Sampling of building materials from archaeological sites in the Mediterranean basin

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INTRODUCTION
The purpose of this document is to describe the sampling campaigns performed at the archaeological sites selected as case studies for the PRODOMEA. Plastering and bedding mortars were collected at the archaeological remains of Giannutri in Italy, Tróia in Portugal, Mekawer and Petra in Jordan and Damascus in Syria. The sampling campaigns were possible thanks to a close collaboration among the partners of the project. Two analytical methodologies were applied in order to characterise the materials employed, evaluate the damage and identify the natural and anthropogenic sources responsible for the deterioration processes. The detailed results obtained at each site and final conclusions, comparing the data and evidencing common and diverse features among sites, are presented.

1. SITES DESCRIPTION
TROIA, Portugal
Located at Tróia peninsula, in the Atlantic coast of Portugal, this archaeological site comprehends one of the most outstanding cases of the known fish-salting industries of the Roman Empire. That fact motivated attribution of National Monument category since nearly one hundred years ago by the Portuguese Government. Tróia was not the single one of its kind in the European Occident. In fact, this fish-salting industry was part of a complex trading chain centred in the Mediterranean Sea (the Roman *Mare Nostrum*), that guaranteed the supply of sea products to a significant set of imperial population centres. Built by the end of the first century before Christ, it was kept fully active until the middle of the third century after Christ. By that time, it began a progressive and irreversible decadence process until the fifth century a. C., as testified by the latest Roman vestiges found at the site.

Ranging in the extension of almost two kilometres, this fish processing industrial complex keeps a considerable dense set of buildings including factories, houses, spa, funerary structures and a religious temple. This complex built set reflects the intense industrial activity developed at the site. The dates and reports of the first archaeological surveys in Tróia are not known. The earlier reference dates back to 1502, in a privilege attribution document issued by Ordem de Santiago, granting to a couple, the land and its use near a lagoon area for building tide mills. More formal excavations campaigns started by the time of D. Maria I, when she was still a princess. *Sociedade Archeológica Lusitana* (Lusitanic Archaeological Society), was officially born in 1851 with the purpose of accomplishing excavations in Tróia. Several survey campaigns took place at the ruins, mostly in Rua da Princesa (residential Area) and over the area of the late Roman temple.

1.1.1. The salt fish plants
The 3 km length of fish processing factories had specialized working areas, including: tanks (*cetariae*), wells, fish preparation areas, heating furnaces to accelerate the sauce production, structures for
cooling, storehouses and residential houses. The fish-salting reservoirs have different sizes and are grouped in distinct factories divided by masonry walls.

1.1.2. Other Roman monuments

Besides the extensive industrial structures, other important structures exists such as two late Roman graveyards, a religious building (Basilica), a Spa and a residential area. The presence of buildings with two floors, some of them covered with opus tesselatum, indicates a probable splendour of the site. The Roman constructions are built in stone masonry using mainly local stone (opus incertum and opus quadratum) and in the later period (IV-V a.D.) brick was used, as well (opus testaceum, opus mixtum) in architectonic reformulations. Different types of stones were used in the masonry, probably brought to Tróia as successive ballast charges by the ships used to transport salt supplies.

1.2. GIANNUTRI, Italy

Giannutri is located in the northern Tyrrhenian Sea and is the southernmost island of the Tuscan Archipelago (fig. 1.2.1.a). The earliest reference to the island was found in the Naturalis Historiae of Pliny the Elder. The Romans inhabited the island until the 3rd century A.D., when it was abandoned for unknown reasons. Architectural evidence of the Roman period consists of the remains of the ancient Roman villa of the 1st-2nd century A.D. owned by the Domizi Enobarbi family. The earliest excavations of the Roman Villa were carried out by Gualtiero Adami, a Garibaldian captain, who landed on the island in 1882. During his stay there, some rooms of the villa were used as lodgings. The archaeological area referred to as Villa Domitia comprises a group of connected buildings with different functions, located between Cala Maestra (western coast) and Cala Spalmatoio (eastern coast). In particular, the western coast is the location of the residential quarter, a group of service posts (cistern and crypto-portico), a small thermal plant and, finally, the Cala Maestra harbour. The ancient masonry is built using tuff blocks (cubilia) arranged in opus reticolatum bordered by the bricks forming testaceum belts. In 1990 (Rendini, 1991) and 2000, the archaeological area underwent restoration work.

