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Characterization of monumental carbonate stones by thermal analysis (TG, DTG and DSC)

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Abstract

Thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC), were found to be suitable instrumental techniques for the study of monumental rocks because they need small amounts of sample and provide extensive qualitative and quantitative information. From DTG curves, the calcite/dolomite ratio in the samples as well as the differences between limestones and dolomites can be quantitatively determined. DSC curves are adequate for the identification of the degradation products in the monumental stones since they are usually salts (sometimes hydrates) which present first-order processes under 600°C. This technique makes it possible to carry out quantitative and semiquantitative analysis of the degradation of monumental rocks since it provides data about its mineralogic composition. © 1997 Elsevier Science B.V.

Keywords: Dolomites; Limestones; Monumental stones; Stone degradation; Thermal analysis

1. Introduction

Carbonate rocks are used in the construction of buildings and monuments. Most monuments forming the Spanish historical heritage, have been built with the limestone of the Hontoria (Burgos) quarry and the dolomites of the Laspra (Oviedo) and Bonar (León) quarries.

The alteration of stone is a natural and non-reversible process. 'Monumental' rocks show at present an accelerated rate of decay due to the proliferation of industrial pollution. Hence, it would be important to solve the so-called "harm of the stone". The way should be based on scientific insights and on previous experimental papers. Thus, any interventions for stone conservation must be preceded by a good diagnosis of the stone damage.

Crystallization of soluble salts in the construction materials is considered at present to be one of the most important decay mechanisms [1–3]. The presence of soluble salts not only disturbs the appearance of the rock fabric (when efflorescences appear on the surface) but induces crystallization within the pores causing significant damage to the stones. Thus, the desquamation, alveolization, disaggregation, etc., of the monuments stones due to the formation of crusts, plates, scales, etc. frequently show high levels of sulphates, chlorides, nitrates, etc., mainly of Ca, Na, K and Mg [4–6].

The main observed damage occurring in Europe is caused by the sulphonation of carbonaceous rocks

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(limestone, marble, dolomite), a chemical process which penetrates and progresses inside the stone from the surface [7]. This kind of deterioration consists in the formation of a fragile gypsum-calcite layer building up on the stone surface and characterized by the presence of oil-fired carbonaceous particles within the layer. These black particles, having a very large surface-to-volume ratio, are recognized to be the main agents of the observed chemical transformation [8].

Limestones are largely composed of calcite ($CaCO_3$). In the samples from the Hontoria quarry no other minerals were detected by X-ray or chemical analysis [9]. This stone is an extremely pure, white limestone. It is homogenous, white and sometimes has a very fine pink or yellow appearance which in air takes grey colour [9].

Dolomites are composed of dolomite and variable amounts of calcite. The Laspra dolomites present a uniform white colour (white-greyish) and those from Bonar have a colour ranging from cream to beige or ochre [10].

Carbonaceous rocks present a porous system with an intricate and variable structure [11] since their genesis involves a great variety of processes and they present a marked tendency to post-depositional changes (dissolution, cementation, etc.).

A classic quantitative chemical analysis needs a relatively large amount of sample to be dissolved (> 500 mg) in order to obtain the whole composition of the material. If we need to know the mineralogic composition, supplementary instrumental techniques must be used.

Instrumental techniques of thermal analysis (thermogravimetry (TG), derivative thermogravimetry (DTG) and differential scanning calorimetry (DSC)) are very adequate for the study of monumental rocks because they are rapid techniques, need small amounts of sample ($\sim$ 25 mg) and provide great qualitative and quantitative information [12–19].

In this paper, we apply the earlier experimental techniques to the study of monumental damaged or undamaged rocks in many monuments forming the Spanish historical heritage.

2. Experimental

The samples were powdered in an agate mortar and then dried at 110°C. Thermal analysis was performed in a Mettler Model TA 4000 and in a TC 11 TA Processor (TG 50, DSC 30; nitrogen atmosphere; rate of heating 5°C min^{-1} in TG and 10°C min^{-1} in DSC). The temperature of TG ranges from room temperature to 1000°C and the temperature of DSC ranges from room temperature to 600°C. The sample containers used for TG are made of alumina and the weight used is $\sim$ 35 mg. For DSC, the samples containers are made of aluminium and the weight used is $\sim$ 15 mg.

