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Thermochimica Acta 321 (1998) 207–214

thermochimica acta

Thermal, microscopic and X-ray diffraction studies on some ancient mortars

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Received 28 February 1997; accepted 30 May 1998

Abstract

Within the framework of research on ancient mortars in Pavia and its district, thermal, microscopic, and X-ray diffraction measurements have been carried out on some mortar samples taken from three walls situated in the historical center of the city, and belonging to the following periods: 4–6th, 9–10th and the 16th centuries.

A careful mineralogical and grain-size analysis showed that local raw materials were regularly used during the Middle Ages. By means of thermal analysis and thermogravimetry it was proved that the Roman age and medieval mortars are richer in calcite, whereas the presence of gypsum and dolomite are indicative of a poorer original composition or of compositional changes induced by atmospheric pollution in the mortars of the 16th century. © 1998 Elsevier Science B.V.

Keywords: Ancient mortars; Optical microscopy; Thermal decomposition; Thermogravimetric analysis; X-ray diffraction

1. Introduction

Since the Middle Ages, bricks have been the main construction material in the historical centres of many cities in the plains of northern Italy on account of the presence of important clay sediments of the Quaternary period. In medieval masonry, mortars used to assemble brick layers represented the portion which was prepared often from significantly different raw materials. These materials frequently undergo dramatic physical and chemical changes induced by climate and atmospheric agents.

Scientific studies on ancient mortars in Italy are relatively rare. Only a few recent works have been reported: X-ray diffraction measurements performed on mortars from Pisa [1]; thermogravimetric analyses of mortars from two Italian regions [2]; and thermal and X-ray studies on mortars from Rome [3].

Research groups active in several disciplines at the University of Pavia have recently undertaken a series of investigations on construction materials of monuments and old buildings in the historical centre of Pavia. Within the framework of a long-range study on ancient mortars in this city, the present work deals with microscopic, X-ray diffraction and thermal measurements carried out on some mortar samples taken from walls of a building situated in the Roman area of the centre of Pavia, namely the cloister of the 'Ugo Foscolo' Grammar School, formerly the Monastery of the Barnabites religious order, with the adjacent church of S. Maria di Canepanova.

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0040-6031/98/$ – see front matter
PII: S0040-6031(98)00461-4

Among the foundation walls of the southwestern corner of this building, three layers have been recognized by archeologists [4]: an older wall of Roman times, built in the last period of the Roman Empire, 4–6th centuries on the western side; a medieval wall, built just above the former one after some centuries, 9–10th centuries; and the foundation walls of the adjacent church, probably built in the second half of the 16th century on the south side. Samples taken from these wall layers were used in the present work and are representative of different construction periods.

The aim of this study is the characterization, by various experimental techniques, of the above-mentioned mortars in order to attain a better understanding of the remarkable differences in their chemical composition and mechanical properties. It may be noticed that physico-chemical and structural investigations of the properties of ancient construction materials could give a valuable contribution to a thorough knowledge of their behaviour. By considering materials produced in the same place in different historical periods, one can recognize the different methods of working in the building industry in relation to the technical evolution and economic development of the society. A collection of physical and chemical data on ancient mortars and plasters existing in one town may be useful, in particular, for dating buildings or parts of them [5]. Moreover, such data may be of great interest in order to set-up a data base on the properties of these materials, and to find out the best compatible materials for use in restoration.

Monitoring the formation of weak structural domains in the walls of ancient monuments, thus preventing their decay and destruction, is another important target of this type of investigation.

2. Experimental

2.1. Samples

The mortars were taken from three different walls, as previously indicated. The site is a cellar characterized by a steady microclimate and a remarkably high relative humidity. The walls are covered with a black crust of deposited particulates, the presence of which is probably due to the fact that the oil burner of the heating system is located in this part of the building. Organic substances of possible biological origin can also be observed on surfaces of the walls. In order to avoid contamination of the samples, a surface layer, 5–10 mm thick, was carefully removed from each sampling area, thus reaching the inner layer of the material from which the powders were taken.

The collected samples were representative of mortars displaying significantly different morphologies.

