J Therm Anal Calorim (2011) 104:467–474
DOI 10.1007/s10973-011-1348-5

Thermal study of unaltered and altered dolomitic rock samples from ancient monuments

The case of Villarcayo de Merindad de Castilla la Vieja (Burgos, Spain)

**J. L. Perez-Rodriguez · A. Duran ·
L. A. Perez-Maqueda**

Cultural Heritage Special Chapter

Abstract In this study, the decomposition behaviour of unaltered and altered dolomitic rock samples used in Cultural Heritage buildings was studied by simultaneous TG–DTA experiments at different atmospheres, X-ray diffraction in a high-temperature chamber, and evolved gas analysis. The components of dolomite rock samples and hydrated calcium oxalate formed during the alteration processes of the rocks were characterized, and the decomposition mechanisms of these components were determined. The TG–DTA experiments carried out at CO_2 atmosphere were used to determine the carbonate compounds in the rock samples. The TG–DTA study characterized the presence of organic compounds formed during the biological degradation of the rock samples, possibly responsible of the hydrated calcium oxalate formation.

Keywords Cultural Heritage · Oxalates · Dolomite · Calcite · Alteration

Introduction

Dolomite is a double salt of calcium and magnesium carbonate. Natural dolomite has many industrial applications, such as in the production of cements, pharmaceuticals, iron, refractories, etc. The dolomitic rock has been widely used to build monuments and stone works of art [1]. The firing of dolomite at different temperatures yields materials of various compositions that can be used in a variety of applications. Several investigators [2–11] have conducted thermal decomposition experiments on dolomite minerals. The thermal decomposition of dolomite minerals shows different characteristics depending on the atmosphere during the heating [12–14]. It has been claimed that the DTA curves of dolomite show two peaks, the first one is due to decomposition of the carbonate ions associated with magnesium and the second one to the decomposition of those associated with calcium [15]. The two dolomite peaks are more clearly resolved in a carbon dioxide atmosphere [2]. Mechanical treatments of minerals produce modification in their thermal behaviour [16–19]. Thus, grinding of dolomite results in the disappearance of the first peak and its replacement by a peak at a lower temperature [20].

The façade of Cultural Heritage buildings are unavoidable destined to be covered with layers produced by different degradation processes [21–26]. The formation of patinas has been particularly well studied in large European cities, where largely historical monuments were constructed of calcareous rocks. For this rock, one of the most common patinas formed during degradation was that constituted by hydrated calcium oxalates. This patina was produced by growth and activity of living organisms. Microorganisms formed biofilms on the surface of stones with resulting aesthetic and structural damage. Some authors have sustained that the formation of oxalate patinas was also produced by the degradation of the agents which were applied for conservation/restoration [24–27]. The type of oxalates formed depends on the material involved. In dolomitic substrate, the oxalic acid produced by microorganisms attacks the rock and precipitates as calcium oxalates (Whewellite, $CaC_2O_4 \cdot H_2O$; Weddellite, $CaC_2O_4 \cdot 2H_2O$). The formation of the mineral glushinskite ($MgC_2O_4 \cdot H_2O$) occurs only in special experimental

---

J. L. Perez-Rodriguez (✉) · A. Duran · L. A. Perez-Maqueda
Materials Science Institute of Seville (CSIC-UNS), Americo Vespucio 49, 41092 Seville, Spain
e-mail: jlperez@icmse.csic.es

conditions such as trough fungal interaction with dolomite rock and sea water substrate [28].

Thermal treatment has been used as a method for characterization of oxalates [29–33]. Several authors have reported three mass-loss steps during the thermogravimetric studies of hydrated calcium oxalates. In the first mass-loss step, water was evolved, whilst in the second and third steps CO and CO_2 were evolved [31, 34, 35]. Frost and Weier [29, 32] used thermogravimetric and mass spectrometry analysis to identify the presence of carbon dioxide in the second and third mass-loss steps.

Several experimental techniques have been used to study the degradation of materials used in Cultural Heritage artefacts [36–38]. The DTA–TG thermoanalytical investigation and X-ray diffraction experiments carried out during the heating allow to characterize the materials and its alteration products formed on stone works of art [39, 40].

The thermal studies of dolomite and hydrated calcium oxalates have been widely studied by several authors as mentioned previously. However, studies on thermal behaviour of unaltered and altered dolomitic rock samples on cultural heritage monuments have been scarcely studied. Hence, this study aims at the identification and thermal transformations of minerals and patinas formed on dolomites rocks from several monuments by TG–DTA carried out in air, N_2 or CO_2, and by X-ray diffraction carried out at different temperatures in a high-temperature chamber.

Experimental

Unaltered and altered dolomite samples were collected from monuments (mainly Churches) located in Villarcayo de Merindad de Castilla la Vieja (Burgos, Spain). In this study, three dolomitic rock samples were studied: an unaltered one (sample 1), a sample with a small degree of alteration (sample 2) and a highly altered sample (sample 3). Both altered samples (2 and 3) were collected from the external façades of the monuments. Commercial $CaC_2O_4 \cdot H_2O$ sample (provided by Fluka) was used. Simultaneous TG–DTA measurements (STD Q600, TA Instruments) were carried out at a linear heating rate of 10 °C min^{-1} over the temperature range from ambient temperature to 1000 °C, at flowing air, N_2 or CO_2.

