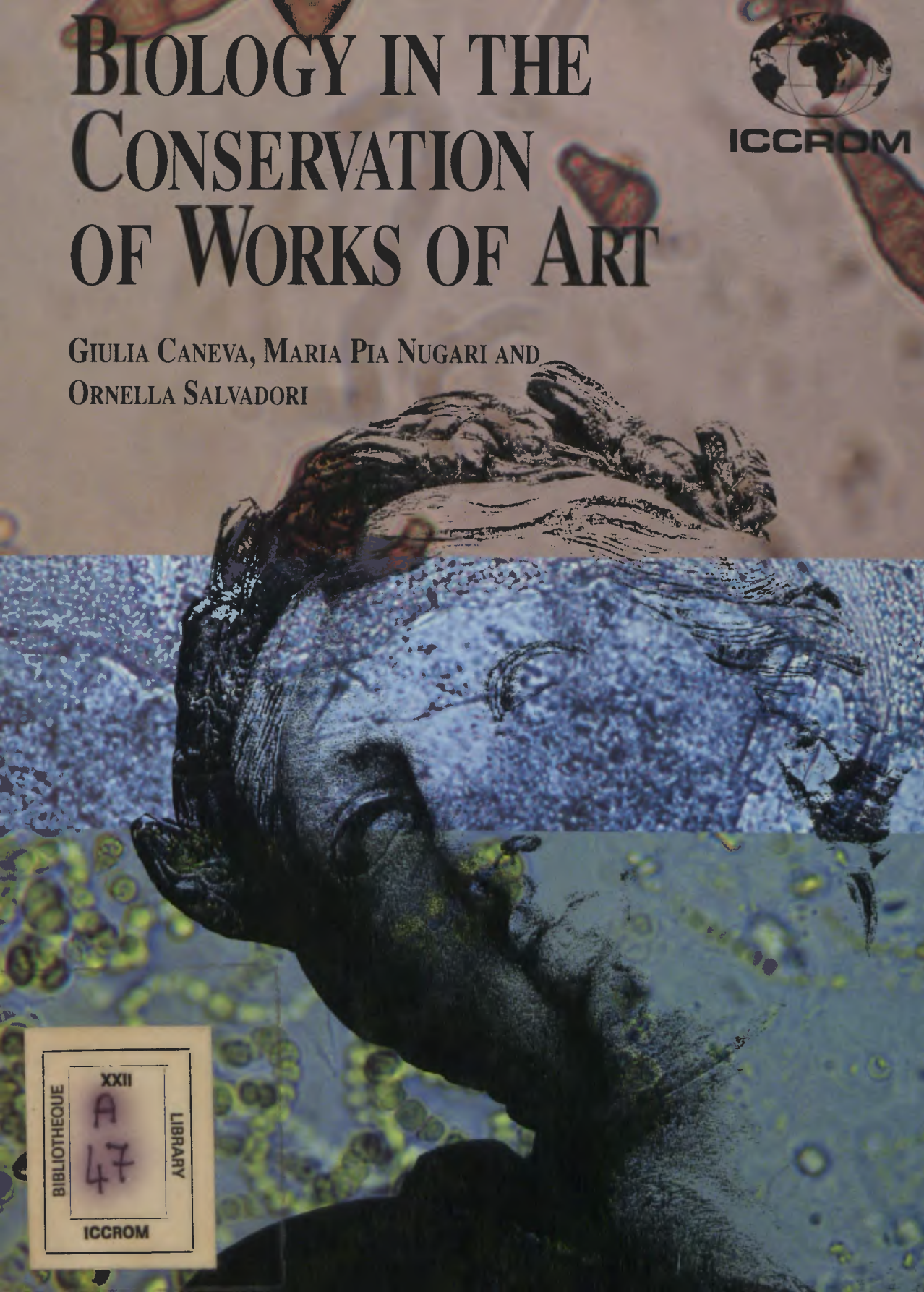
Biology in the Conservation of Works of Art

Giulia Caneva, Maria Pia Nugari and
Ornella Salvadori



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Giulia Caneva, Maria Pia Nugari and Ornella Salvadori

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FOREWORD

Products and methods for the conservation of works of art must be chosen on the basis of careful diagnoses aimed at defining the intrinsic chemical and structural properties of their constituent materials and at understanding the reasons for the alterations that have been observed.

The conservation of works of art and the performance of diagnostic studies in this field are, by definition, interdisciplinary activities that require the transfer of basic scientific knowledge from the restricted sphere of any single discipline to a larger number of persons involved in the same problems, but specialized in different areas.

Among the disciplines forming what we can now rightfully call "Science for Conservation" is biology, due to the significant role played by biological factors in the deterioration of works of art.

To know the most important biological agents and to understand the relationship of their physiology to environmental conditions is essential in order to adopt the most suitable methods to prevent and control biodeterioration without producing any negative interference with the constituent materials of the objects to be conserved.

The present book fills the gap between theoretical treatises in the field of biology and the practical activities of conservation. It gives "non biologists" the basic information necessary for a serious approach to the problems of biodeterioration and, at the same time, it gives "biologists not specialized in this field" references and specific indications on the most important constituent materials and suitable treatments for them. Moreover, the extensive bibliographic references will allow readers to deepen their knowledge of various topics.

Apart from the Appendix, with elements of general biology and systematics of biodeteriogens that are very useful in helping non-biologists to "break the ice" with the discipline, I appreciated very much the first chapter, in which biodeterioration is approached and set against the broader problem of interactions between each artifact and its environment. Those involved in practical conservation activities will also find chapters 5 and 6 of particular interest, as they describe and critically discuss the methods available at present to prevent and control biodeterioration.

The book is the result of the authors' experiences, acquired in more than a decade of activity in scientific laboratories of the Italian Ministry of Cultural Property: the Laboratory for Biological Investigations of the Istituto Centrale per il Restauro, in Rome, for Giulia Caneva and Maria Pia Nugari, and that of the Soprintendenza ai Beni Storico-Artistici di Venezia for Ornella Salvadori.

It is in just such a type of scientific laboratory, where scientists daily work closely with restorers and where they are asked to face together practical, urgent problems arising from conservation activities, that the richest study and research experiences can ripen, where a solid theoretical background must match a sense of practical organization. This combination makes it possible to meet the many special requirements involved in conservation of artifacts that are frequently precious and unique.

Marisa Laurenzi Tabasso

INTRODUCTION

This is a didactic text addressed to any person interested in the problem of biodeterioration of works of art. More precisely it was written for conservators without specialization in biology and for biologists lacking experience in the field of conservation.

Given the vast scope of the subject, this volume aims to provide a general overview of the study of biodeterioration and conservation of constituent materials rather than a critical analysis or a discussion of specialized literature.

The term '*biodeterioration*' refers to any undesired change in material properties due to the activity of microorganisms and/or organisms belonging to various systematic groups.

The biological aspects of conservation of works of art can be approached in different ways. First, the negative effects of biological populations, e.g., biodeterioration of materials, must be evaluated for prevention and control. Second, the potential positive contribution of biological populations to diagnosis and conservation treatments must be considered.

The processes of biodeterioration will be analyzed. Doing so will provide the basic information for understanding how a biological population can be used to evaluate weathering capacity and to interpret environmental parameters.

Microorganisms and organisms normally play an important role in the mechanisms of weathering of organic and inorganic materials. In fact, they can cause not only aesthetically undesirable effects, but overall, a progressive loss of cohesion and the transformation of component materials.

Biological alterations differ according to ecological peculiarities such as the substrate, the kind of microorganisms and organisms involved and the characteristics of the environment where the object is located (micro- and macro-environment, atmospheric pollution, etc.).

Environmental parameters and the nature of the substrate both drastically influence the potential attack by biological populations in relation to the presence of favoring or limiting factors and to their metabolic characteristics. These factors will be analyzed before describing the mechanisms and the phenomenology of biodeterioration.

Moreover, the biodeterioration of materials in nature cannot be considered as an isolated phenomenon; in fact, it always occurs together with other physical, chemical or physico-chemical deterioration processes, with which it is strictly correlated. The inter-relationship of these various weathering processes must always be borne in mind.

Therefore, an ecological approach is necessary to have a complete view of the biotic and abiotic parameters and later for understanding which of these parameters have the greatest impact in a given situation.

Chapter 1

ENVIRONMENTAL FACTORS IN BIODETERIORATION

1.1 GENERAL PRINCIPLES OF ECOLOGY

1.1.1 Characteristics of ecosystems

Ecology is the scientific study of the interrelationship of organisms and their environment. Given this perspective, the environment is a system composed of elements that interact and condition each other.

Any system that is defined through ecological parameters is called an *ecosystem.* An ecosystem is an abstract concept; it is not a definite object and it does not have defined limits in space. (It can be very small or, on the contrary, include the entire universe.)

In other words, the term 'ecosystem' can be used when we analyze the functional relationships characterizing the flow of energy and the transformations of the materials and elements of a system. Therefore, the analysis of the relationships between the work of art and the abiotic and biotic environment is the basis of an ecological approach to the system, or ecosystem.

This kind of study is complex and interdisciplinary because it takes into account the numerous interrelationships between various biological populations and between these populations and the physical and chemical factors of the surrounding environment. These relationships can be summarized as in Fig. 1.1, next page.

The work of art (the object to be conserved) represents the "soil," i.e. the material that is in the bio-geochemical cycle, exposed to environmental factors and potentially transformed by biological populations.

Generally speaking, biological factors (organisms and microorganisms) are considered potential *biodeteriogens*, but sometimes the presence of a biological factor influences the system in a different way, e.g., trees in archaeological areas modify some environmental parameters so that the conservation of the artifacts is improved (see ¶4.1.5).

The *biotope* is the environmental unit of an ecosystem and represents an area in which the physico-chemical parameters are uniform and where a certain *biocoenosis* lives. A biocoenosis is a biological community formed by various species living together in a biotope. In a work of art it is possible to find one or more biotopes and biocoenoses,

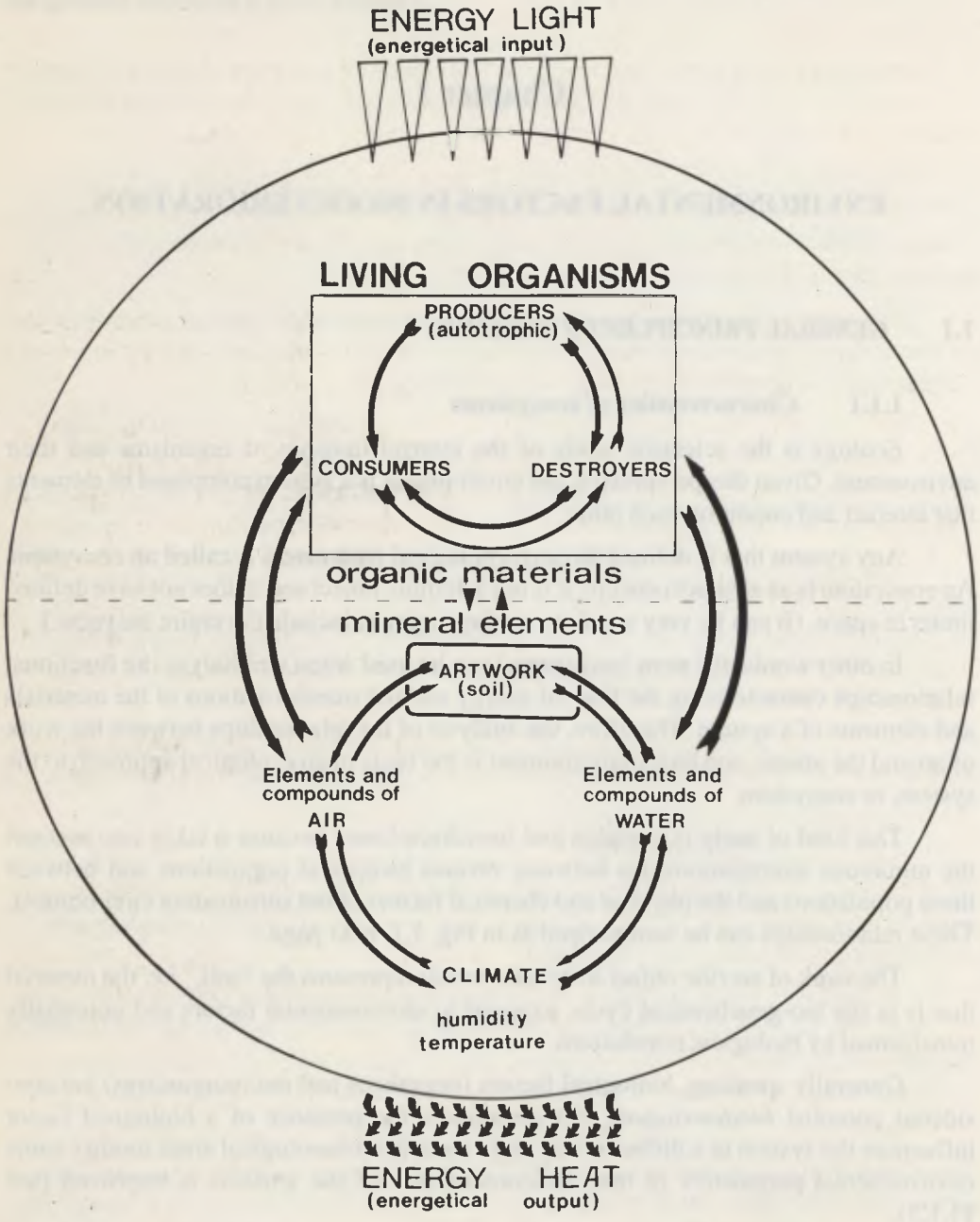


Fig.1.1

A work of art as an ecosystem.

depending on the dimensions and the structure of the object and, by consequence, on significant variations in environmental parameters (exposure, height, inclination).

In fact, each species occupies a specific *habitat* and also a specific *ecological niche,* considering the other biological interactions that define its ecological space.

Regarding the *trophic chains*, which explain the nutritional position of an organism in a system, living organisms present on works of art, as in any other ecosystem, can be both producers (*autotrophs*) and destroyers or consumers (*heterotrophs*).

The *producers* do not directly utilize the materials for their metabolic requirements (with the exception of water and mineral salts), but they can indirectly damage the substrate by their metabolism products or through mechanical penetration. Autotrophic bacteria, algae, lichens, lower and higher plants are producers.

The *destroyers* utilize organic matter for their nutrition, severely changing the structure of substances due to breakdown and oxidation of organic materials. The majority of bacteria, fungi and insects involved in biodeterioration are destroyers.

The *consumers* are the least important category in this field because they utilize the living matter of other micro- and macro-organisms. They do not attack the substrate but can be present on materials as predators of other biological communities. They can play an important role in controlling the growth of other biodeteriogens (e.g., grazing animals, snails that eat lichens, or acari that eat algae), even though it is difficult to use them specifically for this purpose.

From the viewpoint of energy, this trophic chain gives rise to an ecological pyramid; in each step there is a dispersion of energy following the thermodynamic law of increase of entropy.

For the same reason, the conservation of materials for an infinite time is impossible because matter tends to revert to its original state, to a simpler and more stable structure.

1.1.2 The limiting factors

Limiting factors for biological growth are those that condition and inhibit the presence of a biological species. Generally any parameter becomes a limiting factor if its values are near (above or below) the limits of tolerance of a species; pH, temperature, humidity, light and salinity are examples of limiting factors. In an ecological study it is not necessary to analyze all the environmental parameters, but only those that are significant in the specific case.

The interactions between limiting factors and biological populations are described by two laws.

Liebig's law (of minimum) says that under conditions of stationary equilibrium, the essential substances become limiting factors if their quantity is close to the minimum. In other words, the growth of an organism depends on any essential factor that is present in limited quantity.

For example, for an algal species, the humidity, content of salts and temperature (see ¶1.2.3 and Figs. 1.13 and 1.14) present in a subterranean environment are usually

not close to the minimum in quantity, and, therefore, are not limiting factors. In contrast, light is often close to or lower than the minimum limit of survival (photosynthesis cannot be performed), and light, in this case, is a limiting factor.

For a correct application of this law, it is necessary for the system to be in a true condition of stationary equilibrium (i.e., the flux of energy and materials entering balances that of those exiting).

Shelford's law (of tolerance) is an extension of the previous law and says that organisms have not only an ecological minimum but also a maximum which determines an interval representing the limits of tolerance.

In Fig. 1.2, the behavior of various species of different taxonomical groups with respect to the environmental parameter 'temperature' shows that any species has specific values under and over which it dies for opposite reasons (values too low or too high). The optimality value obviously lies somewhere between those values, but not necessarily in the arithmetical middle. For example, in this case, the optimality value for a biological species is usually nearer to the maximum limit of tolerance.

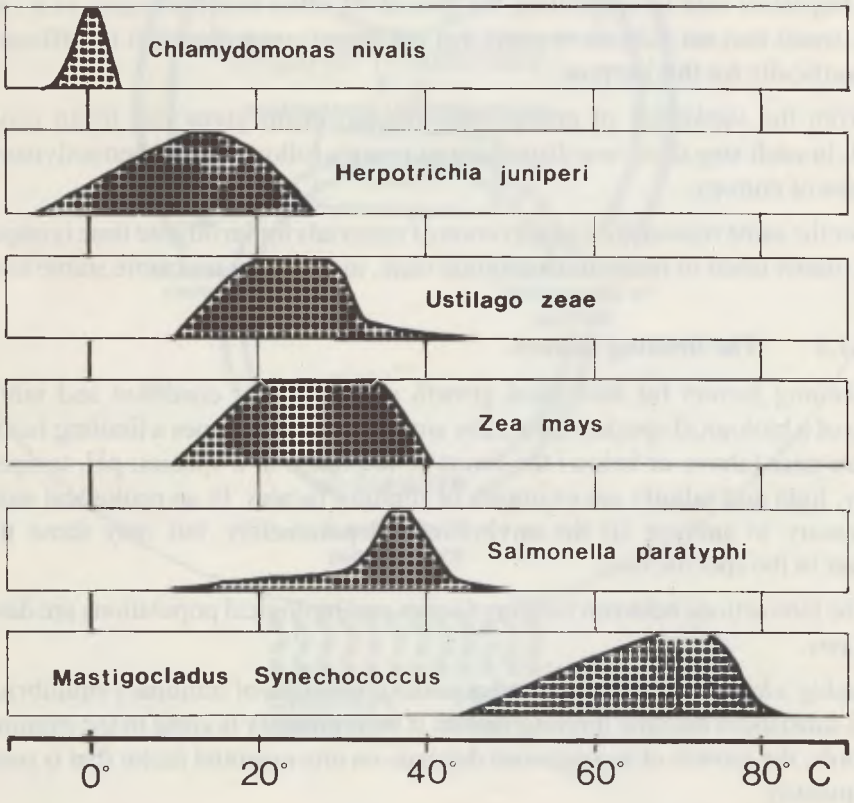


Fig.1.2

Ranges of tolerance of some organisms to temperature (from Larcher, 1976).

Organisms can have a wide range of tolerance for one factor and a narrow one for another. Those with narrow limits are linked to precise conditions, making it possible to interpret the values of environmental parameters to which they are sensitive. Thus, when present, they can be used as *bioindicators* (i.e., biological species or communities that indicate certain values of an environmental parameter). The terms *xerophilous* and *hygrophilous*, used to describe a species, mean that the water content is a limiting factor for opposite reasons (high or low values). *Acidophilous* and *basophilous* describe the effect of the pH factor, and so forth. Sometimes the absence of a species can also be used as a bioindicator of certain negative environmental parameters, such as the absence or reduction of lichens where there is pollution (see ¶1.2.4).

Moreover, it is necessary to consider that the interaction between the factors can cause different effects. Generally, if the values of a certain environmental parameter are not optimal for a species, the limits of tolerance for the other factors also become narrower. Synergistic or compensatory effects, however, can also occur. In the first case, the result of the interaction between two factors is not equal to the sum of the effects of the single factors, but higher. In the second case, a certain value of one factor may compensate the value of another limiting factor at a level close to ecological minimum. Taking two environmental factors, biological growth can also develop at an unfavorable value of one factor if the second compensates for the not optimal value of the first. The example of Fig. 1.3 illustrates how at low values of water activity, growth can appear only at a higher level of temperature. A high value (optimal value) of temperature can compensate for an unfavorable value of water activity (see ¶1.2.2).

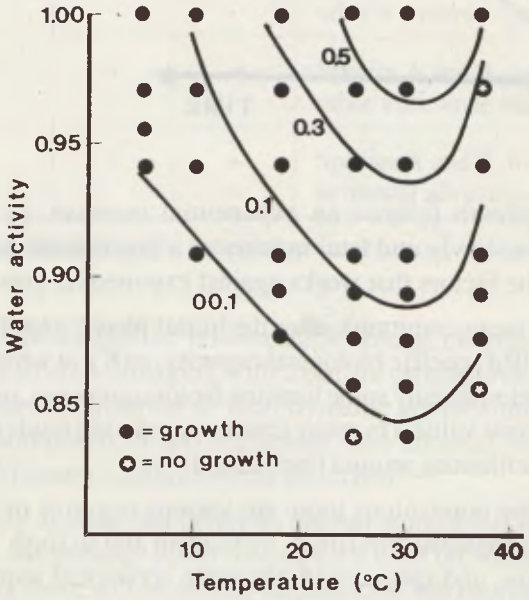


Fig.1.3

Interaction between temperature and water activity (from Ayerst, 1968).

1.1.3 Growth and dynamism of populations and communities

The biotic component of an ecosystem changes density and composition as a function of time.

A biological population is composed of organisms of the same species that live in a given place. A community or *coenosis* is composed of different populations having similar but not equal ecological requirements (i.e. occupying different ecological niches).

Biological populations grow according two kinds of models which are as follows (Fig.1.4):

- exponential growth (J curve- a in figure)
- logistical growth (Sigma curve - b in figure)

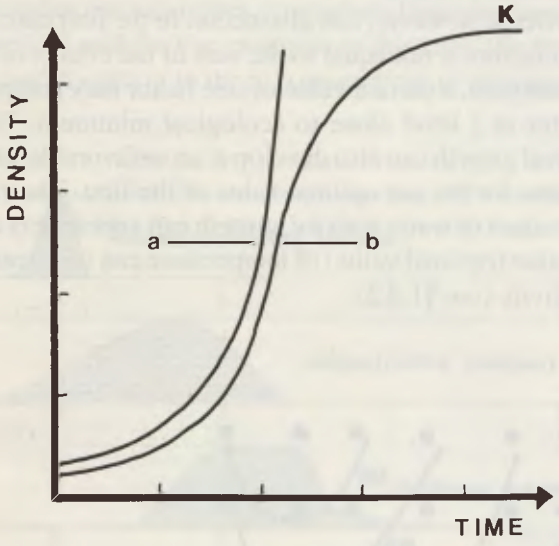


Fig.1.4

Exponential and logistical growth of a biological population.

In the first case, growth follows an exponential increase, i.e. the number of organisms increases at first slowly and later quickly as a logarithmic trend. The density of a population is one of the factors that works against exponential growth.

In the second case (more common), after the initial phase, growth is rapid until it reaches a certain value (called specific biological capacity, or K), at which it is stationary. At a certain level of population density some limiting factors intervene, restricting growth, which is then stabilized at that value. (In many cases a population tends to reach a certain density after a series of oscillations around that value.)

Moreover, among the populations there are various negative or positive interactions due to competition, parasitism, predation, mutualism and so forth. More frequently the interactions are negative, and species with the same ecological requirements cannot live together because at a certain moment the direct or indirect competition between them tends to eliminate one or the other.

In the case of *predation, parasitism* and *antibiosis*, the interaction between the populations produces negative effects on the growth and life of only one population. Generally in an ecosystem, different ecological niches arise in order to permit the growth of various populations together.

In contrast, *commensalism, cooperation* and *mutualism* are advantageous relationships among species having different nutritional and ecological requirements. Cases of *symbiosis* are extreme examples of such positive interactions (e.g., lichens, termites).

Table 1.1 Types of interaction between two biological species

Type of interaction	Species A → B	Species B → A	Description of interaction
Predation	+	--	Species A kills and eats species B
Parasitism	+	--	Species A grows at direct expense of species B
Antibiosis	+	--	Species A releases toxic substances against B
Commensalism	+	0	Species A benefits from the presence of species B, which is not affected
Cooperation	+	+	Species A and B mutually benefit from the other's presence but can survive alone
Mutualism	+	+	Species A and B mutually benefit from the other's presence and cannot live alone
Symbiosis	+	+	Species A and B live together in an organism to mutual advantage

+ = positive interaction; -- = negative interaction; 0 = no interaction

Over time, the results of relationships among biological communities and the environmental parameters changing with them are progressive successions and substitutions of biocoenosis. A situation of final dynamic equilibrium is reached and the final populations are composed of the organisms best adapted to the final environmental conditions, which remain constant unless disturbed.

This theoretical trend can invert its normal tendency if man or some other natural factor intervenes, for instance when biocides are used on works of art. When biological growth starts again there will be similar successions, but beginning from different stages because the previous colonizations modified the substrate, increasing such features as porosity or its content of organic materials.

1.2 PHYSICO-CHEMICAL LIMITING FACTORS

1.2.1 Edaphic factors

Edaphic factors are those related to the "soil" (see ¶1.1.1), i.e., in this case the component materials of the work of art and/or what has been subsequently superimposed during restoration or exhibition. For an organism, these factors represent potential nutritive substances, i.e. those providing energy and the elements necessary for biosynthetic or catabolic reactions (see the composition of living matter in the Appendix).

The primary division of materials relates to carbon compounds, so organic materials (which contain carbon) will be discussed separately from inorganic materials (see Chaps. 3 and 4). Nevertheless, the presence of other nutritional elements in the substrate must also be considered in order to understand whether there are nutritional deficiencies. The composition of a work of art influences the possibility of development of autotrophic or heterotrophic organisms and, consequently, substantially conditions the kind of biodeterioration that occurs.

Among nutritive substances, the elements and compounds necessary in high quantity are called *macronutrients.* The most important are the salts of phosphorus and nitrogen (phosphates and nitrates). Hypertrophication can occur due to the anomalous increase of these substances arising from human activity (pollution) (see ¶ 1.2.4) or animal excrement (e.g., birds).

Potassium (K), calcium (Ca), sulfur (S) and magnesium (Mg), are the other nutritive substances required in certain amounts.

Elements and compounds required in very low quantities (e.g., as cofactors of enzymes or as constituents of vitamins) are called *micronutrients.* It is not always possible to distinguish between micro and macro nutrients, and such a division does not have the same validity for all organisms (e.g., animals require higher quantities of Na and Cl than plants do). Apart from those two elements, other essential micronutrients are Mn, Fe, Zn, V, Mo, B, Co, Cu, Si (I for Vertebrates).

Despite the small quantity required, micronutrients can be important limiting factors. In many cases the total productivity of an ecosystem is greatly reduced if there is a shortage of these limiting substances. As is true of other environmental factors, nutritive substances can also be very toxic in excessive concentrations (e.g., copper).

1.2.2 Water

Water plays a fundamental role in life; in fact, an organism's weight is 70% to 90% water. All organisms need water for their metabolism, and all enzymatic reactions in the cell happen in an aqueous environment. Water is broken down in photosynthetic reactions and is produced by the respiration processes (*catabolism*) (see Appendix).

In this section, the role of water will be analyzed in relation to the physiological and ecological aspects of an organism. In the next paragraph, the relation between climate (and, therefore, water as a climatic parameter) and biological growth will be discussed.

Organisms use the water present in the substrate or in the air. The nature of the component material influences its water content, but capillary absorption, high RH (especially nearing dewpoint) or rain can increase this value.

It is important to distinguish the role of water in activity as opposed to the mere survival of organisms. Survival is possible under a wide range of unfavorable conditions, but activity is not. Some species are more resistant to drying than others. In fact, organisms are classified as *aquatic, hygrophilous, mesophilous* and *xerophilous* according to a positive gradient of tolerance to water deficiency. An increase of dryness heavily decreases microbial growth and finally limits it to specialized organisms. Some bacteria are able to form endospores, cysts, as stages resistant to desiccation. Moreover, a low water content can condition the habitus of a species or favor the colonization of a different, more adapted species, such as the development of endolithic forms of algae or lichens on stone (see ¶4.1.3 and 4.1.4).

When discussing water we must consider *water activity* (a^w) which is the real quantity available for chemical and biochemical reactions. This quantity is a function not only of the water content of a material, but also of solution and adsorptive factors. The range of this parameter varies between 0 and 1; microbial growth is possible between 0.6 and 0.998 a^w. The majority of bacteria need water activity higher than 0.98. Fungi and halophilous bacteria can tolerate the lowest values.

When considering the chemical aspects of water solutions in relation to biological growth, the pH and osmotic solutions are analyzed. The *pH* of a solution is the inverse logarithm of the hydrogen ion concentration ($pH = \frac{1}{\log [H^+]}$) and expresses its acidity or basicity. Most microorganisms and organisms prefer conditions of neutrality, but some species prefer lower or higher pH values (*acidophilous* or *basophilous* species, which can also be used as bioindicators). Many fungi prefer acidic conditions, whereas, on the contrary, the majority of bacteria prefer neutral or slightly alkaline conditions. The pH is also important in relation to the buffering capacity of the substrate.

The *osmotic pressure* (π) of a solution is linked to the number of dissolved particles present and appears when solutions with different concentrations are separated by a semipermeable membrane (like biological membranes) which permits the passage of water but not of solutes.

In fact, when a cell is immersed in a water solution with a lower concentration of particles (hypotonic = lower osmotic pressure), water tends to enter and inflate the cell. The cellulosic wall structures of plant cells and the rigid murein wall of bacteria balance the pressure (walls are permeable); other kinds of cells, without stiff walls and lacking systems for pumping out water, will die. A higher concentration of the outside solutions (hypertonic) is more dangerous for biological cells, because water is extracted from them, ultimately causing death (Fig. 1.5). This is why salt, for example, is used to preserve food, because it impedes the attack of microflora.

Only a very few specialized organisms tolerate a high value of osmotic pressure (halophilous species) due to their ability to crystallize and excrete salts or to high values of internal osmotic pressure.

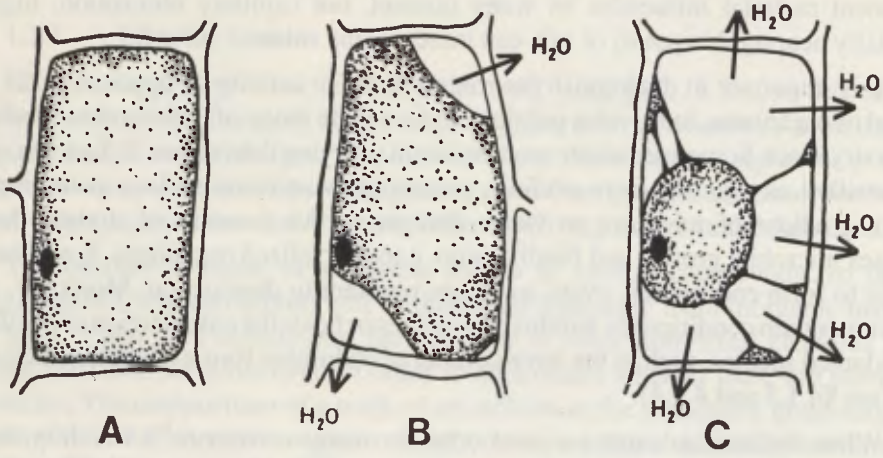


Fig.1.5

Plasmolysis of a plant cell in relation to differential osmotic pressure.

A high saline concentration and low or high pH values are very important because these factors can be limiting factors for biological growth, discouraging growth even if the other parameters are at values of optimality.

1.2.3 Atmospheric factors

1.2.3.a Chemical components

At the chemical level, the atmosphere is composed of two main molecules, nitrogen and oxygen, and secondarily by carbon dioxide and other minor components (under normal conditions).

Nitrogen (N_2) in the molecular form is the main component of air (about 78%), but it is in a very stable and non-reactive form which can be used only by a few specialized prokaryotes (nitrogen-fixing bacteria and cyanobacteria with heterocysts). It can react with oxygen, forming various oxides (NO_x) and nitric or nitrous acids. In polluted environments, these nitrogen compounds are, together with SO_2, among the main elements responsible for chemical attack of monuments.

Oxygen (O_2), also in the molecular form, is of basic importance for the respiration processes of living organisms, due to its high oxidation capacity. *Oxidation* is a process in which a compound or radical loses electrons which are accepted by another compound, such as oxygen, with a higher electron affinity. The accepting compound is *reduced.* Oxygen is also produced by photosynthesis from water photolysis (see Appendix) and is, in fact, the final acceptor of electrons coming from oxido-reductive reactions. Oxygen is present in the air at a concentration of about 21%. In aqueous environments its concentration is about 20 times less (which also depends on temperature and salinity). In the soil,

its concentration is greatly reduced until anaerobic conditions are reached at variable depths.

The relationships of organisms with oxygen vary. *Strictly aerobic* organisms must have oxygen for respiration processes; they are in the majority. *Strictly anaerobic* organisms are inhibited by an oxygen concentration of more than about 5%. *Facultative aerobic* or *anaerobic* organisms usually grow in both the presence and the absence of molecular oxygen, but if it is lacking (2-7%) they may utilize some fermentable compound. *Microaerophilous* organisms are aerobic but favored by low levels of oxygen.

Oxygen can, therefore, become a limiting factor for all aerobic organisms in water or soil. In the absence of oxygen, only anaerobic organisms can survive and so they occupy a well-distinguished ecological niche, taking part with specific roles in biogeochemical cycles (e.g., the sulfur cycle, see ¶4.1.1). In contrast, it seems that at a low oxygen concentration the speed of photosynthesis increases.

Carbon dioxide (CO_2), unlike molecular oxygen, is produced by respiration processes and consumed by photosynthetic reactions. It is, therefore, equally important because it is the chemical form in which carbon is fixed for producing organic substances through photosynthesis. An increase of carbon dioxide concentration in the air (the normal values are around 0.03%) or in water solutions, due to increases of oxidative reactions such as combustion, will give rise to a higher growth of photosynthetic organisms, as well as having the well-known impact on the climate (greenhouse effect). Due to its rather low concentration it may soon become a limiting factor. Moreover, it carries out an important role in weathering because of the production of carbonic acid in water solutions (see ¶2.1). Excesses of carbon dioxide in the soil can have toxic effects on organisms.

1.2.3.b Climate

Climate is defined as the result of the average atmospheric conditions considered at the physical level. Climate arises, therefore, from the interaction of various factors, the most important of which are *temperature* and *rainfall* (Fig. 1.1). For photosynthetic organisms (and consequently for all the others that have nutritional links with them), *light* plays a fundamental role. *Wind* is significant, not only for problems of aeolian erosion, but also because it influences the evaporation of surfaces, transpiration process of organisms and the direction and force of rainfall.

It is possible to divide climate into three levels: *macro-*, *meso-* and *micro-* climate as a function of the breadth of the area considered.

Macroclimate is the climate at a regional level. It is characterized by different local climatic conditions in relation to exposure, altitude, morphology of the landscape, etc. On the other hand, it is composed of various microclimates.

Mesoclimate is the result of a modification of the macroclimate in relation to topographical variations (hills or valleys) or other significant factors (lakes, cities, forests).

Microclimate is the climate at the level of a certain biotope (see ¶1.1.1). In consideration of the scale of analysis, humidity will also be considered for the hydric factor and artificial inputs (heating, cooling or lighting systems) for temperature and light.

Moreover, *bioclimate* deals with climatic factors in relation to their capacity for encouraging biological growth. Temperature and rainfall are the main parameters in a bioclimatic classification (Fig. 1.6) and depend, with light, upon geographical location (latitude and altitude) and seasonal variations. Generally, biological growth is more pronounced in warm and humid zones, while it is heavily reduced in those that are cold and especially in those that are dry.

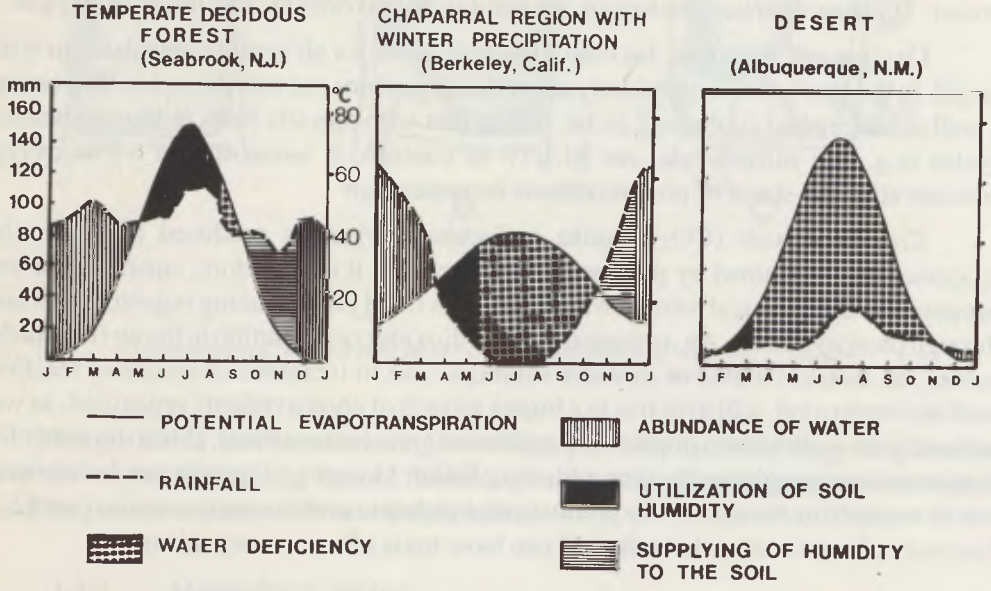


Fig.1.6

Different bioclimates according to Walter (from Odum, 1971).

Temperature

Temperature affects living organisms by influencing the structure of the molecular components of a cell (carbohydrates, proteins, lipids, etc.) and the kinetics of reactions. Theoretically, life exists in a relatively wide range of temperature, but active metabolism develops in a much more limited range. As in the case of water, it is important to distinguish between active growth and survival in a quiescent stage as a result of an unfavorable temperature value. Organisms adapted to low temperatures (*psychrophilous* species) have active metabolism between 0 and 10°C, and those adapted to high temperatures (*thermophilous* species) between 30 and 70°C. Most organisms, however, have an optimum between 15 and 25°C (*mesophilous* species).

Usually, low temperatures do not favor biological growth, and only microorganisms that can dehydrate their biological structure are able to resist very cold conditions. In fact, the formation of ice crystals inside the cell (which also relates to osmotic values) causes it to rupture.

When temperature increases, biological growth generally increases up to a certain level because chemical reactions are accelerated, re-doubling in speed with every increase of 10°C. Enzymes, however, have an optimal value of activity at specific temperatures which determines their preferentiality with respect to this factor.

A very high temperature (above 50-60°C) is dangerous because it gives rise to various negative phenomena such as rupture of weak links, fluidification of lipids or modification of the active sites of enzymes.

The geographical distribution of an organism (areal) can be limited by an excess or deficiency of cold or warmth. In the first case, its distribution relates to the isotherm (average temperature) of the coldest month of the year. Also, small increases of temperature in the warm seasons, as in high latitudes, can become a limiting factor for several species.

Indoor temperature is rarely a limiting factor for biological growth, but heating can favor development if other environmental parameters (especially humidity) are advantageous. The same condition occurs in low-latitude countries (tropics). Optimum values of temperatures for the insects and microorganisms that are found in museums and libraries are usually between 20°C and 30°C.

Moreover, temperature strongly influences the RH of the air and the water content of the substrate. At a constant water content, an increase in temperature causes a diminution of relative humidity, whereas a decrease in temperature has the opposite effect (Fig. 5.1).

Water

When considering *water* at the climatic and microclimatic level, we will discuss *rain* and *relative humidity*.

Rainfall is expressed by the millimeters of rain that fall in a given place during a year. Rainfall varies significantly in different climatic regions. Desert conditions are found when there is less than 250 mm of rainfall per year. Xeric conditions, consisting of only 250-750 mm of rainfall (e.g., Mediterranean regions), also exhibit an unfavorable period without any rainfall. Mesophilic conditions exist when the rainfall is 750-1250 mm, and water is rarely a limiting factor. Humid conditions prevail above 1250 mm.

In the case of vertical surfaces, however, the combined effects of rain and *wind* condition wetness. In fact, when a building's wall receives water only through rainfall, biodeterioration varies in the various *exposures*. In the absence of other input of water or very high humidity conditions, only the walls subject to driving rain are colonized by microorganisms (Fig 1.7, p. 71) (Caneva et al., in press).

Absolute humidity (AH) represents the grams of water contained in a cubic meter (m^3) of air. The relative humidity (RH) is the ratio between the content of water in a certain volume of air and the maximum quantity that can be contained in that volume reaching condensation. The RH clearly influences evaporation and transpiration processes and, therefore, the water content of materials. For example, hygroscopic materials such as paper can absorb high quantities of water as a function of an increase of RH (from

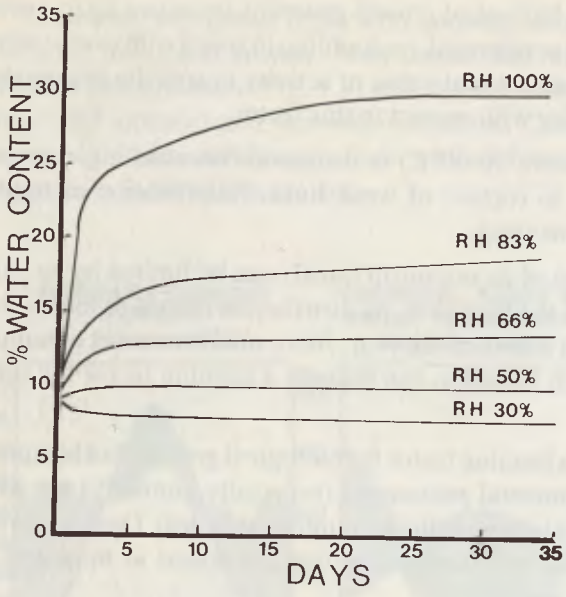


Fig.1.8

Water content of paper in relation to different values of relative humidity (from Monte and Tonolo, 1969).

8% to 30% - see Fig. 1.8). Temperature also affects RH: when the temperature increases, the kinetic energy of the water molecules increases, and a higher quantity of water can be contained in the same volume. The absorption of water by a substrate depends on many other factors such as porosity, hygroscopicity of materials or *hysteresis* phenomena.

To evaluate a material's susceptibility to biodeterioration, it is not merely sufficient to know its chemical composition; it is also necessary to take into account its capacity to retain water. Mortar is much more easily colonized by microorganisms than marble, especially in relation to its higher porosity (Fig. 1.9, p. 71). The porosity of a material is not only an inherent property but also depends on ageing and other stressing agents, which increase it.

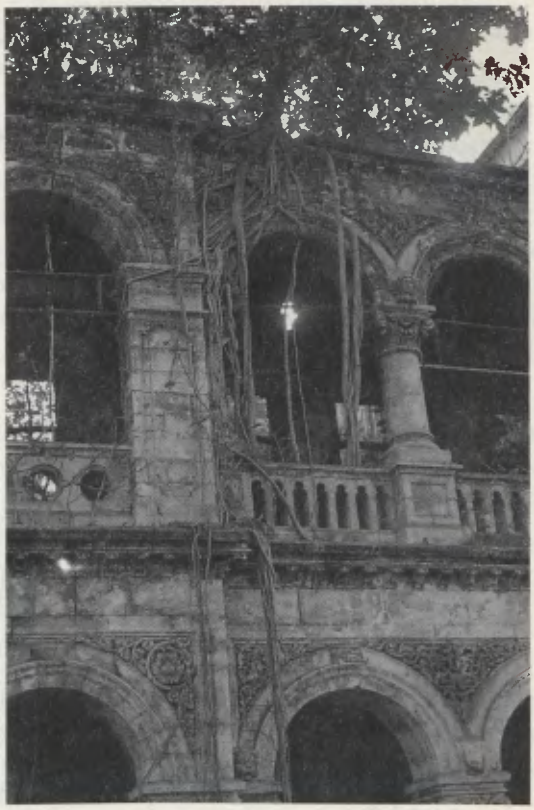
Optimum values of RH for biological growth (with the exception of xerophilous species) are those higher than 65-70%. Combined conditions of both high temperatures and high humidity as in tropical countries are the most favorable for a biological attack on materials (Figs. 1.10, p. 71 and 1.11).

