INTERNATIONAL JOURNAL OF CONSERVATION SCIENCE

ISSN: 2067-533X Volume 6, Issue 3, July-September 2015: 335-348 www.ijcs.uaic.ro

THE CONTRIBUTION OF EARTH SCIENCES TO THE PRESERVATION OF UNDERWATER ARCHAEOLOGICAL STONE MATERIALS: AN ANALYTICAL APPROACH

Mauro Francesco LA RUSSA[1*], Michela RICCA[1], Cristina Maria BELFIORE[2], Silvestro Antonio RUFFOLO[1], Mónica Álvarez DE BUERGO BALLESTER[3], Gino Mirocle CRISCI[1]

[1] Università della Calabria, Dipartimento di Biologia, Ecologia e Scienze della Terra (DiBEST), Via Pietro Bucci, 87036 Arcavacata di Rende (Cs), Italy
[2] Università di Catania, Dipartimento di Scienze Biologiche, Geologiche e Ambientali, Corso Italia 57, 95129 Catania, Italy
[3] Instituto de Geociencias (CSIC-UCM), Facultad de Ciencias Geológicas, planta 7, despacho 17.4c/ José Antonio Nováis 12 28040, Madrid, Spain

Abstract

This work focuses on the study of alteration and degradation forms affecting underwater archaeological marble fragments mainly due to biological activity. The studied artefacts were recovered from the submerged archaeological park of Baia (Naples, Italy). It includes ruins of the ancient city of Baiae, which, since the 4th century AD, started to be submerged due to the bradyseism phenomenon. Diagnostic investigations were carried on 50 marbles specimens, collected from covering slabs of different pavements, from a specific area of the site called "Villa con ingresso a protiro". Several techniques, including stereomicroscopy, polarizing optical microscopy, scanning electron microscopy and mineralogical analysis, were used to study the superficial weathering, as well as the bioerosion phenomena due to the action of marine organisms and their interaction with the substrate in relation to textural features. Results revealed that the main degradation processes can be attributable to endolithic activity, capable of excavating cavities and tunnels causing irreversible damage to the archaeological materials. In addition, samples revealed a different degree of bioerosion related to their specific intrinsic characteristics.

Keywords: *Bioerosion; Composition; Damage; Marble; Texture; Underwater environment.*

Introduction

In recent decades, following the UNESCO 2001 Convention on the Protection of the Underwater Cultural Heritage, there has been an increasing interest in the preservation and management of the submerged heritage [1, 2]. As known, in fact, the marine environment promotes the development of deterioration phenomena on submerged archaeological structures, such as biological colonization by microorganisms, ionic corrosion and oxidation, which, sometimes, can cause serious alteration. In particular, the deterioration of natural and artificial stone materials is related to several factors associated to their intrinsic characteristics, such as texture, composition, technological properties, porosity, hardness and strength, as well as to the environmental conditions they are exposed to. Some important advances have been reached in

* Corresponding author: mlarussa@unical.it

this research field [3-7] and well known is the high reactivity of materials against the chemical and mechanical alteration.

This paper wants to underline the importance of protecting the underwater stone heritage, firstly highlighting how to undertake a study aimed to investigate the state of conservation of the archaeological underwater items. It focuses on the characterization of different decay forms affecting archaeological marbles as a result of the biological activity and the textural features of investigated materials. The analysed artefacts were collected from the submerged archaeological park of Baia (Naples, Italy) (Fig. 1), which is one of the greatest underwater sites in Italy including all the material evidence of human activities during the Roman times. The ancient Roman city of Baia testifies the great morphological transformations that occurred in the coastal area of Phlegraean Fields throughout the centuries, because of natural occurrences. The whole area of the Campanian coast is, in fact, long time dominated by the bradyseism phenomenon [8-10]. For this reason, Baia currently lies in submerged environment, at about five meters depth below the water surface [11-13]. Although many archaeological structures and architectural elements are still preserved, they show evident alteration phenomena mainly due to biocolonization as well as to many environmental influences [4, 5, 13].

Archaeological setting and sampling

The Archaeological Park of Baia (Fig. 1), located about 15 km west of Naples, is one of the most relevant submerged archaeological sites in the Mediterranean basin. It includes ruins of the ancient Roman city of *Baiae*, which, since the 4th century AD, started to be submerged due to the bradyseism phenomenon [4,11, 14].