1.2.1. Harbour Quarter

The Harbour quarter includes “Le Stanze” and the “Darsena” archaeological sites (fig. 1.2.2). The site called “Le Stanze” is located near Cala Maestra, on the western coast of Giannutri, and consists of a small ancient harbour quarter (fig. 1.2.1.b). The site consists of a small complex of similarly sized, interconnecting rooms, located next to a vaulted structure and a cistern. The “Darsena”, on the western side of the island, is located in the landing place of the ancient harbour of Cala Maestra. It is characterised by a rectangular basin, obtained from digging into the calcareous rock. The cutting of the natural rock is clearly visible, together with the excavated materials used in the building of the masonry, which is formed by sections of volcanic tuff blocks (cubilia) set between brick belt borders.
1.2.2. Residential Quarter
The ancient residential zone, located in proximity of the Punta Scaletta site, is one of the most indicative areas of the entire site for the study of the environmental impact, being one of the most deteriorated areas. The masonry at this site is subject to continual deterioration, caused by atmospheric and biological agents.

1.3. DAMASCUS, Syria
Damascus, the capital of the Syria, is considered the world’s oldest continuously inhabited cities, believed by some to date back to the seventh millennium BC. The documented history of the city starts in the second millennium BC, in the Amorite period, when Damascus, thanks to its geographical position, became an increasingly important city in the Aramaean Kingdom, which was defeated by the Assyrians in 841 BC. It is believed that the remains of the Aramaean town lie buried under the eastern part of the old walled city. The main buildings of the Aramaean era were the Temple of Hadad and the Royal Palace. The Temple was built on the site now occupied by the Great Omayyad Mosque, and ruins thought to have belonged to the Temple were found in 1949 during the restoration of this building.

1.3.1. The roman period and the Jupiter Temple
In 64 BC, Syria became a province of the Roman Empire. Damascus, thanks to the political stability and economic growth brought by the expansion of the Roman Empire, gained significant commercial importance as the nodal point of the east-west trade route. The Romans incorporated the Aramaean and Greek sectors of the city into a coherent city plan, and built a wall encircling the whole area. Seven gates were built at intervals along the wall. The major construction during the Roman era was the Temple of Jupiter (fig. 1.3.1), some of whose remains are still standing near the entrance of the Omayyad Mosque (fig. 1.3.2) and Souk al-Hamidieh. It was built on the same site where the Aramaean temple once stood. Another important construction was the Forum, located east of the Great Mosque. A colonnaded street connected the Forum to the Temple of Jupiter, and its columns can still be found in al-Qaymariyyeh quarter. With the break up of the Roman Empire in 395 AD, Syria became a part of the eastern province of the Byzantine Empire and Damascus maintained its economic and strategic significance, remaining much the same as it had been during the Roman period, except for the mass construction of churches and the transformation of the Temple of Jupiter into a cathedral dedicated to St. John the Baptist, in the fourth century.

1.3.2. The Muslim Empire and the Omayyad Mosque
In 635, Muslim armies entered Damascus and annexed Syria to the fast expanding Muslim empire. The way of life changed in accordance with Islamic teachings of the Koran. However, the Muslims treated Jews and Christians, who now became a minority, with tolerance. Christians and Muslims
prayed side by side in the Cathedral of St. John, before Muslim rulers decided to build the Great Mosque on the same site. In 661, a golden age started for Damascus thanks to the Omayyad Dynasty, which continued to rule the Muslim empire for about one century. The Omayyad rulers introduced new styles of art and architecture, which were mainly inspired by Islam. The new styles combined with Byzantine and Persian influences to produce the Great Omayyad Mosque. The Mosque, built between 705 and 715, was the first of its type and became a model for other mosques throughout the Islamic world.

1.4. MEKAWER, Jordan
The village and fortress of Mekawer are located at the summit of jebel al-Mishnaqa. Mekawer was founded in 90 BC, as a stronghold of Asmonean power against the Nabateans of Petra. Destroyed by the Roman in 57 BC, it was rebuilt during the reign of Herod the Great. After his death, the fortress passed on to Antipa, and eventually fell under the control, in 37 AD, of Agrippa, king of Judea and vassal of Rome. During the Judean revolts, from 66-74 AD, the fortress was one of the bulwarks against Roman rule, until its destruction in 72 AD.

