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Study of ancient dolomitic mortars of the church of Santa María de Zamarce in Navarra (Spain): comparison with simulated standards

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Abstract

Ten ancient mortars from the Church of Santa María de Zamarce (Navarra, Spain) have been studied by means of chemical analysis, X-ray diffraction and simultaneous thermogravimetric and differential thermal analysis (TGA–DTA). All the studied samples have shown to be dolomitic mortars. Sixteen simulated standards of typically present compounds in dolomitic mortars were prepared and studied. Particularly the occurrence of hydrated magnesium carbonate hydroxide (hydromagnesite (HY), $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$) as result of the setting of dolomitic mortars is discussed. No HY has been checked in mortars from Santa María de Zamarce. However, TGA–DTA studies have clearly shown the thermal decomposition of HY in the prepared mixtures, specially the exothermic peak at 500 °C. The experimental conditions in TGA–DTA, with a high CO_2 pressure around the sample, seem to play an important role in the occurrence of this phenomenon. Suitable experimental conditions for thermal studies of these materials have been indicated.

Keywords: Dolomitic mortars; Thermal analysis; Hydromagnesite; Self-generated atmosphere; X-ray diffraction

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1. Introduction and objectives

The knowledge of the chemical composition of the mortars used in the construction of historical–artistic monuments has an enormous interest. Now, the restorations carried out on this type of constructions often use similar materials to the original ones in composition and properties, according to the conclusions of the symposium “Mortars, cements and grouts used in the conservation of historic buildings” [1]. Rodríguez-Navarro et al. [2] state the advantages related to the use of lime mortars instead of Portland cements in the restorations: in addition to historic and aesthetic reasons, lime mortars do not release soluble salts and they are more chemically, structurally and mechanically compatible with much ancient masonry.

In general, lime mortar is the most widely used in historical–artistic constructions. To this type of mortar and its composition and properties have been dedicated numerous works of research; Franzini et al. [3] have studied lime mortars from some medieval buildings in Pisa and they have proposed a method for determining the chemical composition of binder and aggregate; Frizot [4] and Gutiérrez-Solana et al. [5] have analysed the chemical and mineralogical–petrographical compositions from ancient lime mortars.

Mortars with a dolomitic lime are less abundant than the aforementioned mortars. Nevertheless, the study of the variations of their behaviour, the characteristics

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of the present phases and the methods of determination of the same ones have an undeniable scientific interest. Certain discrepancies in the specialised literature have also motivated this work. The controversy is about the occurrence of phases originated during the setting of this type of mortars (for example hydromagnesite, HY), whereas Bruni et al. [6] and Dheilly et al. [7] have indicated that the carbonation of a dolomitic lime (i.e., containing magnesium hydroxide—brucite, $Mg(OH)_2$) can originate usually HY, and Vecchio et al. [8] have determined the presence of HY in Italian dolomitic mortars (11th and 14th centuries), Newton and Sharp [9] have only found magnesite and brucite in some dolomitic mortars and Alessandrini et al. [10] have not determined HY in the binder fraction from some dolomitic mortars. Botha and Strydom [11] state as conclusion in their work that HY only can be prepared from magnesium hydroxide if the experimental conditions are chosen carefully (and with a CO_2 flow of 190 ml min^{-1}). Also the work by Dheilly et al. [7] has shown HY obtained after curing in a CO_2 atmosphere, and Caceres and Attiogbe [12] have produced HY after recarbonation of $Mg(OH)_2$—from calcined dolomite—in a CO_2 excess.

The advisable analytical techniques to characterise dolomitic binding materials (and also the information which is provided by these techniques) is also matter of controversy: Vecchio et al. [8] have determined HY by means of XRD and DTA–TGA, but unexpectedly they have not observed the exothermic peak at 500 °C. However, Bruni et al. [13] state the difficulty in determine HY by using XRD due to the poor crystallinity of the HY, and also, the conditions for the occurrence of the exothermic peak in the thermal decomposition of HY have been presented in the work by Sawada et al. [14] and in a recent paper by Khan et al. [15].

In order to define the composition and characterise the type of binder employed, 10 ancient mortars of dolomitic origin, used in the building of the Church of Santa María de Zamarce (1141–1167), have been studied. The church is in the rural Romanesque style of Navarra (Spain), with a single nave of three sections with semicircular apse (Fig. 1) [16].

In a previous work by the research group a methodology for characterisation of the mortars have been detailed [16]. In the present paper, the results obtained by means of chemical analysis, X-ray diffraction (XRD) and simultaneous thermogravimetric and differential thermal analysis (TGA–DTA), are offered.

Considering the references of the literature and the experimental results, 16 different patterns from phases that could be present in materials of these characteristics have been prepared. The objectives are to clarify the possibilities of occurrence of these phases in mortars, as well as the suitability of the use of the XRD and the TGA–DTA in their determination. Experimental conditions that allow the occurrence of the exothermic peak and the set of phenomena of HY thermal decomposition have been settled down.

This work shows the type of mortars used in the Church of Santa María de Zamarce, as well as the comparative study between the bibliographical data and the simulated standards of these materials. The obtained results confirm the complementary use of XRD and thermal studies for the adequate characterisation of these binding materials.

2. Experimental

The sampling procedure for binding materials has been carried out taking a part of the mortars with a chisel and throwing away the external portion of the joints, with the aim of obtaining non-altered material. Fig. 1 shows the sampling points.

The sample, ground in an agate mortar, was dried in a heater at 105 °C until constant weight and then 1 g of sample was taken for its subsequent chemical analysis.

The chemical analysis of the main components has been carried out by attack with a sodium carbonate–borax alkaline flux, and afterwards by traditional chemical procedures [16]; a titration with ethylenediaminetetraacetic acid (EDTA) (using murexide and eBT (eriochrome black T) as indicators) in order to determine calcium and magnesium concentrations; sodium and potassium levels were determined by flame atomic emission spectroscopy (Perkin Elmer 460, Überlingen, Germany); R_2O_3 (Fe, Al and Ti oxides) was determined by gravimetry (precipitation in the solution and calcination); sulphates (SO_3) were evaluated by precipitation as $BaSO_4$ with a 10% (w/w) $BaCl_2$ solution; SiO_2 was determined by weight difference of the sample (final − initial

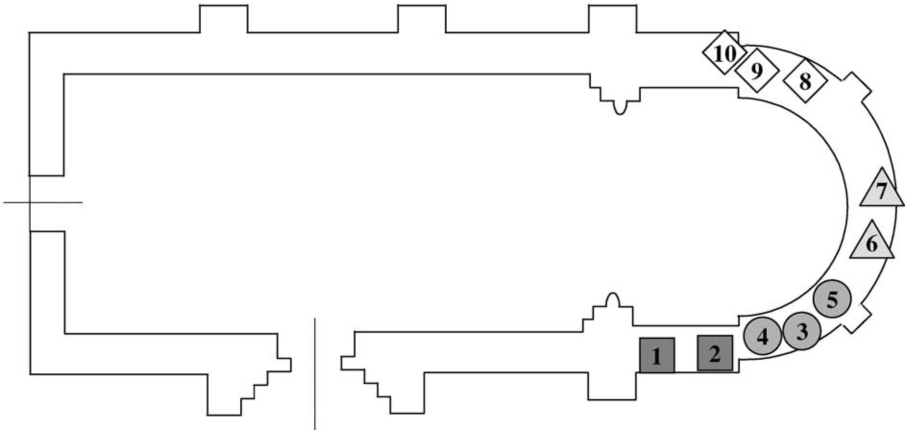

Fig. 1. Plan of Santa María de Zamarce. Sampling areas.

weight) after treatment in platinum crucible with HF (40%, w/w) and a few drops of H_2SO_4.

