanium, manganese and mercury were detected.
Reddish tones are characterized by high amounts of arsenic (As-based pigments). Small quantity of mercury, in association with sulphur, is related to cinnabar. Silicon, iron, potassium, titanium and manganese are related to earth pigments. Phosphorous and chlorine traces were detected.

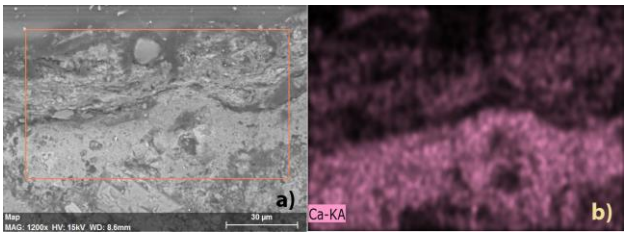

Fig. 3. MY31, SEM micrograph

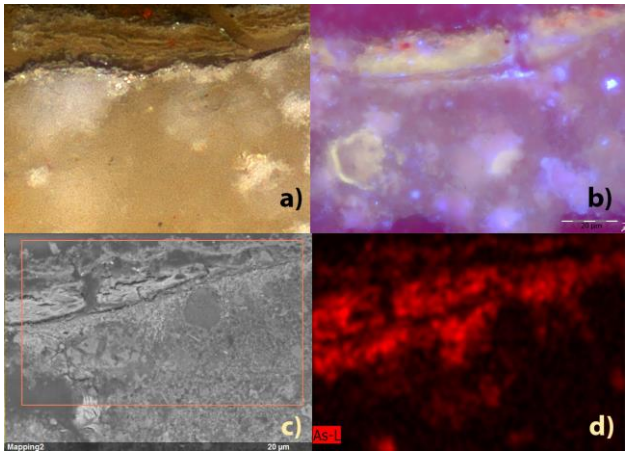

Fig. 4. Sample MY33: Optical microscope micrograph: (a) visible light: (b) UV light; (c) SEM micrograph; (d) As elemental map distribution (EDS)

Micro-invasive investigations using optical microscope and SEM-EDS were carried out on paint layers cross sections (MY33, MY44, MY45, MY45e).
In all the investigated samples, a whitish non-homogeneous plaster is present (level 0). The aggregate is poorly sorted and quartz, silicates and earth pigments constitute it.
A weak yellowish UV fluorescence was observed in areas of plasters areas that are probably related to the organic materials used in the preparation of plaster itself.
SEM-EDS pointed out the presence of a mainly Ca-based matrix confirming the use of carbonate/oxalate-based binder. Elements (Si, Mg, K, Al and Ti) related to mud clay binder were detected too while phosphorous was found only in traces. Also particles, whose composition is referred to silicates and aluminosilicates, iron oxides, micas, titanite/ilmenite were identified. Phosphorous traces were detected.
In MY33 plaster few fibrous arsenic-based particles were identified, probably related to arsenite/arsenates.
An overlaying finishing carbonate/oxalate layer (level 1, thickness 25 µ) is present, sometimes containing As-based fibrous particles too (fig. 3).
UV optical microscope observations revealed the presence of yellowish fluorescence, probably related to

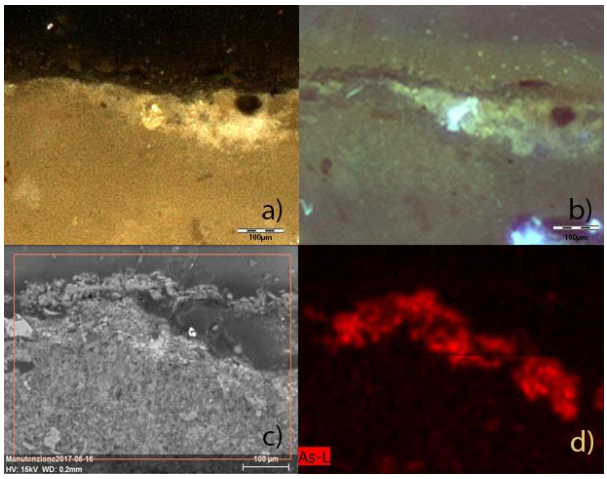

Fig. 5. Sample MY45e: Optical microscope micrograph: (a) visible light: (b) UV light; (c) SEM micrograph; (d) As elemental map distribution (EDS)

organic compounds.

The paint layers (level 2) are mainly composed of calcium and arsenic-based compounds.

The paint layers (level 2) are mainly composed of calcium and arsenic-based compounds.

In reddish tones (MY33), EDS element maps (Fig. 4) revealed the abundance of arsenic whose distribution has no correspondence with sulphur. Calcium, silicon, iron, aluminium, titanium, magnesium, carbon, chlorine and sodium have homogeneous distribution. An additional paint layer (level 3) in sample MY33 was observed. SEM-EDS revealed the presence of some Ca and As-rich particles as well as cinnabar and phosphorous, sodium and chlorine traces.