X-ray diffraction patterns (XRDs) were recorded on a Panalytical diffractometer X'Pert Pro MPD, using Ni-filtered Cu Kα radiation using an X'Cellerator detector with an angular aperture of 2.18° (2Θ) and step size of 0.016°. Heating experiments were carried out in a HTK 1200 high-temperature chamber (Anton Paar). Experiments were performed at flowing air and at temperature ranging from room temperature to 1000 °C with a heating rate of 10 °C min^{-1}. XRDs were recorded every 50 °C.

Morphological and chemical analysis were done with a scanning electron microscopy (model HITACHI S-4800) coupled to X-ray energy dispersive analyser (EDX). Evolved gas analysis (EGA) was carried out by heating the sample at synthetic air flow, in a tube furnace coupled to a Quadropole mass spectrometer (QMS).

Results and discussion

XRD characterization of rocks

X-ray diffraction patterns of the unaltered rock sample (sample 1, Fig. 1a) showed the presence of dolomite; in addition, small amounts of calcite were detected. The analysis by SEM showed the typical morphology of a dolomitic rock, whilst the chemical analysis by EDX showed the presence of Mg, Ca and small amounts of silicon in the sample. XRDs of the altered rock sample 2 showed diffractions of low intensities (Fig. 1b) that were not present in the unaltered sample. The intensities of these

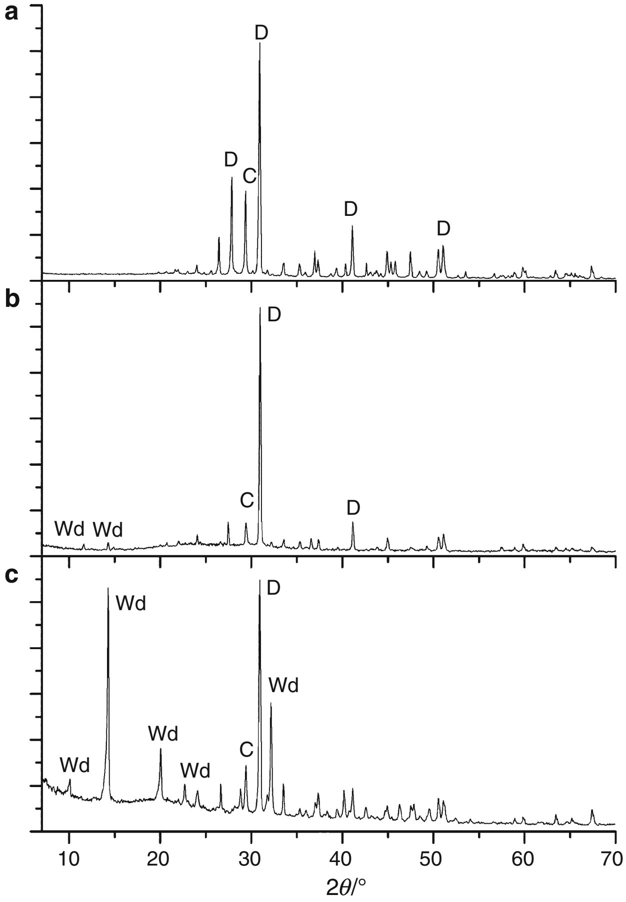

Fig. 1 XRD corresponding to **a** unaltered rock sample 1; **b** altered rock sample 2 and **c** altered rock sample 3 (*D* dolomite; *C* calcite; *Wd* weddellite; *W* whewellite)

new diffraction patterns increased with the alteration degree of the rock. Thus, the XRD study of the more altered sample 3 (Fig. 1c) confirmed that the new diffractions corresponded to a hydrated calcium oxalate compound, i.e. weddellite. In addition, dolomite and calcite were also detected. In this sample, only Ca and Mg were recorded by EDX analysis. The formation of weddellite could be attributed to degradation processes of dolomite. The mineral glushinskite (hydrated magnesium oxalate) was not found as previously reported by other authors [28, 41, 42].

Thermal studies

Thermal study of unaltered rock samples

The TG and DTA curves of unaltered rock sample 1 (Fig. 2) showed a very small mass-loss and an endothermic effect at about 150 °C, attributed to free and adsorbed water. In addition, the curve recorded in air (Fig. 2a) showed a large mass loss (about 45%) in a temperature range between 600 and 790 °C that corresponded with an endothermic effect in the DTA curve attributed to carbonates decomposition. The observed decomposition temperature around 750 °C indicated that the carbonates phases were well crystallised, which was in agreement with XRD data (Fig. 1a) and SEM observation. In the large mass loss and the corresponding endothermic effect was included the decomposition of the carbonates from the dolomite and also from the small amount of calcite in the sample as detected by XRD and SEM. The temperature of mass-loss and endothermic effect of carbonates may vary depending on the grain size, the experimental atmosphere and other concomitant factors. The use of carbon dioxide atmosphere during heating raises the calcite peak temperature and sharpens it considerably [16, 41–45]. The TG curve of the unaltered sample carried out at CO_2 atmosphere (Fig. 2b) showed two endothermic effects at 750 and 935 °C that corresponded with two mass losses. The first effect showed a mass loss of 21.3% and the second one of 22.48%. The first and second mass losses were respectively related to the magnesium and calcium content in the sample, due to the shift at higher temperatures for the calcium carbonates at CO_2 atmosphere [16, 41–45]. The second mass loss was higher than that expected for a stoichiometric dolomite due to the presence of small amount of calcite in the sample, as shown by X-ray diffraction (Fig. 1a). According with the values of the first and second weight losses, about 2.68% of calcite was present in the unaltered sample (1.18% of mass loss, due to CO_2 produced from calcite decomposition).

