VAKHTANG BERIDZE
1ST INTERNATIONAL SYMPOSIUM
OF GEORGIAN CULTURE

Georgian Art

in the Context of European and Asian Cultures

Proceedings

JUNE 21-29, 2008 GEORGIA

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PROCEEDINGS

TBILISI 2009

UDC(უაკ)7(479.22)+008.1(479.22:100)
ქ-279

PUBLISHED BY:
GEORGIAN ARTS & CULTURE CENTER through
INTERNATIONAL INITIATIVE FOR GEORGIAN CULTURAL STUDIES
7, N.Nikoldaze str.,
Tbilisi, 0108, Georgia
e-mail: gacc@gaccgeorgia.org
www.gaccgeorgia.org

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DESIGN AND TYPESETTING:
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Photography on the cover:
David Garedji Monastery. Bertubani 13th c

Printed in: PETITE Ltd

ISBN 978-9941-0-2005-6
ISSN 1987-829X

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BIODETERIORATION OF MURAL PAINTINGS IN THE CHURCH OF THE VIRGIN IN MARTVILI (GEORGIA)

ABSTRACT

The biological attack of the mural paintings of the church of the Virgin in Martvili was analysed, with a floristic and ecological approach. This problem was particularly relevant in the case of the western porch of the church, where diffuse growths of blackish, green and pink patinas, due to cyanobacteria (Chroococcales) and other bacterial forms were detected. These biological colonisations were studied through optical microscopy and SEM, and differences between the different phenomenologies appeared mainly quantitative, with exception of the pink ones. These latter seem in fact to be referred to other bacterial forms, with carotenoid pigments, linked to high light input and lower values of humidity. In general, the changes in biodeterioration appear to be correlated mainly to light and air circulation, especially to the direction of humid air and fog during winter. Considering the porosity of the materials (mortars and stone) and the different environmental conditions in the porch, a map of the humidity level of the walls has been developed, using these organisms and their distribution as bioindicators.

Some conservative treatments were carried out with preliminary tests of efficiency, using two biocides (Rocima 110 and Preventol R80, quaternary ammonium salts, in the first case plus an organotin compound) widely tested and used in the past. Further interventions of environmental conditioning were also suggested, in order to limit the ecological ability of these organisms to grow, and solve this problem in a long lasting way.

HISTORICAL NOTES

The Church of the Virgin in Martvili (7th- 19th century) is one of the most significant monuments in Georgia and one of the oldest and most important centres in Western Georgia. It served as the Episcopal Chair of the Georgian Orthodox Church from the 10th Century until its abrogation by Russian governors at the beginning of the 19th Century. At one time, the interior of the church was almost entirely decorated with paintings made in various periods from the 14th to the 17th Centuries. The frescos are executed in a combination of both fresco and secco methods, and are depicted with a distinctly Georgian combination of Byzantine style and unique individual details.

Climatic analysis of the site MARTVILI (Samegrelo Region, Georgia)

In order to better understand the ecological relationships between the biodeterioration problems, a general climatic analysis of the site was carried out, and for the definition of the microclimate, we also utilised the data previously collected by Ing. I. Massari (Massari, 2004).

The elaborated data (collected from 2001 to 2005, including monthly precipitation, temperature and humidity) show that rainfalls have a quite homogenous distribution (Autumn = 278.9 mm; Spring = 291.1mm), with an increase during Summer (300.1mm) and a reduction in Winter (154.7 mm).

The rainiest month is June (131,4 mm), while the least one is January (41,2 mm), with average rainfall of 1024,8 mm per year. The medium monthly humidity is very relevant and the values are always higher than 70%, with a maximum in February (80,4%) (60-65% are threshold values for the spore's germination).