The mineralogical phases contained in the samples were determined by means of XRD, that was undertaken using a Bruker D8 Advance diffractometer (Karlsruhe, Germany), according to the diffraction powder method, with a Cu Kα1 radiation and 0.02 increment and 1 s/step, sweep 2–90, $2\theta/°$.

The DTA–TGA were carried out using a simultaneous TGA–sDTA 851 Mettler Toledo (Schwerzenbach, Switzerland) thermoanalyser, using alumina crucibles, with holed lids, at $20\,°C\,min^{-1}$ heating rate, under static air atmosphere, from ambient temperature to 1050 °C.

The standard mixtures were prepared using chemical reagents that figure next:

- C (calcite): $CaCO_3$ calcium carbonate PA Merck Ref. 2066;
- Q (quartz): SiO_2 silicon dioxide from sea sand washed QP Panreac Ref. 1214;
- P (Portlandite): $Ca(OH)_2$ calcium hydroxide PA Merck Ref. 2047;
- MgO (Periclase): MgO magnesium oxide PA Merck Ref. 5865;
- HY: $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$ hydrated magnesium carbonate hydroxide PA Merck Ref. 5827.

Simulated standards were prepared according to weight ratios indicated: pure HY; HY + C (1:1); HY + C (1:2); HY + C (1:3); HY + C (1:4); HY + C (1:5); HY + C + Q (1:1:1); HY + C + Q (1:6:12); HY + Q (1:1); HY + Q (1:2); HY + P (1:1); HY + P (1:2); HY + P + Q (1:6:12); HY + MgO (1:1); HY + MgO (1:2); HY + MgO (2:1). After weighing the required amounts of the components, they were intimately mixed in an agate mortar, and they were transferred to sealed glass containers in order to avoid hydrations and carbonations.

3. Results and discussion

3.1. Study of Santa María de Zamarce ancient mortars

3.1.1. Chemical and XRD studies

Table 1 shows the results of the chemical analysis of the samples of mortars of Santa María de Zamarce. Table 2 shows the results of XRD patterns of the same samples. Main components of these samples are calcium carbonate as crystalline phase of calcite (calcium oxide and calcination loss, in the chemical analysis), silicon dioxide as α-quartz, and calcium and magnesium carbonate (oxides of calcium and magnesium and calcination loss, in the chemical analysis), that appears identified as dolomite in XRD pattern.

Z1 and Z2 samples of Santa María de Zamarce present significant amounts of gypsum (calcium sulphate dihydrate) in the study by XRD. Chemical analysis confirms this presence, with a sulphate (SO_3) content of 1.44 and 6.52%, respectively. Other phases as bassanite [$CaSO_4{\cdot}0.5H_2O$ ICDD 41-0224] and

Table 1
Chemical analysis of the main components of the mortars of Santa María de Zamarce[a]

Sample	Loss[b]	SiO_2[c] (%)	CaO (%)	MgO (%)	R_2O_3[d] (%)	SO_3 (%)	Na_2O (%)	K_2O (%)
Z1	23.97	35.27	16.38	10.18	10.00	1.44	0.60	1.26
Z2	13.88	51.33	14.08	3.52	8.18	6.52	0.77	1.33
Z3	30.45	23.11	30.56	4.82	9.15	0.92	0.50	0.90
Z4	30.50	31.79	22.48	9.35	4.06	0.41	0.11	0.21
Z5	45.56	3.08	34.39	14.32	1.53	0.61	0.24	0.31
Z6	26.32	34.93	26.84	3.53	7.66	0.10	0.07	0.18
Z7	24.67	38.03	26.88	2.53	7.56	0.37	0.22	0.67
Z8	42.97	3.46	36.35	15.63	0.64	0.33	0.24	0.10
Z9	35.10	18.04	34.83	5.33	5.57	0.58	0.24	0.41
Z10	43.33	2.07	36.57	13.57	3.44	0.24	0.04	0.04

[a] Sodium carbonate–borax alkaline flux. Percentages related to original dry mortar.
[b] Loss indicates the loss due to calcination at 975–1000 °C.
[c] The percentages of SiO_2 refers to the total silica in the sample.
[d] R_2O_3 expresses the percentage of Fe, Al and Ti as oxides.

anhydrite [$CaSO_4$ ICDD 37-1496] appear in very scarce quantity. The presence of small quantities of gypsum could indicate its incorporation as an additive, with functions already highlighted in the literature (gypsum rends the lime mortar more white and increase the plasticity and the adherence of the mortar) [17]. Also this presence can indicate a certain degree of sulphatation of the carbonated material [18]. And, of course, it could be incorporated to the mortar through the aggregate that would have a certain amount of phases of gypsum in its composition.

However, the primary origin of the gypsum phases most probably should not be the limestone source of the binding material, because it could not have rehydrated to form $CaSO_4{\cdot}2H_2O$ after have been heated till near 1000 °C in the calcination of the limestone [17].

They are also observed by means of XRD clay minerals coming from some impurities, so much derived from the binder as from the aggregate. Their determination has been complicated because [19]:

i) The most intense diffraction peaks of most of these compounds appear within a narrow range, and generally the samples contain mixtures of these compounds in different proportions.
ii) The small quantity usually present means that either the diffraction peaks may not have stood out enough, or they may have been masked by the main components.

However very scarce quantity of muscovite [$(K_{0.94}Al_{1.96})(Al_{0.95}Si_{2.85}O_{10})((OH)_{1.744}F_{0.256})$], anorthite [$Ca(Al_2Si_2O_8)$] and anorthoclase [$(Na_{0.85}K_{0.15})(AlSi_3O_8)$] can be seen. Other clay minerals appear in a lower amount than the previously mentioned, as albite [$Na(AlSi_3O_8)$ ICDD 76-898], feldspar [$(Na_{0.5}K_{0.5})AlSi_3O_8$ ICDD 84-710], kaolinite [$Al_2(Si_2O_5)(OH)_4$ ICDD 83-0971], and illite [$K_{0.5}(Al, Fe, Mg)_3(Si, Al)_4O_{10}(OH)_2$ ICDD 09-0343], in some samples.

