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# Chemical–physical and mineralogical investigation on ancient mortars from the archaeological site of Monte Sannace (Bari—Southern Italy)

P. Bruno [a], D. Calabrese [b], M. Di Pierro [e], A. Genga [c], C. Laganara [d], D.A.P. Manigrassi [a], A. Traini [a], P. Ubbrìaco [b,*]

[a] *Dipartimento di Chimica, Università di Bari, via Orabona 4, 70126 Bari, Italy*
[b] *D.I.C.A., Politecnico di Bari, via Orabona 4, 70126 Bari, Italy*
[c] *Dipartimento Scienze dei Materali., Università di Lecce, via per Arnesano, 73100 Lecce, Italy*
[d] *Dipartimento dei Beni Culturali, Università di Bari, Piazza Umberto, 70100 Bari, Italy*
[e] *Dipartimento Geomineralogico, Università di Bari, via Orabona 4, 70126 Bari, Italy*

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**Abstract**

This study concerns experimental results of a chemical–physical and mineralogical characterisation of some mortars, sampled by different masonries brought to light during excavations of the site of Monte Sannace. The aim of the research is to provide, through the characterisation of the mortar samples and the relative raw materials, useful information in order to define the stages of construction and the workers' technological knowledge during different historical periods. DTA/TG/DTG thermoanalytical investigations and X-ray diffractometry analyses can allow to define the nature of both the binder and aggregate materials. As regards a specific mortar with hydraulic behaviour such a study has allowed to recognise also the residual reactivity towards lime of the 'pozzolanic' sand, rich in volcanic ashes, used as aggregate in the original mortar. The thermoanalytical and X-ray diffractometric results together with the granulometric and chemical determinations allow to get information about the preparation techniques of binding materials of old masonries.


*Keywords:* Ancient mortars; Thermal analysis; X-ray diffractometry; Mineralogical composition; Chemical characterisation

## 1. Introduction

Monte Sannace is an ancient human settlement, which lies at about 5 km from the small town of Gioia del Colle (Bari-Apulia), and whose origins date back to the thriving Apulian Peucetian age (seventh to third century B.C.). The archaeological relevance of the site is already testified by 17th century documents, but excavations for scientific purposes started in the second half of the 19th century and intensified during the last decades of the 20th century.

During the various excavation campaigns, it has been possible to reconstruct the successive stages of occupation of the site: Iron Age (from the end of the ninth century to the second half of the seventh century B.C.); Archaic and Classic Age (from the beginning of the sixth century to the middle of the fourth century); Hellenistic Age (from the second half of the fourth century to the first decades of the first century B.C.); Early Imperial Age (from the first century B.C. to the first century A.D.); Late Ancient Period; High Middle Ages (10th–11th century) [1,2].

Some ancient masonries situated in an area of the site supposedly inhabited in the High Middle Ages proved particularly complex for the archaeologist to interpret. Studying the characterisation of materials can help discover the techniques of retrieval and usage of raw materials.

The aim of this archaeometric investigation, thus, is to provide useful information in order to define the stages of construction and the workers' technological knowledge, through the chemical–physical and mineralogical characterisation of mortar samples taken from various masonries.

DTA/TG/DTG thermoanalytical investigations and X-ray diffractometry analyses can allow the characterisation of the binding materials, by specifying their main mineralogical components, as shown in other studies on ancient mortars [3–5].

* Corresponding author.
*E-mail address:* p.ubbriaco@poliba.it (P. Ubbrìaco).

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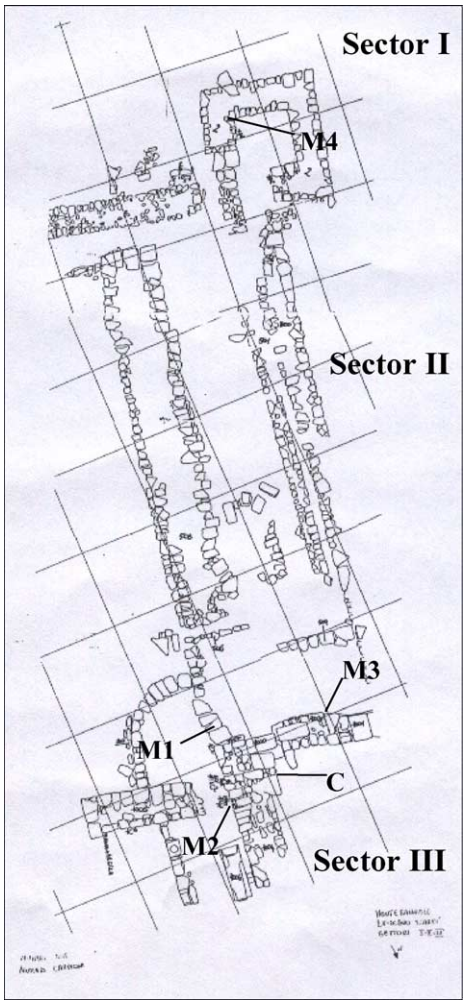


Fig. 1. Map of the archaelogical site.

## 2. Experimental

Fig. 1 shows the plan of the masonries under examination and the area from which mortar samples (M1–M4), calcarenite materials (C) and soil samples (G) were taken.

Each mortar sample was dried in two stages: (1) ground (<1000 μm) and dried for 4 h in vacuum over calcium chloride; (2) ground (<100 μm) and dried for 6 h in vacuum over calcium chloride. The various samples (about 100 mg each) were immediately submitted to DTA/TG thermoanalytical investigations at the heating rates of 10 °C per minute and 5 °C per minute in static air (Netzsch STA 409 apparatus) and to X-ray diffractometry analysis (Philips PV-1710 using Cu Kα radiation).

The chemical composition (reported in Table 1) of these fine fractions was determined on samples dissolved by means of acid attack ($HCl/HF/HNO_3$ 1:2:1, v/v/v) in order to determine metal ions by ICP-AE spectrometry (Varian Liberty 100) and through basic attack (lithium metaborate, in oven) to determine anions by HP Ion Chromatography (Dionex, DX-300). Carbonate content of the mortar samples was determined through $CO_2$ volumetric method [6], while silicon content through spectrophotometric determination [7].

