Appl. Phys. A 92, 151–154 (2008)
DOI: 10.1007/s00339-008-4466-6

Applied Physics A
Materials Science & Processing

M.O. FIGUEIREDO[1,2,✉]
T.P. SILVA[1,2]
J.P. VEIGA[2]

Analysis of degradation phenomena in ancient, traditional and improved building materials of historical monuments

[1] Crystallography and Mineralogy Centre, IICT, & INETI-Geological Survey, Apt. 7586, 2721-866 Alfragide, Portugal
[2] CENIMAT, Materials Sci. Dept., New University of Lisbon, 2829-516 Caparica, Portugal

Received: 12 November 2007/Accepted: 15 January 2008
Published online: 29 March 2008

ABSTRACT A review is presented on constructive techniques plus materials and the processes involved in degradation phenomena observed in two historical monuments: the Zambujeiro dolmen (Portugal) and the Roman Aqueduct of Carthage (Tunisia).

Dolmens are particularly impressive megalithic constructions for the dimensions of granite blocks. At Zambujeiro, the upright stones have undergone a catastrophic evolution after the archaeological exploitation due to accelerated weathering through a process apparently distinct from natural granite decay in nearby outcrops. The biological attack of granite minerals by lichen exudates has emphasized the hazardous character of bromine and more has been learnt about construction techniques, namely, the insertion in the mound of an impermeable clay stratum that hinders water penetration into the dolmen chamber.

The characterization of original Roman ashlar blocks, including masonry and the diagnosis of Byzantine and medieval reconstruction testimonies in the Aqueduct of Carthage were the object of a detailed study by X-ray diffraction and synchrotron radiation X-ray fluorescence. Traditional constructive techniques and local construction materials were studied and successive historical, modern and recent rehabilitations were reappraised.

PACS 83.80.Nb; 64.70.Kb; 78.70.En; 41.60.Ap

1 Introduction

The diversity of solid–solid transformations involved in decay processes occurring along the lifetime of ancient monumental buildings are actually a challenge to material scientists.

As a result, the characterisation of ancient materials at the atomic level is increasingly embodied in studies on archaeological and historical specimens.

Environmental effects like climate and pollution significantly contribute to accelerate degradation phenomena and to make difficult a correct assignment of causes and mechanisms mixed up in those complex processes. Prior to the implementation of any preservation or conservation action, a considerable effort to identify the materials originally used and to assess the constructive techniques employed should be made, along with a careful analysis of the compatibility with new (actual) materials and a critical evaluation of stability and permanence of restoration works to be undertaken.

A review is presented on materials degradation observed in two historical monuments located in the Mediterranean basin: the Zambujeiro dolmen nearby Évora (southern Portugal) and the Roman Aqueduct of Carthage in Tunisia. As an overall output, emphasis is given to the need of conforming space rehabilitation procedures to ancient local construction methodologies, simultaneously taking into account the problematic of materials compatibility and durability.

2 The Zambujeiro dolmen (Évora-Portugal)

Megalithic monuments are unique testimonies of cultural manifestations dating from more than five millennia. Dolmens are particularly impressive amongst megaliths for the huge dimensions of granite "building" stones.

One of the largest dolmens in Europe was discovered quite accidentally about 60 years ago at the locality named Zambujeiro, nearby Évora, in the south of Portugal (Fig. 1).

2.1 *Materials*

The upright granite blocks typical of megaliths went through a catastrophic decay at Zambujeiro dolmen, following the archaeological excavation of the mound. The degradation mechanisms involved in such accelerated weathering were found to be distinct from natural granite alteration observed in nearby outcrops [1].

The ongoing solid–solid transformations are the consequence of exposure to the Earth's surface conditions – namely, temperature and humidity cycles, both daily and yearly – under a Mediterranean dry climate, following the release of mechanical stresses as a result of excavating the dolmen mound. Rock decay mechanisms were studied to delineate suitable conservation strategies (including the use of water-