All chemicals used were of reagent grade. Calcium and magnesium were analyzed by EDTA complexometry. The rest of the cations (except NH_4^+) were determined by atomic absorption spectrometry using a Varian Spectra A 300 ($\lambda = 766.5$ nm for K and 589.0 nm for Na). The anions and some of the cations (alkalis and NH_4^+) were analyzed by HPLC, using a Waters instrument provided with a double-piston bomb (W^{TM} 600 controller) and a conductivity detector (W 431). Columns of cationic (Waters IC-$Pack^{TM}$ M/D 3.9×150 mm) and anionic (Waters IC-$Pack^{TM}$ HC 4.6×150 mm) ion exchange were used. In both cases the working mode is isocratic. For the cation analysis the eluent is AEDT 0.1 mM/3.0 mM HNO_3, with a flux of 1.0 ml min^{-1}. For the anion analysis the eluent is borate-gluconate, with a flux of 2.0 ml min^{-1}. In both cases, 100 μl of the standards and test solutions are injected. The software used for chromatography analysis is $Millenium^{TM}$ 2010.

The diffractometer used was a Philips PW Model 1729/1720 equipped with a graphite monochromator, a rate of 3° min^{-1} and CuK_α radiation ($\lambda = 1.5418$ Å).

3. Results and discussion

Limestone rocks are mainly constituted by calcite ($CaCO_3$) while dolomites comprise dolomite [$CaMg(CO_3)_2$] and variable amounts of calcite. Since the formula weights of $CaCO_3$ and $CaMg(CO_3)_2$ are different (100.09 and 184.4 g mol^{-1} respectively), the calcination at 900°C should give information about the nature of the sample: the limestone has a loss of weight of 43.97% and dolomite 47.73%. Nevertheless, this simple procedure shows two main problems: (a) the range of the parameter variation measured is very narrow (< 4% of weight loss) and (b) the value of the entire weight loss depends on the sample purity.

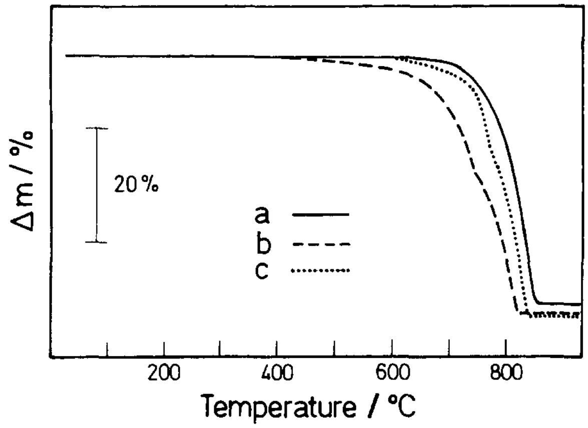

Fig. 1. Thermogravimetric curves (TG) of the quarry samples from: (a) Hontoria (limestone); (b) Laspra (dolomite); and (c) Bonar (dolomite).

Thermogravimetric curves of limestones and dolomites show a similar shape (Fig. 1) except small differences in the zone of decomposition temperature and in the kinetics of the process. These differences are more significant when the DTG curves of the samples are obtained. Experimental data (Fig. 2) indicate that DTG curves of the quarry limestones show only one peak with a minimum about 800°C while those of quarry dolomites present two peaks (not perfectly resolved) at 750 and 800°C.

