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The Monumental UNESCO Site of Panamá Viejo: Investigation of the Masonry Mortars

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Abstract: The presented study illustrates the characterisation of several artificial materials (bedding, joint mortars, and plasters) belonging to the masonries of the UNESCO site of Panamá Viejo, located in Panama City (Panama). This monumental site represents the first Spanish settlement on the Pacific Coast, founded 500 years ago, in 1519. Through mineralogical and petrographic analyses of the collected samples, as stereomicroscope and polarized light microscopy (PLM) observations of bulk and thin sections, respectively, environmental scanning electron microscopy and micro-chemical investigations (ESEM-EDX) and X-Ray Powder diffraction (XRPD) analysis, it was possible to identify the composition of the materials utilized for the production of mortars and plasters, in addition to the determination of their state of conservation. Therefore, this work represents a substantial step for the preservation of the Panamá Viejo site, in order to support the selection of the most suitable restoration products, such as consolidants, protectives, etc., but also for choosing the most compatible materials for possible replacements/integrations in the masonries.

Keywords: mortars; plasters; central America heritage; Spanish colonial architecture; world heritage

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1. Introduction

Panamá Viejo (or Old Panama) is part of the World Heritage property named the "Archaeological Site of Panamá Viejo and Historic District of Panama". These two component parts are located at opposite areas of Panama City, in the Republic of Panama. The first one, subject of this study, also known as the "Panamá Viejo Historical Monument Complex[1]", arises on a prosperous territory, where archaeological studies revealed that the first human's settlements date back to more than a thousand years ago. During the XVI century, the Panamanian isthmus became a crucial crossroad for commercial routes between the "New World" and the "Old World". Consequently, Panamá Viejo was founded in 1519, and it is the oldest European settlement on the Pacific coast of the Americas. Abandoned in the mid-17th century, during its existence, it was affected by fire and an earthquake, and it was definitely destroyed during a pirate attack in 1671. After this, several materials belonging to the buildings of Panamá Viejo were used to construct a new settlement closer to the Ancón Hill, the currently named "Casco Antiguo", or the "Historic District of Panama" [1].

Nevertheless, the remains and the original layout of this exceptional historical site arevisible to date. Its current location and plan are reported in Figure 1.

Figure 1. Ensembled image showing the geographical location of the archaeological site of Panamá Viejo (source of aerial photo: Bing maps; source of floor plan sketches: UNESCO official website archive).

Natural stone started to be used in masonry construction towards the end of the XVI century, and it was utilized only for government buildings, churches, convents, and in the finest houses.

According to Mena García [2] all the available documentation on the Panamanian buildings, from the 16th century until the end of the colonial era, underlined the existence of three types of construction: entirely built in wood; entirely built in stonework; and another one, a mixed type, with the first floor in stone and the upper floor in wood.

Regarding the stonework, the raw materials utilized come from the region, which is described as abundant of these materials, and their quality was also appreciated by the neighboring regions, such as the Virreinato of Peru, where the Panamanian stones were exported during the XVII century [2]. In addition, according to a research work performed by Arroyo [3], the historical documents/records contemporary to the construction phases did not mention the purchase of stones for the masonries. This strengthens the hypothesis of using local stones, also supported by a letter addressed to the Spanish King from Bartolomé Morquecho, dated 1608, where it was reported that there was a stone of good quality and low cost in the outskirts of the town: *"piedra la hay en los arrabales de esta ciudad muy buena y a poca costa"*.

Observing the geology of the area, the outcropping formations are both of sedimentary and volcanic origin, respectively formed by marine facies (siltstones, algal and foraminifera limestones, alluvium or fill sediments) and volcanic facies (agglomerates, generally andesitic in fine-grained tuffs and streamed deposited conglomerates) [4].

The masonries still visible nowadays belong to the stonework and mixed typologies among the building types aforementioned, the majority of which were built or re-built after a disastrous earthquake occurred in 1621.

Over recent years, Panamá Viejo has been completely embedded in Panama City. In particular, during the 60 years between 1950 and 2012, the archaeological site was crossed by Vía Cincuentenario, a traffic-congested street, which was successively moved and nowadays runs along the northern side of the site [2,5–8].

Finally, in order to complete the analysis of the environmental context of Panamá Viejo site, we need to take into account the Panamanian climate. According to the update of the Köppen–Geiger climate classification, performed by Kottek et al. [9], the area of Panama Viejo is considered: fully humid equatorial rainforest (Af) and equatorial monsoon (Am). In addition, according to the Panamanian geographer and historian Alberto McKay [10], the climate of this area is also defined as a tropical climate with a prolonged dry season, characterized by quite high yearly temperature (average values 27–28 °C) and two seasons: the dry (from January to March) and the rainy season (April–December, approximately), with annual values of precipitation around 2500 mm.

The aim of this work is to characterize the composition and to evaluate the state of conservation of the mortars of the sites' masonries, which are exposed to a warm and humid climate and embedded in a rather congested metropolis. Further, we address the integration of the studies previously conducted by the authors at the Panama Viejo Complex on the characterization of stone building materials and the evaluation of impacts due to climate change [11,12]. Indeed, the analysis performed by Ciantelli et al. [11], utilizing damage functions validated for natural stones, showed that the Panamá Viejo area is likely to undergo, in the near and far future, an increment of surface recession of carbonate rocks and of biomass accumulation on the volcanic ones. Both phenomena depend mainly on the rain amount, a factor that can affect also the mortars of the site, since heavy rains drive a considerable amount of moisture within the masonries.

2. Materials and Methods

2.1. Sampling Campaign

Samples of mortars have been collected from seven buildings/monuments and from archaeological excavations during a sampling campaign performed in July and August 2014 (except for 5 samples belonging to previous campaigns, as specified in Table 1). The photos and plans reported in Figure 2 display the location of the investigated buildings and related sampling points.

Figure 2. Map of Panamá Viejo Historical Monument Complex (modified from Google Maps) showing the monuments sampled and the corresponding plans, with specimen locations and some pictures of the referred monuments. Plans are courtesy of the Patronato de Panamá Viejo. Legend: Fortín de la Natividad (FN); Convento de la Merced (CM); Convento de San Francisco (FC); Compañía de Jesús (JM); Aljibe del Convento de la Concepción (CC); Casas Reales (CR); Torre de la cathedral (TC).