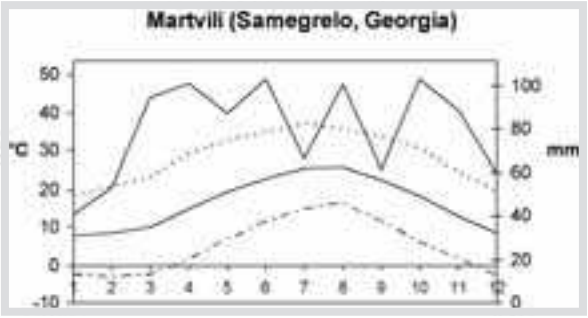
The average minimum monthly temperatures are under 0°C during the winter period and also in March (all these months are characterized, in fact, by a strong Cold Stress), while they are little warmer in November (1,6°C) and during April (1,3°C). The coldest month is February with an average minimum temperature of - 3,1°C. The higher temperatures instead are the summery ones, with values higher than 30°C for May and from June to October. The month with the higher maximum temperature is July (36,7°C).

From the analysis of these data (Tab. 1) it has been possible to characterize the climatic station of Martvili according to the Rivas Martinez classification (Rivas Martinez, 1995), which, on the basis of bioclimatic indexes, subdivides the world-wide climate into five macrobioclimates (Tropical, Mediterranean, Temperate, Boreal and Polar).

The Samegrelo Region is in the West part of Georgia and in part it stands along the Black Sea coast, where subtropical climate features are dominant: high humidity and heavy precipitation. This influence decreases going into the interior part of the Region and in the Martvili station it seems not relevant. Data of the Martvili climate show, indeed, that the Macrobioclimate is Temperate- boreal, and the Bioclimate is oceanic - semicontinental, with superior *Thermo- moderate Thermicity* i*ndex* and *inferior Humid Ombrothermic index.*

Tab. 1 – Resume of climatic data, Martvili station.

	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	Oct	Nov	Dec	Year
	Precipitation of the months (mm)												
Average	41,2	53,7	94,5	109,2	87,4	131,4	65,8	102,9	61,4	128,9	88,5	59,8	1024,8
	The average temperature of the months (0° C)												
Average	6,6	6,1	8,4	12,7	18,3	21,8	24,4	25,1	22,8	17,3	11,8	6,9	15,2
	The max. temperature of the months (0° C)												
Average	17,8	20,4	22,8	28,7	32,3	34,6	36,7	35,3	33,5	30,3	24,2	19,5	28,0
	The min. temperature of the months (0° C)												
Average	-2,7	-3,1	-2,8	1,3	6,6	11,0	14,6	16,1	11,7	6,0	1,6	-2,7	4,8
	Average relative humidity of the months (%)												
Average	79,2	80,4	78,2	74,8	75,8	76,8	73,4	75,2	75,8	79,4	77,6	79,2	77,2
	max. relative humidity of the months (%)												
Average	94,2	95,6	95,8	96,2	92,6	96	89,4	89,4	91,8	95,4	94	94,4	93,7
	min. relative humidity of the months (%)												
Average	62,6	56,4	53,4	43,2	56,4	53,8	55,8	58	54	60,2	51,6	54,6	55



1 Thermopluviometric diagram of Martvili (Samegrelo Region).

Biodeterioration problems of mural paintings

Literature describes wall paintings as frequently subject to biodeterioration, whether as a result of their high porosity, or because in their indoor environments, conditions favoring biological growth are often found (high RH, phenomena of capillarity and/or condensation) (Ciferri, 1999; Nugari et al. 2005).

The previous investigation carried out in Georgian churches confirmed the relevance of the biological colonization in the deterioration of these substrata (Meggiolaro et al., 1998; Gittins et al., 2002). In fact, during the restoration activities in the churches of Kintsvisi and Timotesubani, supported by the World Bank and the Getty Conservation Institute, the biological attack to the mural paintings was observed to be one of the most relevant conservative problems (Vedovello & Gittins, 2006).

In the case of the Martvili church, the biodeterioration problem looked particularly heavy on the mural paintings in the western porch, where diffuse growths of blackish, green and pink patinas of biological origin were easily detectable (Fig. 2). According with the literature, the degradation of frescoes was greater in areas adjoining windows and doors, and in proximity to the ground. In these areas microorganisms are found in greater quantities, evidence of the importance of air-flow either because of the easier deposition of spores linked to air movement, or the greater degree of humidity linked to a fall in temperature (Nugari et al. 2005).