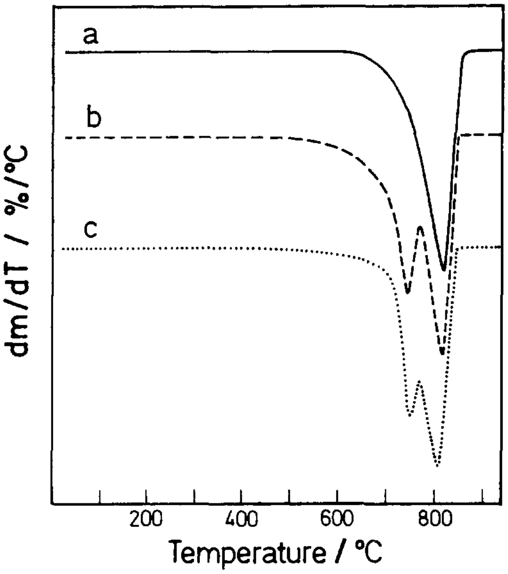

Fig. 2. Derived thermogravimetric curves (DTG) of the quarry samples from: (a) Hontoria (limestone); (b) Laspra (dolomite); and (c) Bonar (dolomite).

The fact that dolomites show two steps in the carbonate decomposition and the temperature of one of them concurs with the characteristic of the $CaCO_3/CaO$ transformation lead us to argue that the smaller size of magnesium with respect to calcium, facilitates the magnesium mobility and thus the formation of CO_2 associated to MgO is kinetically favoured against the formation of CO_2 associated to CaO. Accordingly, the separate integration of the peaks area at 750 and 800°C should lead to data corresponding to the material composition. Thus, the ratio calcite/dolomite in the rocks may be quantified (or at least semiquantified) by means of a thermogravimetric study of the decomposition process of the dolomites.

Since the shape of the peak corresponding to the $CaCO_3$ decomposition for an experimental condition can be easily reproduced, we have used the shape of the curve ranging from the temperature of maximum rate of weight loss (peak minumum) to the temperature of stabilization (right part) in order to reproduce the left band of the peak associated with the CaO formation, so that the mass loss of both processes can be individually determined.

Synthetical samples (standards) were prepared to perform a calibration curve including the composition range from a pure limestone to a pure dolomite. We have worked with two series: Series A are rocks from Laspra and Hontoria quarries and Series B rocks from Bonar and Hontoria quarries. Each series is formed by eleven samples with compositions varying from 0 to 100% in weight of limestone.

Plotting the losses of mass at 800°C obtained from thermogravimetric analysis as a function of the weight percentage of Hontoria limestone (Fig. 3), two straight lines are obtained, one for each series, with a slightly negative slope. This parameter is only valid for the correct characterization of the type of carbonate rocks analyzed when it's purity is very high, since the presence of additional salts will give rise to variations in the value of the mass loss at 800°C which are difficult to relate with the composition.

Chemical analysis of the samples used in the calibration curves leads to obtain the molar fraction of Ca in solid phase $\bar{X}_{Ca}$ defined as the ratio of the number

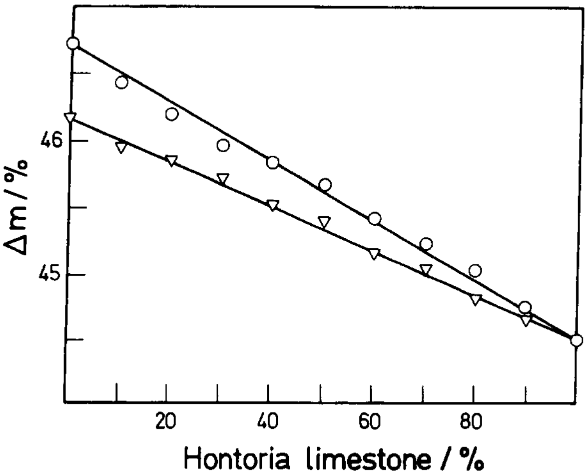

Fig. 3. The percentage of weight loss at 800°C vs. the weight percentage of Hontoria limestone: (a) Laspra–Hontoria (▽); and (b) Bonar–Hontoria (○) rocks.