The Mekawer Fortress is one of the most important of a great system of fortresses built by Herod the Great (37-4 BC). Current knowledge on the fortress depends on the digs of the Studium Biblicum Franciscanum (1978-1981) and the Cooperativa Archeologica of Florence (1992-93), which have begun to shed light on the its various construction phases: a) the Asmonean (parts the towers and walls); b) the period of Herod the Great (the water system, strengthening of defences, re-organisation of the peristilum and thermal area); c) the period of Herod Antipa and Agrippa (general reorganisation); d) the period of the Roman administration and the revolts (destruction and temporary reoccupation); e) the Byzantine period and salvaging of materials for the building of the village.

The village of Mekawer is a good example of a settlement developing around an original nucleus of a few houses, which provide an excellent example of traditional stone building methods. An effective system of water management comprising cisterns along the mountainside, dug into ancient stone quarries, as well as cisterns on the flat land. There are also a number of decanting tanks, thermal baths, with a calidarium and frigidarium, a ritual bath and a dense network of small canals.

Since 1991, the recovery of the remains of the village and fortress of Mekawer has been part of a project (Machaeerus, Plan for restoration, maintenance and tourist development) carried out by Florence University's Department of the History of Architecture and Restoration of Architectural Structures for the Ministry of Tourism and Antiquities of the Hashemite Kingdom of Jordan, in collaboration with the Studium Biblicum Franciscanum and the support of the Italian Embassy in Amman. Up to now, the restoration work has been based on a micro-intervention with the aim to tidy up, clean and consolidate. At the present, the archaeological digs and the restoration works are suspended (Marino, 1992-1993-1997a-1997b, Marino et al 1992, Marino and Matella, 2000).
1.5. PETRA, Jordan

Petra is situated half way between the Dead Sea and the Gulf of Aqaba, about 95 miles south of Jerusalem and 60 miles north of Aqaba. The ancient city of Petra was located at the crossing of two important ancient trade routes, and was a thriving commercial centre from 100 BC and to 100 AD, during which time it was the capital of the Nabatean Kingdom in Edom. The Nabateans excelled in many areas, including trade, architecture, agriculture, as well as developing innovative methods of water management. Public spaces, temples and tombs occupied large areas of the city, yet it was also full of residential areas with multi-room houses and paved streets. Some time after the arrival of the Romans, Petra was abandoned, the site no longer being considered of strategic and commercial importance. The major discovery from Petra is its distinctive pottery, but there are three other areas of relevance to the study of the city: the tombs, the water systems and the very recently discovered papyrus scrolls. The following description of the sampled sites was done with the contribution of Dr. May Shaer.

1.5.1. The Petra Great Temple

Excavations at the Great Temple started in 1993 and have continued since. The monument is located in the centre of Petra, occupying an area of 7560 mq, which includes the monumental entrance (propylaeum), the sacred area (lower temenos) and the upper temenos comprising the temple itself (Joukowsky, 1998).

1.5.2. The Petra Garden and Pool Complex

The Petra Garden and Pool Complex is located in the centre of Petra, overlooking the colonnaded street. A preliminary survey and excavation of the site started in 1998, revealing an elaborate hydraulic system associated with a swimming pool and island pavilion (Bedal 1999; 2001; 2002).
1.5.3. **Qasr el-Bindt**

Qasr el-Bind is located at the western end of the temeneous gate, at the end of the colonnaded street. It is thought to be the only freestanding structure that withstood the earthquakes of AD 363 and 747. The first to describe the structure was Kohl (1910), followed by Wright (1961), while excavations in and around the site began in the 1960s. The plane of this temple is square-shaped, built of massive sandstone blocks, sometimes reaching ca 2m. Parr (1967-68: 17) dates the temple to the time of King Obodas III (30-9 BC), while McKenzie (1990: 35-35) gives it a terminus ante quem of the first century AD.

1.5.4. **Temple of the Winged Lions**

The Temple of the Winged Lions is located on a slope lying north of the colonnaded street. It was named after the sculpted lions with wings that once decorated the capitals of the altar’s columns. A survey of the site began in 1973, while the first excavation of the site was conducted in 1974. It continued in subsequent years, uncovering the whole temple with its adjoining rooms, including the residential quarters and workshops (Hammond 1975; 1977-78; 1996). The Temple is dated to AD 28, by an inscription found in the marble workshop.