In particular, the sites selected are described as follows [11,13,14]. Samples' labels, according to the site of collection, are indicated within brackets:

- Fortín de la Natividad (PV FN): the fort, built during the XVII century, arises in the eastern side of the archaeological site. Nowadays, it is located in proximity to the new Vía Cincuentenario and just in front of a gas station.

- Convento de la Merced (PV CM): built during the XVII century. Both specimens were sampled from a buttress, originally located at the North corner of the Convent and removed in April 2013, in order to allow the passage of the new Vía Cincuentenario.
- Convento de San Francisco (PV FC): the convent is located in the eastern side of the archaeological site, close to the new Vía Cincuentenario.
- Compañía de Jesús (PV JM): located close to the Plaza Mayor, it was founded in 1578 and built out of wood. From the beginning of the 17th century, the convent was converted in stone masonries and pre-made structures, where the use of clay is mentioned for the production of joint mortar. The remains visible today correspond to the church and the main cloisters, dating from the period after the 1621 earthquake.
- Aljibe del Convento de la Concepción (PV CC): the cistern of the Convento de la Concepción is located on one side of the church, in the center of the land occupied by the convent, where the patio was probably located. It can be deduced that its capacity was 124,000 L. It is known that, in 1604, there was a well of 10 feet or approximately 2.70 m of depth, but the exact date of construction of the well is not known, probably after 1640. Furthermore, in the past, it has been buried, as shown in an image of the beginning of the 1900s, showing the presence of soil and vascular plants within the cistern [15].
- Casas Reales (PV CR): these structures were the most important architectural complex in the town, representing the highest position in the public hierarchy. Its location was the most salubrious because it was erected on bare rock foundations. With a dominant position on the town and the sea, these buildings were built in order to realize a fortress with sufficient capacity to store goods and treasures. Seriously damaged during the 1621 earthquake, the complex was subjected to constant remodeling during the XVII and XVIII centuries. After the abandonment of the town, their walls underwent tidal wave erosion.
- Torre de la cathedral (PV TC): the tower was built, as we currently know, in stone masonry between 1619 and 1626, after several wooden structures. In particular, the tower (used as a belfry and watchtower) was much more solidly built than the rest of the building. From the tower of the cathedral, joint mortar samples were taken at the first level, since the other three levels underwent interventions between 2001 and 2006, and now, they are covered by a protective layer of lime mortar.
- Excavaciones arqueológicas (PV AE): in conjunction with the Department of Archeology, 3 samples of mortars were chosen, which were collected during the archaeological excavations carried out in recent years.

Detailed descriptions of each sample and sampling or macro image are reported in Table 1.

2.2. Performed Analysis

With the purpose of characterizing the composition and the state of conservation of the mortars, the following analyses were carried out. First, the petrographic and mineralogical features of the mortars were studied by observation of thin sections through Polarized Light Microscopy (PLM) in transmitted light, utilizing an Olympus BX 51 microscope, equipped with PixeLINK PL-A642-STA scanner and the Alexasoft software "X-Series" vers. 9.01.08. for acquiring, archiving, analyzing, and processing images with interactive measurement functions. Thin sections were prepared by impregnating the specimens under vacuum with a resin and then cutting and polishing the samples to obtain thin sections of 25–30 μm thick. The petrographic analysis has been focused on the determination of the compositional characteristics and texture of both aggregate and binder (e.g., mineralogy, size distribution and shape of grains and pores).

Table 1. Description of the sampling of the 21 specimens, of the macro observation and the state of conservation, using the ICOMOS-ISCS' terminology for deterioration patterns [16]; macro images of each sample are reported.

Site	Sample Code	Type	Sampling Location and Description	Macro Observations/ State of Conservation	Sampling/Macro Picture
Fortín de la Natividad	PV FN 3M	Bedding/ Joint mortar	Sampled from the South wall (3.45 m distant form East wall), 70 cm of height above the natural ground level.	Dark grey-black aspect of the external side, probably due to *biological colonization.*	
Convento de la Merced	PV CM 1	Joint mortar	Collected from a buttress before its dismantlement. Height ≈ 1 m above natural ground level.	Greenish *biological colonization* present on the external surface	
	PV CM 2	Joint mortar/ repointing mortar	Collected from a buttress before its dismantlement. Height ≈ 3 m above natural ground level.	Dark grey-black aspect of the external side, probably due to *biological colonization.*	
Convento de San Francisco	PV FC 1	Joint mortar/ repointing mortar	Collected from the external wall of the Church (perpendicular to the previous *vía Cincuentenario*), probably from a side chapel.	Greyish aspect of the external side, probably due to *biological colonization*.	
	PV FC 2	Joint mortar	Sampled towards the interior part of the west wall (perpendicular to the previous *vía Cincuentenario)* at 3.04 m of height above the natural ground level. Probably, it was part of the cloister and the wall sampled could the most ancient one.	During the sampling, the mortar appeared highly deteriorated, showing *powdering*.	
	PV FC 3	Joint mortar	Sampled from an internal wall of the convent, which probably divided the church from the cloister. Height 1.32 m above the natural ground level.	The joint shows *material loss*. No significant superficial alteration was observed.	
	PV FC 10M	Bedding/ repointing mortar	Collected from a corner of the South wall. Height 1.20 m above the natural ground level and distant 10 m from the new *vía Cincuentenario*.	Dark grey-black aspect of the external side, probably due to *biological colonization.*	

Table 1. *Cont.*

Site	Sample Code	Type	Sampling Location and Description	Macro Observations/ State of Conservation	Sampling/Macro Picture
Compañía de Jesús	PV JM 1	Joint mortar	Collected from the south-east corner of the convent church, located towards the external part or towards the street of the Empedrada. Height of sampling 1.30 m above the natural ground level.	The joint shows *material loss*. No significant superficial alteration was observed.	
	PV JM 2	Plaster	Sampled during a previous study in 1999. Possibly, it was located on the altar and the height of sampling is assumed to be at a level no higher than 1.80 m.	The sample was described as showing plaster and painting layers. No significant superficial alteration was observed	
	PV JM 3	Joint mortars	External west wall of the convent, which corresponds to the inner wall of the altar. The height above natural ground level was 3.06 m.	The joint shows *material loss*. No significant superficial alteration was observed.	
Aljibe del Convento de la Concepción	PV CC 1	Plaster	Sampled from the south wall of the inner part of the cistern, next to the central arcade at 50 cm above ground level	Sampled in proximity of a *detachement* of the plaster. The external surface shows a dark grey-black probably due to *biological colonization*.	
	PV CC 2	Joint mortar	Collected from the external part of the north wall of the cistern, 1.40 m above the level of natural ground.	Mortar showing *alveolization* and a grey-black aspect probably due to *biological colonization*.	
	PV CC 3	Mortar from pavement	Collected from the cistern during the archaeological excavations of 2013.	The specimen was described as a grayish mortar of lime and sand with small stones and some shells, heterogenous, with a thickness of approx. 11 cm. [17]. No significant superficial alteration was observed.	

