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A study on microclimatic parameters and conservation state: the case of wall paints of the Archeological Site of Baia (Italy)

Paola Cennamo[1], Roberta Scielzo[1], Giorgio Troisi[1] and Elena Chianese[2]
[1]*Department of Humanities, University of Naples Suor Orsola Benincasa, 80132 Naples, Italy; paola.cennamo@unisob.na.it (P.C.); scielzoroberta@gmail.com (R.S.); giorgio.troisi@docenti.unisob.na.it (G.T.)*
[2]*Department of Science and Technology, Parthenope, University of Naples, 80143 Naples, Italy; elena.chianese@uniparthenope.it (E.C.)*

Abstract –

The present study investigated the correlation between the degradation processes of cultural heritage and environmental parameters. The case study of this research was a semi-underground room (*ninphaeum*), decorated with marine motifs, dating back to the third century, painted with frescos technique of third century. This site, also indicated as SB-E0-R07, is located in the northern area of the Mercury sector of the archaeological park of Baia, in Italy; the nearby nymphaeum, 10 meters away, was also investigated to highlight any correlations between the two rooms. The main diagnostic techniques used to investigate the environmental parameters were Ion Chromatography (for the chemical characterisation of deposits) and Thermography, alongside other investigations based on knowledge of the original materials of the artefacts and biodeteriogens (here not discussed). The data obtained showed that the underground environment, which also has rising brackish water, was affected by the presence of biodeterogens whose distribution and growth is strongly favoured by the environmental parameters above all as well as by the substrate. All the data were then cross-referenced to obtain a complete knowledge of the conservation frameworks of the environments, essential for identifying the most compatible and effective restoration methodologies to be applied in the conservation of the SB-E0-R07 environment.

INTRODUCTION

The purpose of this study was to study the environmental parameters and the degradation processes in a semi-hypogeum room located in the North zone of the Mercury's Sector of the archeological park of Baia, Italy. During this research, both room SB-E0-R07, the main subject of the present work, and the near nymphaeum were investigated to find any possible correlation among the degradation phenomena identified in the primary environment. The two nymphaeums are located at a short distance from each other (2 m), but at a different height from the sea due to the phenomenon of bradyseism. Due to this difference, the second chamber has about 20 cm of brackish water on the lining. A further difference is given by the presence of wall paintings on the main wall of the SB-E0-R07, a room decorated with frescos paintings of the Roman era, and the near nymphaeum (the two rooms are directly adjacent and, probably connected), while the second has decorations only on the upper frame. These sites were probably part of a thermal complex and, despite their proximity, they are very dissimilar.

Figure 1 – Detail of the room SB-E0-R07. It is possible to notice the massive presence of biodeteriogens in particular on back wall and on the ceiling.

Figure 2 - Detail of the nerby nymphaeum. It is possible to notice the presence of brackish water on the

lining.

In the analysis of the conservation state of architectural surfaces, in fact, the examination of environmental context is one of the major elements to investigate to find out the causes of degradation of artistic artifacts (mainly caused by humidity [1]) and, consequently, to plan adequate conservative strategies to preserve cultural heritage. In the archeological park of Baia, in particular, the environmental context is notably complex due to the presence of thermal groundwater, as well as other factors like the existence of vegetable species and the proximity of the port area.

2. MATERIALS AND METHODS

During the present study, we investigated the variations of humidity levels and temperature on the horizontal and vertical axis of room SB-E0-R07 for one year, collecting the data during two weeks per season (on an hourly base), to trace a daily seasonal and annual profile using four data logger ORIA©. Each datalogger was put in the border area of the room across the horizontal and vertical axis to ensure the monitoring of the whole environment.

Unfortunately due to the absence of electricity in the surrounding areas, it wasn't possible to place a monitoring system to collect the external air to analyze its composition and the presence of pollutants.

In addition to the investigations of environmental parameters, the analysis of saline efflorescence was performed to gain information about the predominance and spatial distribution of detected species.

Surface samples were collected at different heights and at different distances from the room entrance, following the vertical and horizontal axis to find out the variation of the Salt species and to verify any correlations with other degradation phenomena. Samples were then analysed by means of Ion Chromatography technique for the determination of minor and major ions concentration.

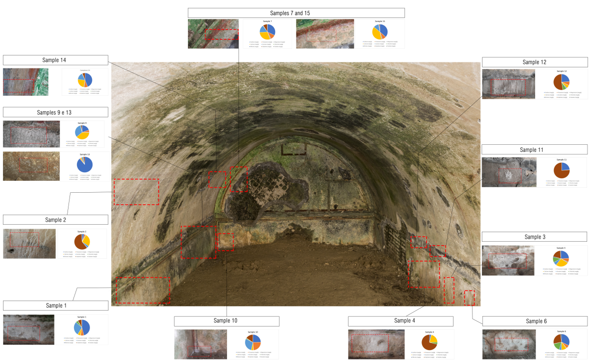

Figure 3 – Map of pickig areas of Salts present in room SB-E0-R07

Before major and minor ions determination (Cl^-, F^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-} $HCOO^-$, CH_3COO^-, $C_2O_4^{-2}$, Na^+, K^+, NH_4^+, Ca^{2+} and Mg^{2+}), samples were treated with ultrapure water and sonicated to allows the extraction of soluble constituents.