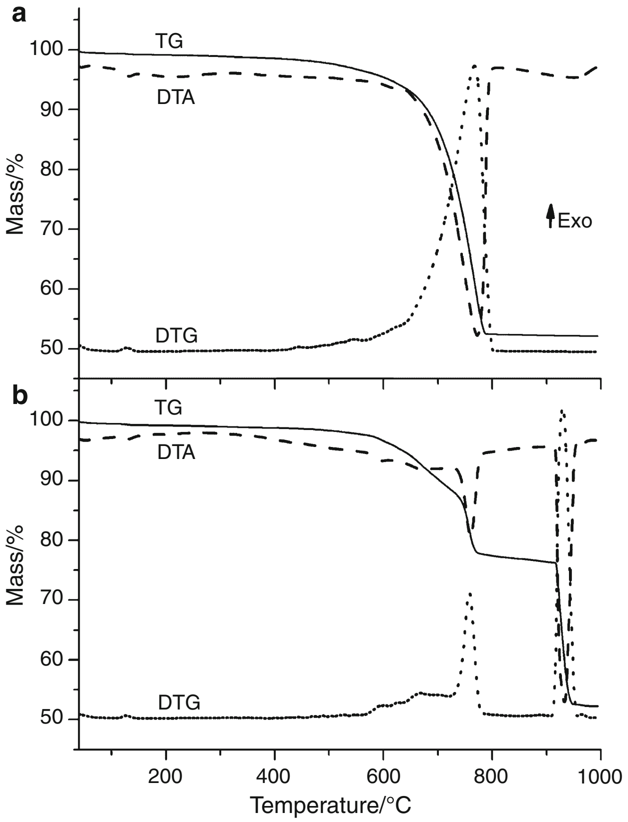

Fig. 2 TG/DTA/DTG curves of unaltered rock sample 1 carried out at air (**a**) and CO_2 (**b**) atmospheres

In the high-temperature XRD study of the unaltered rock sample (Fig. 3), the diffraction patterns attributed to dolomite and calcite remained till about 700–750 °C. At higher temperatures, the carbonates were decomposed into CaO and MgO that corresponded to the thermal decomposition showed by TG–DTA curves carried out at air atmosphere (Fig. 2a).

Thermal study of standard $CaC_2O_4{\cdot}H_2O$ and mixture of $CaC_2O_4{\cdot}H_2O$ with an unaltered rock

The X-ray diffraction study showed the presence of hydrated calcium oxalates in the altered samples (Fig. 1b and c). Thus, it was considered of interest in this study to use a standard $CaC_2O_4{\cdot}H_2O$ sample to characterize its thermal decomposition. The DTA curve of $CaC_2O_4{\cdot}H_2O$ at air atmosphere showed two endothermic effects at 190 and 750 °C, and one exothermic effect at 480 °C (Fig. 4a). These effects corresponded to three well-defined mass-loss steps in the TG curve (Fig. 4). No additional DTA effects or mass losses were detected in the studied temperature range in the curves (Fig. 4a). These results were in agreement with the mechanism proposed by several authors [29–32]: (1) $CaC_2O_4{\cdot}H_2O \rightarrow CaC_2O_4 + H_2O$; (2) $CaC_2O_4 \rightarrow CaCO_3 + CO_2$; (3) $CaCO_3 \rightarrow CaO + CO_2$. The high-temperature XRD of this sample, heated in the

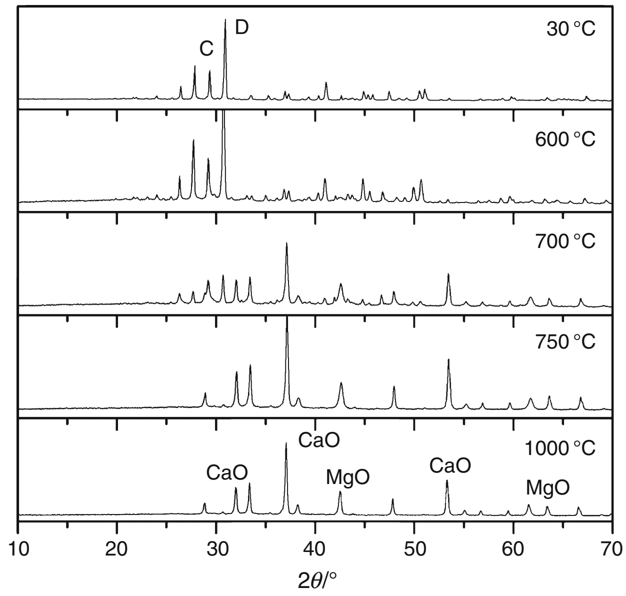

Fig. 3 XRD of unaltered rock sample 1 collected at different temperatures. (*D* dolomite; *C* calcite; *CaO* calcium oxide; *MgO* magnesium oxide)