Actually, while sampling these materials, several characteristics became apparent: (i) Roman mortars (No. 1 in the text) were crumbly, but presented a fairly good aggregation and consistency; (ii) the medieval ones (No. 2) were characterized by a good state of conservation, they looked hard and very compact, i.e. difficult to be sampled; and (iii) mortars of the Renaissance (No. 3), viz. the more recent ones, which were very humid, friable, and disaggregated, as if they had practically lost their binding ability and main properties.

The mortars of the Roman and Renaissance periods were 1–2 cm thick layers, lying between regular layers of bricks ~8 cm thick, whereas the medieval mortars were thicker (2–5 cm) and consisted of larger masses including rough layers of rounded stones taken from the river, as shown in the schematic diagram of Fig. 1.

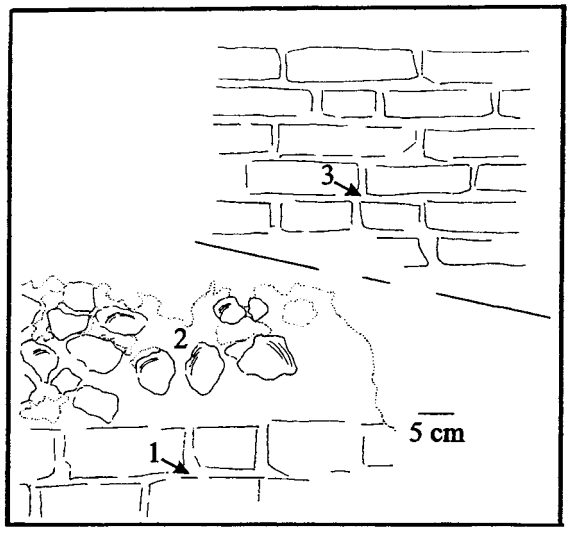

Fig. 1. Scheme of the sampling on the wall structure. (1) Roman wall, (2) medieval wall, and (3) Renaissance wall. The site (1) is ca. 0.6 m high on the cellar pavement, and ca. 2.5 m below the present level of the street. Site (2) lies just above site (1). Site (3) is 1.1 m high on the pavement, and ca. 2 m below the level of the street.

At least five samples were taken from each site indicated in the figure, and the results reported are to be considered as indicative of the distinctive features of each site.

A preliminary characterization was carried out taking into account the grain-size distribution in order to separate the main components (skeleton and binders) and to get a better definition of them. The mineral aggregates were thoroughly ground in an ultrasonic cleaner for ca. 1 h. The powder obtained was fractionated in a column of sieves stirred for ca. 30 min, and the masses of the collected fractions were determined.

2.2. Techniques

2.2.1. Thermal techniques

Differential thermal analysis (DTA) experiments were carried out in static air, using a scan rate of 10 K min^{-1}, with a high-temperature DTA 1600 cell of DuPont (USA) assembled with a 910 DSC module. The cell was calibrated for temperature with the melting point of a gold standard (99.9% by weight) supplied by Metalli Preziosi (Milan, Italy). Thermogravimetric analysis (TGA) measurements were made in a pure nitrogen flow of ca. 30 ml min^{-1}, scan rate of 20 K min^{-1}, with a DuPont 951 TGA thermobalance. A preliminary calibration of the TGA module for temperature was carried out by running some samples of calcium oxalate provided by DuPont. Both modules were controlled with a Thermal Analyst 2000 system of TA Instruments. The uncertainty of the temperature measurements, at the mentioned scan rates used, was within ± 0.2 K.

2.2.2. X-ray diffraction

X-ray diffraction data were collected on powders at room temperature by means of a Philips PW 1800 diffractometer, CuK_α radiation; analysis conditions 40 kV, 20 mA. The mineralogical analyses were carried out on the fine fraction (<0.038 mm) obtained by grain-size separation as previously described. The collected diffraction data were analyzed considering the intensity of reflections for each mineral; the semi-quantitative percentages of the various mineral phases were checked using a homemade software derived from the SIROQUANT Software Package [6].

2.2.3. Optical and electron microscopy

A Leitz Laborlux 12 POL S instrument was employed for optical microscopy.

Energy dispersive spectrometry (EDS) was performed with a JEOL JXA 840A instrument.

2.2.4. Separation techniques

After breaking the aggregates by means of an ultrasonic cleaner Minimaxi St., the particle-size selection was carried out using sieves of the ISO 565 series.

3. Results and discussion

In the present work, the first approach was devoted to thin section analysis of the mortars in order to characterize their textures and define their content in inert fraction.