Table 1
Chemical composition of the mortar, calcarenite and soil samples

| | M1 | M2 | M3 | M4 | C | G |
|---|---|---|---|---|---|---|
| CaO (%) | 40.10 | 26.34 | 40.00 | 28.16 | 52.00 | 25.52 |
| $Al_2O_3$ (%) | 3.82 | 6.68 | 2.56 | 8.17 | 1.59 | 4.42 |
| $Fe_2O_3$ (%) | 1.57 | 1.42 | 1.03 | 2.70 | 0.64 | 1.79 |
| MgO (%) | 0.68 | 0.45 | 0.37 | 0.63 | 0.58 | 0.51 |
| $SiO_2$ (%) | 15.00 | 36.62 | 14.00 | 32.58 | 0.70 | 34.21 |
| $Na_2O$ (%) | 0.57 | 1.17 | 0.45 | 0.55 | 0.22 | 0.69 |
| $K_2O$ (%) | 0.95 | 2.79 | 2.92 | 1.65 | 2.15 | 1.49 |
| $CO_2$ (%) | 32.01 | 20.68 | 31.56 | 16.06 | 41.93 | 15.04 |
| L.O.I. (%) | 35.98 | 24.11 | 36.37 | 25.67 | 42.50 | 30.00 |
| MnO (ppm) | 448 | 778 | 243 | 1032 | 351 | 662 |
| $TiO_2$ (ppm) | 128 | 185 | 97 | nd | 32 | 2455 |
| $Cl^-$ (ppm) | 212 | 79 | 140 | 234 | 108 | 566 |
| $NO_3^-$ (ppm) | 82 | 314 | 169 | 437 | 160 | 134 |
| $PO_4^{3-}$ (ppm) | 58 | 525 | 1 | 727 | 57 | 2364 |
| $SO_4^{2-}$ (ppm) | 49 | 114 | 193 | 230 | 221 | 92 |

The mortar samples were also investigated by means grain-size analysis (Fig. 2), after having been submitted to a light crushing in order to separate the aggregate fraction from the binders.

## 3. Results and discussion

The M1 mortar taken from the foundation structure (sector III-M.S.U. 1016) appears to adhere still quite well to the calcareous ashlars, summarily squared, which constitute the masonry.

Grain-size analysis (Fig. 2) shows an aggregate with an acceptable grain-size distribution, similar to sand sampled from blocks of yellowish calcarenite (calcareous tufa: type '*carparo*') largely diffused in the archaeological site, also in more ancient structures. In the aggregate a small amount of siliceous sand and some fragments of brickwork can also be observed. The latter can be probably traced back to baked clay vases and bricks, which are also present in the area of the archaeological site. Thus, the aggregate is likely to derive mainly from yellow calcarenite elements, whose easy crushability and recovery enrich the aggregate with siliceous and clayey components. Moreover, the macroscopic examination of the aggregate provides evidence of the presence of a limited amount of carbon residues.

DTA/TG/DTG thermoanalytical investigations (Fig. 3) indicate the presence of a limited amount of clay minerals, shown by the endothermic effect of dehydration at about 100 °C and also of dehydroxylation at 500 °C. Small endothermic effects in the range between 200 and 400 °C can be attributed to aluminium and iron hydrated oxides. The small exothermic effect at about 430 °C corresponds to the oxidation of a limited amount of carbon residues.

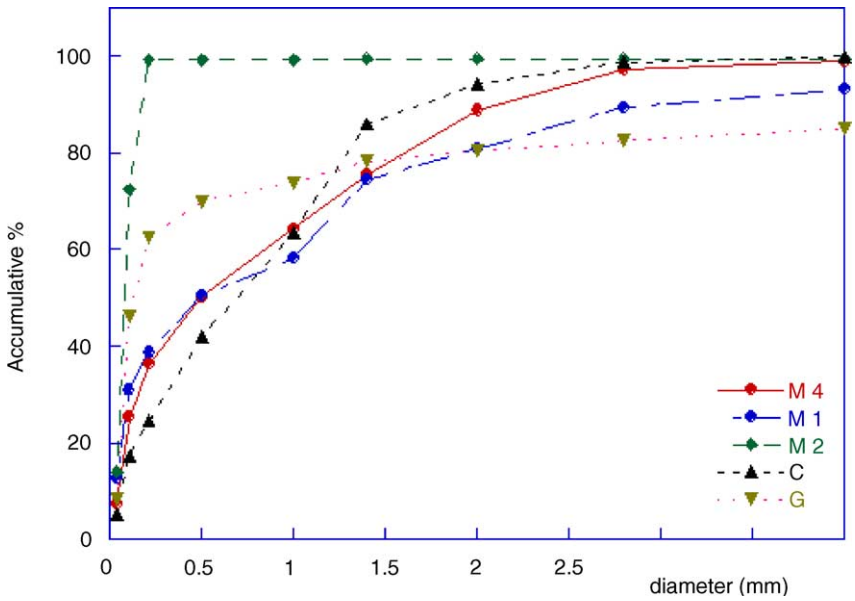


Fig. 2. Granulometric behaviour of the examined mortars, calcarenite and soil samples.

A weak endothermic effect at about 700 °C is due to the decomposition of magnesian calcite [8] while at about 900 °C a notable effect of decomposition of calcite was observed. Carbonate is the constituent of the binding matrix, resulting from the carbonation of the original binder (lime putty), as well as of the aggregate fraction. Moreover, X-ray diffractometry results (Fig. 4) indicate the presence of calcite ($2\theta = 29.40$), quartz ($2\theta = 26.50$) and a limited amount of clay minerals ($2\theta = 19.80$), feldspars ($2\theta = 27.60$).

Some thermoanalytical and X-ray diffractometric investigations were carried out also on samples of yellow calcarenite, taken from big ashlars of more ancient structures, present in other areas of the site. XRD (Fig. 5) and thermoanalytical results (Fig. 6) indicate calcite as their main constituent. Furthermore, a very small amount of magnesian calcite, aluminium and iron hydrated oxides (endothermic effect in the interval 250–400 °C) can be observed. The good grain-size distribution (Fig. 2) of the sand obtained through a light crushing may have been the peculiarity that encouraged workers to use yellow calcarenite as aggregate in the preparation of mortars. In observing the masonry it was noticed that, at times, pieces of this kind of calcarenite were also used as '*wedges*' between the mortar and stone blocks.

