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Thermochimica Acta 418 (2004) 53–60
thermochimica acta
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Thermal and microchemical investigation of Phoenician–Punic mortars used for lining cisterns at Tharros (western Sardinia, Italy)

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Received 27 February 2003; received in revised form 4 September 2003; accepted 25 November 2003

Available online 21 April 2004

Abstract

The microchemical and minero-petrographic characterisation of mortars used at Tharros (western Sardinia, Italy) for lining the walls of Phoenician–Punic cisterns has been carried out by means of the combined use of differential thermal analysis–thermogravimetry (DTA–TG), X-ray diffraction (XRD), scanning electron microscopy + energy dispersive spectrometry (SEM + EDS) and optical microscopy (OM). The microchemical and minero-petrographic results combined with the thermal information are used for identifying the nature of the mortars and for clarifying some technological aspects of the manufacturing technique. The results disclose the complex structure of the mortars and evidence weight changes due to dehydration, dehydroxylation and carbonates decomposition that allow to group the major part of the mortars in the well-distinct area of the hydraulic lime mortars with only a small group of mortars, used for bonding the stones of the cistern walls and also in few cases as first layer, to be grouped as lime mortars without hydraulic properties.

Keywords: DTA–TG; Historic mortars; SEM + EDS; Ancient technologies; Tharros; Chemical–physical investigation; Phoenician–Punic cisterns

1. Introduction

Tharros, located on the western Sardinian coast, is now one of the most important archaeological sites in Sardinia and was one of the most rich and populated city of ancient Sardinia that was continuously inhabited by Proto-Sardinians, Nuragics, Phoenicians, Punics, Romans, early Christians, Vandals and Byzantines from the 12th century BC to the 11th century AD when the city was abandoned as a consequence of the continuous attacks of Saracens. Site excavations, carried out since the early years of the last century have shown the presence of a large numbers of Phoenician–Punic cisterns used to save and to stock rain water necessary to meet several needs of the Tharros inhabitants [1].

In the present work, the characterisation of mortars used for lining in Phoenician–Punic cisterns has been carried out using simultaneous differential thermal analysis and thermogravimetry (DTA–TG) combined with X-ray diffraction (XRD), scanning electron microscopy + energy dispersive spectrometry (SEM + EDS) and optical microscopy (OM).

The aim of the study is to characterise the microchemical and minero-petrographic structure of the mortars constituting the cistern linings in order to identify their nature and to clarify some technological aspects of mortar manufacturing processes [2–7]. Indeed, ancient mortars are composite materials constituted by hydraulic or aerials materials, aggregates and additives, inert phases and binders, whose nature and manufacturing techniques could largely vary in ancient times [2–11]. Furthermore, it is worth noting that to our best knowledge Phoenician–Punic mortars used for lining cisterns have been never studied in details even though, according to the historical sources, for the first time about 3000 years ago, Phoenicians produced lime mortars characterised by hydraulic properties [1–3]. According to this literature information [3], hydrated lime ($Ca(OH)_2$), powdered and crushed bricks were mixed to produce mortars to be used for isolating the cistern walls of the Phoenician settlements located on the Syrian–Palestinian coast. Unfortunately, till now scientific studies have been not carried out to identify the nature and manufacturing processes of

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doi:10.1016/j.tca.2003.11.053

these mortars as well as those of the mortars used in the Phoenician–Punic settlements in Italy, Spain and Tunisia.

2. Experimental

According to archaeological information [1], the most interesting Phoenician–Punic cisterns of Tharros have been selected to be sampled. In particular, only the mortars used for lining the walls normal to the earth have been considered and the samples were classified according the number of the cistern (CS) given by the archaeologists, to the position and to the macroscopic nature determined via visual inspection. The cisterns to be sampled were selected considering only the cisterns whose shape is similar to that of the cisterns found during archaeological excavations in other Phoenician–Punic settlements in the Mediterranean basin and whose general aspect seems apparently not modified by Romans. During the sampling carried out using clean and new stainless steel tools and surgical lancets, considerable attention has been paid to avoid the sampling of mortars affected by the phenomenon caused by capillary rise. For this reason, the samples were mainly taken from the upper parts of the cistern walls at about 100 cm from the bottom wall level. Because the sampled Phoenician–Punic cisterns of Tharros are generally characterised by a height variable from 1.80 to 2.5 m, the sampled areas were located at about half distance from the bottom level and the roof of the cistern. Furthermore, the cisterns are characterised by an elongated shape with a width ranging from 1 and 1.5 m and a length that varies from 3 to about 5 m.