The important heterogeneity of the studied samples, as can be seeing through the chemical analysis and the XRD, may be highlighted:

- There are samples with calcite and quartz as main components, but with significant presence of dolomite, that reveals the dolomitic origin of the raw limestones (samples Z1, Z2, Z6, Z7, Z9).
- In other samples, the dolomite appears as the main phase (Z4, Z5, Z8, Z10), in fact with variable amounts of other important mineralogical phases.
- And even in the sample Z3 appears dolomite only in traces, the hexagonal calcite being the main mineralogical phase.

It can also be observed by means of XRD the presence of other magnesium carbonates different to dolomite, although in amount of traces. Usually nesquehonite [$(MgCO_3{\cdot}3H_2O)$ ICDD 20-0669] appears but, in some cases could be HY [$(Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O)$ ICDD 70-1177] or, less probably, artinite [$(Mg_2CO_3(OH)_2{\cdot}3H_2O)$ ICDD 06-0484].

In any event, none of these compounds are clearly appreciated by XRD. It could be made the hypothesis

Table 2
Results of XRD in mortars of Santa María de Zamarce[a]

Sample	α-Quartz (SiO_2) ICDD 85–798	Calcite ($CaCO_3$) ICDD 05–0586	Dolomite ($CaMg(CO_3)_2$) ICDD 36–0426	Gypsum ($CaSO_4 \cdot 2H_2O$) ICDD 21–0816	Muscovite ($K_{0.94}Al_{1.96}$) ($Al_{0.95}Si_{2.85}O_{10}$) ($(OH)_{1.744}F_{0.256}$) ICDD 86–1386	Anorthite Ca ($Al_2Si_2O_8$) ICDD 76–948	Anorthoclase ($Na_{0.85}K_{0.15}$) ($AlSi_3O_8$) ICDD 75–1635
Z1	*[b]	*	S[c]	T[d]	–[e]	T	–
Z2	**[f]	*	S	S	T	T	S
Z3	*	**	T	–	–	T	S
Z4	*	S	*	–	–	T	T
Z5	T	S	**	–	–	–	–
Z6	*	*	S	–	T	T	–
Z7	*	*	S	–	T	T	T
Z8	T	*	**	–	–	–	–
Z9	*	**	S	–	–	T	–
Z10	T	*	**	–	–	–	–

[a] >75%.

[b] 20–50%.

[c] Small amount (5–20%).

[d] Traces (<5%).

[e] Undetectable.

[f] 50–75%.

that they are not in a very crystalline state and/or they are present in a very scarce amount.

Contrary to what are pointed out in some works of the literature of dolomitic mortars [6–8], HY do not appear clearly in the XRD study.

3.1.2. Thermal studies

Initial tests carried out with standards in several experimental conditions (type of crucible, atmosphere and heating rate), show the included conditions as the most appropriate for this type of materials (alumina crucible covered with a holed lid of alumina, heating rate 20 °C min^{-1} in static air atmosphere). The use of an alumina holed lid on the crucible has shown great importance as can be seen later on. The summarised results of the thermal analysis are collected in Table 3.

Sample Z1 (Fig. 2) presents a DTA curve characterised by two important endothermic peaks, with associated weight losses at ca. 145 °C and at ca. 850 °C. First of them appears as a doublet (clearly visible in the DTG curve) at 130 and 150 °C. This doublet could be associate, besides a possible loss of moisture, to the dehydration of the gypsum ($CaSO_4{\cdot}2H_2O$) that takes place in two stages (Eqs. (1) and (2)) [20]:

$$\mathrm{CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot \tfrac{1}{2}H_2O + \tfrac{3}{2}H_2O}, \quad T^{a} \approx 162\,^{\circ}\mathrm{C} \tag{1}$$

$$\mathrm{CaSO_4 \cdot \tfrac{1}{2}H_2O \rightarrow CaSO_4 + \tfrac{1}{2}H_2O}, \quad T^{a} \approx 174\,^{\circ}\mathrm{C} \tag{2}$$

Table 3

Summary of the results of the thermal analysis (DTA, TG and DTG curves) (associate compounds to the thermal events)

Samples	Curve	Approximate temperatures (°C)						Other effects
		145	320	440, 510 and 530	573	700	900	
Z1	DTA[a]	↓	vs↓	–	vs↓	s↓	↓	–
	TG[b]	↓	vs↓	–	–	s↓	↓	–
	DTG[c]	Doublet (130, 50)	–	–	–	Peak	Peak	–
	Compounds	G	N?	–	Q	D	C	–
Z2	DTA	↓	–	–	s↓	vs↓	↓	see text
	TG	↓	–	–	–	vs↓	↓	see text
	DTG	Doublet (162,176)	–	–	–	Peak	Peak	see text
	Compounds	G	–	–	Q	D	C	see text
Z3	DTA	↓	–	–	vs↓	vs↓	↓	–
	TG	s↓	–	–	–	vs↓	↓	–
	DTG	Peak	–	–	–	Peak	Peak	–
	Compounds	G	–	–	Q	D	C	–
Z4, Z5	DTA	vs↓	vs↓	–	–	↓	↓	–
	TG	vs↓	vs↓	–	–	↓	↓	–
	DTG	Peak	–	–	–	*Doublet (690, 730)	Peak	–
	Compounds	Traces of G	N?	–	–	* see text	C	–
Z6, Z7, Z9	DTA	–	vs↓	–	vs↓	vs↓	↓	–
	TG	–	vs↓	–	–	vs↓	↓	–
	DTG	–	Peak	–	–	–	Peak	–
	Compounds	–	Clay minerals	–	Q	Traces of D	C	–
Z8, Z10	DTA	vs↓	–	–	–	↓	↓	–
	TG	–	–	–	–	↓	↓	–
	DTG	–	–	–	–	Peak	Peak	–
	Compounds	Traces of G?	–	–	–	D	C	–

[a] TA curves: ↓, endothermic peak; s↓, slight endothermic peak; vs↓, very slight endothermic peak; –, no phenomenon observed.

[b] TG curves: ↓, weight loss; s↓, slight weight loss; vs↓, very slight weight loss; –, no weight loss observed.

[c] Compounds: G, gypsum; N, nesquehonite; Q, quartz; D, dolomite; C, calcite.