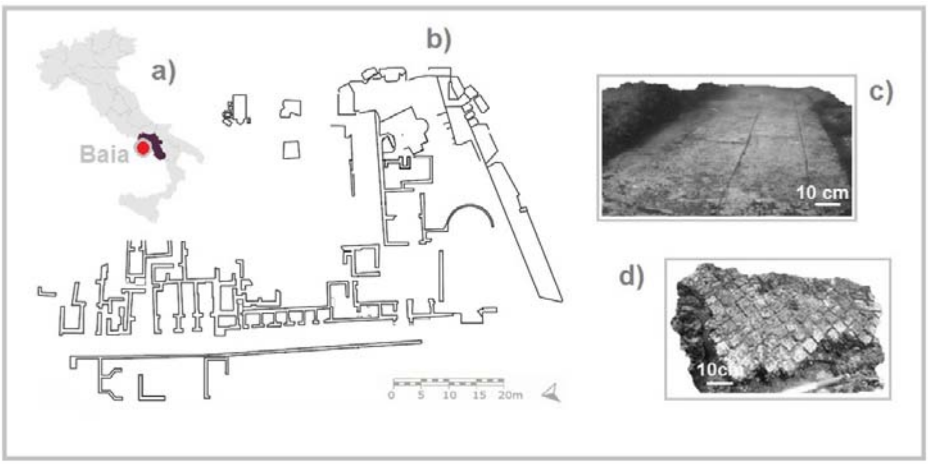
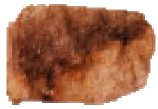
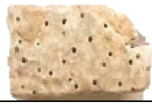
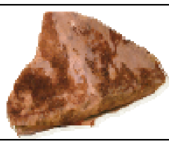


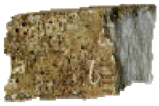
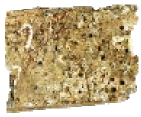
Fig. 1. a) Location of Baia in the Campanian region, Italy**; b)** Plan of the *Villa con ingresso a protiro*; **c)** and **d)** Portions of the *covering slabs* belonging to the Villa.

Many architectural structures are still preserved in the site, such as luxurious maritime villas, imperial buildings, private houses, *thermae* and *tabernae* [15], which were carefully mapped during the numerous underwater archaeological surveys [16, 17]. In 2000, the Italian Ministry of Environment created the ‘‘Baia Underwater Park” for the safeguard of the archaeological site. The *“Villa con ingresso a protiro”* is one of the best facilities that testify to the greatness of the Roman Empire, whose name was given for the presence of two columns – no longer existing – that were placed on two short parting walls built in front of the threshold

[13]. At present, the villa is located at a depth of five meters, with rooms extending for 40 meters. However, it is thought that in ancient times, during its heyday, the whole area was much wider. The Villa was chosen as case study for its large variety of architectural types and especially for the assortment of marble flooring and wall coverings, in almost all the rooms. Fifty marble samples (Table 1), with noteworthy alteration forms on the surface, were taken from pavement covering slabs (Fig. 1c, d), mainly in the northern, southern and south-eastern areas of the Villa. Sampling was carried out on representative portions of material of variable size (averagely ca. 0.7x2x1.5 cm), in relation to the different macroscopic appearances of decay forms, without compromising the integrity of artefacts.

Table 1. List of the examined archaeological marbles taken from the monumental complex of *Villa con ingresso a protiro.*

Sample	Object	Photographic representation	Sample	Object	Photographic representation
MV1	Fragment of pavement covering slabs		**MV34**	Fragment of pavement covering slabs	
MV2	Fragment of pavement covering slabs		**MV35**	Fragment of pavement covering slabs	
MV3	Fragment of pavement covering slabs		**MV36**	Fragment of pavement covering slabs	
MV4	Fragment of pavement covering slabs		**MV37**	Fragment of pavement covering slabs	
MV5	Fragment of pavement covering slabs		**MV38**	Fragment of pavement covering slabs	
MV6	Fragment of pavement covering slabs		**MV39**	Fragment of pavement covering slabs	
MV7	Fragment of pavement covering slabs		**MV40**	Fragment of pavement covering slabs	
MV8	Fragment of pavement covering slabs		**MV41**	Fragment of pavement covering slabs	
MV9	Fragment of pavement covering slabs		**MV42**	Fragment of pavement covering slabs	