The mortars of the Roman age contained ca. 70% of inert fraction. In those of the medieval and Renaissance ages the percentage of this fraction could be evaluated as ranging between 80 and 90% of the material.

The inert fraction may be characterized with optical microscopy inasmuch as the individual phases bring out their optical and structural features (cleavage traces, pleochroism and interference colours), whereas the binder fraction, because of its fine-grain sizes, needs to be analyzed with more sophisticated techniques, such as electron microscopy and microanalysis.

More than five thin sections of each available sample were analyzed by means of both electron and optical microscopy. A deeper examination of the results obtained with microanalysis is in progress and will be presented in a subsequent paper [7].

The observations carried out by means of optical microscopy and EDS gave the results, illustrated in Fig. 2(d), in which the presence of binders and aggregates, their relative fraction and interactions, can be observed.

The clasts were generally angular in shape, and varied in size and composition, as shown in Fig. 2(a and b).

In the samples of the Roman age, there were numerous crystals of calcite. They were associated with micas, such as biotite and muscovite. The heavy minerals were represented by brown and green

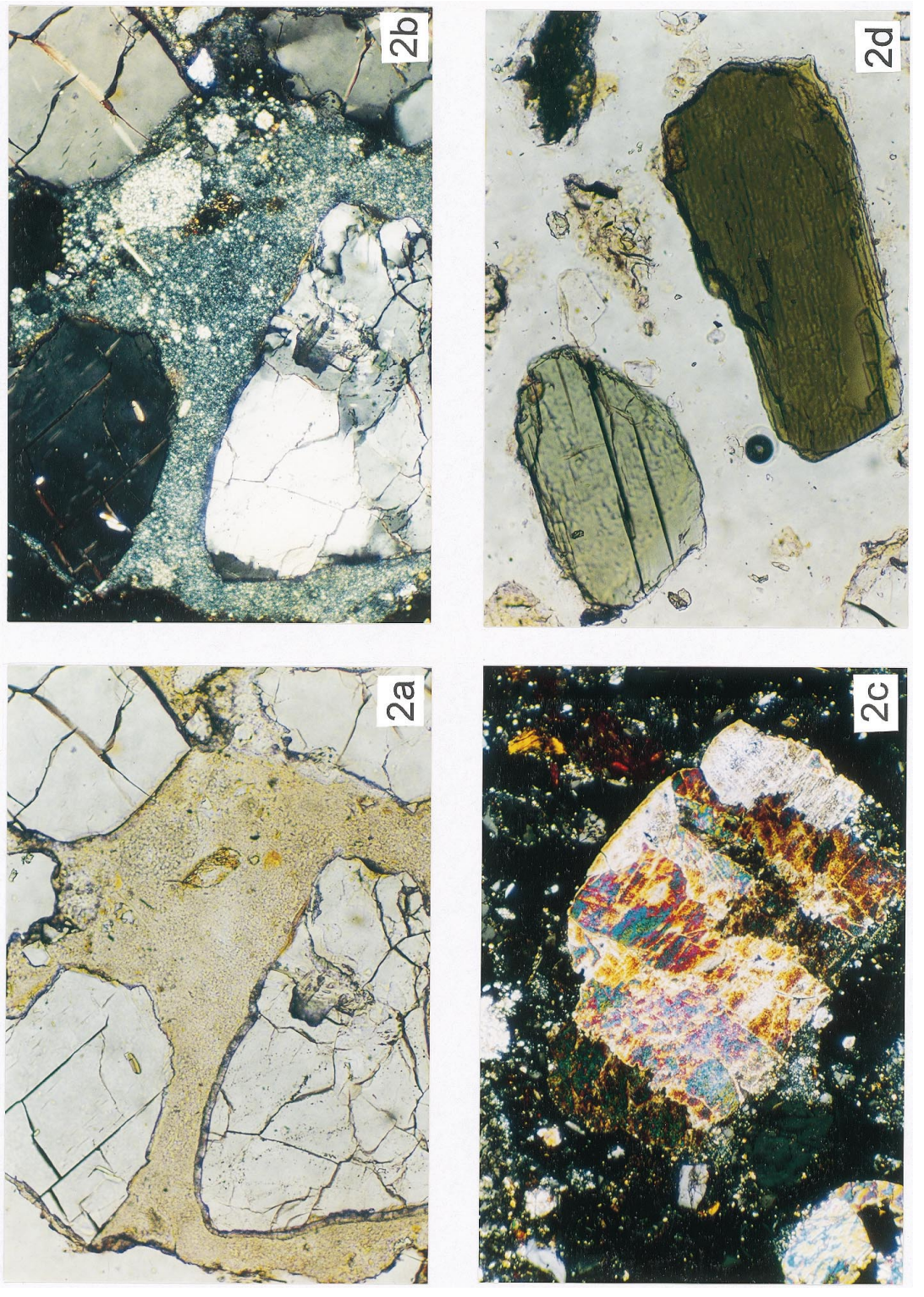

Fig. 2. Thin sections. (a) Texture of the mortar of Roman age, parallel nicols, 220*x*. The sharp edges of the sand clasts are apparent. (b) The same as in (a) with crossed nicols. The distribution of the calcite binder, partially in form of irregular white grains, is clearly shown. (c) A primary calcite crystal in the same mortar of (b). (d) the same mortar, parallel nicols, 220*x*. Two crystals of green amphibole, which are abundant in the inert fraction, are illustrated.

amphiboles (Fig. 2(d)). Among the lithic clasts, schistose rocks associated with metamorphic quartz were prevalent. Lithic fragments of igneous origin, including quartz, K-feldspar and plagioclase were also present as shown in Fig. 2(a).