Table 1
Comparison between the results obtained from DTG curves and from chemical analysis ($_{Ca}$)

Samples	$(X_{CO_2})_{Ca}$	$\bar{X}_{Ca}$	$(X_{CO_2})_{Ca}/\bar{X}_{Ca}$
A1	1.000	1.000	1.00
A2	0.987	0.968	1.02
A3	0.983	0.919	1.07
A4	0.976	0.879	1.11
A5	0.953	0.851	1.12
A6	0.930	0.823	1.13
A7	0.887	0.778	1.14
A8	0.841	0.744	1.13
A9	0.812	0.719	1.13
A10	0.765	0.671	1.14
A11	0.680	0.597	1.14
B1	1.000	1.000	1.00
B2	0.984	0.955	1.03
B3	0.978	0.940	1.04
B4	0.973	0.910	1.07
B5	0.967	0.879	1.10
B6	0.934	0.841	1.11
B7	0.927	0.828	1.12
B8	0.907	0.797	1.13
B9	0.867	0.774	1.12
B10	0.835	0.739	1.13
B11	0.816	0.722	1.13

moles of Ca to the number of moles of Ca and Mg in the solid.

The splitting of the DTG curves in two individual bands allows the determination of the CO_2 fraction associated with each step of the decomposition processes. If we call $(X_{CO_2})_{Ca}$ the relative weight of the peak detected at 800°C $[(X_{CO_2})_{Ca} = m_{800}/m_T]$ for each sample, the $(X_{CO_2})_{Ca}$ and $\bar{X}_{Ca}$ values should be the same assuming that the formation of the MgO and CaO takes place in consecutive and totally separated steps. The comparison between both magnitudes can be seen in Table 1.

The agreement is relatively good (differences about 10%, relative) but the data obtained by thermal analysis are always higher than those obtained by chemical analysis. This may indicate that the MgO formation is not completed when the $CaCO_3$ decomposition starts.

The experimental data might be explained by assuming the formation of mixed oxides of Ca and Mg as a consequence of the calcination, but X-ray patterns of the calcinated materials (Fig. 4) show that this does not occur. In all cases the existence of mixtures of the pure oxides (CaO and MgO) is observed.

When the data from Table 1 are plotted (Fig. 5) it is observed that the experimental points describe a curve from which one can obtain the Ca molar fraction in dolomites ($\bar{X}_{Ca}$) from thermal analysis measurements $[(X_{CO_2})_{Ca}]$. To be specially noted is that the curve situation is independent of the origin of the dolomite (Laspra or Bonar) so that the DTG data can be used to determine the dolomites composition independently of geologic factors.

Once the calibration curve is determined, we can establish the calcite/dolomite ratio in a dolomite only from its DTG curve.

DSC of quarry samples (limestones and dolomites) do not give information because the highest temperature that our instrument can get is 600°C and the minerals forming these rocks are decomposed at temperatures > 600°C. If this technique is applied at damaged monument samples, the curves present a variable number of bands.

The soluble salts arising from the degradation usually are hydrated, so that they undergo modifications at low temperatures (~ 100°C). Moreover, nitrates, sulphates and phosphates undergo phase transitions, they decompose or melt under 600°C. These changes give rise to the processes detected by calorimetric techniques.

