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Culture Sector
World Heritage Centre

H.E. Ms Tea Katukia
Ambassador Extraordinary and
Plenipotentiary of Georgia to
France
Permanent Delegate of Georgia to
UNESCO
UNESCO House

Ref: CLT/WHC/EUR/20/12998 7 December 2020

Subject: State of conservation of the World Heritage property 'Gelati Monastery'

Dear Ambassador,

I have the pleasure to transmit herewith the ICOMOS Technical Review on the temporary scaffolding and roofing project at the Church of the Virgin, as part of the World Heritage property 'Gelati Monastery'.

Please kindly be informed that ICOMOS concludes to construct the scaffolding with temporary roofing, covering not only the areas of the damaged roofing but the entire roof of the Church of the Virgin (perhaps with the exception of the dome) to prevent the further penetration of rainwater or humidity during the coming winter, and that temporary cover should be constructed in a way that allows the implementation of assessment work to identify the sources of water penetration and any additional damage to the roofing caused by the destruction of the tiles, and defects in the gutter construction in the joints between the stone walls and the roofing.

Furthermore, ICOMOS recommends formulating a comprehensive Conservation Management Plan divided into different implementation phases and followed by a combined action plan, to be submitted upon the finalisation to the World Heritage Centre and Advisory Bodies for review, in compliance with Paragraph 172 of the *Operational Guidelines*.

Finally, ICOMOS considers that the proposed "Hazards Mitigation Short-Term Action Plan" adequately responds to the requirements of the immediate rescue operations, as well as to the preconditions for the study of a Conservation Management Plan for the Church of the Virgin. Therefore, it is advised that the State Party can proceed to fulfil the recommendations and actions following the framework of the proposed Short-Term Action Plan, in order to continue elaborating the proposed Conservation Management Plan.

We would appreciate if you would share the enclosed ICOMOS Technical Review (see Annex) with your relevant authorities for their consideration and keep the World Heritage Centre informed of ways by which these recommendations are being taken into account.

…/...

Thanking you for your continuous collaboration and support in the implementation of the *World Heritage Convention*, I remain,

Yours sincerely,

M. Rössler

Mechtild Rössler
Director

Enc.

cc: Georgian National Commission for UNESCO
National Focal Point for World Heritage
ICOMOS

Annex

ICOMOS Technical Review on the state of conservation of the Church of the Virgin as part of the Word Heritage property ‘Gelati Monastery’

ICOMOS Technical Review

Property	**Gelati Monastery**
State Party	**Georgia**
Property ID	**710**
Date of inscription	**1994**
Criteria	**(iv)**
Project	**Information report on the state of conservation of the Church of the Virgin and scaffolding and temporary roofing project**

Background

On 8 September 2020, the World Heritage Centre transmitted to ICOMOS information submitted by the State Party on the state of conservation of the Church of the Virgin in Gelati Monastery World Heritage property, comprising a letter with two annexes: an information report on the state of conservation of the Church of the Virgin, and the implemented project documentation for the temporary scaffolding and roofing of the Church of the Virgin.


The monastery complex in 2015.

The conservation-restoration works on the Church of the Virgin *inter alia* considered the replacement of previous metal roofing with handmade glazed ceramic tiles produced using traditional technology based on the archaeological findings.

While the entirety of the works on the new roofing had been successfully completed by the end of 2019, at the end of February 2020 there were confirmed problems regarding the arrangement of the roofing and the breaking or damage to part of the glazed ceramic tiles, and signs of water infiltration on the west arm of the Church of the Virgin.

Roofing arrangement

Issues with the roofing arrangement are identified on the chapels, porches, narthex, and the altar of the church, consisting of full and partial loss of roofing tiles, while on the joints between the tiles, loss, cracks, and loss of adhesion are observed.

On-site assessment revealed that the batch of the glazed tiles used (produced with white ceramic) are of low quality and are not suitable for roofing with lime mortar.

Stone conservation
On the fillings made during the stone conservation, stone colour alteration (assumedly due to moisture) and loss of cohesion and adhesion are observed.

Interior wall-paintings condition
Salt efflorescence has been detected as the main cause of deterioration, which is related to water infiltration through damaged roofs and the environmental conditions of the interior. Salt crystallization cycles have caused problems with the cohesion and adhesion of paint and plaster layers, loss of repair materials applied during previous interventions in the 20th century and loss of small wall painting fragment pieces from the original technology. Bioactivity has also been observed.

The phenomena have been detected in various places, however, the most critical issues are found on the church's west arm vault.

The regular monitoring carried out by the National Agency's specialists, and interviews with the monastery representatives, did not reveal the damage to the mosaic and/or the loss of any of its fragments.

Analysis

The following comments arise from ICOMOS' study of the "Temporary Roofing and Scaffolding Design for Gelati Main Church (Church of Virgin)" project, as well as from the evaluation of the situation, taking into consideration the assessments and recommendations of the previous ICOMOS Advisory missions.

Remark 1 – Building blocks:
The report of the last mission to the monument (joint ICOMOS/World Bank Advisory mission, 21-25 January 2015) underlined the main problems the Church of the Virgin was facing in terms of the condition of the roof, and that special attention should be paid to the condition of the building stone blocks of the monument.

"The stone has been significantly damaged for various reasons: mechanical, seismic actions, atmospheric downfall, seasonal temperature alterations and biological factors (lichens). The eaves stones are in the poorest condition (fig.11).

It is known that throughout history the building has been affected by earthquakes as well as man-made interventions. These traces are clearly visible on the body of the church and are marked on the measured drawings (fig.12). The connections of the secondary volumes with the main structure of the church have been weakened and the weathering of the facing masonry is evident (fig.13). However the most significant impact on the building has been caused by rain and wind (fig.14)" (page 6 of the 2015 mission report).

"Within the framework of the survey project, information is included related to the kind of damage of each stone of the masonry face of the main church and its location height. This documentation vividly shows that a significant number of stones are damaged by atmospheric downfall (Fig.12)" (page 8 of the 2015 mission report).

The report pointed out that special attention should be paid to the places where the roofs meet the vertical surfaces of the walls. The report focused especially on the western part of the cross and on its southern and northern sides - that is, exactly where the most serious problems of moisture inflow from the roofing system and from the open joints between the ashlar stones have recently appeared:

Detail of the upper western part – view from south (Fig.11 of the 2015 mission report).

Facing masonry to the tin covering – existing condition (Fig.13 of the 2015 mission report).

Disconnection between the blocks of a wall [west wing-north side] and alteration of the structural behaviour (Fig.58 of the 2015 mission report).

Remark 2 – Glazed roof tiles:
The report of the 2015 joint ICOMOS/World Bank Advisory mission notes that:

"The experience of the traditional coloring composition, the layer-applying technique, and the old firing technology were obtained after long-term research and experimental work: a) the palette of colors, implying for each tile not only one color, but a whole range of colors achieved by means of natural pigments with iron and other admixtures (fig.88), and b) greater transparency of the colors, distinguishing the Georgian glazing technique from the Asian one […] *The method (with green-tone glazed tiles) was first applied to replace the tin roofing of the two-storey St. Nicolas church (fig.89), in front of the Cathedral, and after that to the roofing of the side bell tower (fig.90), and that of St. George church (fig.91) - with excellent results"* (page 15 of the 2015 mission report).

"The ICOMOS representative […] *visited the private clay atelier producing the glazed tiles, where he was informed in detail about the procedure (fig.93, fig.94, fig.95, fig.96, fig.97, fig.98)"* (page 46 of the 2015 mission report).

Pictures from the process of production of the glazed tiles for the restoration of the church roofing (Figs. 88 and 95 of the 2015 mission report)

It should be noted that no issues have been reported to date concerning the subsequent covering of the dome of the Church of the Virgin with the same quality glazed tiles with red ceramics.

ICOMOS notes that in the information report on the state of conservation of the Church of the Virgin there is no explanation as to why the layer of the first batch of glazed tiles with red ceramics, which had been proven to function well and could be efficiently applied with lime mortar, was not continued to be applied. No mention is made regarding the reasons that dictated the change to white ceramic new tiles, nor regarding the specifications on the basis of which the second batch of white ceramic tiles was selected and approved by the Georgian Arts & Culture Centre, the contractor organization working on the roof of the World Heritage property.