Table 1. *Cont.*

Site	Sample Code	Type	Sampling Location and Description	Macro Observations/ State of Conservation	Sampling/Macro Picture
Casas Reales	PV CR 1	Joint mortar	Collected on the east wall, facing the beach. Height of sampling 95 cm above natural ground level.	Mortar showing *alveolization* and a grey-black aspect probably due to *biological colonization.*	
	PV CR 2	Plaster	Collected from the interior part of the west wall at an approximate height of 1.20 m above the level of natural ground.	Sampled in proximity of a *detachement* of the plaster which showed also *thin cracks*. Dark grey-black aspect probably due to *biological colonization.*	
	PV CR 3	Joint mortar	Sampled on the east wall, which faces the beach. Height of sampling 3.17 m above the level of the natural ground.	Dark grey-black aspect, probably due to *biological colonization.*	
Torre de la Cathedral	PV TC 1	Joint mortar	South wall of the tower at a height of 1 m above the level of natural ground.	Dark grey-black aspect, probably due to *biological colonization.*	
	PV TC 2	Joint mortar	Collected from the west wall of the tower at a height of 3.05 m above the level of natural ground.	Partial *differential erosion* observed. No significant superficial alteration was observed.	

Table 1. *Cont.*

Site	Sample Code	Type	Sampling Location and Description	Macro Observations/ State of Conservation	Sampling/Macro Picture
Excavaciones arqueológicas	PV AE 1	Plaster	Collected from a wall disassembled in March 2012, during the project vía Cincuentenario (2012–2013), Section 5 of Casal Norte, coordinate micro 825N-1020E.	No information regarding the state of conservation of the plaster during the sampling was reported.	
	PV AE 2	Mortar from pavement	Collected near the main square, at a level 40–60 cm below the level of natural ground, in October 2013.	No information regarding the state of conservation of the mortar during the sampling was reported.	
	PV AE 3	Mortar from pavement	Collected from a pavement found in the Puente del Rey (October 2012), at a depth of 40 cm below the level of natural ground.	No information regarding the state of conservation of the mortar during the sampling was reported.	

Along with this investigation, specific samples were selected according to their representativeness and an adequate material amount for performing X-Ray Powder Diffraction analysis (XRPD) in order to identify the mineralogical composition of the samples. A Philips PW 1050/37 diffractometer was utilized with a Panalytical X'Pert PRO and High Score software data acquisition and interpretation system, operating at 40 kV–20 mA, with a Cu anode, a graphite monochromator, and with 2°/min goniometry speed in a scanning range between 5–70° 2θ; the slits were 1-01-1, and the detection limit was 4%. For this technique, a partial separation of the coarse aggregate fraction was performed by soft mechanical grinding and manual removal by tweezers.

For confirming and detecting in detail the elemental composition of specific areas already highlighted by PLM observations, Environmental Scanning Electron Microscopy and microchemical investigations (ESEM-EDS) were carried out on uncovered thin sections. An EVO LS10 Zeiss Scanning Electron Microscope coupled to a QUANTAX XFlash 6|30 Energy Dispersive Spectrometer (Bruker Microanalysis). The software employed for data acquisition and treatment was Bruker ESPRIT 1.9.

3. Results and Discussion

The following section illustrates the microscopical observations by PLM and ESEM-EDS techniques for the characterization of the materials (Section 3.1) and for the evaluation of their state of conservation (Section 3.2) [18,19]. The final sub-paragraph (Section 3.3) describes the XRPD results, which confirm and enhance the outcomes of the previous observations [20,21].

3.1. PLM and ESEM-EDS Characterization of Materials

The majority of samples were formed by bedding and joint mortars (Section 3.1.1), except for seven samples. A plaster, PV CR 2, and two masonry mortars showing traces of a finishing layer on the external surface, PV JM 2 and PV AE 1, are investigated and described in Section 3.1.2. Furthermore, two samples belonging to the pavements from previous archaeological excavations, PV AE 2 and PV AE 3, were analyzed (Section 3.1.3). Finally, two samples were collected from the internal part of the *aljibe* (cistern) of the *Convento de la Concepción*, specifically from the masonries (PV CC 1) and from the pavement (PV CC 3) (Section 3.1.4).

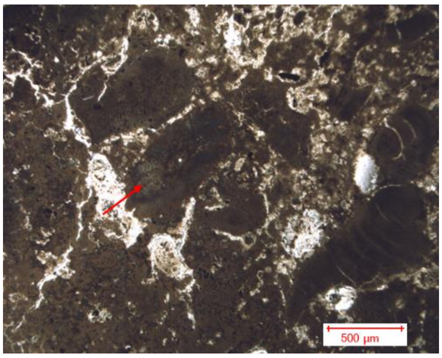
3.1.1. Bedding and Joint Mortars

Considering the bedding and joint mortars collected from the masonries, the binder/aggregate ratio is variable; thus, from PLM observations, it is possible to highlight both fat and lean mortars [22]. In addition, two samples, PV TC 1 and PV JM 1, showed scarce and almost absent aggregate; however, they presented lumps as remnants of burnt stones (from the process for obtaining lime) and the remains of fossils/of shells (e.g., foraminifera, echinoderms, etc.—Figure 3).