Then, solutions were filtered using membranes with 0.2 mm pores size. Pre-treated samples were analyzed using an ion exchange chromatography Dionex IC-1100 with a double line for anions and cations determination; compliance method and accuracy were discussed in [2].

The thermographic investigations, on the other hand, were conducted divided the artifact into six sections, each subjected to heating cycles, through the use of a convector, until a temperature increase of about 6°C is reached in each area. The resulting thermal response of each section was register during the period and warm up with a 10Hz frame rate used LAVIO TVS500 LWIR camera with an array of microbolometer sensors 307, electrically cooled by Peltier cells and using a 50 focal length lens mm and IFOV 0.3 rad. From the image sequences thus acquired, a heat recovery maps were obtained, through the use of a home-made calculation procedure built with MATLAB R2019b software.

3. RESULTS AND DISCUSSION

The graphs of indoor humidity and temperature show, in particular, variations of RH along the vertical axis of room SB-E0-R07. The thermal data indicate a difference of only 2°C both in the perpendicular and parallel sections of the room, while the difference in humidity rates, equal to 3% on the horizontal axis, shows a difference of 6% along the longitudinal axis.

From the curve of the hygrometric rates variation, it can be seen that, over the year (Fig.4), there are decreases in overall values around 4 pm with a slow degradation to the minimum at about 2 pm.

These data are fully reflected by the curves of thermal variations; in fact, at this time, there is a maximum of the temperature value.

The room SB-E0-R07 is particularly exposed to solar radiation, precisely between 1 p.m. and 3 p.m., leading to an increase in temperatures and a lowering of humidity, particularly in the areas close to the entrance. After 2 p.m., follows a slow increase in the hygrometric rates and a decrease of the overall temperatures in correspondence with the evening time slots.

It is important to highlight, on the other side, that the indoor temperature is constant during all the seasons (Fig. 5), a sign of the influence of thermal water present in the nearby nymphaeum and under room SB-E0-R07.

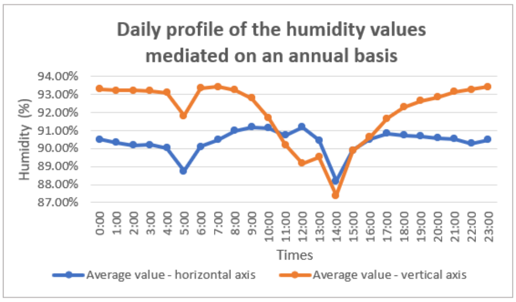

Figure 4 - Variations of the daily profile of the indoor humidity of the room SB-E0-R07 on an annual basis.

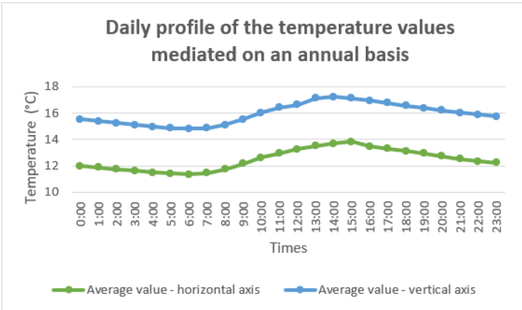

Figure 5 - Variations of the daily profile of the indoor temperature of the room SB-E0-R07 on an annual basis.

Microclimatic factors are the main causes of the proliferation of the biodeteriogens (mainly Cyanobacteria and algae [3]) on the frescos paintings on this site. The high humidity levels (with a maximum value of 94% over the year) and mild temperatures (the room has a constant temperature of 12-14 °C all over the year) are due to the presence of thermal water in the area under room SB-E0-R07 and in the near nymphaeum. These values influence the distribution of the water content in the surfaces of the environment, as shown by the thermography analysis (Fig 6). Previous analyses conducted by De Luca et al 2023 [4] indicated that the two nymphaea host different microbial communities. In particular, the 1st nymphaeum presents a greater microbial complexity thanks also to the presence of less water inside and the external part similar to soil and colonized by plants, it contains, among others, bacterial taxa commonly found in soils such as Rhizobiales, Burkhorderiales and Frankiales [4] which are not present in the inner part. Cyanobacteria were the dominant phylum in almost all samples regardless of origin, followed by Actinobacteriota and Alphaproteobacteria. The cyanobacteria are fine known settlers of ancient and modern stone monuments, where play an important role in the biodeterioration of these substrates [5].