✉ Fax: +351-21-471-9018, E-mail: ondina.figueiredo@ineti.pt

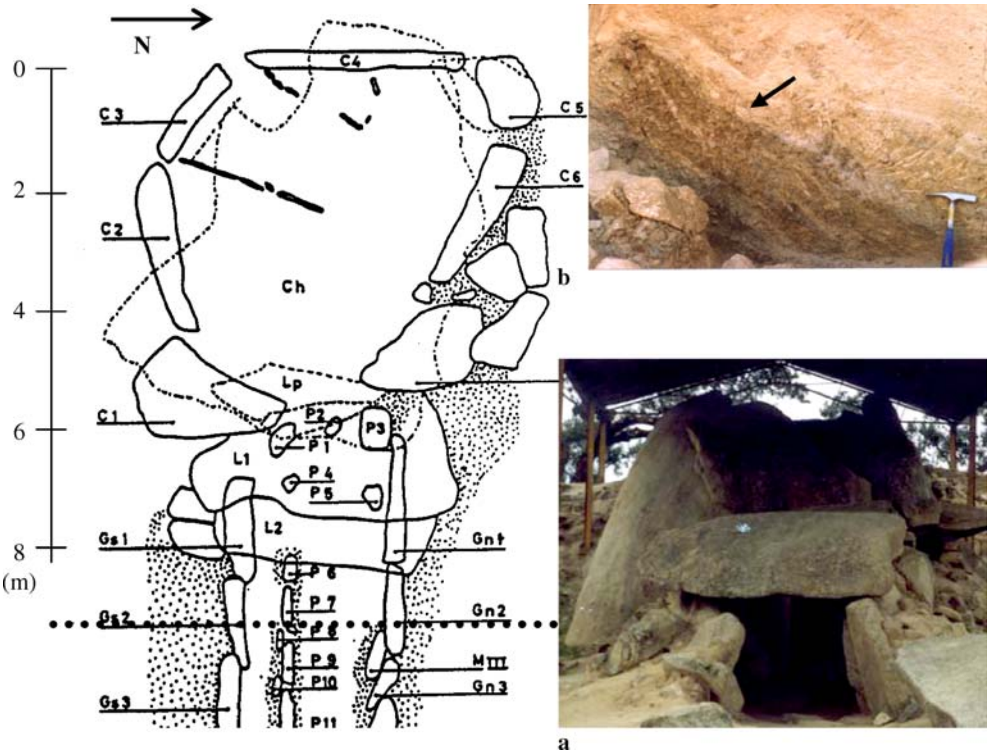

FIGURE 1 Sketch map of Zambujeiro dolmen (polygonal chamber and part of the corridor), at present protected by a metallic shelter (**a**). The excavation of the mound has exposed, close to C-4 stone, an impermeable smectite-rich clay stratum assigned by an *arrow* (**b**)

repellent organic additives when consolidating the stone blocks) [2].

The biological attack of granite component minerals by micro-organisms and lichen exudates – namely, of biotite by lichenic acids with formation of ferrous oxalate hydrate [3] – plus the weathering role played by these biogenic actions in stone decay [4] were addressed, showing that bromine is a relevant chemical agent in surface processes.

At the same time, more has been learnt about dolmen construction techniques: In particular, it has been noticed that an impermeable smectite-rich clay stratum was deposited when building up the mound. Supposedly, this layer aimed at hindering the penetration of raining water into the dolmen chamber.

2.2 *Techniques and results*

X-ray diffraction to identify the constituent minerals of the clay stratum included in the dolmen mound (Fig. 1b) was performed with a non-automated Philips Bragg–Brentano diffractometer equipped with a large-anode copper tube and a graphite crystal monochromator.

The occurrence of a smectite clay was unequivocally assigned, together with kaolinite and illite.

The chemical characterization of stone alteration materials and lichen encrustations has been carried out in a non-destructive way using synchrotron radiation X-ray fluorescence (SRXRF) at the former LURE (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Orsay/France). The instrumental set-up of the microprobe installed in the D15A experimental station at the DCI storage ring [5] was equipped with a solid state Si (Li) detector and the area to irradiate in the sample was positioned with the aid of a laser-beam by using a computer-controlled micrometer stage. Peak assignment was based on the usual diagnostic emission lines: K_α in the X-ray emission spectrum of elements with medium atomic number and L_α for elements with $Z > 42$. Data handling and processing programs developed at the LURE [6] were used for spectra deconvolution and analysis.