Micas, i.e. biotite, and muscovite in lower percentage, together with a lot of fragments of chlorite and calcite characterized the samples of the medieval ages. The lithic clasts belonged mainly to schistose rocks, but fragments of igneous rocks and low-grade metasediments were also observed, with only rare grains of amphiboles.

The Renaissance mortars contained abundant biotite and muscovite associated with brown and green amphiboles, clinopyroxene and metamorphic quartz. Lithic fragments were represented by schistose rocks.

As for the binders, those from the Roman and Middle ages samples presented a heterogeneous composition due to calcite phases (Fig. 2(c)) in primary idiomorphic crystals and in calcite micrograins of secondary crystallization. The latter was particularly apparent in the medieval samples within the pores of the mortar.

On the other hand, in the samples of the Renaissance, the binder displayed a very homogeneous look. Newly formed crystals of calcite were absent. With crossed nicols, the binder appeared as a fine-grained aggregate which was difficult to analyze with an optical microscope.

Table 1
Percentage distribution (in wt/%) of the grain-size range for the considered samples. Sample 1: Roman mortar; sample 2: medieval mortar; sample 3: Renaissance mortar

Sample No., particle size range, *X*/mm	1, W%	2, W%	3, W%
$X \geq 8$	0.00	0.00	4.40
$4 < X < 8$	5.10	4.30	6.80
$2 < X < 4$	5.20	5.60	4.00
$1 < X < 2$	6.10	9.28	3.99
$0.5 < X < 1$	9.60	19.55	8.90
$0.25 < X < 0.5$	24.13	31.08	37.65
$0.125 < X < 0.25$	16.50	14.15	17.81
$0.075 < X < 0.125$	5.38	2.70	4.41
$0.038 < X < 0.075$	4.22	1.44	2.71
≤ 0.038	23.86	11.89	9.33

Grain-size data are reported in Table 1. A comprehensive view of the results obtained from the particle-size analysis is illustrated in Fig. 3, where the wt% of each particle-size range is listed for every sample.

By means of this technique, it was shown for the Roman age mortars (No. 1) that a symmetric distribution around the range of 0.25 mm was obtained. In this case, the fine fraction, i.e. <0.038 mm, represents up to 24% of the total weight.