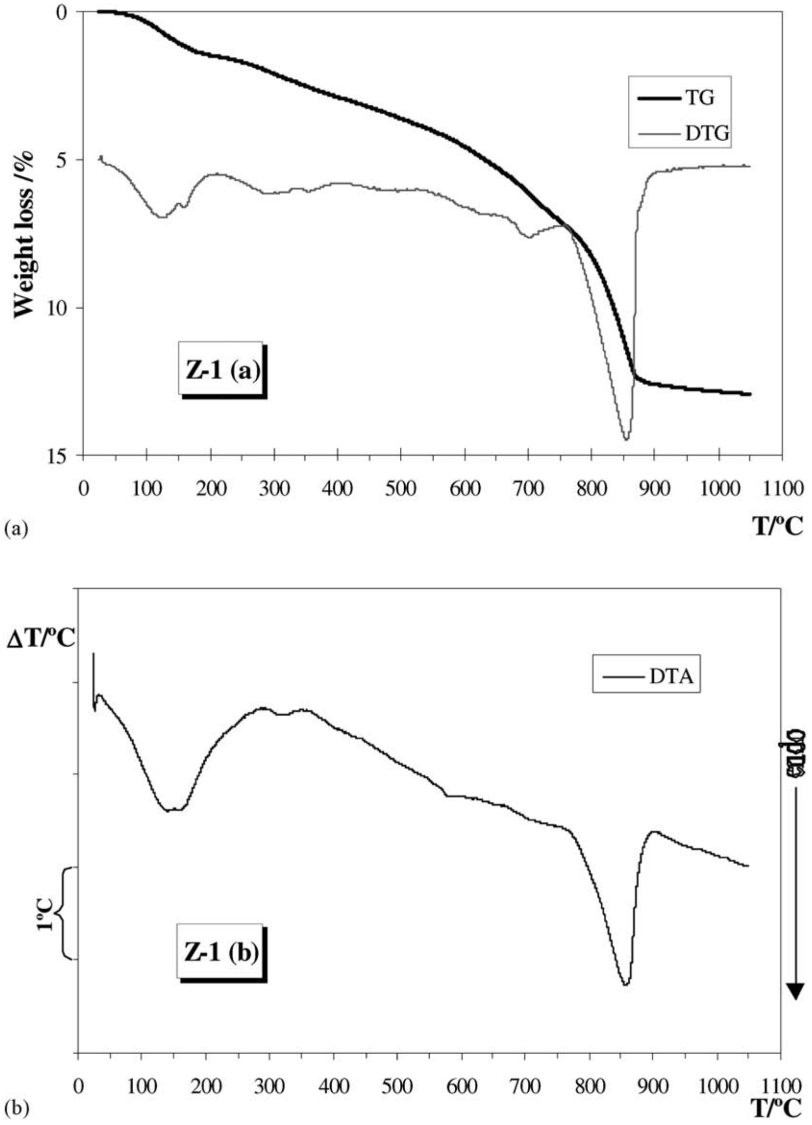

Fig. 2. (a) TG and DTG curves; (b) DTA curve from Z1 sample.

The second one would be associate to the decarbonation of the calcite and the weight loss has been related to the CO_2 evolution from the structure (Eq. (3)) [21]:

$$CaCO_3 \rightarrow CaO + CO_2, \quad T^a \approx 860\,^{\circ}C \tag{3}$$

Besides these two important endothermic peaks, other peak at ca. 700 °C can be observed. This peak could correspond to the thermal decomposition of the dolomite, $CaMg(CO_3)_2$ [22,23] determined by means of XRD, although in small amount. The peak could correspond to decomposition of the $MgCO_3$ from the dolomite, the weight loss being due to the CO_2 evolution. At the same temperature (850 °C) that the $CaCO_3$ from the calcite, the remaining calcium carbonate from the dolomite lattice could lose the CO_2; so the peaks appear overlapped [21].

In the DTA curve, an endothermic peak without associated weight loss has been observed at 573 °C.

This peak could be related with the transformation (Eq. (4)):

$$\alpha\text{-Quartz} \rightarrow \beta\text{-Quartz}, \quad T^{a} \approx 573\,^{\circ}\mathrm{C} \qquad (4)$$

The energy involved in this polymorphous inversion is small; obviously the corresponding endothermic peak is also very small [24].

The weight loss associated with the endothermic peak at approximately 145 °C is, nevertheless, too important for the amount of gypsum determined in the sample (by XRD and chemical analysis—percentage of SO_3). Therefore, in this same range of temperatures, it could have other weight losses corresponding to other compounds. For example $Mg(HCO_3)(OH)\cdot 2H_2O$ (nesquehonite, $MgCO_3\cdot 3H_2O$), that appears in the XRD pattern in scarce amounts ($<5\%$). This substance loses two molecules of water around 200 °C, and it could be the cause of the increase of weight loss. This compound has been pointed out as one of the possible resultants of the $Mg(OH)_2$ carbonation [21].

Either the endothermic effects at 440 and 530 °C for HY or the exothermic peak with weight loss associated at 510 °C have not been observed [21]. The presence of HY in this mortar has not been determined by means of thermal analysis. This result shows an agreement with XRD determination.

In the thermal studies of the sample Z2 similar results were obtained (Table 3). Gypsum, quartz and calcite clearly show their thermal effects. Dolomite is present in small amount and apparently not very crystalline, as the irregularity of the curve shows, but the endothermic peak in DTA curve can be determined.

A last endothermic peak between 900 and 1000 °C, with associated weight loss, has been observed in the study. There are two possible explanations for this endothermic effect:

i) The muscovite $(K_{0.94}Al_{1.96})(Al_{0.95}Si_{2.85}O_{10})((OH)_{1.744}F_{0.256})$ detected by XRD releases structural water at 900 °C, breaking the crystal lattice [20].
ii) After melting, NaCl and KCl evaporate at these temperatures, what would justify the weight loss and the high contents of Na and K determined by the chemical analysis [8,20].

Although the first hypothesis is qualitatively sound with the XRD results, quantitatively it seems an excessive weight loss for the detected muscovite by XRD. So, perhaps, the effect can be due to the combination of the two hypothesis.

In the study of Z3 sample, gypsum in small amount, quartz and calcite have been also showed their endothermic effects. In the study by XRD, dolomite appears in amount of traces. The weight loss observed at ca. 700 °C could be due, as in the previous sample, to the $MgCO_3$. The remaining $CaCO_3$ should have foreseeably overlap with the peak of calcite decomposition.

In connection with the samples Z4 and Z5 (Table 3), traces of gypsum could be present. The weight loss around 320 °C (sample Z5, Fig. 3) could be attributed to the dehydration of some magnesium carbonate that could have been formed, as for example the nesquehonite, $MgCO_3\cdot 3H_2O$ (determined in traces by XRD). The endothermic peak in DTA curve is not well defined, hence the material could have a poor crystallinity.

The three endothermic peaks at ca. 690, 730 and 900 °C (Fig. 3) could be justified for a dolomite with a poor crystallinity, like a dolomitised magnesite or a mixture of magnesium and calcium carbonates, due to the decrease of the characteristic initial temperature of the first peak of dolomite and to the appearance of a relatively erratic weight loss. The absence of magnesite phases (Table 2, results of XRD), the typical presence of dolomite in magnesium limestones (and not of magnesite), and the consideration of the poor crystallinity of the material, take better to think therefore on a poor crystallinity dolomite [21].

Thermal studies of the samples Z6, Z7 and Z9, with calcite and quartz as main phases, and a little amount of dolomite, show an agreement with the studies by XRD and chemical analysis. The presence of small amounts of clay minerals as muscovite, illite and kaolinite, determined by XRD, could justify the high contents of R_2O_3 (Al_2O_3, Fe_2O_3 and TiO_2) in these samples in the chemical analysis results, and the partial loss of the water of these compounds around 300 °C.

