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An unusual mortar with a magnesium binder in the *Perseus* of Giovan Battista Pieratti in Boboli Gardens (Florence)

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Abstract

The restoration of Perseus Boboli Gardens (Florence, Italy), a sculptural complex realized by Giovan Battista Pieratti in the 30th of the XVII century mostly as reuse and reinterpretation of fragments of ancient Roman sculptures, offered the opportunity to face the problem of the structural consolidation of a fragmented sculpture. During disassembly of this sculptural complex it was possible to observe an overlapping of techniques and materials that covers more than three and a half centuries, from the first half of the XVII century until the 80s of the XX century. One of the materials used as glue of the pivots showed an unusual composition, characterized by a magnesium hydroxide based binder (brucite) and brucite and barite as aggregate. It is probably an old mortar still in excellent conservation conditions.

Key words: Giovan Battista Pieratti; Boboli Gardens; adhesion mortar; brucite binder.

Introduction

Perseus is a sculptural complex sited in the pond of the Island in the Boboli Gardens (Florence, Italy) (Figure 1a). It was realized by Giovan Battista Pieratti in the 30th of the XVII century in the context of the expansion of the Boboli Gardens (AA.VV., 1989; Medri, 2003).

Perseus indeed born as reuse and reinterpretation of fragments of ancient Roman sculptures according to iconographic solutions following the fashion of the time. Archive documents testify that in occasion of the XVII century phase of expansion of the Boboli Gardens, collections of statues and numerous fragments from the excavation of Roman villas owned by the Medici family came to Florence (Del Panta, 1989; Medri, 1989).

The restoration, carried out during the years 2006-2009 by Opificio delle Pietre Dure (OPD)

Figure 1. The Boboli Gardens (Florence, Italy): a) Perseus riding Pegasus represented as an hippocampus; b) Andromeda attacked from a sea monster.

of Florence, offered the opportunity to face the problem of the structural consolidation of a fragmented sculpture.

The direct observations made possible by the restoration, showed an overlapping of techniques and materials that covers more than three and a half centuries, from the first half of the XVII century until the 80^s of the XX century.

During disassembly of this sculptural complex it was possible to distinguish four different types of adhesive products (two types of mortar and two synthetic resins) and numerous pivots of different forms and materials (ranging from copper to stainless steel).

One of the materials used as adhesive and as glue of the pivots, showed a very unusual composition, characterized by a magnesium hydroxide based binder. It is probably an old mortar, which is still in excellent conditions of conservation. The material is still under study with the main purpose of being able to reproduce and promote its use.

The sculpture and the execution techniques

The sculpture depicts Perseus that, riding Pegasus, is going to save Andromeda from a sea monster (Capecchi, 2008) (Figure 1 a,b). It is evident the iconographic inconsistency of Pegasus represented as an hippocampus and not as a winged horse; this is due to reuse as it was common in Baroque epoch when the restoration of the ancient sculptures (even if in fragments) were carried out with such freedom and fantasy that is better to speak about reuse and “pastiches” (Muñoz, 1916; Cagiano De Azevedo, 1948; Rossi Pinelli, 1986; Dolcini, 1986). The composition is dynamic and vital: Perseus seems precariously balanced, in the excitement of the moment, clinging to the mane, stretched legs and right arm to grab an attribute now missing. The figure is naked and wearing only a cloak, fluttering in the breeze, enhances its dynamics. The youthful features of the face and hair tousled and not too refined are almost a signature of Pieratti.

Pegasus is pawing, nerves and muscles tense and vibrant energy, flowing mane, back arched and tail contracted, wrapped in a spiral. The work is of excellent quality and anatomical definition very accurate and realistic: swollen veins on face and the muscles of the front legs are clearly visible while the back of the animal, with a fish-tail, presents an exceptional scaled surface. The two figures are combined in a harmonious way, giving rise to a group of remarkable dynamic and expressive strength.