Furthermore, ICOMOS notes that in a news article published in July 2020, it was reported that the Georgian Arts & Culture Centre said that the damage to tiling was *"'impossible to predict' as none of the* [white ceramic] *tiles later revealed to have failed had shown signs of visual defects during inspection after they were produced, and had undergone laboratory testing on 'mechanical characteristics' before being used in the rehabilitation works"*.[1] Just after the damage to the roofs appeared in 2020, *"on-site assessment revealed that these glazed ceramic tiles are of low quality and are not suitable for roofing with lime mortar"* (page 2 of the information report).

Additionally, ICOMOS notes that the kind of specifications and the methodology of the analysis under which the white ceramic glazed tiles were tested for their strength and shape before being used are not mentioned anywhere in the information report on the state of conservation of the Church of the Virgin. Likewise, new tile pieces are being prepared to replace the current ones. The new contractor for the repair of the roof is called to check the durability of the new replacement tile and its compatibility with lime mortar; however, there is no indication of the new specifications they must meet in order to avoid future failures: *"*[…] *first of all, it is necessary to carry out a laboratory test of the new, replacing tile and obtain an expert opinion on its durability and the possibility of arranging it on a lime mortar solution"* (page 4 of the project documentation).

Suggested recommendations

Suggested recommendation 1:
As an indication of the methodology and care with which the reconstruction of damaged original glazed tiles should be treated, ICOMOS would suggest the experience of the Parma Cathedral in Italy, for which an exemplary analysis of the production techniques of medieval glazed tiles was elaborated (attached to this Technical Review).

A similar analysis could help formulate the specifications that must be met by the new produced glazed tiles and the mortars in order to avoid future failures.

Suggested recommendation 2:
If it turns out that the applied white ceramic tiles do not meet the specifications, then the whole batch of these tiles should be changed (i.e. removed from all surfaces) regardless of whether the tiles have been already damaged or not, because it is very likely that the rest of these tiles will cause similar problems in the future. The total replacement of the tiles with white ceramics is not clearly foreseen by the project, which makes it unclear whether the tiles would be changed throughout or only in the places where they are damaged:

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[1] 'Only 16 percent of Gelati monument roof damaged, says cultural heritage agency head', Agenda.ge, 25 July 2020.

- *“Considering the severity of damage, complete replacement of the tile made of white ceramics (preferably with tiles made of red ceramics which have already been tested and used on the upper parts of the Church)”* (page 4 of the project documentation);
- *“*[…] *arrange temporary roofing on the sections of the roofing where the tiles are damaged, as well as on the western arm (completely), in order to prevent further infiltration of water”* (page 3 of the project documentation);
- *“*[…] *replacement of tile coating should be initiated in stages (damaged tiles should be removed in such a way that the works do not cause vibration and in case of drilling, it is inadmissible to use the so-called perforator mode)”* (page 4 of the project documentation).

Suggested recommendation 3:
It is unclear why no stainless-steel nails were used for the general fixing of the tiles, but rather common rusty iron nails. The need to change to stainless-steel nails therefore constitutes an additional reason for removing and re-fixing the entire roof covering with tiles: *“Replacement of rusted tile securing nails with noncorrosive nails”* (page 4 of the project documentation).

Suggested recommendation 4:
During the construction of the joints at the edges of the roof that connect to the walls of the church, it would have been advantageous to have implemented special measures to prevent the inflow of water through these dangerous areas. Possible ways to address the problem include flashings. Flashing a roof refers to the act of installing various waterproof materials in valleys, joints, edges, roof penetrations and any other gaps to prevent water damage or leaks. This form of protection is a necessary construction practice, and it is widely applied.

Possible ways of addressing this issue are the following:

- As the tiles are impossible to cut precisely, it would have been beneficial to produce special pieces of ceramic tiles to form a "gutter" in a way that collects rainwater. Taking into account that the general roof covering required 7 kinds of main tiles and 6 additional different elements (e.g. antefixes for the edges of the tile rows; special pieces where the tile rows open and double in size, etc.), the production of an extra element for the purpose described could be considered.
- Flashings are metal sheets that are cut to size to fit along the edges of the roof. They are usually drawn under the structure of the roof, preventing any water from getting in. More importantly, flashings stop condensation because they are watertight. This means that they remove the moisture problem. In this case, the seal must be right because water tends to accumulate between different layers of roofing materials.

  Once flashings are installed, an additional layer of caulk is applied to seal the slightest holes. Most water damage to the roof occurs due to minuscule holes that remain after the flashing is installed. That is why caulking the roof is an essential step to close all the gaps.

  Metal flashings are by far the most reliable kind. The metals used are aluminium, copper stainless steel, and lead. Copper flashings are the most popular, but the choice of metal depends on the type of roofing material.

  In the case of the green tiles of the Church of the Virgin, a good-quality lead flashing can last longer and is virtually impossible to damage, due to lead’s properties as one of the strongest metals used for roofing purposes. Additionally, it has immense durability — up to 500 years. It would be fixed with stainless steel nails via hard plastic washers to the building ashlars.

Wall-paintings in the interior of the Church of the Virgin

Existing condition:

- A certain amount of fallen fragments of plastering with original paintings was observed on the platforms of the scaffolding arranged in the west arm of the Church of the Virgin.
- Analysis of the condition of the wall paintings in the Church of the Virgin**,** St. George Church and the Southern Porch was carried out; condition phenomena have been identified, documented and categorized according to:
    - Areas that have been historically damaged/deteriorated;
    - Newly damaged/deteriorated areas (occurred after roof rehabilitation).

  Apart from this, the rate and distribution of detrimental change has been determined in order to establish whether deterioration is active or not.
- According to the condition assessment of the façades and interior, a possible correlation between those two has been identified.

Church of the Virgin: Barrel-vaulted western cross arm (from the Report of the joint World Heritage Centre /ICOMOS/ICCROM Advisory Mission to Bagrati cathedral and Gelati monastery, March 2010)

Suggested recommendations concerning the current state of the murals

Suggested recommendation 5:
The necessary time must be ensured to allow the phenomena of moisture and the formation of salts to be relieved mainly by themselves, in a natural way. The abrupt drying of the murals can cause them "shock", as a result of which salts could remain inside the pigment or create peeling conditions.

Suggested recommendation 6:
The process of moisture release can be "facilitated" by careful and periodic removal of salts from the surface of the murals, by mechanical methods. However, great care must be taken so that during these rescue operations no damage and peeling of the original material of the frescoes (either the pigment or the substrate) occurs, as it may have lost its original cohesive ability. That is why salt reduction should be probably combined accordingly with local consolidation of the wall-paintings by appropriate compresses with Japanese tissue paper.

Suggested recommendation 7:

- Implement long-term condition monitoring of the wall paintings in the whole monastery complex.
- Make an accurate diagnosis of the causes of their deterioration and an indication as to whether old hotbeds have been reactivated or new ones created, as well as the reasons for their creation (e.g. defects in the roof covering, cracks on the ashlars, open joints between the wall surfaces and the domes or between the wall surfaces and the roof construction, etc.).
- Draw up a detailed plan for the treatment of the phenomenon.

Suggested recommendation 8:
The wall-painting diagnosis, immediate rescue operations, and conservation and restoration work should be performed by a specialized group of mural conservators.

Suggested recommendation 9:
It is absolutely necessary throughout the wall-painting conservation and restoration work that the respective external wall surfaces of the church remain completely dry and unaffected by rain (both from vertical and lateral incidences), or by any possible incoming moisture from the roof.

Suggested recommendation 10:
All of the above lead to the conclusion that it is necessary to cover the entire external surface of the church roof (except perhaps the dome) with protective temporary roofing and scaffolding until the above-mentioned works on the roof and on the wall-paintings in the interior of the church are finished. This is also supported by the following remark in the project text: *"However, as the condition of roofing has not yet been thoroughly inspected due to lack of scaffolding, the categories of works to be performed through the scaffolds specified in the design have not been determined"* (page 3 of the project documentation).