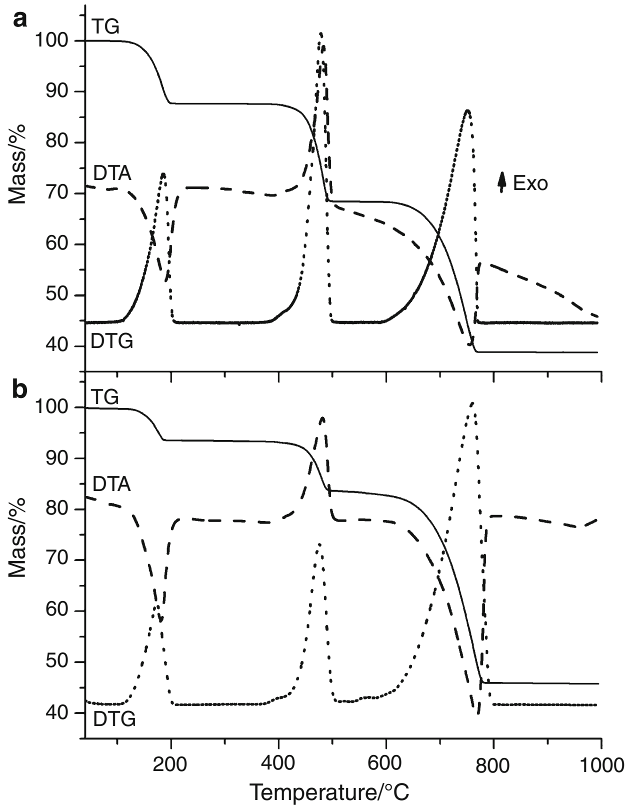

Fig. 4 TG/DTA/DTG curves of $CaC_2O_4 \cdot H_2O$ carried out at air (**a**) and CO_2 (**b**) atmospheres

range between 30 and 1000 °C (Fig. 5), confirmed the mechanisms proposed by thermal analysis study. The transformation of hydrated calcium oxalate to calcium oxalate appeared between 100 and 200 °C. An increase in the calcite content appeared at about 450 °C due to the decomposition of oxalates. At 800 °C, CaO was recorded by decomposition of $CaCO_3$.

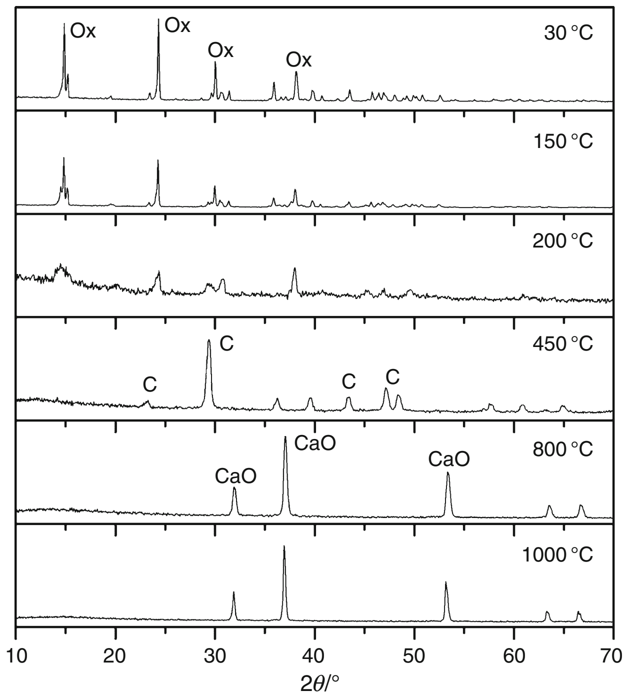

Fig. 5 XRD of $CaC_2O_4 \cdot H_2O$ collected at different temperatures. (*Ox* CaC_2O_4; *C* calcite; *CaO* calcium oxide)

The TG, DTA and DTG curves of an artificial mixture of unaltered sample and standard hydrated calcium oxalate (Fig. 4b) showed all the effects corresponding to the $CaC_2O_4 \cdot H_2O$ with an increased mass loss between 650 and 800 °C due to the carbonates decompositions from the unaltered sample in addition to that corresponding to the oxalate. The XRD of this mixture heated in the range between 30 and 1000 °C (Fig. 6) showed the dehydration of the oxalate at low temperature. The proportion of calcite increased at 450 °C attributed to decomposition of calcium oxalate. At about 750 °C, CaO and MgO appeared due to the decomposition of carbonates.

Thermal study of altered rocks

The TG curve of the altered rock sample 2 in air atmosphere (Fig. 7a) showed three mass losses, at the following temperatures: 150, 460, and a large one between 650 and 780 °C. These mass losses were similar to those from the artificially prepared mixture of unaltered sample with hydrated calcium oxalate. In addition, an additional new mass loss appeared between 200 and 550 °C that partially hide the endothermic and exothermic effects of oxalate decomposition in this temperature range.