DTA–TG simultaneous measurements were carried out in air from room temperature to 1000 °C using an automated thermal analyser (Stanton Redcroft STA-781) computer controlled. Cylindrical Pt crucibles of diameter 4 mm and depth 2 mm were used. Approximately 35 mg of sample was heated in static air at a heating rate of 20 °C min^{-1}.

Scanning electron microscopy and energy dispersive spectrometry characterisation was carried out by using a Leo Cambridge 360 scanning electron microscope equipped with an EDS apparatus, a four-sector back-scattered electron detectors and a LaB_6 filament. The samples has been coated with a thin layer of carbon in order to observe the mortars without charging effects. The carbon coating was deposited by using an Emitech sputter coater K550 unit, a K250 carbon coating attachment and a carbon cord at a pressure of 1×10^{-2} mbar in order to produce a carbon film with a constant thickness of about 3.0 nm.

In order to establish the crystalline phases present in the mortars, XRD patterns were recorded directly on the finely pulverised mortars by multiple scanning using an automated Seifert XRD-3000 diffractometer. The identification of the species was carried out by using a Seifert XDAL 3000 Software Index I.

Thin sections of the mortars were examined under transmitting light by using a polarising Leitz optical microscope equipped by a digital camera in order to obtain the petrographical–mineralogical characterisation of the mortars constituents and the microscopic observation of the different mineral phases in matrix. The thin sections have prepared using a diamond saw blade for first cutting a sample of mortar in order to obtain a fragment with a flat surface. Next, the flat surface has been first polished to remove the roughness of the cut and make it as smooth as possible and then it has been impregnated with epoxy resin and mounted onto a microscope slide with resin or Canada balsam. The mounted sample is cut again perpendicularly to the flat surface in order to have the second face parallel to the first and as thin as possible. This face has been lapped with low grade (20–30 μm) silicon carbide papers followed by polishing with diamond pastes until it is characterised by an approximate thickness of 50 μm. The last stage has been a hand polishing using a diamond paste on a flat glass surface, the thickness of resulting thin section of the mortars was about 30 μm.

To analyse the cross sectioned microchemical structure of the mortars via SEM + EDS, a sample was removed with a clean and new stainless steel lancet, embedded in an epoxy resin with a setting time of 24 h and metallographically polished with low grade carborundum papers and diamond pastes up to 0.25 μm.

3. Results and discussion

The typical aspect of the Phoenician–Punic cisterns of Tharros is shown in Fig. 1. These buried structures are characterised by a typical common shape being elongated for several meters and thin in section. Their covering was obtained by easily removable stone slabs of bio-limestone in order to facilitate in ancient times the cleaning and the restoration procedures.

The results of the mineralogical XRD analysis indicate that calcite is the main mineralogical component of mortars. Quartz (SiO_2) is always present with other constituents such as K-feldspar ($KAlSi_3O_8$), albite ($NaAlSi_3O_8$), analcime ($NaAl(SiO_3)_2$), pagioclase ($CaAl_2Si_2O_8$–$NaAlSi_3O_8$) and a small amount of calcium silicium hydrate ($5Ca_2SiO_4{\cdot}6H_2O$), calcium orthosilicate hydrate ($10Ca0.5SiO_2{\cdot}H_2O$) and tobermorite ($Ca_5Si_6O_{17} + H_2O$).

In Fig. 2 are shown some selected micrographs obtained by using polarising optical microscopy. These results confirm that calcite is the main constituent of the matrix, thus classifying the mortars as typical lime mortars. Furthermore, the micrographs evidence a common structure where microcrystalline calcite is mixed with angle shaped quartz clastic grains of variable size, fine fossils, feldspars, silicate minerals and small fragments of crushed or pulverised ceramic materials added to give hydraulic properties to the mortars in all the samples except in two mortars, CS7-1L and CS12-1. These two latter materials have been sampled between the stones that have been used for building the walls of the

Fig. 1. Typical aspect of the cisterns of Tharros. In particular, the cisterns 3 and 5 are shown on the left and right sides, respectively. The mortar samples were mainly taken from the upper parts of the cistern walls at about 100 cm from the bottom wall level. Because the sampled Phoenician–Punic cisterns of Tharros are generally characterised by a height variable from 1.80 to 2.5 m, the sampled areas were located at about half distance from the bottom level and the roof of the cistern. Furthermore, the cisterns are characterised by an elongated shape with a width ranging from 1 and 1.5 m and a length that varies from 3 to about 5 m.