Light

Light represents the primary energy source necessary for the growth of all photosynthetic organisms. The non-phototrophic species can be affected in different ways by light. It can cause inhibition (e.g., lightfugal fauna) due to secondary reactions (e.g., photooxidation of enzymes, etc.). In other cases, light can be a favorable factor for some species or also an indifferent one. Insects, for example, can be conditioned by the presence of light or darkness; termites, for example, are lightfugal species. There are various diurnal and nocturnal species. Tolerance to light also varies during the life cycle. Darkness, however, usually favors the growth of most insects and microorganisms in libraries (Gallo, 1985).

Fig.1.11

Heavy colonization of lichens and trees (Ficus religiosa) on a building in the tropics - Bombay, India.



Solar radiations are partially absorbed as they pass through the atmosphere; the majority of those that reach the earth belong to the visible spectrum. The light factor cannot be completely separated from temperature due to the nature of solar radiation itself. The quantity of energy reaching the soil varies in relation to latitudes and seasons. Part of this energy is reflected, another part is absorbed or diffused, thanks to atmospheric and environmental conditions (e.g., clouds, vegetation).

From the ecological point of view, the most important parameters describing light are as follows:

- quality (color)
- quantity (intensity)
- duration (in time)

The *quality* of light plays an important role due to the absorption peaks of the chlorophylls that have a lack of absorption in the green radiations. Other pigments, such as phycoerythrins and phycocyanins, present in some photosynthesizing organisms, well complement the absorption spectra of chlorophylls. For that reason, green light is the worst for photosynthesis, but there is no visible wavelength that completely obstructs the growth of photosynthesizing organisms. The various photosynthetic species can have preferences for certain frequencies of radiations as determined by their pigments (Fig. 1.12).

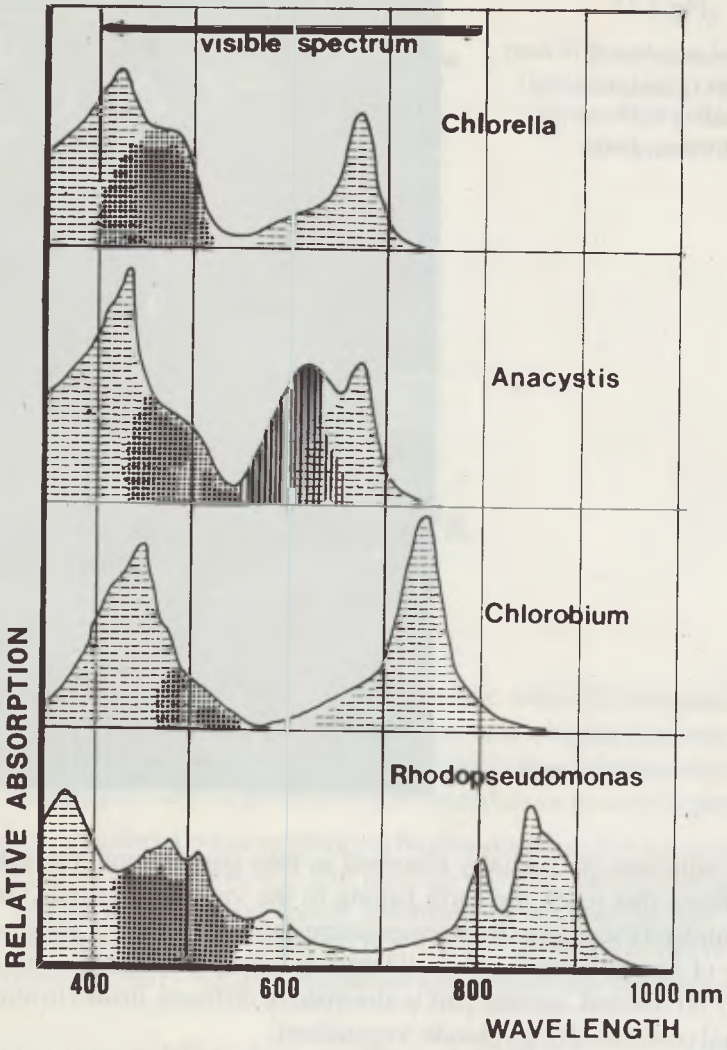


Fig.1.12

Absorption of different wavelengths of light in some cyanobacteria and algae species (from Stanier, Douduroff and Adelberg, 1970).

High-frequency values of light such as UV are, however, dangerous for all organisms because they can induce rupture in the molecular links of the cells (especially nucleic acids), anomalies in growth, or death. Some organisms protect themselves from these radiations and from excessive light intensity by becoming darkly pigmented (e.g., blackish patinas of cyanobacteria when exposed to direct solar radiation) or avoiding direct exposure. In the first case, the dark color induces light absorption and avoids its deep penetration; in the second case, the biological organisms grow under the surface, showing chasmoendolithic or euendolithic behavior (Golubic et al., 1981).

Red and infrared radiations can also be dangerous when they induce overheating of surfaces, thus favoring biological colonization and creating physico-chemical stresses. Therefore, cold indoor lights are preferable.

The values of *light intensity* are important because they determine the quantity of the energy inputs. *Heliophilic* or *heliophobic* organisms are influenced in opposite ways. The intensity of light is in fact very important for the efficiency of photosynthesis, but not all organisms have the same optimality values. The presence of photoautotrophs (photosynthetic bacteria, algae, lichens, lower and higher plants) is usually strongly limited under conditions of low lighting, and light becomes a limiting factor. In cellars (lit artificially or through windows), one frequently finds the presence of this flora limited to those parts receiving a sufficient quantity of radiation (see ¶1.1.2 and Figs 1.13, 1.14, p. 72).

The *duration in time* of light and darkness influences the presence and the activity of organisms due to *photoperiodism* phenomena. This is important not only for plants but also for animals, because some cyclic phenomena (e.g., hormone production) are linked to this factor. In the case of insects, the photoperiod plays a fundamental role because it influences morphogenesis, behavior, egg-laying, movement and respiration.

1.2.4 Pollution effects

Pollution is an undesirable change in the physical, chemical and biological properties of air, soil or water. Everyone is well aware of how much this factor influences the conservation of artifacts; the damage due to industrial activities, vehicular traffic, heating and cooling systems is stressed in the literature.

Pollutants in the air vary, and on the basis of the current division, particulate substances (hydrocarbons, silicates, spores, pollens, etc.) are differentiated from gaseous compounds (SO_2, SO_3, H_2S, NO, NO_2, NH_3, CO, CO_2, O_3, HF, HCl). Some of these are natural components of the air but they are considered as pollutants when their concentration is too high.

The disequilibrium they cause in the environment can trigger different effects on biological populations. These effects obviously change with the nature of the pollutant, and with the kind of species involved. The effects are much higher outdoors than indoors.

Most of the gaseous pollutants often inhibit biological growth. Organisms are not equally sensitive, and some groups (especially mosses and lichens) are more frequently damaged; sensitivity also varies from one species to another. The inhibitory effect can be buffered by the substrate (e.g., limestones neutralize acid pollutants at their own expense).

On the basis of their differential sensitivity and tolerance, some species are used as *pollution bioindicators.* In polluted urban and industrial areas, lichens (and mosses) are considered bioindicators, and the number of lichen species of an area is a good indicator of pollution and in particular of SO_2 levels (Fig. 1.15). Several indices for quantifying relationships between the pollution level and the presence of lichen species have been proposed, such as that suggested by Le Blanc and Sloover (1970) (Index of Atmospheric Purity - IAP):

$$IAP = \left(\frac{n}{100}\right) \sum_{i=1}^{n} Q\,fi$$

n = number of species in the sampling plot
f = frequency of each species
Q = toxitollerance associated with each species

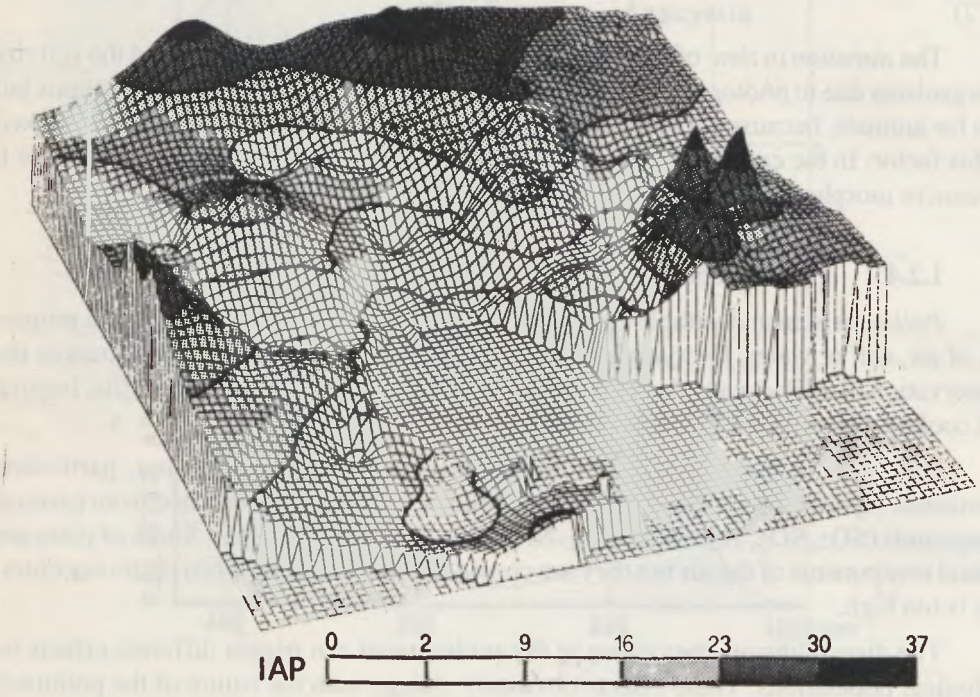


Fig.1.15

Three-dimensional IAP map of the Gulf of La Spezia (Italy) (from Nimis, et al., 1990).

Lichens are also good indicators of heavy metals (lead, copper, zinc, nickel, cobalt) because they accumulate these metals in the thallus; the concentration is correlated to the distance from the emission point (Nimis, 1990; Hawksworth and Rose, 1976).

In the case of higher plants, pollution and particularly acid rain cause the erosion of the cuticular layers of leaves and interfere with the stomatic cells. Damage due to acid rain, observed in forests far from the emission point of pollutants, is also frequently discussed in the professional literature.

Pollutants present in water or soil can be inorganic or organic compounds used or produced by man (e.g., pesticides or toxic substances, by-products of various chemical reactions). These compounds can cause serious problems of environmental health, bringing about undesirable decimation of flora and fauna, changing the ecosystemic equilibrium and favoring the development of more resistant species.

Despite the negative effect of pollutants, they can favor the growth of some biological populations because the more resistant species will survive up to certain levels. This determines over time a diminution of biological diversity and the development of a monospecific invasive flora growing without competition. For example, the presence of organic particulates generally supports the development of heterotrophic microflora. Some sulfur and nitrogen compounds can favor specific microflora involved in their cycles. Hypertrophication and other modifications (e.g., impregnation with dust) give rise to corresponding modification of the biocoenosis. This process has been enhanced in recent years by agricultural practices such as the widespread use of artificial fertilizers. The establishment of nitrophilous flora, previously absent, will be favored, replacing the old populations after nutrient-rich dust has accumulated sufficiently (Deruelle, 1983) (Fig. 1.16, p. 72).

Similar effects are produced by bird droppings, and in cities well colonized by avifauna, one frequently sees areas covered by nitrophilous lichen flora, especially in flat places where the droppings accumulate.

Moreover, the increment of phosphate coming from partially degraded detergents gives rise to considerable problems of water hypertrophication, causing anomalous "flowering" of algal populations. In fountains, when phosphates are added for complexing carbonates, the development of algae and mosses occurs more easily (Fig 1.17, p. 73).

REFERENCES

AYERST, G. (1968). "Prevention of biodeterioration by control of environmental conditions," *Biodeterioration of Materials*, ed. A.H. Walters. Amsterdam: Elsevier. 223-241.

CANEVA G., E. GORI and A. DANIN (in press), "Incident rainfall in Rome and relation to biodeterioration of buildings," *Atmospheric Environment.*

———, and O. SALVADORI (1988). "Biodeterioration of stone," *The Deterioration and Conservation of Stone, Studies and Documents on the Cultural Heritage* N° 16, Paris: Unesco. 182-234.

DERUELLE, S. (1983). *Ecologie des lichens du bassin parisien, Impact de la pollution atmosphérique (engrais, SO_2, Pb) et relations avec les facteurs climatiques*, Thèse de doctorat d'etat, Univ. Paris.

EHRENDORFER (1979). "Geobotanik," *Lehrbuch der Botanik für Hochscholen.* Stuttgart: Gustav Fischer Verlag.

GALLO, F. (1985). *Biological Factors in Deterioration of Paper.* Rome: ICCROM.

GIACOBINI, C., and M.S. SPAMPINATO (1979). "Biodeterioramento," *Fattori di Deterioramento, DIMOS, parte II, modulo I.* Rome: Istituto Centrale per il Restauro. 171-213.

GOLUBIC, S., E. FRIEDMAN and J. SCHNEIDER (1981). "The lithobiontic ecological niche, with special reference to microorganisms," *J. Sedimentary Petrology*, 51. 475-478.

LARCHER, W. (1976). *Oekologie der Pflanzen 2.* Stuttgart: AUFL.

LE BLANC, F. and J. SLOOVER (1970). "Relation between industrialization and distribution and growth of epiphytic lichens and mosses in Montreal," *Can. J. Botany*, 48. 1485-1496.

LEMEE, G. (1978). *Precis d'ecologie vegetale.* Paris: Masson.

HAWKSWORTH, D.L., and F. ROSE (1976). "Lichens as pollution monitors," *Studies in Biology*, 66. London: E. Arnold. 1-60.

HOPTON, J.W. (1987). "Physical conditions and microbial growth: some implications for biodeterioration," *Biodeterioration* 7, eds. D.R. Houghton, R.N. Smith and H.O.W. Eggins. London and New York: Elsevier Applied Science. 511-516

KRUMBEIN, W.E. (1983). *Microbial Geochemistry.* Oxford: Blackwell, Ltd.

MONTE, M., and A. TONOLO (1969). "Sviluppo di microrganismi sulla carta in relazione all'umidità relativa dell'ambiente," *Quaderni del Gabinetto Nazionale delle Stampe.* Rome. 35-46.

NIMIS, P.L. (1990). "Air quality indicators and indices - The use of plants as bioindicators and bioaccumulators for monitoring air pollution," *Workshop on Indicators and Indices for Environmental Impact Assessment and Risk Analysis*, Ispra. 1. 22.

———, M. CASTELLO and M. PEROTTI (1990). "Lichens as biomonitors of sulphur dioxide pollution in La Spezia (northern Italy)," *Lichenologist*, 22 (3). 333-344.

ODUM, E.P. (1971).*Fundamentals of Ecology.* Philadelphia: W.B. Saunders Company.

RAVEN, P.H., R.F. EVERT and S.E. EICHHORN (1986). *Biology of Plants.* 4th ed. New York: Worth Publishers.

SORLINI, C., (1984). *L'azione degli agenti microbiologici sulle opere d'arte*, ENAIP, Ed. del Laboratorio, Botticino (Brescia). 1-48.

SCOSSIROLI, R.E. (1979). *Elementi di ecologia.* Bologna: Zanichelli.

STANIER, R.Y., M. DOUDOROFF and E.A. ADELBERG (1970). *The Microbial World.* Englewood Cliffs, NJ: Prentice Hall, Inc.

WALTER, H. (1973). *Vegetation on the Earth.* London: The English University Press.

Chapter 2

MECHANISMS AND PHENOMENOLOGY OF BIODETERIORATION

Biodeterioration of materials involves mechanisms of different kinds: physical or mechanical processes (disintegration) and chemical processes (decomposition). Generally these two processes occur simultaneously and, depending on the biodeteriorating agent and the kind of substrate and environmental conditions, either can prevail.

Apart from these direct actions, the development of microorganisms or organisms can create conditions favorable to the growth of other species or, in other words, an ecological succession.

Depending on the different chemical composition of materials, we can have different kinds of biodeterioration. In fact, organisms are divided into different nutritional groups depending on their different nutritional necessities, and the nature of the substrate determines the possible deteriorating agents (see Appendix). The biodeterioration of works of art composed of organic materials (paper, wood, textiles, leather, etc.) such as paintings on canvas or on wood, wooden sculpture, library materials and prints is carried out especially by heterotrophic microorganisms able to degrade organic polymers enzymatically. The deterioration of inorganic materials is more easily performed by autotrophic microorganisms, even if it is almost always accompanied by heterotrophic ones as well.

Other characteristics of materials such as pH, presence of impurities and water content will condition the development of biodeteriogens. A certain pH will favor the growth of acidophilous or basophilous microflora. The RH and consequently the water content of materials are very important, and organic materials are much more hygroscopic than inorganic ones. Impurities can be constitutional (e.g., depending on different manufacturing techniques), naturally or artificially superimposed on the substrate and can determine a higher susceptibility to biodeterioration or enlarge the range of microorganisms that can develop. Moreover, other kinds of deterioration (physical or chemical) are very important because they can facilitate biodeterioration. Paper degraded by photo-oxidation or deteriorated stone with a larger porosity are more easily attacked by biodeteriogens than the same materials without such damage.

Some metabolic processes are performed by all living organisms (e.g., CO_2 is produced by respiration); others, on the contrary, are linked to some specialized organisms and depend on the possibility of using a certain substrate as food (e.g., decomposition by enzymatic reactions).

2.1 PHYSICAL PROCESSES

Physical processes cause mechanical abrasion, fracturing and disruption of the substrate due to the mechanical activity of organisms (movements or growth). The fragments produced have the same chemical composition as the original materials and easily detach from the substrate because of the pressure exerted during the growth of organisms or their parts (e.g., roots of higher plants) (Figs. 2.1, 2.2). Generally the damage caused by organisms is more serious than that caused by microorganisms. Moreover, the substrate, when reduced to tiny fragments, offers a greater surface to other factors of deterioration, especially in an outdoor environment (e.g., chemical compounds, rain, wind, freeze-thaw cycles). Detachment of the paint layer due to the growth of fungi is an example of a purely mechanical action performed by microorganisms (Fig. 2.3, p. 73).

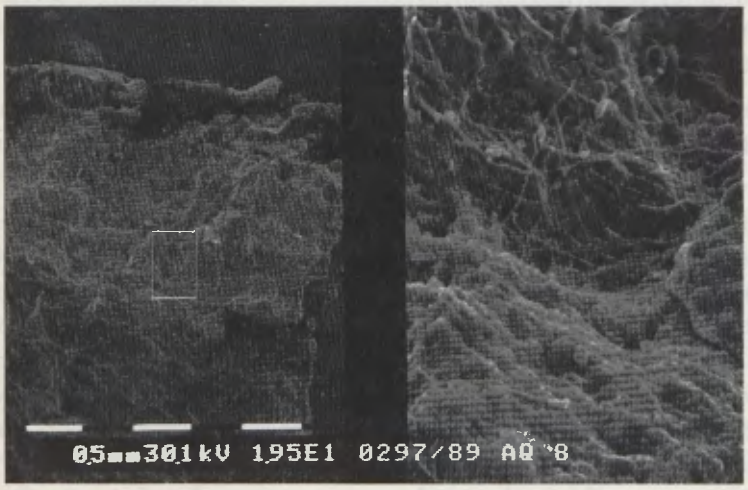


Fig.2.1

SEM micrograph of a fragment of Muggia sandstone covered by Lecanora muralis showing its hyphae penetrating 1.5 mm.

Fig.2.2

Penetration of roots under plaster, causing it to drop off - Dolocoenum, Rome, Italy (M. Baleani, ICR).

The adhesion to the substrate of microorganisms and organisms is very important; indeed, the ability to transform the substrate is strictly linked to a good attachment to it. This close contact with the surfaces happens in different ways: prokaryotes attach to the substrate by sheaths, holdfast substances (generally polymers), fimbriae or pili; fungi attach directly by hyphae; lichens, mosses and plants have a variety of attachment organs (ranging from rhizines to a real root system). Cellulose degradation also requires a direct contact between the bacteria and the cellulose fibers (e.g., the rod cells of *Cytophaga* and *Sporocytophaga* adhere closely to fibers and the cells are oriented in the same direction as microfibrils) (Schlegel and Jannasch, 1981). Insect pests cause damage with a purely mechanical action mainly due to the eating of different substances (paper, textiles, wood), which causes surface erosion, holes and tunnels.

Marine archaeological objects can be bored by some organisms (Pearson, 1987). Shipworms (Teredinidae) and piddocks (Pholadidae) bore into wood by the rasping action of their clam-shell grinders, the crustacean *Limnoria* using the mandibles. Other borers (e.g., *Mytilus* and *Lithophaga*) secrete acids to aid in boring.

Among types of physical damage, those caused by vandalism must also be mentioned. Graffiti on monuments, pedestrian traffic and the touching of surfaces can cause serious damage to surfaces, floors and carved artifacts.

2.2 CHEMICAL PROCESSES

Chemical processes involve a decomposition or transformation of the substrate by the chemical activity (etching, dissolving) of organisms. Bacteria, algae and fungi have a high surface-volume ratio (due to their small dimensions) compared to plants and animals, and this permits a rapid diffusion of metabolic products between cells and the surrounding environment.

Chemical action is due to chemical assimilatory or dissimilatory processes. In the former, the microorganisms or organisms use the material as food, as carbon or as an energy source through enzyme production; in the latter, the material is damaged by excretion of waste or intermediate metabolism products including acids and pigments which can damage, stain or disfigure the materials. Some specialized microorganisms and organisms can actively penetrate into the substrate as a result of chemical action (e.g., endolithic organisms).

The deterioration develops in different ways (Berthelin, 1983; Eckhardt, 1985; Allsopp and Seal, 1986), namely the production of the following:

- organic and/or inorganic acids
- chelating substances
- alkalis
- enzymes
- pigments

Other mechanisms can occur in the microbial corrosion of metals. These are described in ¶4.2.2, which covers these materials.

2.2.1 Acidolysis

Acids vary in strength and react directly with the molecules of the substrate, giving rise to salt formation. During metabolic processes, biodeteriorating agents release inorganic (e.g., carbonic, nitric, sulfuric) and/or organic (e.g., formic, acetic, butyric, lactic, succinic, gluconic) acids in considerable amounts. While some of these acids are weakly complexing (lactic acid), the main damage arises from their direct action on the substrate.

Carbon dioxide (CO_2) is produced by all aerobic organisms through respiration. In an aqueous environment it changes into carbonic acid, which can react with the substrate.

$$CO_2 + H_2O \underset{\leftarrow}{\rightarrow} H_2CO_3$$

Carbonic acid, even if weak, can dissolve the (relatively insoluble) calcium and magnesium carbonates of limestone, marble, lime mortar, plaster, etc., because it forms calcium and magnesium bicarbonates, which are more soluble.

$$CaCO_3 + H_2CO_3 \underset{\leftarrow}{\rightarrow} Ca(HCO_3)_2$$

$$MgCO_3 + H_2CO_3 \underset{\leftarrow}{\rightarrow} Mg(HCO_3)_2$$

In addition to some modifications of the substrate (direct action), the production of acids is important as it may favor the development of acidophilic species, which could not live on the substrate under neutral or basic pH conditions.

2.2.2 Complexolysis

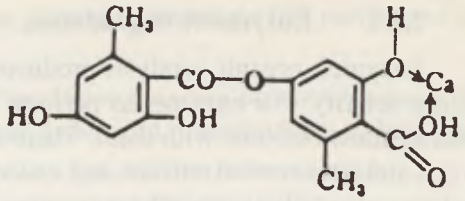
Chelation is a phenomenon by which one atom of hydrogen or of a metal is shared by two atoms of the same molecule. In chelation complexes, the central metal ion coordinates with a polyfunctional organic base to form a stable ring compound. The factors that affect chelate formation include the following:

- the basic strength of the chelating group (there is a relationship between the basicity of a chelating group and the stability of the chelate it forms)
- the electronegativity of the donor atoms of the basic group in the chelating agent
- the ring size
- the metal ion characteristics
- the resonance
- steric effects

Many organic compounds produced by microorganisms and organisms can complex or chelate the metal ions of the substrate. Among the complexing agents, simple organic acids (e.g., oxalic, citric, 2-ketogluconic, tartaric, fumaric, malic, malonic and aspartic) and phenols (e.g., salicylic and 2-3 dihydroxybenzoic acids) can be mentioned. These compounds are more or less active in metal solubilization, depending on the chelating ability of the molecule involved. Oxalic acid is a strong complexing agent and is produced in great amounts by fungi, lichens and higher plants. Lichens also produce many so-called "lichen acids" which have a chelating ability (Fig. 2.4).

Fig.2.4

Chelation of calcium performed by lecanoric acid produced by some lichens.



2.2.3 Alkalinolysis

During metabolic processes, basic compounds (e.g., ammonia and sodium carbonate) can also be released. These bases can react with some molecules of the substrate and generally increase the pH, favoring the development of basophilic microorganisms.

2.2.4 Exchange uptake of ions

Microorganisms and plants can absorb metal cations for their nutrition, or eventually in excess; this is essentially a cation-exchange mechanism.

In microorganisms, mineral ions can accumulate in the cells. The transformation of mica to vermiculite is performed by fungi with a process of this kind (K^+ ions are exchanged with Na^+) (Weed et al., 1969).

In plants, the mineral particles are etched by the acidity of root tips, as the hydrogen ions can be exchanged with cations in solution following the lyotropic series ($Ba^{++} > Ca^{++} > Mg^{++} > Cs^+ > Rb^+ > NH_4^+ > K^+ > Na^+ > Li^+$). The transfer of cations can occur through a network of colloidal particles by a contact-exchange mechanism (Fig. 2.5) (Keller and Frederikson, 1952; Caneva and Altieri, 1988).

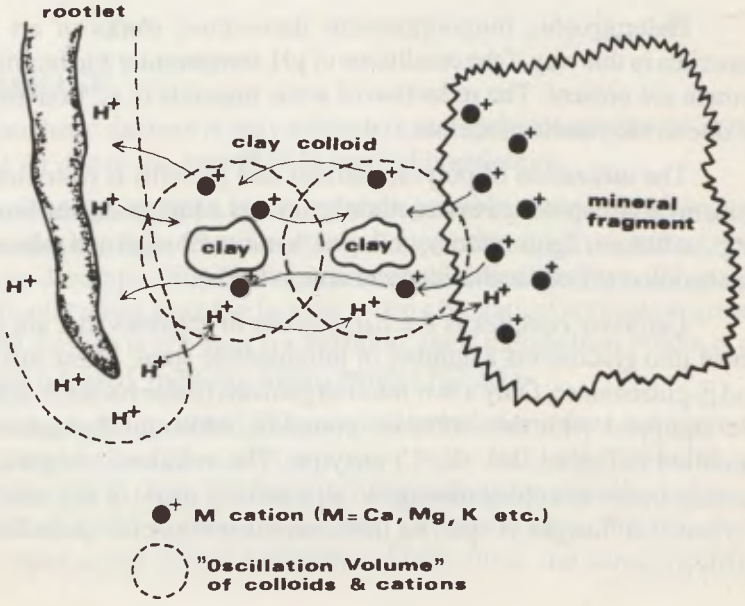


Fig.2.5

Extraction of mineral ions by a plant rootlet through mechanisms of contact exchange (from Keller and Frederickson).

2.2.5 Enzymatic degradation

Enzymes, organic catalysts produced by cells, are proteic molecules with a high specific activity. For enzymes to perform their catalytic activity, the molecules of the substrate must combine with them. There are *endoenzymes*, which are produced within the cell and not excreted outside, and *exoenzymes*, which are excreted into the substrate. The latter, also called extracellular enzymes, play an important role in the biodeterioration of works of art. The main function of extracellular enzymes is to perform chemical changes on nutrients present in the medium in order to allow food to enter the cell. These enzymes transform complex molecules (such as proteins, cellulose hemicelluloses, lignin) into simple ones that are soluble in water (Fig. 2.6).

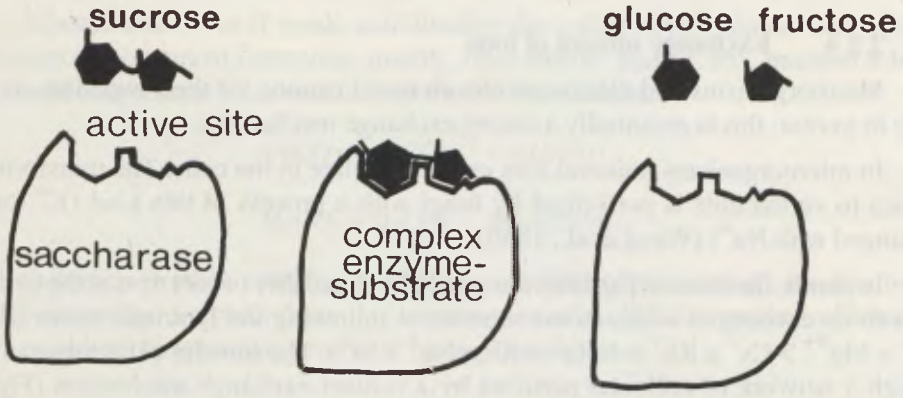


Fig.2.6

Example of the correspondence between the enzyme (invertase) and its substrate (sucrose).

Heterotrophic microorganisms decompose works of art composed of organic materials in this way if the conditions of pH, temperature and humidity useful to microbial growth are present. The reduction of some minerals (e.g., iron and manganese) can also be due to enzymatic processes.

The utilization of polysaccharides and proteins is restricted to all those microorganisms able to produce extracellular enzymes which break the bonds of macromolecules (e.g., cellulose, lignin, starch, collagen, keratin, fibroin) and release components that can be absorbed (monosaccharides and amino acids).

Cellulase complex is the name given to enzymes that are able to break cellulose down into glucose via a number of intermediate steps. These enzymes are called C_1, C_x and β-glucosidase. Only a few microorganisms (some bacteria, actinomycetes and fungi) are equipped with this cellulase complex, while microorganisms able to hydrolyze modified cellulose lack the C_1 enzyme. The cellulase complex hydrolyzes cellulose, causing heavy structural damage to all materials made of this substance. The firmness of the material changes. (Paper, for instance, can become feltish and so brittle that it crumbles easily.)

Proteolytic enzymes hydrolyze proteins, damaging materials like parchment and leather which are composed of them.

Molds such as *Aspergillus niger* and *Penicillium glaucum* produce *tannases* that hydrolyze the tannins of inks into glucose and gallic acid, causing them to lose color (Messner et al., 1988).

2.2.6 Pigments

Many microorganisms (bacteria, algae, fungi) produce organic pigments of different colors during their development. The pigments are characteristic of different species, but the color of stains arises not only from the chemical composition of pigments, but also from many other factors, such as the chemical composition of the material, the presence of metallic trace elements available in the nutrient (iron, zinc, manganese and copper), the acidity or basicity of the medium, the presence of other microbic species or environmental conditions.

Endopigments are located inside the cells and diffuse outside only after cellular lysis. Photosynthetic pigments (e.g., chlorophylls, bacteriochlorophylls, carotenoids, phycobilins) are of this kind.

Exopigments are secreted by cells and diffuse in the substrate. Many fungal strains produce a variety of colored pigments (green, blue, purple, violet, etc.) of different chemical natures, often belonging to anthraquinones, xanthones or carotenes. Melanin is a pigment deposited on the external surfaces of the hyphae of some fungi, giving a pigmentation. Some bacteria also produce pigments (e.g., *Pseudomonas* form pyocyanin, pyoverdin, pyorubin, pyomelanin). Some pigments are enzyme inhibitors or antibiotics, but the functions of other pigments are not yet completely clear. .

The release of pigments on the substrate or the presence of microorganisms containing pigments causes the appearance of different color stains or patches on many works of art.

2.3 AESTHETIC DAMAGE

The concept of aesthetic damage is very subjective and includes alterations in the appearance of works of art due to the growth of biological populations.

As stressed in previous paragraphs, it is not always possible to separate biological damage of a merely aesthetic nature from structural damage that involves irreversible harm to objects, with the decomposition or disintegration of materials (Figs. 2.7, p. 73, 2.8, 2.9, p. 74). The difficulty arises from the fact that when a biological population grows on a surface, even if the surface is not used for nutrition, their metabolism products or CO_2 from respiration are released, inducing some changes (¶2.2.1).

In some cases, indeed, the presence of biological populations does not seem to cause any noticeable change in the chemical composition of the substrate (Realini et al., 1985; Pietrini et al., 1985) (Fig. 2.10, p. 74). But much depends on the time elapsed since the initial biological colonization occurred. Very often (but not always) the growth of microorganisms and lichens under certain conditions is very slow, and damage can be

evaluated only after many years or decades. This occurs especially when there is not a direct nutritional utilization of the substrate by the microflora, as opposed to when an organic material, such as paper or wood, is attacked by specific heterotrophic cellulosolytic microorganisms or organisms.

The concept of aesthetic damage encompasses change due to chromatic alterations, development of biological patinas, or visual obstruction of the materials composing a work of art.

Nonetheless, purely aesthetic damage is often the most emphasized, or the only damaged considered by several authors. In many cases it represents the less important part of the problem (Figs. 2.11 and 2.12, p. 75).

Moreover, it is important to remember that this concept will vary from one person to another in relation to his or her background and sensitivity, and it is also subject to changing fads. In the nineteenth century, for example, the aesthetic value of ruins was prized and the effect of plants climbing on monuments was highly appreciated (Ruskin) (Martines, 1983). Algal or lichen patinas were esteemed and even encouraged, for they gave a better idea of the passage of time. Today, in contrast, we usually prefer to eliminate biological patinas, encrustations or ruderal vegetation, not only for conservation reasons, but also to create an impression of order and care (Fisher, 1972).

In conclusion, when one is dealing with damage due to the growth of a biological population, it is preferable to consider objective data due to physical or chemical processes linked to this growth and not dwell too much on aesthetic damage. Moreover, a first biological colonization, even if not very dangerous and therefore considered as aesthetic damage, can ultimately favor the implantation of other, more aggressive species.

2.4 PHENOMENOLOGY OF BIOLOGICAL ALTERATIONS

The phenomenology of biological alterations represents the appearance with which the biodeterioration occurs. The ability to recognize the nature of alteration has evident practical consequences for a conservator.

To recognize a biological attack and distinguish it from other causes, at least two conditions are required:

- a typical (characteristic) morphology of the alteration
- easy legibility

Considering the first point, we can observe that the morphology is sometimes typical but other times can lead to confusion.

Legibility depends upon the experience of the person observing the phenomenon, and upon the level of taxonomical accuracy required. For example, if one only has to decide whether the cause is biological or not, in many cases an unspecialized person is able to answer (Fig. 2.13, p. 75).

Obviously, vegetable organisms are easier to recognize than microorganisms, due to dimensions that permit observation with the naked eye. Still, algal patinas, mosses and sometimes lichens are frequently confused with each other by the non-biologist.

More detailed systematic information (order, class, family, genus and species), which is necessary to perform correct preventive or control measures (Chap. 6), can be obtained with specific analyses (see Appendix).

The phenomenology of alteration varies according to the biological species involved, the nature of the substrate, the climate and often also the period of the year.

The different weathering patterns of the various species involved are described in the respective paragraphs of Chapters 3 and 4. A summary of the most frequent phenomenology of biological alterations in relation to materials is given in Table 2.1 below. Paintings are not included in the table because the morphology of alteration varies in relation to the kind of material used as a support (wood, paper, textiles, parchment), and the nature of the paint layer (oil, distemper, watercolor).

Table 2.1 Phenomenology of biological alterations - Part I

	Wood	Paper	Textiles
Autotrophic bacteria	ND = Not described	ND	ND
Heterotrophic bacteria	Changes in mechanical characteristics of material	Stains, changes in mechanical characteristics (feltish and fragile)	Stains, discoloration, loss of strength
Actinomycetes	Idem	Idem	Idem
Fungi	Stains, change of wood color, softening, cracking, change in mechanical characteristics	Idem	Stains, discoloration, loss of strength
Cyanobacteria and algae	Patinas of various colors (mainly green)	ND	Patinas
Lichens	Crusts, patches	ND	ND
Mosses and liverworts	Green-grey thalli	ND	ND
Higher plants	ND	ND	ND
Animals — insects * — marine borers and snails **	* Tunnels, holes, bore dust ** Deep erosion, tunnels	* Superficial abrasion, erosion, holes and tunnels	* Erosion, holes, loss of parts

Table 2.1 Phenomenology of biological alterations - Part II

	Parchment & leather	Stone & related materials	Glass	Metal
Autotrophic bacteria	ND	Black crust, black-brown patinas, exfoliation, powdering	Pitting, opacification, black spots, blackened waterlogged material	Corrosion
Heterotrophic bacteria	Spots, stains, loss of tensile strength, softening	Black crusts, black patinas, exfoliation, color change	Idem	Corrosion
Actinomycetes	Spots, stains, whitish flecks, loss of tensile strength	Whitish-grey powder, patinas, white efflorescence	ND	ND
Fungi	Spots, stains, whitish flecks, loss of tensile strength, increased stiffness	Colored stains and patches, exfoliation, pitting	Opacification, black spots	ND
Cyanobacteria and algae	ND	Patinas and sheets of various colors and consistency	ND	ND
Lichens	ND	Crusts, patches, pitting	Pitting, opacification, corrosion	ND
Mosses and liverworts	ND	Green-grey thalli	ND	ND
Higher plants	ND	Grass, shrubs & woody species induce cracks, collapse, detachment of materials	ND	ND
Animals — insects * — marine borers and snails ** — birds ***	* Erosion, holes, loss of parts	** Holes of typical shape *** deposition of excrement with corrosive effect, holes, scratches	ND	ND

ND = Not described because they play a secondary role in deterioration of works of art or are rarely found on these materials under usual conservation conditions.

Cases in which a biological population might be confused with purely physical or chemical damage are analyzed in the next paragraphs (2.4.1 and 2.4.2). These cases are more frequently found in inorganic materials (e.g., stone, mural paintings, glass) because, as observed in ¶2.3, the growth of microflora is often slow and does not always occur under optimal physiological conditions. In contrast, when biological populations (especially fungi) attack organic materials, their development is usually more easy to detect, given the typical presence of their vegetative and reproductive structures and significant changes in the constituent materials. Due to the evident damage induced by biological populations on organic materials, the concept of aesthetic damage has been applied very rarely in these cases of biodeterioration. As a result, there will be more examples focusing on inorganic materials.

In the last paragraph, the perspectives of using specialized biological analysis in archaeological and monumental areas are analyzed.

2.4.1 Relationships to the nature of materials, kinds of microorganisms and relative habitats

With organic materials, a biological attack is often easily recognized. In the case of microorganisms such as fungi, it is possible to observe the development of fungal mycelia or typical changes in color or structure of the materials. In the case of insects, the deposition of excrement and the formation of tunnels, holes, nests and bore dust are typical signs of their presence (Gallo, 1985; Bravery et al., 1987).

With stains, however, some confusion might arise. In fact, stains can be either chemical in nature, especially due to oxidation or deposition of mineral salts, or biological in nature due to a microbial attack, utilizing, oxidizing or reducing ions or producing pigments. Even with the help of analysis, it is not always easy to identify the cause of alteration. The case of foxing of paper is emblematic (Arai et al., 1988; Hey et al., 1988) (¶3.1.3, Fig. 3.17, p. 78).

When there is a biological attack on wood, "white rot," "brown rot" and "soft rots" are typical alterations caused by different species (¶3.1.2. and Figs. 3.8, 3.9, 3.10, p. 77).

On stone, the most difficult type of biodeterioration to detect is induced by bacteria that produce damage similar to chemical damage; their identification requires specific biological investigations (microscopic and cultural analyses). For example, sulfur-oxidizing bacteria or nitrogen bacteria produce exfoliation and softening of stone similar to those due to an attack of SO_2 or NO_x respectively, both of which are common pollutants in urban and industrial environments. Heterotrophic bacteria are also often associated with black crusts or other forms of weathering similar to a chemical attack. Other bacteria such as *Arthrobacter* and mycoplasms give rise to color changes in mural paintings that could appear to be purely chemical in nature (Petushkova and Lyalikova, 1985) (¶4.1.1).

The problem of recognition of the etiological agent of stains is similar to that discussed for organic materials. The case of the Certosa of Pavia (Italy) is an example of stains on marble due to pigments of biological origin whose nature was not readily explained. The cause was finally identified when heterotrophic bacteria producing orange-red pigments were isolated (Realini et al., 1985).

Other potentially confusing cases are productions of biological patinas or efflorescence that resemble those of various chemical compounds. For example, black patinas of cyanobacteria are sometimes confused with deposits of pollutants, even though it is easy to recognize the presence of a biological attack by simply considering that it is associated with water, contrary to deposits of particulates (Fig. 2.14, p. 76).

Whitish efflorescence and patinas in subterranean or humid environments in contact with the earth can originate from mineral salts or also by the growth of Actinomycetes. The typical smell of the latter, verified by microscopic observation, can reveal the true nature of the attack (Fig. 2.13, p. 75).

For metals, the difficulty of distinguishing microbial corrosion from purely electrochemical corrosion is discussed in ¶4.3.

Another fact that can contribute to the difficulty of recognizing the presence of a biological attack is the specific habitat of the organisms involved. When organisms do not grow on the surface but in depth, their presence is often detected only in the final stages of decay. This occurs with termites which, being heliophobic organisms, avoid emerging on the surface. Often the damage is observed only when the inner layers of wood are already consumed (¶3.1.2, Figs. 3.12, 3.20, p. 79). This is also the case of endolithic organisms, such as some bacteria, cyanobacteria, algae or lichens, whose presence can only be detected by experienced biologists, who collect samples and carry out specific analyses (Fig. 2.15, p. 76) (¶4.1.3 and 4.1.4) (Golubic et al, 1981; Saiz-Jimenez, 1990). Another instance is found with the roots of plants in subterranean environments. They grow abundantly under plasters and become recognizable only when they inflate or break down these layers, due to thickening with lignification (¶4.1.5, Fig. 4.22) (Caneva, 1988).

2.4.2 Relationship of physiology of organisms to environmental conditions

A biological colonization also varies as a function of the physiological condition of the organisms involved, which is correlated with internal factors (e.g., age of the populations) and with external factors, such as the availability of nutrition or the micro- and macro-climate, which vary from season to season, especially in temperate climates (see ¶1.2).

Especially when an organism is growing under unfavorable conditions, its morphological appearance changes in color or form. This fact gives rise to the words "typical" or "atypical" growth for indicating respectively the morphology of the organisms under good or poor physiological conditions (Giacobini, 1974).

The most problematical and interesting situation from our point of view occurs when the change makes the biological origin of deterioration difficult to recognize.

Such confusion frequently arises with algal patinas that can change color in response to situations of physiological stress. For example, green patinas of *Haematococcus pluvialis* (Chlorophyceae) become red when the alga enters into a quiescent state, forming cysts where carotenoids are accumulated. This state seems to be induced especially when the salt content of the substrate varies (Pietrini et al., 1985).

Green patinas can also become black, grey or pink and therefore sometimes resemble saline efflorescence. This phenomenon was observed in the case of several mural paintings in Italy due to the ageing of the microorganisms (cyanobacteria and green algae), the pH of the substrate and its mineral composition (Giacobini et al., 1979; Tomaselli et al., 1979).

It is, however, important to remember that biological patinas of photoautotrophic organisms — algae and cyanobacteria in particular — are not always green even if the organisms are in a good physiological state, because chlorophylls may be obscured by other photosynthetic pigments (e.g., carotenoids, ficobilins). For example cyanobacteria often form black patinas, as previously pointed out; there are also green algae such as *Trentepohlia* that appear orange or red-brown under normal conditions.

Apart from algae, other organisms also clearly vary in relation to physiological stresses (e.g., mosses, plants, lichens), but their biological origin usually remains detectable, given the thickness of their thallus or vegetative structure.

When physiological stress arises from unfavorable climatic conditions, such as water deficiency or overheating, some poikilohydric species such as cyanobacteria and lichens are better able to tolerate such stress. Other species can be damaged and therefore change in morphological appearance when the stress is great and prolonged.

