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## RESEARCH ARTICLE

### MEASURES TO PRESERVE PAINTED AND UNPAINTED TOMBS AFFECTED BY DEGRADATION PROBLEMS AT THE ARCHAEOLOGICAL SITE OF MONTE SANNACE

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#### ABSTRACT

Research findings of microbial monitoring at the archaeological site of Monte Sannace have indicated high levels of bacteria, especially on the inner walls of the painted tombs, as tomb no. 8 (range: 16 - 56 CFU/ml). Tomb no. 105 was rich in organic matter (range: 10.34 - 16.33 g/Kg), organic carbon (range: 6 - 9.47 g/Kg) and biological growth was not very high (range: 0 - 15 CFU/ml). Research findings have demonstrated that deterioration in each kind of tomb was very different. In no. 8 deterioration was caused by natural agents and, at the same time, by anthropogenic factors: the roof as well as chemical products used for conservation has helped speed microorganism growth. Principal aim of this study was to provide information on the degradation processes and to predict areas at risk in conservation. We also studied potential risk of biological colonisation of newly exposed rock samples. Surveys were performed in three stages: before, during and after restoration.

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## INTRODUCTION

Conservation of wall paintings in archaeological sites can be difficult due to the severe damage caused by living organisms, which can degrade substrates as a result of their growth and metabolic activity (Mora, 1986). The study of the phenomena of degradation and the behaviour of microorganisms is essential in the design of strategies for prevention and restoration. The purpose of this study was to provide information on the degradation processes affecting the artefacts of an archaeological site and to predict areas where conservation is at risk and precarious. The study focussed on the archaeological site of Monte Sannace (Apulia - Southern Italy) and its ancient tombs. The walls and mural paintings provide a great environment for the growth of many microorganisms that metabolise a wide range of organic and inorganic substances, in combination with particles of dirt and other environmental contaminants, which accumulate on surfaces. The biological colonisation of mural paintings induces structural and aesthetic damage through mechanical and chemical alteration (Ciferri, 1999). In some cases, the

chemical compounds used to preserve and restore the stone and the frescoes interacted with the original materials, changing the physical and chemical properties thereof (Caneva *et al*, 1994). During the last restoration, at painting tombs of Monte Sannace, chemical cleaning with ammonium carbonate was performed to remove surface deposits, and the stone was treated with biocides based on ammonium salts ("Desogen") and triazine derivatives ("Lithium 3") (Ciancio *et al*, 1986). We analysed samples of rock from the tombs and the soils surrounding them using chemical and microbiological analysis techniques (CNR *et al.*, 1986; CNR *et al.*, 1989; CNR *et al.*, 1987). In archaeological sites, soils are very important because they contain artefacts and may also contain the remains of degraded archaeological materials. Thus, soils contain a store of information about the depositional and post-depositional history of artefacts and therefore should be examined. Such techniques can also be applied to anthropogenic materials (Cowie *et al*, 2009). Phosphorus is the only element that serves as a sensitive indicator of human activity and is persistent. In its common form of phosphate, phosphorus is generally stable and immobile in soils and is detectable even after long periods (Holliday *et al*, 2007). To evaluate the degradation of materials at different stages (before, during and after restoration), specimens of newly exposed stone similar in composition to the worn material, left in place for sixty days near the tombs,

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were examined. We analysed two cylindrical samples of newly exposed limestone placed near tomb no. 8, along the south side and inside tomb no. 105. The samples were analysed again after sixty days and after the restoration. Moreover, the effects of a cover at the archaeological site relative to its conservation function and the control of biological growth were also examined. In this study a multidisciplinary approach was implemented. Specifically, analytical techniques were used to examine both biological and chemical characteristics of soils and to obtain information on the causes and mechanisms of degradation.

## MATERIALS AND METHODS

### Location and duration of study

This study was conducted at Monte Sannace archaeological site, one of the most important and well-known archaeological sites of ancient Apulia, that is in a very precarious state of conservation, especially in the area where large painted graves are located.

### Experimental design and Grouping

Diagnostic analyses were performed on worn material and on samples of newly exposed material, gathered in situ with a scalpel, sterile swabs and cellulose micro-membranes. Sampling was carried out as described in CNR and ICR, 1989.