cisterns and in very few cases also constitute a thin first layer on the lateral walls to create a smooth and flat surface to be coated by a thick mortar layer. Furthermore, the optical micrographs evidence that pulverised ceramic materials and lime mortars show a compact matrix traversed by reaction rims where calcium silicate hydrate and calcium aluminium silicate hydrate are present. This coherent calcite matrix with well-adherent phases such as quartz and pagioclase components is the typical microstructure of the mortars and is shown in Fig. 3, where a back-scattered electrons image is reported with ED spectra. These latter data evidence the elemental chemical composition of some different inorganic phases such as quartz, calcite, iron–calcium–aluminium silicate and aluminium–calcium silicate.

In order to gain further insight into the nature of the Tharros mortars, DTA–TG analysis has been performed and in Figs. 4 and 5 are shown the characteristic thermal curves for mortar CS2-1 and CS12-1, respectively.

Figs. 4 and 5 show broad peaks indicating weight loss of absorbed water in the temperature range from 60 to 180 °C and water bound to hydraulic components in the temperature range from 200 to 600 °C and then, the weight loss due to the carbonates thermal decomposition. For what concerns the CS2-1 mortar, the broad exothermic peak from about 200 to 500 °C could be due to the combustion of organic contamination compounds. For what concerns the CS12-1 mortar, the thermal curves indicate the absence of any relevant weight loss before the carbonate endothermic decomposition that mainly occurs in the temperature range from 630 to 900 °C. This large temperature range could be related to the presence of re-carbonate lime [12] characterised by a microcrystalline structure and also to the thermal decomposition of carbonates present in the ceramic materials.

Furthermore, in some cases (for example, mortars CS15-2 and CS15-L, not shown) a small endothermic peak at about 570 °C has been observed that can be related with the transformation of α-SiO_2 to β-SiO_2 [11]. On the contrary, the endothermic peaks in the temperature range from 250 to 440 °C caused by the decomposition of the hydromagnesite or peaks related to gypsum phases have been not detected.

From the DTA–TG curves have been calculated the percentage of weight loss in the temperature ranges selected to give relevant [4–9] information for identifying the nature of the mortars and these data for 30 mortars of 10 cisterns sampled at Tharros are summarised in Table 1. It is worth noting that the total number of sampled mortars and cisterns can be considered enough to avoid errors caused by heterogeneity.

The data of Table 1 evidence that the weight loss due to the thermal decomposition of re-carbonate lime [6] that produces CO_2 is rather low being this value ranging from 0 to 10% for 4 samples and from 10 to 20% for 16 samples, thus indicating the presence of ceramic and silicate hydraulic components in the mortar mixture [4,6]. Only two samples show a value of weight loss due to the production of CO_2