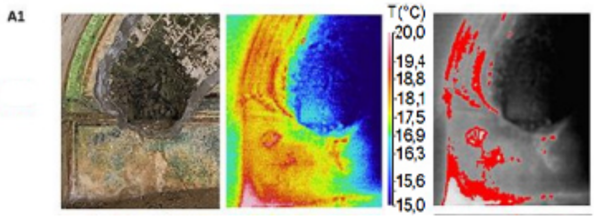

Figure 6 – Section of the room SB-E0-R07 investigated during the thermography analysis. On the left image, is the photo of the investigated area, on the central one, is the thermic frame, and on the right one is the map of heat recovery of the analysed zone.

The peculiar environmental characteristics of the archaeological Park of Baia led also to the formation of different species of salts.

In Fig 7 and Fig 8, ionic composition (expressed as percentage) of sample 3 and 6 (collected from the lower part of the wall adjacent to the nymphaeum) are reported. For sample 3, it is possible to notice the high level of calcium (Ca^{2+}), attributable to the substrate composition (calcium carbonate); in addition, there are great amounts of sodium (Na^{+}) and sulphate (SO_4^{2-}). These species can be related to the permeation of thermal water (chemical composition is showed in Fig. 8) from the next nymphaeum, as confirmed by the presence of the highest of all percentage of chloride (Cl^{-}).

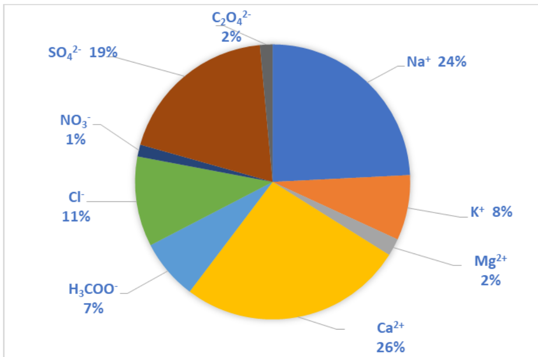

Figure 7 – Ionic composition for sample 3, collected from the lower part of the wall adjacent to the nymphaeum.

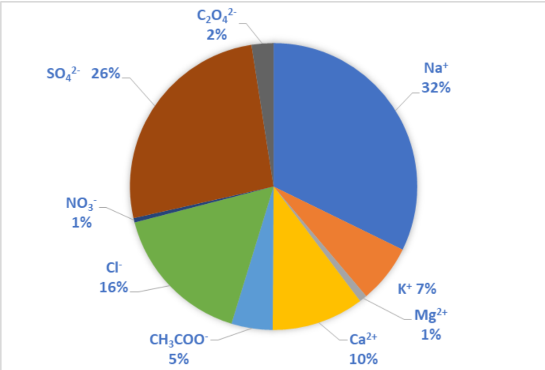

Figure 8 - Ionic composition of sample 6, collected from the lower part of the wall adjacent to the nymphaeum.

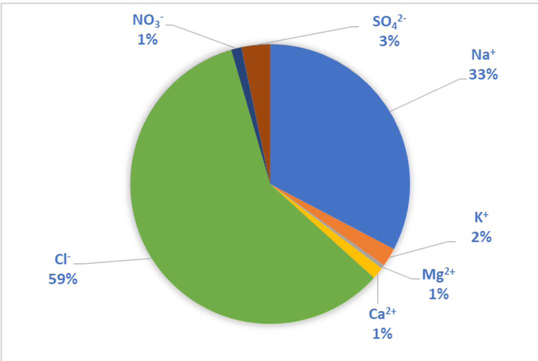

Figure 9 – Ionic composition of the thermal water presents in the down area of the nympheum.

To better understand the presence of the high concentration of sulphate (SO_4^{2-}) and to assess the contribute of thermal water on salts deposition, a mass balance was performed.

In particular, the contribution of sea-salt (expressed as mg of sea salt per gram of sample) was determined by means of the relation [6]:

$$\text{sea salt (mg/g)} = [Cl^-] + 1.47 \times [Na^+]$$

For samples 3 and 6 the contribution of sea-salt is in the range 1-6 mg/g; these values indicate that there are other contributions in addition to the permeation of water from the near nymphaeum. It should be noted that the points 3 and 6 were previously interred, so the chemical composition of surface samples here collected can be affected by the chemical species of the soil.

Among the samples here considered, the samples 13, 11 and 4 show the highest sea-salt contribution, with values of 325, 39 and 20 mg/g respectively; these samples are all collected from the lower section of the walls and present clear signs of moisture (see Fig 3).