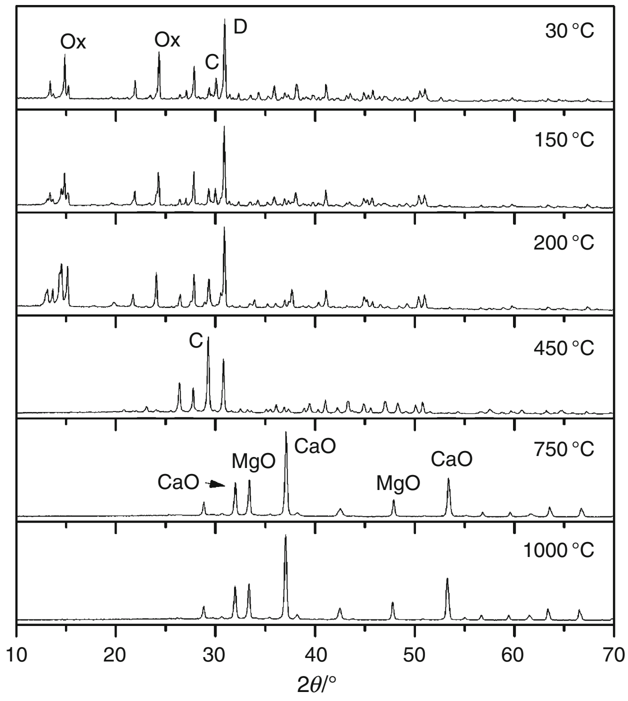

Fig. 6 XRD of mixtures composed by unaltered rock sample 1 and $CaC_2O_4 \cdot H_2O$ collected at different temperatures. (*D* dolomite; *C* calcite; *W* whewellite; *Ox* CaC_2O_4; *CaO* calcium oxide; *MgO* magnesium oxide)

The TG, DTA and DTG curves of the most altered sample 3 recorded in air (Fig. 7b) were similar to those of sample 2 (Fig. 7a). However, the effects of oxalate decomposition were more easily detected due to its higher oxalate content in the sample. It stood out the higher intensity of the exothermic effect in the range between 200 and 550 °C with a maximum about 350 °C accompanied of an important mass loss as compared with those in the sample 2. In addition, there was a continuous mass loss between 200 and 600 °C (Fig. 7b), unlike the well-defined mass loss steps in the artificially prepared mixtures of hydrated calcium oxalate and unaltered rock sample 1 (Fig. 4). These data confirmed that other components, not detected by XRD (Fig. 1c), possible due to their amorphous character, were present in the altered samples. The high-temperature X-ray study carried out between 30 and 1000 °C showed almost identical results to those for the artificial mixture of unaltered sample and $CaC_2O_4 \cdot H_2O$ (Figure not shown): dehydration of calcium hydrated oxalate, followed of the decomposition of the oxalate into $CaCO_3$ and finally decomposition of the carbonates into calcium and magnesium oxides.

The thermal study of the altered sample 3 at CO_2 atmosphere (Fig. 7c) showed that the exothermic effect at about 350 °C is much smaller than that recorded in air (Fig. 7b). In addition, two endothermic effects were present at higher temperatures, i.e. 780 and 935 °C, that corresponded to two mass losses, the first one attributed to the CO_2 loss (8.15%) from the magnesium content in the dolomite, and the second one (20.6%) attributed to CO_2 loss from calcium content (8.15%) in the dolomite, together with that corresponding to the calcite produced by the oxalate (11.38%) and the calcite that was originally present in the sample (1.07%), as calculated considering the mass loss at CO_2 atmosphere of unaltered and altered samples. The mass loss between 155 and 400 °C that appeared in the altered rock samples changed between 6.5% (sample 2) and 17.4% (sample 3) depending on the alteration degree of the dolomitic rock. These results confirmed that other amorphous compounds were present in the samples, produced during the alteration process.

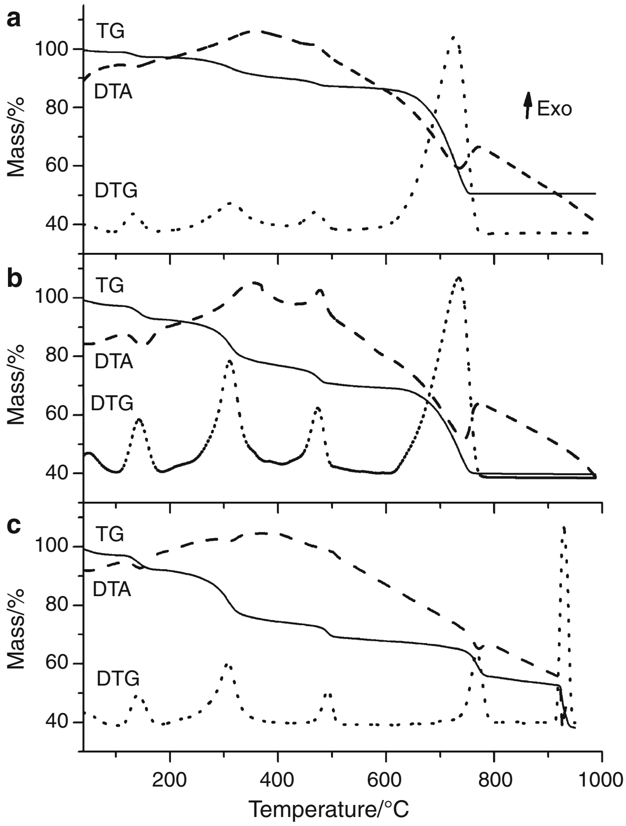

Fig. 7 TG/DTA/DTG curves of **a** altered rock sample 2 carried out at air atmosphere, **b** altered rock sample 3 carried out at air atmosphere and **c** altered rock sample 3 carried out at CO_2 atmosphere