As regards the brown-greyish mortar (M2), which was taken from the core of the same structure from which the M1

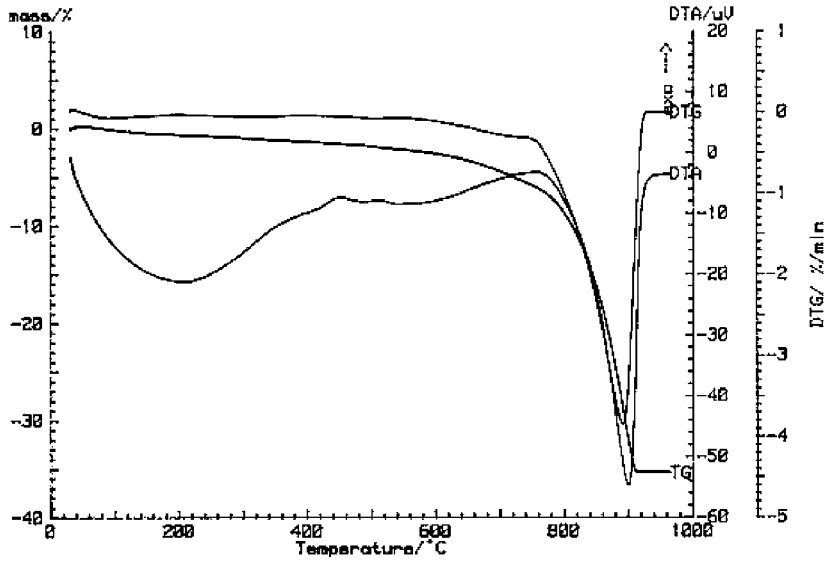


Fig. 3. Thermal curves of the mortar M1.

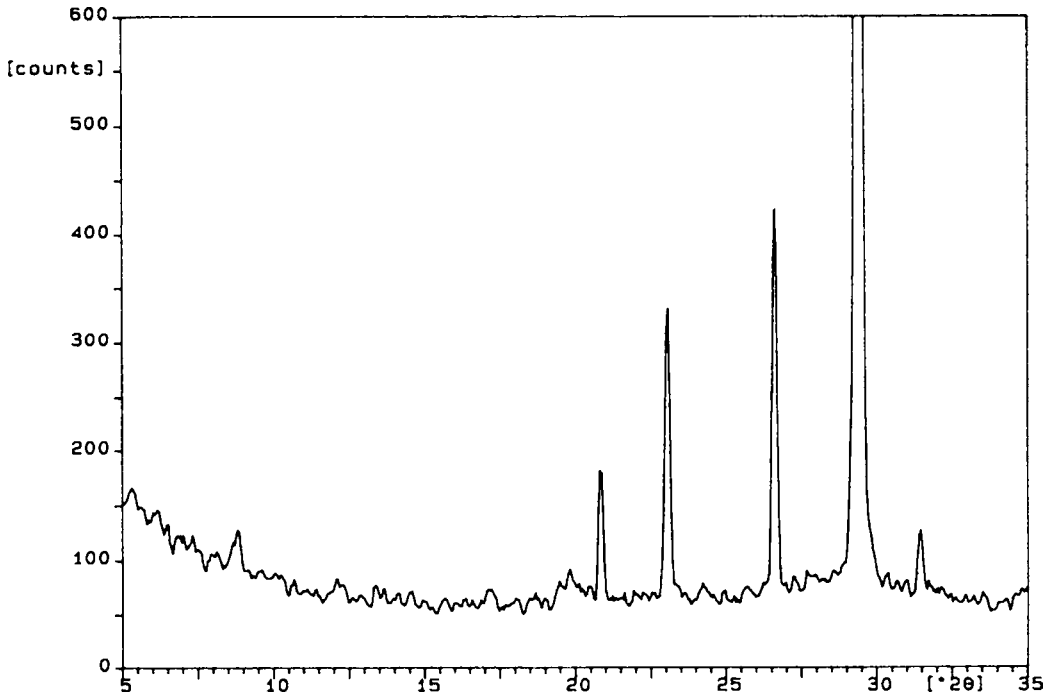


Fig. 4. XRD of the mortar M1.

mortar was taken, but at a higher stratigraphic level (M.S.U. 1004), granulometric distribution of the aggregate-binder constituents was not homogeneous. It must be pointed out that, already in the sampling stage, it was possible to observe how gross the preparation of this mortar was: a fraction of soil was used as filler between mortar and stone blocks, as well as numerous pieces of coal. These fragments of coal, measuring up to about 1 cm, may be the result of the production of lime used as binder; this is plausible, in consideration of the fact that in small calcining furnaces the recovery of lime caused a contamination with the carbon residues present in the combustion room [9].