1.5.5. **The Turkmanyya Tomb**

This tomb is located on the west bank of the Wadi abu-‘Ullayqa, and the eastern rock-side of Jabal al Mu’aysra ash-Sharqiyya. Its façade consists of two sets of large steps, a cavetto cornice, an attic storey and classical cornice. Almost one third of the façade has disappeared. Above this portion is a five-line Nabatean inscription. Both McKenzie (1990: 35) and Zayadine (1991: 282) date the tomb to the time of King Malichus II (40-70 AD).

1.5.6. **The Palace Tomb**

This is one of the largest facades in Petra. A major portion of its upper section is constructed in masonry, much of which has collapsed. It underwent restoration work to rebuild its top left structure.

2. **SAMPLING**

Representative fragments of bedding mortars, plasters and renders were collected from ancient masonry in archaeological sites of the Herodian Age (from 50 B.C. to 100 A.D.), located in the Mediterranean basin:

- Troia, nearby Lisbon in Portugal;
- *Villa Domitia* on the Giannutri Island within the Tuscan Archipelago in Italy;
- Jupiter Temple within Damascus in Syria;
- Mekawer Fortress and Petra in Jordan.

The LNEC and IPPAR team visited the Archaeological Site in April 2003. During this visit the team carried out a thorough inspection of the site with the aim of defining the sampling strategies. The sampling collection was decided to be carried out on three places, selected with basis on the chronology, the typology of construction and the location of the monuments inside the peninsula (near
or far from the river shore). On May 2003, a sampling campaign was carried out and several mortar samples were collected from the residential area as well as from the inland and harbour fish plants. The I.S.A.C. sampling campaigns at the different archaeological sites were carried out in July and October 2003. During the first campaign (2nd –3rd July 2003), samples were collected from the ancient masonry of the Roman Villa of Giannutri Island, in the Tuscan Archipelago (Italy). The collaboration with the “Soprintendenza per I Beni Archeologici per la Toscana” was essential in reaching an efficient planning and implementation of the sampling campaign.

The second campaign was performed between 23 and 28 October 2003, in Syria and Jordan. In particular, the archaeological remains of the Jupiter Temple, in Damascus (Syria), and of the Mekawer Fortress and Petra in Jordan, were taken into account. This work was possible thanks to a close collaboration with Queen Rania’s Institute of Tourism and Heritage of Hashemite University (HU) for the Jordan sites, and the Architectural Research Centre of Old Damascus (ARCOD) of Damascus University for the Syrian site.

2.1. TRÓIA, Portugal
At the Tróia archaeological site, samples were collected from original Roman masonry, aiming to characterize the building materials and technologies.

2.1.1. Plan of the inland fish plant and the sampling locations
A view of the inland fish plant is presented and figure 2.1.1.2 shows a plan of this fish plant with the sampling locals.

2.2. GIANNUTRI, Italy
At the Island of Giannutri in Italy, samples were collected from the ancient masonry of the archaeological remains referred to as Villa Domitia. On the basis of information on the restoration intervention at this site (Rendini, 1991 and Sabelli, personal communication), fragments of bedding and plastering mortars from restored areas were also collected, in order to evaluate their compatibility with the original ones.

Residential Quarter
The samples were collected from the cistern located near the Roman Villa and from both ancient and modern materials in the villa’s masonry.
2.3. DAMASCUS, Syria
Sampling was performed at the archaeological area including the Omayyad Mosque and Jupiter Temple wall remains. The Roman archaeological site located south of the Omayyade Mosque was also considered. The original masonry consists of limestone blocks, with the exception of some areas realised in bricks, which could either be original Roman remains or restoration filling works. Generally, no plastering mortars are present. On visual assessment, soiling and blackening were observed to be present on almost all areas of the walls, representing the most important damage processes. The sampling mainly focused on the bedding and pointing mortars between stones or bricks. In addition fragments revealing a co-presence of black crust and stone substrate were collected.
2.4. MEKAWER, Jordan
At the archaeological remains of Mekawer, sampling was performed in several areas of the ancient Herodian Palace (*triclinum, peristilum, calidarium, frigidarium*), by collecting fragments of original and repair bedding and plastering mortars. Samples of original stone blocks were also collected.