For the realisation the traditional gradine, chisel, mallet and drill have been used. The traces of sculpting are more evident in the hair of Perseus and the mane and tail of Pegasus. The composition is formed by assembling several elements made of different types of marbles; among them there is the main block of Pegasus, in a white veined marble, to which the curl of the tail, the hocks (made with a statuary marble) and clogs have been added.

As for Perseus, the situation is more complex because the figure is composed of seventeen parts: head, thorax, abdomen, arms, cloak, thighs, legs, feet, and small pieces of marble placed in correspondence of the grafting of arms to change their posture, or between thorax and abdomen to give continuity to the left side. This is all assembled with clamps and metal pins fixed with various techniques and materials.

Conservation issues

The sculpture was placed in the pond in conditions of partial immersion and showed degradation phenomena due to the combined action of physical, chemical and biological factors.

The biological attack affected the whole of the surface and consisted in the presence of black fungi and gray-brown bacteria which was superimposed by a sharper lichen attack, more accentuated on the sub-horizontal surfaces: in particular the hair, arms, thighs, shoulders and the coat of Perseus, the nose, the mane, the tail of Pegasus were colonized by Verrucaria nigrescens, Candelariella Aurella, Aspicilia with disseminated pitting (Nugari and Salvadori, 2009; Onesti, 2009).

In the areas less exposed to direct sunlight there were colonies of green algae. In the areas of greatest deposit of dirt and organic material, in particular in the hair of Perseus and the mane of Pegasus, mosses were present. The surfaces exposed to the runoff showed a marked roughness due to the dissolution of the marble by the acid atmospheric pollutants. This phenomenon, particularly evident on the nose, ears and mane of Pegasus and on the face, hair and on the right hand of Perseus, resulted in a consumption of surfaces with loss of material and therefore of the signs of the sculpting process.

The areas protected from runoff had gray crusty deposits consisting of recrystallized calcium carbonate (left side of the neck of Pegasus and the unexposed surface of the coat of Perseus) and black crusts with sulfation and pulverization phenomena (tail of Pegasus).

The portion of the figure immersed in the pond was covered with a calcareous concretion characterized by an irregular cavernous surface, rich in globular deposits green-brown in colour. The underlying marble resulted rich in cavities (Figure 2a).

The physical degradation of the sculptural complex was evidenced particularly by problems of structural stability: the adhesives in polyesteric resins had totally lost the mechanical and adhesive properties due to a depolymerization causing the collapse of the structure with consequent separation of the different marble pieces. Moreover many marbles blocks of Perseus presented strong decohesion phenomena due. Due to these problems, the displacement phase preliminary to the restoration had further urged the bonding, resulting in the detachment of the mantle and the left arm of Perseus and the collapse of the bonding at the pelvis.

The “restoration process” was carried out in several phases (Pasolini, 2009):

- transport in the OPD restoration laboratories (Figure 2b);
- disassembling of fragmented sculpture (42 pieces) (Figure 2c);
- removing of the damaged pivots;
- cleaning;
- removing of the calcareous incrustations;
- structural consolidation of the fissure network;
- reassembling (Figure 2d).