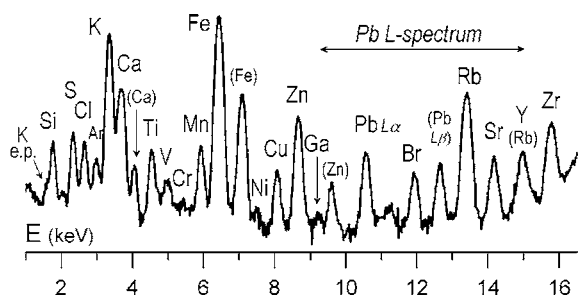

FIGURE 2 SRXRF spectrum (excitation energy 18.9 keV) collected from an encrustation of Xanthoria parietina lichen over a granite stone

SRXRF spectra collected from lichen encrustations over granite blocks (Fig. 2) showed the contribution of biogenically concentrated elements (Pb and Br, both characteristic of lichen biological activity).

3 The roman aqueduct (Carthage, Tunisia)

Built in the 2nd century [7], the Roman Aqueduct of Carthage, in Tunisia, is a unique piece of hydraulic engineering and architectural archaeology.

Integrating the common cultural patrimony of Mediterranean basin countries, this monument has been the object of detailed international studies focused on the description of Roman ashlars (Fig. 3) – blocks of sandstone, occasionally limestone – plus masonries (opus caementicium, op. signinum, op. incertum), on the characterization of medieval re-

a b c

FIGURE 3 Aqueduct of Carthage: (**a**) Roman arches in risk of dismantling being subjected to consolidation works; (**b**) fallen-down blocks of opus caementitium and original sandstone ashlars (**c**) detail of ashlar blocks displaying stone alteration by alveolization

construction works and on the diagnosis of Byzantine rehabilitation testimonies.

3.1 *Materials*

Traditional constructive techniques and local building materials were studied and successive historical, modern and recent rehabilitations were appraised [8]. Hypothetic geotechnical constraints (earthquakes and subsequent hazards, even not historically registered) and environmental features – particularly anthropogenic actions – were considered in relation to the structural failures observed along the Aqueduct aerial trajectory, 17 km long.

The building material used in medieval (Hafsid) reconstructions (Fig. 4a) was a mixture of lime and reddish argillaceous earth with hydraulic properties (still used nowadays under the name of torba). The adopted constructive technique is clearly expressed in fallen blocks manufactured in that period (Fig. 4b): Pillars were built using wood moulds progressively displaced from bottom to top; after a section had dried a thin layer of chalk or lime was spread over the surface before starting the new section.

3.2 *Techniques and results*

Mineralogical and chemical characterization of masonry and mortar materials was performed preferably using non-destructive X-ray techniques. Diffraction (XRD) spectra for phase identification and fluorescence (XRF) scanning for elemental qualitative analysis were directly collected from sample fragments. Synchrotron radiation X-ray fluorescence was also applied with the aim of ascertaining water provenance by studying the trace elements population in calcitic crusts deposited on water conduits [9] and also to characterize the fine isolating Roman stucco containing pozzolana and its medieval succedaneum incorporating crushed fragments of incompletely fired red ceramics mixed up with dispersed small carbon fragments.

Applied destructive instrumental methodologies included bulk chemical analysis together with the assessment of trace elements by X-ray fluorescence (wavelength dispersive mode, WDS). Table 1 is a summary of bulk XRF-WDS data representative of various constructive materials: Roman (including pozzolanic) and Hafsid mortars, masonries from various provenances (water conduits and stone joints), plus a hy-

Sample description	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	SO_3	LOI
Stone joint masonry	69.96	1.65	0.54	n.d.	15.95	0.35	0.18	n.d.	0.46	10.85
Hydrated lime masonry*	55.30	2.92	0.71	n.d.	24.84	0.50	0.80	n.d.	n.d.	14.89
Mortar (pozzolanic?)	36.60	4.31	0.84	0.47	35.69	0.24	0.46	n.d.	n.d.	21.34
Roman mortar	28.37	4.65	1.18	0.55	37.54	2.09	0.64	0.04	0.16	24.73
Mortar (fallen block)	36.82	1.46	0.41	0.42	33.55	0.37	0.17	n.d.	0.19	26.51
Water conduit masonry	20.79	4.56	2.05	1.00	38.61	0.20	0.41	0.13	0.13	32.07
Hafsid mortar (pillar)	19.18	2.79	1.01	0.95	40.30	1.04	0.15	0.03	0.36	34.03
Actual torba	12.66	2.34	0.86	0.94	44.94	0.44	0.25	n.d.	n.d.	37.54

* 19th century masonry from a Lisbon building; n.d., not detected; LOI, loss-on-ignition