![Map of the Mekawer Fortress archaeological site: the arrows show the different sampling sites](site plane for courtesy of Prof. L. Marino).

2.5. PETRA, Jordan
At the archaeological area of Petra, bedding mortars, plasters and renders were sampled from several buildings: the Petra Great Temple, the Petra Garden and Pool Complex, the Qasr el-Bint Temple, the Turkmanyya Tomb, the Temple of the Winged Lions and the Palace Tomb. Attention mainly focused on masonry building materials and covering mortars of pipeline systems and reservoirs (tanks, cisterns), both original and restored.
3. ANALYTICAL METHODOLOGIES

3.1. Laboratorio Nacional de Engenharia Civil (L.N.E.C.), Methodology Applied

In order to characterise the different materials, samples were observed following a systematic protocol where colour, texture, aggregate morphology; aggregate sorting and the function of the mortar (plaster, render, structural, decorative, etc) were recorded. Three different preparation steps were carried out according to the tests to be performed namely:

i) disaggregation and separation of aggregates from the binder;

ii) grinding the bulk sample, aggregates and binder;

iii) grinding the bulk sample and extraction with water for soluble salts determination.

With the aim to separate the aggregates from the binder, the original sample (totally or a fraction of it depending on the size of the sample) was weighted and disaggregated manually by using a little hammer with care so as to avoid breaking of the aggregates. Once disaggregated the sample was sieved by using sieves with the following meshes: 16mm, 8mm, 5mm, 2.5mm, 1.25mm, 630 µm, 315 µm and 106 µm. The fractions retained on the sieves 630, 315 and 106 µm were ground together in an agate mortar and passed through sieve 106 µm. The fraction that still remains on sieve 106 was constituted of siliceous sand. All the fractions were weighted. After disaggregation, the aggregate fractions were washed with a diluted solution of hydrochloric acid and dried. This procedure and the tests performed are presented in the flow chart.

The optical microscopy observations (OM) were carried out with the aid of a stereo-zoom microscope OLYMPUS 52H-111 equipped with a video system CCD SONY. The granulometric fractions obtained were observed and registered. Also small fragments of the samples were observed by OM after samples being cut, polished and impregnated under vacuum with an epoxy resin and the observations were carried out by means of reflected light optical microscopy. By using a scanning electron microscope (SEM) JEOL JMS 6400 with EDS and X-ray NORAN micro-analyser, the microstructure of the sample and its elemental composition were observed by using a representative fragment of the sample covered with a conducting thin carbon film.

The mineralogical characterisation of samples by XRD was carried out with a PHILLIPS PW3710 diffractometer with a scanning 2θ range between 3 and 74º and a velocity of 0.05º 2θ/s, and a tension and filament current of 35 kV and 45 mA, respectively. The constituents identification was done by using the JCPDS database of standard X-ray powder patterns with the search/match procedure PC-APD Phillips software. Thermo gravimetric tests (TG/DTG) were carried out with the equipment SETARAM TG-DTA, under an inert atmosphere of argon with 3 L/h, and a uniform heating rate of 10 °C/min, from room temperature until 1000 °C. The thermogravimetric analysis measures continuously the mass variation of the sample, under a uniform heating rate. Any reaction that implies a mass loss (dehydration, dehydroxilation, decarbonation) or a mass increment (oxidation, carbonation, hydration) can be quantified. Many of these mass losses or increments occur at temperature intervals that are characteristic of certain compounds, fact that permits to identify and quantify them.

Some mortar samples were collected with the aim of analysing the content of soluble salts trying to evaluate the causes of damage. Samples were collected along a vertical profile of the wall having in mind the objective of identifying eventual phenomena of raising damp. An Ion Chromatograph (IC) from ALTECH with a modular system and a conductivity detector with gold plated electrode with a constant of 30cm-1 was used to characterise the soluble salts.