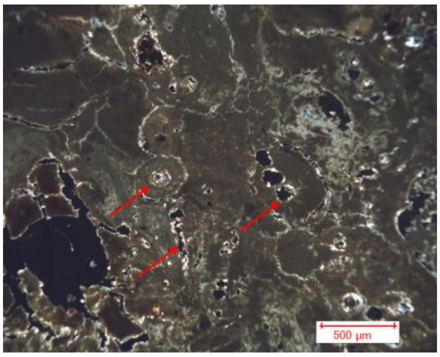
In general, the binder is attributable to lime-based mortars, presenting a brownish color, often inhomogeneous. Nevertheless, the presence of clay minerals, thus of a marly lime binder, has not be excluded since the ESEM-EDS analysis performed on the binders confirmed the carbonate nature of it but, in some cases, also revealed traces of Si, Al, and Fe. In addition, the fat mortars, with a higher presence of binder than the aggregate, are more affected by shrinkage (as in Figure 3b) than the lean ones [19,22–24].

The presence of lumps, as remnants of burning and sometimes also over burnt fragments, was diffused in almost all samples, proof of a poor production technology, as inhomogeneity in the distribution of temperature within the kiln and/or due to a difficult calcination of the stone [19,22–24]. In addition, lumps often show fissuring due to shrinkage (Figure 4).

The aggregate is largely formed by both carbonate and silicate fragments (Figure 5). The first ones are represented by fragments of shells/fossils, as foraminifera, bivalves, echinoderms, etc., with rounded/subrounded shapes and dimensions varying between tens/hundreds to thousands of microns, probably ascribable to the use of beach sand (Figure 5a,b). Notwithstanding, the presence of these fragments can be due also to the use of local rocks, as polygenic breccias, characterized by the presence of both clasts of volcanic rocks and fragments of bioclastic rocks (Figure 5c), as reported in Ciantelli [11,12]. This hypothesis is also supported by the manifestation of remnants of fragments of local rocks and of shells/fossils, as described before (Figure 5d).



(**a**)



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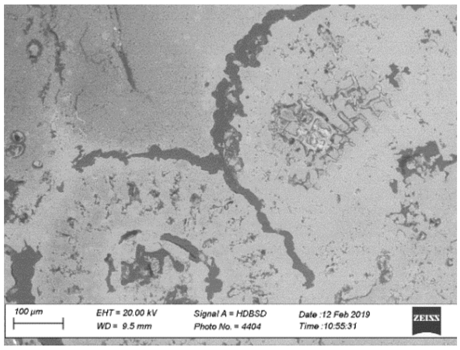
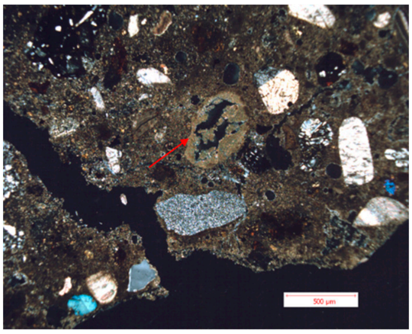


(**c**)

Figure 3. PLM micrographs showing rests of shells/fossils (highlighted by red arrows), respectively, in sample (**a**) PV JM1 and (**b**) PV TC 1: (**a**) xpl, clearly shows a rest of an echinoderm; (**b**) xpl, shows the rest of several fossils, including echinoderms. (**c**) ESEM micrograph of PV TC 1 showing a detail of echinoderm fossils.



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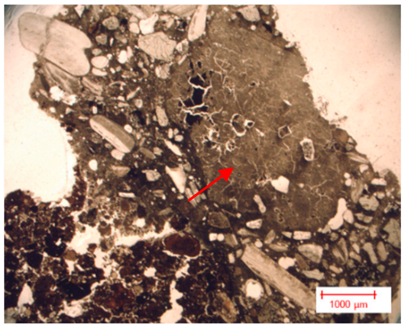

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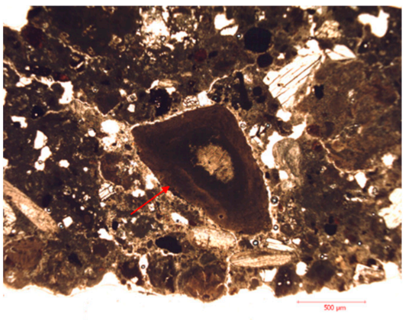

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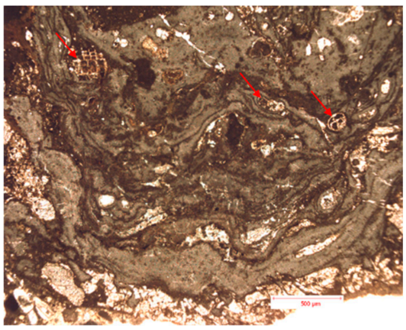


(**d**)

Figure 4. PLM micrographs showing lumps with dissolution and fissuring (highlighted by red arrows), respectively, in samples (**a**) xpl, PV JM3 and (**b**) ppl, PV FC 10M; (**c**) ppl, remnant of a rest of fossil shell fragment in sample PV JM2; (**d**) ppl, PV CM2 shows the rest of bio-clasts embedded in a lump of unmixed binder.