Conclusions

As a result of its analysis as set out above, ICOMOS presents the following advice to the State Party:

1) As a matter of emergency, ICOMOS advises to complete the construction of the scaffolding with temporary roofing, covering not only the areas of the damaged roofing but the entire roof of the Church of the Virgin (perhaps with the exception of the dome) in such a way as to prevent in any way the further penetration of rainwater or humidity during the coming winter.

2) The temporary cover should be constructed in a way that allows the implementation of assessment work to identify the sources of water penetration and any additional damage to the roofing caused by the destruction of the tiles, and defects in the gutter construction in the joints between the stone walls and the roofing, etc., as well as the finishing of relevant studies and lab testing. The temporary cover should also be able to protect the frescoes inside the church from any possible incoming moisture.

3) The works proposed above should formulate the basic components of a comprehensive Conservation Management Plan that would address issues that can be categorized into three broad groups:
    - the covering of the Church of the Virgin;
    - the condition of the ashlars of the masonry of the Church of the Virgin;
    - the state of conservation of the frescoes inside the Church of the Virgin.

The Conservation Management Plan, after analysing the existing conditions and identifying the causes of the problems, should suggest the proposed methodology for addressing each group of issues. The Conservation Management Plan could be divided into different implementation phases (for each one of the components or for some of the proposed actions addressed to them) following a combined action plan. Upon completion, the Conservation Management Plan should be submitted to the World Heritage Centre and the Advisory Bodies for review before any action is taken, in conformity with Paragraph 172 of the Operational Guidelines.

4) ICOMOS considers that the proposed *“Hazards Mitigation Short-Term Action Plan”* adequately responds to the requirements of the immediate rescue operations, as well as to the preconditions for the study of a Conservation Management Plan for the Church of the Virgin. Therefore, it is advised that the State Party can proceed to fulfil the recommendations and actions following the framework of the proposed Short-Term Action Plan, in order to continue elaborating the proposed Conservation Management Plan.

ICOMOS remains at the disposal of the State Party for further clarification on the above or assistance as required.

ICOMOS, Charenton-le-Pont
December 2020

Annexe: *“The steeple spire of the Parma Cathedral: An analysis of the glazed bricks and mortars”*, in: Journal of the European Ceramic Society, Volume 33, Issues 13–14, November 2013, Pages 2801-2809.

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Journal of the European Ceramic Society 33 (2013) 2801–2809

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The steeple spire of the Parma Cathedral: An analysis of the glazed bricks and mortars

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Received 18 February 2013; received in revised form 9 April 2013; accepted 18 April 2013
Available online 19 May 2013

Abstract

In October 2009, a terrible lightning struck the steeple spire of the Parma Cathedral, causing a fire. The fire-fighting operation made possible the discovery of the original spire ceiling made up by dichromatic glazed bricks, white and black, dating from the 14th century. Original materials presented a relevant decay, both for the high temperatures reached during the fire and for lack of maintenance. The research presents the first study of glazed bricks of the 14th century in Po Valley (Italy) with the purpose of collect chemical, mineralogical and petrographic data on the dichromatic glazed bricks. Brick samples with different kind of glazes and mortars exposed at different condition of fire were analyzed. The following techniques were used in the study: X-ray powder diffraction, optical microscopy, scanning electron microscopy analysis, inductively coupled plasma atomic emission spectroscopy and Raman spectroscopy. Glazes, applied on to Ca-rich paste, have a high lead content (41–57 wt%), with an high amount of tin (19–24 wt%) for the white opacified glazes and manganese (about 4.0 wt%) for the black ones. Typological and historical analysis allowed us to define the production technique of bricks and glazes. Mortars are mainly composed of lime binder and carbonate aggregate.

Keywords: Glaze; Brick; Mortar; SEM-EDS; ICP-AES

1. Introduction

In October 2009, a lightning struck the spire of the Parma Cathedral (Fig. 1). Following the fire-fighting operation was possible to discover the original roof of the conical spire, built in the 14th century with rounded profile brick elements with white and black glazes (Fig. 2). The precious dichromate roof was covered at the end of 16th century.

In literature, the glazing technique of the Asian, Syrian and Egyptian areas was studied extensively: early Islamic,[1,2] pre-Islamic[3] and both.[4] Several studies have been performed on glazed ceramics from Spain and Portugal.[5–8]

A detailed description of the history and production techniques of glazing can be found in literature.[2,10–12] In particular, some studies analyze high lead glazes and alkali-lead glazes,[2] tin-opacifier glazes,[4,9] coloring,[8,12,13] methods of glaze application, directly over the air-dried ceramic body or after a first firing (biscuit-fired bodies)[2] and the interaction between glazes and the ceramic body.[2,5]

In Italy most of studies have been performed on glazed pottery of the central regions,[14] e.g. Gubbio and Orvieto,[15] Siena,[16] no studies have been done on glazed bricks in the Po valley.

The literature also reports a series of studies to define the firing temperature of ceramics, especially in archeology: mineralogical, textural and chemical transformation of clay-rich materials during firing.[17–19]

The study presents the first original study of 14th century glazed bricks in Po Valley, North Italy. From the original masonry a number of samples were collected, glazed bricks and mortars, to characterize the original materials of the cover of the ancient spire of the Parma Cathedral by determining the production technique through a mineralogical, petrographic and chemical analysis of bricks and glazes. In particular, the firing process was defined by means of the study of the shape of the bricks and the discovery of some defects of glazing.

14th century and 16th century mortars of the spire were also characterized to define the provenance of the materials and the original recipes.

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http://dx.doi.org/10.1016/j.jeurceramsoc.2013.04.019

Fig. 1. Panoramic view of the Cathedral of Parma before the fire. The spire still had the copper covering, now removed.

2. Historical note

The Cathedral of Parma was edified starting from 1050 on the site of an early Christian cathedral, which dates back to the fifth century.

The edifice was built following a unique compositional scheme with three naves completed by apses, a protruding transept and a crypt, in agreement with the tradition of the Romanesque churches in the Po area.

Fig. 2. Particular of the conic spire, realized with dichromatic glazed bricks: white and black. The masonry shows deterioration, cracks and erosion of the bricks.

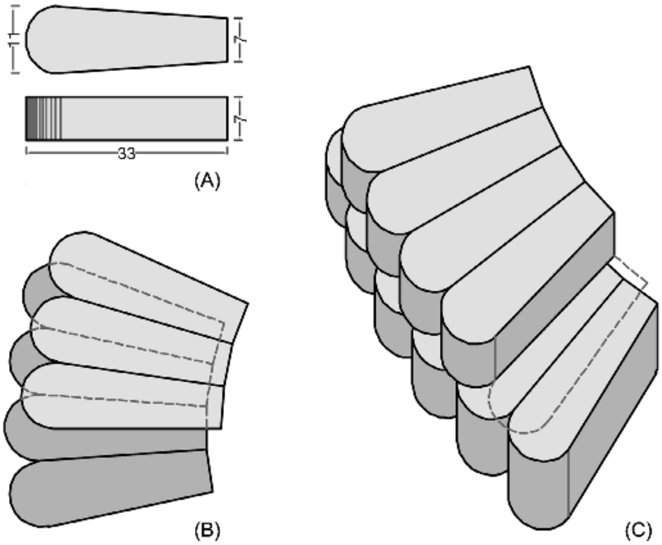

Fig. 3. (A) Dimensions and shape of the bricks. (B) and (C) Overlapping model of the bricks.

The building of the bell tower began in 1284, when the tower of the ancient cathedral was demolished. In 1291 the edifice was progressed to the height of the castle of the bells.

Documents attest that the whole mural-architectonic parts of the tower were already ended in 1294.[20] According to the *Chronicle* by Salimbene De Adam,[20] the conical spire was built after 1336 and before the 15th century.