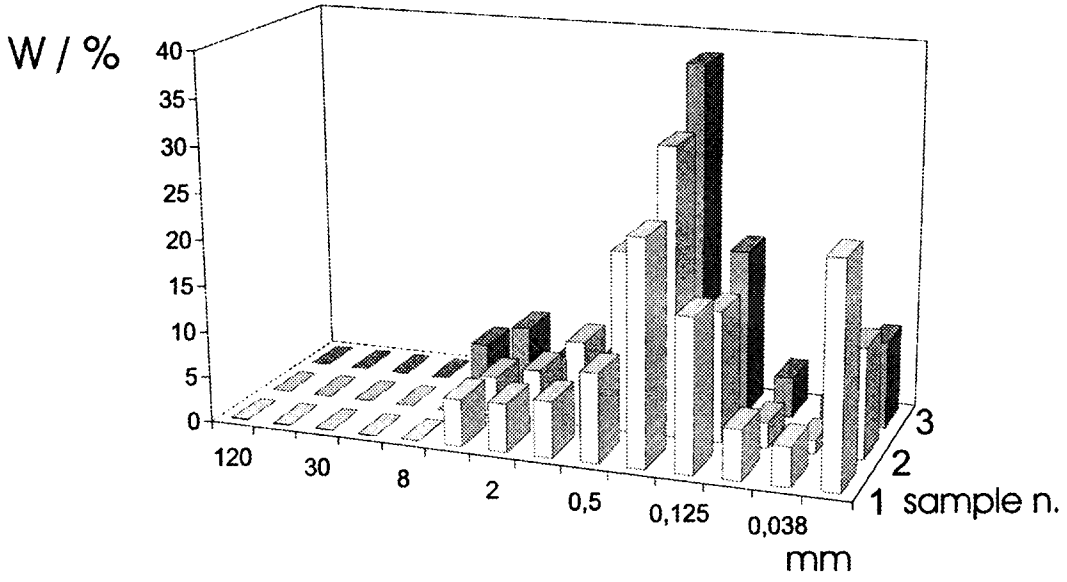

Fig. 3. Grain-size distribution of the three considered mortars among the selected sizes.

In the medieval mortars (No. 2), the distribution was also unimodal and similar to that of the Roman mortars, but the fine fraction was remarkably lower, ~12%; the absence of grains >8 mm could also be noticed.

As for the mortars No. 3, the distribution was bimodal, inasmuch as two maxima were apparent around 0.25 and 4 mm. It may be remarked that this kind of bimodality, which is similar to that of the fluvial sediments of the Quaternary period, was described as resulting from a variety of causes [8].

The fine fraction of all the available samples, namely that with grain size <0.038 mm, was investigated by means of powder X-ray diffraction measurements.

In Fig. 4, X-ray diffraction patterns for a sample of each mortar are reported. Quartz, feldspars and calcite can be recognized as common phases present in both, the Roman age and medieval mortars (Nos. 1 and 2). The main peak of calcite was significantly higher for the Roman age mortar, a higher concentration of calcite can be derived for this material. On the other hand, calcite is missing in the trace of sample No. 3, where the peaks of gypsum and dolomite are apparent.

In Table 2, the percentage distribution of the mineral compounds found in the fine fraction of the examined mortars is reported.

By means of thermogravimetric analysis (TGA), the thermal decomposition of the binders has been recorded. The TGA scans carried out on the same fine fraction with grain size <0.038 mm showed a thermal behaviour which is in good agreement with the results obtained from the above-mentioned techniques. Fig. 5 illustrates typical records of wt% vs. temperature taken on the considered mortars in the 300–1300 K range.

Table 2
Percentage distribution of the mineral compounds, as determined from the X-ray diffractions patterns. These data should be considered as semiquantitative, since the accuracy of this method is limited by the number of phases and absorption effects

Sample	Q	K-F	Pl	Cc	D	G	H	Total
1	47	25	20	8	0	0	0	100
2	53	17	23	7	0	0	0	100
3	15	5	4	0	6	63	7	100

Q, quartz; K-F, K-feldspar; Pl, plagioclase; Cc; calcite; D, dolomite; G, gypsum; and H, hematite).