The “disassembling” of the sculpture made it

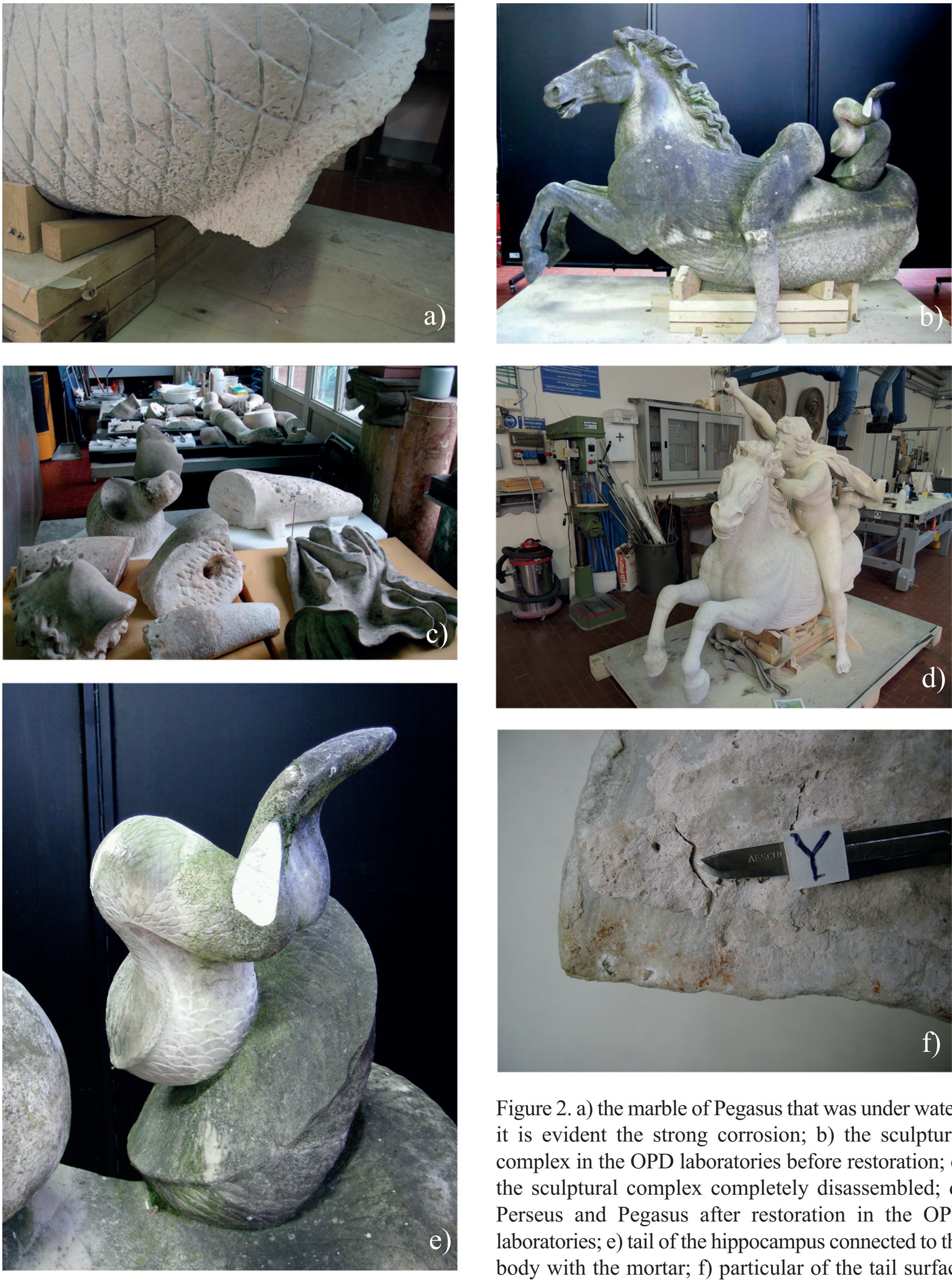

Figure 2. a) the marble of Pegasus that was under water: it is evident the strong corrosion; b) the sculptural complex in the OPD laboratories before restoration; c) the sculptural complex completely disassembled; d) Perseus and Pegasus after restoration in the OPD laboratories; e) tail of the hippocampus connected to the body with the mortar; f) particular of the tail surface with the strange whitish adhesion mortar.

possible to study all the technical aspects utilised in the composition, evidencing a large number of different materials and techniques along three centuries.

The working of the contact surfaces between the different marble blocks looks very interesting, testifying the phases of the original assembly and the following interventions suffered by the sculpture. There are clear traces of the extremely accurate smoothing of the surfaces with gradine (to be referred possibly to Pieratti) and those with chisel (coarser and result of later interventions as reported in Pasolini, 2009), the holes and channels for the pouring of molten lead, traces of the violin drill for the realization of the holes for the pins.

With regard to the pins, there were pins in copper, brass, iron, stainless steel, characterized by different shapes (circular or square in section, straight or curved, flared etc.) and put in place by lead and adhesive products like mortars, natural and synthetic resins (polyester and epoxy).