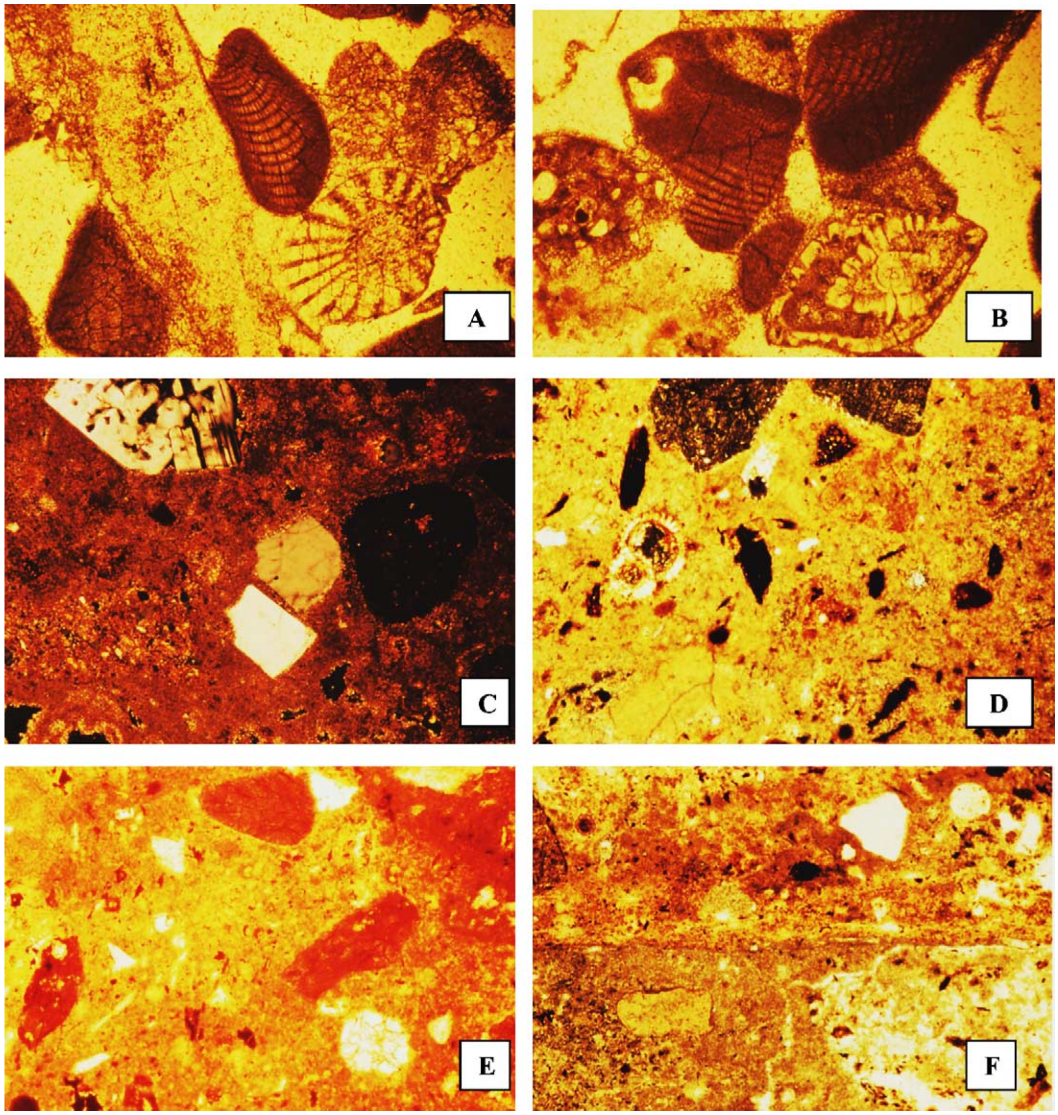

Fig. 2. Micrographs of mortar thin sections obtained by using polarising optical microscopy. The results indicate that calcite is the main constituent of the matrix. Furthermore, the micrographs evidence that microcrystalline calcite is mixed with angle shaped quartz clastic grains of variable size, fossils, feldspars, phyllo-silicate minerals and small fragments of crushed ceramic materials added to give hydraulic properties to the mortars. (A) CS12-1 (200×); (B) CS12-01 (200×); (C) CS1-23 (100×); (D) CS5-1 (100×); (E) CS5-12 (100×); (F) CS3-23 (100×).

higher than 37% and therefore, these mortars (CS7-1L and CS12-1) can be surely classified as typical lime mortars without hydraulic properties being constituted by more than 77% of $CaCO_3$.

According to Bakolas and co-workers [4–6,8,9], the data of Table 1 can be reported as a function of the percentage of weight loss due to the different chemical–physical reactions suffered by the mortar under heating. In particular, in the range from 30 to 120 °C, the weight change is due to the loss of adsorbed water, from 120 to 200 °C to the loss of other hygroscopic water, from 200 to 600 °C to the loss of structurally bound water to the hydraulic components of the mortar when there are no other compounds that undergo weight variation and finally, to the carbonates decomposition with CO_2 production above this latter temperature.

Furthermore, the CO_2/hydraulic H_2O ratio calculated as percentage of weight loss in the temperature range from 600 to 1000 °C/structurally bound water calculated as weight loss in the temperature range from 200 to 600 °C, is reported in Table 1 for better classifying the mortar nature. In order to discuss these DTA–TG results, the data reported in Table 1 have been also plotted in Figs. 6–8. In particular, in Fig. 6, the percentage of weight loss related to the structurally bound water to the mortar hydraulic components is shown versus the percentage of weight loss due to the production of CO_2 from the decomposition of carbonates. In Fig. 7, this latter values are related to the CO_2/hydraulic H_2O ratio and in Fig. 8, the amount of hydraulic water is plotted versus CO_2/hydraulic H_2O ratio.