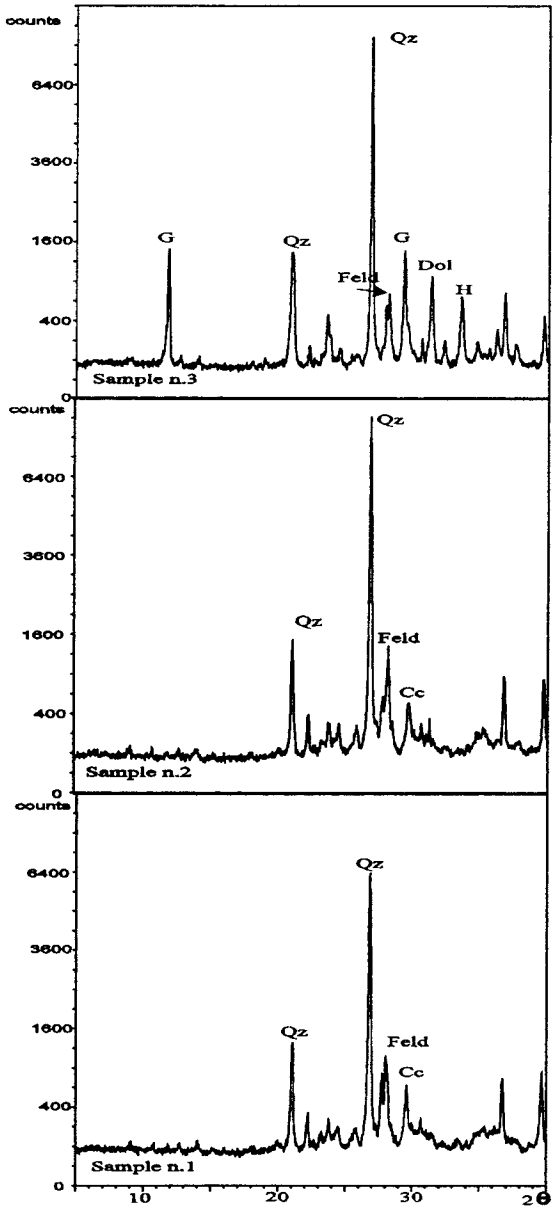

Fig. 4. X-ray diffraction patterns for the three mortars. The following main peaks are indicated. Qz, quartz; Feld, feldspars; Cc, calcite; Dol, dolomite; G, gypsum; and H, hematite.

After the first region of the diagram, in which adsorbed water is removed from the three samples, the trend of the weight loss as a function of temperature is remarkably different in the three cases examined.

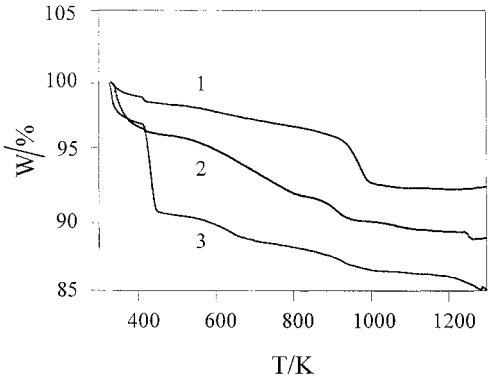

Fig. 5. Thermogravimetric records of: (1) Roman mortars; (2) medieval mortars; (3) Renaissance mortars. Scan rate 20 K min^{-1}.

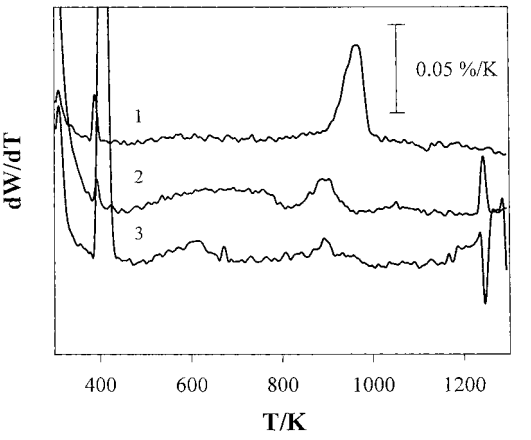

Fig. 6. Plot of the first derivative of weight loss of samples 1, 2, and 3 vs. temperature.

The Roman age mortar (curve 1) displays a rather regular decrease in weight, followed by a step between ca. 900 and 1000 K, due to the decomposition of calcium carbonate which can be estimated in the order of 9% of the total original weight.

The medieval mortar (curve 2) shows a smoother thermogravimetric plot, after a step at ca. 400 K which is probably due to the loss of structural water.

In the Renaissance mortar (curve 3), near 420 K, a large step occurs. The total mass loss, occurring between room temperature and 500 K, may be related to the loss of 1.5 molecules of water from $CaSO_4{\cdot}2H_2O$; this hydrated salt represents ca. 60% of the initial mass. It is followed by the further slow loss of the remaining water from calcium sulphate hemihydrate between 500 and 900 K. This behaviour is in agreement with the trend of water loss described in this compound by Webb and Krüger [9].