A more difficult problem is when the aim is to recognize the presence of an old biological attack, after the death of the biological populations. This is sometimes possible, but only through a serious biological and ecological investigation, carried out by specialists in the sector. In fact, a specific morphology of weathering or "specific imprinting" can be left on the work of art. For example, the previous existence of borer organisms can be recognized through the shape of tunnels, holes and craters produced on wood, paper, stone, etc. In the case of cyanobacteria, fungi, algae, lichens or roots, specific weathering patterns (pitting and cavities of different shapes) can permit recognition if the damage is not in an initial stage (Danin, 1986). Here again, there is sometimes a risk of mistaken identification by the inexperienced investigator.

2.4.3 Perspectives in using the phenomenology of alteration as a bioindicator

The cases discussed above emphasized the difficulty of an immediate recognition of a biological attack, especially for a person without specific knowledge of biology and biodeterioration of materials.

In many cases, however, specific experience in this field makes it possible to recognize the characteristic weathering patterns of biodeteriogens. These patterns arise from the different morphological characteristics of the organisms (structure of thalli, fruiting bodies, etc.), from specific metabolites emitted and from physiological peculiarities.

Such patterns also permit one to recognize the biodeteriogens inducing them and the environmental parameters that are compatible with the ecological ranges of the organisms (¶1.1.2). As a result, there is a possibility of using biological populations as

bioindicators of those environmental parameters that condition their presence (e.g., water, pH, mineral salts, temperature, light, etc.).

The potential contribution of this information to the phase of monitoring environmental parameters before restoration can easily be understood (Caneva and Salvadori, 1989). In practice, however, studies carried on with this ecological approach are very rare.

The identification of specific weathering patterns of stone caused by different biological populations has been proved in different localities in Israel (Danin and Garty, 1983; Danin, 1986). Terms such as "jigsaw", "honeycomb", "spongy pattern" were used to indicate the different typical alterations of stone arising from the activities of different microorganisms (especially cyanobacteria, lichens and fungi). Considering that the distribution of lithobiont communities is influenced by environmental conditions, through the knowledge of their climatic affinities it was possible to use their specific weathering pattern (even in the absence of living organisms) for the reconstruction of paleoclimates. Specific investigations were also made in archaeological sites in order to compare biogenic weathering of stones buried in walls or by soils dating to 10,000 to 1,500 years ago and to assess the climatic regime that prevailed in the different periods (Danin, 1985).

REFERENCES

ALLSOPP, D., and K.J.SEAL (1986). *Introduction to Biodeterioration.* London: Edward Arnold.

ARAI, H., N. MATSUI and H. MURAKITA (1988). "Biochemical investigations on the formation mechanisms of foxing," *The Conservation of Far Eastern Art.*

BERTHELIN, J. (1983). "Microbial weathering processes," *Microbial Geochemistry*, ed. W.E. Krumbein. Blackwell Scientific Publications. 223-262.

BRAVERY, A.F., R.W. BERRY, J.K. CAREY and D.E. COOPER (1987). "Recording wood rot and insect damage in buildings," *Building Research Establishment Report.*

CANEVA, G., and A. ALTIERI (1988). "Biochemical mechanisms of stone weathering induced by plant growth," *Proc. VIth Int. Cong. on Deterioration and Conservation of Stone. Torun.* 32-44.

——— (1988). "Tree roots and hypogeans conservation," *Proc. IAVS Spontaneous Vegetation and Settlements, Frascati (Italy)*, (in press).

——— and O. SALVADORI (1989)."Sistematica e sinsistematica delle comunità vegetali nella pianificazione di interventi di restauro," *Proc. "Il Cantiere della Conoscenza, il Cantiere del Restauro," Bressanone.* Padova: Lib. Progetto Ed. 325-335.

DANIN, A. and J. GARTY (1983)."Distribution of cyanobacteria and lichens on hillsides of the Negev Highlands and their impact on biogenic weathering," *Z. Geomorph.* N.F. 27 (4) 423-444.

——— (1985)."Palaeoclimates in Israel: Evidence from weathering patterns of stones in and near archaeological sites," *Bull. Amer. Sch. Oriental Research*, 259. 33-43.

——— (1986). "Patterns of biogenic weathering as indicators of paleoclimates in Israel," *Proc. Royal Society Edinburgh,* 89B. 243-253.

ECKHARDT, F.E.W. (1985). "Mechanisms of microbial degradations of minerals in sandstone monuments, medieval frescoes and plasters," *Proc. V Int. Congr. Deterioration and Conservation of Stone, Lausanne*. vol 2. 643-652.

FISCHER, G.G. (1972). "Weed damage to materials and structures," *Int. Biodet. Bull.*, 8 (3) 101-103.

GALLO, F. (1985). *Biological Factors in Deterioration of Paper.* Rome: ICCROM.

GIACOBINI, C. (1974). "Prospettive di riconoscimento morfologico di alcuni tipi di alterazione dei monumenti," *Proc. XXIX Cong. A.T.I. Firenze*. 129-132.

———, C. ANDREOLI, G. CASADORO, B. FUMANTI, P. LANZARA and N. RASCIO (1979). "Una caratteristica alterazione di murature ed intonaci," *Proc. III Int. Congr. Deterioration and Conservation of Stone, Venice*. 289-299.

GOLUBIC, S., E.I. FRIEDMANN and J. SCHNEIDER (1981). "The lithobiontic ecological niche, with special reference to microorganisms," *J. Sedimentary Petrology*, 51. 475-478.

HEY, M., G. PASQUARIELLO, F. GALLO, G. GUIDI and F. PIERDOMINICI (1988). "Paper analysis in relation to foxing," *III Conferenza Internazionale sulle Prove non Distruttive. Perugia. II/9.1-9.10.*

KELLER, N.D., and A.F. FREDERICKSON (1952). "The role of plants and colloid acids in the mechanisms of weathering," *Amer. J. Sci.*, 250. 594-608.

MARTINES, G.G. (1983). "Marmo e restauro dei monumenti antichi: estetica delle rovine, degrado delle strutture all'aperto, una ipotesi di lavoro," *Proc. "Marmo Restauro - Situazione e Prospettive," Carrara.* 83-92.

MESSNER, K., L. ALBERIGHI, G. BANIK, E. SREBOTNIK, W. SOBOTA and A. MAIRINGER (1988). "Comparison of possible chemical and microbial factors influencing paper decay by iron-gall inks," *Biodeterioration* 7, eds. D.R. Houghton, R.N. Smith and H.O.W. Eggins. London and New York: Elsevier Applied Science. 449-454.

PEARSON, C., ed. (1987). *Conservation of Marine Archaeological Objects*. London: Butterworths.

PETUSHKOVA J.P. and N.N. LYALIKOVA (1985). "Microbial degradation of lead-containing pigments in mural paintings," *Studies in Conservation*, 31. 65-69.

PIETRINI A.M., S. RICCI, M. BARTOLINI and M.R. GIULIANI (1985) "A reddish alteration caused by algae on stoneworks - Preliminary studies," *Proc. V Int. Congr. Deterioration and Conservation of Stone, Lausanne,* vol. 2. 653-662.

REALINI M., C. SORLINI and M. BASSI (1985). "The Certosa of Pavia: a case of biodeterioration," *Proc. V Int. Congr. Deterioration and Conservation of Stone, Lausanne,* vol. 2. 627-629.

SAIZ-JIMENEZ, J. GARCIA-ROWE, M.A GARCIA DEL CURA, J.J. ORTEGA- CALVO, E. ROEKENS and R. VAN GRIEKEN (1990). "Endolithic cyanobacteria in Maastricht limestone," *The Science of the Total Environment,* 94. 209-220.

SCHLEGEL, H.G., and H.W. JANNASCH (1981). "Prokaryotes and their habitats," *The Prokaryotes*, eds. M.P. Starr, H. Stolp, H.G. Truper, A. Balows and H.G. Schlegel. Springer-Verlag. 43-82.

TOMASELLI, L., M.C. MARGHERI and G. FLORENZANO (1979). "Indagine sperimentale sul ruolo dei cianobatteri e delle microalghe nel deterioramento di monumenti ed affreschi," *Proc. III Int. Congr. Deterioration and Conservation of Stone, Venice.* 313-325.

WEED, S.B., C.B. DAVEY and M.G. COOK (1969). "Weathering of mica by fungi," *Soil Sci. Soc. Amer. Proc.*, 33. 813-814.

Chapter 3

BIODETERIORATION OF ORGANIC MATERIALS

Many works of art, such as paintings on canvas or wood panel, wooden sculpture, library materials, prints and archaeological objects, are composed of organic materials.

Cultural property made of organic substances is more susceptible to attack by heterotrophic microorganisms and organisms than is inorganic material. The biodeterioration phenomena occur as soon as microclimatic conditions (temperature and RH) are favorable to biological growth. These conditions are not rare in indoor environments: an RH over 65%, associated with a temperature of 20°C or above, is enough to cause the growth of microorganisms such as fungi, which can cause serious damage to works of art. An artifact's liability to biodeterioration is also strictly related to its chemical composition and to the type and quantity of organic molecules present.

Based on their composition, organic materials can be divided into those of vegetable origin (e.g., paper, wood, cotton, flax) and those of animal origin (e.g., leather, wool, silk).

3.1 MATERIALS OF VEGETABLE ORIGIN

3.1.1 Chemical components and their susceptibility to biodeterioration

Cellulose, lignin and hemicellulose are the main compounds that form materials of vegetable origin.

Cellulose is a linear polysaccharide (made of carbon, hydrogen, oxygen) consisting of D-glucose units linked together in long chains by (1-4-β) glucosidic linkages (Fig. 3.1). The chain length varies according to the type of cellulose (natural or manufactured).

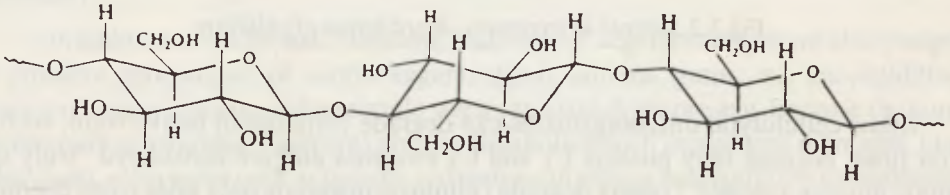


Fig.3.1 *The cellulose molecule.*

In nature, cellulose molecules are linked together in parallel sheaves called microfibrils. The areas in which the chains are most closely bound are called "crystalline" because they look crystalline when examined under X-ray diffraction; those in which the chains are separated and not strictly parallel are called "amorphous." The crystalline areas are strongly held together and highly resistant to breakdown by chemical substances and enzymes. The amorphous areas are loosely bound and easily penetrated by chemicals (cellulolysis).

Native cellulose is mainly crystalline with some amorphous sites, but many more amorphous sites are created along the macromolecule by physico-chemical processing. These changes make cellulose more susceptible to biological attack.

Cellulose is one of the components of cell walls in all plant tissues, structural and conductive. Its percentage varies in relation to the plant species and the kind of tissue involved. Therefore, in materials of vegetable origin, the cellulose percentage differs depending on the plant or plant fibers used. It is higher in materials made of herbaceous dicotyledons and lower in those made of conifer wood: cotton 95%, linen 80%, hemp 77%, jute 60%, esparto 46-58%, conifer wood 58-60%.

The deterioration of cellulose is caused mainly by microorganisms. Cellulose biodegradation relates to the production of a system of several extracellular and intracellular enzymes known as *cellulase complex*. These enzymes break cellulose down into glucose. Over the past 20 years, much research has been conducted on cellulolytic enzymes, and it is now thought that several enzymes are involved; a C_1 component acts on crystalline cellulose, de-aggregating the cellulose chains and paving the way for attack by the hydrolytic enzymes, while a subsequent action of endo- and exo- 1,4-β-glucanases (generally referred to as C_x) effects the hydrolysis of cellulose and a 1,4-β-glucosidase converts water-soluble cellodextrins to glucose (Fig. 3.2) (Eriksson and Wood, 1985).

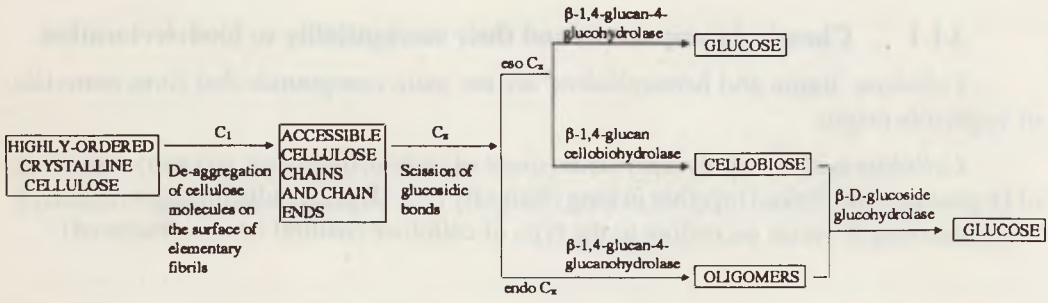


Fig.3.2 *Scheme of enzymatic degradation of cellulose*

Some cellulolytic microorganisms can degrade cellulose in native form, such as cotton fiber, because they possess C_1 and C_x enzymes and are considered "truly cellulolytic microorganisms"; others degrade cellulosic materials only after some chemical modification because they are unable to produce C_1 enzymes (Allsopp and Seal, 1986; Sagar, 1987).

The cellulases of microorganisms are *inductive* enzymes and are produced only in the presence of cellulose. The production of this complex of enzymes by microorganisms is self-regulated by the amount of glucose (the end product of cellulose biodeterioration) in the substratum. Production is repressed if glucose is present in sufficient quantity.

The breakdown of cellulose is also strictly related to the availability of other nutrients in the environment. A low quantity of available nitrogen severely limits the ability of microorganisms to attack cellulose. As a result, the presence of a nitrogen source and mineral elements favors cellulose degradation.

Lignin is a very complex three-dimensional polymer composed of aromatic alcohols (three different phenylpropane monomers). It forms an irregular reticulate molecule. The monomeric units in lignin are not joined by a single intermonomeric linkage but by several different carbon-to-carbon and other linkages, most of which are not readily hydrolyzable.

Lignin represents the essential part of woody fibers and its content in woody stems of arboreous gymnosperms and angiosperms varies from 15 to 36%. Its percentage in materials varies according to the origin of the raw material and the chemical/physical treatments used in manufacture. In timber, for example, the percentage of lignin depends upon the arboreous species of origin and on the part of the plant used; in paper it can depend upon the purification (delignification) treatment employed.

Lignin is resistant to degradation by most microorganisms. Only some fungi and some strains of bacteria are able to decompose lignin in nature; the best known and the most important degrading microorganisms are the wood-decaying fungi. More recent studies have shown that only wood-destroying Basidiomycetes are able to metabolize lignin efficiently, whereas other fungi and some species of Actinomycetes cause only a partial degradation; lignin can also be degraded by consortia of microorganisms, which alone are unable to metabolize it completely (Kirk and Shimada, 1985).

Hemicelluloses are polysaccharides soluble in alkali that are associated with the cellulose of the plant's cell wall. They include the noncellulosic β-D-glucans, the pectic substances and several complex heteropolysaccharides. Some hardwood plant species contain up to 35% hemicellulose (Dekker, 1985).

Most of the bacteria and fungi (including yeasts) are capable of hydrolyzing hemicelluloses by the production of extracellular enzymes (hemicellulases). These hemicellulases can be either constitutive enzymes (produced irrespective of the growth substrate) or inductive enzymes (produced only when hemicelluloses are present in the substrate).

In addition to these basic elements, materials of vegetable origin are also composed of different percentages of simple sugars, starch, tannins, gums, etc. Susceptibility to biodeterioration increases when simple sugars and starch are present, because the number of microorganisms and organisms able to metabolize such substances increases. On the other hand, substances such as tannins and resins can reduce susceptibility to biodeterioration.

3.1.2 Wood

Wood represents a complex system of tissues present in most vascular plants. It is formed by the activity and proliferation of an undifferentiated tissue, called cambium, which produces outside the phloem (internal bark) and inside the xylem or wood. The cambium is responsible for the secondary growth (radial growth) of the plant.

Wood is the principal water-conducting tissue and chief supporting tissue of higher plants. It is composed of vascular elements (vessels or tracheids), mechanical elements (fibers and fibro-tracheids) and parenchymatic elements. The only living elements are the parenchymatic cells or rays. When vessels and fibers die, their protoplasm is absorbed and only their cell walls remain.

Every year the plant produces a new layer of wood, the "growth ring." The thickness, density and, as a consequence, color of this layer vary in relation to the growth period (spring or autumn), the species and age of the plant, soil composition, wind, etc.

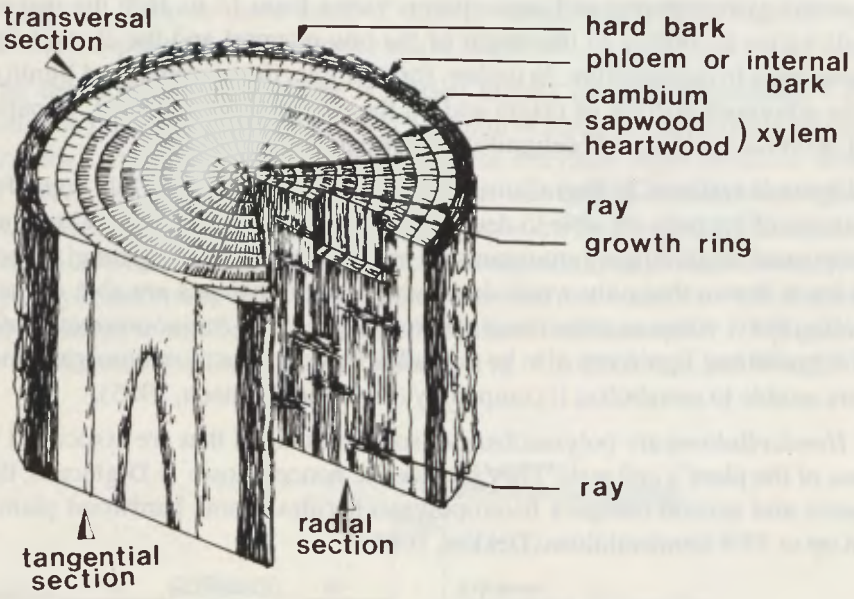


Fig.3.3 *Macroscopic structure of wood.*

The external part of the wood in the tree is called sapwood and is physiologically active, while the inner part, called heartwood, is physiologically dead (Fig. 3.3). In the formation of heartwood, the reserve food materials stored in ray parenchyma are removed and the cell walls are impregnated with materials called extractives, such as tannins.

When we speak of wood as commercial timber, the meaning is quite different; indeed, the principal source of commercial timber is the entire stem of the tree. The commercial wood derived from coniferous trees (gymnosperms) is called *softwood*, whereas *hardwood* is produced from dicotyledons (angiosperms). These general terms, softwood and hardwood, do not refer specifically to the comparative densities or hardness of the two groups of wood, but, rather, they are accepted and used as categories of timber.

Softwood (Fig. 3.4), also called *homoxylous*, is more uniform in structure than hardwood, being composed of tracheids which communicate through valvelike structures called pits, with parenchyma restricted to rays. Certain species also have resin ducts. Hardwood (Fig. 3.5) is composed of fibers, vessels with more simple pits and parenchyma; its structure is relatively heterogeneous, hence hardwood is also called *heteroxylous*.

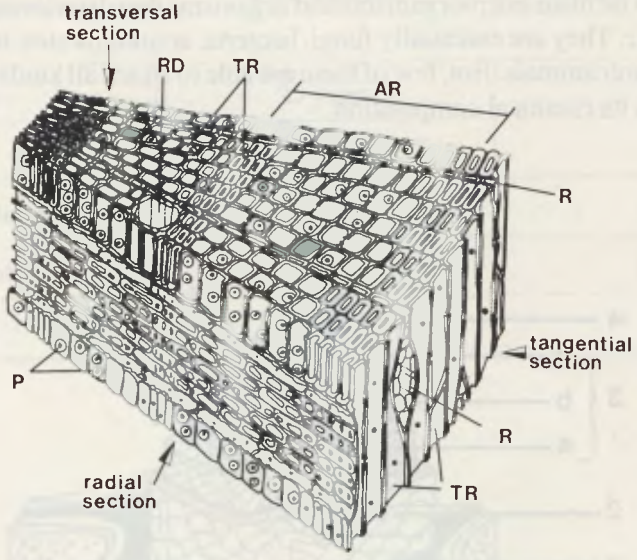


Fig.3.4 *Wood of conifers (softwood):*
AR - annual growth ring; P - pits; RD - resin duct; TR - tracheids; R - rays.

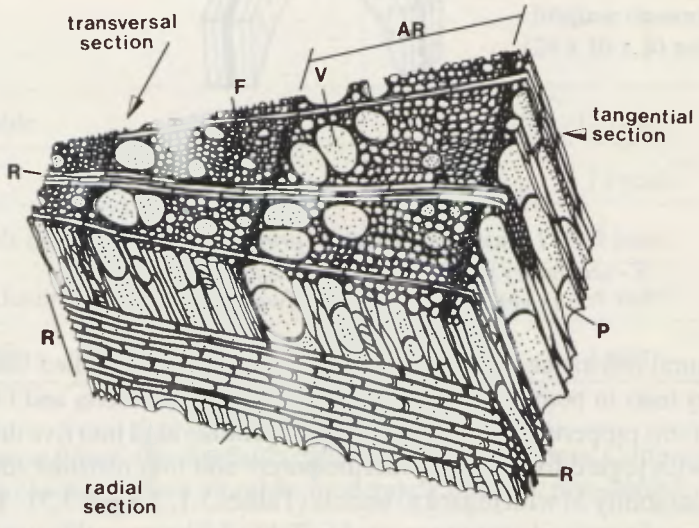


Fig.3.5 *Wood of dicotyledons (hardwood):*
AR - annual growth ring; F - fibers; P - pits; R - rays; V - vessels.

The percentages of the main chemical constituents (cellulose, lignin and hemicellulose) vary in relation to the original species (angiosperms or gymnosperms), the part of the stem used (sapwood or heartwood) and ageing (seasoning). The different chemical constituents are also not uniformly distributed in the complex structure of the wood cell walls (Fig. 3.6). Biological attack occurs in different parts of the cell wall, depending on the kind of deteriogen microorganisms or organisms involved and on their metabolic characteristics. The main microorganisms and organisms that deteriorate wooden objects are *heterotrophic*. They are essentially fungi, bacteria, actinomycetes, insects and, in sea water, marine borer animals. But, few of them are able to attack all kinds of wood because of differences in its chemical composition.

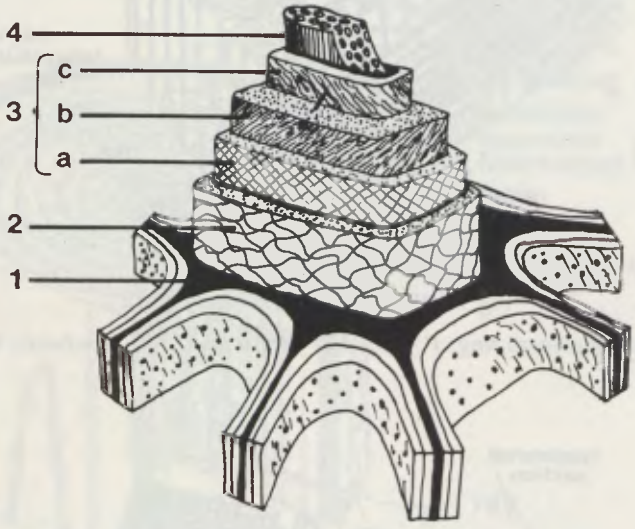


Fig.3.6 *Structure of wood cell wall:*
1 - middle lamella; 2 - primary wall;
3 - secondary wall: a. S1 layer, b. S2 layer, c. S3 layer;
4 - verrucous layer (not always present).

The natural resistance that wood offers to deterioration is called "durability," and is evaluated by tests in both the field and the laboratory (Gambetta and Orlandi, 1982). On the basis of this property, the species of wood can be divided into five different classes of durability with regard to fungi and marine borers and into resistant (durability 1) or not resistant (durability 5) with regard to insects (Tables 3.1, 3.2 and 3.3). Tests on fungal biodeterioration of sapwood are not reported in Table 3.3 because this type of wood is so vulnerable.

Table 3.1 Durability classes of wood against fungi (from Gambetta and Orlandi, 1982, modified)

	Field tests on wooden samples: lifetime (mean) (5 x 5 x 50 cm)	Laboratory tests on wooden samples: % weight loss after 4 months (1.5 x 2.5 x 5 cm)
1. very durable	25 years	1
2. durable	15-25 years	1-5
3. moderately durable	10-15 years	5-15
4. not very durable	5-10 years	15-30
5. non-durable	5 years	30

Table 3.2 Durability classes of wood against marine borers (from Gambetta and Orlandi, 1982)

	Field tests on wooden samples: lifetime (mean) (20 x 10 x 20 cm)
1. very durable	15 years
2. durable	8-15 years
3. moderately durable	4-8 years
4. not very durable	1-4 years
5. non-durable	1 year

In the near future, the standards of the European Economic Community will reduce the durability classes to three: durable, moderately durable, non-durable.

Table 3.3 Natural durability of woods (from Gambetta and Orlandi, 1982, modified).

Wood species	Fungi	Insects				
		Lyctidae		Cerambycidae		Anobiidae
	heart-wood	sap-wood	heart-wood	sap-wood	heart-wood	
SOFTWOODS:						
Abies alba Mill.	5	R		5	5	5
Cupressus sempervirens L.	2	E				
Larix decidua Mill.	2	S		5	1	5
Picea abies Karst.	5	I		5	5	5
Pinus pinea L.	4	S		5	1	5
Pinus radiata D. Don	4	T				5
Pinus pinaster Ait.	4	A		5	1	
Pinus laricio Poir.	5	N		5	1	5
Pinus sylvestris L.	4	T		5	1	5
Pinus strobus L.	4			5	1	5
Pseudotsuga spp.	4			5	1	
HARDWOODS:						
Acer campestre L.	5	5				5
Betula alba L.		1	1			
Castanea sativa Mill.	3	5	1	5	1	
Fagus sylvatica L.	5	1	1	5	5	5
Fraxinus excelsior L.	5	5				5
Juglans regia L.	3	5	1	5	5	5
Platanus orientalis L.	5					

Wood species	Fungi	Insects				
		Lyctidae		Cerambycidae		Anobiidae
	heart-wood	sap-wood	heart-wood	sap-wood	heart-wood	
Populus euroamericana Guinier	5	1	1	5	5	5
Prunus avium L.		1	1	5		5
Quercus cerris L.	4			5	5	5
Quercus petraea Liebl.	2	5	1	5	1	5
Quercus robur L.	2	5	1			5
Tilia plathyphyllos Scop.		1	1			5
Ulmus spp.	4	5				5

Susceptibility to microbial attack also depends on the moisture content of the wood. Wood is a hygroscopic material and, after seasoning, its moisture content keeps equilibrium with the RH of its surroundings. Microbial deterioration usually occurs when the water content of wooden materials is above 20%. The fiber saturation point of wood, about 30%, is required for the optimum development of most fungi (Garg and Dhawan, 1985-1987).

Among microorganisms, fungi are the major agents of deterioration of wooden cultural property. They develop on the surface of wood or within it in the openings (Fig. 3.7, p. 76) such as rays, parenchyma cells, tracheids. They find organic materials in the products stored in the cell protoplasms of the parenchymatic cells, such as starch and sugars, or in the components of cell walls. In the latter case, by production and emission of exoenzymes, fungi can partially and sometimes totally destroy the cell walls, breaking down their components into simpler nutritive compounds.

Based on both the preferential chemical reactions of fungi with the constituents of wood and the resultant general color effects, two types of wood decay can be recognized: white rot and brown rot (also called dry rot).

"*White rot*" fungi are able to destroy both the cellulose and lignin of wood, leaving it generally whitish in color and light in weight; sometimes it develops a fibrous appearance (Fig. 3.8, p. 77) (Kirk and Shimada, 1985; Bravery et al., 1987). The most commonly reported fungal species responsible for white rot are Ascomycetes and some Basidiomycetes such as *Pholiota* sp., *Fomes* sp., *Coriolus versicolor* or *Pleurotus* sp.

"*Brown rot*" fungi attack only the cellulose and short chains of polysaccharides, leaving a brownish residue of lignin (Fig. 3.9, p. 77). Wood appears darker and, upon

drying, forms a typical cuboidal cracking along and across the grain. The most common fungi causing this kind of damage are some species of Basidiomycetes: *Serpula lacrymans* (syn. *Merulius lacrymans*), *Poria* spp. and *Coniophora puteana* (Allsopp and Seal, 1986; Garg and Dhawan, 1985-1987; Bravery et al., 1987).

Wooden objects are less likely than timber to suffer from these two types of structural decay because the decay occurs only under poor conservation conditions (high RH, soil contact, poor ventilation, prolonged neglect).

More significant types of fungal attack on works of art are soft rot and staining.

"*Soft rot*" of wood is a kind of surface decay which tends to occur in continuously damp or wet conditions and in ground-contact wood (Fig. 3.10, p. 77), so it is very frequent in archaeological sites during excavations, in subterranean and in marine or water-saturated environments. Soft rots are caused by a wide range of fungi, including some genera in the Ascomycetes group, such as *Chaetomium, Xylaria, Hypoxyeon*, and in the Deuteromycetes group, such as *Alternaria, Coniothyrum, Humicola, Stemphylium* or *Stysanus* (Moriondo et al., 1967; Bravery et al., 1987). The main structural parts of the cell wall are destroyed, cavities are formed in the S2 cell wall layer. The attacked wood becomes soft and typically cracked when dried.

Other fungi cause stains on wood, either by liberating pigments, as in the case of *Chlorociboria aeruginascens* (Allsopp and Seal, 1986), or by the presence of dark fungal hyphae. Belonging to the latter group, among Deuteromycetes, are some species of the genera *Aspergillus, Aureobasidium, Fusarium, Penicillium, Trichoderma,* etc. and, among Ascomycetes, mostly the genus *Chaetomium* (Garg and Dhawan, 1985-1987; Bravery et al., 1987). They colonize the rays, feeding on the food reserves, and can penetrate the cell wall with their hyphae, which pass from one ray to another. This kind of attack is very frequent, but has little or no appreciable effect on wood properties.

Apart from those fungi with a specific activity on wood, there are secondary molds that are able to utilize the wood cell cellulose only after a partial breakdown by other fungi. These kinds of fungi — *Trichoderma viride* and *Gliocladium roseum* are reported as predominant — complete the destruction of wood.

Bacteria and actinomycetes are less frequent than fungi in the deterioration of wood and particularly in wooden works of art because they require a high water content. These kinds of microorganisms have been found as wood deteriogens in terrestrial and marine environments (see below).

Certain bacteria, such as aerobic species of *Pseudomonas* and *Achromobacter*, are able to degrade the structural elements of wood: cellulose, hemicellulose and lignin. They cause erosion and cavitation in the wood cell walls and attack the secondary wall layer of the cell, changing its permeability. By breaking down the layers in the cell walls and increasing the permeability of the wood, bacteria can stimulate the colonization of other microorganisms.

Actinomycetes attack wood in particularly wet conditions and in the presence of soil contamination. The most common deteriogen genus is *Micromonospora.*

Insects, however, are the most serious source of damage to wooden objects kept in museums or indoor environments; they use wood as a nutrient source, for shelter and egg laying. In feeding, some insects utilize only the compounds obtained from the cell contents (sugars and starch), the cellulose cell walls not being digested; others utilize both materials. Among insects able to use cellulose, the way in which adult insects and/or their larvae digest wood varies. Some of them are able to digest partially decomposed cellulose; others, like termites, have a complex symbiotic relationship with microorganisms that secrete cellulase enzyme complex in their gut.

The main insects involved in wood decay are reported in Table 3.4 (Allsopp and Seal, 1986; Bravery et al., 1987).

Table 3.4 Insects frequently found on wooden materials

Orders	Families	Common names	Type of damage
Coleoptera	Anobiidae	furniture beetle	Winding and circular tunnels; circular emergence holes
	Lyctidae	powderpost beetle	Tunnel with oval section
	Botrychidae	wood borer	Circular holes and tunnels
	Cerambycidae	longhorn beetle	Large, oval tunnels and holes
Isoptera	Kalotermitidae	termites or white ants	Deep and crater-shaped holes; sometimes entire interior of object is destroyed but outer surface is left intact
	Rhinotermitidae	"	"
Hymenoptera	Siricidae	wood wasp	Circular tunnels and holes of wide dimension

Among Coleoptera or beetles, many species have larvae that destroy wood by living inside it and feeding on it. The life cycle of the beetles comprises four phases: egg, larva, pupa and adult. The beetles lay their eggs in cracks or sheltered places. After some weeks the larvae emerge, bore into the wood and live in it until they mature. After a short pupa stage, they become adult, bore to the surface and fly away. The sexually mature beetle reproduces and the life cycle begins again (Fig. 3.11). For most of their life cycle, these insects are not visible and infestations are usually detected only by the small flight holes (Fig. 3.12).

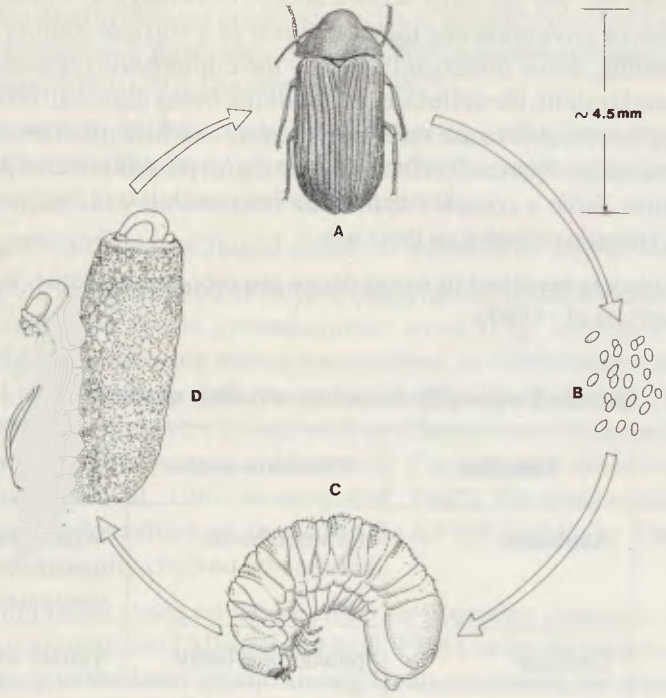


Fig.3.11

Life cycle of Coleoptera in wood: A) adult (two to three weeks); B) eggs (about 10 days); C) larva (one to five years); pupa (about six weeks).

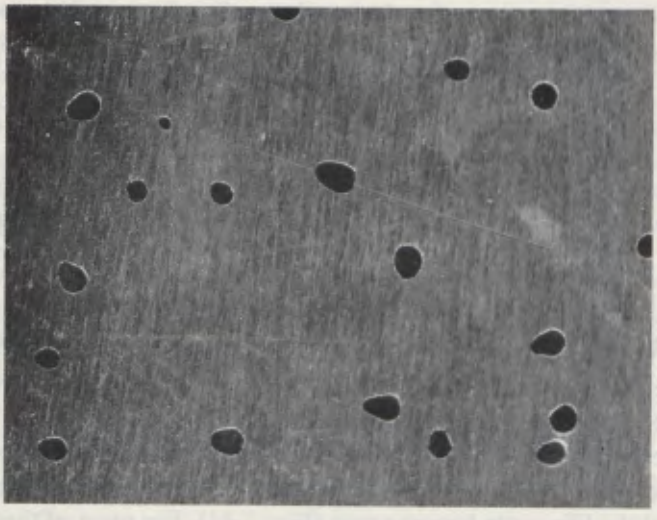


Fig.3.12

Wood showing emergence holes of Anobium punctatum.
(A. Gambetta, E. Orlandi, CNR Istituto per la Ricerca sul Legno - Florence)

Fig.3.13

Wood attacked by termites. (A. Gambetta, E. Orlandi, CNR Istituto per la Ricerca sul Legno, Florence).

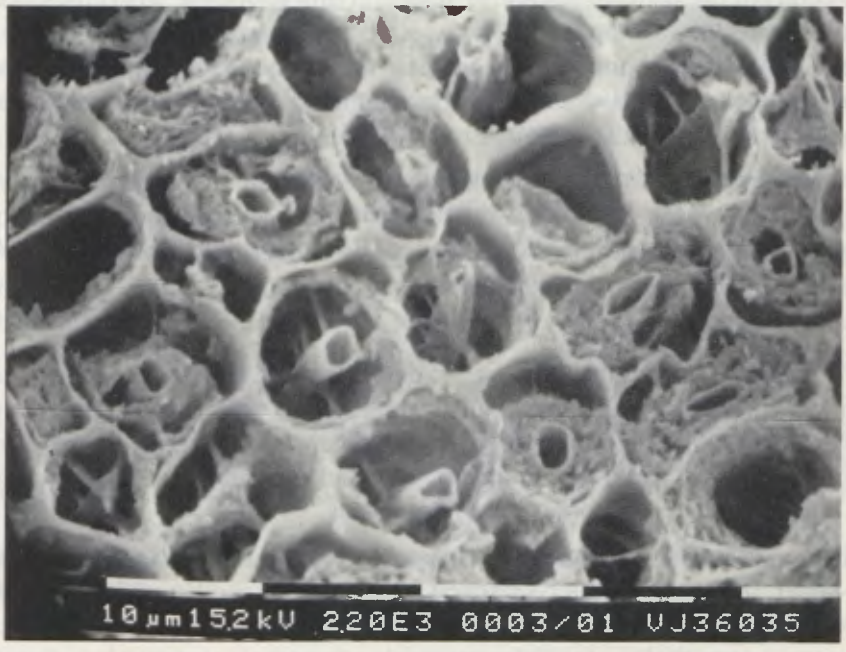


Fig.3.14

SEM micrograph of transverse section of waterlogged coniferous wood. Visible erosion of cell wall by bacteria. (G. Giachi, CNR Istituto per la Ricerca sul Legno, Florence)

Belonging to the Coleoptera order, the Anobiidae are the insects most frequently found in deterioration of furniture, sculpture and other wooden objects. High RH and moderate temperature favor their development. Unlike the Anobiidae, the powderpost beetles (Lyctidae) even thrive in dry conditions and attack mainly sapwood. Longhorn beetles (Cerambycidae) can cause serious damage, mainly to structural timber such as roofs or floors.

Termites are most common in the tropics and subtropics because they require high temperature and humidity. They are social insects, forming communities which include reproductive individuals (queen and males), nymphs and wingless specialized sterile forms (workers and soldiers). Workers are confined to the ground or wood where they devote their energy to feeding and foraging for the community. They often hollow out the wood completely, leaving a thin outer shell of wood undamaged (Fig. 3.13). Termite attack is often not detected until the whole structure collapses. This happens because many termite species are *photophygous* (heliophobic), i.e. they shun the light.

There is also a range of omnivorous insects that can cause incidental damage while scavenging for other food; cockroaches (Dictyoptera) belong to this group. These insects only cause surface erosion of variable depth.

A different situation occurs with Dermestidae, a family of Coleoptera, which are destructive to dry materials of animal origin and occasionally to wood and materials of vegetable origin; the larvae frequently bore "refuges" into timber adjacent to a food source.

In contrast, the damage caused by insects living inside the wood includes emergence holes of different shapes and sizes as well as superficial or deep tunnels. The presence of holes does not necessarily indicate an active infestation, but the bore dust produced from holes may give a clue. The main insect damage is due to the breakdown of the wood fibers, which affects structural strength.

On worked wood kept outdoors, a biological attack of autotrophic organisms can occur if environmental conditions permit. Instances where wooden objects were colonized by algae and lichen have been reported (Brightman and Seaward, 1977; Allsopp and Seal, 1986).

Waterlogged wood is the term used to describe wood kept under the surface of the soil or in water, for example archaeological wood such as shipwrecks or pile-dwellings. Under these particular conditions (high water content and lowered oxygen pressure), wood can easily be attacked by microaerophilic and anaerobic heterotrophic microorganisms and, in sea sites, by some marine organisms.

The microflora able to attack waterlogged wood vary in relation to the maintenance site (sea-water, fresh-water, water-saturated soil, etc.) and specific environmental conditions (oxygen concentration, temperature, concentration of mineral salts, etc.). In sea water, bacterial degradation of wooden materials can occur in water or in sediment up to a maximum of 60 cm deep; fungi occur under aerobic conditions in the sediment-water interface (Florian, 1988).

The microorganisms that can degrade waterlogged wood are either some wood-destroying species such as soft rot fungi, sea-water fungi or bacterial strains (Fazzani et al., 1975; Kohlmeyer and Kohlmeyer, 1978; D'Urbano et al., 1989).

Among bacteria, the most common are cellulolytic aerobic (*Cytophaga, Cellvibrio, Cellfalcicula*) or anaerobic species (*Plectridium, Clostridium*) and common microorganisms such as strains of *Bacillus, Pseudomonas, Arthrobacter, Flavobacterium, Spirillum.* Bacteria are also categorized according to the type of alteration they cause. Thus, there are erosion bacteria, cavitation bacteria and tunnelling bacteria (Fig. 3.14) (Abbate Edlmann et al., 1989).

In sea-water and fresh-water environments, some micro-algae strains can also cause damage to immersed woods. They form slimy green patinas and cause superficial modification of wood characteristics. The alterations caused by these microorganisms are not too serious, but they contribute to chemico-physical decay.

In sea water, marine borer animals are the most destructive organisms for waterlogged wood. They are widely distributed in salt water, although more prevalent in warm water than in cold, and include different species of Mollusca and Crustacea.

The main genera of Mollusca are *Teredo, Bankia* and *Martesia*, which produce tunnels that penetrate deeply within the wood. The tunnels may have a chalky-white shelly (calcareous) lining (Fig. 3.15, p. 78). The first two genera comprise a number of species known as "shipworms". After a free-swimming larval stage, the young organisms become able to attack timber and make very small entrance holes in the surface of wood, but once within it they increase rapidly in size. They use wood for shelter and feed on the minute organic particles and plankton found in the sea water. Their whitish, worm-like bodies are equipped with a pair of shelly valves at the anterior end that excavate wood. The mollusks of the genus *Martesia* are small clams with their bodies entirely encased within the bivalve shell. The damage caused is relatively small compared to the other two genera.

Among Crustacea the main wood-destroying genera are the isopods *Limnoria, Sphaeroma* (common name "wood lice") and *Cherula* (common name "sand fleas"). The wood-boring crustaceans differ from the molluscan borers either in their methods of attacking wood or in their general structure. They do not become imprisoned in the wood but, instead, are able to move about. The young and the adult are equipped with a pair of strong-toothed mandibles designed for chewing wood, which provides nourishment; they burrow in the timber, making galleries of various depths with narrower bores than those of Mollusca. They attack the timber in such great numbers that the infested wood becomes honeycombed and can be broken by the mechanical action of water at the point of attack. The damaged area is usually concentrated at the water line. The damage caused by these marine borers is more evident to inspection and proceeds more slowly than that of shipworm, so it is less spectacular and serious (Edlmann Abbate, 1967; Allsopp and Seal, 1986; Feilden, 1982).

3.1.3 Paper

Paper is primarily composed of cellulose and other substances related to the origin of the raw materials used in its manufacture: lignin, hemicelluloses, pectins, waxes, tannins, proteins and mineral constituents. In fact, paper can be manufactured from textiles or from wood through various and complex operations.

The content of these components varies according to the paper-making process, the type of paper and the period of production. In the Middle Ages, for example, the quality of paper was particularly good; it was manufactured from carefully selected cotton rags and contained a great amount of cellulose and only a few impurities. Subsequently, the quality of paper changed for the worse. Modern papers produced by industrial manufacturing processes since the end of the seventeenth century are derived from the stem of wood or wood pulp and contain a great amount of polymers and non-fibrous material other than cellulose, as well as impurities. Modern papers are thus more vulnerable to microorganism attack than older ones (Kowalik, 1980a).

Paper is a good source of nourishment for heterotrophic microorganisms and organisms, not only because of its own nature, but also because of the organic nature of all the components that enter into its manufacture, such as animal and vegetable glues, inks, fillers or dyestuffs. Impurities and these organic components represent an organic nutrient source for many microorganisms, whose growth prepares substrates for typical cellulolytic strains.