Particularly, the mortar used for the adhesion of the tail to the body of the hippocampus (Figure 2e), whitish in colour (Figure 2f), showed excellent conditions of conservation and strength of adhesion. This mortar has been found below a more recent restoration realised with synthetic resins. This fact together with the kind of pivots (apparently made of copper) and other technical aspects relative to the junction between the two marble elements, would suggest for the mortar an age not younger than the XVII century.

The curiosity forced us to study the nature of this mortar.

Analytical methods

Several samples of adhesion mortar (fragments) have been taken from the junction between the tail and hippocampus body.

Some fragments have been embedded in polyester resin to prepare cross and thin sections, other have been powdered to perform chemical and mineralogical analysis.

The following analytical techniques have been used both at the ICVBC-CNR and OPD laboratories:

- cross section microscopic observation in both incident light (dark field) and UV radiation (365 nm) (ICVBC-CNR);
- infrared spectrophotometry analysis (FTIR): it has been carried out using the KBr micro-pellet method (13 mm in diameter) and a Thermo Nicolet Nexus (software OMNIC™) software (OPD);
- elemental analysis through SEM-EDS: EVO® MA 25, Zeiss with an energy dispersive X-ray detector (80 mm^2 SDD detector) and ATZEC software Oxford Instruments (UK). The elemental maps have been acquired on an area 1100 mm x730 mm in size (image 512 x 340 pixels) with the following beam conditions: 20kV accelerating voltage and 600pA current probe. The cross section were mounted on aluminium stubs with a conductive adhesive and then carbon coated (OPD);
- mineralogical analysis through X-ray diffractometry (XRD) (X'Pert PRO by PANalytical with Cu anticathod) according to the following operative conditions: 2q = 3-70, time per step = 60.325 sec, step size = 0.033, 40 KV, 30 mA (ICVBC-CNR);
- transmitted light microscopic observation (Zeiss AXIO Scope.A1 microscope) (ICVBC-CNR).

Results

The mortar appears to be constituted by a white matrix with dispersed translucent, whitish and secondarily brown grains (Figure 3).

The UV fluorescence is white indicating the absence of organic substances.

FTIR analysis, carried out in order to check the presence of organic substances and non crystalline compounds, point out the presence

Figure 3. Cross section image of the adhesion mortar.

only of magnesium hydroxy carbonate, barium sulphate and magnesium hydroxide (brucite) and confirms the absence of organic substances (Figure 4).

The XRD analysis of the sample, in agreement with the FTIR analysis, points out the presence of brucite [$Mg(OH)_2$], barite [$BaSO_4$], hydromagnesite [$Mg_5(CO_3)_4(OH)_2 \bullet 2H_2O$], wulfingite [$Zn(OH)_2$], and traces of quartz [SiO_2], calcite [$CaCO_3$], and goethite [$FeO(OH)$] (Figure 5).

The maps of the elemental composition of the mortar obtained by SEM-EDS have been acquired in order to get information on the distribution of the mortar components (Figure 6).

The elemental maps highlight that magnesium is widespread throughout the mortar: most of the translucent grains, dark in the backscattered SEM image, as well as the binder, are characterized by the presence of this element and traces of S, Ca, Si, Zn and Cu. This is in agreement with the FTIR and XRD results and points out the presence of magnesium hydroxide and hydromagnesite as main components of the mortar. The distribution maps of barium and sulfur are perfectly overlapped, thus indicating that the diffuse fine fraction of the mortar aggregate is made of barium sulphate. Some translucent silicon rich grains can be observed in the fragment; they are constituted by quartz, the presence of which has been revealed by XRD and FTIR analysis. Finally, the brown-red grains observed both in cross section and thin section result very rich in iron which could be linked to the presence of goethite (XRD). On the upper surface of the fragment a calcium rich layer is probably due to the recrystallization of calcium carbonate.

The mortar contains, as minor elements, also zinc and copper. Zn in the XRD analysis seems to be associated to the presence of $Zn(OH)_2$ while, due to their low amount, no phases associated to these two elements has been detected by FTIR analysis.