The evolved gas analysis was used for the detection of the release of gases during the heating. In the temperature range up to 200 °C, for the hydrated calcium oxalate, the first mass loss and the corresponding endothermic effect respectively in the TG and DTG traces (Fig. 4a) were assigned to the loss of water (EGA figure not shown). At about 480 °C, the mass-loss and the exothermic effect were attributed to the transformation of calcium oxalate to calcite, as indicated by the release of CO_2 and CO at this temperature. Finally, at about 765 °C, the mass-loss and the endothermic effect were attributed to the carbonate decomposition, as indicated by the release of CO_2. These results are in agreement with those of Frost and Weier [29, 32].

The evolved gas analysis of the more altered rock sample 3 (Fig. 8) showed the release of water in the low-temperature range (up to 200 °C) due to physically adsorbed and crystallization water of the hydrated calcium oxalates. At 465 °C, CO and CO_2 were detected due to the decomposition of oxalates, and at 765 °C CO_2 was recorded due to the decomposition of carbonates. At 320 °C water, CO, CO_2 and a signal corresponding to heavier organic compounds ($m/z = 56$) were recorded. The simultaneous presence of these compounds, in a temperature range where no crystalline phase was detected by XRD, suggested that this event corresponded to the combustion of some organic compounds present in the altered rock samples. In addition, the presence of organic compounds in the sample was also confirmed by different experimental results such as the intense exothermic peak with a maximum at about 350 °C (Fig. 7), the continuous mass loss occurred between different steps (Fig. 7) that was not observed for unaltered rock sample (Fig. 2) and neither for the standard oxalate sample (Fig. 4) and the small release of water at high temperature (Fig. 8).

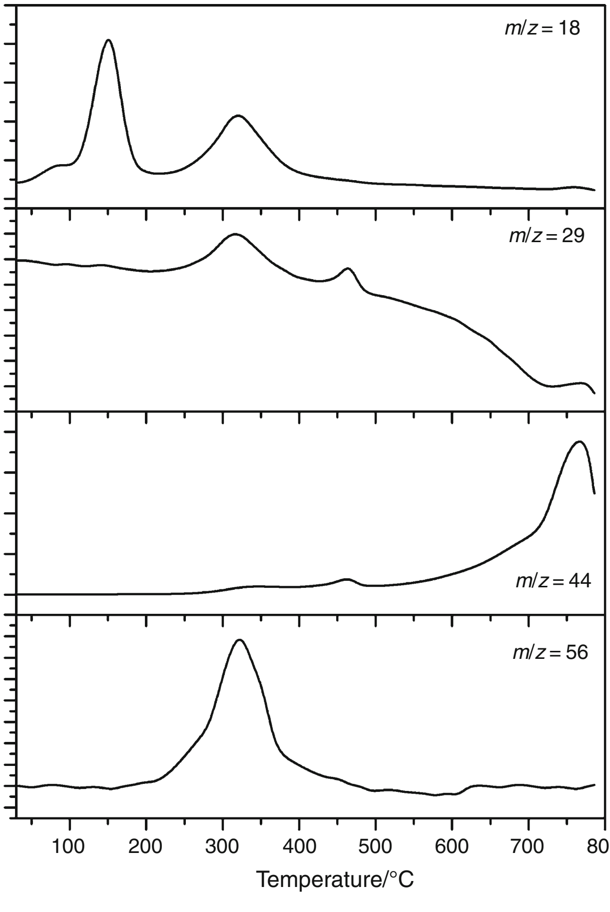

Fig. 8 EGA curves corresponding to $m/z = 44$ (CO_2), $m/z = 29$ (CO), $m/z = 18$ (H_2O) and $m/z = 56$ (organic matter) for the thermal decomposition of sample 3 at air atmosphere

The biological activity produced by environment conditions could be responsible of the hydrated calcium oxalate formation and of the organic matter in the samples. The presence of these organic compounds was not detected by XRD, due to their amorphous character.