The indispensable condition for a microbial attack is a high water content, and the hygroscopicity of paper makes it more liable to biodeterioration.

The main biodeteriogen microorganisms for paper are bacteria, micro-fungi and actinomycetes, either cellulolytic strains which damage the chemical structure of paper or non-cellulolytic ones with non-specific action. But, the most common are fungi because they show a great tolerance to environmental conditions. They can live with a lower water content than bacteria and actinomycetes.

Among cellulolytic strains of micro-fungi, many species of Deuteromycetes (e.g., *Alternaria* spp., *Aspergillus* spp., *Fusarium* spp., *Humicola grisea, Myrothecium verrucaria, Penicillium* spp., *Stachybotrys atra, Stemphylium spp.., Trichoderma* spp., *Ulocladium* spp., etc.) and Ascomycetes (e.g., *Chaetomium* spp.) are frequently isolated from books, documents and prints (Kowalik, 1980b; Gallo, 1985).

Certain cellulolytic species of *Aspergillus* and *Penicillium* are particularly harmful to paper because they are able to grow on substrates having a 7-8% moisture content, which can be reached in some types of paper at an RH as low as 62-65%; such conditions are not rare in many places where paper is kept (Gallo, 1985).

In books, the bindings are the first to take on moisture from the air whereas the interior parts do so later. As a result, fungal growth spreads more quickly on bindings than on sheets of paper (Dhawan, 1986).

Some species of *Chaetomium*, *Trichoderma viride* and *Stachybotrys atra* cause a deep decay of cellulosic materials, which then lose their mechanical properties.

In general, fungi cause alterations on paper that appear as various kinds of stains, either round or irregular in shape and colored red, violet, yellow, brown, black, etc. (Fig. 3.16, p. 78). These stains are due either to the presence of dark mycelium or to the release of colored pigments (Gallo, 1985). The color of pigments can change depending on the conditions of growth and the properties of paper (e.g., pH, presence of starch or gelatin sizing, presence of metal, etc.).

A particular kind of alteration due to fungi is the discoloration of inks due to tannase, an enzyme that catalyzes the hydrolysis of gallotannate, produced by some strains of *Aspergillus* and *Penicillium.*

Bacteria attack paper less frequently than fungi, but several bacteria have been isolated from paper materials where the RH was quite high, more than 85% (Kowalik, 1980a; Strzelczyk, 1981; Dhawan, 1986). The cellulolytic species are obviously more harmful than non-cellulolytic ones; the genera *Cytophaga, Cellvibrio* and *Cellfalcicula* belong to the first group, the latter one is rarely found.

Frequently, bacterial and fungal attack makes the paper feltish and fragile.

During metabolism, all microorganisms produce different organic acids (oxalic, fumaric, succinic, citric, etc.) which reduce the pH of paper, conditioning the dynamics of bacterial and fungal growth in secondary attacks.

One particular and very common chromatic alteration of paper is *foxing*; it appears as rust-colored marks of different shapes, frequently as spots, but always restricted in the area concerned (Fig. 3.17, p. 78). The causes of foxing have not yet been clarified, although several opinions have been put forth. Many authors consider fungi a possible cause, but others believe that the presence of heavy metal, most commonly iron, might be among the factors favoring this kind of alteration (Arai, 1987; Hey et al., 1988; Arai et al., 1988). Nevertheless, foxing never develops into a characteristic mold attack, nor does it look like metal-induced degradation, because of the extremely localized development of discoloration.

One of the most serious types of damage to ancient library collections occurs when books are "consolidated" into blocks, losing their structure and becoming a solidified mass. This damage affects books that have been flooded or heavily moistened. The alteration is brought about by growth of bacteria and fungi. The "consolidation" relates to the production, during cellulose degradation, of oligosaccharides with mucous properties and, on substrates particularly rich in sugar, to the formation of secondary metabolic products of a slimy nature. Moreover, bacteria can form mucilaginous capsules when the amount of carbon is substantially greater than the amount of nitrogen and salts. It is clear that the composition of paper (fiber content and type of glue) affects the intensity of the degradation (Strzelczyk and Leznicka, 1981).

Insects are frequently involved in the deterioration of paper. Many insects are able to attack cellulose with processes like those used on wood. Others also cause damage by utilizing fillers, glues, boards, textile fibers, leather or other constituent elements of paper materials. Based on frequency, there are customary and occasional insects. Customary insects are those most often found on paper, using this material for nourishment. Occasional insects (e.g., wood or textile borers) sometimes damage paper when different

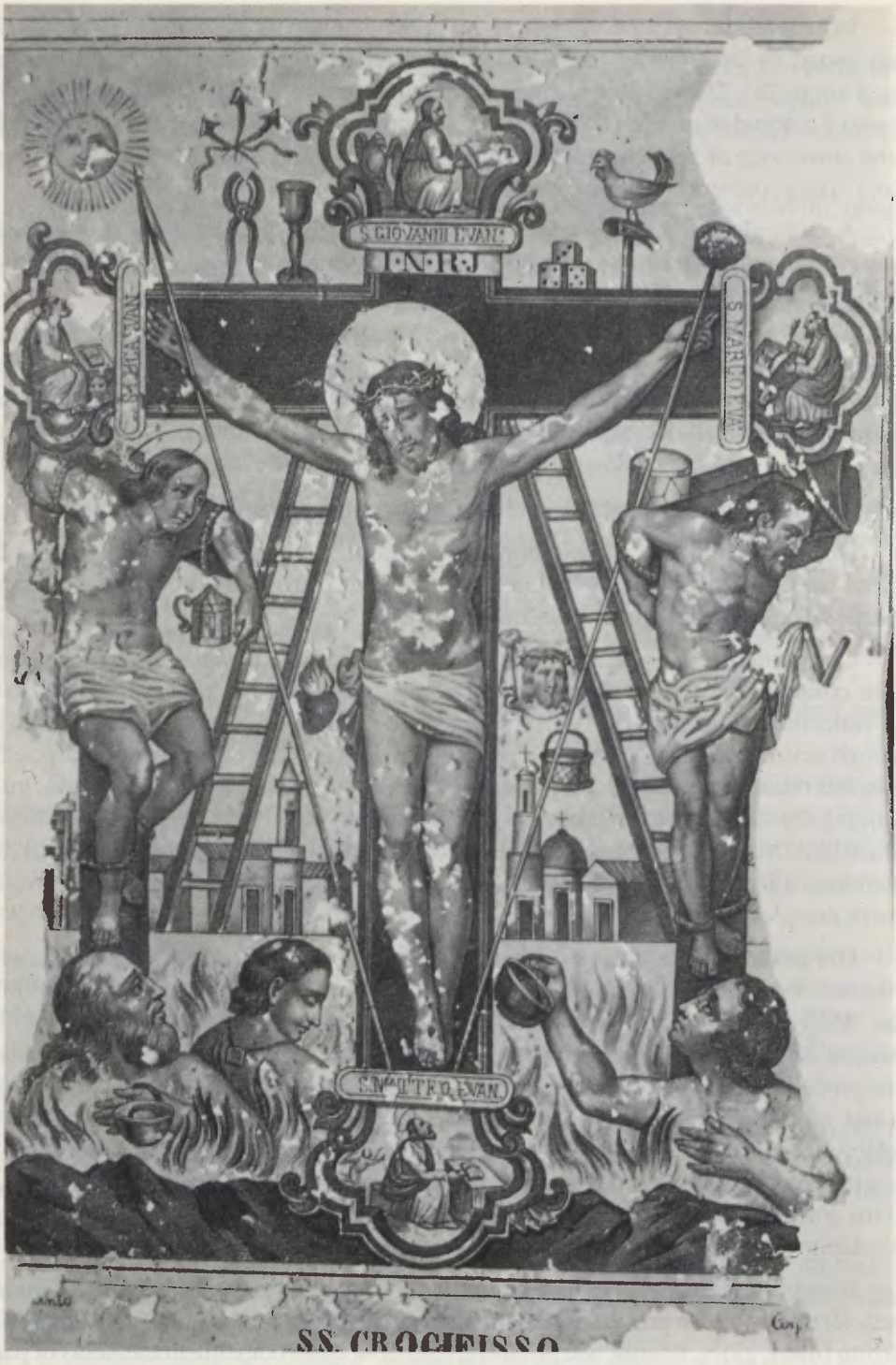


Fig.3.18

Tiny surface abrasion due to silverfish (Lepisma saccharina) on a print (G. Donati, Istituto per la Patologia del Libro, Rome).

materials are components of the same object, such as in ancient book covers, or when they are near each other (e.g., wooden shelves in libraries).

The morphology of insect damage ranges from tiny superficial abrasion and surface erosion to holes and sometimes tunnels (Fig. 3.18).

In Table 3.5, the main orders and families of insects responsible for deterioration of paper works of art are listed (Gallo, 1985; Menier, 1988).

Table 3.5 Insects frequently found on paper materials

Orders	Families	Common names	Type of damage
Thysanura	Lepismatidae	silverfish	Small surface erosion with irregular outline
Isoptera	Kalotermitidae Rhinotermitidae Termitidae	termites	Deep crater-shaped holes and erosion; destruction of the interior of object while the outside remains intact
Coleoptera	Anobiidae	furniture beetles	Winding, circular tunnels
	Lyctidae	powderpost beetles	Tunnel with oval section
	Dermestidae	skin beetles	Short blind tunnels with circular section and irregular perforation
Corrodentia	Liposcelidae	book lice	Tiny surface abrasion
Blattoidea	Blattidae Blattelidae	cockroaches	Surface erosion

Anobiidae, Lyctidae and Dermestidae complete their life cycle inside books. Dermestid beetles mainly eat leather bindings, but they burrow into books, making tunnels where they pupate. Blattidae, Blattelidae, Lepismatidae and Termitidae live in environments where books are kept, and paper, cardboard and glue of vegetable or animal origin represent their source of nourishment (Figs. 3.19, 3.20, p. 79). Liposcelidae are the smallest insects in book biodeterioration (1-2 mm), and are very common. They feed on paper, glue, etc., and live especially on bindings. These insects also feed on the microfungi of infected surfaces, so they appear frequently under high-humidity conditions.

3.1.4 Textiles

Textiles can be of either vegetable or animal origin. Those of vegetable origin are cotton, flax, hemp, jute and sisal. They are mainly composed of cellulose derived from plant fibers; for example, flax and jute are phloem fibers, sisal and manila are leaf fibers and cotton is made from seed fibers.

Like other materials of vegetable origin, the susceptibility or resistance of textiles to biodeterioration depends on the content of cellulose, lignin and other organic constituents. The presence of non-cellulosic components such as lignin and waxes decreases susceptibility; in contrast, pentosans and pectins increase susceptibility. Natural cotton contains about 5% of non-cellulosic products, flax 15%, so cotton is less susceptible to microorganisms than flax.

Fibers with a high amount of lignin are more resistant to microbiological attack than purified fibers. Considering this factor, the order of resistance would be: jute, hemp, cotton, flax (Vigo, 1977; Kowalik, 1980b). The resistance of textiles is often modified in the manufacturing process. For example, jute, if the lignin is removed, becomes more liable to decay than cotton due to the presence of hemicelluloses and mineral salts. Susceptibility is also increased if textiles contain sizing, which is composed of starch and dextrin.

The following structural features of fibers and textiles also affect biodegradation: degree of polymerization, length of cellulose chain, fiber crystallinity and orientation. Mechanical, photochemical or other types of degradation increase susceptibility to biodeterioration because they lower these structural features (Vigo, 1980).

In the manufacture of textiles, the types of weave can affect resistance to microbial attack. Loosely woven fabrics are less resistant than tightly woven fabrics because they hold more dirt and biological pollutants between fibers, creating conditions of higher risk.

The most frequent biodeteriogens of cellulosic textiles are micro-fungi (Ascomycetes and Deuteromycetes) and bacteria of cellulolytic and non cellulolytic species, many of which are mentioned above in wood and paper biodeterioration.

The most active agents of textile deterioration are fungi (Fig. 3.21, p. 79). Among Deuteromycetes, we find several species of *Alternaria, Aspergillus, Fusarium, Memnoniella, Myrothecium, Neurospora, Penicillium, Scopulariopsis, Stachybotrys* and *Stemphylium*, etc. Quite frequent and particulary harmful because of its high cellulolytic activity is the genus *Chaetomium* of Ascomycetes (Mahomed, 1971; Kowalik, 1980b; Vigo, 1980). Zygomycetes such as *Mucor* and *Rhizopus,* which use carbohydrates and nitrogen compounds, sometimes occur on textiles.

Bacteria and actinomycetes need a high water content in fabrics, and their occurrence in museums should be rare. But in damp environments or when textiles are buried in the soil (archaeological textiles, for instance), the most serious decomposition of cellulose is caused by bacteria belonging to the species of *Sporocytophaga myxococcoides* and then by *Cellvibrio, Cellfalcicula, Microspora* and anaerobic *Clostridium* (Kowalik, 1980b). Degradation of fabrics exposed outdoors has also been associated with species of Myxomycetes and Actinomycetes and even a blue-green alga, *Tolypothrix byssoides* (Vigo, 1980).

Under conditions of damp, heat, lack of ventilation and contact with decaying matter, the microbiological attack can occur in a few days.

The biodeterioration of textiles can take several forms, such as discoloration, staining and loss of strength.

Metal fibers were sometimes used for embroidery in the manufacture of textile objects such as standards, flags, frontals, vestments and ancient costumes. These fibers can inhibit microbial growth, particularly when copper or other heavy metals are present.

Cellulosic textiles are also susceptible to attack by insects such as silverfish and cockroaches. The probability of attack is increased if these materials contain glues made of starch or dextrin. The main insect families involved in textile biodeterioration are Blattidae, Blattelidae (cockroaches), Lepismatidae (silverfish) and Mastotermitidae, Hodotermitidae, Rhinotermitidae (termites), but many others may occur occasionally (Hueck, 1972). In general, their attack ranges from surface erosion to loss of parts of the object. In termite infestations, complete devastation often progresses from the dark reverse or interior of materials.

3.2 MATERIALS OF ANIMAL ORIGIN

3.2.1 Chemical components and their susceptibility to biodeterioration

Many cultural properties are made from raw materials of animal origin. Parchment, leather, some archaeological remains and textiles such as wool and silk belong to this category. In this case, biodeterioration is related to the main chemical components: proteins or their monomers, amino acids or partially polymerized components such as polypeptides.

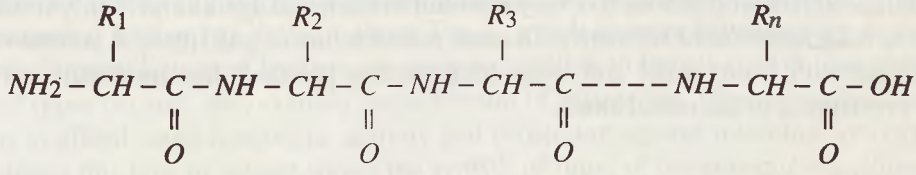


Fig.3.22 *Molecular structure of protein.*

Proteins are high-molecular-weight polymers composed of about 22 amino acids joined by peptide linkages to form a chain (Fig. 3.22). The sequence of amino acids is called the "primary structure." Protein compounds can be used as a source of organic nitrogen or carbon by heterotrophic microorganisms and organisms. Their utilization depends on the production of specific enzymes (*proteinases* and *peptidases*). The function of proteolytic enzymes is to convert non-diffusible proteins into products that can diffuse into the cell. These enzymes are able to catalyze the hydrolysis of the peptide linkages of polypeptide molecules (Fig. 3.23).

$$W-CO-NH-W + H_2O \xrightarrow[\text{enzyme}]{\text{Proteolytic}} \begin{matrix} W-COOH \text{ free carboxyl group} \\ W-NH_2 \text{ free amino group} \end{matrix}$$

Fig.3.23 *Scheme of enzymatic degradation of proteins.*

The types of proteins found in materials of animal origin vary according to the source (e.g., mammalia, insects, etc.), the part of the animal used (e.g., skin, hair, fur) or other factors such as secretions (e.g., silk).

Parchment and leather are produced from the skin of mammals. They have the protein collagen as a basic component. Collagen is an impure protein of high molecular weight (approximately 310,000-350,000) and contains some polysaccharides. It is a scleroprotein composed of three peptide chains of 1000 amino acid units. The chains are held together in fibrils by a peptide with low molecular weight. The chemical structure is nearly crystalline. Collagen is one of the proteins most resistant to microorganisms.

Wool, produced from the hair of different mammals (e.g., sheep, alpaca, vicuna, etc.), consists mainly of keratin, a highly insoluble protein containing sulfur linkages in the molecule.

Commercial silk is a proteinaceous filament secreted by the domesticated "silkworm" *Bombyx mori* in making its cocoon. Wild silk is produced by a caterpillar of the Antheridae family. The silk fiber is composed of two filaments made of a protein (60-70%), fibroin, linked together by another protein (25-30%), sericin. Fibroin is a highly crystalline scleroprotein which is very resistant to chemical agents and highly insoluble. Sericin is an albuminoid substance. In some manufacture of silk fibers, it is removed by treatment with warm water and soaps (degumming process); this treatment increases silk's resistance to microbial attack.

3.2.2 Parchment and leather

Parchment as a writing support was produced from sheep or goat skin, particularly valuable parchment having been made from embryos of lambs and calves. It is composed of collagen, some amount of keratin and elastin, and a minimal amount of albumin and globulin.

Collagen can only be hydrolyzed by specific enzymes, *collagenases*, produced by some anaerobic bacteria of the genus *Clostridium* (Kowalik, 1980a and 1980b).

Some treatments, such as mechanical disintegration of skin during the manufacture of parchment, depolymerize the collagen. This denatured collagen can be decomposed by non-specific proteolytic enzymes produced by many bacteria and some microfungi in aerobic conditions. Other factors such as temperature (increases), humidity (violent

change), pH and exposure to UV rays can also influence the stability of collagen in parchment; they cause changes in the structure, and resistance to biodeterioration is lowered as a result.

In addition to collagen, some other components (other proteins, lipids, carbohydrates, mineral constituents and impurities) are involved in the decay of parchment. These components either derive from the original skin or are added during manufacture. As a consequence, parchment's liability to biodeterioration depends upon the raw material, on its method of production and on conditions of preservation.

Under aerobic conditions, only partially decomposed collagen can be attacked by bacteria, among which are strains of *Bacillus* (e.g., *B. mesenthericus*), *Pseudomonas, Bacteroides, Sarcina.* Ancient parchment materials can also be attacked by certain species of fungi of the genera *Cladosporium, Fusarium, Ophiostoma, Scopulariopsis, Aspergillus, Penicillium, Trichoderma, etc.*, but the most intensive deterioration has been observed under the action of some strains of the first four (Kowalik, 1980b; Varonina et al., 1981).

As a result of biodeterioration, parchment loses its original properties and becomes hard and brittle, often with deformation of the object. The microbial attack also causes variegated spots, white films and fading of the texts (Fig. 3.24, p. 80).

Leather has a chemical composition similar to parchment and, as a result, its susceptibility to biodeterioration and the species involved are very similar. To produce leather, skins are cured by subjecting them to tanning, which causes chemical and physical changes. There are different methods of tanning: smoking, oil process, mineral process, vegetable tanning and chrome tanning. Vegetable tanning is probably the earliest tannage used. In contrast, chrome tanning was only discovered in 1858 and introduced in the industry in 1884 (Florian, 1988).

The attack of microorganisms varies depending on whether the skins were tanned or not. Untanned skins are attacked by bacteria under conditions of high humidity. Tanned leathers are not readily subject to bacterial attack, but are degraded by fungi. Usually, after tanning, leather has a pH of about 3 to 5, which is more advantageous to fungal growth. Vegetable-tanned leathers are more susceptible to fungal growth than chrome-tanned types because they contain some amount of glycosides. Chrome-tanned leather seems to afford some fungistatic activity and protection against microbial activity but sometimes this type of leather shows the growth of fungi of the genera *Penicillium* and *Paecilomyces*, which are tolerant to the chromium compounds. Fungi that attack tanned leather often belong to lipolytic species and utilize the fats present in leather as a source of carbon. In this case the proteins are not directly affected, but can be damaged by organic acid released as a metabolic waste product and the artifact becomes stained and stiff (Zainal et al., 1983; Von Endt and Jessup, 1986; Allsopp and Seal, 1986; Strzelczyk et al., 1987). The principal effects of microbial deterioration on proteic materials are the presence of different stained spots, loss in tensile strength, and, if the proteins are attacked, hydrolysis of the leather.

Proteinaceous materials like parchment and leather are also susceptible to attack by insects: Dermestidae and Tineidae are the main families that can selectively attack either collagenous or keratinous materials (Von Endt and Jessup 1986, Allsopp and Seal

1986). Occasionally, cellulose feeders cause damage to parchment and leather materials. Often insects invade proteinaceous materials, chewing proteins, while they are looking either for food or for an environment for reproduction. The insect damage appears as superficial erosion, deep erosion, holes or loss of material.

3.2.3 Textiles

Wool and silk are the main textiles of animal origin.

The main agents of deterioration are microorganisms (bacteria, actinomycetes and fungi) and insects, but insects are considered the most serious pests in museums.

Although protein fibers, such as silk and wool, are not as susceptible to microorganism deterioration as cellulosics, they can be attacked if they contain a high degree of impurities (such as sericin for silk or sizing, soap and suint for wool) and if they are stored under warm and humid conditions (Vigo, 1977). Like cellulosic textiles, they become less liable to biodeterioration when their molecules are more polymerized.

In general, wool fibers are more subject to attack by bacteria than cotton fibers and less subject to fungal attack. An indispensable condition for a bacterial attack to take place is a high water content; this condition is enhanced by the high hygroscopicity of wool.

Bacteria may be keratinophiles that are able to produce enzymes that break down keratin, such as some dermatophytic fungi (*Trichophyton* and *Microsporum*) which can cause disease in human beings.

The microorganisms most frequently mentioned in degradation of wool and other protein fibers are bacteria of the genus *Bacillus* (*B. mesenthericus* and *B. subtilis*), *Proteus* (*P. vulgaris*) and some species of Actinomycetes (*Streptomyces albus* and *Streptomyces fradiae*) (Vigo, 1980; Kowalik, 1980b). *Pseudomonas aeruginosa* frequently causes green, red or other colored stains according to the pH of the substrate.

Micro-fungi are not very frequently involved in biodeterioration of protein fibers but species of *Aspergillus, Fusarium* and *Trichoderma* are sometimes reported (Kowalik, 1980b; Vigo, 1980).

Silk is fairly resistant to microorganisms if impurities and sericin are removed in manufacturing processes such as the degumming process. The strains degrading silk include the species that attack other protein fibers, but the specific deteriogen microorganisms for silk are less known. The microbiological damage appears as discolorations, stains of different shapes, color and diffusion (Fig. 3.25, p. 80). Tensile strength may be reduced: for example, silk becomes more fragile.

The most serious damage to animal-origin textiles is related to insects. In museums, especially in moderate climates, a microbial attack on protein fibers rarely occurs, but insects can cause significant damage under these conditions.

The insects most frequently found are some species within the families Dermestidae, Oecophoridae (brown house moth) and Tineidae (clothes moth). The better-known species of moths are *Tinea pellionella, T. bisselliella* (Tineidae) and *Hofmannophila pseudospretella* (Oecophoridae) which degrade extensively wool and rarely unscoured silk. The damage is done by larvae, which use wool as food and complete their life cycle

in the infested textiles themselves. Carpet beetles, too, cause damage to textiles. Among the most frequent species of Dermestidae are *Anthrenus verbasci, A. museorum, Attagenus pellio*, which cause damage only through their larvae because the adults usually spend their life elsewhere. Infestation by these insects is rather widespread and not confined to textiles. Silk can be attacked by Lepismatidae and Dermestidae (Hueck, 1972; Vigo, 1977 and 1980; Allsopp and Seal, 1986).

Susceptibility is increased and the range of deteriogen insects can become larger if these materials contain sizing, composed of starch or dextrin, and other organic components. The type of damage involves the production of holes of irregular shape, superficial abrasion or deep erosion.

3.3 COMPOSITE MATERIALS

Works of art are often made of a combination of different organic and inorganic materials, rather than just one. It is impossible to list all the types of cultural property made of different materials and to give information about their susceptibility to biodeterioration. In general, the risk of biological attack is linked to the most vulnerable component and is the result of the combined liability of all the substances present. The biodeterioration phenomena on composite materials are similar in their character and effect to those of the main and more susceptible component. Among works of art made of different components, we will discuss paintings as an example.

3.3.1 Paintings

Paintings are composed of a support (canvas, wood, paper or parchment) and a paint layer, the chemical composition of which varies according to the mode of painting, the kind of paints used (oil paints, distemper or watercolor), the period of the artifact and sometimes the artist.

Over the support in paintings, there are generally several layers. In canvas paintings, stretched in a frame and sized with animal glue, there is usually a ground layer of lime or gypsum with an addition of animal or plant glue. On this smoothed layer, several layers of color are present, which consist of pigments mixed with binders of oil or distemper (egg or glue). The surfaces are usually spread with a thin, translucent varnish. In paintings on wooden supports, a similar multi-layer structure is observed.

Paintings on paper can be watercolors, gouaches or pastels. The paint is laid directly on paper and the state of preservation of the paper determines the durability of the whole painting. In watercolors, the transparent paint layer also contains a small amount of binder, usually gum arabic. Pastels are made with crayons consisting of pigment without binder and are, therefore, extremely difficult to store and preserve.

In painted works of art, the biodeterioration processes can involve either a portion of the painting or all of its components. Thus, paintings may show traces of a biological attack on the reverse side, the support, or on the painted side, and a part or all components may be damaged (Figs. 3.26, 3.27, p. 81).

The organic components in paintings represent a good source of nutrition for a wide range of heterotrophic microorganisms and organisms (Table 3.6). But, biological attack occurs only when there are favorable environmental conditions, and such conditions are often found in museum rooms, old churches or in storage without control of humidity and temperature. Condensation of water on cold surfaces, such as the glass over pictures or outside walls, is caused by a drop in temperature, which can occur frequently inside old damp buildings.

Table 3.6 Organic components of paintings as nutrient sources for microorganisms (from Strzelczyk 1981)

Organic materials	Occurrence and use
Cellulose	in canvas, timber and paper
Starch	in bookbinding as glue as relining paste
Gums (arabic, cherry, tragacanth)	in distemper paintings
Sucrose	in distemper paints as plasticizer
Glucose	in watercolors as plasticizer
Glycerine	in watercolors and emulsion paints as plasticizer
Gelatine	in paper as sizing glue, in canvas as sizing glue, in grounds
Linseed oil	in oil paints
Egg	in distemper paints as binder

The microflora attacking paintings include virtually all species of micro-fungi because the variety of organic components of these works of art can represent a carbon source for practically all species. In addition, they show a great tolerance for environmental conditions and can use condensation moisture. In contrast, the moisture content of these objects is rarely so high as to favor development of bacteria, which are unable to use condensation water (Strzelczyk, 1981).

Generally, the essential part on which the microbial deterioration depends is the support of the paint. In paintings on wooden board, the decay of the support can be distinct from the paint layer. The alteration of wood interferes with the paint layer by changing the mechanical property of wood, forming cracks, slits, etc. In paintings on canvas, the microbial attack usually starts from the reverse side, because the natural susceptibility of textiles is increased by the glue sizing. As they penetrate inside textiles, microorganisms often reach the back side of the paint layer, causing cracks and detachment of paint

particles. Cellulose hydrolysis creates differences of adhesion between the paint layer and the canvas (Makes, 1981). In contrast, in paintings on paper, the microbial deterioration of the support is strictly linked to the paint layer.

The microorganisms involved in biodeterioration processes are those mentioned above in biodeterioration of materials of vegetable and animal origin. Sometimes the presence of substances, such as sizing glue or lining paste used for different treatments of the support, can increase liability (Strzelczyk, 1981; Makes, 1984).

Biological attack on the paint layer is less frequent than on the support and depends on the nature of pigments. The most liable to biological attack are casein and egg distemper, emulsion distemper and linseed oil in that order. Pigments composed of earth sienna, umber and boles are particularly liable. In contrast, the presence of heavy metals, such as in lead white or zinc oxide, can increase the resistance of the paint layer. Watercolors contain only a small amount of organic binder and are, therefore, as liable to microbial deterioration as pastels (Strzelczyk, 1981).

Among the species of micro-fungi most frequently involved in deterioration of the paint layer, we find that some species of *Penicillium, Aspergillus, Trichoderma* and *Phoma pigmentovora* disintegrate distemper and oil binders, *Aureobasidium* decompose oil binders, *Geotrichum* develop on casein binders, *Mucor* and *Rhizopus* attack glue (Ionita, 1971; Strzelczyk, 1981; Dhawan and Agrawal, 1986).

The development of micro-fungi on the surface of paintings appears with a wide and varied morphology because these organisms act mechanically, biochemically and chemically. Sometimes, especially when growth is in the initial stage, filaments spread over the paints, masking design and color. At other times, the growth of hyphae and fruiting bodies inside the painting supports causes fissuring, friability and loss of the paint layer.

Exoenzyme activities can cause more serious damage by decomposition of some components of the paint layer or of the support material, whereas the emission of metabolites, such as organic acids which react with various painting components, produces transformation in its structure. For example, these acids can dissolve lime ground and accelerate peeling of the paint layer.

In fungal attacks, dark hyphae and colored fruiting bodies form circular spots of different colors while the emission of pigments irreparably stains the painted surfaces (Fig. 3.28, p. 81).

In biodeterioration of painted materials, insects are also often reported but they only occasionally injure the paint layer, preferentially attacking wood in the frame or support, paper and vegetable glue.

REFERENCES

ABBATE EDLMANN, M.L., A. GAMBETTA, G. GIACHI and E. ORLANDI (1989). "Studio del deterioramento di alcune specie legnose appartenenti ad un relitto navale del VII sec. a.C., effettuato con il microscopio elettronico a scansione," *Il restauro del legno. Atti del 2° Congresso Nazionale Restauro del Legno.* Florence: Nardini Editore. 121- 127.

ALLSOPP, D., and K.J. SEAL (1986). *Introduction to Biodeterioration*. London: Edward Arnold.

ARAI, H. (1987). "On the foxing-causing fungi," *ICOM Commitee for Conservation, 8th Triennial Meeting, Sydney, Sept. 1987*, ed. K. Grimstad, U.S.A.: The Getty Conservation Institute. 1165-1167.

———, N. MATSUI and H. MURAKITA (1988). "Biochemical investigations on the formation mechanisms of foxing," *The Conservation of Far Eastern Art. Preprints of the contributions to the Kyoto Congress, 19-23 September 1988*, eds. S. Mills, P. Smith and K. Yamasaki. London: IIC. 11-14.

BRAVERY, A.F., R.W. BERRY, J.K. CAREY and D.E. COOPER (1987). "Recording wood rot and insect damage in buildings," *Building Research Establishment Report.*

BRIGHTMAN, F.H., and M.R.D. SEAWARD (1977). "Lichens of man-made substrates," *Lichen Ecology*, ed. M.R.D. Seaward. London: Academic Press. 253-293.

DEKKER, R.F.H. (1985). "Biodegradation of hemicellulose," *Biosynthesis and Biodegradation of Wood Components*. Ed. T. Higuchi. London: Academic Press. 505-533.

DHAWAN, S. (1986). *Microbial deterioration of paper material - A literature review*. Government of India, Department of Culture, National Research Laboratory for Conservation of Cultural Property. Ed. M.M. Khan. Lucknow, India. 1-18.

———, and O.P. Agrawal (1986). "Fungal flora of miniature paintings and lithographs," *Int. Biodet. Bull.*, 22 (2) 95-99.

D'URBANO, S., C. MEUCCI, M.P. NUGARI and G.F. PRIORI (1989). "Valutazione del degrado biologico e chimico di legni archeologici in ambiente marino," *Il restauro del legno. Atti del 2° Congresso Nazionale Restauro del Legno.* Florence: Nardini Editore. 79-84.

EDLMANN ABBATE, M.L. (1967). "Primo contributo allo studio delle alterazioni da Teredini in vari legnami immersi nel Mare Ligure," *Contributi Scientifico-Pratici per una Migliore Conoscenza e Utilizzazione del Legno.* VII, No. 10. Rome: CNR. 9-35.

ERIKSSON, K.E., and T.M. WOOD (1985). "Biodegradation of cellulose," *Biosynthesis and Biodegradation of Wood Components*. Ed. T. Higuchi. London: Academic Press. 469-503.

FAZZANI, K., S.E.J. FORTADO, R.A. EATON and E.B.G. JONES (1975). Biodeterioration of Timber in Aquatic Environment. Microbial Aspects of the Deterioration Materials. Eds. D.W. Lovelock and R.J. Gilbert. London: Academic Press. 39-59.

FEILDEN, B.M. (1982). "Insects and other pests as causes of decay," *Conservation of Historic Buildings*. London: Butterworth Scientific. 131-151.

FLORIAN, M. (1988). "Deterioration of organic materials other than wood," *Conservation of Marine Archaeological Objects*, ed. Colin Pearson. London: Butterworths. 21-54.

GALLO, F. (1985). *Biological Factors in Deterioration of Paper*. Rome: ICCROM.

GAMBETTA, A., and E. ORLANDI (1982). "Durabilità naturale di 100 legni indigeni e di importazione a funghi, insetti e organismi marini," *Contributi Scientifico-Pratici per una Migliore Conoscenza ed Utilizzazione del Legno*. Rome: CNR Istituto per la Ricerca sul Legno. XXX, no.79. 47-71.

GARG, K.L., and S. DHAWAN (1985-1987). "Microbial deterioration of wooden cultural property," *Conservation of Cultural Property in India*, ed. T. Singh. Vol XVIII-XX. New Delhi: Indian Association for the Study and Conservation of Cultural Property. 4-85.

HEY, M., G. PASQUARIELLO, F. GALLO, G. GUIDI and F. PIERDOMINICI (1988). "Paper analysis in relation to foxing," *III Conferenza Internazionale sulle Prove non Distruttive, 17-20 Aprile, 1988. Perugia.* Preprints. Rome: ICR, AIPnD. II/9.1-9.10.

HIGUCHI, T. (1985). "Biosynthesis of lignin," *Biosynthesis and Biodegradation of Wood Components*, ed. T. Higuchi. London: Academic Press. 141-160.

HUECK, H.J. (1972). "Textiles pests and their control," *Textiles Conservation*. London: J. E. Leene. 76-97.

IONITA, I. (1971). "Contribution to the study of the biodeterioration of the works of art and of historic monuments. II. Species of fungi isolated from oil and tempera paintings," *Rev. Roum. Biol. Botanique*, 16 (5) 377-381.

KIRK, K.T., and M. SHIMADA (1985). "Lignin biodegradation: the microorganisms involved, and the physiology and biochemistry of degradation by white-rot fungi," *Biosynthesis and Biodegradation of Wood Components*. Ed. T. Higuchi. London: Academic Press. 579-605.

KOHLMEYER, J., and E. KOHLMEYER (1979). "Fungi on wood and other cellulosic substrata," *Marine Mycology. The Higher Fungi*. New York, San Francisco, London: Academic Press. 111-173.

KOWALIK, R. (1980a). "Microbiodeterioration of library materials. Part 1," *Restaurator*, 4. 99-114.

——— (1980b). "Microbiodecomposition of basic organic library materials. Microbiodeterioration of library materials. Part 2," *Restaurator*, 4 (3-4). 135-219.

MAHOMED, R.S. (1971). "Antibacterial and antifungal finishes," *Chemical Aftertreatment of Textiles*, eds. H. Mark, N.S. Wooding and S.M. Atlas. New York, London: Wiley Interscience. 507-552.

MAKES, F. (1981). "Enzymatic consolidation of paintings," *ICOM Committee for Conservation. 6th Triennal Meeting. Ottawa, 21-25 September 1981.* Preprints. Paris: ICOM. 81/2/7- 1 - 7/7.

———, (1984). "Enzymatic removal of lining paste from painting," *ICOM Committee for Conservation. 7th Triennal Meeting. Copenhagen, 10-14 September 1984*. Preprints. Paris: ICOM. 84.2.26-2.30.

MENIER, J.J. (1988). "Sur quelques insectes déprédateur des archives," *Patrimoine culturel et alterations biologiques. Actes des journees d'etudes de la S.F.I.I.C., Poitiers, 17-18 November 1988*. 45-52.

MORIONDO GAMBETTA, A., and E. ORLANDI (1967). "Studi sulla carie soffice - I: Su alcuni Ascomiceti e deuteromiceti reperiti su legno a contatto con il suolo," *Contributi Scientifico-Pratici per una migliore conoscenza ed utilizzazione del legno*. Florence: CNR Istituto per la Ricerca sul Legno. VII, no.11. 39-56.

SAGAR, B.F. (1987). "Textiles. Biodeterioration of textile materials and textile preservation," *Biodeterioration* 7. 683-702.

SORLINI, C. (1984). *L'azione degli agenti microbiologici sulle opere d'arte.* ENAIP, Ed. del Laboratorio, Botticino (Brescia). 1-48.

STRZELCZYK, A.B. (1981). "Painting and sculpture," *Microbial Biodeterioration. Economic Microbiology*, vol. 6. Ed. A.H. Rose. London: Academic Press. 203-234.

———, and S. LEZNICKA (1981). "The role of fungi and bacteria in the consolidation of books," *Int. Biodet. Bull.*, 17 (2) 57-67.

———, J. KUROCZKIN and W.E. KRUMBEIN (1987). "Studies on microbial degradation of ancient leather bookbindings: part I," *Int. Biodet. Bull.*, 23, (1) 3-27.

VARONINA, L.I., O.N. NAZAROVA, U.P. PETUSHKOVA and N.L. REBRIKOVA (1981). "Damage of parchment and leather caused by microbes," *ICOM Committee for Conservation, 6th Triennial Meeting. Ottawa, 21-25 September 1981*. Preprints. Paris: ICOM. 19/3.1-19/3.11.

VIGO, T.L. (1977). "Preservation of natural textile fibers - Historical perspectives," *Preservation of Paper and Textiles of Historic and Artistic Value*, ed. J.C. Williams, Advances in Chemistry. Series 164. Washington, DC: American Chemical Society. 189-207.

———, (1980) "Protection of textiles from biodeterioration," *Conservazione e Restauro dei Tessili. Convegno Internazionale, Como*. 18-26.

VON ENDT, D.W., and W.C. JESSUP (1986). "The deterioration of protein materials in museums," *Biodeterioration* 6, *Proceedings of the Sixth International Biodeterioration Symposium,*. eds. S. Barry and D.R. Houghton. Great Britain: Cab International. 332-337.

ZAINAL, A.S., M.A. GHANNOUM and A.K. SALLAL (1983). "Microbial biodeterioration of leather and leather-containing exhibits in Kuwait National Museum," *Biodeterioration* 5, eds. T.A. Oxley and S. Barry. London: John Wiley & Sons Ltd. 416-426.

Fig.1.7

Differential biological growth on plaster in relation to exposure to driving rain - Rome, Italy .

Fig.1.9

Differential biological growth on restored column in relation to porosity of materials - Ostia Antica, Italy.

Fig.1.10

Heavy colonization of algae, mosses and lichens on stone in the tropics - Java, Indonesia.

Fig.1.13

Growth of algae on a mural painting near a lighting system in a subterranean environment - Domus Aurea, Rome, Italy (ICR).

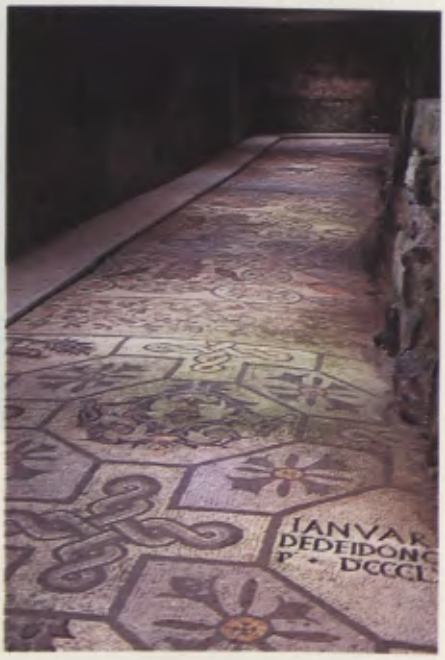


Fig.1.14

Growth of algae on mosaics limited to those parts receiving sufficient light intensity - Aquileia, Italy .

Fig.1.16

Growth of nitrophilous lichens due to bird droppings on statue - Villa Cordellina, Vicenza, Italy (ICR).

Fig.1.17

Effect of eutrophication on a fountain due to addition of phosphates that favor the growth of algae and mosses - Fountain of the Naiads, Rome, Italy.

Fig.2.3

Growth of fungi on canvas painting, causing detachment of paint layer (M. Baleani, ICR).

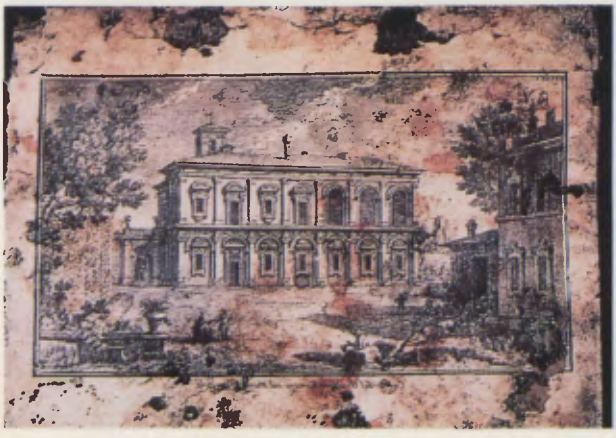


Fig. 2.7

Print with stain of microbiological origin (G. Donati, Istituto per la Patologia del Libro, Rome).

Fig.2.8

Textile with stain due to fungal growth (M. Baleani, ICR).

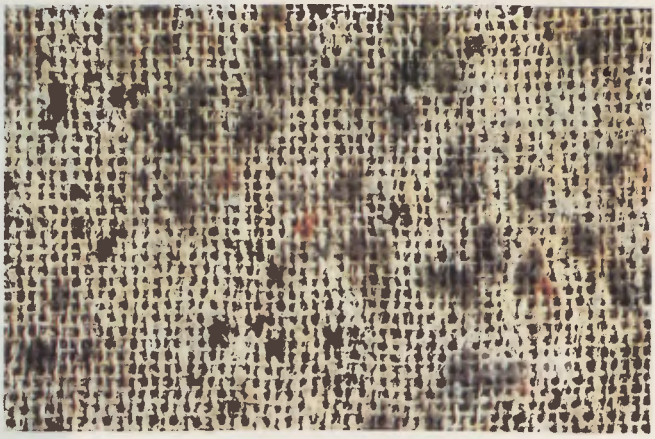


Fig.2.9

Black patina due to fungi (Cladosporium sp.) on mural painting during a restoration - Cantù, Italy (ICR).

Fig.2.10

Red stains caused by Haematococcus pluvialis on stone due to physiological stress.

Fig.2.11

Green patina of algae (Chlorophytes) on marble stairs - Venice, Italy.

Fig.2.12

Lichens disfiguring the face of a sandstone statue - Brittany, France (F. Sacco, ICR).

Fig.2.13

Example of very evident attack of algae and roots on a mural painting, contrasting with a whitish patina of actinomycetes that could be confused with salt efflorescence - Domus Tiberiana, Rome, Italy.

Fig.2.14

Black patinas of cyanobacteria and green algae on stone, often erroneously confused with deposition of pollutants - Roman Forum, Rome, Italy (A.M. Pietrini, S. Ricci, ICR).

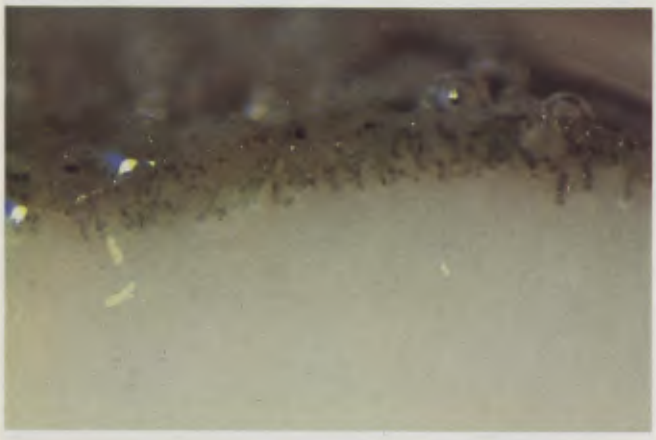


Fig.2.15

Growth of endolithic algae on limestone as shown in a polished cross section.