Their presence and distribution in the cross section would have been a key feature for a chronological attribution of the mortar. In fact, the presence of zinc would have been related to the use of lithopone, a pigment, white in colour, consisting of a mixture of barium sulfate

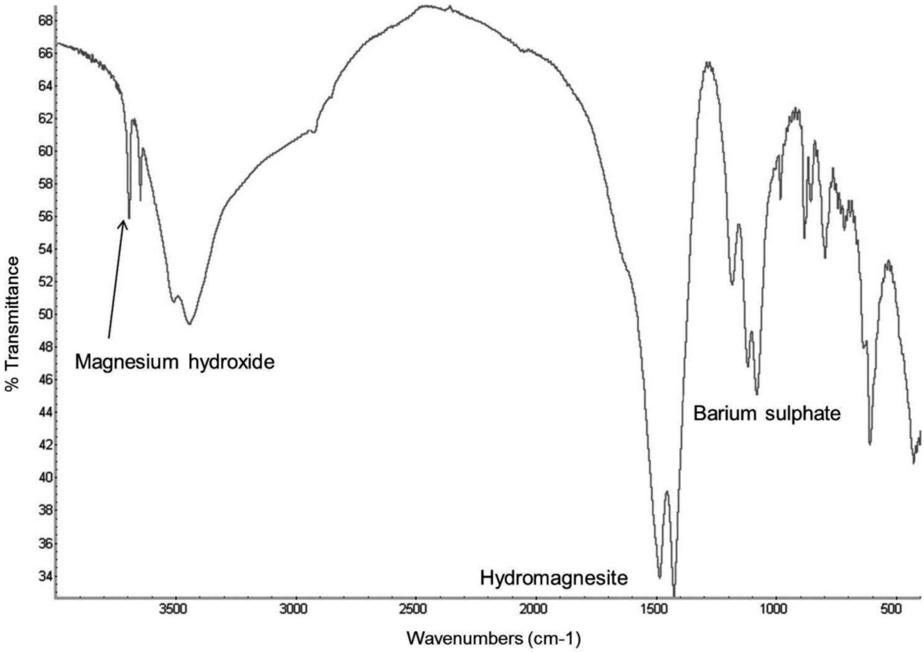

Figure 4. FTIR spectrum of the mortar.

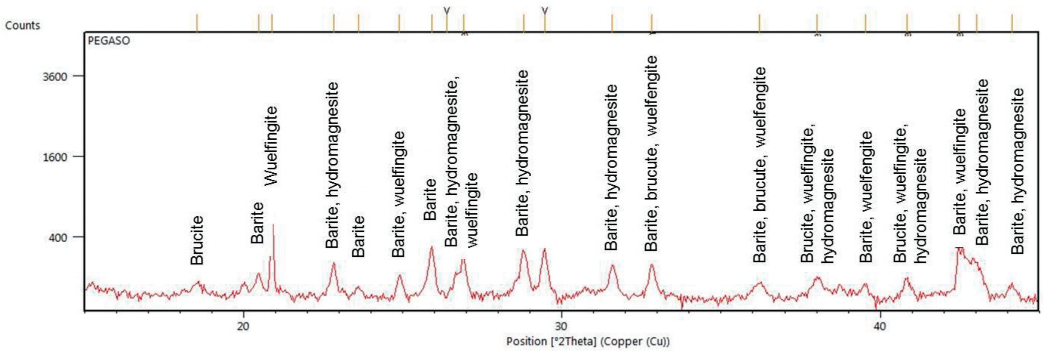

Figure 5. XRD spectrum: for sake of clarity only the peaks of the principal minerals (brucite, barite, hydromagnesite, wulfingite) have been indicated. Calcite and quartz have not been indicated due to their very low amount and for sake of clarity.