In the study of the samples Z8 and Z10, two endothermic peaks, with associated weight losses, have been determined. The peaks could correspond to the decomposition of $MgCO_3$ of the dolomite, very abundant in the sample, around 800 °C, and to the decomposition of the $CaCO_3$ coming from the calcite and the dolomite, which decompose at the same temperature

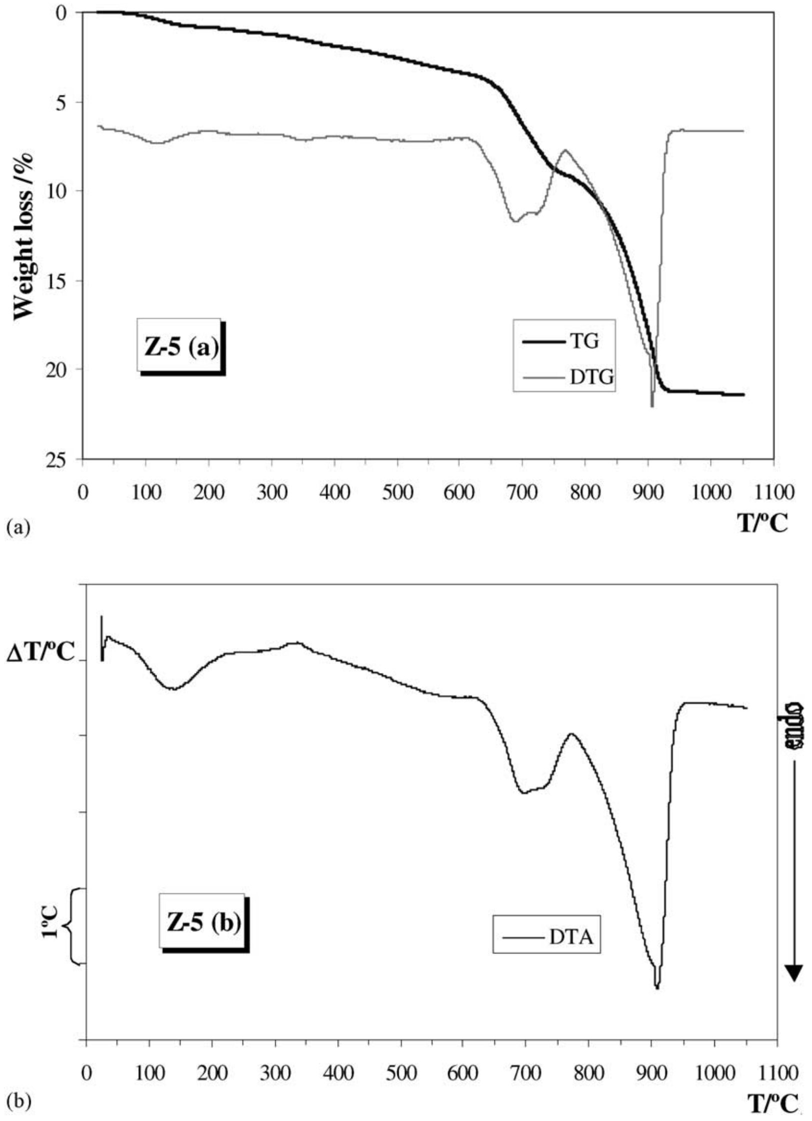

Fig. 3. (a) TG and DTG curves; (b) DTA curve from Z5 sample.

and justify the absence of a point of inflection, around 900 °C.

3.2. Preparation and study of simulated standards

As it has already been pointed out, contrary to what it is noticed in several works of specialised literature [6–8,13,25], that it has not been able to determine the presence of HY in mortars of dolomitic origin of Santa María de Zamarce. It has motivated the preparation of samples with different mixtures of typically present compounds in limestone or dolomitic mortars. The aim of the preparation of these mixtures was to clarify the sensitivity and specificity of the analytical techniques used in the study for the determination of HY (XRD and TGA–DTA, mainly). According to the results, the preliminary conclusion of the absence of HY in mortars of Santa María de Zamarce could be

Table 4
Simulated standards (weight ratios) and XRD results

Simulated standards	Hydromagnesite (HY) $Mg_5(CO_3)_4{\cdot}(OH)_2{\cdot}4H_2O$ ICDD 70–1177	Calcite (C) ($CaCO_3$) ICDD 05–0586	α-Quartz (Q) (SiO_2) ICDD 85–798	Portlandite (P) ($Ca(OH)_2$) ICDD 44–1481	Periclase (MgO) ICDD 45–0946
Pure HY	***[a]	–[b]	–	–	–
HY + C (1:1)	*[c]	**[d]	–	–	–
HY + C (1:2)	S[e]	***	–	–	–
HY + C (1:3)	T[f]	***	–	–	–
HY + C (1:4)	T	***	–	–	–
HY + C (1:5)	–	***	–	–	–
HY + C + Q (1:1:1)	S	**	*	–	–
HY + C + Q (1:6:12)	–	**	*	–	–
HY + Q (1:1)	**	–	*	–	–
HY + Q (1:2)	*	–	**	–	–
HY + P (1:1)	*	T?	–	**	–
HY + P (1:2)	S	T?	–	***	–
HY + P + Q (1:6:12)	–	T	**	*	–
HY + MgO (1:1)	**	–	–	–	**/*
HY + MgO (1:2)	*	–	–	–	**
HY + MgO (2:1)	**	–	–	–	*

[a] >75%.
[b] Undetectable.
[c] 20–50%.
[d] 50–75%.
[e] Small amount (5–20%).
[f] Traces (<5%).

considered or not as definitive. The prepared mixtures and their proportion (w/w) are presented in Table 4, together the semiquantitative results of XRD.

3.2.1. *XRD studies*

The obtained results show that it is really possible to determine HY by means of XRD (70–1177 ICDD standard, pure HY). Nevertheless when HY is mixed with other compounds, the intensity of its peaks of diffraction is very weak, being undetectable in some cases [HY+C (1:5), HY+C+Q (1:6:12), HY+P+Q (1:6:12)] (as example, Fig. 4 shows XRD patterns of the mixtures of HY + C, with the gradual decrease of the intensity of the HY diffraction). This event had been already indicated in a previous work [13]. In this paper, Bruni et al. explain that, in comparison with the calcite specially, the poor crystallinity of the HY is the cause of the weak intensity of the peaks, emphasising that the HY peaks could not be detected in small amounts. Actually, in the present work, when calcite is present, the attenuation of the HY peaks is so high that the peaks are undetectable or almost undetectable for amounts in weight between 20 and 16% [(HY + C (1:4) and (1:5)]. This fact could be justified by the poor crystallinity of the hydroxisal and the large presence of hydrogen atoms by weight formula.

So, the results of XRD of the samples of Santa María de Zamarce can not be considered definitive to verify the absence of HY in these mortars, because relatively large amounts could escape to the detection by XRD, especially considering that calcite is present in all those mortars. Surprisingly, the previously cited works [7,8] have not shown problems in the determination of HY by XRD in samples with important contents of calcite.