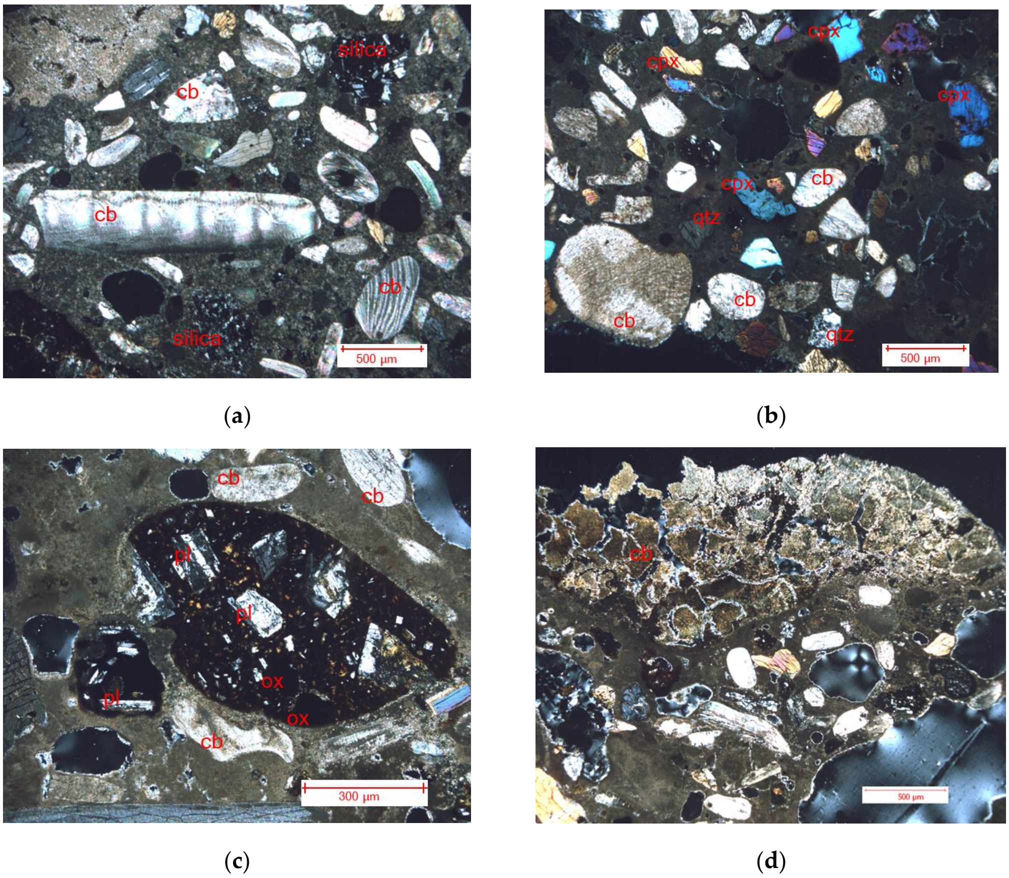


Figure 5. PLM micrographs (xpl) of: (**a**) PV FC 10M showing the aggregate formed by carbonate (cb) and silicate fragments; (**b**) PV CC 2, detail of the aggregate formed by sub-rounded shell fragments (cb) and silicate fraction, mainly formed by pyroxenes (cpx); (**c**) PV CM 2 volcanic rock fragment rich in feldspars (pl) and iron oxides (ox); (**d**) PV CM 2 remnant of an under-burnt carbonate fragment, showing calcite re-crystallization within the cracks and fissures.

The silicate fraction of the aggregate can be generally ascribable to altered volcanic rock fragments and presence of single crystals of quartz, plagioclases (frequently showing sericitization), and pyroxenes, also with the sporadic presence of micas and zeolites. This fraction is mostly characterized by sub-rounded shapes and millimetric dimension for the rock fragments, and by angular/sub-angular shapes with maximum dimension of about 500 µm for the single minerals. The exception was the zeolites; indeed, these latter ones are usually present within amygdales as secondary minerals. Furthermore, the presence of iron oxides was largely diffused. Our results agree with a previous study, performed in 2001 by Garcia de Miguel, who characterized samples from the *Torre de la Cathedral* and evaluated their state of conservation [25]. This research work analyzed two plasters and two embedding/pointing mortars, classifying them as lime mortars with heterometric rests of carbonated fossils, from marine or fluvial sand and fragments of volcanic rocks. Moreover, the presence of crystals such as plagioclases, pyroxenes (e.g., augite), quartz, and iron oxides was detected. The author hypothesized that the plagioclases and pyroxenes derived from the disaggregation of the volcanic rock fragments, whereas quartz was probably obtained by using fluvial quartz-sand. Finally, the mortars showed the presence of iron oxides and high porosity.

In addition, the obtained results concerning the aggregate composition are in agreement with the characterization of the stone mansonries (identified mainly as local volcanic rocks) conducted by Ciantelli [11,12], showing, therefore, the provenance from local quarries also for the raw materials used for mortar production [12]. Even historical documents support this theory; indeed, Arroyo [3] reports sources affirming that, in the second half of XVI century, excellent and copious quarries were found near the town for producing lime and bricks. In addition, for the construction of *Casas Reales*, commercial documents indicate that materials such as lime, tiles, and bricks were brought in small boats through the rivers. In particular, lime was transported from Pacora (east of *Panamá Viejo*) and/or from the west, near the Cárdenas River.

In addition, samples of PV FC 10M and PV AE 1 showed cocciopesto fragments, which can be ascribed to be the main reason of the presence of hematite detected in these samples by XRPD (Table 2). Finally, it has to be mentioned that some specimens (PV FN 3M, PV FC1) showed a preferential orientation of the aggregate, parallel to the external surface, deriving from the application on the wall.

3.1.2. Plasters

Regarding the masonries, three samples were collected from a plaster (PV CR 2) and from wall mortars showing a finishing layer on the external surface (PV JM 2 and PV AE 1), respectively.

PV CR 2 was a covering/finishing layer, ascribable to a lime plaster. The aggregate was almost absent, and the binder was quite compact, with few fissures/pores but showing quite inhomogeneous color and structure. Indeed, it presented remnants of burning and unmixed lime lumps. Finally, iron oxides were detected (Figure 6a).