MV10	Fragment of pavement covering slabs		**MV43**	Fragment of pavement covering slabs	
MV11	Fragment of pavement covering slabs		**MV44**	Fragment of pavement covering slabs	
MV12	Fragment of pavement covering slabs		**MV45**	Fragment of pavement covering slabs	
MV13	Fragment of pavement covering slabs		**MV46**	Fragment of pavement covering slabs	
MV14	Fragment of pavement covering slabs		**MV47**	Fragment of pavement covering slabs	
MV15	Fragment of pavement covering slabs		**MV48**	Fragment of pavement covering slabs	
MV16	Fragment of pavement covering slabs		**MV49**	Fragment of pavement covering slabs	
MV17	Fragment of pavement covering slabs		**MV50**	Fragment of pavement covering slabs	

Note: 2.5 cm

Methods

For a complete characterization of the selected items, different techniques were applied in order to: a) define the microscopic features; b) investigate the state of conservation; c) recognize the alteration forms due to biological activity. In particular, analytical methods here used include:

• Observations under a stereomicroscope (EMZ-5D, MEIJI EM), performed in order to preliminarily identify and quantify the biological communities in relation to the total surface of the fragments. Observations were preceded by samples treatment in a formalin solution, according to standard procedures [18], to preserve the stability of tissues of the biomass thus allowing the identification of the species. All samples underwent to a system of virtual crosshatching (Fig. 2) in order to detect the rate of coverage of the different species for unit area investigated. The estimation was performed using a scale of abundance (Fig. 2a), in which each coverage percentage of a specific species corresponds to a numerical unit. Several studies, in fact, show that this method, proposed by *J. Braun-Blanquet* [19], has good potential even for the estimation of submerged species [20].

• Polarising optical microscopy (POM) on thin and stratigraphic sections in order to: i) determine the textural characteristics of stone substrates, ii) understand the alteration mechanisms, and iii) evaluate the extent of decay. Observations were performed using a Zeiss AxioLab microscope equipped with a digital camera to capture images.

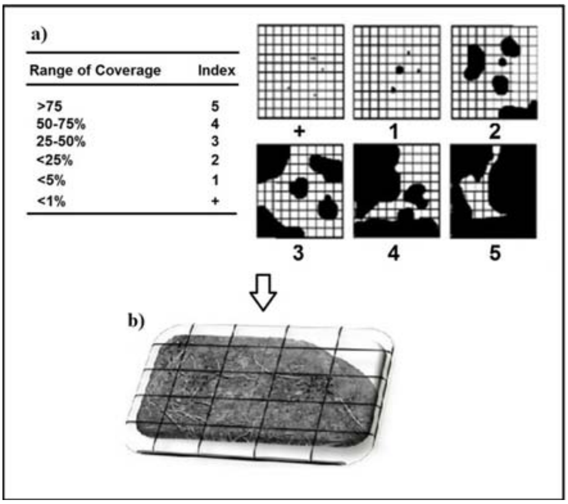


Fig. 2. a) Range and index of coverage of species on substrates;
b) Example of specimen underwent to a system of virtual crosshatching.

• X-ray powder diffraction analysis (XRPD) of stone materials to identify the constituent mineralogical phases. Analyses were performed on a D8 Advance Bruker diffractometer with CuKα radiation, using the following operative conditions: step-size of 0.02° 2θ, step time of 2s/step and an analytical range of 3–65°.

• Scanning electron microscopy (SEM 360 Cambridge Instruments Stereoscan), equipped with an EDAX Philips microanalysis working in energy dispersive spectrometry (EDS), to investigate the morphology of the species and the nature of their skeletal components and to assess the extent of the decay. Analyses were carried out with an acceleration voltage of 20 kV under high vacuum conditions (10^{-5} mbar pressure).

Results

Stereomicroscopy Observations

Observations of sample surfaces through stereomicroscopy revealed some variability in the type and rate of biocolonization between the different examined items. The rate of coverage of the different species for unit area in all investigated samples, determined through the method proposed by Braun-Blanquet [19], is reported in Table 2.

Some marble specimens (Table 2) show a slight biological growth characterized by thin superficial deposits, while others exhibit a great colonization in which, in addition to superficial concretions, bioerosion phenomena can also be observed. The presence of surface deposits is due to epilithic encrusting organisms (whose rate of coverage in all samples ranges from 5 to over 75%), mainly consisting of serpulids (Fig. 3a) and algae (Fig. 3c), and subordinately barnacles (Fig. 3a, b) and bryozoans (Fig. 3c). All these organisms produce carbonate deposits associated to their skeletons with variable thicknesses [4, 5, 21-23]. Furthermore, in several samples, a loss of material relating to the action of endolithic communities was observed (Fig. 3d). This phenomenon is mainly produced by organisms which develop and grow-up within the stone material [13, 15, 21, 24-26]. However, only a few endolithic organisms were recognized under stereomicroscope, such as some algae and molluscs, causing pitting and macro-boring. Even in this case, the coverage rate ranges from ~ 5 to over 75% among the specimens.