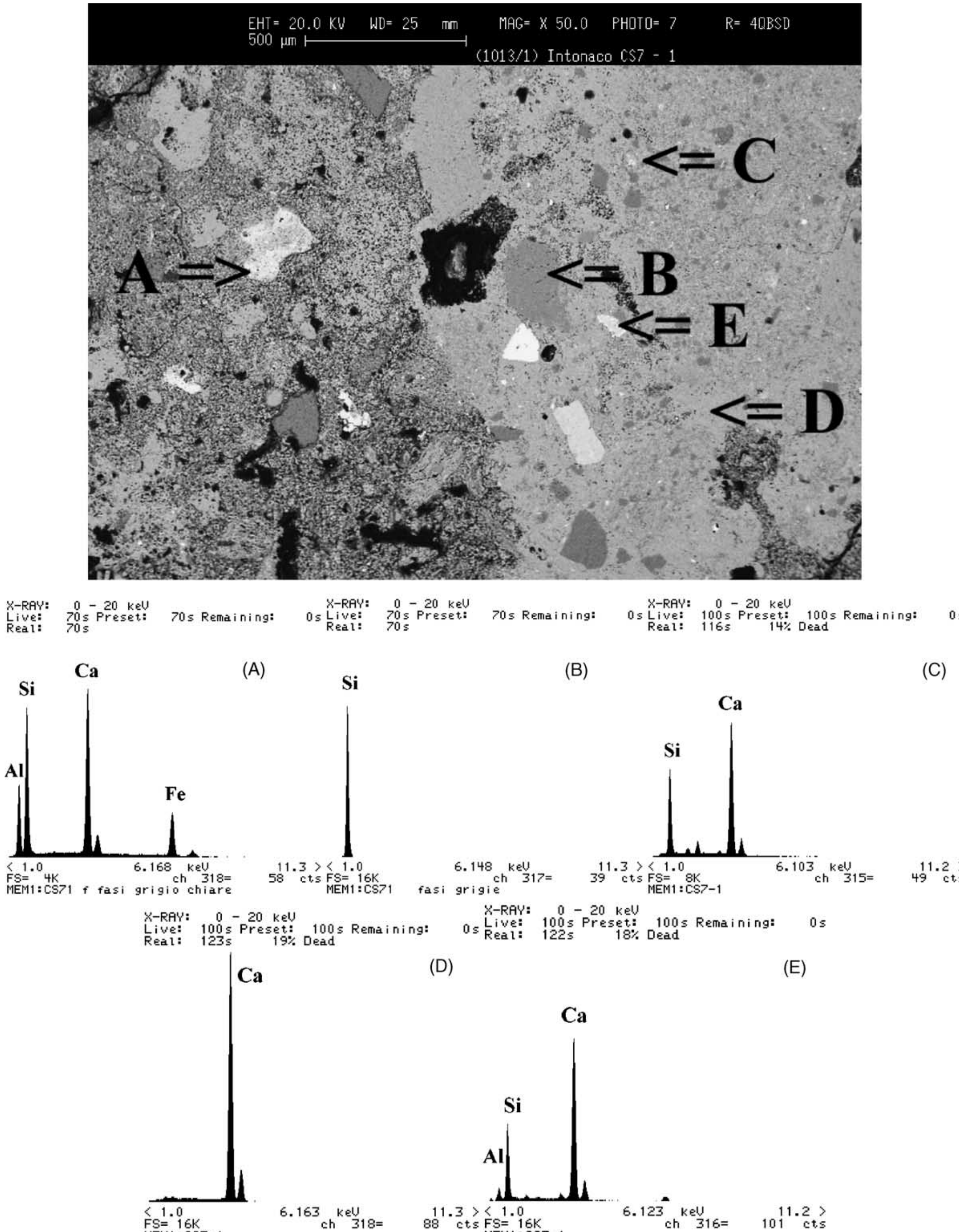

Fig. 3. SEM back-scattered images and ED spectra showing the cross-sectioned microchemical structure of the mortar CS7-1S(1). The different degree of brightness of the back-scattered image is related to the presence of atoms with different atomic number as also evidenced by the EDS results (spectra A–E). These latter data clearly show the elemental chemical composition of some different inorganic phases that constitute the mortars such as quartz, calcite, iron–calcium–aluminium silicate and aluminium–calcium silicate. Indeed, the spectrum A reveals the presence of silicon, aluminium, calcium and iron, thus indicating likely the addition of powdered ceramic materials to the lime for producing hydraulic mortars. The spectrum B confirms the presence of fragments of quartz. The spectrum C reveals the presence of silicon and calcium. The spectrum D is originated from the lime and finally, the spectrum E is similar to that for the phase A as shows the presence of Si, Al, Ca and a small amount of Fe and confirms the addition of powdered ceramic materials.