Four different types of samples were examined (Table 1):

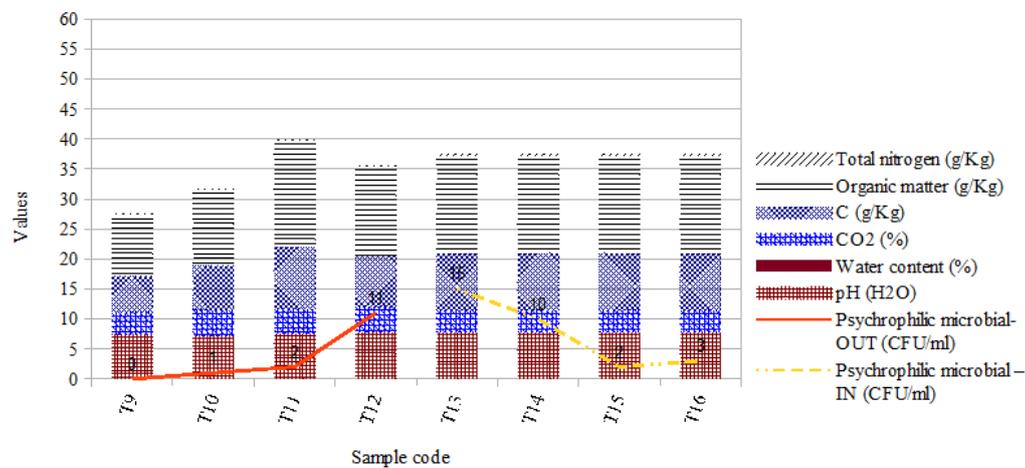
- stone fragments from the walls of the tombs,
- stones from newly exposed areas,
- microbiological samples from the tombs
- Soil samples.

### Procedures

The study was carried out in the following steps. First, samples were examined in situ, and two samples of newly exposed material were examined immediately after being left near the tombs (at time  $t = 0$ ). After sixty days, the newly exposed samples were analysed again. Each sample (weight = 50 g) from the tombs, from the newly exposed material and from the

**Table 1 Description of samples and type of investigation**

Samples code	Unpainted stone	Painted stone	Soil	Investigation
T1, T2, T3, T9, T10, T11, T12	x			Chemical, microbiological
T4	x			Microbiological
T5, T6, T7, T8, T14, T15, T16		x		Microbiological
T13		x		Chemical, microbiological
N1, N2	x			Chemical, microbiological
S1, S2			x	Chemical



**Graph 1. Chemical and microbiological analysis of tomb no. 105**

In this study two different kinds of tombs were analysed: tombs no. 105 and no. 8 (Fig 1). Tomb no. 105 is located on the acropolis, in excavation area "D". It is a semi-chamber tomb with walls composed stones arranged in regular parallelepipeds, plastered on the inside and decorated with a red horizontal band. Tomb no. 8 is located in the acropolis, in excavation area "G", placed inside a building of the VI century b.C. The tomb is oriented from east to west and is composed of regular squared stones, without overlapping binding, plastered and painted inside. To preserve the frescoes in the tomb no. 8, a roof structure made of iron and plastic was built above it. Both tombs are located outdoors and thus exposed to the weather and are in a very precarious state of preservation.

soil was analysed with respect to pH level, total carbonate, CO<sub>2</sub> content, available phosphorus, total nitrogen, water content, Organic matter. Biological contamination was evaluated by measuring the microbial growth (Psychrophilic microbes) on the samples obtained using the nitrocellulose membranes (Fig 2). After purification of the different morphotypes of colonies identified, isolated microorganisms were identified by observed wet mounts under a light microscope according to the method reported in CNR and ICR 1987 (Fig 3). Newly exposed sample N1, placed near tomb no. 8, and sample N2, near tomb no. 105, were sterilised before the analysis.

### Monte Sannace Archaeological site



Figure 1. Tomb n. 8 (A) and n. 105 (B) of Monte Sannace Archaeological site. Tombs were sampled for each side (North, South, East and West) and on outer and inner sides. For conservation reasons in tomb n.8, inner side, were analyzed only non-destructive microbiological samples, because it is fresco painted