($BaSO_4$) and zinc sulfide (ZnS). It is used as a constituent of paints, varnishes and white enamels, but also for inks and cosmetics. The various types of lithopone differ according to the % of ZnS, which generally varies from a minimum of 15% to a maximum of 30%. Discovered by de Douet in 1853 by the reaction of vitriol of zinc with barium sulphide: improved by J.B. Orr of Glasgow (1874), who subjected the mixture of barium sulfate and zinc sulfide to

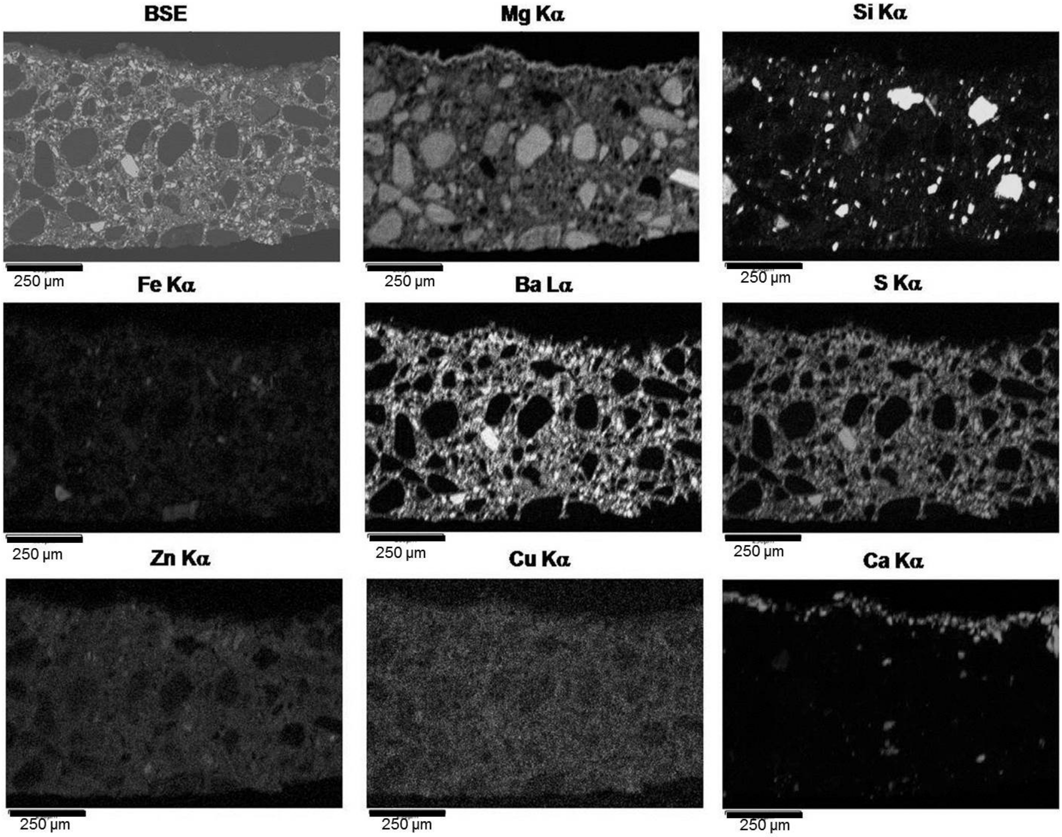

Figure 6. Backscattered electrons image (BSE) and maps of Mg, Si, Fe, Ba, S, Zn, Cu, Ca).

tempering process in order to make the product thicker and whiter. It was called lithopone by Boulez in 1877 (Mazzetti, 1934; AA.VV., 1986).

In the Perseo's mortar a semiquantitative assessment of zinc concentration provided values clearly lower (about 3%) than those reported for the lithopone composition. Zinc is mainly present diffused in the binder, even if traces have been revealed in the coarse grains of the aggregate (Figure 7). On the contrary, the distribution of barium shows that this element is definitely absent in the magnesium hydroxide-hydromagnesite grains. Moreover, the copper distribution results very similar to that of zinc, both in the binder and aggregate of the mortar.

Therefore, an alternative explanation for the presence of zinc and copper could be the origin from the corrosion of the pivot which has not been analyzed but seems to be made of a copper alloy.