Table 2. Estimation of species identified on the 50 examined marble fragments by using the method proposed by Braun-Blanquet (1932) and the related scale shown in Figure 2.

	Superficial biomass					*Range* of coverage (%)	Index	Degradation forms
Sample	**Alg**	**Bal**	**Br**	**Mol**	**Ser**			
MV1	xx	/	x	/	xxx	> 75	5	Superficial deposit
MV2	xxx	/	/	/	xx	50-75	4	Superficial deposit, *pitting*
MV3	xx	/	/	/	xxx	50-75	4	Superficial deposit
MV4	x	/	x	/	/	25-50	3	Superficial deposit
MV5	/	/	/	x	/	< 25	2	*Macroboring*
MV6	xx	/	xx	/	x	50-75	4	Superficial deposit
MV7	xx	/	/	/	xxx	> 75	5	Superficial deposit
MV8	xx	/	/	/	xxx	> 75	5	Superficial deposit
MV9	xx	xx	/	/	xxx	> 75	5	Superficial deposit, *pitting*
MV10	xx	/	/	/	/	25-50	3	Superficial deposit, *pitting*
MV11	xx	/	xx	/	/	< 5	1	Superficial deposit, *pitting*
MV12	xxx	/	x	/	x	50-75	4	Superficial deposit, *pitting*
MV13	x	/	/	/	xxx	50-75	4	Superficial deposit, *pitting*
MV14	/	/	x	/	/	< 5	1	Superficial deposit, *pitting*
MV15	/	/	xx	/	xxx	> 75	5	Superficial deposit, *pitting*
MV16	x	/	/	/	/	< 5	1	Superficial deposit, *pitting*
MV17	xx	x	xx	/	xxx	> 75	5	Superficial deposit
MV18	x	x	xx	/	xxx	> 75	5	Superficial deposit, *pitting*
MV19	x		xx	/	x	25-50	3	Superficial deposit, *pitting*
MV20	/	x	xx	/	xx	25-50	3	Superficial deposit
MV21	xxx		x	/	/	50-75	4	Superficial deposit
MV22	X	/	/	/	/	< 5	1	Superficial deposit
MV23	xxx	x	xx	/	xxx	> 75	5	Superficial deposit, *pitting*
MV24	x	/	x	/	xxx	50-75	4	Superficial deposit, *pitting*
MV25	x	/	x	/	/	25-50	3	Superficial deposit
MV26	/	/	/	/	x	< 25	2	Superficial deposit
MV27	x	/	x	/	/	< 25	2	Superficial deposit
MV28	xx	/	/	x	/	25-50	3	Superficial deposit, *macroboring*
MV29	x	/	/	/	x	< 25	2	Superficial deposit, *pitting*
MV30	/	/	x	/	x	< 25	2	Superficial deposit, *pitting*
MV31	/	x	/	/	x	< 25	2	Superficial deposit, *pitting*
MV32	x	x	x	/	x	25-50	3	Superficial deposit
MV33	xxx	/	/	/	xx	> 75	5	Superficial deposit
MV34	xxx	/	/	/	/	50-75	4	Superficial deposit, *pitting*
MV35	/	x	/	/	xx	25-50	3	Superficial deposit
MV36	xx	/	/	/	x	25-50	3	Superficial deposit, *pitting*
MV37	xx	/	/	/	/	25-50	3	Superficial deposit, *pitting*
MV38	/	xx	x	/	/	25-50	3	Superficial deposit
MV39	x	/	/	/	/	< 5	1	Superficial deposit
MV40	/	/	/	/	xx	< 5	1	Superficial deposit, *pitting*
MV41	xxx	/	/	/	xx	50-75	4	Superficial deposit, *pitting*
MV42	xx	/	/	x	x	25-50	3	Superficial deposit, *pitting*, *macroboring*
MV43	xx	/	x	/	/	25-50	3	Superficial deposit, *pitting*
MV44	x	/	/	/	/	< 1	+	Superficial deposit
MV45	xxx	/	/	/	x	25-50	3	Superficial deposit, *pitting*
MV46	/	/	/	xx	/	25-50	3	*Macroboring*
MV47	x	x	/	/		< 25	2	Superficial deposit, *pitting*
MV48	x	/		/	xx	25-50	3	Superficial deposit
MV49	/	/	x	/	xx	25-50	3	Superficial deposit
MV50	xx	/	x	/	x	25-50	3	Superficial deposit