### Microbiological analysis

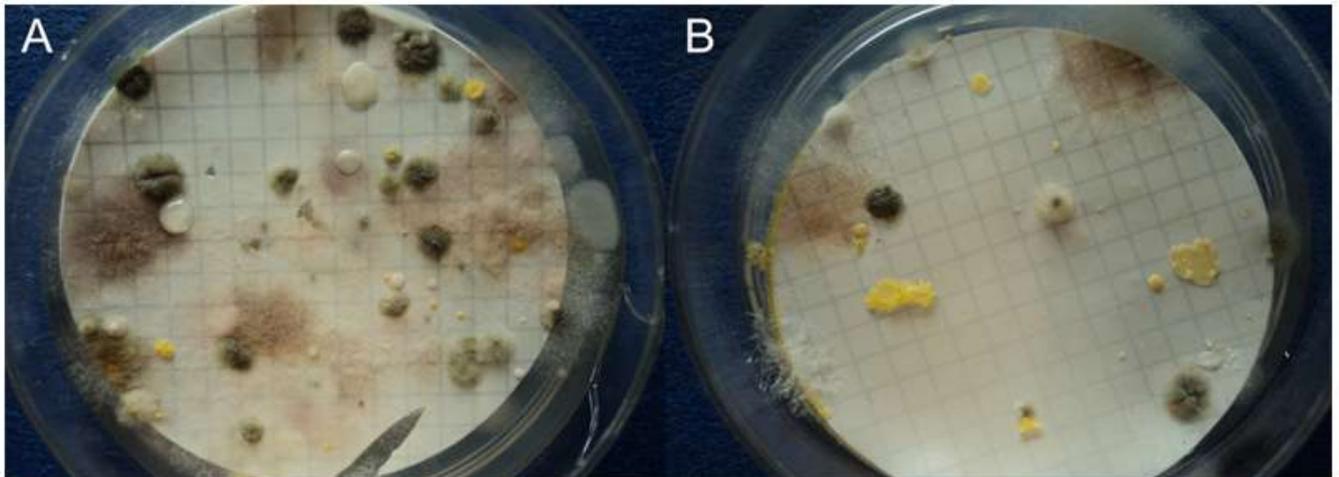


Figure 2. Microbial colonies on Petri dishes with agar growth media. Sample T8 of tomb n. 8 (A), sample T14 of tomb n. 105 (B)

### Micro-photograph

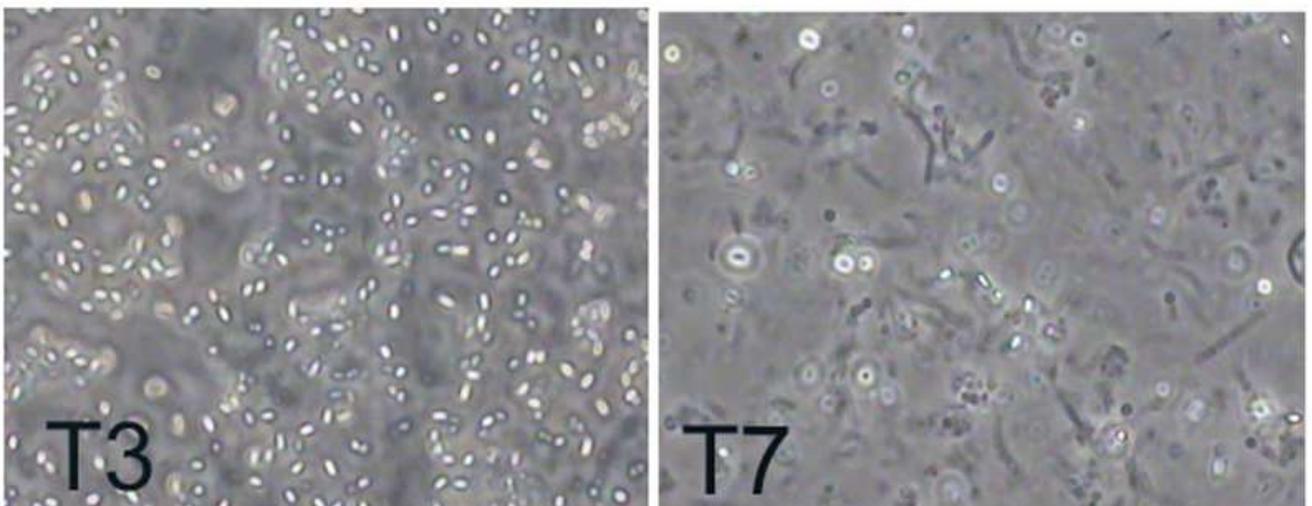


Figure 3. Micro-photograph acquired by optical microscopy, magnification 1000x, showing microbiological colonisation of the stone surface of tomb no. 8, samples T3 and T7