Conclusions

In this research, characterization of unaltered and altered dolomitic rock samples from Cultural Heritage buildings were investigated by thermal methods. The XRD study revealed the presence of dolomite in the unaltered rock sample. This mineral was altered in the façade of the monuments producing hydrated calcium oxalate. The TG–DTA analysis and the XRD carried out in high-temperature chamber showed in the altered rock samples the three following steps: (i) dehydration of hydrated calcium oxalate to form calcium oxalate, (ii) transformation of calcium oxalate to calcium carbonate and, finally, (iii) formation of CaO by decomposition of calcium carbonate and of CaO and MgO produced by decomposition of the dolomite. These steps were confirmed in artificially prepared mixtures with unaltered rock sample from the monuments and standard monohydrated calcium oxalate. The TG carried out at CO_2 atmosphere permitted to quantify the percentages of magnesium content and calcium content in the dolomite, the content of calcium carbonate formed by decomposition of oxalates, and the small percentage of calcite originally present in the unaltered rock samples. In addition, the DTA and TG curves of altered rock samples showed an exothermic effect accompanied of a mass loss at about 350 °C. This effect that was not present in the unaltered rock or in the artificially prepared mixture became more significant as the alteration degree of the rocks increased. The EGA showed in the temperature range of the new exothermic effect, the release of water, CO, CO_2 and a signal corresponding to heavier organic compounds, attributed to the combustion of organic compounds that possibly were formed during the biological degradation of the monument rocks.

Thermal techniques have proved to be very useful for characterization of unaltered and altered rock samples from Cultural Heritage monuments, including the detection of the organic compounds produced due to the biological activity that was only detected by thermal analysis methods whilst XRD or SEM only gave information on the presence of the hydrated calcium oxalate, dolomite and calcite.

Acknowledgements The authors gratefully acknowledge Prof. M. D. Robador (University of Seville) for providing the samples. A.D. is indebted to the CSIC (MICINN) of Spain for the “Junta de Ampliacion de Estudios” contract (JAE Doc 088). We thank M. C. Jimenez de Haro for her help in SEM measurements. Financial support from projects TEP-03002 from Junta de Andalucía and MAT 2008-06619/MAT from the Spanish Ministerio de Ciencia e Innovación is acknowledged.