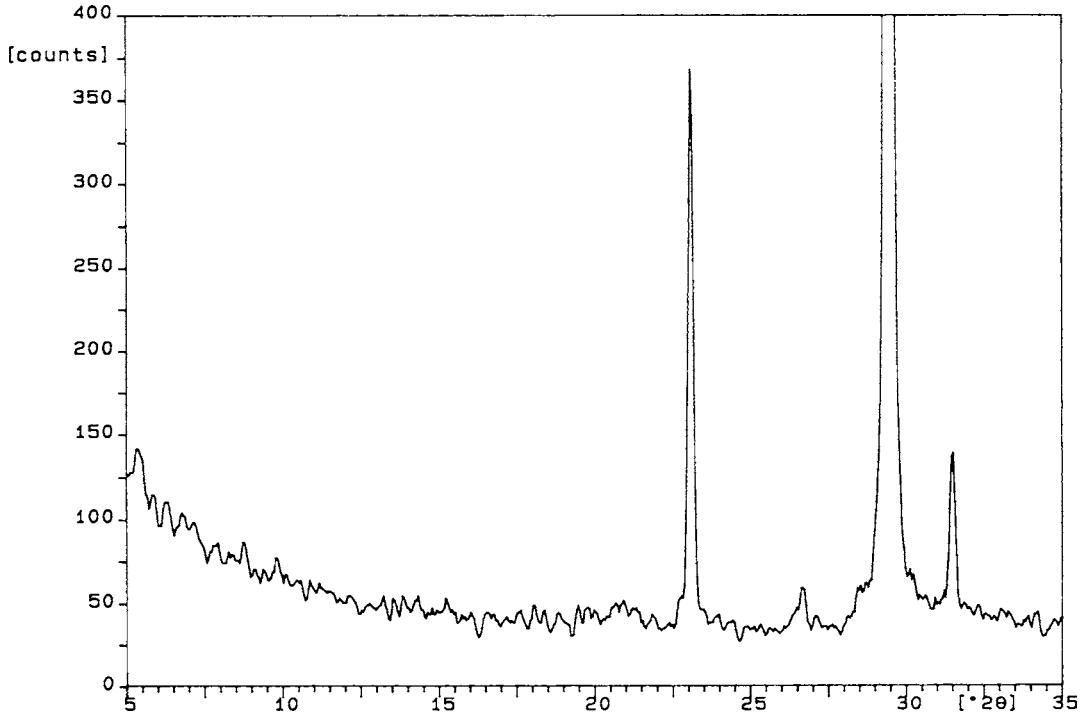


Fig. 5. XRD of the calcarenite sample.

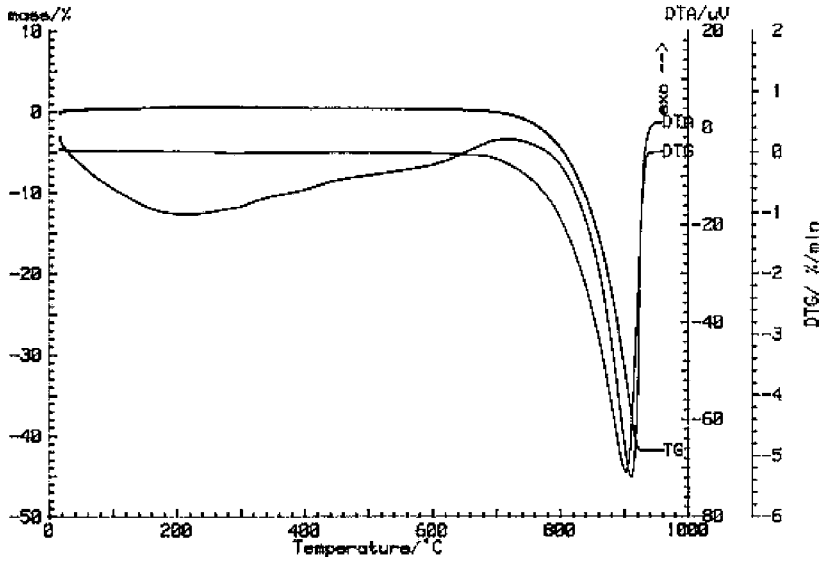


Fig. 6. Thermal curves of the calcarenite sample.

Thermoanalytical investigations (Fig. 7) on this mortar show the presence of a smaller amount of carbonate component, and the presence of clay minerals, aluminium and iron hydrated oxides and magnesian calcite. Moreover, XRD analyses (Fig. 8) provide evidence of a relevant presence of quartz and feldspars, and of a smaller amount of clay minerals.

Both the macroscopic features of the M2 mortar sampled at a higher stratigraphic level (M.S.U. 1004) than the one of the M1 mortar (M.S.U. 1016) and the alignment of the ashlars at this latter stratigraphic unit, reinforce the hypothesis that the respective structures were built in markedly different periods. The upper part may have been built on the already existing foundations, which may have been partly underground, and which must have been regarded by the builder as resistant enough for a new structure to be built on them. The new masonry is characterised by a lower quality mortar, while the structure converted into foundations shows a higher quality mortar. The poor quality of the preparation procedure of the M2 mortar and its setting up may indicate a historical period, in which workers did not comply with the "golden rules" of preparation of the binding materials.

Due to the presence of inclusions of soil fractions in the masonry from which the M2 mortar was sampled, some XRD and thermoanalyses were carried out on samples of soil (G) taken from the area near the examined structures. These investigations were also aimed at analysing the contaminations the soil produced on the mortar. The granulometric

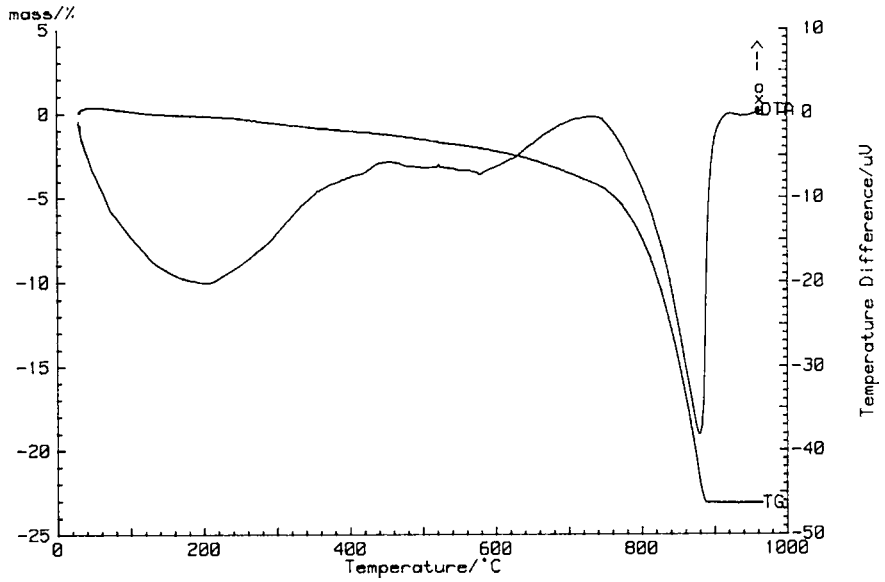


Fig. 7. Thermal curves of the mortar M2.