Notes: Alg. Algae; Bal. barnacles; Br. bryozoa; Mol. molluscs; Ser. sepulids; xxx. very abundant; xx. abundant; x. scarce; /. not present

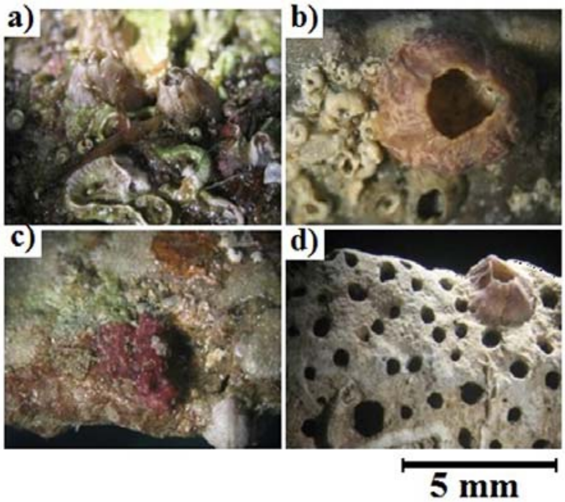


Fig. 3. Stereomicroscope photographs showing the surface colonization:
a) Calcareous skeletons of marine worms and barnacles;
b) Ventral view of a conical calcareous shell of barnacles and marine worms;
c) Encrusting red and green algae and bryozoa;
d) Bioerosion phenomenon related to endolithic sponges.

Mineralogical-petrographic analysis

Petrographic analysis of thin and stratigraphic sections trough polarizing optical microscopy allowed to investigate structural and textural features of archaeological samples as well as to correlate the intrinsic characteristics of materials with the different degree of alteration observed. Marble items cover a broad range of microfabrics (Fig. 4, Table 3) and also their state of conservation is rather variable among the examined artefacts. Samples range from coarse-grained (Fig. 4a, f; Table 3) to fine-grained (Fig. 4g, i; Table 3), with textures varying from heteroblastic to homeoblastic, depending on the sample. The maximum grain size (MGS) is comprised between 0.2 and 6.0 mm; the crystals show sutured, embayed and curved boundaries which indicate different and not always equilibrated metamorphic conditions [27]. Boundaries with triple junctions at 120° and traces of cleavage can be also observed.

Table 3. Main minero-petrographic features of the examined samples.

Group	Samples	Crystals grain size (mm)	Main mineralogical composition
Fine-grained	MV1, MV3, MV4, MV6, MV7, MV8, MV17, MV20, MV21, MV22, MV25, MV26, MV27, MV32, MV33, MV35, MV38, MV39, MV48, MV49, MV50	ranging from 0.2 to 0.9 mm	Calcite, with the exception of MV13, MV36, MV40, MV42 which are dolomite marble
Coarse-grained	MV2, MV5, MV9, MV10, MV11, MV12, MV13, MV14, MV15, MV16, MV18, MV19,MV23, MV24, MV28, MV29, MV30, MV31, MV34, MV36, MV37, MV40, MV41, MV42,MV43, MV44, MV45, MV46, MV47	ranging from 1.7 to 6.0 mm	

Regarding the degradation forms, petrographic observations allowed to point out some differences in relation to the grain size of samples. Specifically, the coarse-grained marbles show pronounced bioerosion phenomena consisting of pitting and macro-boring (Fig. 4a, f). Conversely, the fine-grained marbles are less sensitive to biological activity of endolithic species and are mainly interested by the development of layers (with variable thickness) on the surface (Fig. 4g, i).

All archaeological artefacts also underwent to XRD analysis in order to determine their mineralogical composition and understand at which extent the decay can vary according to this. Obtained spectra reveal that samples mainly consist of calcite with subordinate amounts of dolomite, micas and quartz, except for four samples (MV13, MV36, MV40, MV42) which have a pure dolomitic composition. Table 3 lists the mineralogical phases occurring in each sample and the relative abundances estimated on the basis of intensity of reflection peaks.