The model of the conic spire, realized with curved radial bricks (Fig. 2), was common in the Po Valley since the 13th century: see the bell tower of the Cathedral of Piacenza and the San Donnino Basilica in Fidenza, Parma. Other more recent examples are the majolica spires in Sicily, documented since 1579 for the construction of the spire of S. Giacomo in Collesano (Palermo), now collapsed.[21]

In Parma the primitive glazed brick masonry of the spire endures to the end of the 16th century when, because of the materials deterioration, spire was covered with a copper roofing. The project, by Giorgio Edoari da Erba, was executed in 1596.

Since the end of the 16th century to the recent fire the original covering was not visible.

The dichromatic brick decoration remained occulted for centuries.[22]

The conic spire, 15 m high, was realized in masonry with trapeze-shaped quoins, which have a curved external profile disposed in alternated courses (Fig. 3). The external part of bricks is covered by a dichromatic glaze, white and black (Fig. 2). The bicolor courses consist of 4 rows of white bricks and 4 of blacks.

Some cuneiform bricks are more tapered to close the circumference of the spire without an excessive amount of mortar and to correct the radial position of the bricks.

The structure leans on a polygonal basement with 16 sides, composed by regular courses of bricks which have smooth surface and reduced mortar joints. The masonry is about 33–35 cm thick, i.e. the depth of the bricks which constitute the structure.

At the top of the spire a cone of stones (arenaceous stone and Vicenza stone) supports a golden anemograph angel.

2.1. Conservation state

After the fire, the whole copper cover was removed; except a wooden beam of the basement, nothing of the ancient frame was left. Iron nails remained linked to masonry; they were inserted in the 16th century as anchorage for the cover to the masonry.

The ancient masonry structure was in poor state of preservation and, thus, the fire worsened an already advanced deterioration (Fig. 2).

The masonry showed deep fractures and some areas presented deep erosions and lacunas. Glazes showed superficial cracks and alterations which were probably due to the high temperature reached during the fire and by the following thermal shock produced by the water used to extinguish it. Glazes have portions of copper (from the cover) recast on the surface, pink shades are present on the surface, probably due to a reducing environment during the fire (the fire burn up in the space between the copper covering and the masonry), the glazes show small surface cracks with detached parts and swellings.

Mortar was affected by decohesion (powder consistency) and blackening on the surface caused by the thermal shock and the smoke.

3. Analytical methods

Nine samples of glazed bricks of different colors, white and black, six samples of mortars and two sample of plaster were collected at different level from the steeple spire (Fig. 4).

Sampling was planned in order to represent the two construction phases of the spire: the building (14th century) and the later intervention of covering (16th century).

Glazed bricks and mortars were investigated by petrographic, mineralogical and geochemical methods with the aim of defining glaze, brick and mortar characteristics. The methods of investigation were:

- In situ macroscopic observations; in particular, color, structure, glaze-brick interaction, surface aspect, manufacturing techniques, and pathology.
- Optical mineralogical microscopy, transmitted and reflected light (Nikon Eclipse LV100 POL), three thin sections for each sample.
- Scanning electron microscopy (JEOL 6400, Jeol Ltd., Tokyo, Japan) and energy-dispersive system microanalysis (Oxford Isis 300, Oxford Instruments, Abingdon, UK) on polished thin section, gold or carbon coated.
- X-ray powder diffraction (Philips PW-1710 diffractometer, Cu K_α radiation, [Philips Analytical Inc., Natick, MA]; Step Size: 0.05°.; Scan Rate: 0.750000; Scan Mode: Step; λ: 1.540562) with XPowder Ver. 2004.04.47 Pro program (PDF2 data base).[23]
- Raman spectroscopy (Jobin-Yvon Horiba LabRam Raman micro-spectrometer).
- Chemical analysis of major and trace elements by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES – FUS-ICP analysis method) of the bricks and mortar powder (8 g each sample, binder and aggregate together).

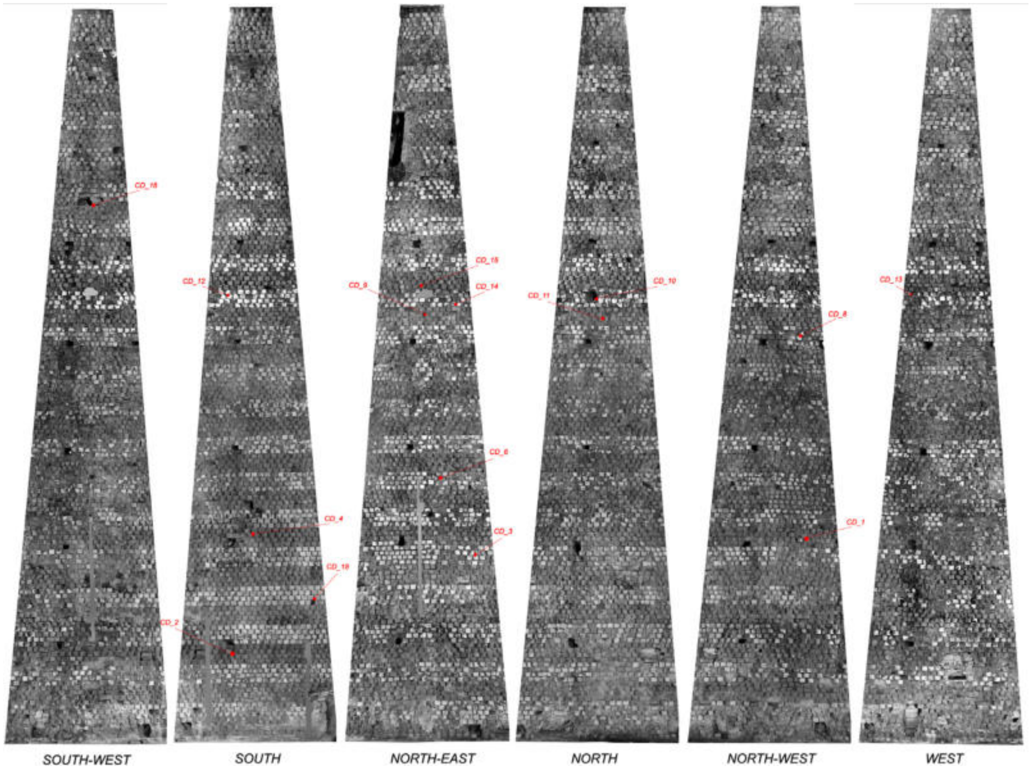

Fig. 4. Survey of the spire with sampling location.

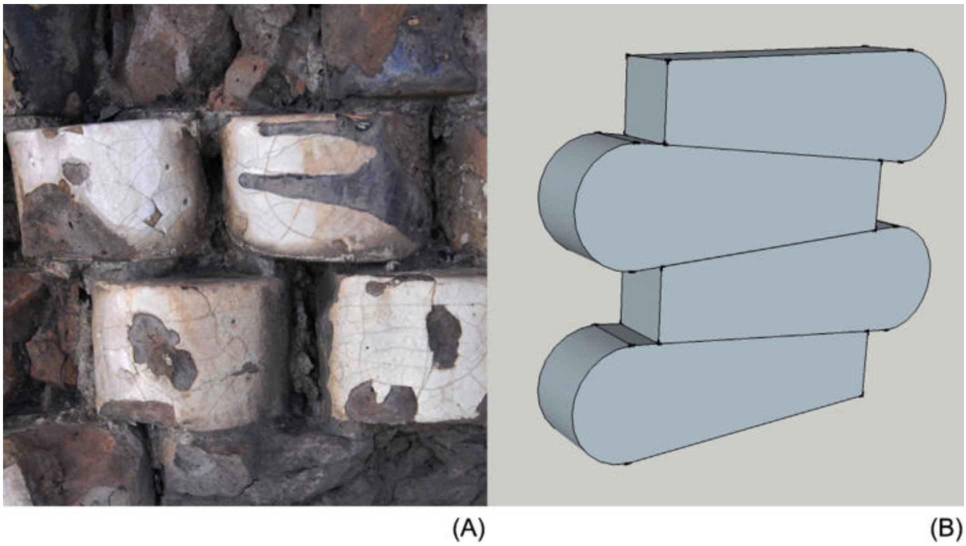

Fig. 5. (A) Black drops of black glaze over some white glazed bricks. (B) Reconstruction of the stacked bricks in the kiln during firing.