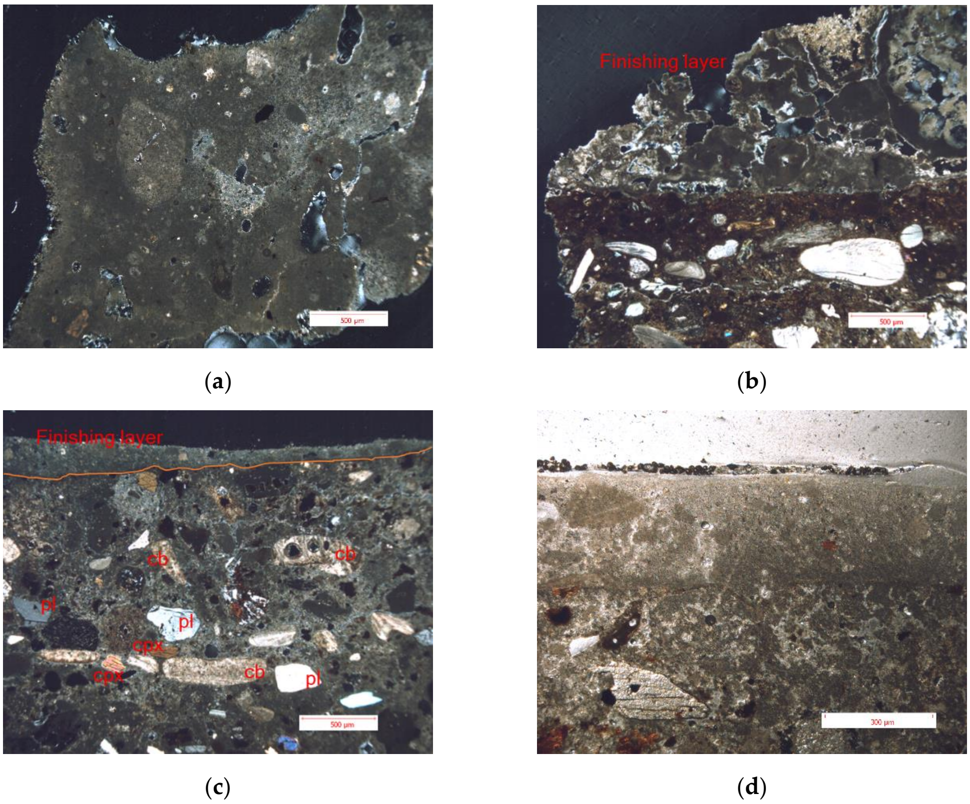


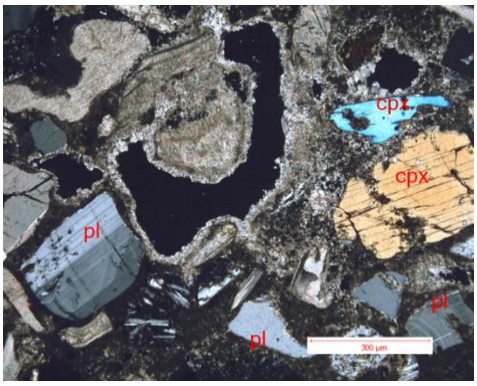
Figure 6. PLM micrographs (xpl) of plaster samples: (**a**) PV CR 2, the aggregate is almost absent, the binder shows inhomogeneity color, with the presence of lumps and pores; (**b**) PV AE 1 sample, the calcite finishing layer showing an irregular and porous surface, rich in dissolution and recrystallization phenomena; (**c**,**d**) PV JM 2, two main layers of mortar are clearly visible in both micrographs: the lean mortar with an aggregate constituted by bioclasts (cb), and silicate fragments (pl, cpx), whereas the thin external layer showing a homogeneous and quite regular and plane surface. In micrograph (**d**), the magnification of the finishing layer shows the presence of the remnant of another thin surface layer over the finishing one.

PV JM 2 and PV AE 1 are almost lean mortars with a superimposed finishing layer with scarce or absent aggregate mainly constituted by carbonate (bioclasts) and silicate fragments (plagioclase, piroxene) (Figure 6b–d). The thickness of the finishing layer varied from about 100 μm to 350 μm in sample PV JM 2 and from about 700 μm to 2500 μm in sample PV AE 1. Considering the first sample, the analysis in cross-section confirms the presence of a thin surface layer over the finishing one, which can be likely ascribable to the presence of painting layer as detected during the sampling campaign conducted in 1999.

3.1.3. Pavements

Considering the mortars from the pavements belonging to previous archaeological excavations, PV AE 2 and PV AE 3 are both lean mortars, with scarce lime binder and abundant aggregate (Figure 7a,b). This latter one is formed by a carbonate fraction (sub-rounded fragments of shells/fragments, also remnants of burning) and a silicate fraction (subangular and angular shaped crystals of quartz, pyroxenes, plagioclase, volcanic rock fragments). In addition, iron oxides and of altered zoned plagioclase are observed (Figure 7b).

(**a**)



(**b**)

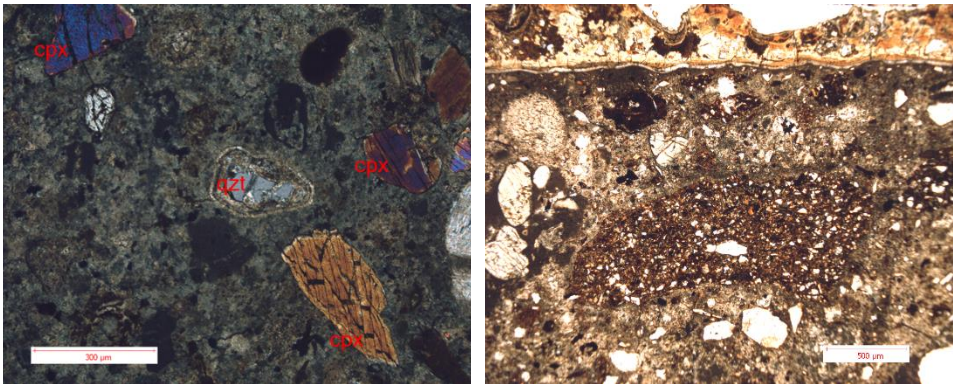
Figure 7. PLM micrographs (xpl) of: (**a**) PV AE 2, detail of the aggregate. The traces of under-burnt of the shell (cb) are evident; (**b**) PV AE 3, silicate fragments of the aggregate, formed by altered pyroxenes (cpx), volcanic rocks, and plagioclases (pl–a zoned one on the right bottom). The pore rims show the crystallization of secondary calcite.

3.1.4. Mortars from the Cistern

Lastly, as previously mentioned, two samples were collected from the inner part of the cistern of the *Convento de la Concepción*. Precisely, they were sampled from the masonries, the plaster PV CC 1, and from the pavement, PV CC 3.