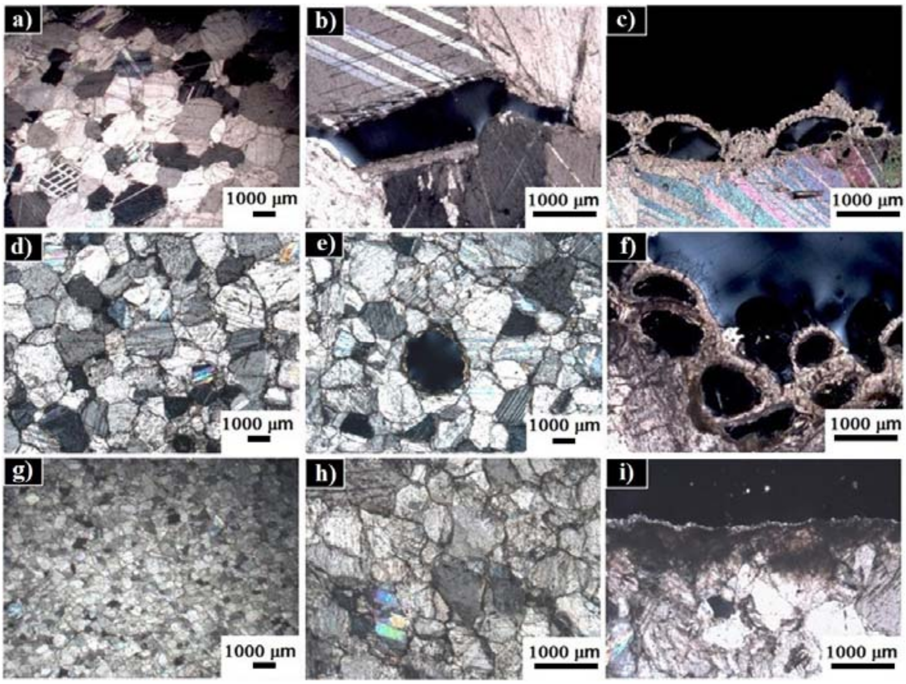


Fig. 4. Representative photomicrographs in cross polars light of different marble samples analyzed: **a)** coarse-grained marble (sample MV19) with microcracks **(b)** along grains and irregular and heterogeneous superficial layer **(c)**; **d)** coarse-grained marble (sample MV24) with boring phenomena **(e)** and irregular superficial layer **(f)**; **g)** fine-grained marble (sample MV48) with absence of perforation **(h)** but only a superficial and regular layer **(i)**.

Morphological analysis by SEM

Bioerosion phenomena described by Golubic et al [28] show the boring behaviour of endolithic species, emphasizing that different organisms penetrating into the same substrate under identical environmental conditions, produce distinctive boring patterns. Moreover, several authors have mentioned to a correlation between perforations and biological colonization [29-35].

In the present study, the identification of the biomass as well as the detailed observation of alteration forms and the estimate of the damage on the archaeological samples, were carried out through a scanning electron microscope. In particular, high-resolution scans of the borings within the samples allowed the systematic identification of the species through the recognition of their footprints or skeletal components.

Bioerosion phenomena have been identified in different intensity, size and shape among the fifty marble fragments. The distribution of the damage is quite irregular since tunnels and cavities at times appear isolated, while in other cases seem to cluster next to each other, with diameters exceeding 500 μm.

The most frequent bioerosion structures are those related to the activity of endolithic sponges (Fig. 5a, 5b) and bivalve molluscs (as regards the marine fauna), while less invasive are those related to algal colonisation (marine flora). All these organisms were recognized through the identification of skeletal and inorganic structures, calcareous or siliceous, or by studying their footprints left inside the stones.

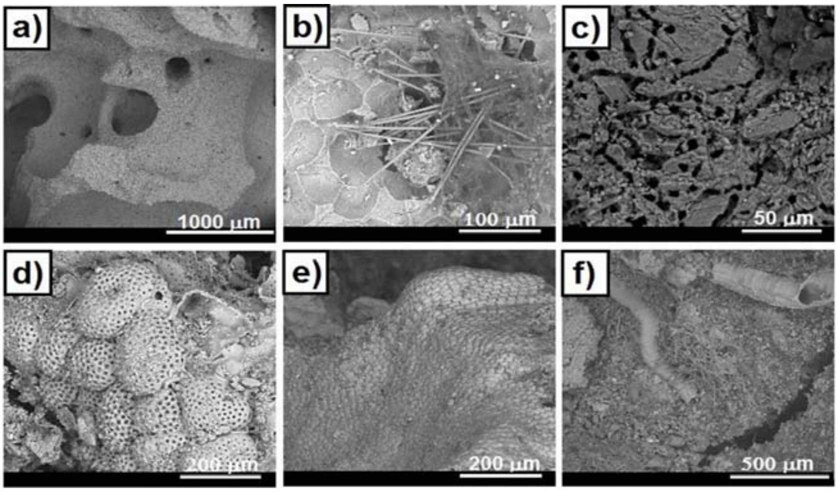


Fig. 5. SEM images of skeletal components and bioerosion phenomena on marble fragments: **a)** Sponge cavities; b) Sponge spicules and footprints; c) Micro-perforations; d) Bryozoa scheletal components; e) Algae flattened thalli; f) Marine worms.