The samples were ground in a porcelain mortar and a portion of exactly 400 mg of sample was taken to an Erlenmeyer and adding 20 ml of hot distilled water. The mixture stayed during 2 hours in a steam water bath and was stirred from time to time. The mixture rested 16 hours at room temperature and was filtered to a volumetric flask of 200 ml. This procedure was repeated two times with the residue on
the filter and the filtrate added to the 200ml volumetric flask. All the washings of the residue were collected in the same flask and the volume completed to the mark with distilled water.

3.2. Institute of Atmospheric Sciences and Climate (I.S.A.C.), Methodology Applied

In the analytic procedure the samples undergo different techniques in order to characterize the mortar types, both ancient and modern (Martinet and Quenee, 2000; Middenford et al., 2000; Van Balen et al., 2000), and evaluate the damage affecting the masonry at the chosen archaeological sites (Sabbioni et al., 2001).

For the petrographical and mineralogical characterization of the material and damage products, thin cross sections of the most representative sample for each site, were prepared and submitted to optical microscopy observations (OM) in transmitted light, using an Olympus BX 51 microscope, equipped with scanner and the MICROMAX software “Primoplus_32” vers.8.11.02.

The mineralogical features previously identified by OM observation were integrated by x-ray diffraction analyses, performed in order to identify the crystalline phases. The instrument used is a Philips PW 1730 diffractometer equipped with a copper anticathode and a nickel filter. The analytic method in question requires at least 3 g of powdered sample on a Plexiglas stub. The measurement conditions have a diffraction interval of 2θ, between 5° and 50°, and a 2°/minute step at 40kV voltage and 30mA current intensity. The methodology permits the acquisition of qualitative and semi-quantitative data on the crystalline phases present in a concentration of at least 3-4%.
Scanning electron microscope observation is used to study the morphological features and the qualitative elemental chemical composition of samples. The instrument used is a scanning electron microscope SEM, Philips XL 20, equipped with an energy-dispersive analyser (EDX). Analyses are carried out on bulk samples. Samples are mounted on aluminium stubs and coated with a thin graphite or gold film to allow surface conductivity. For the measurement of sulphur, graphite films are necessary, because the emission spectrum of gold would interfere with that of sulphur.

Finally, taking into account that one of the main causes of the damage encountered on mortar surfaces in urban areas is related to sulphation processes, and that hydraulic mortars can contain insoluble salts (ettringite or calcium monosulphoaluminate hydrate), a specific procedure was followed for the determination of water soluble sulphate and water-insoluble sulphate. The non-water soluble sulphate concentration was evaluated as the difference between the total sulphate fraction, measured by ion chromatography with a specific methodology (Gobbi et al., 1995), and the soluble sulphate.
Considering that:
• the aim of the work is to analyse samples of mortars from Roman masonry of archaeological sites of the Mediterranean Basin;
• although the sites are widespread and complex, the samples of mortars were collected from similar hydraulic structures, such as pipeline systems, cisterns and tanks, and masonry remains;
• the final objective is to produce a complete set of analyses on the samples and each analysis requires a specific quantity of material; for all the sites, representative samples were chosen on which to perform the analyses above described.

4. CONCLUSION
Different archaeological sites were selected in the Mediterranean area for subsequent mortar sampling and analysis, in order to characterize the materials employed, both ancient and modern, and evaluate the damage processes they have undergone. Representative fragments of bedding mortars, plasters and renders were collected from ancient masonry of the Herodian Age (from 50 B.C. to 100 A.D.), located in the Mediterranean Basin: Tróia, near Lisbon, Portugal, Villa Domitia on Giannutri Island, in the Tuscan Archipelago, Italy, the Jupiter Temple in Damascus, Syria, and the Mekawer Fortress and Petra, Jordan.

The results of the analyses on the various samples clearly show that different types of mortar were used at the selected sites, indicating the presence of both air setting and hydraulic mortars. Considering the air setting mortars, pure lime mortars on Giannutri Island, and as bedding and plastering mortars in the Tróia archaeological site.

Gypsum-based mortars were identified in samples from Damascus (Syria), as pointing mortars in the Omayyad Mosque’s masonry, as well as covering mortars in some hydraulic structures sampled in the remains of the Mekawer Fortress in Jordan. In the case of Damascus, the gypsum mortars found are probably due to maintenance works and are not to be considered original Roman mortars. In the case of Mekawer, the finding of gypsum mortar in hydraulic structures is very untypical and requires explanation: one hypothesis is their application for maintenance and restoration purposes, even though no documentary evidence was found to this effect.