3.2.2. *Thermal studies*

In connection with thermal analysis, Dheilly et al. [7] have not used it in their work. A different thermal behaviour between the pure HY and the samples of ancient mortars studied has been observed by Vecchio et al. [8]. The authors have determined a sharp exothermic peak at 500 °C in pure HY. The authors

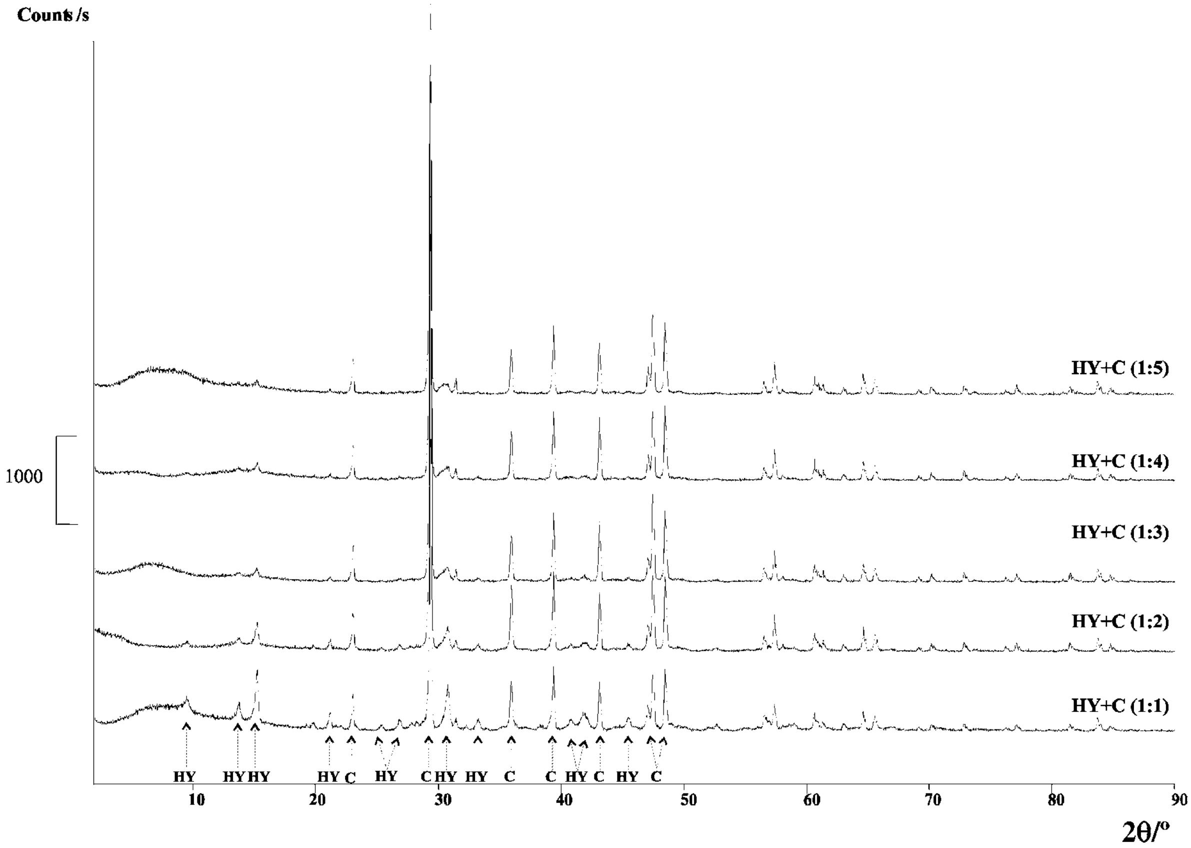

Fig. 4. XRD patterns from (HY) + calcite (C) prepared mixtures in their different weight ratios.

have related it to the crystallisation of a mixed oxocarbonate phase ($x\mathrm{MgCO_3}\cdot y\mathrm{MgO}$). Thermal analysis of pure HY (Fig. 5) is similar to that obtained by these authors and other bibliographical references [14,21]. It can be observed the exothermic peak at ca. 500 °C.

DTA curves of samples from ancient mortars studied by Vecchio et al. [8] have not presented the exothermic peak of HY at 500 °C. The behaviour of mixtures of HY and calcite in different proportions has been used by the authors in order to explain the absence of this sharp exothermic peak. They have indicated that the presence of impurities (chlorides or calcium compounds) hinders the crystallisation of the oxocarbonate phase ($x\mathrm{MgCO_3}\cdot y\mathrm{MgO}$), during the HY thermal decomposition. In the referred study, samples with molar relations Ca/Mg greater than 2 have been shown.

In this regard it is possible to make the following considerations:

i) One of the references of the work by Vecchio et al. [8] is a study about the thermal decomposition of HY made by Sawada et al. [14]. The work by Sawada et al. has not related the crystallisation of a magnesium oxocarbonate phase as responsible of the exothermic peak at 500 °C. In accordance with Sawada et al., the exothermic peak must be the consequence of the crystallisation of an amorphous phase of $\mathrm{MgCO_3}$. No crystallisation of MgO is responsible for the exothermic phenomenon.

ii) The effect of calcium impurities, calcite for example, on the occurrence of the exothermic peak at least is debatable. Some mixtures prepared