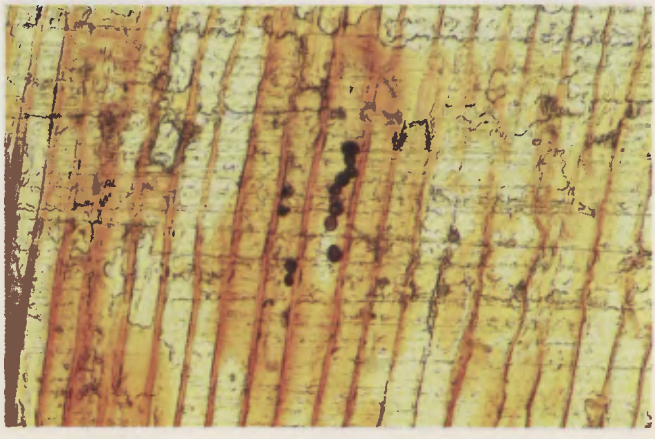


Fig.3.7

Fungal infection within wood structure (M. Baleani, ICR).

Fig.3.8

Example of wood attacked by white rot fungi (A. Gambetta, E. Orlandi, CNR Istituto per la Ricerca sul Legno - Florence).

Fig.3.9

Example of wood attacked by brown rot fungi (A. Gambetta, E. Orlandi, CNR Istituto per la Ricerca sul Legno - Florence).

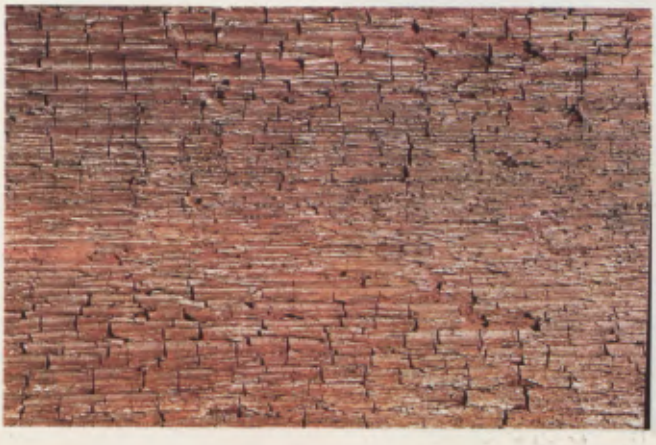


Fig.3.10

Example of wood attacked by soft rot fungi (A. Gambetta, E. Orlandi, CNR Istituto per la Ricerca sul Legno - Florence).

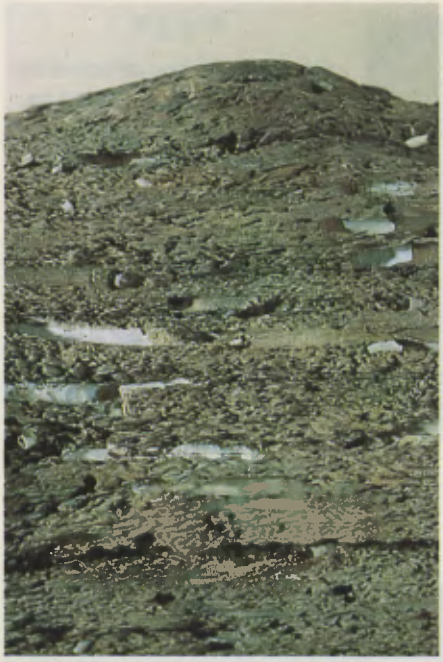


Fig.3.15

Tunnels of Teredo in wood, showing calcareous lining (A. Gambetta, E. Orlandi, CNR Istituto per la Ricerca sul Legno - Florence).

Fig.3.16

Ancient book with stain of microbiological origin: bacteria and sporified fungi (G. Donati, Istituto per la Patologia del Libro, Rome).

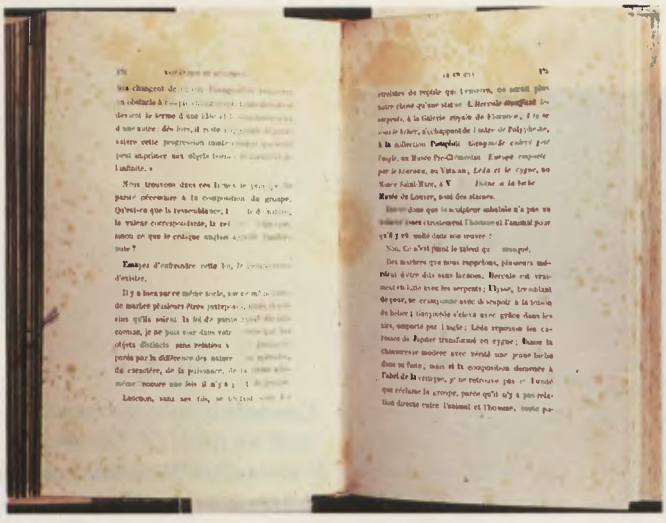


Fig.3.17

An example of "foxing" stains on an ancient book (G. Donati, Istituto per la Patologia del Libro, Rome).

Fig.3.19

Sheet of a herbarium damaged by silverfish (P. Piccione, ICR).

Fig.3.20

Inner erosion of book by termites (G. Donati, Istituto per la Patologia del Libro, Rome).

Fig.3.21

A textile fiber infected by fungi (ICR).

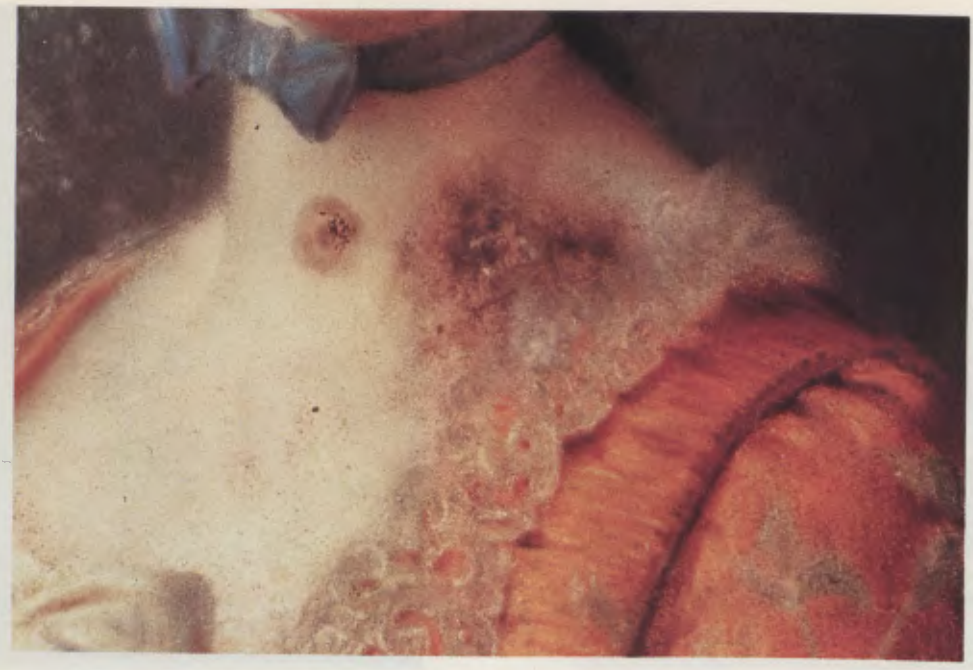


Fig.3.24

A painted parchment with fungal attack (M. Baleani, ICR).

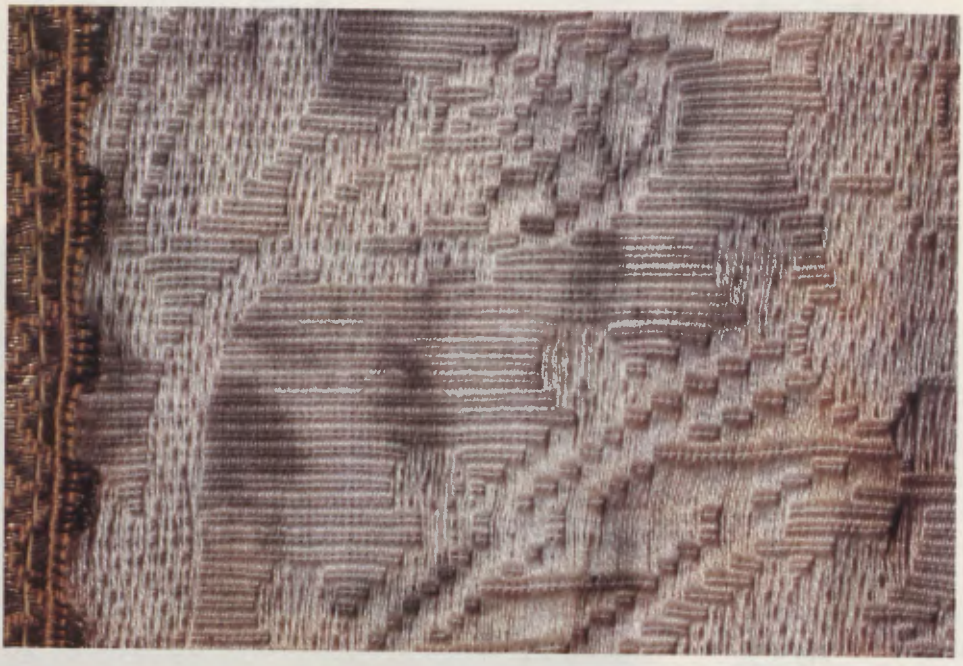


Fig.3.25

Silk textile showing grey stain due to growth of fungi (G. Gusso, ICR).

Fig.3.26

Reverse side of a painting on canvas with stain due to fungal attack - Rieti, Italy (ICR).

Fig.3.27

The right side of the same painting - Rieti, Italy (ICR).

Fig.3.28

A paint layer with different types of stains due to fungal attack: the red ones due to pigment emission and the black due to dark mycelium (ICR).

Fig.4.5

White efflorescence due to the growth of actinomycetes on mural paintings of an Etruscan tomb - Tarquinia, Italy (ICR).

Fig.4.8

Samples of marble treated with a silicon resin showing differential growth of fungi (Deuteromycetes) in relation to airborne spore contamination. Left : not exposed ; right: exposed outdoors.

Fig.4.10

Black patina of cyanobacteria on a statue - Caracas, Venezuela (ICR).

Fig.4.11

Chasmoendolithic algae and cyanobacteria on a marble capital in Trajan's Forum - Rome, Italy.

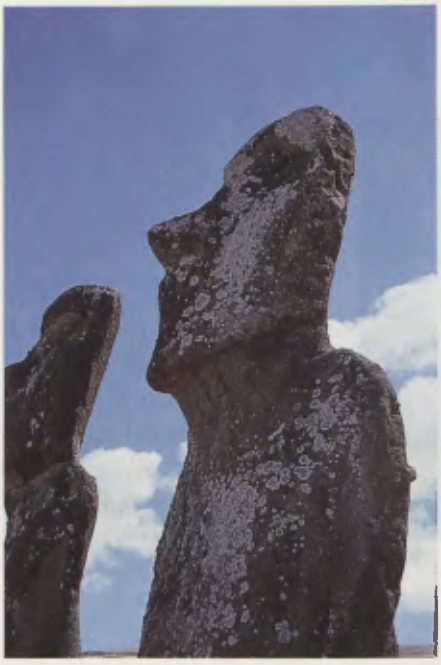


Fig.4.13

Lichens on "moai" - Aku Ahivi, Easter Island .

Fig.4.15

Endolithic lichens on limestone, black fruiting bodies are located in pits .

Fig.4.16

Lecanora campestris on Muggia sandstone. Micrograph of a thin section showing relict clasts (quartz and calcite) among the calcium oxalate crystals (weddellite) within the lichen thallus (N+).

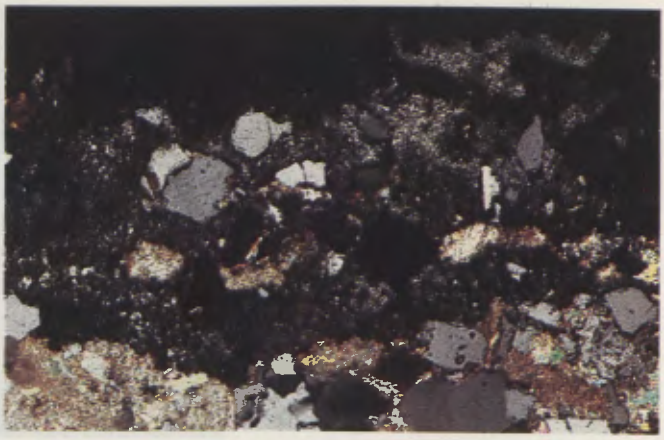


Fig.4.18

Mosses, liverworts and ferns on stone located near a fountain - Rome, Italy.

Fig.4.23

Accumulation of bird excrement on Istrian stone on the church of the Gesuiti - Venice, Italy.

Fig.4.24

Bats attached to a rock cave of religious and archaeological interest, producing a heavy accumulation of blackish excrement - Bali, Indonesia.

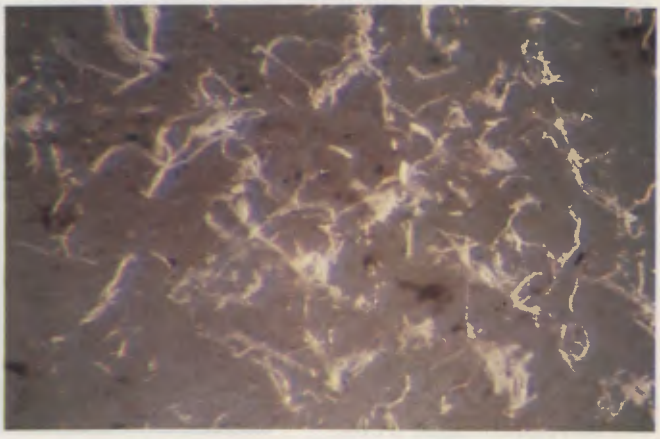


Fig.5.3

Stereomicroscope photo showing fungal growth (Aspergillus sp.) on acrylic resin in a laboratory test (ICR).

Fig.5.5

Archaeological site where plants reduce the strong sun radiation and lower the water table, reducing rising damp - Moenjodaro, Pakistan.

Fig.6.2

Damage caused by ineffective mechanical cleaning with hard brushes to remove lichens from walls - Oviedo, Spain.

Fig.6.3

Field tests to evaluate the effectiveness of different biocides against algae (ICR).

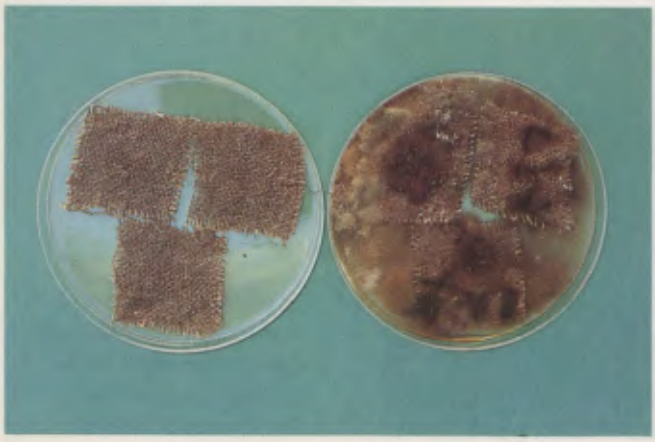


Fig.6.5

Preliminary tests to evaluate the interference of biocides on textile samples (M. Baleani, ICR).

Chapter 4

BIODETERIORATION OF INORGANIC MATERIALS

The inorganic substrates are preferentially colonized by autotrophic organisms. Nevertheless, it is wrong to consider inorganic materials as completely lacking in organic substances. The presence of organic matter on the surfaces of these substrates is very common, especially if the artifacts are exposed to open air. Atmospheric pollution, pollens, vestiges of previous biological colonization, old treatments (waxes, oils, casein, etc.) or new ones (protective coatings, consolidants), hypertrophication by bird droppings and by agricultural practices (the widespread use of fertilizers) favor the development of heterotrophic microflora.

Environmental factors are very important in determining the development of biodeteriogens (see Chapter 1). Also, materials generally not frequently attacked by organisms may be colonized under some extreme conditions. This frequently happens in archaeological sites, when objects are buried.

4.1 STONE AND RELATED MATERIALS

Stone or rocks are aggregations of one (e.g., limestone composed of calcite) or often more minerals. They can be classified as:

(a) **Igneous or magmatic rocks**, formed by cooling and consolidation of magma (e.g., granite, basalt, diorite).

(b) **Sedimentary rocks**, derived from the disintegration or chemical weathering of pre-existent rocks and deposited by water, wind and glaciers (e.g., sandstone, limestone, gypsum, travertine, volcanic tuffs).

(c) **Metamorphic rocks**, derived from transformations of pre-existent rocks due to pressure and heat (e.g., marble).

Stuccos, mortars, plasters, frescoes and ceramic products employed in architecture (bricks and brickworks) do not require a separate discussion because the biodeteriogens that attack them are the same as those that grow on stone. Apart from differences in their chemical composition, these materials generally have a larger porosity which can favor the establishment of microflora, especially in view of their greater ability to retain water. In addition, bindings or pigments represent another kind of substance biodeteriogens can use.

Outdoor walls and floors are colonized in different ways by microflora and plant communities, depending on the mineralogical composition and porosity of the substrate, its exposure and inclination, the macro- and micro-climate and also the period of plant settling. This permits the vegetation to be used (if one knows its ecological requirements) as bioindicators.

4.1.a Bacteria and actinomycetes

Bacteria attack stone by chemical action only. They are, in fact, extremely small in size, and their active penetration in rocks has never been described. The bacteria that play an important role in the weathering of rocks and minerals are autotrophic, but also facultative chemolithotrophic (which use inorganic and/or organic substrates indifferently) and heterotrophic (Krumbein, 1972). Microbial solubilization processes are always coupled with an acidification of the cultural medium (as witnessed by the production of acids) and a weight loss of tested stone.

The alterations produced by bacteria are no different from those of purely chemical origin: black crusts, powdering, exfoliation. The problem of defining the extent to which alterations can be ascribed to chemical or to microbiological processes has been studied at length, but has not been solved. Generally, the abiotic processes are considered the most important, and the role of bacteria is acknowledged only in cases where analyses have shown them to be present. But depending on the different methods used to remove the bacteria from stone, culture and count them, very different results are obtained (Lewis et al., 1985). More and more, it is necessary not only to have a deeper knowledge of the microbial ecology of stone but also to establish common standardized laboratory procedures so that the results obtained by different authors can be compared for a better understanding of the microbial decay of stone.

For bacteria as well as other microorganisms, the quantitative aspect is fundamental to evaluating their importance in the deterioration process. Naturally, even a "sound" stone is not sterile, and the "pathogenic number" of bacteria must be determined in order to establish whether their presence is only incidental or whether, on the other hand, they play an important role in weathering phenomena.

The ability of many bacteria (sulfur-oxidizing, nitrifying and heterotrophic) to decay stone has been demonstrated in the laboratory (Fig. 4.1), and they are always found in higher numbers in weathered than in sound stone.

Biological formation of gypsum, nearly always found among the weathering products of limestones, is due to the action of sulfur-oxidizing bacteria (especially *Thiobacillus* types), which utilize various reduced sulfur compounds or elemental sulfur to produce sulfate ions ($SO_4^{=}$) which, when reacting with the calcium (Ca^{++}) ions of stone, form gypsum ($CaSO_4 \cdot 2H_2O$) (Pochon and Jaton, 1968). The circulation of sulfur compounds in nature (sulfur cycle) is illustrated in Fig. 4.2.

Pochon and Coppier (1950) have postulated that a reduction of sulfates to sulfides by sulfur-reducing bacteria (especially *Desulfovibrio desulfuricans*, an anaerobic microorganism) occurs in soil near the foundations of buildings. HS^- or $S^=$ in solution can penetrate and rise in stone through capillarity and come to the wall surface through

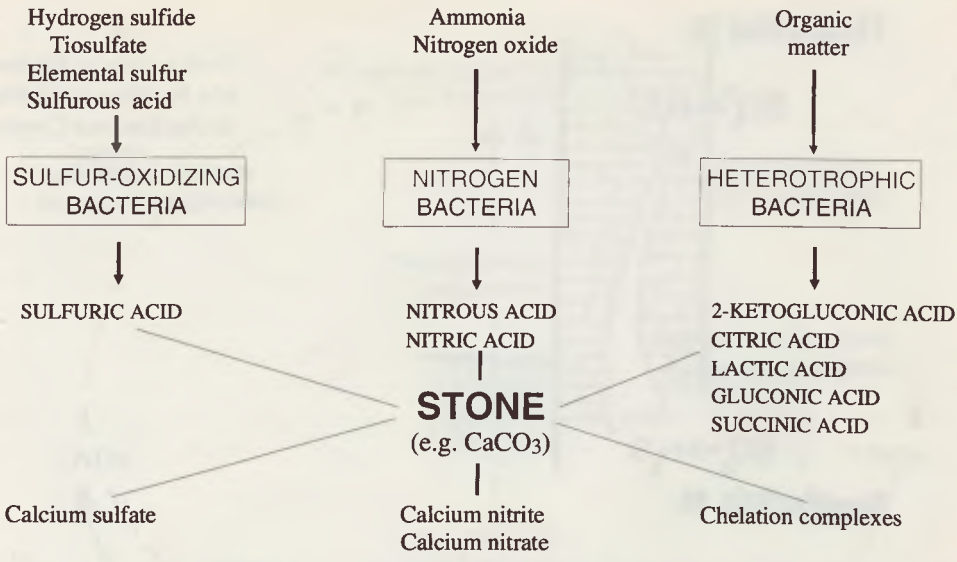


Fig.4.1 *Diagram of the action of bacteria on stone.*

surface evaporation. There sulfides are oxidized by *Thiobacillus* sp. to provide sulfates (Fig. 4.3). Nonetheless, this hypothesis could only explain deterioration at lower building levels affected by rising damp. For deterioration at higher levels, it is necessary to consider a sulfate contribution from pollutants or from other previous biological colonizations. Sulfur-oxidizing bacteria have frequently been isolated in great numbers from French and Italian monuments (Jaton, 1972; Barcellona et al., 1973; Tiano et al., 1975).

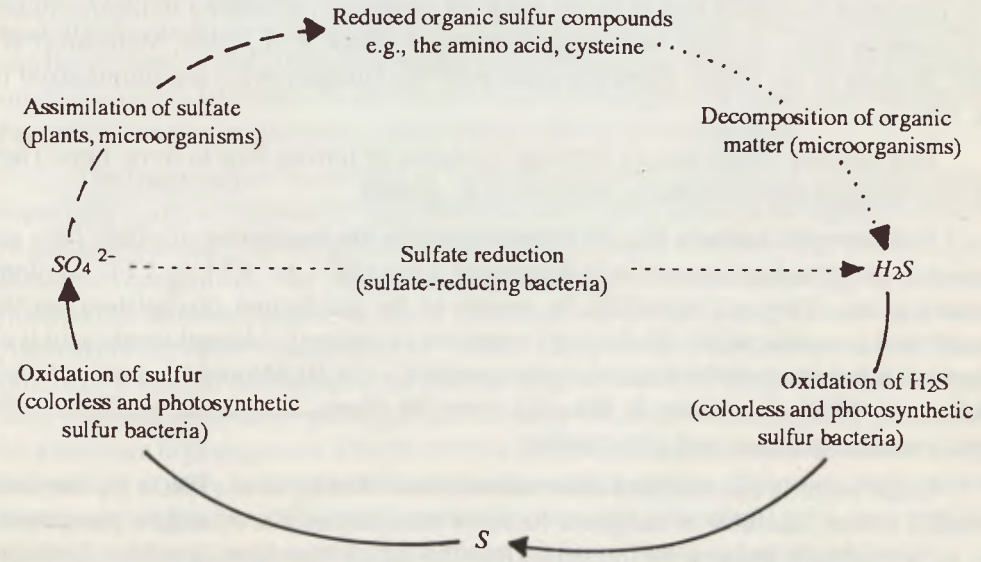


Fig.4.2 *The sulfur cycle.*

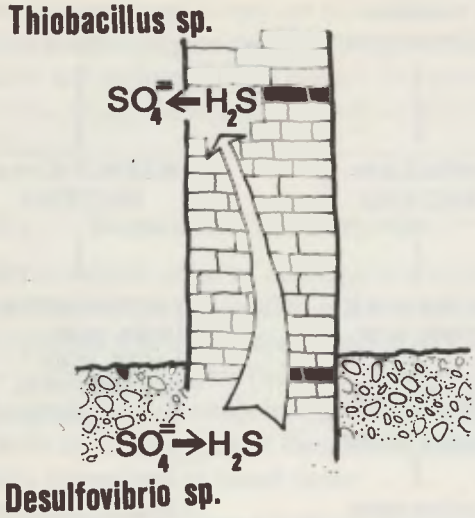


Fig.4.3

Sulfur cycle at the base of a building, according to Pochon and Coppier (1950).

Recently, *Desulfovibrio desulfuricans* have been suggested for use in cleaning crusted marble monuments as they are able rapidly to convert gypsum to calcite (Atlas et al., 1988).

Kauffman (1960) was the first author to demonstrate the role of nitrifying bacteria in the weathering of stone monuments. These bacteria fall into two groups, the ammonia oxidizers (genus *Nitrosomonas, Nitrosovibrio, Nitrosococcus, Nitrosospira, Nitrosoglobus*), which convert ammonia to nitrous acid, and the nitrite oxidizers (genus *Nitrobacter, Nitrococcus, Nitrospira*), which convert nitrous acid to nitric acid. These acids attack limestone and transform its surface into powder: calcium nitrates and gypsum are the alteration products. Nitrifying bacteria, however, have been relatively rarely isolated from weathered limestone or marbles in Italy. In contrast, they seem to be the most important microbial factors in the decay of sandstone, according to recent studies performed on many German sandstone monuments (Bock et al., 1988; Meincke et al., 1988; Wolters et al., 1988). Principal aspects of the nitrogen cycle are summarized in Fig. 4.4.

Iron bacteria obtain energy from the oxidation of ferrous ions to ferric ions. They can oxidize some iron-containing minerals (e.g., pyrite).

Heterotrophic bacteria play an important role in the weathering of stone. They are always detected in high quantities in weathered stone (10^6 - 10^7 CFU/g, CFU = colony forming units). They act especially by means of the production of chelating agents, organic and inorganic acids, alkalis (e.g., ammonia or amines). 2-ketogluconic acid is an effective chelating agent that forms complexes with Ca, Cu, Ni, Mn and many other metals (Duff et al., 1963). In addition to this acid, there are others, such as lactic, glycocholic, citric, succinic, gluconic and galacturonic.

Some bacteria can mobilize silica and silicates (Webley et al., 1963). By the same chemical action, insoluble or inorganic forms of phosphorus (Ca, Al and Fe phosphates) can be solubilized. Bacteria of the genus *Bacillus* attack haematite, goethite, limonite, pyrolusite, etc. (Ehrlich, 1981).

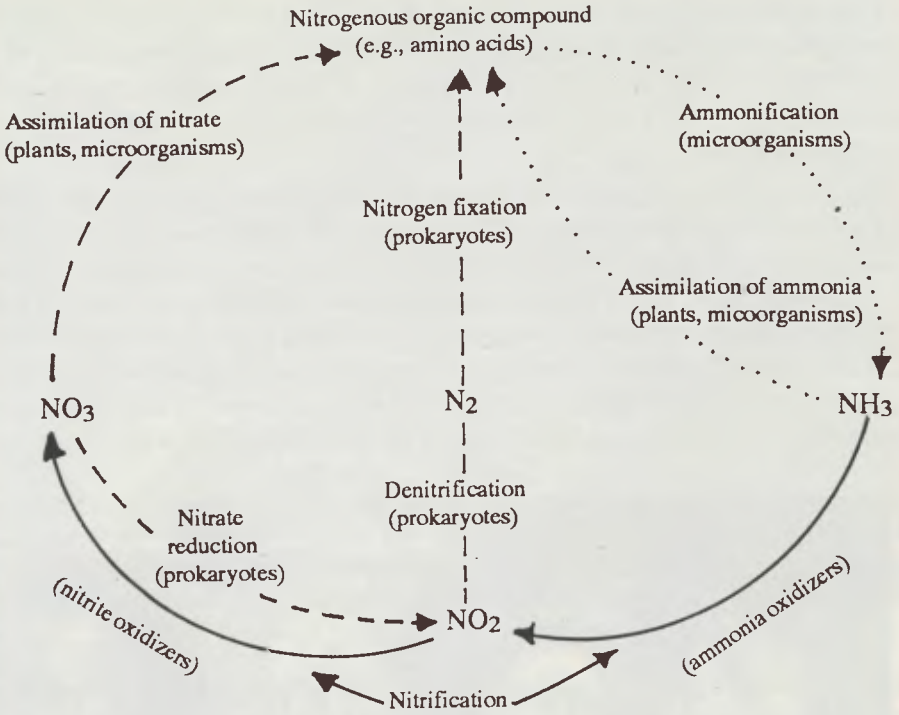


Fig.4.4 *The nitrogen cycle.*

Bacteria can also cause discoloration of the pigments in mural paintings. Lead-containing pigments such as white lead, massicot and minium can be converted into black lead sulfide, due to the interactions of H_2S produced by bacteria. White lead and massicot can be oxidized to PbO_2 (brown), probably by means of hydrogen peroxide produced by microorganisms (Petushkova and Lyalikova, 1985). Some of these were identified as bacteria belonging to the genus *Arthrobacter*, others as mycoplasms.

The frequency of occurrence of Actinomycetes on deteriorated stone and frescoes, especially under conditions of high humidity and a great amount of organic substances (e.g., subterranean environments), is significant (Delvert, 1963; Hyvert, 1966a). Among these microorganisms, the family of Streptomycetes and *Nocardia* spp. are the most involved in biodeterioration of mural paintings located in crypts, grottos and tombs (Agarossi et al., 1984; Giacobini et al., 1988). The growth of Actinomycetes on frescoes produces a whitish or whitish-grey powder (Fig. 4.5, p. 82). They often occur together with other bacteria, fungi and algae, and develop where environments are characterized by a constant high degree of RH (90-100%). Laboratory experiments have demonstrated their ability to utilize nitrites and nitrates, and to reduce sulfates. Therefore, they can attack limestones and silicate minerals (especially mica and orthoclase) with their metabolic products: carbonic acid, nitric acid, sulfuric acid and other weaker organic acids.

4.1.b Fungi

Even though they are heterotrophic organisms, fungi have often been isolated from weathered stones, especially in tropical areas. While the inorganic composition of stone does not offer a favorable substrate for the growth of these organisms, organic residues of various origin are nearly always present on stone and mural paintings, and this factor aids the growth of fungi.

Fungi cause staining on and within stone and mural paintings, frequently with dark spots. The staining caused by fungi of the Dematiaceae family, such as *Cladosporium herbarum, Aspergillus niger, Stachybotrys* spp. and *Alternaria* (frequently detected on stone), is often black and very difficult to remove (Ionita, 1971; Hyvert, 1966b,c). It seems to be due to melanins (very stable indochinone derivatives) inside the mycelium (Leznicka, et al., 1988). The stains caused by non-dematiaceous fungi are more unstable. The mycelium penetrates deeply inside the plasters of wall paintings (10 mm deep and more) and causes loss of cohesion and detachment of the paint layer (Fig. 4.6).

Fig. 4.6

Growth of fungi (Cladosporium herbarum) on a mural painting - Basilica of S. Francesco, Assisi, Italy (ICR).

In dolomitic and calcitic stone, hyphae penetrate the calcite crystals, not only along the crystal planes, and the stone surfaces appear clearly etched when observed under SEM (Koestler et al., 1985). Some fungi are endolithic and produce pitting phenomena (Danin, 1986a), and the filamentous structure of hyphae makes their penetration into the substrate easier (Fig 4.7).

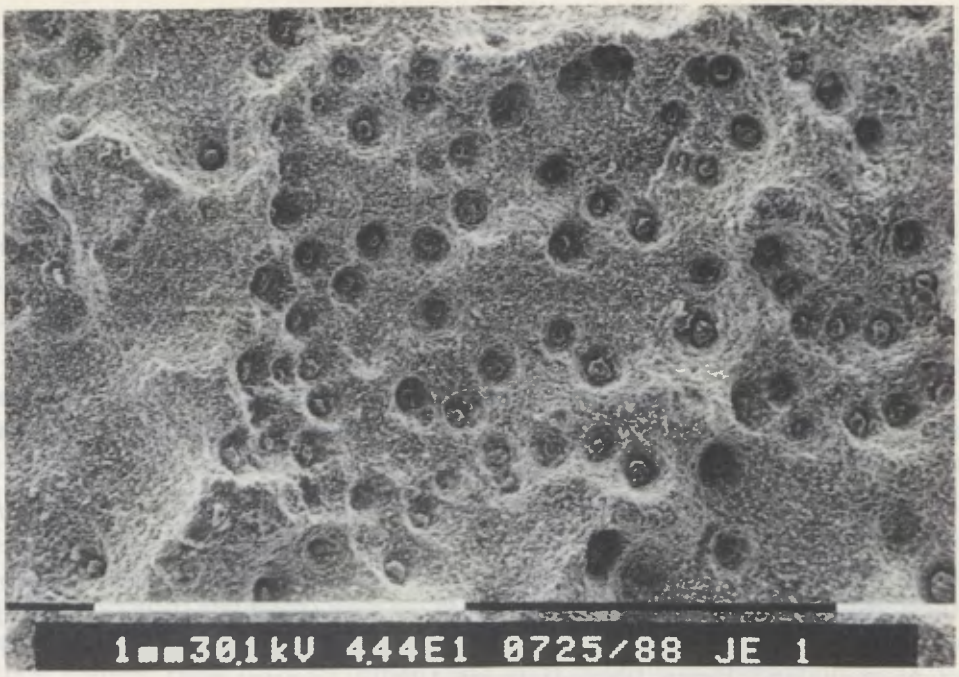


Fig. 4.7

SEM micrograph of pitting produced by Lichenothelia sp. (Ascomycetes) on limestone - Negev Desert, Israel (A. Danin, Department of ESE, the Hebrew University, Jerusalem).

The chemical action of fungi, however, appears to be the most important deteriorative aspect. This phenomenon has been demonstrated in the laboratory: solubilization is always correlated with a decrease of pH, due to production of acids. Fungi produce carbonic, nitric and sulfuric acids, and many other organic acids (citric, oxalic, gluconic, glucuronic, lactic, fumaric). The latter can form chelation complexes with metal cations of the substrate, dissolving limestones, silicate minerals (especially micas, orthoclase, etc.), iron and magnesium-bearing minerals (such as biotite, olivine, pyroxene) and different phosphates (Williams and Rudolph, 1974). Basic igneous rocks are more susceptible to fungal attack than granitic rocks, which seem to be very resistant. Both cementing material and aluminium silicates are deteriorated in sandstone. Some species such as *Aspergillus niger, Penicillium* sp. and *Spicaria* sp. produce great amounts of citric and oxalic acids. The excretion of oxalic acid involves an extensive corrosion of the primary minerals and the complete decomposition of ferruginous clay minerals. Iron oxides, amorphous gels and oxalates are precipitated. The ability of fungi to form calcium oxalates, deposited on the outside of hyphae, has been experimentally demonstrated on calcite and marbles (Mentler et al., 1986; Chiari et al.,1989).

Some fungi, such as *Exophiala jeanselmi, Penicillium* spp. and *Phoma* spp. isolated from deteriorated sandstone, are able to oxidize manganese, inducing extracellular encrustations of hyphae. These fungi could be involved in crust formation and exfoliation of stone (Kuroczkin et al., 1988; Petersen et al., 1988).

Study of the susceptibility of protective coatings and stone consolidants to biodeterioration has only begun in recent years. These studies were performed directly on products applied on glass plates inoculated with a suspension of fungal spores or on treated stone samples (Nugari and Priori, 1985; Salvadori and Nugari, 1988; Koestler et al., 1988). The utilization of these polymers by fungi and bacteria as food is possible especially if the work of art is located in an environment with high RH levels (Fig. 4.8, p. 82). It has been demonstrated that fungal growth can interfere with the structural properties of some polymers.

4.1.c Cyanobacteria and algae

On or within stone we can find microscopic algae belonging mostly to two different systematic groups: Cyanobacteria (or blue-green algae) and Chlorophytes (or green algae). Other kinds of algae only occasionally occur (e.g., diatoms).

Depending on the relation with the substrate, algae can be divided into *epilithic*, growing on the exposed surface and *endolithic*, colonizing the interior of semitranslucent or translucent rocks. Endolithic algae include *chasmoendolithic*, living inside preformed fissures and cavities open to the stone surface, *cryptoendolithic*, colonizing structural cavities within the porous rocks and *euendolithic*, actively penetrating into the substrate (Golubic et al., 1981; Danin, 1986a; Hoffman, 1989).

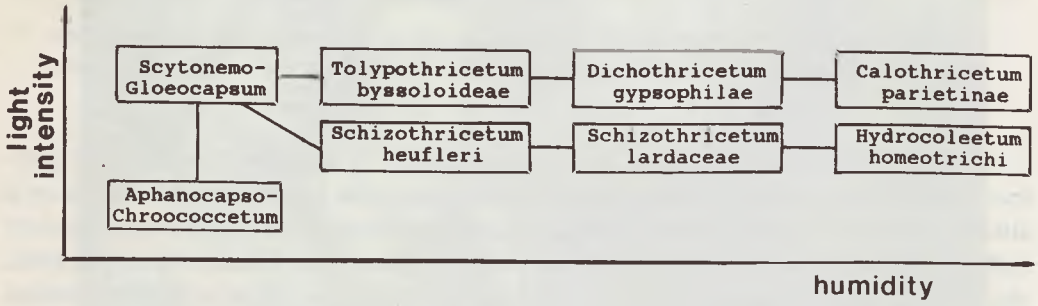


Fig. 4.9

Ecological succession of cyanobacteria associations in relation to light and humidity (from Golubic, 1976).

The most important factors conditioning the establishment of algae are light intensity, humidity, temperature and pH. The relation of the first two factors with different algal associations is summarized in Fig. 4.9. Green algae or, more commonly, cyanobacteria are often the first colonizers of stone because they need only light, water, a few inorganic compounds and prefer an alkaline substrate (pH = 7-8) to develop. Limestone is more often colonized than other kinds of stone (e.g., granite). Cyanobacteria are surrounded by a more or less thick gelatinous sheath, variously colored, able to absorb and retain water for a long time. This permits them to survive under extreme environmental conditions, such as persistent desiccation. In response to changes in environmental conditions, algae can switch their metabolism on and off. In caves or other subterranean environments, the development of algae is tied to the (natural or artificial) light gradient (Lefèvre, 1974; Pietrini et al., 1986; Albertano and Grilli Caiola, 1988).

The species of Cyanobacteria most commonly found on stone and mural paintings of historical or artistic interest belong to the following genera: *Chroococcus, Gloeocapsa, Lyngbya, Nostoc, Oscillatoria, Scytonema, Myxosarcina.* The green algae of terrestrial habitat most frequently isolated from monuments are as follows: *Chlorella, Chlorococcum, Haematococcus, Scenedesmus, Stichococcus, Ulothrix.*

Extensive coverings of diatoms (Bacillariophytes) have been recognized on sandstone, spoilt rocks and building surfaces in the tropics (Wee and Lee, 1980). In temperate climates, they are usually present in fountains or other stoneworks linked to aquatic environments.

Epilithic algae are the most common. They form patinas or sheets varying in extent, thickness, consistency and color, usually easy to recognize under simple observation. Patinas are thin, tough, sometimes green, very often grey or black in well-lit and relatively dry places (Fig. 4.10, p. 82). They are thick, gelatinous and of various colors (green, yellow, orange, violet, red) in poorly-lit and damp places (¶2.4.2). Different colors of patinas depend on the type of biocoenosis, its development stage and the growing phase of the prevailing alga (Ricci et al., 1985). The sheets of algae trap water (with the gelatinous sheaths) and retard subsequent drying, increasing the water-related decay of stone. In addition, dust, soil, organic residues, spores and many other substances adhere to these patinas. These particles help to make the damage worse and simultaneously act as a substrate rich in organic substances, favoring the growth of heterotrophic microflora, lichens, mosses and ferns.

Some alterations of frescoes due to algal growth appear as variously colored powder (white-pink, white-yellowish, light grey), and are present both in the open air and in confined and not very damp places (Giacobini et al, 1979; Tomaselli et al., 1979).

Chasmoendolithic algae form green zones parallel to the surface, frequently under partially detached scales. Often, it is only possible to recognize the presence of these algae after detachment of the scales (Fig. 4.11, p. 83) (Danin and Caneva, 1990).

Cryptoendolithic algae establish on light-colored limestone and sandstone, forming a colored layer parallel to the surface at a depth of some millimeters. Generally they are described as occurring under extreme environmental conditions (e.g., hot and cold deserts), but some recent findings in the limestone of a Belgian basilica (Saiz-Jimenez et al., 1990) and in some Carrara marbles in the quarries (unpublished data) suggest a greater ecological valence of these microorganisms.

Euendolithic algae (only blue-green algae) actively dissolve carbonates, penetrating into the substrate and forming microcavities of differing morphology according to the various species (Fig. 4.12). Light is the limiting factor for penetration into stone; in fact, stone acts as a filter and reduces the light intensity.

Algae contribute to stone deterioration by respiration processes, by retaining water which expands in freeze-thaw cycles or by releasing acids or chelating compounds (Degelius, 1962). Among these are aspartic, citric, glutamic, glycollic, oxalic and uronic acids. In addition to acids, many other organic compounds (e.g., amino acids and polypeptides) are also able to complex or chelate ions.

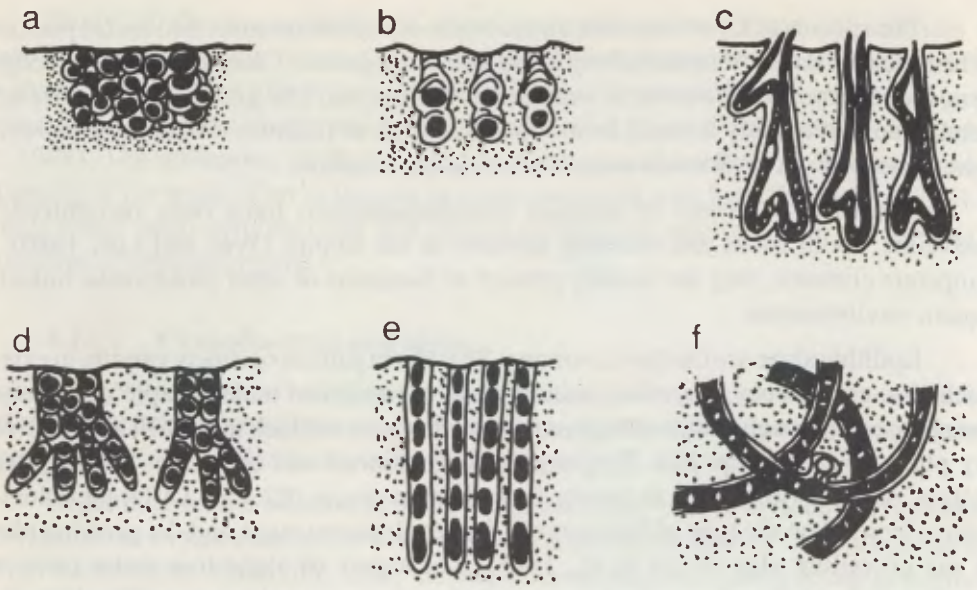


Fig. 4.12

Different boring patterns of euendolithic cyanobacteria:
a, d, Hyella balani; b, Hormatonema paulocellulare; c, Kyrtuthrix dalmatica;
e, Hyella caespitosa; f, Mastigocoelus testarum (from Le Campion-Alsumard, 1979).

4.1.d Lichens

Lichens are poikilohydric organisms (i.e. able to function or survive at varying water content) (Hawksworth and Hill, 1984), and this enables them to occur in extreme environments. Together with cyanobacteria, they play an important role as pioneer organisms in the colonization of rocks and can colonize man-made substrata in a relatively few years (Fig. 4.13, p. 83).

