

Integrated Scientific Investigations on Constitutive Materials from Temple n.1205a Bagan Valley (Myanmar)

Maria Letizia Amadori¹, Paola Fermo², Valentina Raspugli¹, Valeria Comite², Francesco Maria Mini¹, Yoshifumi Maekawa³, KoKiLin⁴

¹*Department of Basic Sciences and Fundamentals, University of Urbino, Urbino (Italy)*

²*Department of Chemistry, University of Milan, Milan (Italy)*

³*Tokyo National Research Institute for Cultural Properties, Tokyo (Japan)*

⁴*Department of Archaeology of Bagan (Myanmar)*

Abstract - On August 24, 2016, a magnitude 6.8 earthquake struck central Myanmar. Bagan Archaeological Zone suffered extensive damage and more than 300 structures were partially destroyed. After the earthquake, information about the damage to cultural heritage was collected from the Department of Archaeology, Japan International Cooperation Agency and the UNESCO Bangkok Office. In addition, a post-earthquake damage assessment survey from Tokyo National Research Institute for Cultural Properties (TNRICP) was dispatched to Bagan from September 2016 in order to collect information on the structural damage to cultural heritage buildings.

As a part of the same project, a diagnostic research was carried on temple n. 1205a located in the archaeological area. The aim of the work was to acquire information on the constitutive materials and construction technology, i.e. compositions of bricks, mortars and stuccoes.

A further goal of the present study was to obtain sufficient technical-scientific knowledge to draw up a “practical code” to be adopted in Bagan valley restructuring plan.

I. INTRODUCTION

Bagan, formerly called Pagan, is an ancient city located in the Mandalay Region of Myanmar. From 1044 to 1287, Bagan was the capital as well as the political, economic and cultural nerve centre of the Pagan Empire. During the kingdom over 10,000 Buddhist temples, pagodas and monasteries were constructed in an area of 104 square kilometres in the Bagan plains, of which the remains of over 2200 temples and pagodas still survive to the present day. The magnificent architecture of pagodas in Bagan proves the achievement of Myanmar craftsmen



*Fig. 1. Temple n. 1205a from Bagan
Archaeological Area*

in handicrafts [1]. Fired bricks and mortars were used to build most of the temples in Bagan; whitish stuccoes covered the exterior surfaces of the walls that today are partially detached and destroyed.

The earthquake that occurred in July 1975 destroyed a lot of monuments [2]. On 24 August 2016, a magnitude 6.8 earthquake struck again central Myanmar. Bagan Archaeological Zone suffered extensive damage and more than 300 structures were partially destroyed.

After the earthquake, Department of Archaeology, Japan International Cooperation Agency and the UNESCO Bangkok Office collected information about the damage to cultural heritage. Furthermore, Tokyo National Research Institute for Cultural Properties (TNRICP) carried out a post-earthquake damage assessment survey in order to investigate the state of conservation of Bagan religious buildings [3]. As a part of the same project, a diagnostic research was carried out to acquire information on temple n. 1205a located in the archaeological area.

The aim of this work was to know the constitutive materials and construction technology, i.e. compositions of bricks, mortars and stuccoes.

II. SAMPLING

Bricks, stuccoes and mortars were firstly submitted to non-invasive analysis performed in situ (with ED-XRF spectrometer) to know the constituting elements on the investigated areas. Some of the constitutive materials are original while some of them are probably non-original.

The materials located in the exterior parts of temple n.1205a were then sampled(table 1).

Subsequently several samples were properly prepared to be analysed using micro invasive investigation techniques as follows.

III. METHODS

- Energy Dispersive X-ray Fluorescence (ED-XRF) analysis was carried out in situ in the temple 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 μ A and 40 kV, 8 μ A. 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 thin sections were performed using polarized 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 microanalyses were carried out, to investigate the chemical composition by a Hitachi Tabletop TMT3030 Electron Scanning Microscope (SEM) equipped with an energy dispersive X-Ray spectrometer (EDS) and dedicated software Quantax 70. The analyses were carried out at acceleration voltage 20 kV with a variable working distance (from 7.3 to 11.4 mm).
- Crystalline phase composition was determined by X-ray diffraction (XRD) on powders samples(bricks, mortars and stuccoes) using a Philips PW 3710 instrument.
- TG analyses were carried out on a selected group of samples by a Mettler Toledo TGA/DSC 3+ instrument