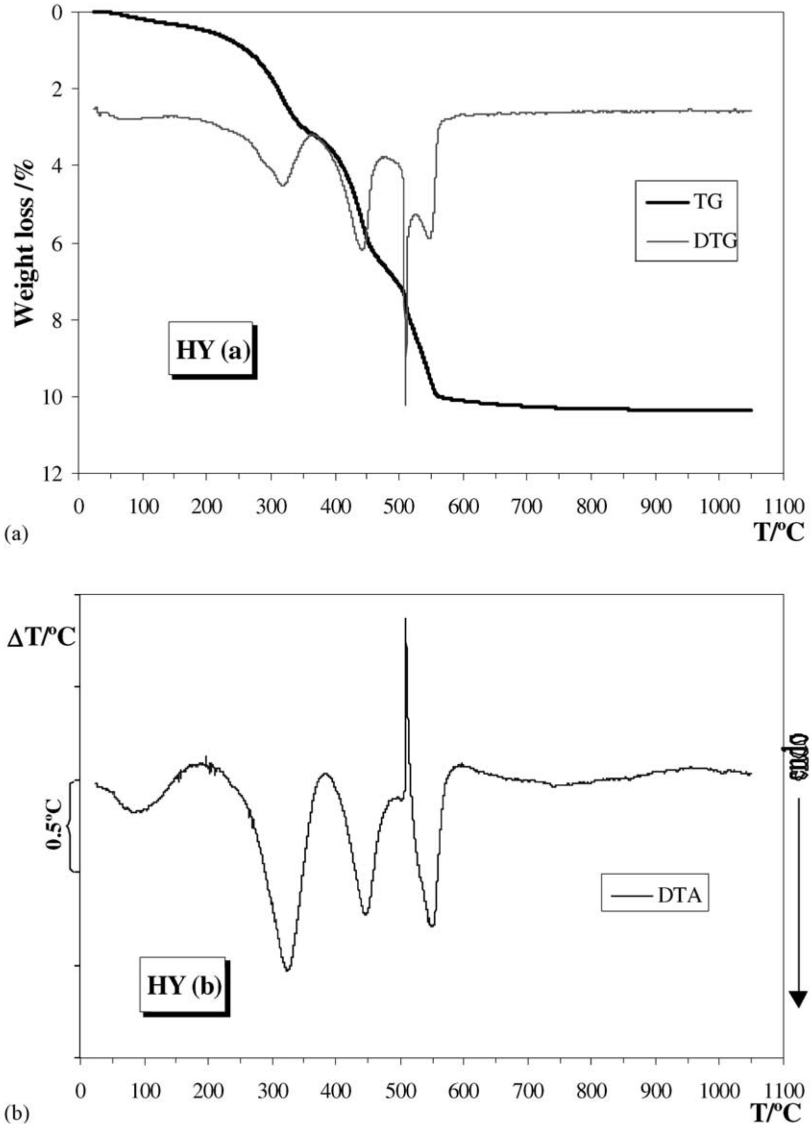

Fig. 5. (a) TG and DTG curves; (b) DTA curve from pure HY.

in the work by Vecchio et al. (HY + C (1:1) and (1:2)) [8] have shown the exothermic peak clearly. The samples studied in the present work allow to observe the exothermic peak at 500 °C in all cases (Table 5). Even being mixtures with low weight percentage of HY with respect to calcite (molar relationships Mg:Ca (1:4) or less), and also with regard to other present phases. In all cases, the exothermic peak at 500 °C is observed. As example, the mixture HY + C (1:5) is showed; it can be seen that the thermal phenomena corresponds to the HY (endothermic at 320, 440 and 550 °C, and exothermic at 510 °C) and the calcite (decomposition at 800–900 °C) (Fig. 6).

iii) This exothermic crystallisation of $MgCO_3$ usually is accompanied of a rapid evolution of carbon dioxide by decomposition of the $MgCO_3$ formed. This decomposition is strongly depen-

Table 5
Simulated standards (weight ratios) and DTA results

Simulated standards	Temperature (°C)							
	320	400	440	480	510	530	573	900
Pure HY	↓[a]	–[b]	↓	–	↑[c]	↓	–	–
HY + C (1:1)	↓	–	↓	–	↑	↓	–	↓
HY + C (1:2)	↓	–	↓	–	↑	↓	–	↓
HY + C (1:3)	↓	–	↓	–	↑	↓	–	↓
HY + C (1:4)	↓	–	↓	–	↑	↓	–	↓
HY + C (1:5)	s↓[d]	–	s↓	–	↑	↓	–	↓
HY + C + Q (1:1:1)	↓	–	↓	–	↑	↓	↓	↓
HY + C + Q (1:6:12)	s↓	–	s↓	–	↑	↓	↓	↓
HY + Q (1:1)	↓	–	↓	–	↑	↓	↓	–
HY + Q (1:2)	↓	–	↓	–	↑	↓	↓	–
HY + P (1:1)	↓	–	↓	↓	↑	↓	–	↓
HY + P (1:2)	↓	–	↓	↓	↑	↓	–	↓
HY + P + Q (1:6:12)	↓	–	↓	↓	↑	↓	↓	↓
HY + MgO (1:1)	↓	↓	↓	–	↑	↓	–	–
HY + MgO (1:2)	↓	↓	↓	–	↑	↓	–	–
HY + MgO (2:1)	↓	↓	↓	–	↑	↓	–	–

[a] Endothermic peak.
[b] No peak.
[c] Exothermic peak.
[d] Slight endothermic peak.

> dent of the temperature; a slight increase of the sample temperature leads to a drastic increase in the decomposition rate [14].

A weight loss due to the aforementioned fact, immediately after the exothermic phenomenon, has been observed in the samples analysed in the present work.

Bruni et al. [6] have also used the thermal analysis as method of identification of phases, specifically HY, on five samples of different centuries taken in different restoration works. In this work, four endothermic peaks at 250, 350, 410 and 480 °C have been mentioned. The authors have ascribed these peaks to the dehydration of the HY, to the loss of hydroxyl water in the HY, to the decomposition of carbonate of HY, and to the decomposition of the magnesite, respectively. These attributions of the endothermic peaks are, partly, similar to the observed ones by Webb and Krüger [21] who take into account as well a work of Beck [26] also cited by the authors.

Avoiding the differences in the temperatures of decomposition, which depend of some factors as the degree of crystallinity and the grain size of the sample, it can indicate that the work of Bruni et al. [6] says nothing about the absence of the exothermic peak at ca. 500 °C.

The attribution of loss of hydroxyl water at ca. 350 °C, after occurring the dehydration at ca. 250 °C, is also questionable. Sawada et al. [14], by means of differential thermal gas analysis (DTGA) and DTA have determined in HY a dehydration at 100–300 °C, and three decarbonation stages at high CO_2 pressure (P_{CO_2}), at ca. 350–510, 520 and 530–650 °C. At low P_{CO_2}, only one decarbonation peak in DTGA has been observed. Moreover, the authors have indicated a change of the HY structure after the complete dehydration, with the appearance of an amorphous diffraction pattern. At approximately 500 °C the specimen was formed by crystalline MgO (crystallite size ca. 50 Å) and an amorphous phase including magnesium carbonate. The composition was approximately $2.6\,MgCO_3{\cdot}3.2\,MgO$. As it has been pointed out, the transformation of $MgCO_3$ from the amorphous phase to the crystalline phase could be responsible for the sharp exothermic peak.

The results of Beck [26] had already been questioned by Sawada et al. [14]. The attributions of