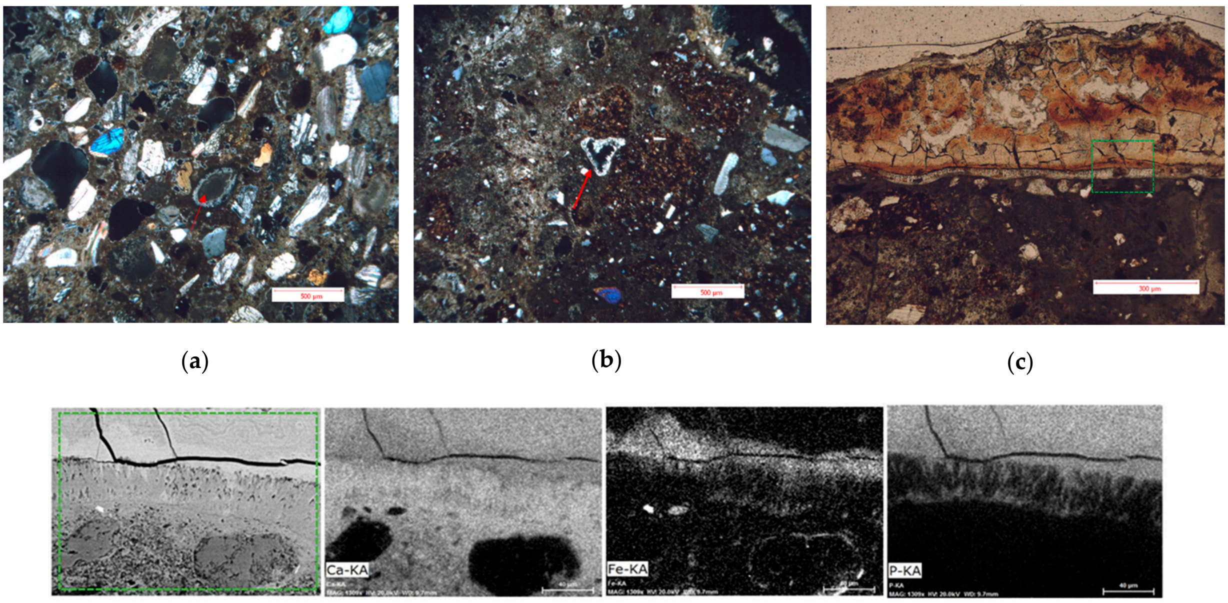
The latter one, sample PV CC 3, was sampled from a mortar described as "greyish mortar of lime and sand with small stones fragments and some shells". Under PLM, the material presents scarce binder and an aggregate constituted by both carbonate and silicate fractions. The first ones consisting of sub-rounded fragments of shells and fossils, whereas the second ones are mainly represented by both single crystals of quartz (observed also as calcedony) and pyroxenes, and volcanic rock fragments. Among this latter one, the quartz crystals result affected by fracturing with subsequent deposition of secondary mineral phases, including calcite, within them and around the crystal rim, as represented in Figure 8a.

PV CC 1 is a plaster, sampled from the south wall of the inner part of the cistern. Through the PLM observations, the mortar showed a superimposing layer, probably intentionally applied (with a variable thickness from hundreds to thousands microns). Within the interface between this external layer and the inner mortar, secondary calcite wasobserved (Figures 8b and 9c,d). The inner internal layer of lime mortar presented as aggregate cocciopesto fragments, volcanic rock fragments and quartz, scarce shells fragments, and pyroxenes (Figure 8b). The presence of cocciopesto gives hydraulicity to the lime plaster, which is expected, as it is covering a wall of the cistern and thus exposed to the almost constant presence of water and moisture [26].



(a) (b)

Figure 8. PLM micrographs of: (**a**) xpl PV CC 3 detail of the silicate aggregate, pyroxenes (cpx), and quartz (qtz) affected by precipitation of secondary minerals; (**b**) ppl PV CC 1, general view of the "mortar with cocciopesto", showing an external layer.



(a) (b) (c)

(d)

Figure 9. (**a**–**c**) PLM micrographs of, respectively: (**a**) xpl, PV FN 3M, presence of lump rounded shaped, showing dissolution and precipitation of calcite (red arrow); (**b**) xpl, PV CC1, secondary calcite re-crystallized within a pore (red arrow); (**c**) ppl, PV CC1 showing the external altered layer. The secondary calcite, re-crystallized within the interface between the mortar and the external layer, is more evident under the ESEM microscope (**d**), where also the presence of iron and phosphorus is detected by EDS maps (analyzed area is indicated by the rectangle, with dashed line, within **c**,**d**).

3.2. PLM and SEM-EDS Analysis of the State of Conservation

During the sampling campaign, several mortars showed evidence of decay and weathering, as material loss, erosion, alveolization, thin cracks, and powdering. Furthermore, several specimens presented a superficial blackening/dark grey-black aspect (see Table 1), which was not detected by PLM and ESEM-EDS analysis. This alteration could be due to the presence of a cyanobacteria, called "alga negra" (*Oscillatoria sp.*), which was identified by a previous study [27] and observed on the stones of the masonries [11]. According to Macedo et al. [28], the presence of algal biofilms on stones can be responsible not only for an aesthetic damage, due to the blackening, but also for an enhancement of soil formation and water retention. Nevertheless, observing the samples, after the thin sections' preparation, the presence of this "alteration layer" was not detectable, as it has been removed.

The majority of the observed samples showed diffused porosity (as pores and fissures/cracks), some of them with the presence of secondary mineral crystallization of calcite within pores (PV FN 3M, PV CM1, PV CM2, PV CC1, PV CR2, PV AE1, PV AE3), as shown in Figure 8a,b. In particular, in sample PV CM1 and in PV CC1, the calcite precipitation is present near the external surface, whereas in the case of PV CC1, it is located in the interface between the inner mortar and the external layer (probably due to decay phenomena, also given by the presence of iron oxides and phosphorous Figure 9c,d). Furthermore, dissolution phenomena of carbonate fragments/lumps are often detected, as in sample PV FN3M (Figure 9a).

3.3. XRPD Investigation

In order to precisely determine the crystalline phases present within these samples, a selection of them have been analyzed through X-Ray Powder Diffraction analysis (XRPD). The obtained results, listed in Table 2, confirmed the PLM observations; indeed, all the specimens show high amounts of calcite due to the carbonate nature of the binder and of the part of the aggregate, sometimes with low amount/traces of aragonite. Traces of aragonite were detected also by the research work by Garcia de Miguel (2001) [25], defined as an index of presence of marine lamellibranch shells from beach sand. Furthermore, low amounts/traces of plagioclase (albite), quartz and pyroxenes (diopside and augite) were detected due to the silicate aggregate already described by the previous observations. Finally, traces/low amounts of hematite were identified, endorsing the diffused presence of iron oxides, also in cocciopesto, whereas only in PV AE 1 were traces of mica (muscovite) found. Considering the PV CC1 sample, the altered superficial layer (called PV CC1 black part) was separated in order to perform a distinct analysis on the two parts. Therefore, XRPD investigation on the altered part revealed a high amount of calcite, followed by low amounts of quartz, zeolite, and brushite.