In Fig. 6 the first derivative of the curves of weight loss is plotted against temperature, in order to give a better view of the mentioned phenomena. The evolution of CO_2 from the Roman age mortar is recorded in curve 1 as a remarkably high peak at ca. 950 K, whereas the corresponding peaks for the medieval (curve 2) and Renaissance (curve 3) mortars occur at ca. 900 K and are much lower in intensity.

From the X-ray data, these weight losses may be related to the decomposition of calcite and dolomite for curves 2 and 3, respectively. In Fig. 5, the loss of carbon dioxide in curve 2 corresponds to a ~5% initial amount of $CaCO_3$. Similarly, in curve 3, the loss of

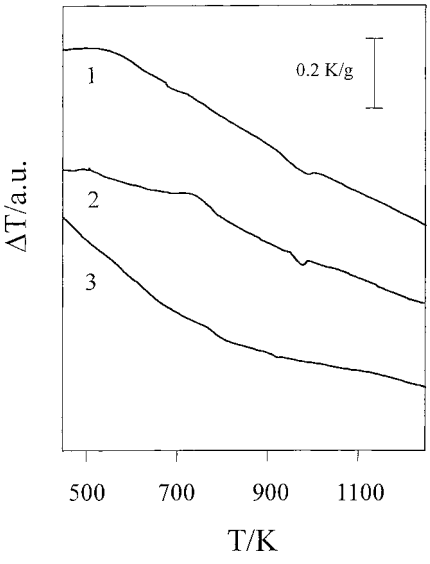

Fig. 7. Typical DTA traces in static air for the considered mortars.

CO_2 corresponds to a ~8% content of dolomite. Thus, a fair comparison was found between the data obtained from TGA and those from X-ray diffraction reported in Table 2.

The results of the thermal analysis scans taken in the 300–1300 K range are shown in Fig. 7. The DTA records display the same phenomena observed in the TGA, although not so clearly, owing to the heterogeneous composition of the analyzed materials. In particular, the curves recorded on the Roman age and medieval samples display well-marked peaks

corresponding to the decomposition temperature of carbonates at ca. 980 K, whereas this phenomenon is hardly noticeable on the curve of the Renaissance material.

The present findings may be compared with the results obtained on mortars taken from the cloister of an 11th century church near Reggio Emilia (northern Italy) in the study by Vecchio et al. [3]. In that work, the weight loss illustrated by the thermogravimetric traces of the 'RE C2' samples recorded in air was attributed to the evolution of CO_2 from the decomposition of calcium carbonate. This decomposition corresponds to the weight loss recorded in the thermogravimetric scans of the sample Nos. 1 and 2 of this study, whereas a different feature of the samples studied by Vecchio et al. [3] was the presence of calcium oxalate.

Moreover, it was qualitatively observed in a recent work [10] that mortars of the Roman age found in the archaeological site of Lomello, ca. 40 km west of Pavia, display a higher percentage of binder vs. aggregate in comparison with the medieval mortars from the same area. It may be interesting to remark that a similar trend was brought about in the present investigation.

4. Conclusions

From the above experimental evidence, the following conclusions can be drawn:

- by means of several complementary techniques, i.e. X-ray diffraction, grain-size analysis, optical microscopy, DTA and TGA, samples of ancient mortars representative of three construction periods, fabricated approximately in the 5th, 10th and 16th centuries, were characterized;
- it was found that the Roman and medieval mortars were richer in calcite; the medieval ones were much harder and compact, due to their higher content of microcrystalline calcite;
- in the mortars of the Renaissance period, the presence of gypsum can be related to the poorer composition and preparation technique of the binding compounds. On the other hand, the presence of dolomite may be seen as indicative of a different choice of raw materials. It may be noticed that compositional changes induced in this mortar by atmospheric pollution cannot be excluded;
- the bimodal distribution observed in the grain-size analysis of the latter mortars confirms this interpretation of the difference in the preparation techniques;
- from the analyses carried out on thin sections, it can be concluded that the choice of the raw materials was made from local sources;
- the observations made by means of X-ray diffraction and microscopy were compared with the data collected with the thermal techniques of analysis. The agreement between these results confirmed the presence of carbonates and of gypsum in these mortars.

Acknowledgements

Thanks are due to Mr. G.W. Palestra for his help in selecting the samples and for fruitful discussions.

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