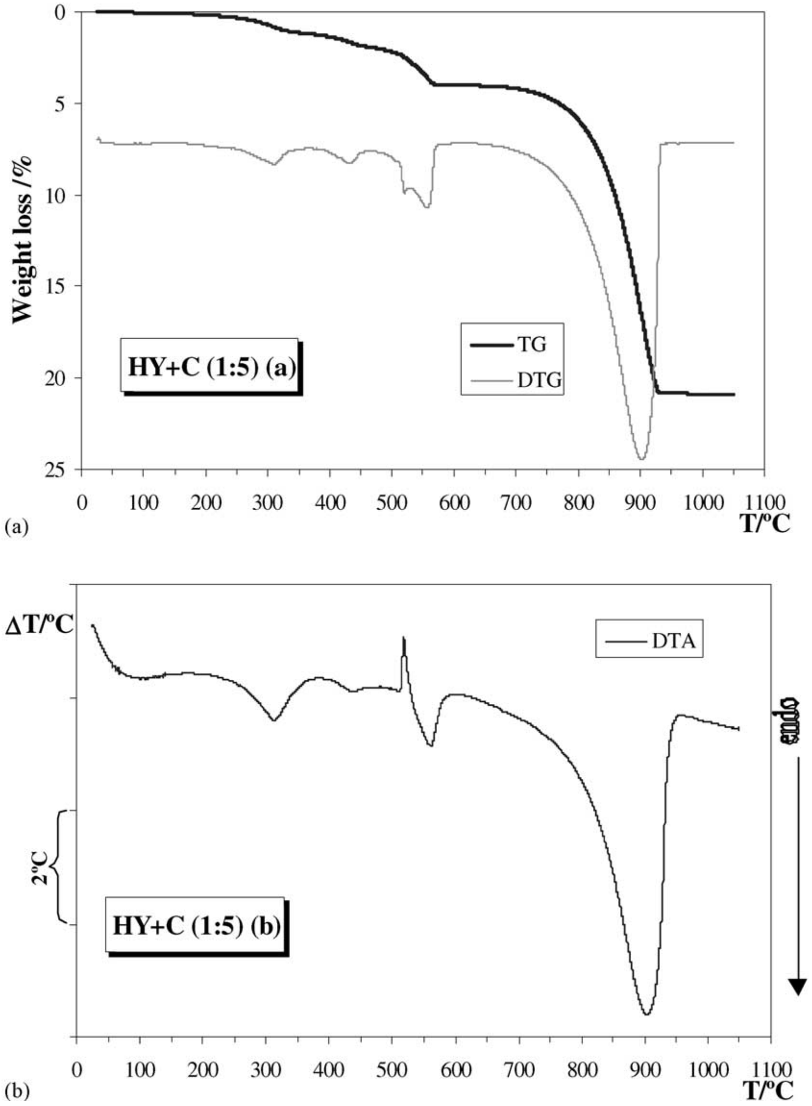

Fig. 6. (a) TG and DTG curves; (b) DTA curve from HY + C (1:5) sample.

endothermic peaks made by Fiori and Macchiarola [25] are equally debatable.

After these considerations it arises the question if the thermal studies are useful to verify the presence of HY in ancient binding materials. The experimental conditions seem to be very important. On this matter it can be indicated:

i) Sawada et al. [14] have studied the thermal HY decomposition in two experimental conditions: one with low CO_2 pressure ($P_{CO_2} = 0.00$ bar), and another one with high CO_2 pressure ($P_{CO_2} = 0.50$ bar). For the occurrence of the exothermic phenomenon at ca. 500 °C a high P_{CO_2} was required, as well as for the occurrence of the three stages of HY decarbonation.

ii) In the simplest case, this high P_{CO_2} can be applied externally. But, in addition to this, the authors set out the establishment of this high P_{CO_2} around the sample (self-generated atmosphere), when the sample powder was densely packed or the heating rate exceeded the rate of ventilation.

iii) In the present work, these experimental conditions have been guaranteed with a static air atmosphere, the packed sample and a high heating rate (20 °C min^{-1}). Furthermore alumina crucibles have been used with holed lids. The obtained results in the studied samples have been satisfactory.

iv) The identification of the set of phenomena of thermal HY decomposition (including the exothermic phenomenon) and other present phases, has been possible in all the studied simulated standards. Practically significant displacements in the temperatures of the different thermal phenomena have not taken place, in accordance with literature data [14,21].

3.3. Discussion

Regarding the obtained results, the determination of HY in prepared specimens has been possible even in samples with small percentage of HY. (Fig. 6 shows the set of phenomena of thermal decomposition of HY in the DTA curve of HY + C (1:5), with scarce amount of HY.) In the experimental conditions considered in this work, the ability of the thermal studies, in order to identify the different present phases in a dolomitic binding material, has been checked. It can be confirmed the absence of HY, at least in significant amounts, in the analysed ancient mortars of Santa María de Zamarce, since the thermal characteristic phenomena of HY have not been observed.

The variability in the showed results in previous works of other authors could be due to different experimental conditions, especially the heating rate and the experimental atmosphere [15].

On the other hand, the absence of HY in ancient dolomitic binding materials of Santa María de Zamarce is surprising. HY has been referred in dolomitic mortars by several authors [6–8,13,25]. Some hypothesis can be considered:

i) In some cases found in the bibliography, it could be nesquehonite ($MgCO_3 \cdot 3H_2O$), with similar losses in those ranks of temperatures, the referred phase instead of HY. Nevertheless, the small amount present in the studied mortars as well as some contradictory results of the literature have complicated this discussion.

ii) The absence of HY in these materials could be justified if it considers the addition of dolomite as aggregate. On this supposition, dolomite would have not undergone previous burnt; therefore during the setting HY would have not formed.

This hypothesis contrasts with (a) the occurrence of one silica aggregate in the samples, (b) the occurrence of samples in which dolomite is the main present phase, (c) the difficulty to have a pure lime in order to be used as binder, and a dolomitic lime in order to be used as aggregate, because usually raw materials available "in situ" were used. Regarding this matter, this hypothesis is very unlikely [10].

iii) It could be put forward the occurrence of dolomite phases as a result of a poor burning process of dolomitic limestone, but it could not justify either the behaviour of the burned fraction or some of the aforementioned problems [10].

Finally, without putting into question the occurrence of HY in dolomitic mortars, its presence in the samples of Santa María de Zamarce studied in this work has not been established, at least in significant amounts. Perhaps the required conditions of preparation of these ancient binding materials were specific, or the raw material was different. On this matter, in the work by Dheilly et al. [7] HY has been obtained after curing in excess of CO_2. The conclusions of the work by Bruni et al. [6] about the carbonation of lime with $Mg(OH)_2$ and the work by Vecchio et al. [8] about the determination of phases are partly questionable. Therefore, there will be necessary further studies with the aim of clarify the reasons and the conditions of occurrence of HY in mortars of dolomitic origin.

4. Conclusions

All analysed ancient mortars of the church of Santa María de Zamarce and found that they are of dolomitic origin, dolomite, calcite and quartz being the main mineralogical phases. It has not been possible to determine by XRD or TGA–DTA the occurrence of HY (hydrated magnesium carbonate hydroxide) in any of the studied mortars, either in its individual study or by comparison with standard mixtures.

On the contrary, the exothermic peak at ca. 500 °C which was observed in the HY thermal decomposition, due to the crystallisation of $MgCO_3$ from the amorphous phase, has been observed in the 16 standard samples, in the aforementioned experimental conditions. Even the samples with small weight percentage of HY have clearly shown the set of phenomena of HY thermal decomposition (including the exothermic peak at 510 °C).

By XRD, an important toning down of the intensity of the HY diffraction peaks has been observed when HY is mixed with calcium compounds (calcite and portlandite). Occasionally, with HY in relatively small amounts (even around 25% in w/w), its diffraction peaks could be masked. In this situation, the use of XRD in conjunction with TGA–DTA is very suitable.

The analysis of these standard samples has revealed as very adequate for the study of dolomitic binding materials the experimental conditions in TGA–DTA with a high P_{CO_2} around the sample (static air atmosphere, packed sample, high heating rate ($20\,^{\circ}C\,min^{-1}$) and alumina crucibles with holed lids).

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