Brushite, a hydrated calcium phosphate mineral with the formula $CaHPO_4{\bullet}2(H_2O)$, is a decomposition product of guano (seafowl excrement), formed at low pH by reaction of phosphate-rich solutions with calcite and clay [29], which can derive from soil, since the aljibe has being buried in the past [15]. The presence of phosphorus within this layer were confirmed also by ESEM investigations previously described (Figure 9d).

Table 2. XRPD results. Abbreviation of minerals according to the list of mineral abbreviations IUGS [30] xxx = high amount; xx = medium amount; x = low amount; tr = trace.

Samples	Cal	Qtz	Arg	Pl	Px	Hem	Brushite	Zeo	Mca
PV CC1	xxx	x	x	x	x	tr	-	-	-
PVCC1 external layer	xxx	x	-	-	-	-	x	x	-
PV CC2	xxx	x	x	x	x	-	-	-	-
PV AE1	xxx	x	tr	x	x	x	-	-	tr
PV CM2	xxx	tr	x	x	x	tr	-	-	-
PV CR3	xxx	tr	-	x	x	x	-	-	-
PV FC10M	xxx	x	x	x	x	tr	-	-	-

Table 2. *Cont.*

Samples	Cal	Qtz	Arg	Pl	Px	Hem	Brushite	Zeo	Mca
PV FC1	xxx	x	x	x	x	tr	-	-	-
PV FC3	xxx	-	x	x	x	-	-	-	-
PV FN 3M	xxx	x	x	x	x	tr	-	-	-
PV JM3	xxx	x	-	x	-	-	-	-	-
PV TC2	xxx	tr	-	x	-	x	-	-	-

4. Final Considerations and Conclusions

The present work analyzed in detail joint/bedding mortars from masonries, plasters, and mortars belonging to pavements (twenty-one total specimens) from seven monuments and from archaeological excavations of the Panama Viejo Historical Monument Complex in Panama.

With the exception of two specimens, which belonged to the walls (both the inner and outer part) of a cistern, all the other joint/bedding mortars and plasters were collected from the masonries of the buildings.

Regarding the characterization of the bedding/joint mortars, both fat and lean mortars were observed. Among them, two samples present scarce and almost absent aggregate; however, they showed lumps from residual fossils/shells (e.g., foraminifera, echinoderms, etc.). The presence of lumps (often affected by fissuring due to shrinkage), such as remnants of burning stone (under-burnt) and fragments of over-burnt of stone for lime, was observed in almost all samples. This may be due to an inhomogeneity in the distribution of temperature within the kiln and/or due to a difficult calcination of the stone because of its composition.

All the samples under study can be attributable to lime-based mortars, presenting a brownish color, often inhomogeneous. The aggregate is largely formed by both carbonate and silicate fragments. The carbonate fraction is represented by fragments of bioclasts (as foraminifera, bivalves, echinoderms, etc.), with rounded/subrounded shapes and dimensions varying between tens/hundreds to thousands of microns, probably ascribable to the use of the beach sand. Nevertheless, the use of local rocks, such as polygenic breccias, which show the presence of these fossils, cannot be excluded. Considering the silicate fraction, generally, altered volcanic rock fragments, quartz, plagioclases (frequently showing sericitization), pyroxenes, with the sporadic presence also of micas and zeolites, were detected. They presented mostly sub-rounded shapes (rock fragments) and angular/sub-angular shapes (single minerals). With the exception of the zeolites, indeed, these latter ones are usually present within amygdales as secondary minerals. Furthermore, the presence of iron oxides was largely observed.

The plasters utilized were lime plasters, without aggregate. With the exception of the plaster used on the cistern wall, indeed, in this case, cocciopesto fragments were identified in order to give hydraulicity to the material.

Finally, the mortars belonging to the pavements, both from previous archaeological excavations and from the cistern, show scarce binder, whereas the nature of aggregate is similar to the one described for the masonries mortars.

Evaluating the state of conservation of these materials, considering the macro-observation, it can be stated that the majority showed an alteration probably ascribable to biological colonization, exhibiting a dark-grey black or greenish aspect of the surface. Furthermore, materials loss, thin cracks, and powdering were detected. By micro-investigations, the majority of the samples showed diffused porosity (as pores and fissures/cracks), some of them with the presence of secondary mineral crystallization of calcite within. In addition, two specimens showed the precipitation of calcite near the external surface. One of them, specifically, the plaster from the cistern, presented a further outer altered layer, rich in iron oxides, which also revealed the presence of brushite, a hydrated calcium phosphate, detected by XRPD investigation, and the presence of phosphorous was also confirmed by ESEM-EDX. This compound could be due to a reaction of phosphate-rich solutions (probably deriving from the presence of guano) with calcite and clay derived from the soil that in the past buried the area.

Finally, by naked eye, several specimens presented a superficial blackening, an alteration that could be due to the presence of a cyanobacteria, called "alga negra" (*Oscillatoria* sp.), also observed on the surface of the stone masonries. Its presence can be responsible for an aesthetic damage, in addition to representing a substrate for further biological deterioration and water retention.

In conclusion, the mortars analyzed were produced utilizing local rocks, both for the carbonate and for the silicate fraction of the aggregate, and for determining the lime binder, even if the technology used was quite poor/limited. The majority of the samples had a similar composition; nevertheless, it is not possible to state that these mortars belong to the same intervention and so to the same period, as the site and the monuments underwent several modifications during the 16th and 17th centuries. Finally, they showed quite a poor state of conservation, exhibiting evidence of alteration due to dissolution phenomena (as the secondary calcite within pores and on the surface), diffused porosity, and the presence of biodeterioration, as a result of the high moisture to which these materials are exposed. The characterization of the original materials and their weathering and decay processes is necessary for choosing the most compatible products for their proper restauration [31]. Therefore, this information can support the regular maintenance and the restoration works performed by the Patronato Panamá Viejo, fundamental for the best conservation of the site, which aims to preserve and enhance the tangible and intangible features of this unique place.

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Note

[1] "Archaeological Site of Panamá Viejo" is the official name of the site, used internationally; nevertheless, the "Monumental Complex of Panamá Viejo" is the nationally used name by law.

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