For sulphate, we used the following relation to evaluate the amount of sea salt sulphate (ss-SO_4^{2-}), namely the sulphate of marine origin:

$$\text{ss-}SO_4^{2-}\text{ (mg/g)} = [SO_4^{2-}] - [Na^+] \times 0.2516$$

and, consequently, the non-sea salt sulphate (nss-SO_4^{2-}), namely the sulphate attributable to other sources:

$$\text{nss-}SO_4^{2-}\text{ (mg/g)} = [SO_4^{2-}]\text{tot} - \text{ss-}SO_4^{2-}$$

Generally, the values of nss-SO_4^{2-} for the samples here considered are very low with, in some cases (samples 1, 9, 13, 14, 15) negative values, indicating a loss of sulphate to respect the balance of a seawater sample.

On the contrary, samples 4 and 13, showed very high values (151 and 80 mg/g, respectively) indicating that the presence of sulphate can be due to other sources; the possibility of the sulfation process on carbonate substrate can be considered but needs to the confirmed.

Finally, the presence of other species may be attributed to the variety of conservation conditions of room SB-E0-R07, among them, the presence of biodeteriogens that can determine the presence of some organic species, as oxalate ($C_2O_4^{2-}$) and acetate (CH_3COO^-).

These aspects determine a consequent variation of ions percentage in the composition of salts, even if collected in adjacent areas of the site [6,7,8].

4. CONCLUSIONS

The analysis of the microclimatic parameters and chemical composition of saline efflorescence is an essential step of the conservative investigations of room SB-E0-R07. The high variations of degradation processes had to find out a specific match in the salts compositions as the variations of thermo-hygrometric parameters, confirming the high influence of these factors in the causes of damage to the Cultural Heritage.

Detachments of the preparatory layers of painted heritage are knowingly caused by the variations of the physical state of salts that can reduce the cohesion of the original material with subsequent loss of decorations, like in-room SB-E0-R07. Salts can also cause a whitening of the surfaces, as seen in the present case.

The influence of the thermo-hygrometric conditions of the nymphaeum, and in particular the presence of thermal water in this room, on the other side, contributed to the manifestation of specific Ionic and biological species, typical of the marine environment.

The identifications of the Ionic species and the variation of humidity and temperature moreover contributed to identifying the most adequate conservative strategies and to planning some future approaches to improve the conservation f room SB-E0-R07 (e.g.

periodic cleaning of the decorative surfaces to reduce the biological growth). The environmental characterization also helps us to understand the phenomena of biodeterioration and, above all, to justify the presence of some microorganisms such as marine eukaryotics and previously reported bacteria from the sea (particularly hot springs).

In fact, their presence can be explained by the presence of numerous saline encrustations in both nymphaeums, which may be the result of infiltrations of brackish water

through the rock and could create a saline environment suitable for the survival of this bacterial species.

REFERENCES

[1] Danti C., Matteini M., Moles A., Le pitture murali: tecniche, problemi, conservazione, Firenze, Centro Di, 1990

[2] Chianese, E., Tirimberio, G., Riccio, A. 2019. PM2.5 and PM10 in the urban area of Naples: chemical composition, chemical properties and influence of air masses origin. Journal of Atmospheric Chemistry, 76, 151-169.

[3] Vincent W. F., Cyanobacteria in «Encyclopedia of Inland Waters» edited by Gene E. Likens, Amsterdam, Elsevier, 2009

[4] De Luca, D., Piredda, R., Trojsi G., Cennamo P., Close but different: Metabarcoding analyses reveal different microbial communities in ancient Roman nymphaea, International Biodeterioration & Biodegradation, 181 (2023) 105619

[5] Crispim, C. A. & Gaylarde, C. C. Cyanobacteria and biodeterioration of cultural heritage: a review. Microb Ecol 49(2005), 1–9.

[6] Lewis, E.R., Schwarts S.E., Sea Salt Aerosol Production: Mechanisms, Methods, Measurements and Models-A Critical Review, Washington, DC, American Geophysical Union, 2013; pp. 9–99.

[7] Manual for the GAW Precipitation Chemistry Programme: Guidelines, Data Quality Objectives and Standard Operating Procedures, Vol. CLX, World Meteorological Organization, 2014

[8] Arakaki T., Azechi S., Somada Y., Ijyu M., Nakaema F., Hitomi Y., Handa D., Oshiro Y., Miyagi Y., Tsuhako A., Murayama H., Higaonna Y., Tanahara A., Itoh A., Fukushima S., Higashi K., Henza Y., Nishikawa R., Shinjo H., Wang H., Spatial and temporal variations of chemicals in the TSP aerosols simultaneously collected at three islands in Okinawa, Japan, Atmospheric Environment, Vol. 97, 2014, pages 479-485.