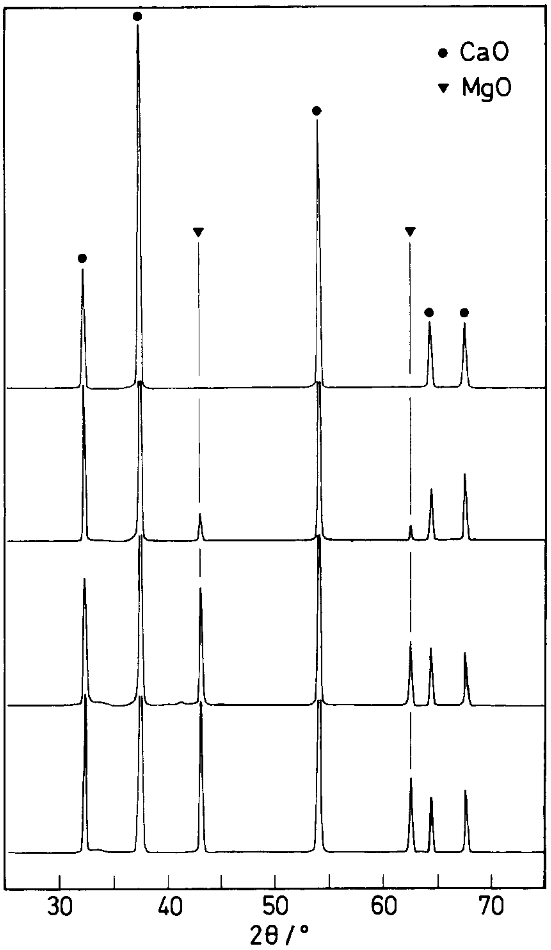

Fig. 4. X-ray patterns of dolomites–calcites treated at 900°C.

The main soluble salts present in monuments [20,21] are Na and K chlorides and Na, K, Ca, Mg and NH_4^+ sulphates and nitrates (sometimes anhydrous and sometimes hydrated). Ca and Mg carbonates are not studied because they are the main components of a great part of the monumental stones.

The main part of literature refers to $CaSO_4 \cdot 2H_2O$, NaCl and Mg and Na sulphates since they are the most abundant and harmful, rather in the monumental stones [22–25] than in the rocks of quarries [26,27].

The temperatures of decomposition and/or phase transition and the enthalpy variations associated to the salt product of the building materials decay, are known and listed [28]. The Na and K chlorides are stable under 600°C so that these salts cannot be detected by our DSC. Decomposition temperatures and enthalpy variations of the salts chosen are compiled in Table 2.

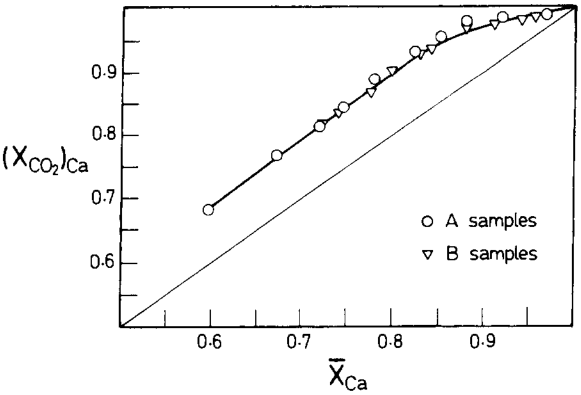

Fig. 5. Calibration curve which allows to fix the dolomite composition ($\bar{X}_{Ca}$) from thermal analysis data $[(X_{CO_2})_{Ca}]$.

We have worked with samples from the most deteriorated zones of the Burgos Cathedral (Gothic Spanish Monument, declared Humanity Heritage by the UNESCO) built with limestones of Hontoria (Burgos) quarry. We have chosen 17 samples and we have classified them as patinas (P) (surface modifications

Table 2
Decomposition temperature and enthalpy variations of the salts which more frequently appear as products of the monumental rocks degradation (data obtained by DSC)

Soluble salts	Temperature (°C)	ΔH ($J\,g^{-1}$)
Sulphates:		
$CaSO_4 \cdot 2H_2O$	143 [a]/178 [a]	641
Na_2SO_4	257 [b]	82
$Na_2SO_4 \cdot 10H_2O$	40 [a], 117 [a], 251 [b]	240, 856, 33
K_2SO_4	583 [b]	53
$MgSO_4$	352 [b]	588
$MgSO_4 \cdot H_2O$	76 [a], 345 [b]	13, 554
$(NH_4)_2SO_4$	355 [b], 505 [c]	876, 1744
Nitrates:		
$NaNO_3$	275 [c], 308 [d]	32, 165
KNO_3	133 [b], 334 [c]	51, 99
NH_4NO_3	267 [d]	711
$Mg(NO_3)_2 \cdot 6H_2O$	93 [a], 423 [d]	154, 949
$Ca(NO_3) \cdot 4H_2O$	49 [a], 153 [a], 549 [c]	145, 492, 399

[a] Dehydration; [b] Phase transition; [c] Melting point; [d] Decomposition.