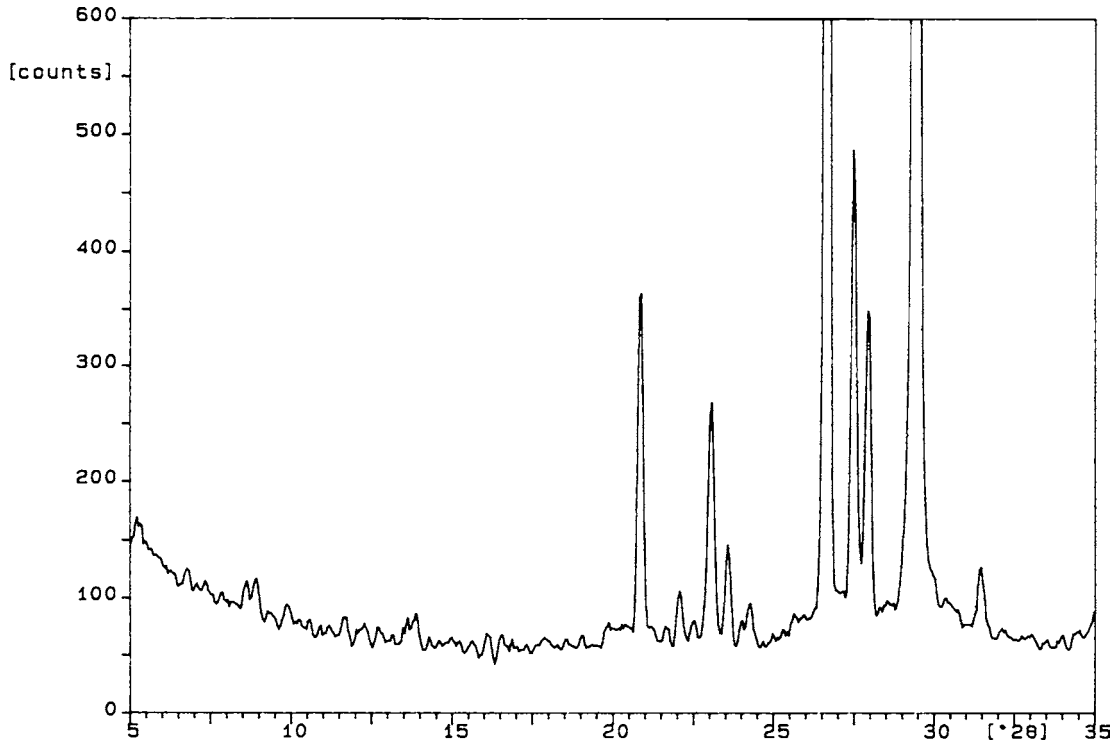


Fig. 8. XRD of the mortar M2.

behaviour of the constituent particles shows a poor dimensional distribution. XRD analyses (Fig. 9) indicate among the main minerals a remarkable amount of calcite and quartz, followed by clayey minerals (mainly illite and montmorillonite), feldspars and iron oxides and by a smaller amount of magnesian calcite and dolomite. Thermoanalytical behaviour (Fig. 10) also indicates the presence of aluminium and iron hydrated oxides, dolomite and magnesian calcite.

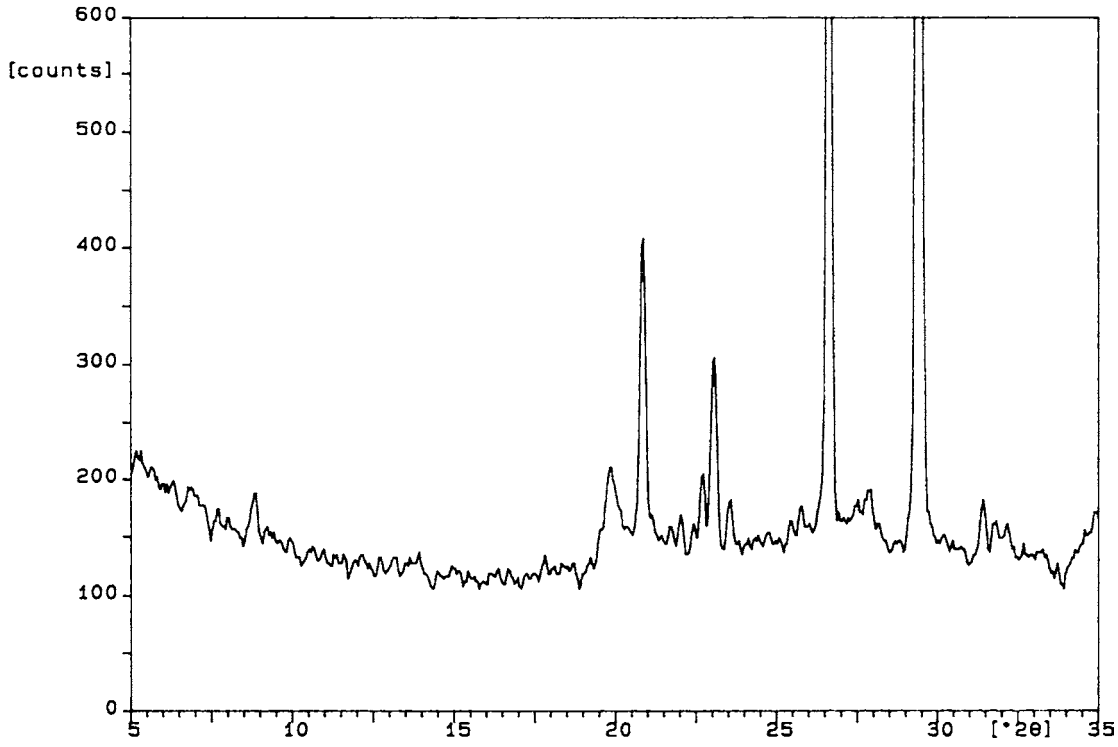


Fig. 9. XRD of the soil sample G.

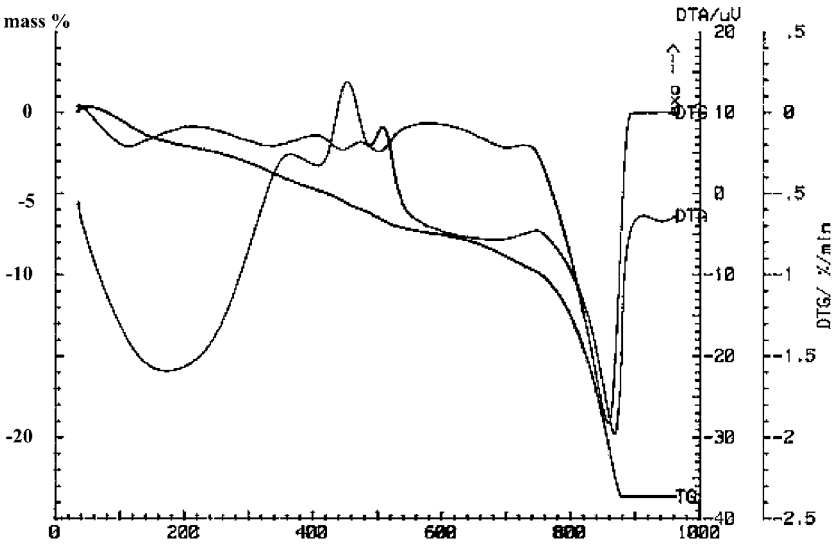


Fig. 10. Thermal curves of the soil sample G.