Mortars characteristics, porosity, grain morphology and size, have been determined using optical analysis, according to the Italian Standard Normal 12/83.[24] To estimate the aggregate/binder ratio, the Volume % estimation diagrams was used[25,26]; image analysis was used to evaluate the porosity.[27]

4. Experimental results and discussion

4.1. Production technique

The bricks and masonry analyses allowed defining the ancient production techniques. Through the survey of the bricks (Fig. 3A) and removing part of the masonry during the restoration works, the assembly system of the masonry has been defined (Figs. 3B and C).

The analysis of the characteristic shape of the bricks and the discovery of horizontal glaze casting over some bricks (Fig. 5A), helped to define the production and firing processes: the bricks, still uncooked, were immersed manually in the glaze, stacked as shown in Fig. 6B and fired in the kiln.

Is presumable that, to optimize the available space in the kiln, the bricks were stacked close to each other. These suppositions have been confirmed by mineralogical analysis of the bricks that show an uneven single-firing.

Furthermore, the presence of horizontal sagging (Fig. 5A) indicate that the white and black bricks were fired together, stacked on each other.

4.2. Bricks

The ceramic paste is a highly calcareous clay, 19–21 wt% CaO and 47–52 wt% SiO_2 (Table 1), with an iron oxide contents lower than 5 wt%. The chemical results show a substantially homogeneous composition. In the calcareous clay bodies the iron oxides are incorporated into calcium iron silicates, for this reason the brick paste has a pale pink color, allowing a minor quantity of opacifier into the glaze to cover the brick.[2,5,14]

Together with the chemical analysis, a mineralogical characterization of the paste was carried out. Powder diffractions reveal significant amounts of quartz, residual calcite, neo-formed diopside and gehlenite, anorthite and sanidine in trace. Trace of neo-formed diopside, gehlenite and anorthite were detected in all the samples. The decomposition of calcite in oxidizing atmosphere occurs at a low temperature, above 800 °C the free CaO can react with clay and SiO_2, forming new phases: gehlenite, diopside and plagioclase (anorthite). Experimental studies showed that gehlenite crystals begins to form at 800 °C through a reaction that occurs at the grain boundaries of CaO, Al_2O_3 and SiO_2 and from 900 °C it begins to disappear quickly.[13,17,28,29]

The presence of diopside, anorthite and gehlenite of neoformation is indicative of a firing temperature of about 900–950 °C. The high content of calcite in the samples CD_1, CD_2 and CD_14, together with high temperature phases, may be indicative of an uneven firing, caused by a low circulation of the air, a stacking of bricks (Fig. 5B) or a different position in the kiln with respect to the fire.

The clayey matrix of the samples has a mainly homogeneous texture characterized by open and closed pores (pores size: 0.02–4 mm), in a few cases they are of primary origin due to the preparation of the dough, while for the most part are of secondary origin, generated after the release of fluids during decomposition of the same phase which produces them. In the brick body are present quartz crystals, lithic fragments, altered mica minerals, apatite minerals, Fe-oxides and-Ti-oxides. Minerals show zoned compositions, as a result of the firing process, and coronal reaction, indices of a slow kinetic.[30]

4.3. Glazes

Brick samples consist of a portion of ceramic body with a layer of high lead glaze (PbO 41–57 wt%) of two different colors: white and black. Glazes have been investigated by scanning electron microscopy with EDS microanalysis to have information about their chemical (Table 2) and mineralogical features.

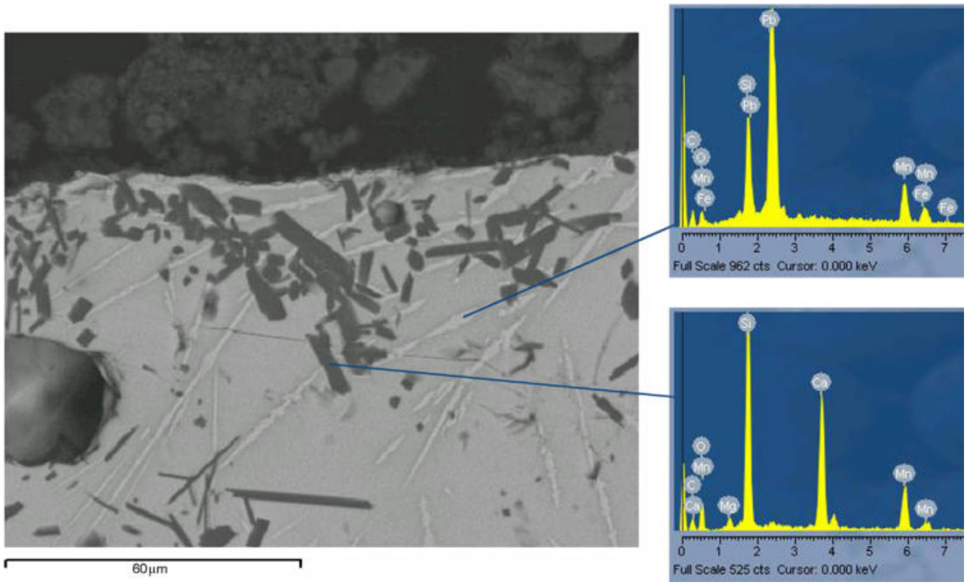

Fig. 6. Sample CD_2. Throughout the black glaze are present thin skeletal crystals formed during the firing; the blacks grains are constituted by Si, Ca and Mn (ED spectrum). Thus, the black pigment is attributable to a MnO–FeO compound.

Table 1
Major (oxide wt%) and trace elements (wt ppm) in the investigated bricks.

Samples	SiO_2	Al_2O_3	Fe_2O_3(T)	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI	Total	Ba	Sr	Y	Sc	Zr	V
Brick																		
CD_2	52.59	12.33	4.86	0.118	2.36	19.32	0.91	1.66	0.608	0.19	5.59	100.54	368	588	25	12	151	82
CD_3	47.01	10.55	4.31	0.122	2.16	21.69	0.91	1.68	0.516	0.28	8.98	98.21	352	672	23	10	139	79
CD_4	51.36	11.65	4.79	0.148	2.43	21.38	1.01	2.38	0.581	0.41	2.25	98.39	435	750	24	11	144	76
CD_8	48.36	11.33	4.49	0.113	2.23	19.76	0.77	1.82	0.555	0.22	10.65	100.30	391	597	24	11	136	88
Mortar																		
CD_13	26.11	3.61	2.37	0.151	1.28	36.54	0.32	0.70	0.150	0.16	29.03	100.42	198	1043	12	5	49	44
CD_18	20.67	3.05	1.76	0.123	1.00	38.61	0.36	0.58	0.133	0.18	32.5	98.97	263	1054	12	4	36	42
CD_9	27.01	3.64	2.23	0.168	1.12	35.08	0.22	0.42	0.153	0.14	29.54	99.72	131	655	13	5	45	53
CD_12	24.00	3.08	1.91	0.144	1.11	36.04	0.28	0.56	0.130	0.19	30.87	98.31	205	780	12	4	41	58
CD_10	5.30	1.29	0.57	0.021	0.98	34.01	0.23	0.36	0.060	0.26	11.49	54.57	58	1034	2	2	22	17
CD_16	5.97	1.45	0.61	0.021	1.02	35.71	0.18	0.46	0.067	0.05	9.42	54.96	65	1076	3	2	19	17

wt% = per cent weight; ppm wt = part per million weight; LOI includes H_2O and CO_2; T = total Fe as Fe_2O_3.

The analyses reveal a similar composition of white and black glazes: samples have the same proportion of SiO_2–PbO and differ only for the presence of FeO–MnO in black glazes and tin as opacifier in the whites.

The total alkaline content is less than about 1 wt% ($Na_2O + K_2O$) and Al_2O_3 about 1% (except CD_2), suggesting the use in all the sample of a quite pure quartz sand for glazes production[5].