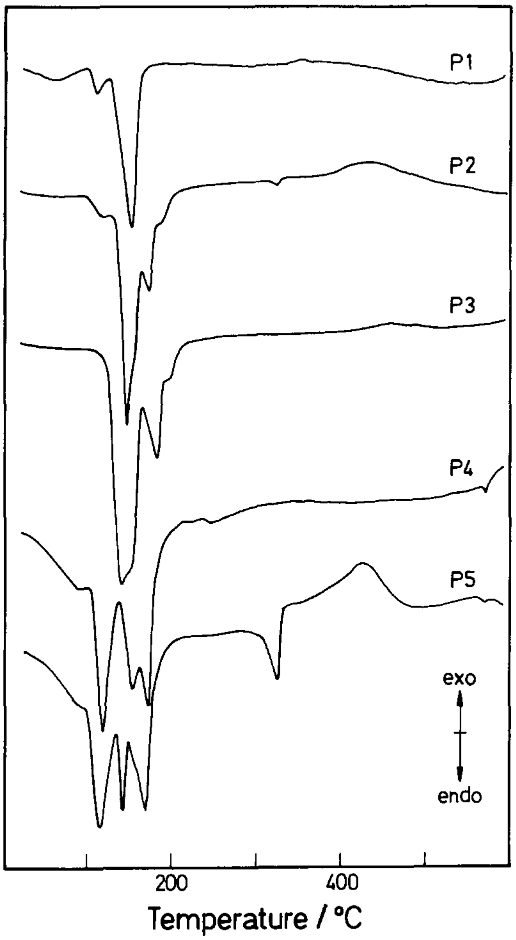

Fig. 6. DSC of patina samples formed on the external surface of the stone in the Burgos Cathedral.

of the stone, change of colour on the surface), saline efflorescences (E) (accumulation of soluble salts on the surface of porous stones) and crusts (C) (compact layer of material placed on the external part of the stone arising from a surface transformation). Figs. 6 and 7 show the DSC of the samples.

If we compare the temperatures corresponding to the minimum of the peaks in DSC curves for each sample with the data listed in Table 2, we can see that $CaSO_4 \cdot 2H_2O$ is present in all type of deteriorated materials; KNO_3 is always present in salt efflorescences and scarcely in patinas and crusts. Hydrous or anhydrous Mg and Na sulphates are also frequent. Hence, the most abundant anions are nitrates and sulphates and cations are Ca, Na, K and Mg. The DSC technique gives additional information about the sample features since the type of salt or salts present can be identified in samples with a good peak separation as a function of the temperature of the processes