Lichens growing on stone are called *saxicolous* and are mainly *crustose* but may also be *foliose* or *squamulose*. Crustose species penetrate into stone with all hyphae of the lower surface; foliose species penetrate with their attachment organs (holdfast and rhizines). The depth of penetration is usually not more than several millimeters (Fig. 4.14). They can be epilithic or endolithic; endolithic lichens are entirely located within the stone, which is almost always calcareous (Fig. 4.15, p. 83).

The wide variety of stone often found in archaeological areas determines the development of many different lichen species. Lichens on silicicolous stone are generally different from those on calcareous stone. Even on the same monument, variations in exposure to driving rain or solar radiation together with morphological features of the work of art itself can cause very particular colonizations which are not easy to summarize.

Among the most common species found in Italian archaeological sites (and also the most investigated from a floristic point of view) are the following: *Acarospora umbilicata, Aspicilia calcarea, A. hoffmannii, Caloplaca aurantia, C. citrina, C. flavescens, C. saxicola, C. teicholyta, Candelariella aurella, C. vitellina, Diploicia canescens,*

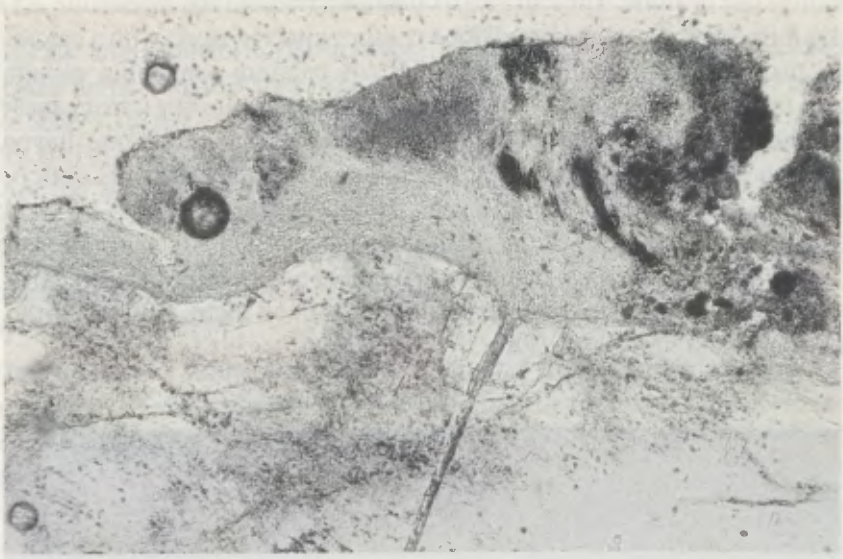


Fig.4.14

Lecanora campestris on Troadense marble. Micrograph of a thin section showing fungal hyphae penetrating into a K-feldspar cleavage (N+).

Diploschistes actinostomus, Dirina massiliensis f. *sorediata, D. stenhammari, Lecanora albescens, L. campestris, L. dispersa, L. muralis, Lecidea fuscoatra, Ochrolechia parella, Tephromela atra, Verrucaria nigrescens, Xanthoria calcicola* (Nimis et al., 1987; Seaward and Giacobini, 1988; Seaward et al., 1989; Nimis et al., in press).

Lichens exert a physical force on the substrate by contraction and expansion of their thalli under either dry or wet conditions. Mineral fragments are detached from the substrate and incorporated into the thallus where they oftenappear heavily corroded (Fig. 4.16, p. 84) (Fry, 1924). Much more important is the damage induced chemically by three main processes: the generation of carbonic acid, the excretion of oxalic acid and the production of lichen compounds with chelating abilities (Jones and Wilson, 1985).

Carbon dioxide dissolves in the moisture held by the thallus and forms carbonic acid, which reacts with minerals and depletes basic cations (K^+, Na^+, Mg^{++} and Ca^{++}) and silica.

Oxalic acid is produced by the mycobiont (the fungus). Generally its production increases with the age of lichens and is greater in calcicolous than in silicicolous species (Ascaso et al., 1982). Nevertheless, we cannot generalize that all lichens produce oxalic acid because many species do not form it; the species (also of the same genus) that do so have different abilities to produce oxalates, and the same species makes different quantities depending on the composition of the substrate (Salvadori and Lazzarini, 1989). Oxalic acid, with its chelating and acidic properties, is more active than other organic acids; it causes a surface etching with the formation of pits beneath the thalli and crystallizes in oxalates deposited in the thallus. There is a close relationship between the kind of insoluble oxalates that accumulate in the thallus and the mineral composition and

the hydration state of stone. The calcium oxalates whewellite and weddellite are the most commonly formed on limestone, sandstone or other kinds of stone with a calcitic matrix; they can also derive from the deterioration of calcium-containing minerals (e.g., plagioclase feldspars). Magnesium oxalate dihydrate (glushinskite), manganese oxalate dihydrate, anhydrous ferric oxalate and copper oxalate hydrate (moolooite) have also been detected in lichens growing respectively on serpentinite, manganese ores, and copper ores (Ascaso et al., 1982; Ascaso, 1984; Purvis, 1984; Wilson et al., 1981). Oxalates can accumulate in various regions of the thallus: on the external surface only (forming the pruina), in the central part of the thallus or at the lichen-rock interface (Fig. 4.17). In any event, it is difficult to ascribe the oxalate films present on many works of art to a lichen origin (Lazzarini and Salvadori, 1989).

Fig.4.17

SEM micrograph of a polished cross-section of volcanite covered by Diploschistes actinostomus showing the distribution of Ca^{++} and its accumulation in the lichen thallus.

Lichens produce many organic compounds, generally called "lichen acids" (although not all are acids), which can be divided into two major series: aliphatic (fatty acids, polyols and triterpenoids) and aromatic (tetronic acid derivatives, depsides, depsidones, quinones, dibenzofurans and diketopiperazine derivatives) (Hale, 1983). Despite their low solubility in water, these substances can act as metal-complexing agents, forming soluble compounds which are frequently colored. Furthermore, the mycobiont can produce other simple organic acids that can chelate metal cations.

On very porous stone, lichen coverage can develop a certain protective effect, reducing the decaying effects of rain, wind and atmospheric pollutants.

4.1.e Lower and higher plants

Mosses and liverworts (Briophytes) and vascular plants grow abundantly on buildings and archaeological areas when the substrates and environmental conditions are favorable (Fig. 4.18, p. 84). Such conditions include a sufficient water content (important overall for Briophytes), adequate lighting for permitting photosynthetic activity and good porosity of the substrate, favoring both the retention of humidity and the mechanical penetration of rhizines and roots. Leaving aside problems of the physical and visual obstruction caused by vegetation, which are sometimes subjective, the role carried out in the weathering processes is of a mechanical and chemical nature (Fisher, 1972; Allsopp and Drayton, 1975).

The mechanical thrust due to the growth and radial thickening of root tips is of great harm (up to 15 atmospheres) (Winkler, 1975). The ruderal plants, however, vary in their ability to cause mechanical or chemical damage, due to their life cycle, the biological forms and the extension and lignification of roots (Caneva and Roccardi, 1991). The most common species on walls in Europe belong to the phytosociological class of *Parietarietea judaicae* in pioneer condition, such as *Parietaria diffusa, Capparis spinosa* (Fig. 4.19), *Antirrhinum* spp., *Centranthus ruber* and *Cymbalaria muralis*, which are respectively characteristic of different associations. Among the most dangerous species frequently occurring in Italian archaeological areas, *Ficus carica, Ailanthus altissima* and *Hedera helix* (Fig. 4.20) should be mentioned. Other woody species belonging to forest plant communities are also found in more evolved situations.

Fig.4.19
Capparis spinosa on tuff walls - Matera, Italy.

Root growth tends to take advantage of the zones with lowest resistance, e.g., plaster or the mortar between bricks and stones (Caneva, 1985). More compact zones can also be penetrated where there is a decrease of cohesion because of the action of physico-chemical factors (e.g., frost, rain).

Apart from the production of carbonic acid by means of cellular respiration processes, the chemical action develops by two main mechanisms: the acidity of root tips and the acidity and chelation ability of exudates (Williams and Coleman, 1950; Keller and Frederickson, 1952).

Fig.4.20

Massive growth of Hedera helix climbing on the ruins of a Gothic abbey - Villers-La-Ville, Belgium (J. Fox, Brussels).

Weathering begins with the attack of H^+ ions surrounding rootlets on silicate and carbonate structures. The acidity can have different values: from the pH = 5-6 of some ruderal plants (Caneva and Altieri, 1988), to the pH = 3-4 of crop plants (Keller and Frederickson, 1952). During growth, the H^+ ions of superficial root layers are exchanged with nutritive metal cations. The organic compounds produced by roots, especially the acids of the Krebs cycle (2-ketogluconate, oxalate or citrate), can have chelating abilities.

Some plants (e.g., ivy) can cause an undesirable coloration of stone due to the release of organic compounds into the pores of the substrate, clearly visible if it is white or light-colored (Lewin and Charola, 1981).

Trees in archaeological sites cause some problems due to the expansion of their root systems, which can develop many meters both in depth and laterally. This can be very dangerous for subterranean environments and for wall structures when trees are too close (Caneva, 1988) (Fig. 4.21). Plants covering catacombs, temples and other buried monuments are an important cause of decay and can produce collapse, detachment of frescoes, damage to walls, etc. (Fig. 4.22).

The presence of plants also induces variations of microclimatic parameters: an increase of RH and water stagnation, a reduction of insolation, windiness and pollutants in the air (the last due to absorption by leaves). From the standpoint of conservation, the effects can be either negative (favoring the growth of algae and mosses) or positive (reducing aeolian erosion, hydric exchanges and consequently the migration of salts). Correct planning of archaeological areas must also bear these aspects in mind.

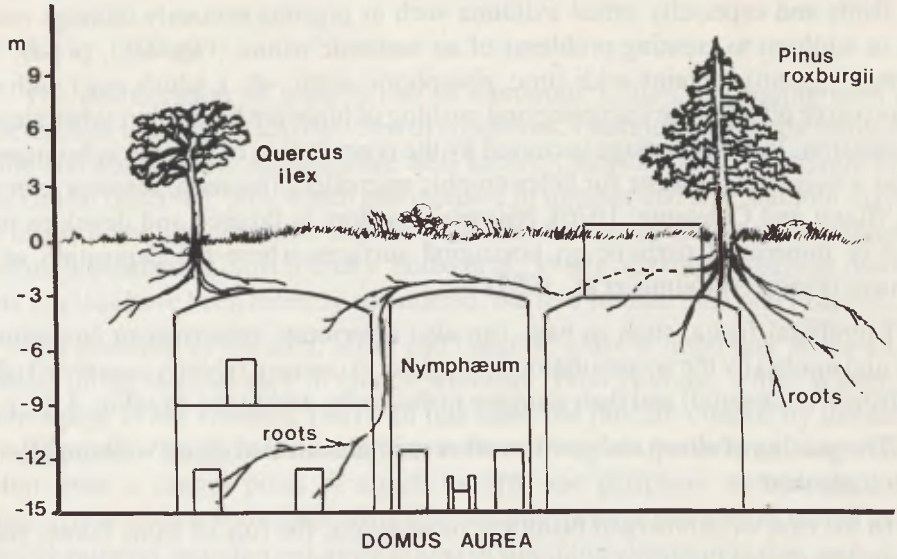


Fig.4.21

Schematic section of the Domus Aurea and Oppius Hill (Rome) showing the wide extension of tree roots in the garden.

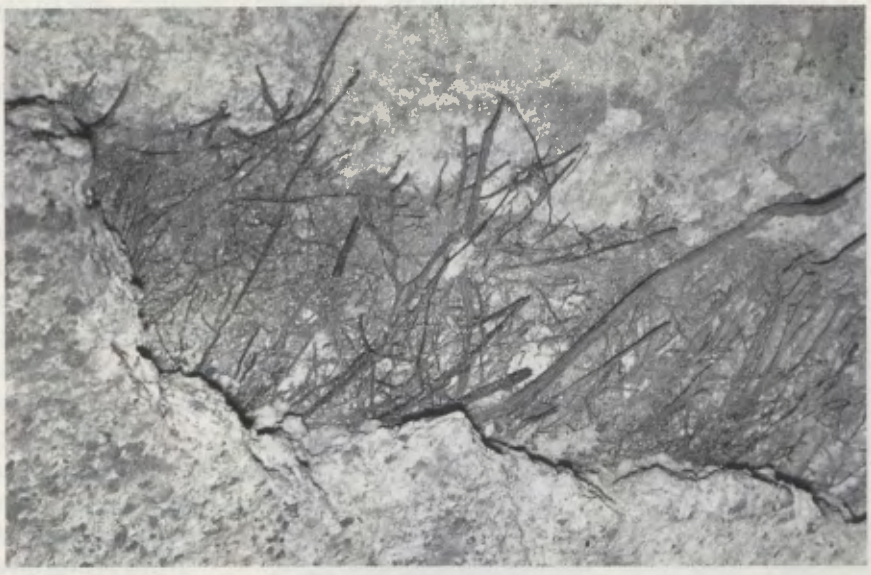


Fig.4.22

Roots of Quercus ilex expanding between wall and plaster - Domus Tiberiana, Rome, Italy.

4.1.f Animals

Birds and especially urban avifauna such as pigeons seriously damage outdoor stone, in addition to creating problems of an aesthetic nature (Fig. 4.23, p. 84). Their excrement (guano) contains acids (uric, phosphoric, nitric, etc.), which react with stone with corrosive effects. The trampling and pushing of birds are harmful to substrates with poor cohesion. Indirect damage is caused by the contribution of organic substances that serve as a nutritive substrate for heterotrophic microflora (bacteria, actinomycetes and fungi) (Bassi and Chiatante, 1976). Nitrophilous flora is favored and develops on the highest or uppermost parts or on horizontal surfaces where the deposition of bird excrement is greatest (Nimis et al., 1987).

Lightfugal fauna, such as bats, can also deteriorate subterranean environments (caves and tombs) by the accumulation of blackish excrement (chiefly composed of urea as a nitrogen compound) and their clinging to the vaults during the day (Fig. 4.24, p. 85).

The grazing of sheep and goats or other animals can also injure walls and floors in archaeological areas.

In the case of submerged historical monuments, the role of stone borers such as molluscs (*Pholas* and *Petricola*), mussels (*Mytilus*), clams (*Lithophaga*) and sea urchins (*Echinus* and *Eucidaris*) must be stressed. Boring, to a depth as great as 10-15 cm, is achieved by the mechanical action of shells, tooth-like structures and by the chemical action of secreted acids (Pearson, 1987).

A complex ecosystem of insects and molluscs, especially spiders and snails, is present on stone monuments without apparent deteriorative effect. They live by eating algae and lichens, exhibiting a micrograzing activity, and take shelter in fissures and cavities of the surfaces under adverse conditions. Snails are sometimes able to excavate cavities in the stone, creating large holes (Fig. 4.25) (Danin, 1986b).

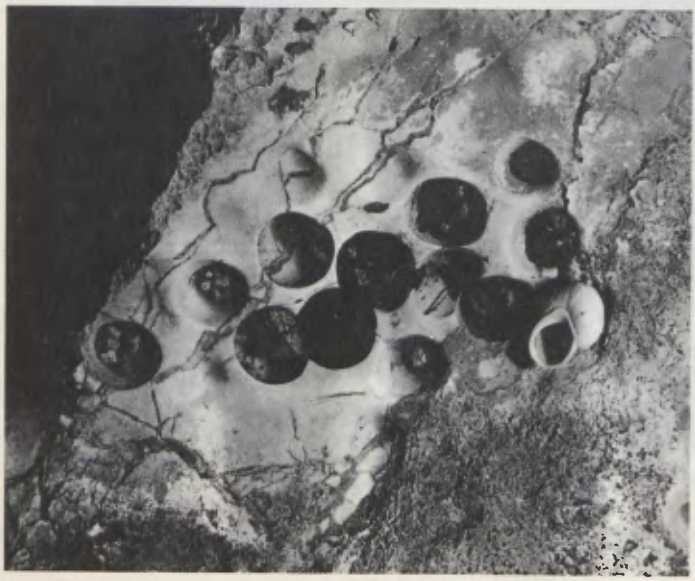


Fig.4.25

Circular holes (2-3 cm in diameter and 2-4 cm in depth) formed by land snails in limestone - Negev Desert, Israel (A. Danin, Department of ESE, the Hebrew University, Jerusalem).

4.2 OTHER INORGANIC MATERIALS

4.2.1 Glass

The deterioration of glass is due to numerous factors, depending both on the characteristics of the glass and on external conditions. Chemical attacks by water, carbon dioxide and atmospheric pollution are well known (Newton, 1982). Different kinds of decay can be observed: pits, which can increase in number and size and join together to form larger holes, opacification of the surface and formation of corrosion products that constitute a weathering crust (Perez y Yorba et al., 1980). Microorganisms as destructive agents of glass have been recently considered, but less studied than other factors.

The presence of bacteria, algae and fungi on glass is important above all in the alteration of the internal face of church windows (Prod'Homme, 1965; Winter, 1965; Bettembourg, 1976; Tennent, 1981). In this case, the pits are created by the action of microorganisms. These holes are different from those on the external face, and they develop from a central point of attack towards the periphery in concentric zones. Biological corrosion is accompanied by opacification of large black spots within the glass. The blackening of waterlogged glass is also of microbial origin: it is due, in fact, to the deposition of ferrous sulfide (Newton and Davison, 1989). Iron bacteria and sulfur bacteria have been hypothesized to play a role respectively in the metabolization of manganese and of sulfur. It has been demonstrated that fungi can etch a line when fungal hyphae traverse a polished glass surface (e.g., the lens in binoculars). The "weathering crust" of glasses is frequently composed of calcium oxalate. Its formation can be attributed to the action of oxalic acid excreted by bacteria, fungi and lichens or to ancient treatments with natural substances containing oxalic acid or with organic materials capable of transforming into oxalates.

The first record of lichens growing on window glass was in 1831, but the identification of lichens on the stained-glass windows of French cathedrals of the twelfth to the sixteenth centuries was permitted by the disassembly of glasses before and after the First World War. In the 1920s, Mellor (1924) and Fry (1924) studied respectively the biochemical and biophysical weathering caused by lichens. The lichen flora of windows is not specialized but composed of ubiquitarian species growing also on stone, often with a crustose thallus. The three most common species identified were *Diploicia canescens, Pertusaria leucosora* and *Lepraria flava*. Glass covered by lichens becomes opaque and iridescent and the surface is pitted by holes up to 6 mm in depth and 5 mm in diameter. Lichens are also active on the lead frames joining the glass pieces, and in the regions near lead the lichen corrosion is greater, perhaps owing to the increase of water retention. Lichens corrode glass very slowly. The chemical action is due to water retention in the thallus, to an increase of carbon dioxide produced by respiration and to chelating agents produced during metabolism; some chelating agents can extract lead from glass. The physical action is due to expansion and retention of the thallus and then of attachment organs depending on variations in water content. This process is illustrated in Fig. 4.26. In addition to their direct action, fungi, algae and lichens favor the maintenance of humidity on glass surfaces.

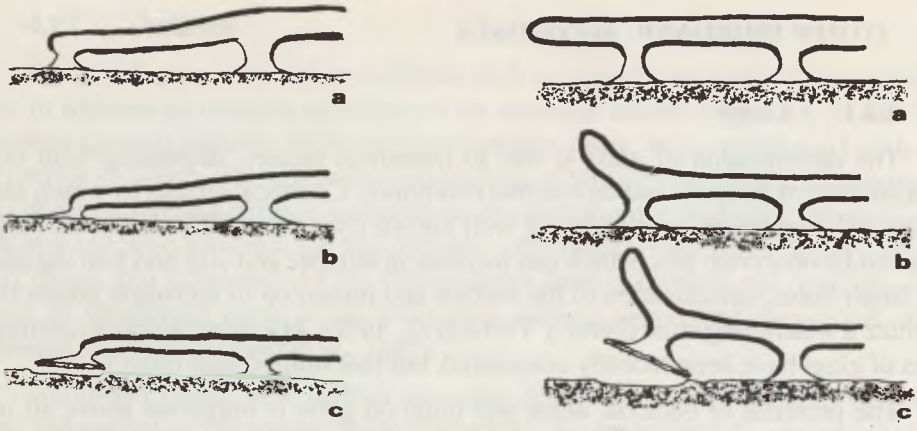


Fig.4.26

Schematic illustration of the mechanical action exerted by foliose lichen thalli with rhizines located at the edges (those at left) or further inside (those at right). a: moist conditions; b and c: progressive stages of dessication (from Fry, 1924).

4.2.2 Metals

The corrosion of metals involves two principal phenomena: dry corrosion and wet corrosion. Dry corrosion is due to the direct reaction of a metal with a chemical (e.g., oxygen, carbon dioxide, hydrogen sulfide, etc.). Wet corrosion occurs in an aqueous environment (with water or humidity) and is essentially due to an electrochemical phenomenon (Stambolov, 1985). Between the points of metals with imperfections, some differences in potential are formed, causing a current to pass through the liquid. The metal goes into solution in the anodic zone and hydrogen ions are formed in the cathodic zone (Fig. 4.27). All substances or mechanisms utilizing cathodic hydrogen depolarize the system, and corrosion starts again.

It has been demonstrated that microorganisms can cause corrosion of metals but it is difficult to separate microbial corrosion from purely electrochemical effects. In fact, it

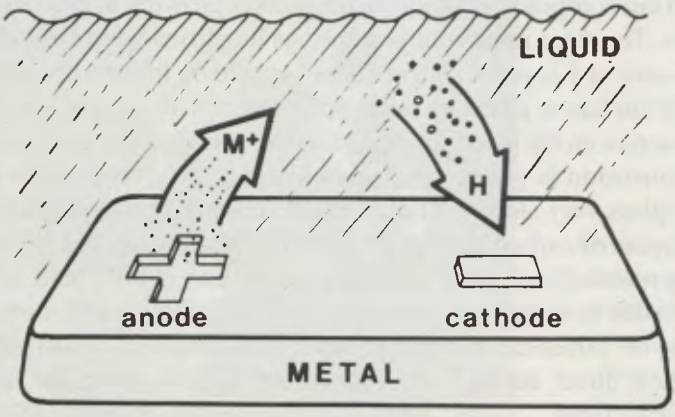


Fig.4.27 *General mechanism of wet corrosion of metals.*

is very difficult to reproduce natural environments in the laboratory, given their continuous changes of physical, chemical and biological parameters.

Microbial corrosion occurs through different mechanisms: (a) release of metabolic products; (b) formation of differential aeration and concentration cells; (c) cathodic depolarization; (d) breakdown of protective films; and (e) utilization of corrosion inhibitors (Allsopp and Seal, 1986; Iverson, 1968). These will be discussed below. In nature, microbial corrosion probably occurs as a result of different mechanisms together, performed by various microorganisms. In all these processes, the role of microbial exopolymers seems to be very important (Ford et al., 1988). In fact, they are able to bind specific metal ions, which induces an irreversible adhesion to metal surfaces. More research is necessary, however, to clarify the role of microorganisms in the corrosion of metals and alloys.

(a) **Release of metabolic products**

Microorganisms produce many acidic products (intermediate substances formed during synthesis or respiration) that are able to corrode and degrade metals. Organic acids (such as oxalic, citric, succinic, fumaric, gluconic, ketoglutaric) are produced by bacteria and fungi and are very effective in causing corrosion of metals. Concentrations of 1,000 ppm of organic acids appear to be necessary to have any detectable corrosion occur (Calderon et al., 1968). Organic acid corrosion plays a more important role in pitting. In laboratory testing, enzymes (such as catalase, hexokinase, hyaluronidase and lactase) were found to be less active than organic acids. Under aerobic conditions, the sulfur-oxidizing bacteria produce sulfuric acid which is very corrosive to metals. Elemental sulfur, hydrogen sulfide, mercaptans and ammonia, produced by many microorganisms, can cause corrosion. The production of oxygen by microscopic algae growing in the presence of light could also increase corrosion (Iverson, 1968).

(b) **Formation of differential aeration and concentration cells**

The growth of a microbial mass on a metal surface causes an oxygen gradient: the concentration of oxygen is lower in the center of the colony (anodic area) and higher at the edges (cathodic areas). The metal goes into solution at the anodic area (Fig. 4.28).

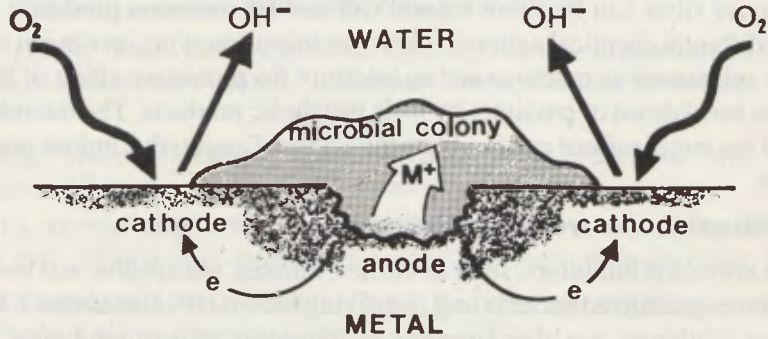


Fig.4.28

Corrosion of metal by microorganisms due to the formation of differential aeration cells in an aqueous environment.

The iron bacteria (*Sphaerotilus, Crenothrix, Leptothrix* and *Gallionella*) seem to corrode metals with this mechanism. During the process, tubercles and, beneath these, pits are formed. The presence of microorganisms on metal surfaces can also produce chemical concentration cells changing the electrolyte beneath and around the living mass.

In addition to bacteria, fungi, algae, protozoa and bryozoa also establish and maintain differential effects.

(c) **Cathodic depolarization**

The sulfate-reducing bacteria (anaerobic and heterotrophic) are able to utilize molecular hydrogen formed at the cathode by means of the enzyme hydrogenase. The removal of hydrogen is coupled to the reduction of sulfate to sulfide. The reactions are as follows:

$$8\,H_2O = 8OH^- + 8H^+$$

$$4\,Fe = 4\,Fe^{2+}\,8\,e^-\ (anode)$$

$$8\,H^+ + 8\,e^- = 8\,H\ (cathode)$$

$$SO_4{}^{2-} + 8\,H = S^{2-} + 4\,H_2\ (cathodic\ depolarization)$$

$$Fe^{2+} + S^{2-} = FeS\ (corrosion\ products)$$

$$3\,Fe^{2+} + 6\,OH^- = 3\,Fe\,(OH)_2\ (corrosion\ products)$$

The overall reaction is:

$$4\,Fe + SO_4{}^{2-} + 4\,H_2O = FeS + 3\,Fe\,(OH)_2 + 2\,OH^-$$

The ferrous sulfide thus produced is extremely corrosive to ferrous metals. The effect of sulfides can also explain pits observed when sulfate-reducing bacteria are present or when produced by other microorganisms (Videla, 1988). According to some authors (Iverson, 1968), and contrary to what has been postulated in the past, cathodic depolarization seems not to be necessarily coupled with the reduction of sulfates. In fact, the electron acceptor may be not only sulfate but also, or more probably, phosphate. Theoretically, any organism capable of utilizing hydrogen should produce a cathodic depolarization.

(d) **Breakdown of protective films**

Protective films can be either natural (formed by corrosion products) or applied (coatings of different chemical natures). Microorganisms growing on a metal surface can utilize these substances as nutrients and so interrupt the protective effect of films. They can cause the breakdown of passivity by their metabolic products. The microbial depassivization of the metal surface can facilitate the action of aggressive anions present in the environment.

(e) **Utilization of corrosion inhibitors**

Some corrosion inhibitors, such as nitrites, nitrates, phosphates and benzoate, are utilized by some specialized bacteria (e.g., nitrifying bacteria oxidize nitrites). Sometimes the corrosion inhibitors can also function as microbial growth inhibitors (e.g., zinc chromate and zinc borate), and the higher durability of coatings can be due to their antimicrobial effect (Stranger-Johannessen, 1988).

REFERENCES

AGAROSSI, G., R. FERRARI and M. MONTE (1984). "The Basilica of St. Clement in Rome: studies on biodeterioration," *Proc. Symp. "Scientific Methodologies Applied to Works of Art", Florence*. 52-56.

ALBERTANO, P., and M. GRILLI CAIOLA (1988). "A hypogean algal association." *Proc. 31 Int. Symp. IAVS "Spontaneous Vegetation in Settlements," Frascati*, in press.

ALLSOPP, D., and K.J.SEAL (1986). *Introduction to Biodeterioration*. London: Edward Arnold.

——— and D.R.DRAYTON (1975). "The higher plants as deteriogens," *Proc. 3rd Int. Biod. Symp. Kingston, Rhode Island*. 357-364.

ASCASO, C., J. GALVAN and C. RODRIGUEZ-PASCAL (1982). "The weathering of calcareous rocks by lichens," *Pedobiologia*, 24. 219-229.

——— (1984). "Structural aspects of lichens invading their substrata," *Surface Physiology of Lichens*, ed. C. Vicente. Madrid: Universidad Complutense. 87-112.

ATLAS, R.M., A.N. CHOWDHURY and K. LAL GAURI (1988). "Microbial calcification of gypsum-rock and sulfated marble," *Studies in Conservation*, 33. 149-153.

BARCELLONA VERO, L., M. MONTE SILA and A. SILVERI (1973). "Influenza dell'azione dei solfobatteri nei processi di alterazione dei materiali lapidei," *Problemi di Conservazione*. Bologna: Edizioni Compositori. 439-451.

BASSI, M., and D. CHIATANTE (1976). "The role of pigeon excrement in stone biodeterioration," *Int. Biodet. Bull.*, 12 (3) 73-79.

BETTEMBOURG, J.M. (1976). "Composition et altération des verres de vitraux anciens," *Verres et Réfract.*, 30. 36-42.

BOCK, E., W. SAND, M. MEINCKE, B. WOLTERS, B. AHLERS, C. MEYER and F. SAMELUK (1988). "Biologically induced corrosion of natural stones - Strong contamination on monuments with nitrifying organisms," *Biodeterioration 7*, eds. D.R. Houghton, R.N. Smith and H.O.W. Eggins. London and New York: Elsevier Applied Science. 436-440.

CALDERON, O.H., E.E. STAFFELDT and C.B. COLEMAN (1968). "Metal-organic acid corrosion and some mechanisms associated with these corrosion processes," *Biodeterioration of Materials*, ed. A.H. Walters. Amsterdam: Elsevier Publishing. 356-363.

CANEVA, G. (1985). "Ruolo della vegetazione nella degradazione di murature ed intonaci," *Atti Convegno Scienza e Beni Culturali "L'Intonaco: Storia, Cultura e Tecnologia," Bressanone*. 199-209.

——— (1988). "Tree roots and hypogeans conservation," *Proc. 31 Int. Symp. IAVS "Spontaneous Vegetation and Settlements," Frascati*, in press.

——— and A. ALTIERI (1988). "Biochemical mechanisms of stone weathering induced by plant growth," *Proc. VI Int. Congr. Deterioration and Conservation of Stone, Torun*. 32-44.

——— and A. ROCCARDI (1991). "Harmful flora in the conservation of Roman monuments," *Int. Congr. Biodet. Cultural Property, Lucknow, India*. 212-218.

CHIARI, G., S. SAMPÒ and G. TORRACA (1989). "Formazione di ossalati di calcio su superfici marmoree da parte di funghi," *Int.Symp. on The Oxalate Films: Origin and Significance in the Conservation of Works of Art*. Milan: Centro C.N.R. Gino Bozza. 85-90.

COSTELLO, J.A. (1969). "The corrosion of metals by micro-organisms. A literature survey," *Int. Biodet. Bull.*, 5 (3) 101-118.

DANIN, A. (1986a). "Patterns of biogenic weathering as indicators of paleoclimates in Israel," *Proc. Royal Society of Edinburg.* 89B. 243-253.

——— (1986b). "Patterns of corrosion and abrasion induced by Mediterranean land snails on limestone rocks," *Malacol Rev.*, 19. 91-98.

———, and G. CANEVA (1990). "Deterioration of limestone walls in Jerusalem and marble monuments in Rome caused by cyanobacteria and cyanophylous lichens," *Int. Biodet. Bull.*, 26 (6) 397-417.

DEGELIUS, G. (1962). "Uber verwitterung von kalk und dolomitengestein durch algen und flechten," *Chemie im Dienst der Archaeologie Bautechnik Denkmalpflege,* ed. J.A. Hedvall. Hakam Ohlssons. Lund. 156-162.

DELVERT, J. (1963). "Recherches sur l'erosion des grès des monuments d'Angkor," *Bull. Ecol. Fran. Extreme Orient.* 453-534.

DUFF, R.B., D.M. WEBLEY and R.O. SCOTT (1963). "Solubilization of minerals and related minerals by 2-ketogluconic acid-producing bacteria," *J. Soil Science*, 95. 105-114.

ECKHARDT, F.E.W. (1985). "Solubilization, transport, and deposition of mineral cations by microorganisms efficient rock weathering agents," *The Chemistry of Weathering*, ed. J.I. Drever. Reidel Publishing Company. 161-173.

——— (1985). "Mechanisms of the microbial degradation of minerals in sandstone monuments, medieval frescoes, and plaster," *Proc. V Int. Congr. Deterioration and Conservation of Stone, Lausanne.* 643-652.

EHRLICH, H.L. (1981). *Geomicrobiology.* New York-Basel: Marcel Dekker Inc.

FISCHER, G.G. (1972). "Weed damage to materials and structures," *Int. Biodet. Bull.*, 8 (3) 101-103.

FORD, T.E., J.S. MAKI and R. MITCHELL (1988). "Involvement of bacterial exopolymers in biodeterioration of metals," *Biodeterioration* 7, eds. D.R. Houghton, R.N. Smith and H.O.W. Eggins. London and New York: Elsevier Applied Science. 378-384.

FRY, E.J. (1924). "A suggested explanation of the mechanical action of lithophytic lichens on rocks (shale)," *Annals of Botany*, 38. 175-196.

GIACOBINI, C., C. ANDREOLI, G. CASADORO, B. FUMANTI, P. LANZARA and N. RASCIO (1979). "Una caratteristica alterazione delle murature e degli intonaci." *Proc. III Int. Congr. Deterioration and Conservation of Stone, Venice.* 289-299.

———, M.A. DE CICCO, I. TIGLIE' and G. ACCARDO (1988). "Actinomycetes and biodeterioration in the field of fine art," *Biodeterioration* 7, eds. D.R. Houghton, R.N. Smith and H.O.W. Eggins. London and New York: Elsevier Applied Science. 418-423.

GOLUBIC, S. (1976). Algenvegetation der Felsen. E. Schweitzerbart'sche Werlagsbuchhandlung (Naegele u. Obermiller). Stuttgart.

———, E. FRIEDMAN and J. SCHNEIDER (1981). "The lithobiontic ecological niche, with special reference to microorganisms," *J. Sedimentary Petrology*, 51. 475-478.

HALE, M.E. (1983). *The Biology of Lichens.* London: Edward Arnold (3rd ed.).

HAWKSWORTH, D.L., and D.J. HILL (1984). *The Lichen-Forming Fungi.* Glasgow and London: Blackie.

HENDERSON, M.E.K. and R.B. DUFF (1963). "The release of metallic and silicate ions from minerals, rocks and soils by fungal activity," *J. Soil Science*, 14 (2) 236-246.

HOFFMAN, L. (1989). "Algae of terrestrial habitats," *Botanical Review*, 55 (2) 77-105.

HYVERT, G. (1966a). "Quelques Actinomycetes isolés sur les grès des monuments cambodgiens," *Revue de Mycologie*, 31 (2) 179-186.

——— (1966b). "Accumulation du fer par *Curvularia lunata* (Wakker) Boedijin," *Revue de Mycologie*, 31 (2) 173-175.

——— (1966c). "Note sur *Cladosporium herbarum* (Pers.) Link, isolé du temple de Banteay Srei," *Revue de Mycologie*, 31 (2) 176-178.

IONITA, I. (1971). "Contributions to the study of the biodeterioration of works of art and historic monuments. III. Species of fungi isolated from stone monuments," *Rev. Roum. Biol. Botanique* 16 (6) 433-436.

IVERSON, W.P. (1968). "Mechanisms of microbial corrosion," *Biodeterioration of Materials*, ed. A.H. Walters. Amsterdam: Elsevier Publishing. 28-43.

JATON, C. (1972). "Aspects microbiologiques des alterations des pierres de monuments," *1er Coll.Int. sur la deterioration des pierres en oeuvre*. La Rochelle. 149-154.

JONES, D., and M.J. WILSON (1985). "Chemical activity of lichens on mineral surfaces. A review," *Int. Biodet. Bull.*, 21 (2) 99-104.

KAUFFMAN, J. (1960). "Corrosion and protection des pierres calcaires des monuments," *Corrosion et Anticorrosion*, 8 (3) 87-95.

KELLER, N.D., and A.F. FREDERICKSON (1952). "The role of plants and colloid acids in the mechanisms of weathering," *Amer. J. Sci.*, 250. 594-608.

KOESTLER, R.J., A.E. CHAROLA, M. WYPYSKI and J.J. LEE (1985). "Microbiologically induced deterioration of dolomitic and calcitic stone as viewed by scanning electron microscopy," *Proc. V Int. Congr. Deterioration and Conservation of Stone, Lausanne*. 617-626.

———, E.D. SANTORO, J. DRUZIK, F. PREUSSER, L. KOEPP and M. DERRICK (1988). "Status report: ongoing studies of the susceptibility of stone consolidants to microbiologically induced deterioration," *Biodeterioration* 7, eds. D.R. Houghton, R.N. Smith and H.O.W. Eggins. London and New York: Elsevier Applied Science. 441-448.

KRUMBEIN, W.E. (1972). "Rôle des microorganismes dans la genèse la diagenèse et la dégradation des roches en place," *Rev. Ecol. Biol. Sol*, 3. 283-319.

——— (1983). *Microbial Geochemistry*. Oxford: Blackwell.

KUROCZKIN, J., K. BODE, K. PETERSEN and W.E. KRUMBEIN (1988). "Some physiological characteristics of fungi isolated from sandstones," *Proc. VI Int. Congr. Deterioration and Conservation of Stone, Torun*. 21-25.

LAZZARINI, L., and O. SALVADORI (1989). "A reassessment of the formation of the patina called 'scialbatura'," *Studies in Conservation*, 34. 20-26.

LE CAMPION-ALSUMARD, T. (1979). "Les Cyanophycées endolithes marines. Systématique, ultrastructure, écologie et biodestruction," *Oceanologica Acta*, 2 (2) 143-156.

LEFEVRE, M. (1974). "La 'maladie verte' de Lascaux," *Studies in Conservation*, 19. 126-156.

LEWIN, S.Z., and A.E. CHAROLA (1981). "Plant life on stone surfaces and its relation to stone conservation," *Scanning Electron Microscopy*. 563-568.

LEZNICKA, S., A. STRZELCZYK and D. WANDRYCHOWSKA (1988). "Removing of fungal stains from stone-works," *Proc. VI Int. Congr. Deterioration and Conservation of Stone, Torun.* 102-110.

LEWIS, F., E. MAY and A.F. BRAVERY (1985). "Isolation and enumeration of autotrophic and heterotrophic bacteria from decayed stone," *Proc. V Int. Congr. Deterioration and Conservation of Stone, Lausanne*. 633- 642.

MAY, E., and F.J. LEWIS (1988). "Strategies and techniques for the study of bacterial populations on decaying stonework," *Proc. VI Int. Congr. Deterioration and Conservation of Stone, Torun.* 59-70.

MEINCKE, M., B. AHLERS, T. KRAUSE-KUPSCH, E. KRIEG, C. MEYER, F. SAMELUK, W. SAND, B. WOLTERS and E. BOCK (1988). "Isolation and characterization of endolithic nitrifiers," *Proc. VI Int. Congr. Deterioration and Conservation of Stone, Torun.* 15-23.

MELLOR, E. (1924). "The Decay of window glass from the point of view of lichenous growth," *J. Soc. Glass Technol.*, 8. 182-186.

MENTLER, A., H.W. MULLER and B. SCHWAIGHOFER (1986). "Verwitterung studien an Naturbausteinen in Wiener Stadtgebiet und in Steinbruchendel Leithagebirges im Burgenland." *Mitt. Oster. Geol. Ges.*, 79. 309-325.

NEWTON, R.G. (1982). *The Deterioration and Conservation of Painted Glass. A Critical Bibliography*. British Academy and Oxford University Press, Occasional Papers, II.

———, and S. DAVISON (1989). *Conservation of Glass*. Butterworths.

NIMIS, P.L., M. MONTE and M. TRETIACH (1987). "Flora e vegetazione lichenica di aree archeologiche del Lazio," *Studia Geobotanica*, 7. 3-161.

———, D. PINNA and O. SALVADORI . *Licheni e conservazione dei monumenti.* Bologna: CLUEB, in press.

NUGARI, M.P., and G.F. PRIORI (1985). "Resistance of acrylic polymers (Paraloid B72, Primal AC33) to microorganisms. First part," *Proc. V Int. Congr. Deterioration and Conservation of Stone, Lausanne*. 685-693.

PEARSON, C., ed. (1987). *Conservation of Marine Archaeological Objects*. Butterworths.

PEREZ Y JORBA, M., J.P. DALLAS, C. BAUER, C. BAHEZRE and J.C. MARTIN (1980). "Deterioration of stained glass by atmospheric corrosion and micro-organisms," *J. Material Science,* 15. 1640-1647.

PETERSEN, K., J. KUROCZKIN, A.B. STRZELCZYK and W.E. KRUMBEIN (1988). "Distribution and effects of fungi on and in sandstones," *Biodeterioration* 7, eds. D.R. Houghton, R.N. Smith and H.O.W. Eggins. London and New York: Elsevier Applied Science. 123-128.

PETUSHKOVA, J.P., and N.N. LYALIKOVA (1985). "Microbiological degradation of lead-containing pigments in mural paintings," *Studies in Conservation,* 31. 65-69.

PIETRINI, A.M., S. RICCI and M.R. GIULIANI (1986). "Domus aurea — Ricerca sulla microflora algale e sui trattamenti algicidi nell'ambiente n.75," *Manutenzione e Conservazione del Costruito fra Tradizione ed Innovazione. Atti Convegno Bressanone*. Padova: Libreria Progetto Editore. 694-696.

POCHON, J., and O. COPPIER (1950). "Role des bacteries sulfato-reductrices dans l'alteration biologique des pierres des monuments," *C.R. de l'Academie des Sciences.* 1584-1585.

———, and C. JATON (1968). "Facteurs biologiques de l'altération des pierres," *Biodeterioration of Materials,* eds. H. Walters and J.J. Elphic. London: Elsevier. 258-268.

PROD'HOMME, M. (1965). "Action des microrganismes sur les surfaces vitreuses," *Proc. 8th Int. Congr. on Glass, Brussels*. Paper N°17.

PURVIS, O.W. (1984). "The occurence of copper oxalate in lichens growing on copper sulphide-bearing rocks in Scandinavia," *Lichenologist*, 16 (2) 197-204.

RICCI, S., A.M. PIETRINI and M.R. GIULIANI (1985). "Il ruolo delle microalghe nel degrado biologico degli intonaci," *L'intonaco: Storia, Cultura e Tecnologia. Atti Convegno Bressanone*. Padova: Libreria Progetto Editore. 53-61.

———, A.M. PIETRINI and M.R. GIULIANI (1988). "Contribution to the knowledge of the algal flora of archaeological remains: the Foro Romano," *Proc. 31 Int. Symp. IAVS "Spontaneous Vegetation in Settlements, Frascati,* in press.

SAIZ-JIMENEZ, C., J. GARCIA-ROWE, M.A. GARCIA DEL CURA, J.J. ORTEGA-CALVO, E. ROEKENS and R. VAN GRIEKEN (1990). "Endolithic cyanobacteria in Maastricht limestone," *The Science of the Total Environment* 94. 209-220.

SALVADORI, O. and M.P. NUGARI (1988). "The effect of microbial growth on synthetic polymers used on works of art," *Biodeterioration* 7, eds. D.R. Houghton, R.N. Smith and H.O.W. Eggins. London and New York: Elsevier Applied Science. 424-427.

———, and L. LAZZARINI (1989)." Lichens deterioration on stones of Aquileian monuments," *Botanika Chronika*, in press.