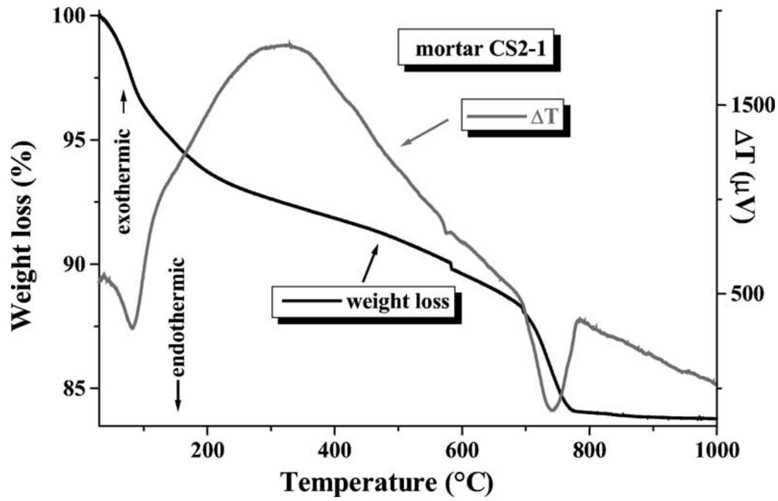

Fig. 4. DTA–TG curves for the mortar CS2-1.

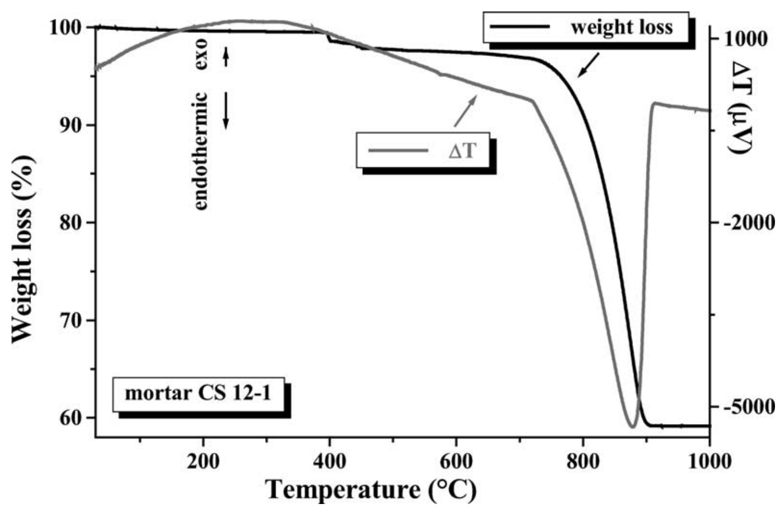

Fig. 5. DTA–TG curves for the mortar CS12-1.

By comparing the results reported in table and the plots shown in Figs. 6–8 with literature data [2,4–6,8–10], it is possible to classify the mortars of the Phoenician–Punic cisterns of Tharros as lime hydraulic mortars and only a small group of mortars used for bonding the stones of the cistern walls and also in few cases as first layer are constituted by lime mortars without hydraulic properties. Indeed, the typical lime mortars are characterised by a loss of structurally bound water to hydraulic components lower than 3% and a weight loss due to the thermal decomposition of carbonates higher than 30% [2,4–6]. The so-called hydraulic lime mortars include all the materials with an amount of structurally bound water to hydraulic components higher than 3% and a lower weight loss due to the thermal decomposition of carbonates with respect to the lime mortars.