In detail, as regards the perforating activity of endolithic marine fauna, the detected borings show singular shapes corresponding, from a taxonomic viewpoint, to the families *Clionaidae* (sponges) (Fig. 5a, b), *Gastrochaenidae* and *Mytilidae* (bivalve molluscs). Instead, concerning the endolithic flora, branched micro-galleries (Fig. 5c), with length between 0.5 and 7 μm, were found inside the fragments but the biological structures required to identify the taxa were not detected inside the micro-borings. Therefore, this type of degradation can only be generically attributed to microflora [25].

Observations highlight that SEM analysis allows to infer the correct taxonomy of the organisms causing bioerosion phenomena on the stone materials, contrarily to stereomicroscopy which permits only to investigate the superficial damage without detecting the taxa which grow within the artefacts.

Regarding the action of encrusting species, the phenomenon seems to be quite complex. In this case, dealing with superficial colonization, the same organisms previously recognised by stereomicroscope were also detected through SEM. However, their morphological features were observed in more detail. All the marine organisms with a calcareous skeletal component (Fig. 5d, e, f) tend to cover the colonized surface with carbonate layers whose thickness is highly variable depending on the species (usually from 50μm to 3 mm). These layers blight the archaeological artefact, losing its legibility and functionality. Therefore, the result is a strong aesthetic damage. Paradoxically, some authors (e.g. [4-5]) demonstrated the protective action of these carbonate layers on the surface, a phenomenon well known as *bio-protective effect*, schematized in Figure 6. When some species reach the life cycle, what remains on the archaeological surface is their inorganic component which is mainly of carbonate nature. These new thicknesses, called "sacrifice layers", become the new areas colonisable by marine organisms. The protective effects of these carbonate layers will strictly depend on the different biological communities that will act on them over time.

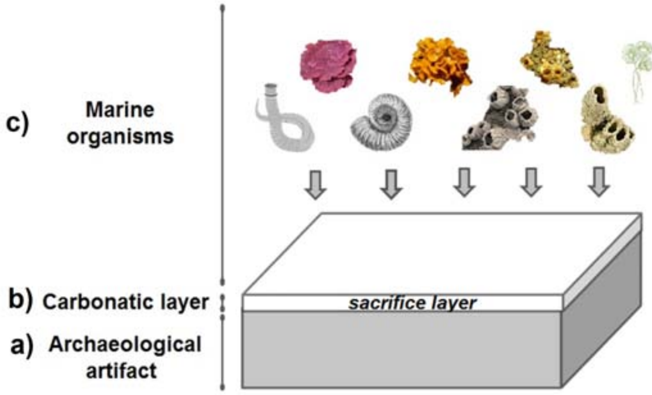


Fig. 6. Schematization of the "sacrifice layers" developing on archaeological items.

A detailed study of interaction patina-substrate on all examined marble fragments was also carried out on thin sections. Specific details on the morphology of the species and on their overlap on the substrate are shown in Figure 7.