In blackish samples (My 31 and 44), SEM-EDS detected the presence of silicon, aluminium, iron, magnesium, potassium, titanium, chlorine, sulphur and sodium. Calcium, As-rich particles, aluminosilicates and traces of phosphorous compounds were detected too.

In brownish tones (MY32 and 45e) optical microscope investigations revealed a whitish paint layer (level 1). SEM-EDS elemental map revealed high calcium and arsenic amounts probably related to Ca and As-based (fig.5) compounds, as well as iron oxides silicates and chlorine traces. In the overlaying layer (level 2), SEM-EDS elemental map revealed the presence of silicon, aluminium, potassium, iron, phosphorous, and As-based particles (MY32, level 3). In My 45e cinnabar presence was detected.

ATR/FT-IR performed on My33 sample (level 0) detected calcium carbonate, calcium oxalate monohydrated and traces of silicates, confirming the high content of calcium in SEM-EDS analysis (fig. 6). The presence of oxalate can justify the use of lime mixed with a natural organic material as binder. The two painted layers (level 1 and 2) are composed by calcium oxalates (mono and bi-hydrates), calcium sulphate (as gypsum)

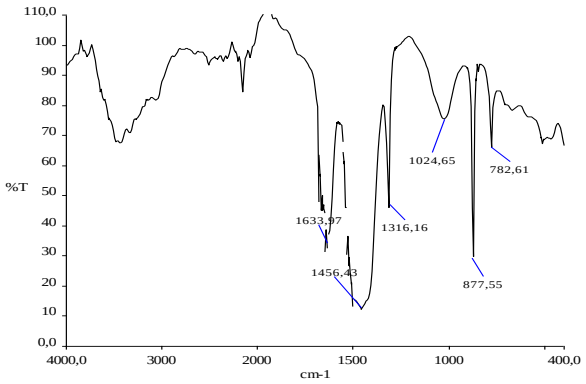

Fig. 6. FTIR spectrum of the white binder (level 0) of the sample MY33.

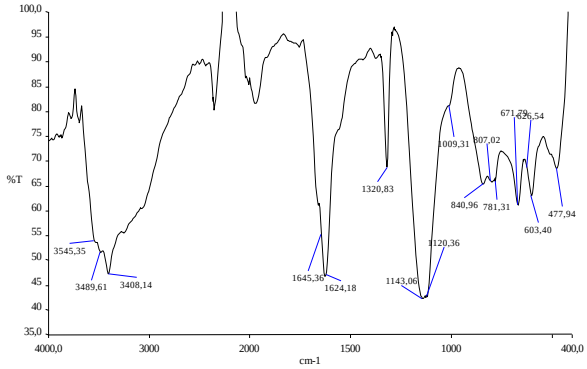

Fig. 7. FTIR spectrum of the grey superficial layers (levels 1 and 2) of the sample MY33

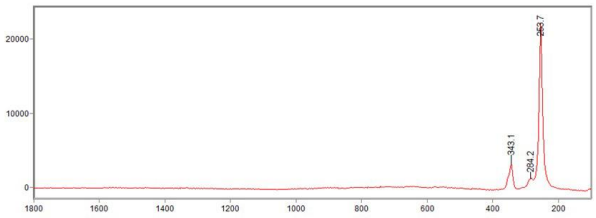

Fig. 8. Raman spectrum of MY45e

and arsenic based compounds (mainly arsenolite, orthoarsenates and orthoarsenites such as Fe(III)-orthoarsenite), traces of silicates (Fig. 7). Gypsum was detected only on the superficial layer.

µ-Raman pointed out an intense Raman fluorescence in panting layers, maybe due to some organic compound. Carbon black (sample MY33), magnetite (sample 44), goethite and cinnabar (sample 45e, fig. 8) were detected.

CONCLUSIONS

Integrated analyses performed on *Me-taw-ya* temple wall paintings suggest the use of lime mixed with natural, organic material and mud clay as binder. Silicates composed of (quartz, feldspar, spinels, Fe-oxides and Mn oxide) were used as aggregate. Some As-based particles were identified too.

Painted layers are very thin and sometimes detached from plaster. They are composed mainly of As-based pigments, cinnabar, probably meta-cinnabar, carbon black, iron oxides as magnetite, hematite and goethite.

Arsenic was indeed detected in all wall paintings, in dark, brown and light area. Probably arsenic is present both as oxide (e.g. arsenolite) or linked with cations such as in orthoarsenites and orthoarsenates (e.g. Fe(III)-orthoarsenite $2FeAsO_3$. $Fe_2O_3 \cdot 5H_2O$) and sometimes as As sulphide (e.g. orpiment).

In dark tones, Hg-based pigments are ascribable to meta-cinnabar because of alteration process. Wall paintings coloured with cinnabar that have been exposed in the open air frequently demonstrate a disfiguring, irreversible darkening of the surface [5]. Chlorine could have played a key role in the darkening process through the formation of light-sensitive mercury chloride compounds, or as a catalyst in the photochemical redox of Hg(II)S into Hg(0) and S(0).

V. REFERENCES

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