Hydraulic and/or semi-hydraulic lime-based mortars were encountered in all the sites sampled, but specific differences were encountered in the mineralogical composition of the aggregate, and the additive used in the mortar preparation to obtain hydraulic properties.
Natural hydraulic lime is obtained from the burning of clay containing limestones, while artificial hydraulic lime results from mixtures of clay and pure limestone. Hydraulic limes can be also obtained from the reaction of slaked lime with pozzolanic material (Charola, 2000). The addition of volcanic ashes or crushed bricks and tiles (cocciopesto) to lime mortars has been identified in constructions as early as the 10th century BC (Furlan et al., 1975), but it was not until the 1st century AD that the practice was documented by Vitruvius (Morgan, 1960). The hydraulic properties of the mortars derive from the new compounds formed by burning pure limestone with clays: quicklime, silica and aluminium, and iron oxides, derived from decomposition of the raw materials react to produce the hydraulic compounds. The quantity of hydraulic components produced varies with the degree of reaction, which in turn depends on the amounts of clays, burning temperature and time-at-temperature (Charola 2000). As mentioned in the Engineer Manual of the US Army Corps of Engineers (Standard Practice for Concrete for Civil Works Structures, 1994), the reaction products are hydrous gels, whose chemical composition always includes silica, alkaline, and at least a little calcium. The silica component is always derived from a reactive aggregate, which is usually an amorphous or metastable crystalline form of silica. Several siliceous components of aggregates may be potentially reactive and may be found in igneous, sedimentary, or metamorphic rocks of various texture and age. The more commonly encountered reactive aggregate components are:

1. Opal. It may occur in cherts, volcanic rocks, shales, sandstone, and carbonate rocks. Opal is the most reactive of the various reactive aggregate components, and may cause damage in concrete when even a fraction of a percent is present in the aggregate.
2. Chalcedony. It is a siliceous component of some cherts. Chalcedonic material is generally very fine quartz, but amorphous silica may be present as well.
3. Volcanic glass. Particles of volcanic glass or sometimes devitrified volcanic glass in an aggregate may be reactive, depending on composition.
4. Tridymite and crystobalite. These are crystalline forms of silica present in various igneous rocks.
5. Quartz. Well crystallized quartz may be reactive and may give rise to problems in concrete if the crystals are strained.
6. Silicates. Various sedimentary or metamorphic rock types containing clays or micas have been observed to be reactive. Such rock types include graywackes, argillites, phyllites, siltstone, etc.
7. Limestones including silica. Several examples of alkali silica reactivity, leading to serious distress, have been observed in limestone aggregate containing small amounts of dispersed silica, often skeletal remains of small organisms.

The mortars types sampled from the masonry of the archaeological sites selected for the PRODOMEA project reveal a significant variability in the preparation of the mortar mixtures, mainly in the components chosen as aggregate. Sometimes, important differences were also observed in the binder employed.

The original mortars found in the masonry of Villa Domizia (Giannutri Island, Italy) and Tróia (Lisbon, Portugal) archaeological sites, were clearly prepared using a lime-based binder. In the case of the archaeological site of Giannutri, pozzolan and cocciopesto were added to the mortar mixture to confer hydraulic properties, while in the Tróia site only cocciopesto was found. Hydraulic lime-based mortars were found in the Jupiter Temple masonry (in Damascus), in Petra Great Temple and Petra Garden and Pool Complex sites and in the remains of the thermal area masonry of the Mekawer Fortress. The experimental data reveal that, in these samples, typical pozzolan tracers (pyroxene, analcite, leucite) are absent and the hydraulic properties of the mortars employed are certainly conferred by the addition of other components in the mortar mixture. Sometimes, fragments of crushed bricks (cocciopesto) as a component of reactive aggregates are observed, but their amount is lower than siliceous clasts. The latter, in the form of chert, quartz (monocrystalline and polycrystalline), and micas are certainly reactive components of the aggregate. In fact, they are often characterized by the presence of well defined reaction rims and evidence of intense dissolution processes. In addition, several fragments of charcoal and/or partially burnt vegetables and wood ashes were encountered as abundant components in the mortar mixture.
Considering the experimental results of the Petra mortar samples, a significant presence of clay mineral (illite, kaolinite) was found alongside limestone fragments characterized by the presence of disseminated silica. This finding indicates that the original stone used in the preparation of the mortars was certainly a marly limestone (clay containing limestone). Furthermore, the significant presence of non-calcinated limestone is evidence of the incomplete burning of the raw material used to produce the hydraulic lime.