TABLE 1 Chemical composition of mortars and masonries

a

b

FIGURE 4 Hafsid reconstruction of the Aqueduct: (**a**) sector enclosing a Roman arch and original water conduit; (**b**) dismantled blocks of Hafsid pillars

Sample description	LOI (% w/w)	Ca	Qz	Ca/Qz
Roman mortar (opus signinum)	26.94	61	39	1.6
Conduit mortar at Mohammedia	32.86	75	25	3.0
Hafsid mortar (filling from a pillar)	36.29	83	17	4.9
Actual torba	37.54	85	15	5.7

TABLE 2 Estimated calcite-to-quartz ratio (Ca/Qz) of mortars

draulic lime masonry from a recent building and an actual torba, both for comparison.

Using LOI values conjugated with CaO content to estimate calcite (Ca) component and SiO_2 content as representative for quartz (Qz), we could define an easy-and-quick test for assessing the period of manufacture on the basis of Ca/Qz ratios calculated for the analysed masonry (Table 2).

4 Conclusions

It is worth remarking that the lack of knowledge about construction raw materials and methodologies employed at the time of emplacement may configure serious drawbacks when foreseeing the implementation of a long term conservation strategy for monuments with such a long history as are the dolmens and the Aqueduct of Carthage. Large-scale rehabilitation projects recently carried out have in definite buried and occasionally destroyed testimonies of construction plus reconstruction materials and techniques that prevailed in the monument for many centuries.

It is then clear that a considerable effort to identify the materials originally used and the constructive techniques employed, along with a careful analysis of the compatibility with new (actual) materials and a strict estimate of durability for restoration works to be undertaken, must precede the implementation of any preservation or conservation action to be undertaken on historic monuments.

ACKNOWLEDGEMENTS Financial support of the EU through Contract nr. STEP-CT90-0110 and Concerted Action IC18-CT-0384 plus Action Access to Research Infrastructures (IHP Program) is acknowledged. Special thanks are due the former LURE beamline scientist Prof. Pierre Chevallier.

REFERENCES

1 M.I. Prudêncio, M.O. Figueiredo, J.C. Waerenborgh, L.C.J. Pereira, M.A. Gouveia, T.P. Silva, I. Morgado, I.R. Costa, J.D. Rodrigues, *ASMOSIA III Athens*, ed. by Y. Maniatis et al. (Archetype Publ., London, 1995), p. 285
2 J.D. Rodrigues, M.I. Prudêncio, M.A. Gouveia, M.O. Figueiredo, T.P. Silva, *Conservation of granitic rocks*, ed. by J. Delgado Rodrigues, D. Costa (LNEC, Lisboa, 1996), p. 13, ISBN 972-49-1685-5
3 M.O. Figueiredo, T.P. Silva, M.I. Prudêncio, M.A. Gouveia, J.C. Waerenborgh, L.C. Pereira, Procd. 6th Nordic Conf. Application of Scientific Methods in Archaeology, Arkaeologiske Rapp. Esbjerg Museum **1**, 153 (1993)
4 M.T. Ramos, M.O. Figueiredo, T.P. Silva, M.J. Basto, P. Chevallier, *Biomonitoring of atmospheric pollution – BioMAP*, (IAEA-TECDOC-1152, ISSN 1011-4289, 2000), p. 197
5 P. Chevallier, P. Dhez, F. Legrand, A. Erko, Y. Agafonov, L.A. Panchenko, A. Yashkin, J. Trace Microprobe Technol. **14**, 517 (1996)
6 J. Wang, D. Piccot, P. Chevallier, F. Legrand, K. Abbas, *Note CEA-N-2756*, (Commissariat à l'Energie Atomique (CEA), Saclay, France, 1993), p. 231
7 F. Rakob, Dossiers d'Archéologie **38**, 34 (1979)
8 M.O. Figueiredo, J.P. Veiga, T.P. Silva, *Historical Constructions 2001*, ed. by P.B. Lourenço, P. Roca, (Univ. Minho, Guimarães/Portugal, 2001), p. 391
9 M.O. Figueiredo, J.P. Veiga, T.P. Silva, A. Alvarez, F. Torrens, S. Khosrof, N. Ferchiou, *Procd. 9th Int. Congr. on Deterioration & Conservation of Stone*, Elsevier, **2**, 641 (2000)