In the other part of the mural paintings and of the walls inside the church, the biological problems were located only in parts where a certain water input from rising damp and sufficient light occur.

To establish the nature of the various forms of biodeterioration of the mural paintings different samples were collected, considering at least one sample for each phenomenology of alteration, and using a sterile scalpel or brushing some powder of the patinas from the surfaces.

These biological colonisations were studied in laboratory through optical microscopy and SEM, in order to define at least the main etiological agent of the alteration. In particular Raman spectroscopy was utilized to identify the nature of the pigments giving rise to the pink coloration.

RESULTS

The samples coming from the green and especially from black patinas showed a not negligible presence of cyanobacteria belonging to *Chroococcus* sp. (Fig. 3).

Choroococcus cyanobacteria are photosynthesing organisms that need light and a certain water input. They have a gelatinous sheath and black melanins (which explains the black patinas that they can form) for protecting themselves from dryness and from too high solar radiations. They have also chlorophylls (which explains the green patinas that they can also form in other ecological conditions) associated with other photosynthetic pigments.

These organisms have been also detected from the pink alterations, but in lower quantity.

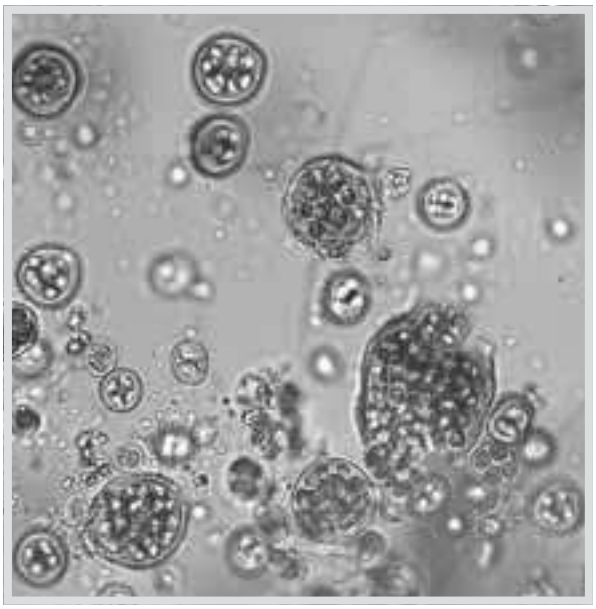
The scanning electron microscopy showed in fact the presence of coccoid forms, of bacterial nature, widely diffused in all the samples. The floristic composition of the different phenomenologies of alteration looked quite similar (especially for the green and black patinas) and the quantitative differences appeared more relevant with respect to the qualitative ones (that means changes in the optimality values of the same species due to ecological gradients).

The scarce information obtained only from morphological observation did not allow, however, reaching a satisfactory taxonomical identification. In this case, such as for the pink alteration, a PCR amplification with specific primers should be needed, as underlined by different Authors (Schabereiter-Gurtner et al., 2001; Imperi et al., in press in this same volume). On the contrary, cultural analysis in these cases appeared not very useful, due to the difficulty of some species to grow on the usual cultural media used in laboratory. This problem explains the isolation, after cultural analysis, only of *Mycelia sterilia* in similar cases of biodeterioration of mural paintings in Georgia.

In the case of the pink alteration, however, the presence of other bacterial species besides cyanobacteria can be supposed. Raman spectroscopy permitted to identify the presence of carotenoids of biological origin, similar to those detected in other cases of biodeterioration of mural paintings (see Matera's, in Imperi et al., in press). In the case of the Crypt of the Original Sin (Matera), the species responsible of the alteration was a *Rubrobacter,* a heterotrophic bacteria containing carotenoids, ecologically linked to light, but preferring a lower level of humidity with respect to cyanobacteria and algae. This species was present in a complex microbiological ecosystem and it was favoured by an increase of dryness, due to climatic variations. The ecology of the bacteria responsible for pink patinas of Georgia appears similar with respect to those of Matera, and the presence of these patinas are limited to areas with sufficient light, but lower humidity.

In the case of Martvili, the residual presence of cyanobacteria we observed in the pink samples can be explained considering the great fluctuation in the composition of the community in relation with local environmental variations.