White glazes belong to the class of 'tin-opacified high lead glazes': in addition to lead, they have a high SnO_2 content. Cassiterite crystals were added to improve glaze flux during firing and to confer an opaque shade to the glaze layer.[31]

Table 2
Energy-dispersive X-ray spectroscopy microanalysis results of glazes (wt%).[a]

Samples		Na_2O	MgO	AlO_3	SiO_2	K_2O	CaO	MnO	SnO_2	FeO	PbO
CD_1	B	0	0.40	1.00	34.60	0	2.52	3.80	0	0	57.48
CD_2	B	0.34	0.90	5.17	33.01	1.41	10.02	4.20	0	2.80	42.19
CD_3	W	0.61	0.34	0.81	29.40	0	2.40	0	24.30	0	42.14
CD_6	W	0.71	0.36	1.06	27.64	0	2.68	0	21.08	0	44.34
CD_8	W	0.62	0	1.27	28.16	0	1.99	0	21.94	0	46.02
CD_11	W	0.71	0.38	1.05	30.11	0	2.55	0	21.35	0	43.85
CD_13	W	0.95	0	2.07	33.75	0	2.57	0	19.38	0	41.28

[a] Normalized to 100%.

B = black color glaze; W = white color glaze.

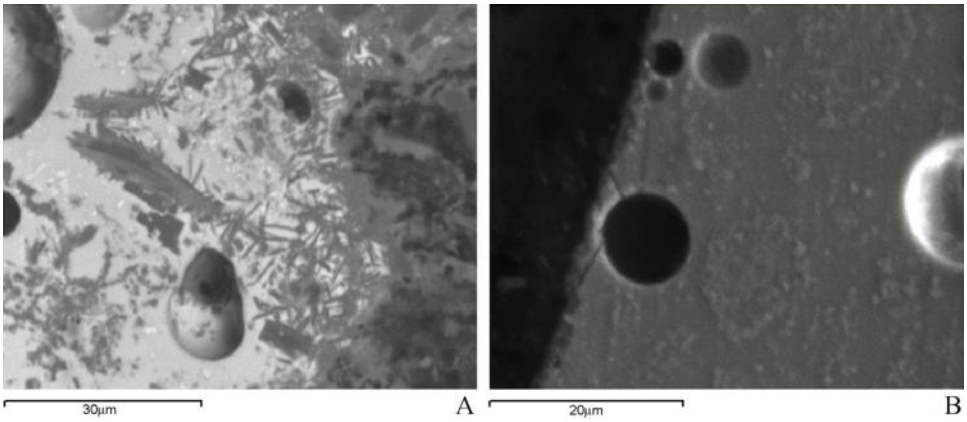

Fig. 7. Sample CD_6. (A) Interface: illite grains from the clay body show the growth of lead–potassium feldspar crystallites around. Within the glaze may be noted bright inclusions of tin oxide. (B) Heterogeneous distribution of tin oxide crystals in the glaze.

The analysis of the samples showed that the composition and microstructure are similar for all the white glazed, which could suggest a common production technique. The tin content are in the range 19–24 wt% SnO_2, with SnO_2/PbO ratios in the range 0.5–0.6 wt%.[14] The content of SnO_2 is very high compared to the contemporary productions from Eastern Spain (13–14th centuries), with SnO_2 in the range between 6 and 7 wt%,[5] to the previous productions from Egypt, with tin oxide rates of 5–9 wt%[4] and to the Italian Renaissance glazed pottery form Gubbio and Deruta (about 5.8 wt% SnO_2).[15]

SEM-EDS analysis evidence the uniform distribution of cassiterite crystals (SnO_2), confirmed by Raman Spectroscopy.[32]

Tin oxide was first dissolved in silica and lead vitreous matrix; during the firing process, tin oxide recrystallized to well develop cassiterite crystals. Recrystallization of cassiterite was dependent on time and temperature. In some samples, CD_3 and CD_13, the punctual SEM microanalysis revealed heterogeneity in the distribution of SnO_2.

The study of geological features and the identification of the quarries already existing at the time of the tower construction, allowed to hypothesize that tin used could be sourced from the mines of Campiglia Marittima (Tuscany), not far from Parma.[33]

Black glazes have an high lead content. From the analyses, the samples have different composition (Table 2): CD_2 has an high content of iron (FeO 2.8 wt%) and alkaline components, instead absent in CD_1. Manganese content (MnO about 4.0 wt%) is similar in the two samples and gives the black color, tinged with brown, to the glaze.[34,35] SEM-EDS analysis evidenced the presence, especially near the external edge, of very thin skeletal crystals containing lead, Mn, Fe, and Si, formed during the firing and black grains constituted by Si, Ca and Mn (Fig. 6). Microanalysis and microscopic examination indicated that an opacifier was not present in black glazes.

4.4. Body-glaze interface

During firing, interaction between glaze and clay body produces an interface layer, that is strongly related to the clay body typology, the temperature and time of firing.[1,2,11] In particular, in dry unfired bodies, elements such as aluminum, iron, potassium, calcium and magnesium diffuse from the body into the glaze and, as the concentration of these elements in the glaze increases, crystals of potassium–lead–aluminum-silicate are formed at the body–glaze interface, this has been detected

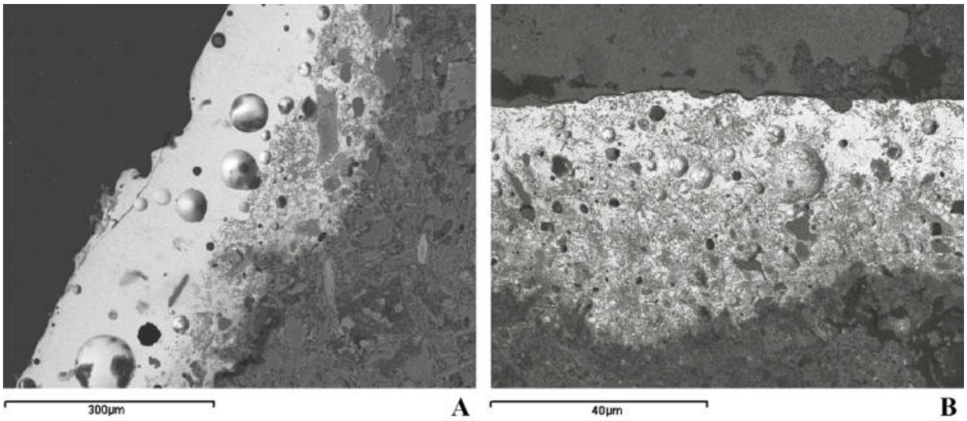

Fig. 8. The thickness of glaze and interface layer. (A) Sample CD_6, unreacted quartz crystals and elongated potassium–lead–aluminum-silicate crystals are present at the interface. (B) Sample CD_2, extended interface with coal particles, manganese dioxide and trace of Fe-oxide.

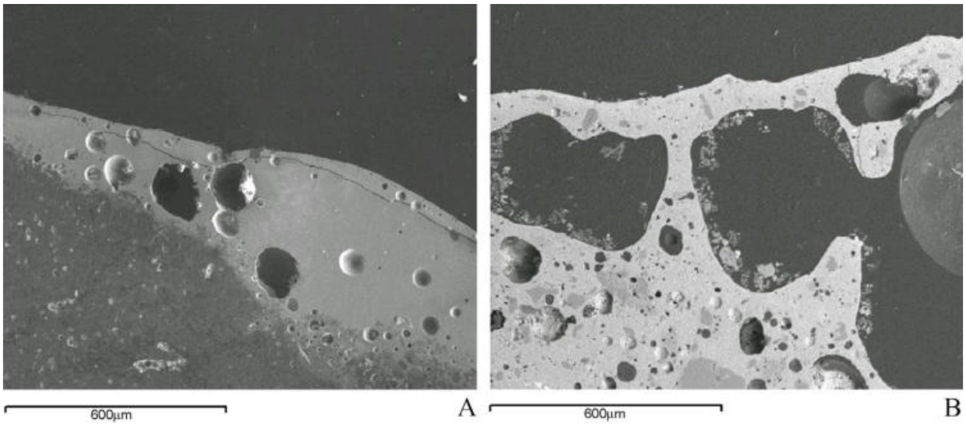

Fig. 9. Glaze damages: (A) fracture parallel to the surface in the sample CD_6; (B) sample CD_4, glaze damages during the fire, with large irregular bubbles and cracks.

in all analyzed samples (Figs. 6 and 7A). The development at the interface is significantly greater when the glaze suspension is applied to the unfired body.[2] In the samples, tin-oxide crystals are heterogeneously distributed, suggesting a non-fritting process for the glaze production or a not accurate preparation technique[5] (Fig. 7B).