Table 1. Sample list collected from Temple n. 1205a

Sample Code	Sample description
MY1	Original red brick with mortar
MY2	Original mortar fragment
M1	Non-original red brick fragment
M2	Non-original red brick fragment
MY3	Original grey stucco
MY4	Original whitish stucco
MY5	Original stucco with decoration
MY6	Grey joint mortar fragment
MY7	Original mortar
MY8	White outer layer of stucco, vertical architectural element, left side, upper level
MY9	Inner layer of stucco, vertical architectural element, left side, upper level
MY10	Original brick sample, between MY8 and MY9
MY11	Inner layer stucco (non-original), left side, lower level
MY12	Outer layer stucco (non-original), left side, lower level
MY13	Joint mortar, between bricks (non-original)
MY14	Thick mortar (non-original) over MY13 brick (2 layers)
MY15	Mortar over MY14 (non-original)
MY16	White stucco (original)
MY17	Original brown joint mortar
MY 17.1	White stucco from outer decorations
MY 17.2	Original brown mortar over stucco
MY 17.3	Original brick, under MY17
MY50	Original brick, from entrance, left side

which allows simultaneous TG and DSC analyses. The analyses were conducted in the range 30°- 800° C, increasing the temperature with a rate of 20°C/minute, using about 2.5 mg of sample for each analysis.

- FT-IR/ATR 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} .

IV. RESULTS

A. Bricks

Non-invasive XRF analyses carried out on bricks both original and not revealed high amounts of silicon and

iron with lower and variable concentrations of potassium, calcium, titanium, aluminium and manganese. Low amounts of strontium, zirconium and barium traces were detected too with traces of chrome, chlorine and phosphorous.

The mineralogical and petrographic characterization analyses of the bricks allowed distinguishing the original ones (MY1, MY10, Y17.3 and MY50 samples) from those employed in restoration interventions (M1 and M2 samples).

In the original bricks (fig. 2) groundmass ranges from anisotropic to semi-isotropic. The a-plastic inclusions grain size varies from 63 µm to 125 µm (silt-very fine sand). A-plastic modal (volume) percentage [4] is about 10-20 % and it is composed of mono- and polycrystalline coarse quartz, biotite, alkali feldspars, fibrous muscovite, opaque minerals (iron oxides) and clinopyroxene. The coarser grains (> 125 µm) are scarce (volume percentage < 5 %) and they are mostly composed of quartz, biotite and argillaceous rock fragments. The voids percentage has amounts of about 5 %. XRD analysis (fig. 3) has confirmed the presence of the mineral phases observed by optical microscope, allowing to distinguish the presence of diopside (as clinopyroxene) and illite in the clay matrix (with exception of MY10 sample). The presence of illite was highlighted by FT-IR analysis (fig. 4).

In non-original bricks the groundmass is semi-isotropic. The a-plastic inclusions have a prevalent grain size from 63 µm to 250 µm (fine sand) with some quartz and K-feldspars coarser grains. A-plastic volume percentage is about 20-25% and it is composed of mono- and polycrystalline coarse quartz, cristobalite, biotite, alkali feldspars and plagioclase, rare lamellar calcic amphiboles, fibrous muscovite, opaque minerals (iron oxides) and rock fragments (i.e. quartzite). The voids percentage is about 10-15%. Also in this case, XRD confirms the observations carried out by OM. Among plagioclases, anorthite was identified while illite wasn't detected.

Traces of rare earths (cerium, lanthanum, neodymium, praseodymium), vanadium, chromium and phosphorous were detected in non original brick sample (fig. 5).

B. Stuccoes

Non-invasive ED-XRF analysis performed on stuccoes revealed the presence of two different typologies. The original stuccoes (MY3, MY4, MY5, MY8, MY9 and MY16 samples) are composed of calcium and silicon as main chemical elements, followed by potassium, iron, strontium, nickel, titanium, zirconium, silver, aluminium,

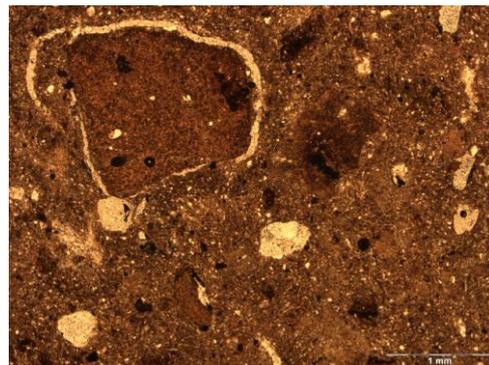


Fig. 2. Representative thin section of original brick, sample MY1,2,5x, nicols //, transmitted light