In particular, some samples of Damascus and Mekawer reveal variable amounts of gypsum and lime as binder, indicating the possible use of both limestone and gypsum rocks in the preparation of the mortar mixture. The mortar samples collected at the thermal area of Mekawer are characterized by brown-dark layers in the binder, indicating the addition of an organic substance, probably added in order to improve the mechanical properties of the material and consequently its workability.

The analysis carried out on the samples collected from the Fish Plant Harbour at the Tròia site found that clay layers were applied at the basis of the cetariae walls, and covered by subsequent mortars layer in order to confer waterproofing properties. The damage characterization shows that halite, due to marine spray deposition, is the main damage product encountered in the samples collected at all the archaeological sites. In addition, in the case of the Tròia site, the rising damp is to be taken into account as another source of salt crystallization, considering the height of the sampling points from the ground.

The IC results show that chlorides, together with nitrates and sulphates, are the most abundant anions detected. The simultaneous presence of nitrites, phosphates and ammonium, alongside chlorides and nitrates, indicate the possible contamination of animal defecation; the possibility of the deliberate addition of animal excrement to the mortar mixture must be taken into account (L. Marino, personal communication).

Furthermore the origin of the nitrates measured in the walls of the residential area at the Tròia site derive from the use of weed-killers. Concerning the amounts of sulphates, the quantities measured are in general agreement with the values present in rural sites, and are always lower than those encountered in European urban sites. At all sites, the highest amount of sulphates was detected in correspondence to the gypsum-based mortars, and is consequently related to the nature of the material and not to atmospheric material interaction. The considerable amounts of sulphates found in the hydraulic mortars probably derive from the crystallization of gypsum due to the water originally present in the hydraulic structures. Since Damascus is the only urban site among the localities selected for sampling, a higher sulphate concentration was expected.

Finally, the procedure used to determine non water soluble sulphates highlights their presence in almost all of the analysed samples of hydraulic mortars. Previous studies on the effects of atmospheric deposition on archaeological, historic and modern European monuments where hydraulic mortars (pozzolan, hydraulic lime and cement) are present demonstrate that most of the non water soluble sulphates can be attributed to ettringite formation within the pores of hydraulic mortars. The formation of ettringite, a strongly hydrated non water salt, gives rise to a considerable swelling of the mortar mass. A limited amount of this salt, referred to as primary ettringite, always forms in cement mortars, due to the small quantity of gypsum (3-5%) added as a setting regulator during mortar preparation. Primary ettringite, forming during the setting time, does not cause damage, as the fluid mortar mixture absorbs the expansion stress produced by its formation. By contrast, when the hydraulic mortar interacts with the sulphates after its hardening, the formation of new ettringite, referred to as secondary ettringite, gives rise to cracks and fractures that seriously damage the material (Older and Jawed, 1991; Taylor, 1994).

In the hydraulic mortars analysed in the present work the amount of soluble sulphates are low compared to the values generally encountered on buildings located in urban sites. It is therefore possible to exclude the formation of insoluble sulphate from the interaction between the calcium
aluminates of the mortar and the gypsum produced by the sulphation process. The insoluble sulphates encountered can be related to the original composition of the material (Van Balen et al., 2000).

5. REFERENCES

Carvalho, J.C.A., 1896, a Sociedade Archeológica Lusitana: As antiguidades extrahidas das ruínas de Tróia e onde é que se acham depositadas. Lisboa.
Esteves, A.M., Cardoso, J., 2004 (a) - “Mortar samples characterization on Archaeological site of Tróia”, July 2004, Report under printing.
Marino L, Mkhijan R., Qusus N., Sabelli R., Al Shava H., Tarawneh A., 1992, Una fortezza erodiana svela i suoi segreti - An Erodian fortress yields it secrets, Marmor 37: 20-34
Marino L., 1997b, La fortezza erodiana di Macheronte, in Ministero Affari Esteri, Missioni Archeologiche Italiane, Roma: 89-92