The microscopic observation in transmitted light allows to verify the presence of the different crystalline phases, to investigate the granulometry of the aggregate, the ratio binder/aggregate, the attention paid in the mixing, the porosity (linked to the amount of water used in the mix).

The grains of brucite appear colourless and non-pleochroic, with low relief, weak interference

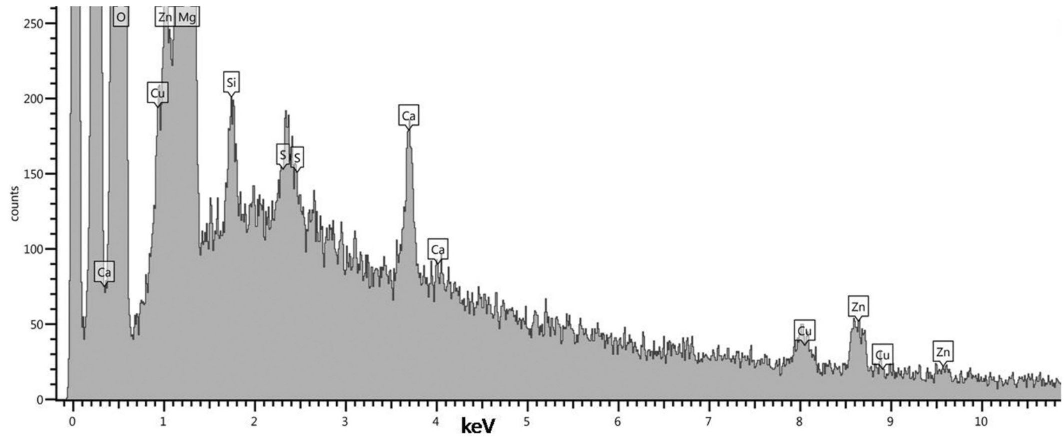

Figure 7. EDS spectrum of the coarse grains of the aggregate: the presence of Zn is evident.

colours and constituted by agglomerates of little crystals (Figure 8a). These optical characteristics are similar to those of hydromagnesite that can be recognised only by conoscopic observations (presence of two optical axes in hydromagnesite). The problem is that for conoscopic observations, sufficiently large crystals are needed, not present in the mortar sample. The shape of the grains is angular and the grain size distribution shows the presence of two classes, one with dimensions of 20-50 mm and the other 150-300 mm.

The grains of barite appear monocrystalline, colourless and non-pleochroic with moderate relief and weak interference colours, prismatic to lenticular in shape with cleavage in one direction (Figure 8b). The grain size is 20-50 mm with rare grains of 150 mm.

Seldom monocrystalline quartz grains, micritic calcite and goethite grains with dimension of 100-400 mm can be observed (Figure 8c).

The binder has a microsparitic structure and looks almost extinct in crossed polarizers (see Figure 8a).

The mortar looks well mixed, with a binder/aggregate ratio of about 1/3 and a low porosity, constituted by rounded pores.

Summarizing, this mortar seems to be made of a Mg-rich binder (brucite/hydromagnesite) and an abundant aggregate with two granulometric fractions: a finer fraction made of barite and magnesite/hydromagnesite, and a coarser fraction made of brucite/hydromagnesite. Moreover there are impurities of micritic calcite, iron oxides and quartz.

The possible raw materials utilised to produce this mortar seem to be:

- a binder made of brucite [$Mg(OH)_2$], obtained by burning magnesite [$MgCO_3$] in order to obtain MgO, then slaked in water:
- brucite as aggregate;
- barite as aggregate;
- impurities of micritic calcite, iron oxides and quartz.

The carbonation of $Mg(OH)_2$ is always incomplete due to its low solubility and it reaches only the stage of hydromagnesite (Balha and Jedlicka, 1994). Nevertheless the cohesion reached by the binder is very good thanks to the interlaced fibres structure of both brucite and hydromagnesite.