As mentioned earlier, the hydraulic property is due to the possible interactions between the calcium hydrate and the components of the pulverised ceramic materials [2,4–6,8–11] that give rise to the formation of calcium

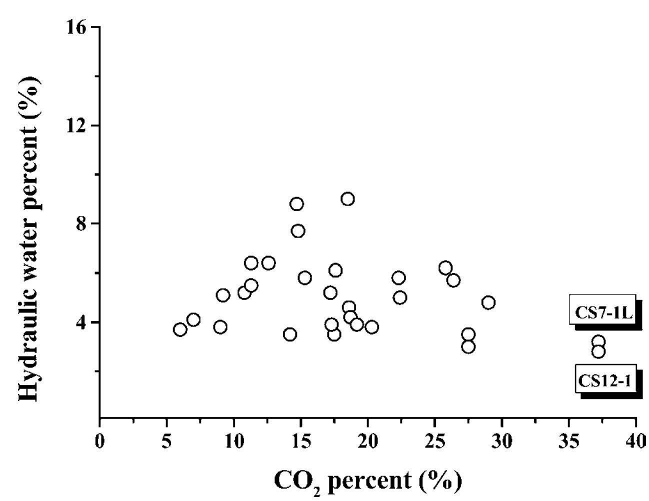

Fig. 6. Structurally bound water (hydraulic water) percentage vs. CO_2 (%). It is worth noting that the mortars CS7-1L and CS12-1 are two examples of the mortars sometimes used for bonding the stones that constitute the lateral walls of the cisterns and in these two latter cases constitute also a thin first layer on the walls.

Table 1
DTA–TG weight losses as a function of the temperature range and expressed in wt.%

Mortar	30–120 °C	120–200 °C	200–600 °C (hydraulic water)	600–1000 °C (CO_2)	CO_2/hydraulic H_2O ratio
CS1-1	3.5	1.0	3.5	17.5	5.0
CS1-23	3.5	0.5	5.1	9.2	1.8
CS2-1	4.5	2.0	3.7	6.0	1.6
CS2-2	2.1	1.0	3.0	27.5	9
CS2-3	2.1	1.5	3.5	27.5	7.9
CS3-1	1.8	1.1	6.2	25.8	4.2
CS3-2	3.2	1.0	4.6	18.6	4.0
CS3-23	6.8	1.1	5.0	22.4	4.5
CS5-1	3.1	0.9	4.2	18.7	4.5
CS5-12	3.5	1.2	3.9	19.2	4.9
CS5-3b	5.8	2.2	5.2	10.8	2.1
CS5-34I	5.9	1.0	4.1	7.1	1.7
CS5-34E	6.1	0.9	6.1	17.6	2.9
CS7-1(SE)	2.9	1.0	6.4	12.6	2.0
CS7-1S(1)	3.9	0.8	3.8	20.0	5.3
CS7-1S(I)	6.1	0.9	3.8	9.0	2.4
CS8-1	3.1	0.9	4.8	29.0	6.0
CS8-2	7.8	1.1	7.7	14.8	1.9
CS11-1a	2.9	0.6	5.5	11.3	2.1
CS11-1b	2.8	0.7	3.5	14.2	4.0
CS11-23	5.8	2.2	5.8	22.3	3.8
CS12-2	3.8	3.2	3.9	17.3	4.4
CS15-L	2.8	2.2	9.0	18.5	2.1
CS15-1	2.4	1.1	5.2	17.2	3.3
CS15-2	2.1	2.9	6.4	11.3	1.8
CS15-123	5.3	2.7	5.8	15.3	2.6
CS16-12E	5.4	0.7	5.7	26.4	4.6
CS16-12I	7.8	2.3	8.8	14.7	1.7
CS7-1L	3.0	1.0	3.0	37.2	12.4
CS12-1	0.7	0.3	2.8	37.2	13.3

Furthermore, the CO_2/hydraulic H_2O ratio (weight loss in the temperature range from 600 to 1000 °C/weight loss in the temperature range from 200 to 600 °C) is reported for classifying the mortar nature. It is worth noting that the mortars CS7-1L and CS12-1 are two examples of the mortars sometimes used for bonding the stones that constitute the lateral walls of the cisterns and in these two latter cases constitute also a thin first layer on the walls.

silicate hydraulic components [2,4–6]. This property was empirically discovered in ancient times by the Phoenicians [2,3] that added different silicate compounds such as crushed bricks and ceramic fragments to the lime to imparts strength, elevated bearing capacity and hy-