2 Different biodeterioration pattern in the western porch (left with respect to the entrance).



3 Samp1e observed under optical microscopy, showing a great growth of cyanobacteria belonging to Chroococcales.

Indirect information on the environmental characteristic of the various parts of the mural paintings in the porch, which appears very relevant for suggesting conservative treatments, arises from the typical distribution of the various phenomenologies of alteration, related to a differential ecology of the species.

Taking into account the supposed ecological requirements, the humidity gradients occurring in the walls can be assumed, together with direction of air circulation.

In fact, the changes between green and black patinas appear to be related to a different water input, and when it is higher the cover of these organisms looks higher. When it is reduced, but in conditions of lighting, the pink bacteria take advantage and become prevalent. This finds an explanation considering the distribution of these organisms, limited to the entrance of the church (being the only position with a sufficient lighting).

The distribution of the biological patinas (always connected to situations with a sufficient lighting) in the porch appears to be linked to air circulation and to the direction of humid air and fog, that should be very relevant in the cold winter periods. Considering the very high values of air humidity in winter, the very high risk of condense in such months and the presence of dense fogs arriving from the outside, the entrance room is very exposed to biodeteriorative phenomena. At the same time, rising damp is also relevant, but especially the permanence of fogs, seems to be a discriminating factor (the lower parts are often less colonised that the higher ones), with exception of few points were rising damp occurs. The differential porosity of the stone with respect to the plaster explains also the differential cover of the different patinas. It is interesting to note that the plaster appear to have, in this case, a lower value of porosity with respect to the old ones.

Concluding, the phenomenology of alteration seems to be the resultant between air humidity entering from the door and carrying humidity to the walls, the porosity of the surfaces that condition the water content of the substrate and a sufficient lighting.

These ecological hypotheses are reconstructed in Figs. 4 and 5, elaborated from the photographs of the different kinds of biological colonisation, considering both qualitative and quantitative data.

Conservative treatments

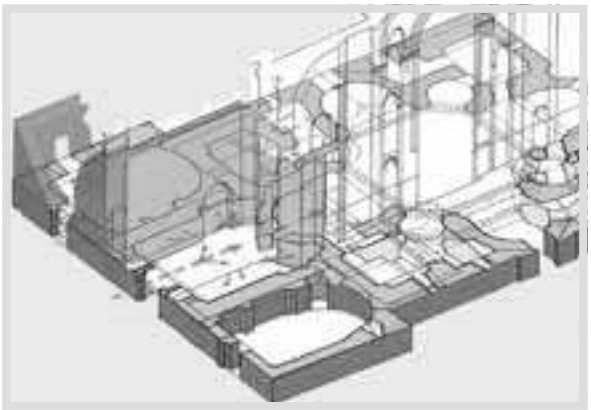
A correct methodology in carrying out a treatment considers various aspects such as (Caneva et al., 2005):

- Efficacy in relation to deteriogenic macro- and micro-organisms of the various materials;
- Possible interactions with the substrate;
- The best method of application in relation to the different kinds of biological colonisation, the nature of the materials and the state of conservation of the work;
- The long term effects and the possible interactions with other products utilised during restoration;
- Innovative and alternative methods as opposed to the traditional methods of disinfection and disinfestations.

In this case, after the identification of the biodeteriogens, some biocide tests (Preliminary tests of efficiency) were performed, considering the following products:

- Rocima 110 (*quaternary ammonium salt + tin naphthenate*) – Acima;
- Preventol R80 (*benzalkonium chloride*) – Bayer.

Preventol R80 was widely tested and used in the past, also for the treatments of mural paintings, and us-



4 Main directions of air circulation in the western porch.

ing the product in a sufficient concentration the results of efficiency were satisfactory (with more than one application) (Caneva et al., 1996; Nugari & Salvadori, 2002). It is a product with not high toxicological problem.