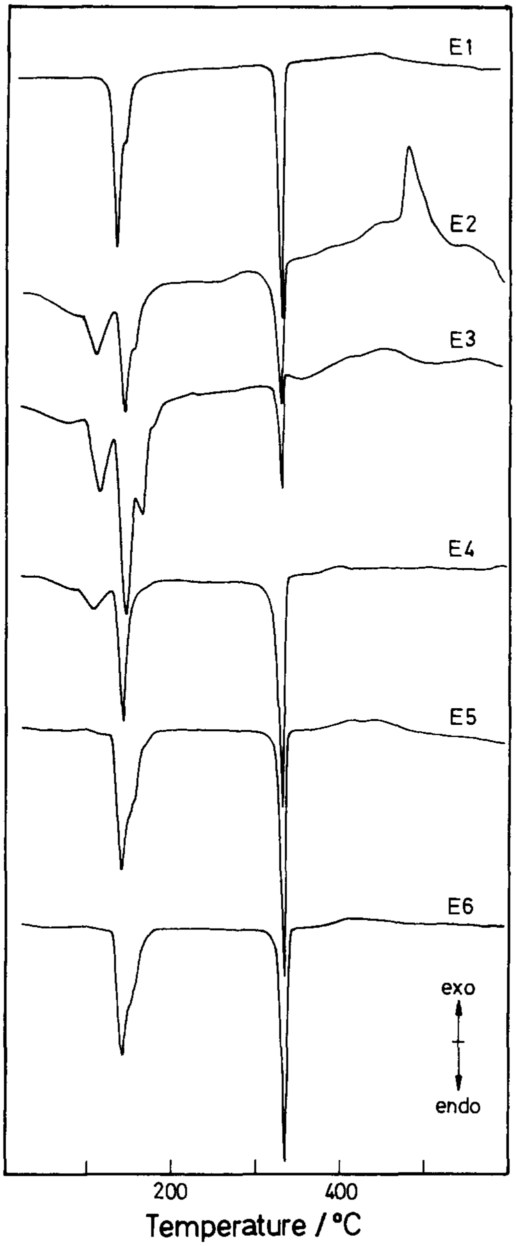

Fig. 7. DSC of saline efflorescence samples formed on the external surface of the stone in the Burgos Cathedral.

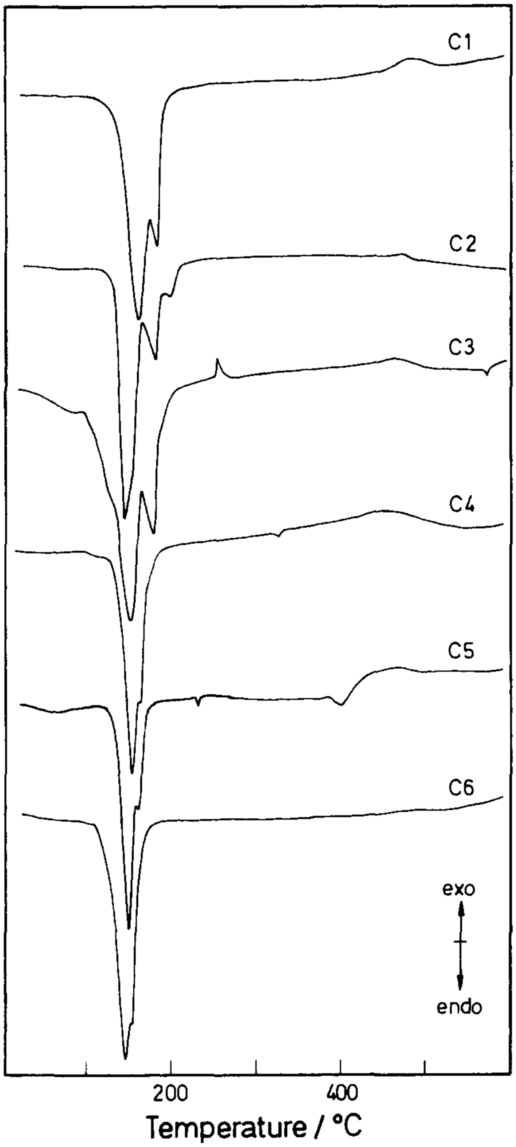

Fig. 8. DSC of crust samples developed on the external surface of the stone in the Burgos Cathedral.

Table 3
Percentage in weight of salts in the samples (obtained by DSC)

Samples	$CaSO_4 \cdot 2H_2O$	KNO_3
P1	4.90	<1
P2	42.10	1.88
P3	79.78	<1
P4	30.65	<1
P5	22.46	<1
E1	9.52	80.64
E2	3.63	47.10
E3	36.10	28.96
E4	2.06	83.20
E5	9.59	52.37
E6	8.45	51.54
C1	66.72	<1
C2	79.33	<1
C3	50.84	<1
C4	27.97	1.15
C5	44.02	<1
C6	17.04	<1

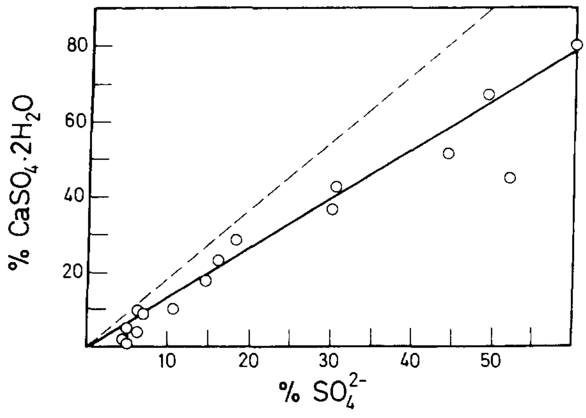

Fig. 9. Ratio between the gypsum concentration obtained from DSC and the percentage of SO_4^{2-} in the samples (HPLC data).

detected in the soluble synthetic salts. The ratio can be quantified from the values obtained for each individual synthetic salt. Table 3 shows the results.