References

1. Maniatis Y, Herz N, Basiakos Y, editors. The study of marble and other stones used in antiquity. Los Angeles: J.G. Publications; 1995.
2. Iwafuchi K, Watenabe C, Otsuka R. Thermal decomposition of ferromanganoan dolomite. Thermochim Acta. 1983;66:105–25.
3. Barcina LM, Espina A, Suarez M, Garcia JR, Rodriguez J. Characterization of monumental carbonate stones by thermal analysis (TG, DTG and DSC). Thermochim Acta. 1997;290:181–9.
4. McCauley RA, Johnson LA. Decrepitation and thermal decomposition of dolomite. Thermochim Acta. 1991;185:271–82.
5. McIntosh RM, Sharp JH, Wilburn FW. The thermal decomposition of dolomite. Thermochim Acta. 1990;165:281–96.
6. Otsuka R. Recent studies on the decomposition of the dolomite group by thermal analysis. Thermochim Acta. 1986;100:69–80.
7. Ozao R, Ochiai M, Yamazaki A, Otsuka R. Thermal analysis of ground dolomites. Thermochim Acta. 1991;183:183–98.
8. Stepkowska ET, Perez-Rodriguez JL, Sayagues MJ, Martinez-Blanes JM. Calcite, vaterite and aragonite forming on cement hydration from liquid and gaseous phase. J Therm Anal Calorim. 2003;73:247–69.
9. Shoval S, Gaft M, Beck P, Krish V. Thermal-behavior of limestone and monocrystalline calcite tempers during firing and their use in ancient vessels. J Therm Anal Calorim. 1993;40:263–73.
10. Shoval S. Mineralogical changes upon heating calcitic and dolomitic marl rocks. Thermochim Acta. 1988;135:243–52.
11. Gunasekaran S, Anbalagan G. Spectroscopy study of phase transitions in dolomite natural. J Raman Spectrosc. 2007;38:846–52.
12. Samtani M, Dollimore D, Alexander K. Thermal decomposition of dolomite in an atmosphere of carbon dioxide, the effect of procedural variables in thermal analysis. J Therm Anal Calorim. 2001;65:93–101.
13. Avila I, Crnkovic PM, Milioli FE. Thermogravimetric study of the effect of temperature and atmosphere on sulfur dioxide absorption by limestone. Quim Nova. 2006;29:1244–9.
14. Maitra S, Chodhury A, Das HD, Pramanik MJ. Effect of compaction on the kinetics of thermal decomposition of dolomite under non-isothermal condition. J Mater Sci. 2005;40:4749–51.
15. Webb TL, Krüger JE. Carbonates. In: Mackenzie RC, editor. Differential thermal analysis, vol. 1. New York: Academic Press; 1970.
16. Perez-Rodriguez JL, Duran A, Sanchez-Jimenez PE, Franquelo ML, Perejon A, Pascual-Cosp J, Perez-Maqueda LA. Study of the dehydroxylation-rehydroxylation of pyrophyllite. J Am Ceram Soc. 2010;93:2392–8.
17. Franco F, Perez-Maqueda LA, Perez-Rodriguez JL. The influence of ultrasound on the thermal behaviour of a well ordered kaolinite. Thermochim Acta. 2003;404:71–9.
18. Perez-Maqueda LA, Balek V, Poyato J, Pérez-Rodriguez JL, Subrt J, Bountsewa IM, Malek Z. Study of natural and ion exchanged vermiculite by emanation thermal analysis, TG, DTA and XRD. J Therm Anal Calorim. 2003;71:715–26.
19. Perez-Maqueda LA, Blanes JM, Pascual J, Perez-Rodriguez JL. The influence of sonication on the thermal behaviour of muscovite and biotite. J Am Ceram Soc. 2004;24:2793–801.
20. Bradley WF, Burst JF, Graf DL. Crystal chemistry and differential thermal effects of dolomite. Am Miner. 1953;38:207–17.
21. Maszalek M. Applications of optical microscopy and scanning electron microscopy to the study of stone weathering: a Cracow case study. Int J Archit Herit. 2008;2:83–92.
22. Toniolo L, Zerbi CM, Bugini R. Black layers on historical architecture. Environ Sci Pollut Res. 2009;16:218–26.
23. Adorni E, Venturelli G. Mortars and stones of the Damascus Citadel (Syria). Int J Archit Herit. 2010;4:337–50.
24. Garcia-Valles M, Urzi C, De Leo F, Salomone P, Vendrell-Sanz M. Biological weathering and mineral deposits of the Belevi marble quarry (Ephesis, Turkey). Int Biodeterior Biodegrad. 2000;46:221–7.
25. Del Monte M, Sabioni C, Sappia G. The origin of calcium oxalates on historical buildings, monuments and natural outcrops. Sci Total Environ. 1987;67:17–39.
26. Chen J, Blume HP, Beyer L. Weathering of rocks induced by lichen colonization—a review. Catena. 2000;39:121–46.
27. Lazzarini L, Borrelli E, Bouabdelli M, Antonelli F. Insight into the conservation problems of the stone building “Bab Agnaou”, a XII century monumental gate in Marrakech (Morocco). J Cult Herit. 2007;8:315–22.
28. Kolo K, Claeys Ph. In vitro formation of Ca-oxalates and the mineral glushinskite by fungal interaction with carbonate substrates and seawater. Biogeosciences. 2005;2:277–93.
29. Frost RL, Weier ML. Thermal treatment of weddellite–a Raman and infrared emission spectroscopic study. Thermochim Acta. 2003;406:221–32.
30. Campanella L, Cardarelli E, Curini R, D’ascenzo G, Tomasetti M. Thermogravimetric analysis of human renal calculi sampled in 19th century patients: discussion on the basis of their alimentary customs. J Therm Anal Calorim. 1992;38:2707–17.
31. Carrasco F. Kinetic-study of the thermal decomposition of monohydrate calcium oxalate by thermogravimetric analysis. Afinidad. 1991;48:19–24.
32. Frost RL, Weier ML. Thermal treatment of whewellite: a thermal study and Raman spectroscopy study. Thermochim Acta. 2004;409:79–85.
33. Kohutova A, Honcova P, Podzemna V, Bezdicka P, Vecernikova E, Louda M, Seidel J. Thermal analysis of kidney stones and their characterization. J Therm Anal Calorim. 2010;101:695–9.
34. Gurrrieri S, Siracusa G, Cali R. Thermal decomposition of $CaC_2O_4H_2O$—determination of kinetic parameters by DTG and DTA. J Therm Anal Calorim. 1974;6:293–8.
35. Mu J, Perlmutter DD. Thermal decomposition of carbonates, carboxylates, oxalates, acetates, formats and hydroxides. Thermochim Acta. 1981;44:207–18.
36. Lombardi G, Santarelli ML. Multi-instrumental analysis of asphalts of archaeological interest. J Therm Anal Calorim. 2009;96:541–6.
37. Budrugeac P, Emandi A. The use of thermal analysis methods for conservation state determination of historical and/or cultural objects manufactured from lime tree wood. J Therm Anal Calorim. 2010;101:881–6.
38. Ion RM, Ion ML, Fierascu RC, Serban S, Dumitriu I, Radovici C, Bauman I, Cosulet S, Niculescu VIR. Thermal analysis of Romanian ancient ceramics. J Therm Anal Calorim. 2010;102:393–8.
39. Franquelo ML, Robador MD, Ramírez-Valle V, Durán A, Jiménez de Haro MC, Pérez-Rodríguez JL. Roman ceramics of

hydraulic mortars used to build the Mithraeum House of Merida (Spain). J Therm Anal Calorim. 2008;92:331–5.

40. Odlyha M, Wang Q, Foster GM, de Groot J, Horton M, Bozec L. Thermal analysis of model and historic tapestries. J Therm Anal Calorim. 2005;82:627–36.
41. Moropoulou A, Bakolas A, Bisbikou K. Investigation of the technology of historic mortars. J Cult Herit. 2000;1:45–58.
42. Genestar C, Pons C, Mas A. Analytical characterisation of ancient mortars from the archaeological Roman city of Pollentia (Balearic Islands, Spain). Anal Chim Acta. 2006;557:373–9.
43. Vágvölgy V, Frost RL, Hales M, Locke A, Kristof J, Horváth E. Controlled rate thermal analysis of hydromagnesite. J Therm Anal Calorim. 2008;92:893–7.
44. Beck CW. Differential thermal analysis curves of carbonate minerals. Am Mineral. 1950;35:985–1013.
45. Duran A, Perez-Maqueda LA, Poyato J, Perez-Rodriguez JL. A thermal study approach to roman age wall paintings mortars. J Therm Anal Calorim. 2010;99:803–9.