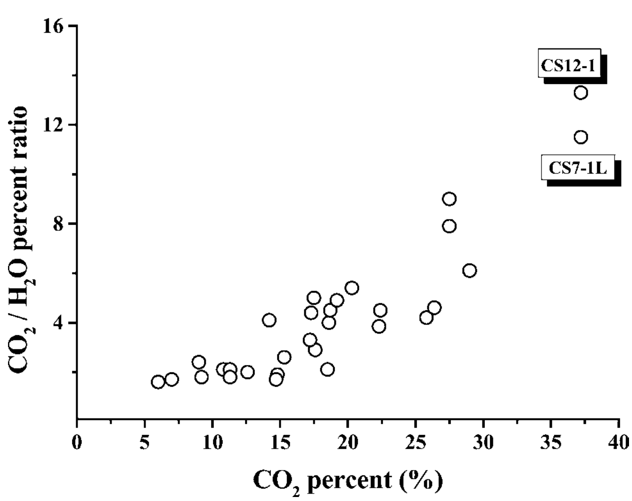

Fig. 7. Ratio of CO_2/H_2O vs. CO_2 percent.

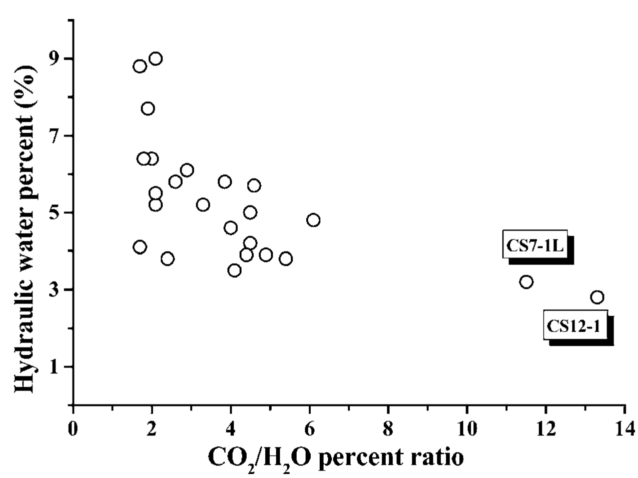

Fig. 8. Structurally bound water (hydraulic water) percentage vs. CO_2/H_2O ratio determined as weight loss percent in the temperature range from 600 to 1000 °C/weight loss in the temperature range from 200 to 600 °C. It is worth noting that the mortars CS7-1L and CS12-1 are two examples of the mortars sometimes used for bonding the stones that constitute the lateral walls of the cisterns and in these two latter cases constitute also a thin first layer on the walls.

draulic properties to the mortars as well as to enhance their resistance against marine atmosphere degradation [2,3].

Finally, from a technological point of view, according to the results obtained by Bakolas and co-workers from ancient, byzantines and later historic mortars different for manufacturing methods and studied via thermal and diffraction techniques, the dispersion of the data reported in Figs. 6–8 could indicate various preparation technologies employed for the obtaining the mortars and then, probably different periods of their production. Indeed, the Phoenician–Punic cisterns of Tharros have been used for several hundred of years and during this large period they have been surely restored in order to ensure good insulating properties to the walls.

4. Conclusions

Thermal and microchemical results obtained via SEM + EDS, XRD, OM and DTA–TG investigation converge to reveal the hydraulic nature of the lime mortars used by for lining the Phoenician–Punic cisterns of Tharros (western Sardinia, Italy) used for several hundred of years to save and to stock rain water necessary to meet several needs of inhabitants. Only a small group of mortars used for bonding the stones of the cistern walls and also in few cases as first layer, are constituted by lime mortars without hydraulic properties. These information are in good agreement with historical sources that indicate Phoenicians as the first users of powdered and crushed bricks to impart hydraulic character to lime mortars about 3000 years.

Finally, the mortars of the Tharros cisterns seem to show slightly different production methodologies used to prepare the mixture of lime and pulverised ceramic materials and this results could be related to different periods of production.

Acknowledgements

The authors express sincere gratitude to Dr. Paolo Bernardini (Soprintendenza Archeologica alle Provincie di Cagliari e Oristano) and Dr. Jacopo Gelli (Centro Sviluppo Materiali S.p.A.) for helpful discussion and to Giuseppe Cauli for the support given during the prospecting in the Tharros district. The SEM + EDS characterisation have been carried out by the authors by using microscope of the University of Roma Tor Vergata installed at the Area della Ricerca di Roma-Montelibretti of the Consiglio Nazionale delle Ricerche. Finally, the authors thanks C. Veroli for their experimental contribution in XRD characterisation.

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