The exothermic effect of oxidation in the range 400–500 °C also indicates the presence of organic substances.

Investigations were also carried out on the M3 mortar, sampled at the foundation level of a masonry not far from the areas from where the already examined mortars were taken. This mortar appears to be intensely altered by meteoric actions, which induced dissolution and reprecipitation processes of some of its main constituents. Due to the mortar's hardness and compactness, the crushing, aimed at separating the binding matrix from the aggregate in order to perform the grain-size analysis, appears quite difficult. The results of thermoanalytical and XRD investigations (Figs. 11 and 12), however, provide evidence of the similarity with the M1 mortar in the mineralogical composition: calcite, quartz, feldspar and small amounts of clay minerals and magnesian calcite are indeed present. The similarity of the two mortars, as regards the mineralogical composition as well as the chemical one, (as reported in Table 1) reinforces the hypothesis—previously put forward—that the two masonries are part of the same ancient structure, which was later used as foundations for a new building.

The grain-size analysis on samples of another mortar (M4), taken from an isolated wall (sector I, which according to some archaeologists may constitute the ruins of a bell tower (1)) but near the main building, shows a good granulometric distribution of the aggregate (Fig. 2).

In the binding matrix a limited amount of small pieces of coal is present; this carbon phase is also made evident, in the thermoanalytical curves (Fig. 13) by the exothermic effect of oxidation at about 430 °C.

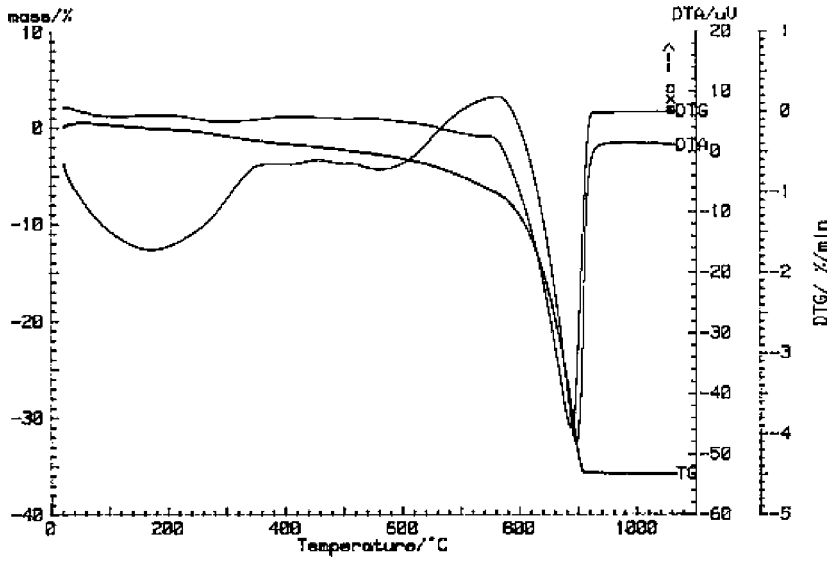


Fig. 11. Thermal curves of the mortar M3.

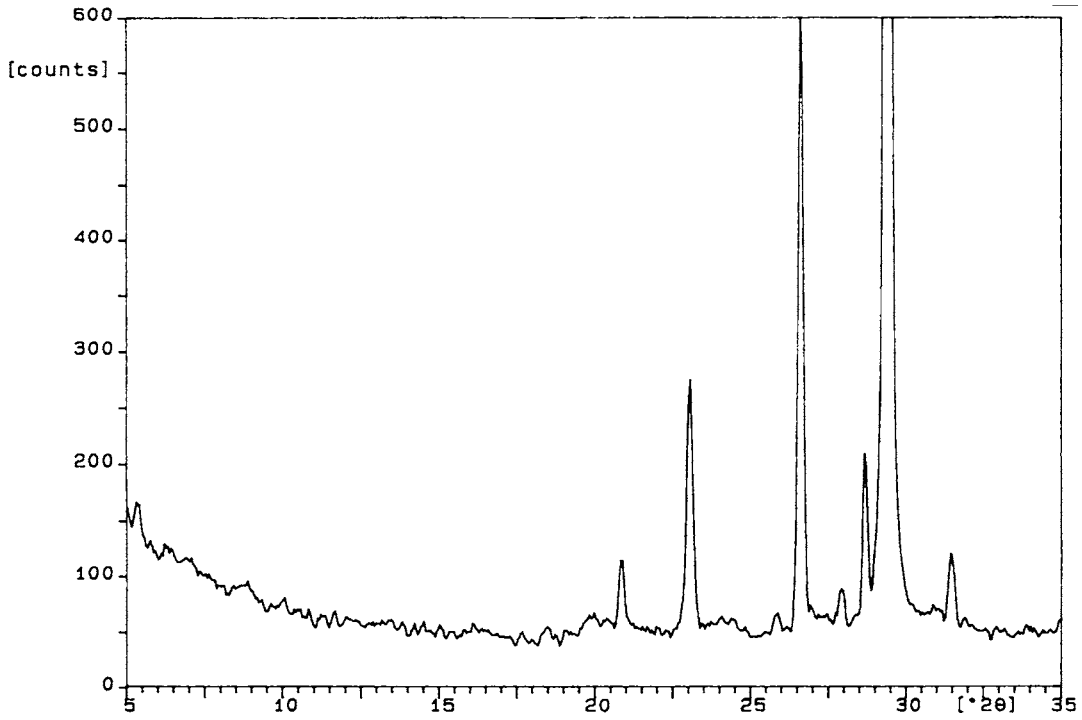


Fig. 12. XRD of the mortar M3.