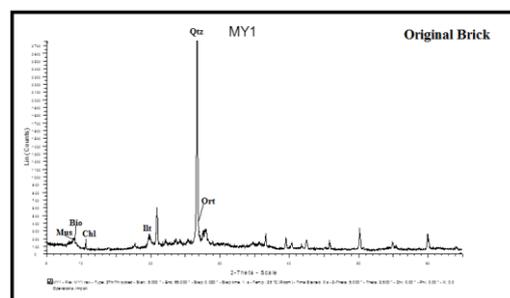


Fig. 3. XRD analyses performed on original brick. Mus=Muscovite; Biotite=Bio; Chl=Chlorite; Ill= Illite; Qtz= Quartz; Ort= Orthoclase

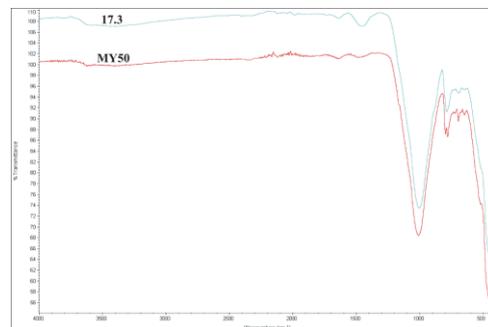


Fig. 4. FT-IR spectra of original brick sample

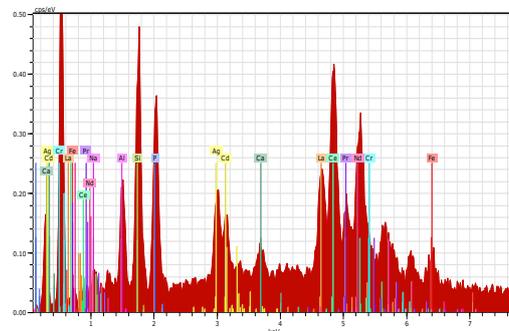


Fig. 5. SEM-EDS of M1 non-original brick sample

manganese and phosphorous. Calcium and sulphur were detected together with silicon,

potassium and iron in non-original stuccoes (MY11 and MY12 samples). Chlorine and trace of nickel, titanium, zirconium, silver, manganese and phosphorous were revealed as well.

Mineralogical and petrographic observations confirm the presence of two different typologies of stuccoes, one original (fig. 6) while the second is a gypsum-based stucco, probably related to a modern intervention of restoration.

In the original stuccoes, binder has carbonate composition, homogeneous distribution, micritic texture and a light brown colour. In general, the aggregate grain size ranges from coarse sand to silt and has silicate composition, mainly consisting (in decreasing order of abundance) of quartz, K-feldspars (orthoclase and microcline), plagioclase, pyroxenes, Ca-amphibole, opaque minerals and garnet. Grog and stone fragments (limestone and quartzite) were detected. Traces of bioclasts (radiolaria, shells and vegetal frustules) are also present. Inclusions volume percentage is about 20-30%. Percentage of voids is about 5-10%. Macro-porosity is mainly given by sub-rounded micro-vacuoles. Also in this case XRD analysis confirms petrographic observations. EDS allowed to detect traces of yttrium and phosphorous in the sample MY5 (fig. 9).

Gypsum has been confirmed by XRD and FT-IR analyses in sample MY12 (fig. 9).

C. Mortars

ED-XRF non-invasive investigations were performed on mortars in situ. Generally high silicon and calcium amounts were revealed, followed by potassium and iron. Titanium, strontium, nickel, manganese and traces of silver, chlorine, sulphur, phosphorous, chrome, zirconium were detected too.

In the original mortars (MY2, MY6, MY7, MY17, MY17.2 samples) a silicate binder was detected instead of a carbonate binder (fig. 10).

The aggregate is poorly sorted and shows a rather inhomogeneous distribution. The grain-size ranges from 63 µm to about 1 mm with a prevalence of medium-to-coarse-sand-like grains. Various rounding grain degrees, from angular to moderately round, was observed. Inclusions volume percentage ranges from 15 to 25 %.