Biocides containing quaternary ammonium salt with organostannic component (such as Rocima 110, or Metatin 58-10) look generally more efficient but the toxicological problems cannot be negligee. Some restriction in the use of those products is now present in many European countries. The new formulation of Metatin 906 (containing isotiazolinone) is more toxicologically safe with respect to the old ones, but it is not yet sufficiently tested. It is a new product, which will substitute the previous ones, but very few data exist on efficiency against these organisms and on the potential interference on these materials. Collections of data are in progress by scientific laboratories of restoration.

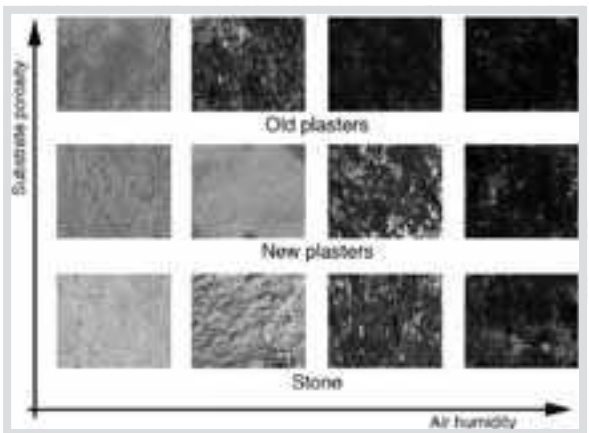
The tests were carried out on 4 sampling zones, in order to cover all the phenomenology of alteration. For each one the 2 products were tested at 2 concentrations, using distilled water as solvent, according to the following scheme: TOP right TOP left Preventol R80 2%4% DOWN right DOWN left Rocima 110 2%3%

A total of 4 tests x 5 sampling areas (20 tests) were therefore carried out, applying the products by brushing. The tests were carried out on August 2007, and the efficiency was evaluated over time, taking photographs in the following days, and watching the changes in the phenomenology of the biological alteration.

The two products showed a similar activity: while Rocima 110 resulted to have a bit slower activity with respect to Preventol R80, in some cases the efficiency of the first one appeared to be only a bit more higher (for example in the case of the green patinas), but not with significant differences. Also, the different concentrations used appeared not so relevant and sometimes the comparison between them resulted difficult because of the application methodology. In fact the brushing systems of application don't permit indeed to dose exactly the quantity of product to lay on the surfaces. Moreover, no treatment have been completely sufficient to remove the biological patinas and more then one application appeared to be necessary to have a complete biocide activity. Furthermore, the black patinas appeared to be the most resistant ones to the biocidal treatment. Finally, laboratory tests observing the changes in fluorescence should be necessary to better evaluate the biocidal activity.

Considering this, we suggested the use of Preventol R80 at 2%, diluted in distilled water for all the alteration forms (taking into consideration that the presence of salts in the normal water can reduce the biocidal activity), as the best compromise in terms of efficiency/safety. The results indicated the need to repeat the treatments (two or sometimes three times), staggered with one week, and finally cleaning with distilled water. In the case of dense patinas, especially the black ones, a partial mechanical removal was also suggested, eventually using a compress for favouring the contact.

In parallel to any biocide treatment, which will function only for a short time if the environmental conditions do not change, it appears urgent to project a



5 Ecological gradient in conditions of sufficient lighting as in the western porch.

system for protecting the porch from the external humidity. In this case the reduction of lighting appears also useful, but not sufficient to eliminate the biological growths, if the humidity remains in such high values.

As it was made in other critical situations (hypogeans, crypts e.g.), a new system of isolation of the entrance door, reducing the direct income of humidity especially in cold winters, without stopping completely ventilation, seems to be necessary.

ACKNOWLEDGEMENTS

We acknowledge the Getty Conservation Institute (Los Angeles), the Staff of the Georgian Arts and Culture Center and of the Department of Preservation of Georgian Monuments at Ministry of Culture of Georgia, and the Faculty of Restoration at Tbilisi State Academy of Arts, for supporting in different ways this work. We also acknowledge the Georgian group of restorers for checking the biocides tests, and Mark Gittins and Sabina Vedovello (CBC) for the help in the field and for the useful suggestions. Thanks to Dr. A. Di Giulio and A. Merante, of our Department, for SEM analyses and for graphical assistance.

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