SEAWARD, M.R.D. (1988). "Lichen damage to ancient monuments: a case study," *Lichenologist*, 10 (3) 291-295.

——— and C. GIACOBINI (1988). "Lichen-induced biodeterioration of Italian monuments, frescoes and other archaeological materials," *Studia Geobotanica*, 8. 3-11.

——— and C. GIACOBINI (1989). "Oxalate encrustation by the lichen *Dirina massiliensis* f. *sorediata* and its role in the deterioration of works of art," *Proc. Symp. "Le Pellicole ad Ossalato: Origine e Significato nella Conservazione delle Opere d'Arte," Milan.* 215-129.

——— C. GIACOBINI, M.R. GIULIANI and A. ROCCARDI (1989). "The role of lichens in the biodeterioration of ancient monuments with particular reference to central Italy," *Int. Biodet. Bull.*, 25. 49-55.

STAMBOLOV, T. (1985). *The Corrosion and Conservation of Metallic Antiquities and Works of Art.* CL Publications.

STRANGER-JOHANNESSEN, M. (1988). "The antimicrobial effect of pigments in corrosion protective paints." *Biodeterioration 7*, eds. D.R. Houghton, R.N. Smith and H.O.W. Eggins. London and New York: Elsevier Applied Science. 372-277.

TENNENT, N.H. (1981). "Fungal growth on medieval glass," *J. Br. Soc. Master Glass Painters*, 17 64-68.

TIANO, P., R. BIANCHI, G. GARGANI and S. VANNUCCI (1975). "Research on the presence of sulphur-cycle bacteria in the stone of some historical buildings in Florence," *Plant and Soil*, 43. 211-217.

TOMASELLI, L., M.C. MARGHERI and G. FLORENZANO (1979). "Indagine sperimentale sul ruolo dei cianobatteri e delle microalghe nel deterioramento dei monumenti ed affreschi," *Proc. III Int. Congr. Deterioration and Conservation of Stone, Venice*. 313-325.

VIDELA, H.A. (1988). "Electrochemical interpretation of the role of microorganisms in corrosion," *Biodeterioration* 7", eds. D.R. Houghton, R.N. Smith and H.O.W. Eggins. London and New York: Elsevier Applied Science. 359-371.

WEBLEY, D.M., M.E.K. HENDERSON and I.F. TAYLOR (1963). "The microbiology of rocks and weathered stone," *J. Soil Science*, 14 (1) 102-112.

WEE, Y.C., and K.B. LEE (1980). "Proliferation of algae on surfaces of buildings in Singapore," *Int. Biodet. Bull.*, 16 (4) 113-117.

WILLIAMS, D.E., and N.T. COLEMAN (1950). "Cation exchange properties of plant root surfaces," *Plant and Soil II*. 243-256.

WILLIAMS, M.E., and E.D. RUDOLPH (1974). "The role of lichens and associated fungi in the chemical weathering of rock," *Mycologia*, 66. 648-660.

WILSON, M.J., D. JONES and W.J. McHARDY (1981). "The weathering of serpentinite by *Lecanora atra*," *Lichenologist*, 13. 167-176.

WINKLER, E.M. (1975). "Stone decay by plants and animals," *Stone: Properties, Durabilities in Man's Environment*. Springer Verlag. 154-163.

WINTER, A. (1965). "Altération des surfaces des verres anciens," *Proc. 8th Int. Congr. on Glass, Brussels*. Paper N°229.

WOLTERS, B., W. SAND, B. AHLERS, F. SAMELUCK, M. MEINCKE, C. MEYER, T. KRAUSE-KUPSCH and E. BOCK (1988). "Nitrification: the main source for nitrate deposition in building stones," *Proc. VI Int. Congr. Deterioration and Conservation of Stone, Torun*. 24-31.

Chapter 5

METHODS TO PREVENT BIODETERIORATION

5.1 GENERAL CONSIDERATIONS

Prevention includes all activities aimed at avoiding biological attack against a work of art. Objects of cultural value are subject to biological attack and consequently to biodeterioration when the physico-chemical conditions of the substrate (object) and the surrounding environment are compatible with the genetic character of an organism or a microorganism (Hopton, 1988). As a result, the conservation of artistic materials is possible if this situation can be kept from arising.

Prevention methods, also named "*indirect methods,*" inhibit or slow down biological growth by modifying, where possible, the environmental conditions and physico-chemical parameters of the substrate so that they become unfavorable to biological spread.

The fact that biological elements have a strong relationship to and dependence on the environment explains why the most effective and reliable methods for eliminating undesirable growth are those that operate on the causes, i.e. the "limiting factors" (¶1.2). These causal factors cannot always be changed because while it is feasible to influence environmental conditions in a confined area (e.g., a museum), it is considerably more difficult in the field (e.g., outdoor monuments, archaeological sites).

The parameters that can theoretically be modified are humidity (RH and water content of materials), temperature and light, whereas nutritive factors, if components of a work of art, cannot be modified without damaging the nature of the object itself. In contrast, nutritive factors can be reduced if they are not related to the work of art (dust, deposits of various kinds, such as pigeon droppings, and unsuitable restoration materials, especially those of an organic nature).

Different types of action are possible depending on whether the environment is indoors or outdoors.

5.2 INDOOR ENVIRONMENTS

In a museum, library, storage room, church, etc., the principal factors favoring the development of biological agents are as follows:

- high relative humidity
- high temperature
- poor ventilation

- strong lighting
- enrichment of the substrate by organic materials (dust, dirt, some restoration materials, etc.)

All these factors should be controlled or modified with routine maintenance and simple or even complex methods, such as complete air-conditioning systems.

High humidity is the main factor causing biological attack. Ancient materials become damp from various sources; some of the causes can be prevented, others are part of the permanent system of factors and are generally impossible to change. In general, the RH should be as low as possible, without falling to such a low level that it would be dangerous for many materials. A reduction of water content modifies the mechanical characteristics of materials: for example, below 50% RH, paper becomes less flexible and wooden panel paintings may shrink. Automatically controlled humidifying systems can be useful in this case. In particular, in storage areas for organic materials that are liable to attack by heterotrophic microorganisms, the RH should not be allowed to rise above 65%.

A high *temperature* is also undesirable because it favors the growth of the main biodeteriogen microorganisms and insects. Temperatures should be kept within a range of 16-20°C and under 20°C in any event. It is necessary to remember that a low temperature can reduce biological growth but not discourage it completely, given the range of tolerance of many microbial species. Therefore, temperature is usually not a limiting factor (¶1.2).

Moreover, where the RH is high, a drop in temperature gives rise to condensation of water, especially on cold surfaces. Proper air circulation and ventilation help to avoid this phenomenon. Paintings should not be hung on damp or outside walls, which are subject to condensation, and never over or near radiators or other heat sources. Sufficient circulation of air should be ensured between the back of a painting and the wall. The same approach should be adopted for showcases and library shelves.

The best conditions are those of atmospheric stability in which a constant low temperature is maintained.

It is necessary to remember that temperature and RH are strictly linked in influencing biological growth. Thus, in environments where works of art are conserved, a slight increase of temperature may be accepted if the RH is below 65%; vice versa, a slight increase of RH may be accepted if the temperature is near 20°C.

The limits of temperature and RH values must be strictly controlled where works of art composed of hygroscopic materials (paper, parchment or wood) are kept. The moisture content of these objects keeps equilibrium with environmental parameters and their water content can easily increase, becoming favorable to microbial attack. For example, at an RH of 62-65%, paper reaches a 7-8% moisture content, a condition favorable to growth of some fungi (¶3.1.3).

Moreover, in environments frequented by visitors, one should remember not only that they affect the temperature and RH, but also that they themselves require comfortable microclimatic conditions (Fig. 5.1).

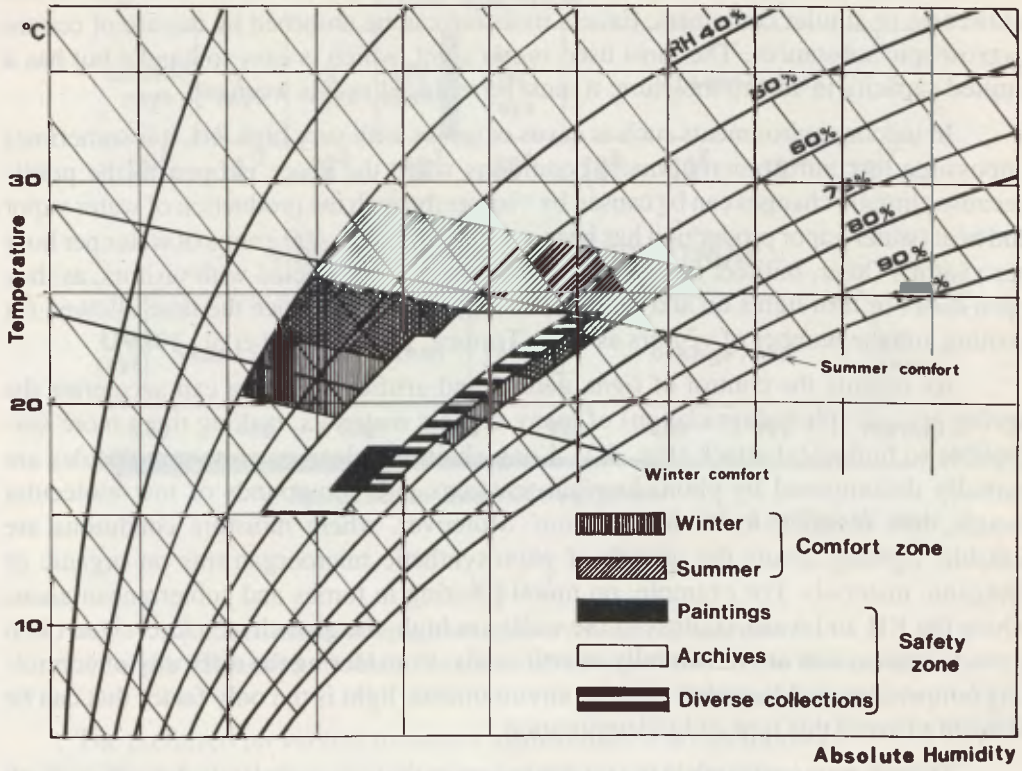


Fig.5.1

Psychrometric diagram (from Plenderleith and Philippot, 1960).

The generally accepted limits of temperature are 18-20°C and of RH constant between 50-65%, with some variations in relation to the chemical character of the objects to preserve (Plenderleith and Philippot, 1960; Gallo, 1985; Kuhn, 1986; Massa and Caneva, 1988).

Depending on the cause of excessive dampness, the following types of intervention are possible indoors: isolation of foundations in the case of rising damp; repair of roofs and gutters in the case of water infiltration from the ceiling; an efficient water drainage system.

It is possible to control excess temperatures by air-conditioning. In the tropics, thick protective walls and roofs or outside corridors parallel to exhibition rooms can be an additional solution in new buildings. In contrast, controlled heating is essential in cold climates. A complete (temperature or RH) air conditioning system is an ideal solution but is expensive to install, and sometimes an unforeseen breakdown of the system can cause even worse damage, producing thermo-hygrometric shock to sensitive materials like paintings on wooden board. Climate-regulating equipment should be checked frequently and readings of temperature and RH taken regularly with thermohygrometers.

In museums for small-sized objects, localized control can be arranged within showcases or similar containers. Excess moisture can be absorbed by the use of certain hygroscopic substances. The most used is silica gel, which is easy to handle but has a limited capacity to absorb moisture; it must be replaced as it is worn out.

In indoor environments such as caves or tombs with very high RH, it is sometimes impossible to control microclimatic conditions when the space is open to the public because climatic changes can be caused by visitors through the production of water vapor and heat (water vapor production has been evaluated at 80 to 400 grams of water per hour per visitor). Other, indirect undesirable effects are also connected with visitors, as they open doors or turn lights on and off. Thus it may be useful reduce the time allowed for visiting and the number of visitors as well (Torraca, 1983; Nugari et al., 1989).

As regards the control of *light*, natural and artificial lighting can accelerate the ageing process (photodegradation) of many organic materials, making them more susceptible to biological attack (Fig. 5.2). Long-chain cellulose or protein molecules are partially decomposed by photochemical reactions into compounds of low molecular weight, less resistant to biodeterioration. Moreover, where moisture conditions are suitable, lighting favors the growth of photosynthetic microorganisms on organic or inorganic materials. For example, on mural painting in tombs and subterranean areas, where the RH and water content of the walls are high, the growth of micro-algae often spreads in areas that are lit naturally or artificially. Considering the difficulty of controlling temperature and humidity in these environments, light is the only factor that can be reduced to avoid this type of biodeterioration.

There is no wavelength in the visible spectrum that can completely deter the growth of photosynthetic microorganisms or organisms, but some wavelengths are less favorable to them than others (Fig. 1.12). The optimal absorption of various species varies, and the presence of different species in a certain environment is a function of the quality, quantity and duration of illuminations (Pietrini et al., 1986; Serra Lerchenthal, 1986; Caneva and Salvadori, 1988). Nevertheless, darkness does not inhibit the growth and development of most insects and some microorganisms (fungi and Actinomycetes).

Intervention methods must always consider the characteristics of the radiation, the materials exposed and the microclimatic condition of their exposure. The ways to reduce light damage are as follows:

- reduction of the time of exposure to light and intensity of radiation
- use of filters for blocking UV radiation
- reduction of emissions of the red and infrared spectrum

For objects that are especially sensitive to light (textiles, paper, paintings on paper, etc.), the maximum illumination recommended is 50 lux (Brommelle, 1968; Gallo, 1985; Kuhn, 1986). Direct sunlight must be entirely excluded by the use of screens and blinds.

Preventive measures in indoor environments based on the control of microclimatic conditions are not always effective in preventing every kind of damaging biological agent. Insects, for example, show a great tolerance to unfavorable conditions of RH and temperature.

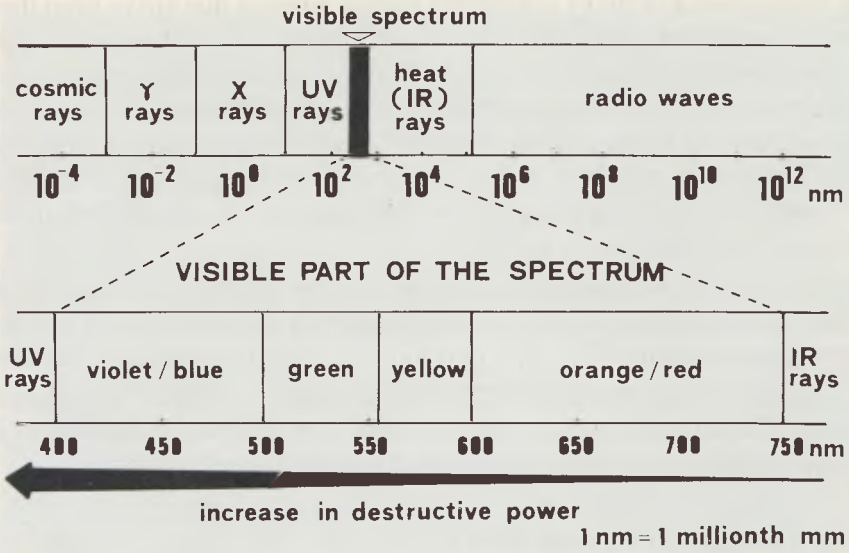


Fig.5.2

Electromagnetic spectrum: the wavelength of radiations is inversely proportional to their damaging effect on materials (from Kuhn, 1986).

The preferred preventive measures against insects are as follows:

- avoid placing infested objects near those that are not infested
- fumigate all newly acquired materials that show signs of infestation
- regularly inspect wood, paper and all materials subject to insect attack, especially in the early summer, to detect and combat possible attack at an early stage
- regularly clean and treat the environment, spraying the walls, ceilings and floors of rooms with contact insecticides when the presence of insects is suspected (Gallo, 1985; Kuhn, 1986)

Some chemical substances can be used to protect organic materials from biological attack, especially by insects, but the effectiveness of these products is limited in time. The substances used to repel insects are called *repellents* and their application is the most important preventive method against insects. Naphthalene, camphor and p-dichlorobenzene are examples of these substances (Hueck, 1972; Zaitseva, 1987). In the past, a number of natural products were used for this purpose, especially in libraries, e.g., flowers of *Chrysanthemum* and *Artemisia.*

The control of termites is particularly difficult, and it is even possible not to detect evidence of a termite attack until the work of art is completely destroyed. Especially in the tropics where termites are very common, particular measures have to be adopted: proper design and construction of buildings where works of art will be kept, use of chemical repellents, frequent inspection to detect the runways.

Yet, even these methods are not always successful. The construction of buildings using concrete rafts or pillars capped with metal skirts or incorporating a concrete slab

between foundations and floors is effective against termites that arrive from the ground but ineffective against winged adults. Moreover, in old buildings, these kinds of solutions cannot be adopted. In such cases, chemical barriers may be adopted, poisoning the soil near foundations. This method, however, becomes ineffective after some years and produces problems of environmental pollution. A careful inspection to detect runways, frass or pellets as soon as they appear and tapping the wooden objects to find hollows is sometimes the only way to prevent irretrievable damage (Hueck, 1972; Feilden, 1982; Allsopp and Seal, 1986).

Cleaning methods in general can also be useful in limiting and controlling biological growth. These are indirect methods because they remove organic and inorganic substances deposited on the surfaces of objects (substances that represent nutritive factors for many organisms or microorganisms) and thus reduce susceptibility to biodeterioration of materials. Cleaning also removes deposits of forms of biological diffusion (spores, hyphae, insect eggs, etc.), which are sources of infection or infestation.

5.3 OUTDOOR ENVIRONMENTS

Outdoor interventions on humidity, temperature or light are very limited and not always feasible, but some of them can at least help to reduce biological growth.

Under conditions of high humidity where building works are impossible, protective covers can reduce excessive dampness or water stagnation, for example protection from rainfall in archaeological sites.

Protective or consolidant treatments of stone can also be useful in reducing its porosity and increasing water repellency. The substances to use for this purpose must be carefully chosen because the composition of these substances can represent a carbon source for some heterotrophic microorganisms and as a result will favor a biological attack instead of preventing it (Fig. 5.3, p. 85) (Salvadori and Nugari, 1987).

Complete thermal control is impossible in open spaces. Measures can include simple sunscreens and other shading methods, which should be carefully evaluated (e.g., planting trees). Screens can also be used to control light, but they do not assure complete elimination of photosynthetic microorganisms or of the growth of organisms, especially where there is stagnant water.

In external interventions, it is necessary to consider that the colonization of a building starts where moisture and organic debris accumulate and is related to stone texture and porosity. The stone surfaces are usually first colonized by bacteria, algae and lichens, followed by mosses, which hold water and favor a secondary colonization of higher plants with a corresponding increase of damage.

Routine maintenance and periodic controls are the principal and sometimes the only way to prevent biological attack in an outdoor environment.

A particular kind of problem is prevention of damage to monuments and historic buildings from birds, especially pigeons. Netting, wires, black nylon thread or spikes to prevent their roosting and nesting are the most commonly used (Fig. 5.4); these methods are unsightly and can create aesthetic problems if not carefully chosen. In recent years,

Fig.5.4 *Anti-pigeon spikes, Venice, Italy.*

anti-perching gels have been used with some success. These are sticky repellents to apply on building ledges but they can stain stone. Recently, new repellent gels have been proposed. They remain soft and make the birds insecure, preventing them from perching. These gels are not sticky and do not stain. Systems of high-voltage wires have also been tested but they are more difficult to keep in operation, due to short-circuit problems (Allsopp and Seal, 1986; Feilden, 1982). The ingress of birds into historic buildings should also be controlled by reducing the possible points of access.

Sometimes biological growth (especially of plants) represents a prevention and protection measure in archaeological sites or in external environments, instead of a source of damage (Fig. 5.5, p. 85). On the basis of an accurate knowledge of correlations between plants and environmental factors, it is possible to use vegetation to solve conservation problems. For example, by introducing suitably-chosen vegetation, one can achieve the following effects:

- lower the water-table by using plants as "biological pumps"
- modify the microclimate by minimizing evaporation or irradiation with sun-screen plants
- reduce wind erosion by using trees as wind-breaks
- reduce air salinity
- reduce pollution

The choice of plants to use for these purposes must be made carefully, in order to optimize results and minimize risks related to the destructive effects of their root apparatus and the colonization of masonry structures (Fosberg, 1980; De Marco et al, 1990).

REFERENCES

ALLSOPP, D., and K.J. SEAL (1986). *Introduction to Biodeterioration*. London: Edward Arnold.

BAYNES-COPE, A.D., and D. ALLSOPP (1984). "Observation on mould in small libraries," *Biodeterioration 6. Proceedings of the Sixth International Biodeterioration Symposium*, eds. S. Barry and D.R. Houghton, Washington, DC: CAB International. 382-385.

BROMMELLE, N.S. (1968). "Lighting, air-conditioning, exhibition, storage, handling and packing," *The Conservation of Cultural Property*. Paris: Unesco. 291-301.

CANEVA, G., and O. SALVADORI (1988). "The deterioration and conservation of stone," *Studies and Documents on the Cultural Heritage 16*, ed. R. Pieper. Paris: Unesco. 203-205.

COREMANS. P. (1968). "Climate and microclimate," *The Conservation of Cultural Property*. Paris: Unesco. 27-39.

DE MARCO, G., G. CANEVA and A. DINELLI (1990). "Geobotanical foundations for a protection project in the Moenjodaro archaeological area," *Prospezione Archeologiche, Quaderni 1*. 115-120.

FEILDEN, B.M. (1982). "Causes of decay in materials and structure," *Conservation of Historic Buildings*. London: Butterworths Scientific. 89-182.

FOSBERG, F.R. (1980). "The plant ecosystem for Moenjodaro," *Unesco Technical Report RP/1977-78/4.121.6, FMR/CC/CH/80/189,15*. Paris: Unesco.

GALLO, F. (1985). *Biological Factors in Deterioration of Paper*. Rome: ICCROM.

HOPTON, J.W. (1988). "Physical conditions and microbial growth: some implications for biodeterioration," *Biodeterioration 7*, eds. D.R. Houghton, R.N. Smith and H.O.W. Eggins. Elsevier Applied Science. 511-516.

HUECK, H.J. (1972). "Textiles pests and their control," *Textiles Conservation*. London: J.E. Leene. 76-97.

KUHN, H. (1986). *Conservation of works of art and antiquities*. Vol. 1. London: Butterworths.

MASSA, S., and G. CANEVA (1988). "Analisi delle condizioni termoigrometriche in relazione alla conservazione del materiale grafico," *2nd International Conference on Non-destructive Testing, Microanalytical Methods and Environment Evaluation for the Study and Conservation of Works of Art, Perugia*. III/11.1- 11.13.

MASSARI, G. (1971). *Humidity in Monuments*. Rome: ICCROM.

NUGARI, M.P., M.R. GIULIANI and C. CACACE (1989). "Domus Aurea: Preservation proposal for control of microflora growth on frescoes in hypogean environments," *International Conference on Biodeterioration of Cultural Property, Lucknow, India, Feb. 1989*. 181-195.

NYUKSHA, J.P. (1979). "Biological principles of book keeping conditions," *Restaurator*, 3. 101-108.

PIETRINI, A.M., S. RICCI and M.R. GIULIANI (1986). "Domus Aurea: Criteri di metodo, apporti disciplinari e prime indicazioni del progetto complessivo di conservazione. - Ricerca sulla microflora algale e sui trattamenti algicidi nell'ambiente n. 75," *Manutenzione e Conservazione del Costruito fra Tradizione ed Innovazione. Bressanone.* 694-696.

PLENDERLEITH, H.G. and P. PHILIPPOT (1960). "Climatology and conservation in museums," *Museum*, XIII/4. 203-209.

SALVADORI, O. and M.P. NUGARI (1987). "The effect of microbial growth on synthetic polymers used on works of art," *Biodeterioration 7,* eds. D.R. Houghton, R.N. Smith and H.O.W. Eggins, Elsevier Applied Science. 424-427.

SERRA LERCHENTHAL, M. (1986). "Domus Aurea: Criteri di metodo, apporti disciplinari e prime indicazioni del progetto complessivo di conservazione. - Impianto di illuminazione sperimentale Domus Aurea," *Manutenzione e Conservazione del Costruito fra Tradizione ed Innovazione. Bressanone.* 651-653.

TANDON, B.N. "The preservation of museum materials," *Prachya pratibha,* vol.III, n.2. 83-90.

TORRACA, G. (1983). "Environmental protection of mural paintings in caves," *International Symposium on the Conservation and Restoration of Cultural Property. Conservation and Restoration of Mural Paintings. Tokyo, Japan.* 1-18.

ZAITSEVA, G.A. (1987). "Chemical measures of protecting USSR museum collections against keratin-destroying insects (Coleoptera, Dermestidae, Lepidoptera, Tineidae)," *ICOM Committee for Conservation. 8th Triennial Meeting. Sydney, Australia.* 1211-1214.

Chapter 6

METHODS OF CONTROL

Control of biological growth is one of the treatments included in restoration. This operation (except for plant removal) is often improperly grouped together with cleaning measures. The aim of such control is the total elimination of biodeteriogens; the methods include sterilization of microflora, extermination of larvae and insects and eradication of higher plants.

The efficacy of these treatments depends on the methods and the products chosen, but new growth will inevitably occur if the environmental conditions favoring biological growth are not changed. In order to obtain lasting results, all the necessary interventions other than direct control of biodeterioration have to be established when restoration is being planned.

Many questions should be considered when undertaking or deciding upon a biodeterioration control treatment (Fig. 6.1).

Is treatment necessary?

The biological alteration needs to be studied, the biodeteriogens isolated and classified and the damage quantified. Only when these operations have been performed can one decide whether intervention is necessary or whether the best choice is not to treat.

Can the object tolerate the treatment?

The physical and chemical properties, as well as the state of conservation of the object, must be considered.

What will be the effect of treatment?

The appearance of the object after treatment and the possible impact of treatment on the ecosystemic equilibrium must be evaluated. The treatment could favor recolonization of the substrate by some more aggressive and resistant species, for instance.

How and when can the object be treated?

In each case, the most suitable method can be chosen by considering both the type and growth density of the biodeteriorating agent, the nature of the substrate and its

condition and the extent of the surface to clean. In some cases (e.g., for plants or insects), it is very important to choose the best period for treatment as well.

How often will the object need treating in the future?

It is very important to foresee the eventual necessity of further treatments, taking into account the possibility of development of resistant species and planning for routine or periodic maintenance to avoid new colonizations.

Can some prevention methods be applied?

An evaluation must be made to decide whether it is possible to apply the measures necessary to modify environmental parameters or some physico-chemical characteristics of the substrate. Such measures actively discourage new biological colonizations.

Generally, after biocidal treatment, some chemical substances (protective coatings or consolidants) are applied to the object to increase its water repellency and cohesion, respectively. These resins may prevent or retard the recolonization of the substrate (because of the decrease of porosity, roughness and water content of the substrate), but when critical environmental conditions persist (especially high RH) they may favor the development of microflora (mostly fungi, but also bacteria and algae).

With regard to the principles and the nature of the means employed, control methods can be classified as mechanical, physical, biological, chemical or biochemical.

6.1 MECHANICAL METHODS

All the techniques described as "mechanical" have in common a method of displacing the biodeteriogen. Traditional mechanical methods involve the physical removal of biodeteriogens either by hand or with tools such as scalpels, spatulas, scrapers, saws or vacuum cleaners. Although frequently used in the past, these methods do not produce lasting results. The mechanical removal of superficial mycelium and lichens or the cutting of vegetation do not completely arrest the vegetative activity of these plants. Moreover, mechanical methods can damage the substrate, as when plants with a developed root system are pulled out or heavy brushing is used (Fig. 6.2, p. 86).

Still, mechanical methods have certain advantages for the substrate because they do not add anything that might cause further deterioration. When properly employed by restorers, they can be useful, especially when coupled with chemical methods. Mechanical cleaning of pieces and accessible galleries of wood can be performed with brushes, hair dryers or vacuum cleaners, followed by injections of insecticides until the object is saturated. Mechanical removal of lichens on stone can be facilitated by applying some alkaline solutions (e.g., 5% of ammonia) beforehand in order to swell and soften the thalli, followed by the application of biocides (Seaward, 1985).

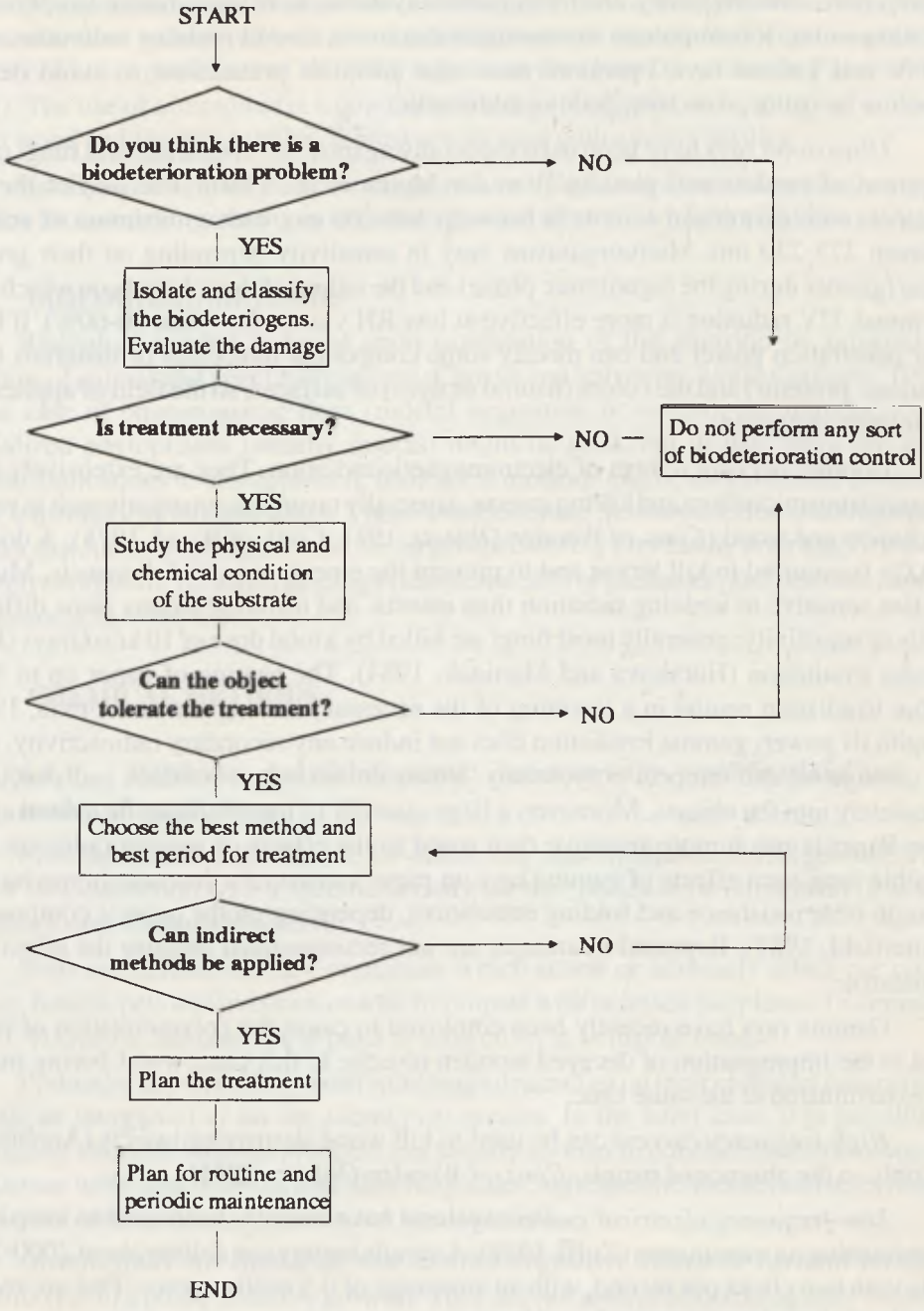


Fig.6.1

Flow chart showing the questions to be considered before deciding to perform a biodeterioration control treatment.

6.2 PHYSICAL METHODS

The methods used experimentally to date are as follows: ultraviolet rays (UV), gamma rays, low-frequency electrical current systems, heat, deep-freeze temperatures and ultrasonics. It is important to remember that in the case of ionizing radiations, such as UV and gamma rays, operators must take adequate precautions to avoid dermal exposure by using protective clothing and masks.

Ultraviolet rays have been used especially against bacteria, algae and fungi in the treatment of renders and plasters (Van der Molen et al., 1980). The part of the UV spectrum with germicidal activity is between 300-200 nm, with a maximum of activity between 275-230 nm. Microorganisms vary in sensitivity depending on their growth phase (greater during the logarithmic phase) and the nature of the substrate on which they are found. UV radiation is more effective at low RH values (less than 50-60%). It has a poor penetration power and can modify some component molecules of materials (e.g., cellulose, proteins) and the colors (natural or dyes) of surfaces, so the field of application is naturally restricted.

Gamma rays are a form of electromagnetic radiation. They are extensively used for sterilizing microflora and killing insects, especially on organic materials such as paper, parchment and wood (*Cons. of Wooden Objects*, 1971; *Cons. of Wood*, 1978). A dose of 500 Gy is required to kill larvae and to prevent the emergence of adult insects. Moulds are less sensitive to ionizing radiation than insects, and different strains show different levels of sensitivity; generally most fungi are killed by a total dose of 10 kilo Grays (kGy) gamma irradiation (Horakova and Martinek, 1984). The heating of paper up to 50°C before irradiation results in a lowering of the necessary dose (Justa and Urban, 1991). Despite its power, gamma irradiation does not induce any secondary radioactivity, does not damage oil and tempera polychromy, leaves no hazardous residues and penetrates completely into the objects. Moreover, a large quantity of materials can be treated at one time. Paper is much more sensitive than wood to the effects of gamma radiation. The possible long-term effects of gamma rays on paper consist of a decrease in mechanical strength (tear resistance and folding endurance), depending on the paper's composition (Butterfield, 1987). Repeated treatments are not recommended because the effects are cumulative.

Gamma rays have recently been employed to cause the polymerization of resins used in the impregnation of decayed wooden objects; in this case, wood-boring insects are exterminated at the same time.

High-frequency current can be used to kill wood-destroying insects (Anobiidae), but only in the absence of metals (*Cons. of Wooden Objects*, 1971).

Low-frequency electrical current systems have recently been used to keep birds from roosting on monuments (Zuffi, 1988). A simple battery can deliver about 2000-3500 volts with two clicks per second, with an amperage of 0.5 milliamperes. This arc-over is completely harmless for animals and humans.

Heat (dry or wet) is used in the disinfestation and disinfection of organic materials. The application of moist heat for disinfection of books is still one of the most widely used techniques (Flieder, 1969; Hueck, 1972). A temperature of 95°C and 40% RH for 4 h is

recommended. This method must be used carefully with antique textiles. Dry heat should not be used because of the high temperatures involved.

Other methods used to eliminate infestations of books are exposure to *deep-freeze temperatures* or to *reduction in pressure* using vacuum dryers. Reduction in pressure causes cells to explode and so all living organisms die (*New Directions in Paper Cons.*, 1986). The use of *ultrasound* is a possibility for the cleaning of archaeological artifacts, damp wood and modern textiles. It must not be used with ancient textiles.

Finally, we might mention the suggested use of *light traps* together with other types of traps for controlling insects in museums that are attracted by light (Zaitseva, 1991).

6.3 BIOLOGICAL METHODS

Biological combat is based upon exploitation of the parasitic or antagonistic faculties of animal and vegetal organisms (Caneva and Salvadori, 1988; Catizone, 1990). In the case of phanerogamic flora (ruderal vegetation or weeds), the introduction of specialized phytophages (usually insects) might be used, but to date there are some counter-indications to this approach. Biological methods can be useful for the control of birds, especially in infested cities. These would include the introduction of antagonistic species that hinder reproduction of the target species (e.g., by eating their eggs), the use of deterrent systems based on ethology (simulated calls of predators) and periodic capture and removal to other sites.

6.4 CHEMICAL METHODS

6.4.1 Pesticides and disinfectants: characteristics, qualifications and modes of application

Pesticides are chemicals used for destroying undesirable biological growth. They have a biocidal action with a specific toxicity for the species to be eliminated (it is also possible to use the term *biocides*).

Pests are defined as "any organisms which attack or adversely affect our crops, bodies, homes, pets and livestock or which compete with or attack our plants" (Stimmann, 1983). Therefore, the concept of pests is subjective, as is that of weeds.

Pesticides are classified in different ways depending on their *chemical nature* (e.g., organic or inorganic) or on the *target pest species.* In the latter case, it is possible to distinguish about 20 kinds of products, but usually in order to control biodeterioration we need to use wide-spectrum bactericides, fungicides, algicides, herbicides and insecticides (acaricides and repellents for birds can be also used).

Disinfectants are chemicals that destroy vegetative forms of harmful microorganisms (i.e. in a phase of active growth). They are not always effective against bacterial spores (i.e. in a resistant quiescent phase).

The term pesticide is used especially in the agricultural field; in contrast, the term disinfectant is used in the health field. The products used in the control of biodeterioration can be either pesticides or disinfectants in relation to the primary field of use.

It is also possible to classify pesticides according to their *chemical groups,* their *mode of action* and sometimes their *use* or *formulation* (e.g., liquid formulations would include solutions, flowables, aerosols, emulsions, fumigants; dry ones would include dust, baits, granules, pellets, wettable or soluble powders, microencapsulations). In addition to the pesticide, other ingredients, such as carriers or additives to improve the effectiveness of the product, are present in the chemical formulation. These are called *coformulants.* The same pesticide can be sold in different formulations and in mixtures with different trade names (e.g., pentachlorophenol in the formulation DowicideEC7™ by Dow Chemical, or Santobrite™ by Monsanto). The names "Dowicide" or "Preventol" or "Hyamine" correspond to typical names assigned by the producer, respectively Dow Chemical, Bayer and Rohm and Haas. They are often used for several different chemical compounds, being specified by letters or numbers (e.g., Preventol PN and Preventol R80 are, respectively, a sodium pentachlorophenate and an alkyldimethylbenzylammonium chloride).

In choosing chemicals, the following characteristics must be taken into account:

- high efficiency against biodeteriogens
- low toxicity for the operator
- low risks of environmental pollution
- no interference with materials

Efficiency is defined as biocidal activity against the target organisms (Fig. 6.3, p. 86. It is defined by taking into account the *dose* of the product (quantity of pesticide/unit of surface or volume of air), the *spectrum of action* (the amplitude of specificity against organisms) and the *persistence of action*). This latter aspect is positive with regard to efficiency but can be a risk from the health point of view. Biocides with a wide spectrum of action and persistent activity seem better for avoiding new colonizations of organisms favored in the absence of competition (Agarossi et al., 1988).

Toxicity is the capacity of a pesticide to injure or kill (Cornwell, 1979). Any substance, however, can be considered as a poison, and the right dose distinguishes a poison from a remedy (Paracelsus). There are no harmless substances, only harmless ways of using substances. Usually, we consider a poison to be a substance that is dangerous at a very low dose. Toxicity can be *acute* (due to short exposure and with quite immediate effects) or *chronic* (due to long-term exposure and with a longer period of appearance).

A great number of parameters define the toxicity of a compound. The most common indices for quantifying acute toxicity are obtained by calculating the amount of active compound (administered orally or cutaneously) that is lethal for 50% of the experimental animals tested (e.g., rats, rabbits) (LD_{50} = Lethal Dose; r = rats). It is expressed in mg of product/kg of weight of the animal. Clearly, the higher this value, the lower the toxicity of the compound. In the case of gaseous compounds, toxicity is expressed by the LC_{50} (Lethal Concentration), and the duration of exposure must also be considered. For these latter compounds, the Threshold Limit Value (TLV) is specified by public health authorities if they are to be used in enclosed spaces. On the basis of these indices, toxicological categories have been established (usually three, but also four in some countries) in decreasing order of risk (Table 6.1)

Table 6.1 Acute Toxicity

Category	Signal Word Required on the Label	LD50 Oral mg/kg	LD50 Dermal mg/kg	LC50 Inhalation µg/l	Probable Oral Lethal Dose
I Highly Toxic	DANGER - POISON skull and crossbones	0-50	0-200	0-2,000	A few drops to a teaspoonful
II Moderately Toxic	WARNING	More than 50 to 500	More than 200 to 2,000	More than 2,000 to 20,000	More than one teaspoonful to one ounce
III Slightly Toxic to Relatively Non-toxic	CAUTION	More than 500	More than 2,000	- - - -	More than 1 oz

These products must be registered by governmental institutions which require toxicological data and specifications on efficiency. Health authorities will indicate instructions for handling as well as the toxicological class, which are written on labels. The way pesticides are used influences the hazards involved. Operators must take adequate precautions according to the level of toxicity. To avoid dermal pesticide exposure, the use of protective clothing is recommended; this would include impermeable gloves and systems to protect the eyes, mouth and face. Other special covers and boots are necessary when spraying highly toxic pesticides (categories I and II). This kind of pesticide (restricted-use pesticide) should be applied only by licensed personnel with proper training and experience. Eating, drinking and smoking should be avoided while one is handling pesticides in order to reduce the risk of oral exposure.

The risk of *environmental pollution* from pesticides is linked to different factors such as drift, undesirable effects on plant life and damage to beneficial insects and animals.

Moreover, one of the most serious problems with the use of pesticides is the *persistence* of the product in the soil or water. This problem is especially prevalent with herbicides and insecticides that are applied or dispersed in external environments, where the risk of contamination of soil and water is high. This is correlated to the chemistry of the soil, its moisture content, the pH, the climate, the present microflora, etc. (Fig. 6.4).

The survival and growth of individuals with internal *resistance* to pesticides can be another problem when treatments are frequent; rotation of products helps to avoid this risk.

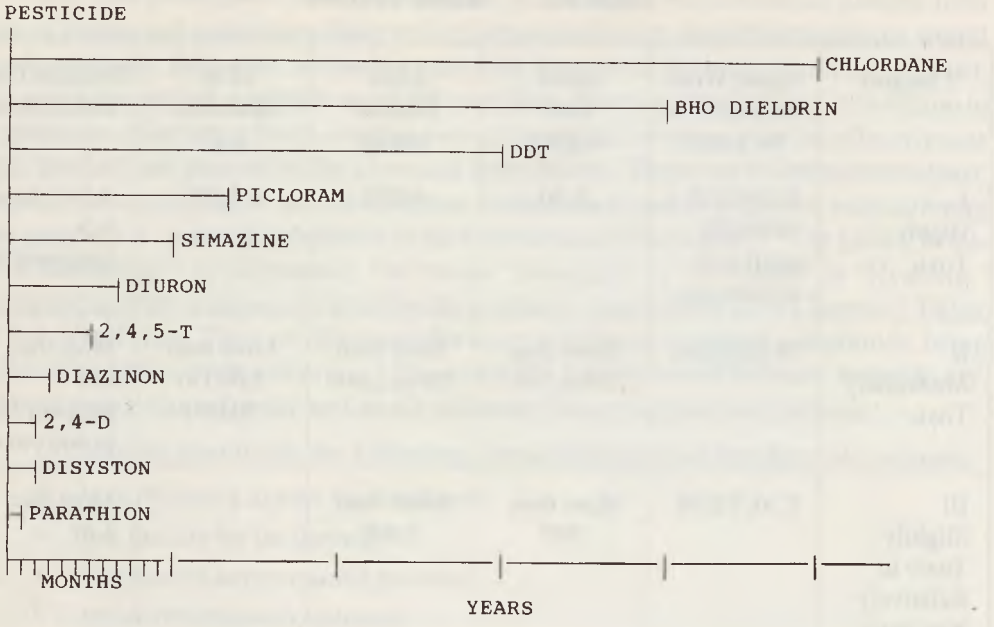


Fig.6.4

Persistence of pesticides in soils (from Stimmann, 1983).

Interference with materials depends upon the chemical reactivity of the biocide or on the presence of colored or oleaginous compounds as coformulants in the commercial product. They can react chemically with the substrata or cause aesthetic damage (solvents can also interfere). Therefore, it is necessary to check the product for chemical neutrality, absence of undesired chemical reactions and absence of color. When information is not available, these aspects must be evaluated carefully with specific laboratory tests on samples of the same kind of material as that to be treated (Fig. 6.5, p. 86) (Rossi Doria and Ciarrocca, 1972; Fearn, 1978).