Quartz is the most represented crystalline phase followed, in decreasing order of abundance, by K-feldspar, plagioclase, Na-pyroxene, clinopyroxene, opaque minerals (magnetite and ilmenite), epidote, titanite and micas. Fragments of limestone, shells and well-preserved vegetal frustules were also detected. Coarser inclusions are represented by grog composed of brownish clay

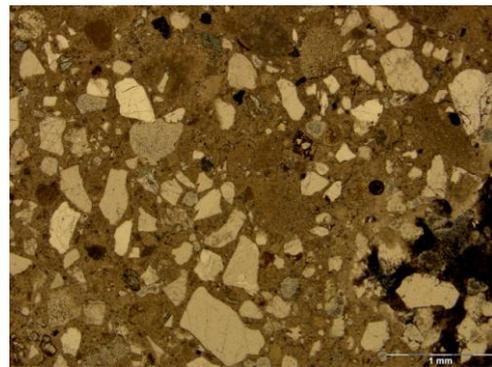


Fig. 6. Representative thin section of original stucco, sample MY3, 2.5x, nicols //, transmitted light

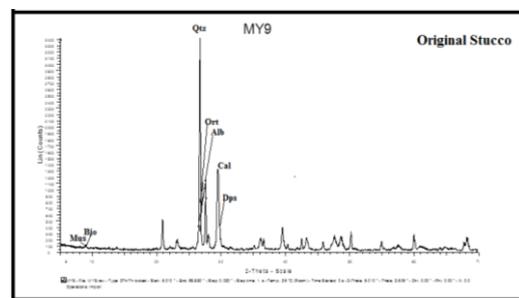


Fig. 7. XRD analyses performed on original stucco. Mus=Muscovite; Bio=Biotite; Qtz= Quartz; Ort= Orthoclase; Alb=Albite; Cal=Calcite; Chl=Chlorite; Dps=Diopside

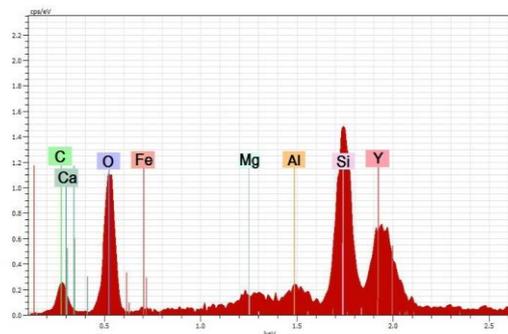


Fig. 8. SEM-EDS analysis of MY5 stucco sample, showing the presence of yttrium particle

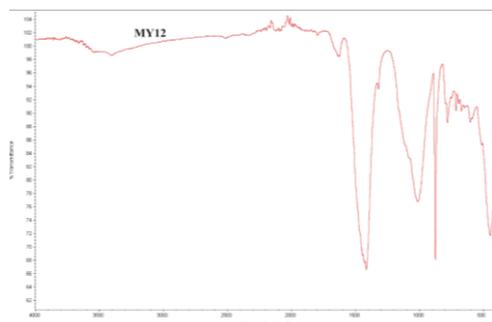


Fig. 9. FT-IR spectra of non-original stucco

matrix and angular fine a-plastic grains (63-125 μm). The most represented crystalline phases are quartz, muscovite, biotite, plagioclase and Ca-amphibole. The porosity is relatively high.

The second mortar, probably non-original, (MY13, MY14, MY15, MY17.1, MY17.2 samples), shows a carbonate binder associated with a silicate phase.

XRD and FT-IR (Figs. 11 and 12) analyses confirm the different composition of the two typologies.

The aggregate is poorly sorted and shows a rather inhomogeneous distribution. The grain size ranges from 63 μm to 1 mm with a prevalence of medium-sand-like grains.

Quartz is the most represented crystalline phase followed, in decreasing order of abundance, by K-feldspar (orthoclase and microcline), plagioclase, Na-pyroxene, amphibole, opaque minerals (magnetite and ilmenite), epidote, titanite and micas. Fragments of metamorphic rock (quartzite) and rare bioclasts were also observed. Inclusions volume percentage ranges from 15 to 25 %.

V. CONCLUSIONS

This study allowed to distinguish original and non-original materials used in the temple n. 1205a in Bagan region.