Morphological analysis of these crystals and their "dragging" into the glaze, allowed to hypothesize that, in the production process, the cooling of the ceramics has been slow, probably inside the kiln.[36]

Many sub-rectangular particles corresponding to quartz in form of 'unreacted quartz' are detected at the interface glaze-brick, these depend on the glaze composition, in this case the SiO_2 content is 12.9–16.9 wt%. In all samples, calcium incorporated into the glaze formed Ca-rich pyroxene.

The noticeable amount of bubbles in the glaze, produced by release of carbon dioxide generated by decomposition of carbonate of the clay, and the large amount of crystals developed at the interface indicate a single firing process (Fig. 8).

In the samples, the thickness of glaze and interface layer is variable and irregular (Fig. 8): (1) glaze thickness: 30–700 μm and (2) interface layer: 20–150 μm. White glazes have a higher thickness than the black ones, with a more developed interface layer.

A particular case concerns the sample CD_4, profoundly altered during the blaze. The sample shows signs of re-firing, with swellings and large irregular bubbles in the glaze and an accentuated vitrification of the brick (Fig. 9B).

Notwithstanding the high lead glazes have a low coefficient of thermal expansion than the alkali lead glazes, the few cracks present in the glaze are probably due to the shrinkage of the ceramic body during firing or to thermal shock suffered during the recent fire (Fig. 9A).

4.5. *Mortars*

Joint mortars and repair mortars have been investigated by optical microscopy, electron microscopy (SEM-EDS), ICP-AES analysis and X-ray diffraction (Table 3) to have information on their chemical (Table 1), mineralogical and petrographic features.[37,38]

Plaster samples were took in correspondence of one of the ancient scaffolding hole; mortar samples were taken at different heights of the spire, sampling points are reported in Fig. 5.

Samples, despite having different compositions and mixtures, are mostly composed of carbonates both in aggregate and binder.

On the basis of the sampling point, two main typologies of mortars could be identified: mortars from the original masonry, 14th century, collected inside the masonry; samples taken in correspondence of the covering structure installed in the 16th century.

The ancientest mortars (CD_13, CD_15, CD_18; 14th century) are composed of a lime-based binder with carbonate and silicate aggregate, in a 1:1 ratio. The interaction between binder and aggregate is poor and reaction rims are not developed around grains boundaries. Small amounts of phyllosilicates, talc and

Table 3
Principal mineralogical composition of the mortars (XRD).

Sample	Phases					
	Anhydrite	Calcite	Chlorite	Gypsum	Phyllosilicates	Quartz
CD_13	–	+++	–	*t*	++	+++
CD_15	*t*	+++	–	+	*t*	+++
CD_9	–	+++	*t*	*t*	+	++
CD_12	*t*	+++	*t*	–	+	++
CD_10	+++	+	–	+++	–	–
CD_16	+	++	–	+++	–	–

+++ = major; ++ = small; + = minor; *t* = trace.

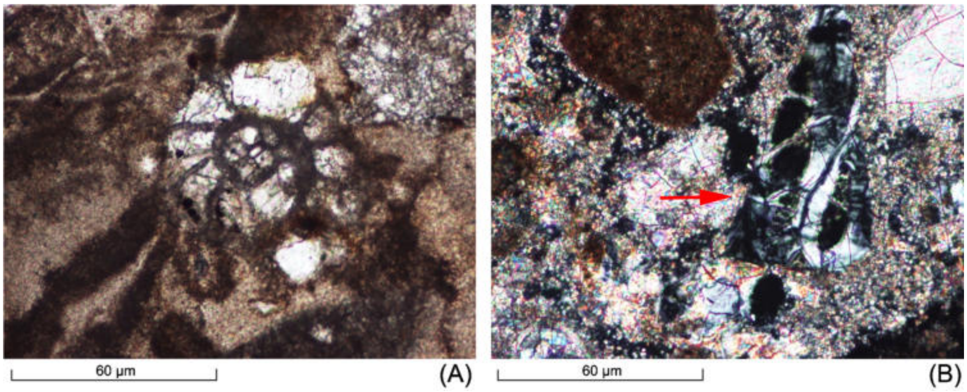

Fig. 10. (A) Sample CD_13. Microfossils (*Pliocene gastropoda*) (optical microscope, 10×, transmitted light, parallel polarizers). (B) Sample CD_9. Ophiolite grain found in the mortar of the end of the XVI century (optical microscope, 10×, transmitted light, crossed polarizers).

microfossils are found in all three samples (Fig. 10A). By optical analysis and visual estimation,[25,26,38] the size of the grains (aggregates size: 0.2–3 mm) and the pores (macropores size: 0.1–2 mm) are homogeneous.

Mortars, CD_9 and CD_12, employed during the installation of copper roofing in the 16th century, are very similar in composition and grain size distribution (aggregates size: 0.08–6 mm), with a good interaction between binder and aggregate, as observed at the carbonate–phyllosilicates interface; high porosity (macropores size: 0.1–0.8 mm) and fracture are present. The ratio between binder and aggregate is visually estimated to 1:2. Ophiolite grains are present in both the samples, reveling the use of aggregate maybe from Parma Apennine area (Fig. 10B).

As shown by chemical analysis, for samples CD_9, CD_12, CD_13, CD_18, CaO is mostly related to carbonates suggested by the high value of LOI.

Plaster samples CD_10 and CD_16 have predominant content of gypsum and anhydrite (Table 3), as observed by XRD and SEM-EDS analysis and also showed in the chemical analysis by the high content of CaO as well as low LOI and high Sr values (Table 1). In the samples, the dimension of the aggregates varies from 0.1 to 7 mm, with a macroporosity (size > 1/16 mm) of 10–15%. The binder and aggregate ratio is 1:2.

The presence of anhydrite in CD_15, CD_12, CD_16 and especially in CD_10 (Table 3) could be related to the gypsum dehydration as effect of the recent fire.

5. Conclusions

The results of this study allow characterizing the dichromatic glazed masonry of the conical spire of the steeple of the Parma Cathedral and defining the production techniques of the 14th century glazed bricks.

Samples consist of a portion of calcareous clay body with a layer of high lead glaze of two different colors: white and black.

White glazes belong to the class of 'tin-opacified high lead glazes', analysis reveal an high tin content (19–24 wt% SnO_2), probably extracted from Campiglia Marittima tin mines in Tuscany (Italy), not far from Parma. The high content of SnO_2 distinguishes this production from the contemporary from Eastern Spain, from the Italian Renaissance glazed pottery and from the previous Egyptian production, which have lower values (SnO_2 about 5–9 wt%).

For black glazes, the color tinged with brown is conferred by the addition of manganese, without trace of opacifier. The samples have different composition: compared to CD_1, CD_2 contains iron (2.8 wt%) and alkali.

The calcareous paste has a low content of iron oxides and a pale pink color.

Traces of neo-formed gehlenite, diopside and anorthite, detected by XRD, together with calcite suggest a uneven firing temperature, about 900–950 °C. Little difference of firing temperature could be probably due to poor air circulation in the kiln and closeness between the bricks.

The interface between brick and glaze has a variable thickness of 20–150 μm, in general higher in the white glazes.

The thickness of the interface and the presence of crystals of potassium–lead–aluminum silicate are indicative of a single cooking, with glaze applied on an un-fired body. Unreacted quartz are also present at the interface and into the glaze, together with bubbles generated by carbonate decomposition of the clay.

Mortars of the 14th and 16th centuries have been analyzed. All the samples are composed of a lime-based binder with different aggregate, in particular: the mortar of 14th century (CD_13, CD_15, CD_18) has a low content of silicate, small amounts of phyllosilicates, talc and microfossils and poor interaction between binder and aggregate; the mortars of the 16th century (CD_9 and CD_12) are very similar in composition and grain size distribution, with a good interaction between binder and aggregate, aggregates contain ophiolite grains, probably deriving from Parma Apennines.