By analysing TG/DTG e DTA/DDTA curves, the small endothermic effects in the interval 250–400 °C, probably connected with aluminium and iron hydrated oxides, can be better observed, while at about 700 °C the presence of magnesian calcite is also shown.

TG/DTA analysis also shows that, at about 850 °C, an endothermic effect develops, which corresponds to the decomposition of calcite. The appearance of smaller decarbonation effects concords with the results of the chemical composition determination (Table 1): since the value of the content in carbonate is the lowest, the thermoanalytical effect may be mainly due to the carbonated binder fraction.

If the remarkable endothermic effect of dehydration at 140 °C is correlated to the limited amount of clay minerals, also shown by the dehydroxilation effect at 500 °C, it can be inferred that the former results from the overlapping of the dehydration effect of the clay mineral and of the one related to calcium silicate hydrate (CSH). Moreover, also in

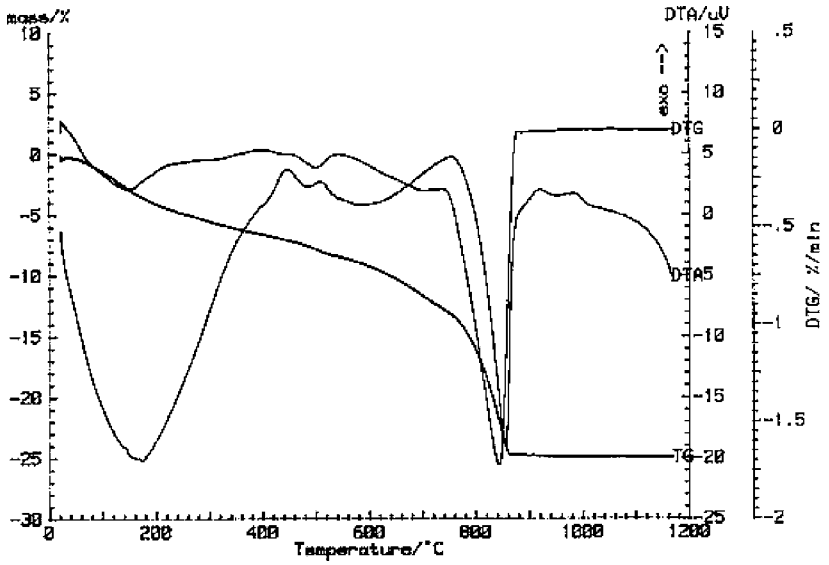


Fig. 13. Thermal curves of the mortar M4.

the XR diffractograms, some peaks can be observed, which, in spite of their limited intensity, attributable to the prevalently amorphous state of the CSH, can be traced back to the presence of this hydrated phase.

The formation of the CSH phase may be due to the use of a sand particularly reactive towards lime. Thus, it was judged important to carry out a reactivity test of the sand aggregate fraction of the mortar.

To this purpose, samples of the M4 mortar were crushed (<100 μm) and then mixed with hydrated lime ($Ca(OH)_2$ 93%) (lime/mortar mass ratio, 10) and distilled water (water/solid, 0.35, w/w) to produce a paste which was appropriately cured in a controlled environment ($T = 20\,^{\circ}C$, R.H. > 90 °C). Samples of the paste, taken at different curing times, were submitted to XRD and DTA/TG analyses, in order to monitor the hydration process. Already the initial setting time (less than 24 h) [10] of the paste shows a behaviour more typical of a hydraulic mortar than of a lime mortar. Moreover, the excellent hardening of the paste during this process signals that a hydration process is taking place, supposedly due to the siliceous and aluminate reactive phases. The analysis of the TG/DTA curves (Fig. 14) and of the respective XR diffractograms (Fig. 15) shows the development, in the hydrated paste, of the following phases: hydrated calcium monocarboaluminate ($3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$) (dehydration temperature: 160 °C) and CSH (dehydration temperature: 110 °C). The formation of calcium monocarboaluminate is intense and fast during the first days of the hydration process. Already after 4 days a complete consumption of the 'free' $Ca(OH)_2$ in the paste can be observed. The formation of the aforementioned hydrated phases, responsible for the good hardening and the hydraulic properties, indicates that the aggregate in the M4 mortar is still characterised by a good residual reactivity and is rich in aluminate phases, reactive towards $Ca(OH)_2$ and $CaCO_3$, thus producing monocarboaluminate [10]. Moreover, there are siliceous amorphous phases, which, in the presence of $Ca(OH)_2$, develop the CSH phase. On the whole, it can be stated that the sand used as aggregate in the original mortar had good 'pozzolanic' properties.

Further investigations were aimed at studying the pozzolanic aggregate, in order to trace back the provenance of this piroclastic sand, which is not significantly diffused in Apulia, where there are no volcanic areas. Various grains of aggregate were severed from the mortar through a light crushing and separation from the binding matrix, even though a minimal contamination of the carbonatic matrix may be anyhow present in the grains. X-ray diffractogram of this fraction shows the presence of quartz, K-feldspars (sanidine and orthoclase), a limited amount of clay minerals, pyroxene and iron oxides, apart from a remarkable amount of amorphous constituents, attributable to siliceous and aluminate phases, responsible for the remarkable hydraulic characteristics of the aggregate. On the whole, the results of XRD and thermoanalysis on the M4 mortar indicate that the pozzolanic material which characterises this mortar was essentially made up of volcanic ashes. Then, these volcanic ashes have been revealed by optical observations by means of a mineralogical microscope.

Through grain-size analysis, it has been possible to ascertain that most grains, of various sizes, correspond to nodules of pozzolanic sand, agglomerated into the binding matrix (lime putty) during the preparation of the original mortar.