In Figs. 9 and 10 the data obtained by chemical analysis of anions and cations are compared to those obtained from DSC analysis of the salts.

Gypsum is the main decay compound. The gypsum concentration obtained from DSC curves is related only with the sulphate ion content. It cannot be related with the Ca concentration due to the constant presence of $CaCO_3$ in the samples. It can be seen that the experimental points form a straight line with a slope of 1.32. The molecular weight ratio between $CaSO_4 \cdot 2H_2O$ and SO_4^{2-} ion is 1.79. Therefore, the experimental data form a straight line with a slope of 1.79 (undashed line in the figure) if all sulphate ions detected in the samples were in gypsum form. The experimental data indicate that about one of each four sulphate ions forms salts different from gypsum.

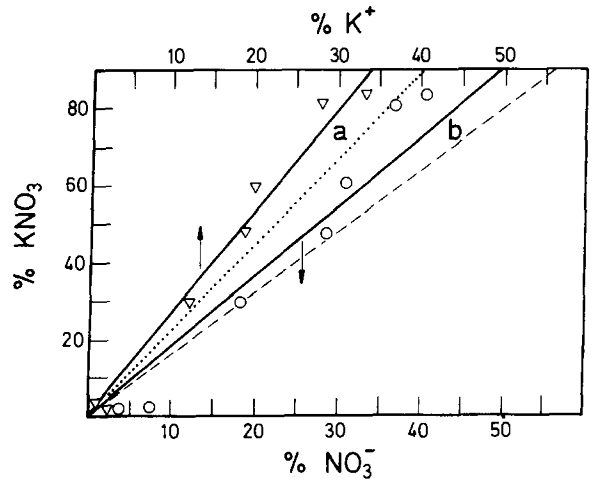

Fig. 10. Ratio between the KNO_3 concentration obtained from DSC and the percentage of NO_3^- (a) or K^+ (b) in the samples (HPLC and AA data respectively).

KNO_3 behaves in a different way. The apparent amounts of KNO_3 obtained from DSC are higher than those derived from the transformation in salt percentage of the NO_3^- (Fig. 10a) or K^+ (Fig. 10b) chemical analysis data (dashed and dotted lines respectively). This only can be explained if the band at 334°C used for the KNO_3 quantitative determination involves another process apart from the KNO_3 melting.

The absence of bands close to 580°C verifies that there is no K_2SO_4 in the solids. Thus, it can be assumed in a good approximation that all potassium is in the KNO_3 form. The deviation of experimental data from the dashed line must be associated to the presence of magnesium and/or ammonium sulphates in the materials since the phase transition temperature of these compounds and the melting temperature of KNO_3 is similar.

DSC is an adequate technique to carry out quantitative and qualitative analysis of the damaged monumental stones, giving data about the mineralogical composition of the materials and therefore is a good complement to the conventional chemical analysis which only provides global ionic compositions of the substrate. This is very important for the establishment of the decay mechanisms since, in addition to the total analysis of the material, one needs to know the nature of the salts formed in order to determine its origin which is the preliminary step to prevent decay before intervention in the monument.

4. Conclusions

The shape of the TG and DSC curves allows the monumental rocks to be classified as limestones or dolomites. A calibration curve obtained from standards covering the range from a pure limestone to a dolomite can be used to determine the composition of monumental rocks only by obtaining their DTG curve. The DSC technique (together with chemical analysis) was used to determine the compounds generated by the exposition of the monumental rocks to the industrial pollution.

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