### Painted tomb



**Figure 4. Sampling procedure performed on stone surface of painted walls of the tomb n. 8 using nitrocellulose membrane. The surface of wall is very faded due to biological and chemical deterioration**

## RESULTS

The wall of tomb no. 105 were rich in organic matter (range: 10.34 g/Kg - 16.33 g/Kg) and organic carbon (range: 6 g/Kg - 9.47 g/Kg). However the extent of biological growth, and particularly that of fungi, lichens and bacteria, is not very high (range: 0 CFU/ml - 15 CFU/ml). The highest values of phosphorus were measured in tomb no. 105 and in the soil sample collected from within it (sample T12 = 25.67 mg/Kg, sample S1 = 25.4 mg/Kg). Values of organic matter were not very high (range: 1.28 g/Kg - 4.74 g/Kg) in tomb no. 8. Moreover an high extent of microbial growth was measured on the surfaces of the stone and frescoes (range: 16 CFU/ml - 56 CFU/ml) and especially in the inner walls (T6 = 56 CFU/ml). On the outer southern wall (sample T3), a large number of viable microorganisms (56 CFU/ml), a high organic matter content (4.74 g/Kg), a low value of total nitrogen (0.16 g/Kg) and a low cation exchange capacity (10.32 cmol(+)/Kg) were detected. The value of total nitrogen measured along the southern wall is lower than that of the other walls, in agreement with the high microbial growth observed. The soluble salts content in tomb no. 8, obtained from conductivity measurements, in the northern outer wall, is high (T1 = 1.22 mS/cm). At  $t = 0$ , no bacterial colony (0 CFU/ml) was detected in samples N1 and N2. After sixty days of exposure ( $t=60$ ), 87 colonies (CFU/ml) were detected in N1, placed near tomb no. 8, and 15 (CFU/ml) in N2, placed near grave no. 105.

## DISCUSSION

The result of organic matter and organic carbon shows that tomb no. 105 was substrate for the growth of micro-algae and lichens, which formed a coloured (e.g., green, brown) layer and broke up the stone, making it porous. The microorganisms, after dead, were remained on the surface, leaving a black residue and forming an over-layer on the stone. The highest values of phosphorus measured in tomb no. 105, and in the soil sample collected from within it, was due to the remains of human bones, mixed, in powder form, in the soil and near the tomb walls.

The walls of tomb no. 8 have been restored and consolidated many times in recent years, with biocides based on ammonium salts and triazine derivatives. Due to the chemical cleaning, all of the microorganisms that lived on the stone were killed. Immediately after the cleaning, the extent of microbial growth was approximately equal to zero. The CFU/ml value detected in this study for tomb no. 8 represented the extent of microbial growth that occurred from the last cleaning to today. The chemical compounds used did not remove organic residues left on the stone, which must be removed mechanically and heterotrophic microorganisms metabolise the organic residues. The soluble salts content in tomb no. 8, obtained from conductivity measurements, was greater than that in the other archaeological structures examined and the surrounding soils, especially in the northern outer wall. Due to the difference in volume between the salt crystals and the stone, the plaster and paints on the stone walls become detached. Efflorescence occurred all over the walls of the tomb, especially on the northern wall.

The frescoes of tomb no. 8 appear to have been intensely altered by biological reactions, which induced the discolouration of the paints of bacteria, as sulphur-oxidising, with calcium ions of the limestone, transforming it into calcium sulphate (gypsum) (Fig 4). The gypsum forms a white layer on the surface of the limestone and obscures the colours of the frescoes. The organic matter detected, particles of animal and vegetable origin, increased with the number of microorganisms detected. The decrease in the nitrogen content, and consequently the cation exchange capacity, indicated the activity of nitrifying microorganisms. Nitrifying bacteria use organic ( $\text{NH}_2^-$ ) and ammoniacal nitrogen ( $\text{NH}_4$ ), transforming them into nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^-$ ). Total nitrogen measured only organic and ammoniacal nitrogen, not the oxidised forms (nitrate and nitrite).

## Conclusion

The extents of deterioration of the two tombs, no. 8 and no. 105, are very different. In tomb no. 105, the sources of degradation are mainly natural: the stone directly exposed to atmospheric and biological agents is subjected to breaking, colour alteration and an increase in porosity. In tomb no. 8, the deterioration is caused by natural agents and, at the same time, by human factors: the roof that covers the tomb as well as the chemical products used for conservation help speed microorganism growth.

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