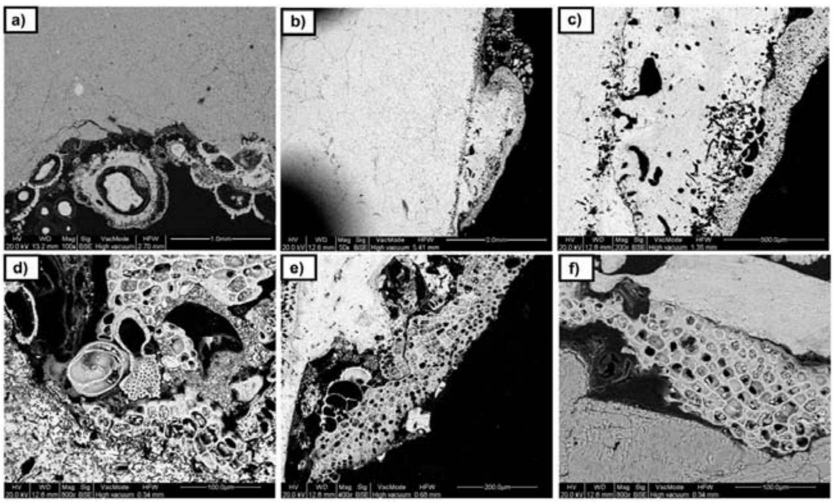


Fig. 7. SEM images of the encrusting deposits on the substrate: **a)** Irregular and heterogeneous carbonatic layer; **b)** Interaction patina-substrate; **c), d, e)** and **f)** Detailed transversal sections showing flared epithelial cells and cell fusions of red algae, gastropods shells, bryozoans and micro- and macro-boring phenomena.

The superficial deposits reveal thicknesses ranging between 0.05 and 3 mm as well as very heterogeneous and irregular trends. Intense bioerosion phenomena, micro-cracks and penetrations into the substrate, due to biological activity, were also detected. In particular, red algae covering wide surfaces with their compact and flattened structures are shown in Figure 7, along with gastropods shells, bryozoans and micro- and macro-borings related to some sponges, algae and molluscs.

Discussion

The data obtained by all analytical investigations display that some marble specimens (Table 2) show a slight biological growth characterized by thin superficial deposits, while others exhibit a great colonization in which, in addition to superficial concretions, bioerosion phenomena can also be observed. This is due to the fact that, although the main cause of degradation in underwater environment is biodeterioration, it develops differently according not only to a variety of environmental conditions in seawater (such as silting, sun exposure, seasonality, wave motion, etc.), whose actions could inhibit biological growth on materials or, conversely, encourage it, but also to the intrinsic textural features of the archaeological materials. Specifically, petrographic analysis of thin and stratigraphic sections through polarizing optical microscopy revealed that the degradation forms in marbles vary in relation to the grain size of samples. In particular, fine-grained marbles are less sensitive to biological activity of endolithic species (Fig. 4g, h, i) than coarse-grained marbles which, conversely, show pronounced bioerosion phenomena with irreversible loss of material (Fig. 4a, b, c, d, e, f). This is probably due to the greater compactness of the fine material and to the higher difficulty of species to penetrate into the grain boundaries. In more detail, it was shown that the main causes of decay in marbles coming from underwater environment are typically related to the action of endolithic sponges, algae and molluscs that produce pitting and macro-boring phenomena. Among the fifty examined marble samples, a strong damage accompanied by disaggregation and loss of material, was estimated for about the 65% of the total. The remaining 35% shows only an aesthetic damage, which interests exclusively the surface and is mainly caused by encrusting biomass (marine worms, barnacles, algae, bryozoans).

While texture and, particularly, grain size strongly influence the biocolonization developing on marbles, results obtained by XRD analysis revealed that the mineralogical composition of such stone materials does not affect the type of degradation forms developing on the surface. Calcite and dolomite marbles show, in fact, similar behaviour in terms of biological decay.

As a last consideration, the possibility to study the effects of biodegradation on materials with different textural features has allowed us to assess the importance of ordinary maintenance of the archaeological items. In particular, it is recommended to perform a proper cleaning of the materials, followed by a restoration work by using methods and products suitable to the specific underwater environment. In addition, when artefacts are subject to considerable loss of material due to biological activity (as in the case of marbles), it is recommended to use replacement materials that are less sensitive to bioerosion phenomena of endolithic species and, specifically, it is suggested using fine grained marbles.

Conclusions

The case study reported in this paper is highly representative of the importance of the use of the Earth Sciences' techniques in the study of archaeological samples coming from underwater environment since they are able to provide advanced scientific results, giving a major contribution to the preservation of Cultural Heritage.

In particular, different and complementary investigations have been performed to characterize the degradation forms of 50 marble fragments collected from the submerged archaeological site of Baia in order to define their state of decay mostly due to biological activity.

Observations through stereomicroscope and scanning electron microscope revealed, in some samples, an intense bioerosion phenomenon, mainly attributable to endolithic forms, capable of excavating cavities and tunnels causing irreversible damage to the archaeological materials. In addition, very thick encrustations due to epilithic species have been detected. The latter colonize the material surface, spoiling and leading to an aesthetic damage. Furthermore, on the basis of minero-petrographic investigations, it was possible to assess how the decay can widely vary within the same type of material depending on its proper textural features. Specifically, the results obtained suggest that the damage of a stone material due to biological colonization is inversely correlated to its compactness.

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Received: February, 21, 2015
Accepted: July, 24, 2015