Some studies [11,12] report the presence of limited deposits of volcanic ashes, accumulated in the Apulian territory as a consequence of eruptions of the volcanoes Vulture and Vesuvio, in the neighbouring regions Basilicata and Campania, respectively. This strengthens the hypothesis that the

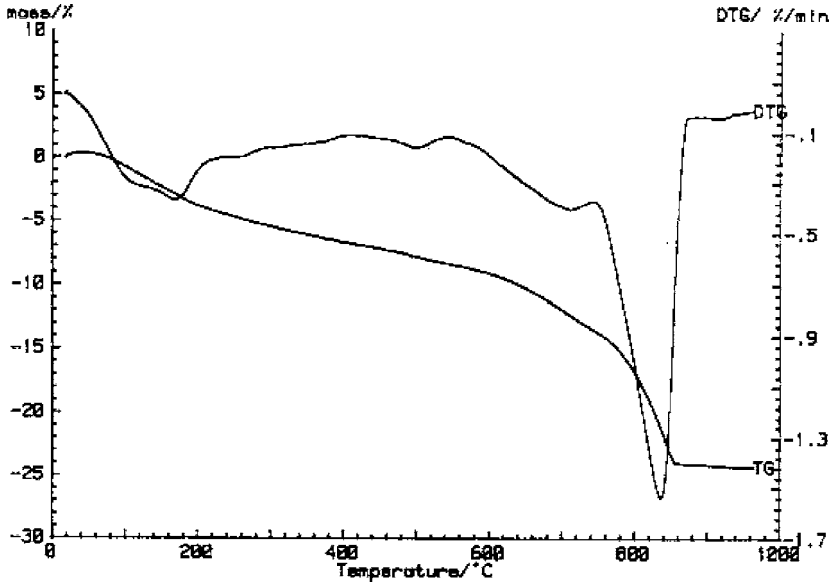


Fig. 14. Thermal curves of the hydrated paste of the M4 powder–lime.

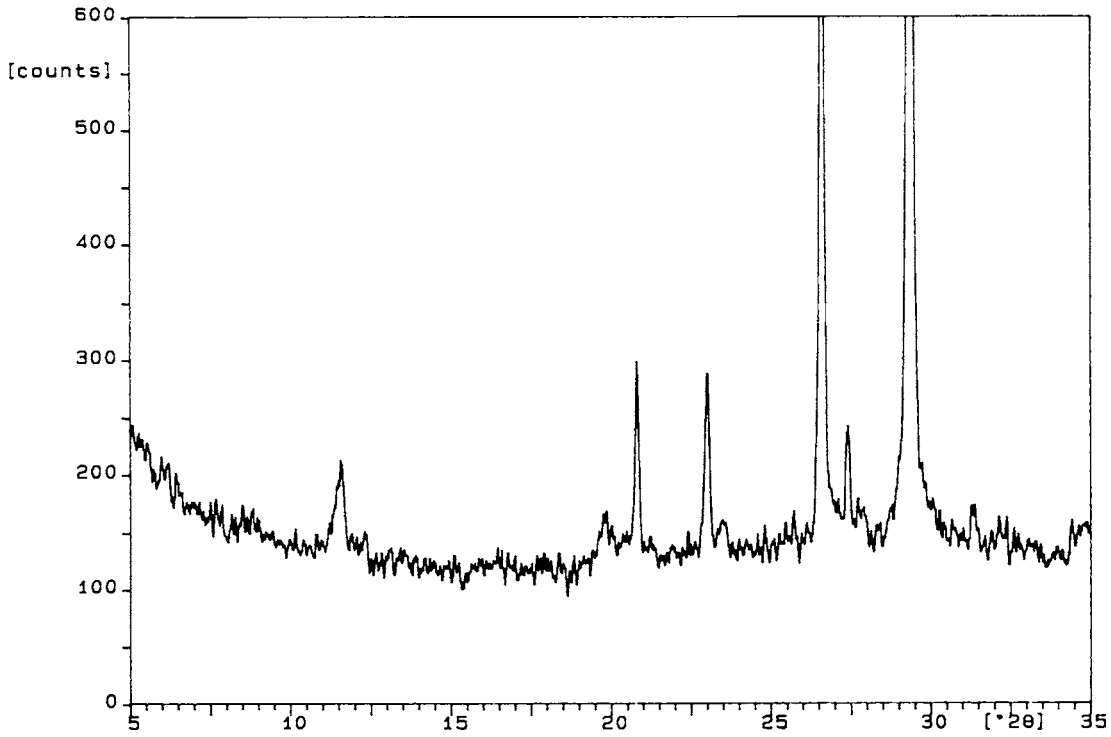


Fig. 15. XRD of the hydrated paste of the M4 powder–lime.

examined sand, well-known by the ancient builders for its good hardening properties shown in lime mortars, may come from an area not so far from the site of Monte Sannace.

The signalled peculiarity of this hydraulic mortar may lead us to suppose that it was probably used in order to obtain a more resistant masonry at the foundations' level, for a very high building, such as a bell tower. However, further historical and scientific investigations will be necessary in order to identify the function of this square-based structure.

## 4. Conclusions

The investigations carried out and the results obtained make it possible to achieve two goals: first, to characterise the technological aspects of mural structures; second, to define the chronological relationship between those masonries which cannot be easily dated through common archaeological parameters.

The results, indeed, provide interesting information about the preparation techniques of the binding materials used in the various mural stratigraphic units and, thus, about the 'technological knowledge' of the ancient workers, which is connected with the different phases of construction.

Thermoanalytical DTA/TG/DTG investigations and X-ray diffractometry analysis proved of fundamental importance in the characterisation of the mineralogical constituents of the examined mortars, showing differences and similarities. The M4 mortar, whose peculiar characteristics are attributable to the usage of a particular sand, rich in volcanic ashes, proved very interesting due to its hydraulic behaviour. This pozzolanic sand probably derives from the excavation of limited deposits in Apulia. The preparation of the mortar, with an aggregate particularly reactive towards lime, testifies a deep knowledge of the raw materials and a deliberate selection of the building materials, among the ones available on the territory.

Further studies will be aimed at going deep into the aspects concerning other usages of the aforementioned pozzolanic material, also in other masonries in the same archaeological site, as well as the more precise localisation of the most suitable excavation areas. The studies' development will also allow us to understand if this knowledge dates back to more ancient ages and to evaluate the influence this technological knowledge had on building techniques during the various centuries.

As far as the dating of masonries is concerned, the results obtained cannot obviously provide absolute chronological information. Nevertheless, on the basis of these results, it has been possible to establish a chronological relationship between those structures which, being made up of shapeless stones and recycled blocks, could not be dated otherwise.

Analysing the differences between the various construction techniques emerged in this study, it can be supposed that the mural structures date back to different periods, ranging from the Late Ancient Period to the first centuries of the Middle Ages.

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