Plaster samples, CD_10 and CD_16, have predominant content of gypsum and anhydrite, the latter could be related to the gypsum dehydration as effect of the recent fire.

Acknowledgments

Thanks to Silvia Simeti and Stefano Volta of Archè Restauri society for the essential and kind assistance in the building site. A special thanks to professor Judit Molera of the University of Vic for her essential advices and corrections and to professor

Giampiero Venturelli of the University of Parma for his suggestions during the research.

References

1. Kleinmann B. History and development of early Islamic pottery glazes. In: Olin JS, Blackman MJ, editors. *Proceedings of the 24th international archaeometry simposium*. Washington, DC: Smithsonian Institution Press; 1986. p. 73–84.
2. Tite MS, Freestone I, Mason R, Molera J, Vendrell-Saz M, Wood N. Lead glazes in antiquity – methods of production and reasons for use. *Archaeometry* 1998;**40**(2):241–60.
3. Moorey PRS. *Materials and manufacture in ancient Mesopotamia: the evidence of archaeology and art*. Oxford: British Archaeological Reports, International Series; 1985. p. 237.
4. Mason RB, Tite MS. The beginnings of tin-opacification of pottery glazes. *Archaeometry* 1997;**39**(I):41L 58.
5. Molera J, Pérez-Arantegui J, Vendrell-Saz M. Chemical and textural characterisation of tin glazes in Islamic ceramics from Eastern Spain. *J Archaeol Sci* 2001;**28**:331–40.
6. Molera J, Vendrell-Saz V, Garcìa-Vallés M, Pradell T. Technology and colour development of hispano-moresque lead-glazed pottery. *Archeometry* 1997;**39**(1):23–39.
7. Coentro S, Mimoso JM, Lima AM, Silva AS, Pais AN, Muralha VSF. Multi-analytical identification of pigments and pigment mixtures used in 17th century Portuguese azulejos. *J Eur Ceram Soc* 2012;**32**:37–48.
8. Guilherme A, Coroado J, Dos Santos JMF, Lühl L, Wolff T, Kanngießer B, et al. X-ray fluorescence (conventional and 3D) and scanning electron microscopy for the investigation of Portuguese polychrome glazed ceramics: advances in the knowledge of the manufacturing techniques. *Spectrochim Acta B: Atomi Spectrosc* 2011;**66**(5):297–307.
9. Cuomo Di Caprio N. *Ceramica in archeologia 2: antiche tecniche di lavorazione e moderni metodi di indagine*. Roma: L'Erma di Bretschneider; 2007.
10. Kingery WD, Vandivier PB. *Ceramic masterpiece: art, structure technology*. New York: Macmillan; 1986.
11. Molera J, Pradell T, Vendrell-Saz M. The colours of Ca-rich ceramic pastes: origin and characterization. *Appl Clay Sci* 1998;**13**:187–202.
12. Bevilacqua N, Borgioli L, Adrover Gracia I. *I pigmenti nell'arte dalla preistoria alla rivoluzione industriale*. Il Prato ed. Padova; 2010.
13. Ricci C, Borgia I, Brunetti BG, Sgamellotti A, Fabbri B, Burla MC, et al. A study on late medieval transparent-glazed pottery and archaic majolica from Orvieto (central Italy). *Archaeometry* 2005;**47**(3):557–70.
14. Tite MS. The production technology of Italian maiolica: a reassessment. *J Archaeol Sci* 2009;**36**:2065–80.
15. Viti C, Borgia I, Brunetti B, Sgamellotti A, Mellini M. Microtexture and microchemistry of glaze and pigments in Italian Renaissance pottery from Gubbio and Deruta. *J Cult Herit* 2003;**4**(3):199–210.
16. Fortina C, Santagostino Barbone A, Turbanti Memmi I. Sienese 'archaic' majolica: a technological study of ceramic bodies and coatings. *Archaeometry* 2005;**47**(3):535–55.
17. Cultrone G, Rodriguez-Navarro C, Sebastian E, Cazalla O, De La Torre MJ. Carbonate and silicate phase reactions during ceramic firing. *Eur J Miner* 2001;**13**(3):621–34.
18. Trindade MJ, Dias MI, Coroado J, Rocha F. Mineralogical transformations of calcareous rich clays with firing: a comparative study between calcite and dolomite rich clays from Algarve, Portugal. *Appl Clay Sci* 2009;**42**:345–55.
19. Rasmussen KL, De La Fuente GA, Bond AD, Korsholm Mathiesen K, Vera SD. Pottery firing temperatures: a new method for determining the firing temperature of ceramics and burnt clay. *J Archaeol Sci* 2012;**39**(6):1705–16.
20. De Adams S. *Chronica fr. Salimbene parmensis ordinis minorum ex codice bibliothecae Vaticanae nunc primum edita*. Parma: Ex offina Petri Fiaccadorii; 1857.
21. Fatta G, Vinci C. *Cuspidi maiolicate nell'architettura religiosa minore in area siciliana in Aymerich C*. Firenze: Architettura di Base; 2007.
22. Testi L. *La Cattedrale di Parma*. Bergamo: Istituto Italiano Arti Grafiche; 1934.
23. Martin JD. *Using XPowder: a software package for powder X-ray diffraction analysis*; 2004 www.xpowder.com
24. Normal 12/83. *Aggregati artificiali di clasti a matrice legante non argillosa: schema di descrizione*. Roma: CNR – ICR; 1983.
25. Ricci Lucchi F. *Sedimentologia parte I: Materiali e tessiture dei sedimenti*. Bologna: Clueb; 1980.
26. Myron Best G. *Igneous and metamorphic petrology*. Oxford: Blackwell Publishing; 2003.
27. Miriello D, Barca D, Bloise A, Ciarallo A, Crisci GM, De Rose T, et al. Characterisation of archaeological mortars from Pompeii (Campania, Italy) and identification of construction phases by compositional data analysis. *J Archaeol Sci* 2010;**37**:2207–23.
28. Riccardi MP, Messiga B, Duminuco P. An approach to the dynamics of clay firing. *Appl Clay Sci* 1999;**15**:393–409.
29. Tarvornpanich T, Souza GP, Lee WE. Microstructural evolution in clay-based ceramic I: single components and binary mixtures of clay, flux, and quartz filler. *J Am Ceram Soc* 2008;**91**(7.).
30. Messiga B. Reaction pathway in conventional ceramics. In: *Engineering mineralogy of ceramic materials, Proceedings of the international school earth and planetary sciences*. 2001.
31. Molera J, Pradell T, Salvado N, Vendrell-Saz V. Evidence of tin oxide recrystallization in opacified lead glazes. *J Am Ceram Soc* 1999;**82**(10):2871–5.
32. Bouchard M, Smith DC. Catalogue of 45 reference Raman spectra of minerals concerning research in art history or archaeology especially on corroded metals and coloured glass. *Spectrochim Acta A* 2003;**59**:2247–66.
33. Strobel G. Antiche miniere di stagno. In: *Bollettino di paletnologia italiana, vol. 4.*; 1879. p. 28–9.
34. Caruso N. *Ceramica viva*. Milano: Hoepli; 2007.
35. Mangone A, Giannossa LC, Laganara C, Laviano R, Traini A. Manufacturing expedients in medieval ceramics in Apulia. *J Cult Herit* 2009;**10**:134–43.
36. Molera J, Pradell T, Salvado N, Vendrell-Saz V. Interactions between clay bodies and lead glazes. *J Am Ceram Soc* 2001;**84**(5):1120–8.
37. Carò F, Riccardi MP, Mazzilli Savini MT. Characterization of plasters and mortars as a tool in archaeological studies: the case of Lardirago Castle in Pavia, Northern Italy. *Archaeometry* 2008;**50**:85–100.
38. Miriello D, Crisci GM. Image analysis and flatbed scanners. A visual procedure in order to study the macro-porosity of the archaeological and historical mortars. *J Cult Herit* 2006;**7**:186–92.