A further result (probably unexpected) that has been reached with this kind of binder is the protection of the pivots from oxidation thanks to the basic environment guaranteed by $Mg(OH)_2$

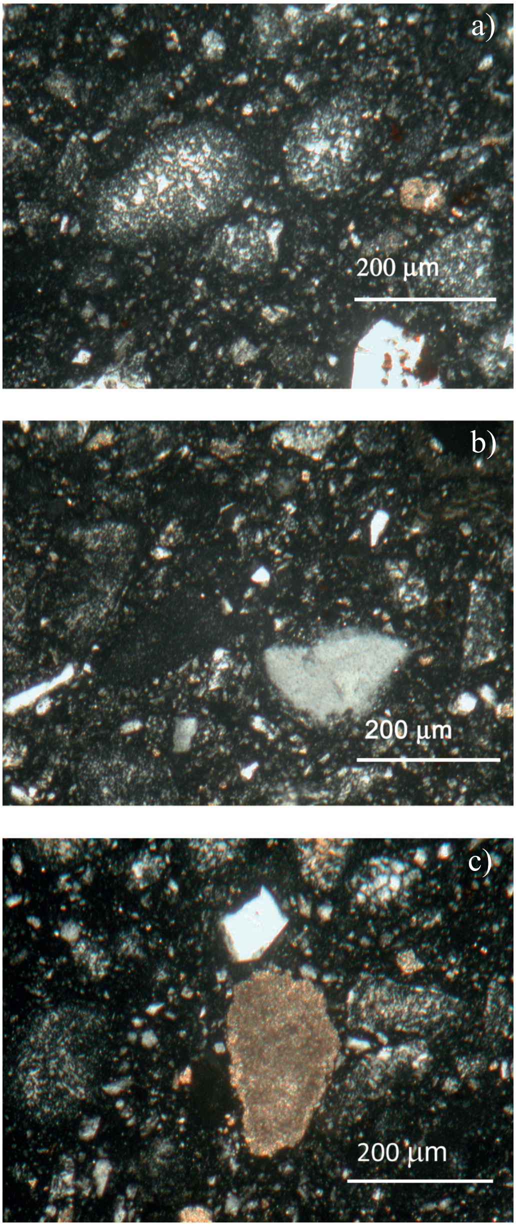

Figure 8. Images at trasmitted light microscopy (crossed polarizers) in a) grains of brucite, characterised by weak interference colours and constituted by agglomerates of little crystals; b) grain of barite in the centre of the image; c) monocrystalline quartz grain (white) and micritic calcite (brown).

which carbonates with difficulty.

Concerning the presence of brucite in the aggregate, we must think to an intentional addition and not to an origin from fragments of MgO slowly hydrated after the setting and hardening of the mortar because this would have caused the disintegration of the mortar itself due to the higher volume of $Mg(OH)_2$ with respect to MgO.

Conclusions

The mortar used for the adhesion of the tail to the body of the hippocampus in the Perseus sculptural complex, still in excellent conditions of conservation and adhesion, showed a very unusual composition, characterized by a magnesium hydroxide based binder and an aggregate made of brucite and barite grains.

For the moment the search for old recipes that could justify this kind of composition, didn't give results. On the other hand, having ruled out the use of lithopone, we can confirm the relative dating of this mortar to the XVII-XVIII centuries, as suggested by the technical aspects relative to the junction between the two marble elements. Unfortunately, as recalled by Mannoni (2000), the written sources concerning the constructions, tell us about the kind of the various operations, their costs, the reasons for their choices but rarely speak of material culture, which was reported only as "rules of the art", often considered as real secrets from the masters. By contract, generally they engaged themselves only to use these rules "as they had done in previous cases" without specifying them. The material culture consisted of the practical knowledge of the characteristics of the materials and of the environmental factors together with the manual know how handed down from generation to generation in the practice of the yard. When this visual, oral and manual transmission has been interrupted, the empirical knowledge accumulated over the centuries has been lost.

Nevertheless our purpose will be to try to reproduce this mortar according to the discovered composition and to the possible raw materials, being conscious that the original recipe (with the tricks of the trade) probably is lost forever.

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