Two typologies of brick were identified, one original and the other related to a restoration intervention. From a textural point of view, in the original brick, a-plastic fraction grain size is fine and does not exceed 125 μm ; in non-original bricks the a-plastic fraction is more abundant than in the original ones and grain size reaches up to 250 μm . Regarding a-plastic mineralogical composition, coarse fragments of quartzite, present only in non-original bricks, could indicate a provenance from the metamorphic region north of Mandalay [5].

The porosity is lower in the original bricks (about 5%) and higher in the non-original ones (10-15%).

Furthermore, the difference in the isotropy of clay matrix could be attributed to a different thermal treatment for the non- vs the original bricks. In fact, ceramic fired in the temperature range of 700-850°C begin to show an isotropic clay matrix [6, 7, 8]. Then, the absence of illite in the non-original bricks suggests that they were probably fired at a temperature higher than 850°C. On the contrary, the original brick matrix shows anisotropic optical properties that allow to estimate a lower firing temperature.

The original stuccoes are composed of carbonate binder, with an appreciable amount of Mg (XRD analyses confirm the presence of Mg-calcite). The aggregate has a silicate composition and grain size ranges from silt to coarse sand. FT-IR analyses detected gypsum in non-original ones.

Mortars are characterized from two different binders.

The original mortars were made using a silicate

binder (clays) and organic binder (not detected probably because of deterioration) that somehow has hardened during the drying phase.

The a-plastic inclusions in original mortars are represented by quartz, muscovite, biotite, plagioclase and Ca-amphibole.

The second type of mortar shows a carbonate binder associated with a silicate phase.

Concerning the traces of rare earths detected in the "new" bricks, we have to remember that in tropical environments such as Myanmar, rocks are deeply weathered. The processes of soil formation commonly concentrate heavy minerals as residual deposits, resulting in an enriched-metal layer over the underlying, unweathered bedrock.

Also the yttrium presence could be referable (with phosphorous) to xenotime (yttrium orthophosphate YPO_4 , a mineral present in some sediments sands of southern Myanmar (Dawei and Myeik) which occurs in association with cassiterite deposits [9]. The mineral occurs in pegmatite veins, as a minor accessory mineral in granites and crystalline metamorphic rocks. It is also found as a heavy residual mineral in the sands of streams.

As a matter of fact, these elements are related to different deposits located in Mandalay Region [10, 11] and they could represent distinctive elements (markers) to recognize the constitutive materials provenance.

REFERENCES

- [1] D. M. Statdner, "Sacred sites of Burma", River Books, 2011, pp. 214-230.
- [2] J.C. Yarmola, "Conservation of Historic Brick Masonry in Pagan, Restricted, UNDP/ BUR/78/023 Technical Report", United Nations Development Programme, Paris 1987.
- [3] "Post-earthquake Damage Assessment Survey of Cultural Heritage Buildings at Bagan Archaeological Zone – Quick Report, Tokyo National Research Institute for Cultural Properties, December 2016.
- [4] Philpotts, A. R. "Petrography of igneous and metamorphic rocks". Englewood Cliffs, N.J: Prentice Hall., 1989.
- [5] H.L. Chibber, "The Geology of Burma", MacMillan and Co, London, 1934, p. 530.
- [6] J.D Seger, "Retrieving the Past: Essays on Archaeological Research and Methodology in Honor of Gus W. Van Beek, Eisenbrauns", 1996, p. 312.
- [7] S.J. Vaughan, "Ceramic Petrology and Petrography in the Aegean", *Am. J. Arch.* 99 (1), 1995, 115-117
- [8] C.A. Rice, Process for surface treating clay minerals and resultant products. U.S. Patent No 4,690,868, 1987.
- [9] Nagaiyar Krishnamurthy, Chiranjib Kumar Gupta,

“Extractive Metallurgy of Rare Earths”, Second Edition, pag.182; <http://www.mineralszone.com>.

- [10] K. M. Kyu, Y. Y. Myint, S. Yee, “The study of the Elemental Concentration in Some Rocks and Cements in Myanmar,”*Jour. Myan. Acad. Arts & Sc.* Vol III N. 3 (1) Physics, 2005, pp. 107- 119.
- [11] A. T. Tara, T. Z. Myob, T. M. Hlaingc, B. B. M. Wind, “Study on Processing of Rare Earth Oxide from Monazite, MongmitMyitsone Region”, *American Scientific Research Journal for Engineering, Technology, and Sciences (ASRJETS)*, Vol 27, N. 1, 2017, 43-51, pp. 2313-4410.