Some traditional treatments also formerly used as biocides in stone conservation (calcium chloride, concentrated ammonia solutions and Zn or Mg silicofluorides) gave rise to secondary damage, such as an increase of the concentration of soluble salts and formation of hard surface skins (Ashurst, 1977). Moreover, copper compounds, widely used as disinfectants in the treatment of wood or varnishes of non-artistic interest, as in the agricultural field, are not reported in this field because they can stain materials and corrode masonry.

The use of different pesticides in order to avoid the growth of resistant species or to control different organisms should be carefully studied, considering problems of *compatibility* and collateral effects of interactions between the chemicals (see ¶6.4.4) even if they are applied at different times.

It seems, moreover, that the use of organic biocides, like other natural organic contaminants, can affect radiocarbon dating unless physically or chemically separated

from the artifact (which might be particularly important in the case of wood of archaeological interest) (Dawson, 1981).

The *mode of application* of pesticides varies depending on the component materials of the work of art, its state of conservation, the organism to be eliminated, the density and diffusion of biological attack and the product chosen. Treatments are carried out by *spraying, brushing, applying poultices, injection* or *fumigation.* In the case of herbicides, granular formulations are sometimes also employed. Non-gaseous biocidal compounds are diluted in water or organic solvents at different concentrations (usually 0.1-3%). Higher concentrations can be employed when the biocide is injected (up to 10%).

Depending upon the type of biological growth, a partial removal of biomass by gentle brushing (avoiding mechanical abrasion and staining due to pigment emission after the breakdown of cells, especially in the case of algae) might be necessary before chemical compounds are applied.

Spraying and *brushing* of diluted biocide solutions are the most common systems of treatment. The spraying method is preferred for paintings with a very deteriorated surface layer and, generally, when the component material is in poor condition. In the case of organic materials, such as paintings on paper, prints, parchment or old books, spraying or brushing biocides is not always possible because some liquid solutions can dissolve pigments and inks.

Application of poultices is carried out especially in the case of hard encrustations in order to increase the contact time and use the dissolving action of water itself. These compresses are made of carboxymethyl cellulose or paper pulp, inert materials that are soaked in the biocide solution. They are covered with sheets of polyethylene or something similar in order to reduce dehydration of the compress itself. The length of application ranges from one day to several days. Sometimes the chosen biocide is added to a gelatinous solvent paste called AB57, widely used for cleaning stone and mural paintings. AB57 is composed of sodium and ammonium bicarbonate, EDTA (a complexing substance), carboxymethyl cellulose and Desogen (a weak disinfectant) (Mora and Sbordoni Mora, 1975; Lazzarini and Tabasso, 1986) (Fig. 6.6). In some cases, the removal of biological or chemical incrustations on stone is obtained through non-selective absorbent clays (e.g., sepiolite or attapulgite) (Paleni and Curri, 1977).

Injection of pesticides within the object can be performed in the case of infested wooden objects, utilizing the insects' own tunnels. When trees or bushes must be eliminated, the plant is cut down and the stumps are drilled and treated (Fig. 6.7). In the case of subterranean termites, injection is performed under pressure into the soil.

Fumigation methods are widely employed for organic materials. The treatment consists of distributing the fumigant (gas) in the air and through materials. This method has some advantages, such as the rapid efficacy of the treatment and the deep penetration inside the object through cracks, crevices, etc. Due to the high toxicity of fumigants, they must be applied in airtight chambers or in perfectly sealed spaces (sometimes created with polyethylene sheets). In an airtight chamber, the pressure can be modified to improve the penetration of gas. Fumigants require highly trained applicators and have no residual effect after aeration (Fig. 6.8).

Fig.6.6

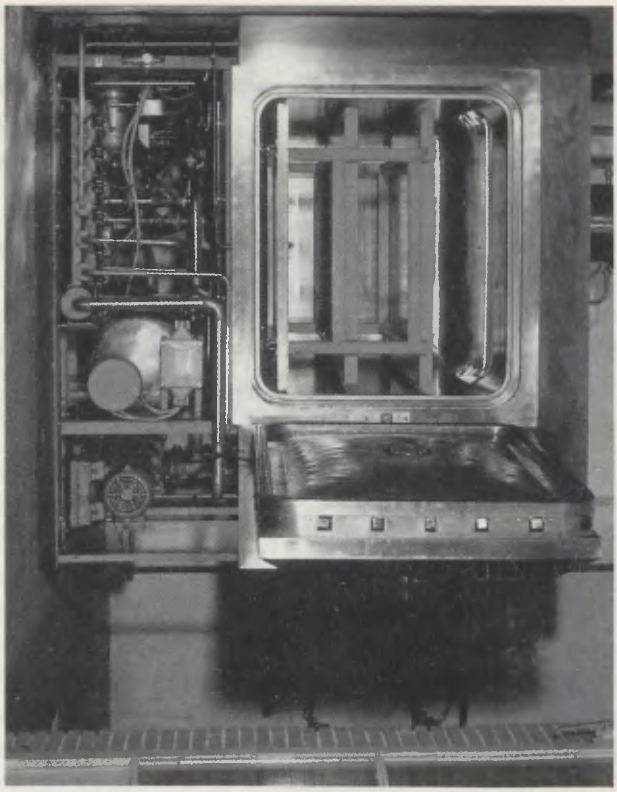
Application of poultices containing biocides (ICR).

Fig.6.7

Ficus carica tree stump being drilled for injecting biocides.

Fig.6.8

Airtight chamber for gaseous treatment (G. Donati, Istituto Centrale per la Patologia del Libro, Rome).



As an alternative to conventional fumigation techniques, researchers have recently investigated the possibility of employing inert gases, such as nitrogen, together with low RH for controlling museum pests (Gilberg, 1989; Valentin et al., 1990). The advantage of this system is that it is safe, inexpensive and not invasive, but more tests are necessary to assess its effect against the various species of microorganisms and insects that might be found.

Treatments with substances active as *vapor* have similar advantages and, moreover, do not require complicated equipment because the products generally used in vapor form are not very toxic. The object can be treated in a polyethylene bag or airtight cabinet to permit the circulation of vapor.

When either spraying and brushing treatments or poultices are used, it is sometimes advisable to wash off the biocide residues in order to avoid secondary reactions (due to the degradation of products) or toxicological difficulties (high-persistence products that are in contact with the public or operators). Obviously, the time of reinfestation will be reduced after the washing, if environmental conditions remain unchanged.

The chemicals used for eliminating biodeterioration of both organic and inorganic materials will be analyzed as a group. Although materials of artistic or archaeological interest vary in nature and chemical composition and are subject to different biodeterioration processes, the same chemical compounds are used in their treatment, with some restrictions for specific materials and sometimes with different application techniques.

Products and application systems vary depending on the kind of biodeteriogen organism present on the material. The text will provide a comparative analysis, differentiating these factors on the basis of the target organism.

The composition of some materials can reduce biocidal effectiveness. Thus, the same biocide will exert a shorter or longer protection against further attack as a function of the material on which it is applied.

The biocides described below are a selection of those used up to the present time. In some cases, however, their suitability can be questioned on the basis of new knowledge of toxicity and interference with materials. This list, therefore, gives guidelines for the choice of biocides but it does not represent a list of products to be applied indiscriminately.

The biocides are listed on the basis of their chemical nature, and are identified with the common name, or if non-existent, with the chemical name. Oral Lethal Dose 50, usually for rats (LD_{50}), or the Lethal Concentration 50 (LC_{50}) for gaseous compounds are given in parentheses. As previously stressed, these data are not sufficient for defining the toxicity of a compound, but are useful for having an idea of hazards in the use of products. The toxicological class can be obtained from LD_{50} oral/dermal (and LC_{50} inhalation) values as indicated in Table 6.1.

The trade names of the formulations containing a certain biocide are reported if they have been specified in the treatment of works of art. This is not only to help the conservator to identify the compound, but also because the practical experimentation was performed with that specific formulation. The trade names listed for each active compound might be incomplete, but arise from the data reported on use of such products in the conservation field. Where common products such as bleach or borax are discussed, the names of manufacturers are not given.

6.4.2 Bactericides, fungicides, algicides

Many organic and inorganic compounds are cited in the literature to be used as antimicrobial agents. The following list includes the products most frequently used.

Inorganic compounds

Hydrogen peroxide is sometimes used (at 120 vol) for killing algae and lichens on stone materials (Tiano, 1986); it is also used in a mixture with *ammonia.* However, some problems can arise from the oxidative capability of this compound, and a general bleaching of the stone has been mentioned. Moreover, it acts only through contact and cannot exert a long-lasting activity.

Sodium hypochloride (bleach) is sometimes used (active chlorine concentration varying from 2-7%) for removing algal and lichen patinas from stone (Spry, 1981; Forero, 1986). It is also considered as a suitable cleaning system (even if without residual activity and with low efficiency against lichens) by the Building Research Establishment Digest (1981). This document also states that there is no evidence that building materials will be harmed by the concentrations normally specified by suppliers. Nevertheless, interference with stone cannot be completely overlooked, owing to a bleaching of the treated materials

and a possible secondary yellowing if this compound is not completely removed. Moreover, all chlorine-containing compounds are considered corrosive and cause irritation to the skin. Chlorine has also been considered as a biocidal treatment for waterlogged wood. It seems that lignin reacts with it to form water-soluble "lignin chloride" (Dawson, 1981). Further study is required to ascertain whether these problems might arise at normal concentrations.

Organometallic compounds

Mercurials are among the most active of organometallic compounds, but are now considered obsolete. Although used in the past for fungicide treatments of wood, canvas and mural paintings (Strzelczyk, 1981) (e.g., *pyridyl mercuric acetate*, or *phenyl mercuric acetate,* LD_{50} = 24 mg/kg), they are now rejected due to their toxicity.

Organotin compounds show a strong biocidal efficiency: *Tri-n-butyl tin oxide* (LD_{50r} = 87-200 mg/kg) (TBTO - Merck; Thaltox - Wykamol, Ltd.) is highly efficient as an algicide and fungicide (it is widely used as an antivegetative paint for boats) and has also been tested successfully for the treatment of algae and lichens on stone and mural paintings (sometimes in a mixture with a quaternary ammonium salt (Jaton et al., 1985; Fry, 1985). In addition, it is reported as a preservative for wood (of non-artistic interest), showing particularly good activity against brown rot fungi and a significant insecticidal action (Gambetta and Orlandi, 1979). *Tri-n-butyl tin-naphtenate* (LD_{50} = 1300 mg/kg) (Metatin N-58-10 - Acima Chemical) has a similar efficiency and, therefore, a similar field of application.

Phenolic compounds and derivatives

Phenol (LD_{50r} = 530 mg/kg) is one of the oldest disinfectants and is used as a standard of comparison to determine the efficiency of other disinfectants. It has been used in the treatment of wood and storage of waterlogged wood but now appears unsuitable because of its high toxicity. Moreover, although not carcinogenic itself, it can increase the potency of carcinogens and corrosivity against metals.

Pentachlorophenol (PCP) and sodium salt (PCPNa). PCP (LD_{50r} = 146-175 mg/kg) (Dowicide EC7 - Dow Chemical) and PCPNa (LD_{50r} = 180 mg/kg) (Dowicide G - Dow Chemical; Santobrite - Monsanto) were frequently used in the past, especially for treatment of organic materials, due to their wide spectrum of effectiveness. However, the toxicity of these compounds is high and their interference with materials, such as some textiles, wood (which can become darker in color) and pigments, has been observed. Pentachlorophenol is easily dissociated to provide chloride ions under conditions of high humidity and in the presence of light; saturated aqueous solutions of PCP are weakly acidic (pH = 4.6). In many countries, the use of these compounds is severely restricted. In fact, usage is prohibited in the case of domestic-class products or a risk of prolonged skin contact. Therefore, their use in the field of art conservation must be carefully considered, even if they are widely employed as a preservative for wooden objects. Pentachlorophenol employed in mixtures with other biocides (e.g., xylamon) is now replaced by less toxic compounds.

Orthophenyl phenols (OPP) and sodium salts (OPPNa). OPP (LD_{50r} = 2480 mg/kg) (Dowicide1 - Dow Chemical; Topane S - ICI) and OPPNa (LD_{50r} = 2500 mg/kg) (Dowicide A - Dow Chemical; Topane WS - ICI; Mystox WFA - Catomance) are active against a broad spectrum of fungi and bacteria, but they show a weak activity against algae. They are usually preferred over the other phenols because of their greater safety and low irritation for operators. Moreover, OPP is usually preferred to its sodium salt in evaluating possible interaction with the substrate. In the case of textiles, treatments with OPP and OPPNa lead to immediate or subsequent ageing effects, with changes in color or brightness. In the case of silk, considering the efficiency parameters, interference and toxicity all together, OPP was found to be the only feasible fungicide (Nugari et al., 1987). These products are widely used as fungicides in glues. OPP in diluted solutions with ethyl alcohol (Lysol - Sterling) has also been reported as successful in removing lichen from granitic stone (Wainwright, 1986).

p-chloro m-cresol (CMC) (LD_{50r} = 1830 mg/kg) has been used for the following purposes: as a fungicide diluted in alcohol solutions on oil, distemper and mural paintings; to protect parchment against microflora; to prevent microbial growth in desalinating wrappings used for cleaning stone; and, for spraying in the air of mildewed book storerooms (Kowalik and Sadurska, 1966; Sadurska and Kowalik, 1969; Strzelczyk, 1981; Agrawal et al., 1989). A mixture with phenyl mercuric acetate was suggested for improving its efficiency (toxicological problems in using mercurials were stressed above).

Thymol (LD_{50r} = 980 mg/kg) has been used frequently as a biocide for library and archival materials and is applied by brushing or as a vapor. Efficiency data in the professional literature report contrasting results. (A strong antibacterial activity is mentioned while the fungicidal activity is considered low in some cases. In other cases, the opposite is true. Unfortunately, the tested target species are only partially defined.) (Sadurska and Kowalik, 1969; Agrawal and Dhawan, 1985). Thymol poses a slight hazard as an irritant and allergen, and moderate toxicity by inhalation or ingestion. In any event, operator exposure during this treatment must be avoided. Thymol can also be a good solvent for organic materials such as varnishes and paints (Dawson, 1981). It has been found to soften oil paints and varnishes and may interfere with parchment (Strzelczyk, 1981). Moreover, it is photooxidized, producing a yellow discoloration, which can be partially removed by acetone. Therefore, its use is not recommended for exhibited material (Daniels and Boyd, 1986).

Dichlorophene (LD_{50mice} = 1200 mg/kg) (Panacide - BDH) is widely used as an algicidal, bactericidal and fungicidal product for the treatment of organic materials.

Salicylanilides (LD_{50r} = 5000 mg/kg) (Shirlan - ICI) are condensation products of salicylic acid and aniline; they are a group of biocides with fungicidal and mildly bactericidal activity. They are not highly toxic but can cause skin irritation. These compounds are used especially in the case of waterlogged wood (added to aqueous solutions) or for textiles and archival materials (Hueck, 1972; Pertegato, 1981; Dawson, 1981).

Quaternary ammonium compounds (quats)

These surface-active disinfectants are widely used for pharmaceutical purposes and applied as bactericide, fungicide and algicide compounds. Their activity against lichens is controversial. They are suggested for various biocidal treatments, due to their absence of color and odor, high stability and combination of biocidal action with detergent activity. They exhibit little long-term activity, however, and do not kill spores. These compounds are active at low concentrations (generally with the exception of gram-negative bacteria). Toxicity varies within this class. Quats are incompatible with anionic detergents such as soap, and show reduced activity in the presence of a great amount of organic matter or certain salts, such as nitrates. Cations, such as calcium and magnesium (present in hard water), also reduce their biocidal activity. The products most frequently used are as follows:

Alkyl dimethyl benzyl ammonium chloride (Benzalkonium chloride) (LD_{50r} = 240 mg/kg) (Preventol R50, R80, R90 - Bayer; Hyamine 3500 - Rohm & Haas; Céquartyl - Rhone Poulenc; Neo-desogen - Ciba Geigy) is most widely used against bacteria, fungi and algae. It is also effective against lichens (Jaton et al., 1985).

Trimethyl 1-(p-tolylalkyl) ammonium methanesulfate (LD_{50r} = variable) (Desogen - Ciba Geigy) is widely used, as in the AB57 compress, showing detergent capability but low bactericidal activity.

Dodecyl dioxyethyl benzyl ammonium chloride (LD_{50r} = 1000 mg/kg) (Bradophen - Ciba Geigy).

Lauryl dimethyl benzyl ammonium bromide (LD_{50r} = 230 mg/kg) (Metatin 101 - Acima Chemical; Proseptyl B - Sicca; Cetlavlon - I.C.I.).

Diisobutylphenoxyethoxyethyl dimethyl benzyl ammonium chloride (Benzethonium chloride) (LD_{50r} = 420 mg/kg) (Hyamine 1622 - Rohm & Haas).

Alkylaryl trimethyl ammonium chloride (DL_{50r} = variable) (Gloquat C - A.B.M. Chem.).

Mixtures

Sodium dimethyldithiocarbamate + sodium 2-mercaptobenzothiazole in the formulation Vancide 51 (Vanderbilt) is classified as a fungicide and is also used in the treatment of algae, lichens and mosses on stone and plaster.

Tributyltin oxide + a quaternary ammonium salt in the formulations Thaltox Q or Murosol 20 (Wykamol, Ltd.) is used against algae, lichens and mosses. Thaltox Q has been tested by Grant and Bravery (1985) and Fry (1985). It seems to be very efficient and persistent in action and is used against resistant organisms.

Tributyltin naphtenate + a *quaternary ammonium salt* (Metatin N 58-10/101 - Acima Chemical) has also been successfully tested in many cases of biodeterioration of stone

and mural paintings in subterranean environments (Bettini et al., 1988; Agarossi et al., 1988).

6.4.3 Insecticides

Apart from methyl bromide, the most common insecticides used today are organophosphorus compounds and carbamates, which are preferred to organochlorine and synthetic pyrethroids, especially due to the shorter length of persistence.

They can be applied in a liquid, solid or gaseous state. When possible, it is preferable to use gaseous compounds in a fumigation chamber (see ¶6.4.4) because solid or liquid-state insecticides emanate noxious fumes for a certain time (Gallo, 1985). Gaseous treatments with hydrocyanic acid, sulfyril fluoride and others are still employed.

Sensitivity to insecticides differs greatly according to the species of insect and its stage of development. Dermestidae and Tineidae larvae show, in general, the greatest resistance. Dermestidae in particular possess higher resistance to organophosphorus compounds. In order to avoid possible resistance to products used repeatedly over a long period, it is necessary to alternate the chemicals applied (Zaitseva, 1987).

Inorganic

Hydrocyanic acid (Highly toxic to humans - exposure for 30 min at 0.36 mg/l is fatal) (LD_{50r} = 6.44 mg/kg) is still mentioned for the large-scale fumigation of historic buildings containing wooden objects (Mori and Arai, 1978; Ognibeni, 1989). Apart from the high toxicological problems, metal artifacts can be discolored or attacked. This latter effect can be avoided by reducing the RH (30% or below) prior to treatment (Bachmann, 1981).

Sulfuryl fluoride (LC_{50} = 417 mg/m^3) (Vikane - Dow Chemical). This odorless and colorless gas is used as an insecticide for fumigating wooden structures to control termites and wood-infesting insects. It has poor ovicidal activity (Mori and Arai, 1978). It is highly irritating to the respiratory tract.

Volatile haloderivatives

Methyl bromide (highly toxic to humans - TLV = 65 mg/m^3) (Dowfume MC2 - Dow Chemical) is also commonly used in fumigation chambers for the treatment of wooden and ethnographic materials. It interferes with proteins or any materials containing sulfur, such as leather, parchment, wool and rubber, and also with metal (Edwards et al., 1981). As a collateral effect, some kinds of leather and parchment have an unpleasant odor after this treatment (Gallo, 1985). Moreover, lead pigments are damaged. Due to its toxicity, use of methyl bromide is restricted to trained personnel.

Organophosphoric insecticides

Although generally more toxic for vertebrates than organochlorines, these insecticides are chemically unstable and non-persistent, reducing problems of environmental pollution. The products chosen in this field are among the least toxic of the class.

Malathion (LD_{50r} = 2800 mg/kg) (Cythion - American Cyanamid) is one of the oldest and safest compounds of this class and is widely employed for domestic use. It is corrosive to iron.

Parathion, Dimeton, Diazitol, Tepp are other compounds in this class.

Carbamates

This is a group of wide-spectrum insecticides acting through a reversible inhibition of the enzyme cholinesterase. The following are among the most commonly used:

Propoxur (LD_{50r} = 90-128 mg/kg) (Baygon - Bayer) is especially used for the control of household insects.

Carbaryl (LD_{50r} = 850 mg/kg) (Sevin - Union Carbide) is widely used against Hymenoptera and parasites of domestic animals.

Organochlorine compounds

These are dangerous because of their high persistence and the consequent risk for animals, such as mammalians and birds, due to accumulation in trophic chains. Their use has been restricted or prohibited for some years in many countries (since 1974 in Italy), but there are still reports of their use to combat insects in the conservation of art work (Cornwell, 1979; Pomarede, 1989).

DDT (LD_{50r} = 113-118 mg/kg) (Gesarol, Neocid - Ciba Geigy). Widely and successfully employed in the fight against malaria, this compound is now used only under very limited circumstances (to counter specific threats to health). DDT is prohibited in many countries, not so much for its actual toxicity, but for its high persistence and accumulation, a result of chemical stability (poorly biodegradable, stable to UV rays, etc.).

Lindane (LD_{50r} = 88-270 mg/kg) (Gammexane - ICI) has a higher vapor action than most of the other insecticides and is used especially when only the vaporized insecticide can reach the insect (e.g., borers in tree trunks) (Ware, 1980).

Chlordane (LD_{50r} = 457-590 mg/kg) (Ochtachlor - Velsicol Chem.) is a slightly volatile compound, persistent in the soil and with significant toxicity. Use is restricted and is practically limited to subsurface ground injection for termite control (*Pesticide Handbook*, 1981-82).

Aldrin (LD_{50r} = 36-60 mg/kg) (Octalene - Hyman & Co.) and *Dieldrin* (LD_{50r} = 46 mg/kg) are less frequently used (only to combat termites) organochlorine insecticides (highly toxic).

Pyrethroids or pyrethrins

Pyrethroids or pyrethrins (LD_{50r} = 584-900 mg/kg) were initially extracted from flowers of a *Pyrethrum cinerariaefolium* growing in Africa and Central and South America and comprise a group of six insecticidal constituents (pyrethrins I and II; cinerin I and II;

jasmolin I and II). They are potent, non-systemic, contact insecticides which cause rapid paralysis. Pyrethrins are highly toxic to fish (Worthing, 1987).

6.4.4 Biocides with both antimicrobial and insecticidal activity

The biocides described below are among the most widely used to date for the protection of organic materials in libraries and museums. In addition to *Pentachlorophenol, pentachlorophenate of sodium* and *TBTO*, which were used principally as fungicides but also employed against insects, the following compounds have been used.

Inorganic compounds

Boric acid (LD_{50r} = 3000 mg/kg) is sometimes used in museums and libraries for controlling insects (Zaitseva, 1987). It is also mixed (7:3) with *borax* (LD_{50r} = 4500-6000 mg/kg) for use in the storage of waterlogged wood (they are compatible with PEG). These compounds show fungicidal, insecticidal and flame-retardant properties (Richardson, 1978) and exhibit very high penetration. In some cases, however, the superficial growth of fungal species was not eliminated. These products can irritate the respiratory system and skin. *Sodium tetraborate* (Polybor) has also been recommended for cleaning algae, lichens and mosses from monuments. Its eradicant action is not very rapid but the inhibitory action persists for several years (Richardson, 1973). Use as a non-selective herbicide for higher plants has rarely been considered in this field.

Organic compounds

Ethylene oxide (TLV = 3 mg/m^2 or 2 ppm) has been used widely as a fumigant for protecting museum materials because of its effectiveness as a fungicide, bactericide and also insecticide (IIC - CG, 1981; Gallo, 1985). It is used in a mixture with carbon dioxide (usually in the proportion of 9:1) or some other inert gas in order to reduce its flammability, explosiveness and toxicity. In fact, its toxicity is considered high due to its recognized mutagenic activity and the suspicion that it may be carcinogenic. Ethylene oxide has the capacity to diffuse and penetrate rapidly through most materials. Experimental tests show that some of the compound, retained in the treated material, can be slowly released after fumigation. Therefore, before being displayed in a museum, treated materials should be aerated for a certain period (at least three days) until they reach a concentration of fumigant below 5 ppm. Special detector tubes, containing chemicals that react with the gas and produce colored stains, are used for indicating the persistence of residues of the toxic gas. Other tests with indicators inoculated with spores are carried out to check the effectiveness of the treatment. Treatment with this gas can also be dangerous in relation to the risk of exothermic reactions with other previous biocides such as sodium pentachlorophenate (PCPNa). To avoid possible burning of organic materials, it is necessary to know whether there are traces of previous treatments with substances containing active atoms of chlorine, -OH groups, -NH_2 groups, or -SH groups, which would give rise to incompatibility (Kleitz, 1987). Moreover, a certain decrease (around 10%) of tensile strength after fumigation was observed in the case of silk and cotton; lower values were obtained with paper and wool (from 3 to 1%) (Green and Daniels,

1987). A reaction with some pastel colors was also observed, and, therefore, a more complete analysis of interference with other pigments is necessary (Pomarede, 1989).

Formaldehyde (max. allowable concentration for prolonged exposure 5 ppm) is a flammable colorless gas; the name *Formalin* (LD_{50r} = 800 mg/kg) is applied to a solution of around 37% formaldehyde in water with 10-15% methanol to prevent polymerization. It has been widely used as an aerosol and in fumigation chambers, especially for the treatment of library materials. It has been employed in the treatment of stone, both sprayed in the air, as used against the algal patinas of Lascaux caves (Lefèvre, 1974), or in aqueous solutions for the treatment of algae on stone (Tiano, 1986). Due to its toxicity, however, and especially to the irritation induced by vapors to mucous membranes, the use of formaldehyde is now restricted. We should also recall that it damages proteic materials (leather, parchments). Moreover, it has been observed that it accelerates the decomposition of PEG in the case of waterlogged wood.

6.4.5 Herbicides

The growth of lichens, mosses and higher plants is usually controlled through herbicides. These products, especially when they interfere with photosynthesis, are also used in some cases against algae. In contrast, in the case of lichens, due to their origin from the symbiosis of algae and fungi, some disinfectants such as quaternary ammonium compounds or mixtures of several chemicals (e.g., Thaltox Q) have been successfully used.

The most commonly used herbicides are nitroorganic compounds, such as amides, diazines, triazines, piridines and urea derivatives. Phosphoorganic compounds also cannot be overlooked.

The selection of these products arises from the agricultural field (excluding those with higher toxicity, which require an operator's license). However, possible interference with materials has not been sufficiently tested, and few papers report experimental results (Fearn, 1978; Tiano and Caneva, 1987). The choice of these products depends especially upon the plants to be treated, so they must be analyzed before proceeding (Caneva and De Marco, 1986). Many experiments with weed control have been carried out especially in Italian archaeological and monumental areas (Villa, 1977; Parrini, 1988; Catizone, 1990; Bettini and Cinquanta, 1990; Caneva, 1991). There are both selective herbicides, which are more active against certain groups of plants, and non-selective herbicides, for total weed control. For the treatment of lower and higher plants growing on masonry, the latter group of compounds is preferable.

Products with residual activity (more persistent in the soil) are better from an efficiency standpoint, but are sometimes unsuitable for precautionary reasons (see ¶6.4.1).

Inorganic compounds

Ammonium sulfamate (LD_{50r} = 3900 mg/kg) (Ammate - Du Pont) crystals have been suggested against woody vegetation, treating the root system locally to avoid regrowth (Ashurst, 1977).

Urea derivatives

Fluometuron (LD_{50r} = 6416-8000 mg/kg) (Lito 3 - Ciba Geigy), *Monuron* and its trichloroacetate salt (LD_{50r} = 3600 mg/kg) (Telvar, Urox - Du Pont) and *Diuron* (LD_{50r} = 3400 mg/kg) (Karmex - Du Pont) have been widely employed against mosses, lichens (and algae). The latter two have also been used against weeds and ruderal vegetation.

Diazine

Bromacile (LD_{50r} = 5200 mg/kg) (Xyvar X - Du Pont) has been used against a wide spectrum of phototrophic organisms such as algae, mosses, lichens and higher plants.

Triazines

Simazine (LD_{50r} - 5000 mg/kg) (Gesatop, Weedex - Ciba Geigy), *Atrazine* (LD_{50r} = 1869-3080 mg/kg) (Gesaprim - Ciba Geigy), *Terbuthylazine* (LD_{50r} = 2000 mg/kg) (Gardoprim - Ciba Geigy), *Secbumeton* (LD_{50r} = 2680 mg/kg) (Etazine - Ciba Geigy), *Hexazinone* (LD_{50r} = 1690 mg/kg) (Velpar - Du Pont), etc., have been used in archaeological areas against higher plants and sometimes against lichens and mosses.

Piridines

Picloram (LD_{50r} = 8200 mg/kg) (Tordon - Dow Chemical; Uniran - Ciba Geigy) has been used especially against woody vegetation (in the past in a formulation with 2-4 D, which is now prohibited).

Imidazolinones

Imazapyr (LD_{50r} = 5000 mg/kg) (Arsenal - Cyanamid) has recently been successfully tested for total control of higher plants and is particularly efficient for injection into woody plants (Caneva, 1991).

Phosphoorganic compounds

Glyphosate (LD_{50r} = 5600 mg/kg) (Roundup - Monsanto, Ravit; Spasor - Siapa) has been tested in archaeological areas for the control of ruderal vegetation (Catizone, 1990; Bettini and Cinquanta, 1990; Caneva, unpublished). It has no residual activity. *Ammonium phosamine* (LD_{50r} = 24,000 mg/kg) (Krenite - Du Pont) has been used against both lichens and higher plants.

Mixtures

Among the various mixtures containing some of the active principles previously listed, *Terbuthylazine* and *Secbumeton* in the formulation Primatol 3588 (Ciba Geigy) are the most commonly used (Villa, 1977).

6.5 BIOCHEMICAL METHODS

In this group, we consider biodeterioration control systems that use chemical compounds of biological origin, which cannot be considered as pesticides. Many of these are now synthetically produced. All of these compounds have been sporadically used and mentioned by researchers.

Antibiotics are substances produced by microorganisms during their growth in order to avoid the competition of other species, which are inhibited or killed. These compounds are active at very low doses, but can lose effectiveness after storage (Gargani, 1968). In this group, *streptomycin* and *penicillin* have been used most successfully to control the growth of bacteria, actinomycetes and fungi on stone objects and mural paintings. Other antibiotics mentioned for the same purpose are *pimafucin, kanamycin, echonazole* and *nystatin* (Gargani, 1968; Curri, 1979; Mak, 1981, Brunet and Vidal, 1989; Dangas and Stefanaggi, 1989).

Pimaricin, widely used in the food industry, has also been tested for the treatment of textiles with good results, considering the absence of collateral interaction with materials, but low efficiency in the protection of materials (Nugari et al., 1987).

Enzymes are proteins that act as catalysts for the biochemical reactions occurring in a cell (see ¶2.2.5). They have been used on rare occasions as biocides and are sometimes mentioned for cleaning or for releasing adhesives. In the latter case, they should be included under control methods as well as other treatments (biological packs or the use of lyophilized microorganisms) used as non-selective cleaning systems.

The proteolytic enzyme *trypsin* has been used for the removal of lichenic crusts, but reports have indicated disadvantages in the practical difficulty of maintaining a good enzymatic activity, i.e. as a function of temperature and pH (Capponi and Meucci, 1987).

Pherormones are substances produced by one individual which have a specific action on other individuals of the same species. Sexual attractants have been tested for controlling insects in museums. Obviously, they cannot be classified as biocides, and they function by inducing the males to exit from the infested object, whereupon they are exterminated with specific insecticides.

These substances are clearly useful, especially in the case of deep infestation, where it is difficult for biocides to penetrate inside the object.

REFERENCES

AGAROSSI G., R. FERRARI, M. MONTE, G. GUGLIANDOLO and M. MAUGERI (1988). "Changes of microbial system in an Etruscan tomb after biocidal treatment," *Proc. VI Int. Congr., Deterioration and Conservation of Stone, Torun*. Torun: N. Copernicus Univ. Press. 82-91.

AGRAWAL, O.P., and S. DHAWAN (1985). *Control of Biodeterioration in Museums*, Technical Note 2. New Delhi: Government of India Press. 1-16.

———, S. DHAWAN, and K.L. GARG (1989). *Microbial Deterioration of Paintings: A Review*. Lucknow, India: Intach Conservation Centre.

ALLSOPP, C., and D. ALLSOPP (1983). "An updated survey of commercial products used to protect materials against biodeterioration," *Int. Biodet. Bull.*, 19 (3/4) 99-146.

ASHURST, J. (1977). *Control of Organic Growth*. DAMHB Technical Note. London.

BACHMANN, H.G. (1981). "Prevention of biodeterioration of wooden objects of art: influence of fumigation with hydrocyanic acid on associated metals," *Studies in Conservation*, 26. 111-118.

BETTINI, C., G. AGAROSSI, R. FERRARI and M. MONTE (1988). "Fenomeni di biodeterioramento in ambienti ipogei dipinti: esperienze di controllo di alcune specie microbiche," *II Int. Conf. on Non-destructive Testing, Microanalytical Methods and Environment Evaluation for Study and Conservation of Works of Art, Perugia*. Session III/1 (1-14). Rome: Comas Grafica.

BETTINI, C. and A. CINQUANTA (1990). *Vegetazione e Monumenti. Esigenze e Metodologie nel Controllo delle Infestanti Ruderali*. Viterbo: Union Printing.

BRUNET, J., and P. VIDAL (1989). "La désinfection des locaux par voie aerienne par la formaldehyde," *Patrimoine culturel et altérations biologiques. Actes des journées d'études de la S.F.I.I.C.* Poitiers: IIC Section Française. 135-144.

BUILDING RESEARCH ESTABLISHMENT (1982). "Control of lichens, moulds and similar growths," *UK Digest*, 139. 1-4.

BUTTERFIELD, F.J. (1987). "The potential long-term effects of gamma irradiation on paper," *Studies in Conservation*, 32 (4). 181-191.

CANEVA, G., and G. DE MARCO (1986). "Il controllo della vegetazione in aree archeologiche e monumentali," *Proc. Congr. Scienza e Beni Culturali - Manutenzione e Conservazione del Costruito fra Tradizione ed Innovazione, Bressanone*. Padova: Lib. Progetto. 553-570.

———, and O. SALVADORI (1987). "I pesticidi nel controllo del biodeterioramento dei monumenti: problemi tecnici e sanitari," *Ecofiuggi*, 87. 81-91.

———, and O. SALVADORI (1988). "Biodeterioration of stone," *The Deterioration and Conservation of Stone, Studies and Documents on the Cultural Heritage N°16*. Paris: Unesco. 182-234.

———, (1991). "Il problema della crescita di *Ailanthus altissima* (Miller) Swingle nelle aree archeologiche e monumentali," *Proc. Convegno Scienza e Beni culturali 'Le Pietre nell'-Architettura: Strutture e Superfici,' Bressanone*. Padova: Lib. Progetto. 225-234.

CAPPONI, G., and C. MEUCCI (1987). "Il restauro del paramento lapideo della facciata della chiesa di S. Croce a Lecce," *Bollettino d'Arte*, Suppl. 41 vol. II. 163-182.

CATIZONE, P. (1990). "Il contenimento delle piante infestanti nelle aree di interesse archeologico." *Archeologia e Botanica*. Rome: "l'Erma' di Bretschneider. 59-64.

Conservation of Stone and Wooden Objects. Contributions to the New York Conference on Conservation of Stone and Wooden Objects. London: IIC. 1971

Conservation of Wood in Painting and the Decorative Arts. Contributions to the Oxford Congress. London: IIC. 1978

CORNWELL, P.B. (1979). *Pest Control in Buildings - A Guide to the Meaning of Terms*. East Grimstead, Sussex: Rentokil Ltd.

CURRI, S.B. (1979). "Aspetti dell'aggressione biologica ai monumenti dell'acropoli di Atene," *Proc. III Int. Congr. Deterioration and Conservation of Stone*. Venice: Fondazione "Giorgio Cini." 261-280.

DANGAS, I., and M. STEFANAGGI (1989). "Un exemple d'intervention in situ: problèmes biologiques des peintures de la crypte de Saint-Savin-sur-Gartempe (Vienne)," *Patrimoine culturel et altérations biologiques. Actes des journées d'études de la S.F.I.I.C.* Poitiers, IIC Section Française. 135-144.

DANIELS, V., and B. BOYD (1986). "The yellowing of thymol in the display of prints," *Studies in Conservation*, 31. 156-158.

DAWSON, J. (1981). "Some considerations in choosing a biocide," *Proc. ICOM Waterlogged Wood Working Group Conference, Ottawa,* ed. D.W. Grattan. 269-277.

EBELING, W. (1978). *Urban Entomology*. Berkeley, CA.: University of California, Division of Agricultural Sciences.

EDWARDS, S.R., B.M. BELL and M.E. KING (1981). *Pest Control in Museums: A Status Report.* Lawrence, KS, USA: Univ. Kansas, Ass. Systematic Collections.

FEARN, J.E. (1978). *The Effects of Herbicides on Masonry*. Nat. Techn. Inf. Service NBSIR. N°78-1449. Washington, DC: National Bureau of Standards.

FLIEDER, F. (1969). *La conservation des documents graphiques - Recherches experimentales*. Paris: Eyrolles.

FORERO, L.E. (1986). Investigación biologica en el parque arqueologico de San Agustin (Huila), Restauración Hoy.1, Bogotà, Colombia: Centro Nacional de Restauración. 5-9.

FRY, M. (1985). "The problem of ornamental stonework - lichen," *Stone Industries*. 22-25.

GALLO, F. (1985). *Biological Factors in Deterioration of Paper*. Rome: ICCROM.

GAMBETTA, A., and E. ORLANDI (1979). "I composti organici dello stagno nella preservazione del legno," *Contributi Scientifico-Pratici per una migliore conoscenza e utilizzazione del legno*, XXV, CNR, Istituto del Legno, Firenze. Rome: CNR. 145-158.

GARGANI, G. (1968). "Fungus contamination of Florence art-masterpieces before and after the 1966 disaster," *Biodeterioration of Materials*, 1, (Proc. 1st Int. Biodeterioration Symp. Southampton). Amsterdam: Elsevier. 252-257.

GILBERT, M. (1989). "Inert atmosphere fumigation of museum objects," *Studies in Conservation*, 34. 80-84.

GRANT, C. (1982). "Fouling of terrestrial substrates by algae and implication for control: a review," *Int. Biodet. Bull.*, 18. 57-65.

———, and A.F. BRAVERY (1985). "A new method for assessing the resistance of stone to algal disfigurement and the efficacy of chemical inhibitors," *Proc. V Int. Congr. Deterioration and Conservation of Stone, Lausanne*. 663-674. Lausanne: Presses polytechniques romandes.

GREEN, L., and V. DANIELS (1987). "Investigation of the residues formed in the fumigation of museum objects using ethylene oxide," *Recent Advances in the Conservation and Analysis of Artifacts*. London: Univ. London Summer School Press. 309-313.

HORAKOVA, H., and F. MARTINEK (1984). "Disinfection of archive documents by ionizing radiation," *Restaurator*, 6. 205-216.

HUECK, H.J. (1972). "Textile Pests and Their Control," *Textile Conservation*, ed. J.E. Leene. London: Butterworths. 76-97.

IIC - CG (1981). "Technical notes. Ethylene oxide fumigation," *IIC - Canadian Group Newsletter*, VII (2) 8-11.

JATON, C., G. ORIAL and A. BRUNET (1985). "Action des végétaux sur le matériaux pierreux," *Vth Int. Congr. Deterioration and Conservation Stone, Lausanne*, Vol. II. 577-586. Lausanne: Presses polytechniques romandes.

JUSTA, P., and J. URBAN (1991). "The use of gamma radiation for conservation purposes," *Proc. Conference Science, Technology and European Cultural Heritage, Bologna, 1989.* 653-656

KLEITZ, M.O. (1985). "Oxide d'ethylène utilisations et limites, Action secondaires avec un residue de traitement antérieur." *ICOM Committee for Conservation. 8th Triennial Meeting, Sydney*. Paris: ICOM. 1175-1181.

———, (1989). "La désinfection au Musée national des arts et traditions populaires," *Patrimoine culturel et altérations biologiques. Actes des journées d'études de la S.F.I.I.C.* Poitiers: IIC Section Française. 177-191.

KOWALIK, R., and I. SADURSKA (1966). "The disinfection of infested storerooms in archives, libraries and museums," *Acta Microb. Pol.*, 15. 193-197.

LAWRENCE, C.A. and S.S. BLOCK, eds. (1971). *Disinfection, Sterilization and Preservation*. Philadelphia, PA: Lea and Fehigen.

LAZZARINI, L., and M. LAURENZI TABASSO (1986). *Il Restauro della Pietra*. Padova: Cedam Ed.

LEFEVRE, M. (1974). "La 'maladie verte' de Lascaux," *Studies in Conservation*, 19 (3).

MAHOMED, R.S. (1971). "Antibacterial and antifungal finishes," *Chemical After Treatment of Textiles*, eds. H. Mark, N.G. Wooding and S.M. Atlas. New York - London: Wiley Interscience. 507-551.

MAK, P. (1981). "Biodeterioration of cultural properties," *Art Gallery Bulletin*, Vol. II (2). Hong Kong: Chinese Univ.

MERCK INDEX (1983). Xth edition, ed. Windholz. Rahway, NJ, USA: Merck and Co., Inc.

MORA, P., and L. MORA SBORDONI (1975). "Metodi per la rimozione di incrostazioni su pietre calcaree e su dipinti murali," *Problemi di Conservazione*, ed. G. Urbani. 339-344.

MORI, H., and H. ARAI (1978). "Biodeterioration of wooden cultural properties and its control," *Conservation of Wood (Int. Symp. Conservation of Cultural Property, Tokyo, 1977)*. 1-16.

MUCCINELLI, M. (1987). *Prontuario dei Fitofarmaci*. Bologna: Edagricole.

New Directions in Paper Conservation. 10th Anniversary Conference. Oxford, England: The Institute of Paper Conservation. 1986.

NUGARI, M.P., G.F. PRIORI, D. MATE' and F. SCALA (1987). "Fungicides for use on textiles employed during the restoration of works of art," *Int. Biodet. Bull.*, 23. 295-306.

OGNIBENI, G. (1989). "Die Bekämpfung von Holzschädlingen-gefasste Holzobjekte unter Einsatz von Gas," *Restauro*, 4. 283-287.

PACKER, K., ed. (1980). *Nanogen Index - A Dictionary of Pesticides and Chemical Pollutants*. Freedom, CA, USA: Nanogens Int.

PALENI, A., and S. CURRI (1976). "Attapulgus clay on cleaning biological aggression control desalination of stone," *2nd Int. Symp. Det. Build. Stone*. Athens: N.T.U. of Athens. 153-162.

PARRINI, P. (1988). "Il degrado biologico: tipi di prodotti, loro impiego ed efficacia nella prevenzione e nella eliminazione della vegetazione infestante le murature," *Atti Convegno Nazionale sulla Salvaguardia dei Monumenti Storici dalla Vegetazione Infestante*. Cremona: Turris. 41-50.

PERTEGATO (1981). "Restauro dei materiali tessili," *Notizie CISST*, a.II. 26-33.

Pesticide Applicator Training Manual, Cat 7. Ithaca, NY: Cornell University, New York State College of Agriculture and Life Sciences. 1977.

Pesticide Handbook (Entoma) (1981-82). Entomological Society of America.

POMAREDE, V. (1989). "La désinfection des collections: un problème de méthodologie et de déontologie," *Patrimoine culturel et altérations biologiques. Actes des journées d'études de la S.F.I.I.C.* Poitiers: IIC Section Française. 135-144.

RICHARDSON, B.A. (1973). "Control of biological growths," *Stone Industries*, 8 (2) 1-6.

———, (1978). *Wood Preservation*. Lancaster, England: Construction Press, Ltd.

ROSSI DORIA, P., and R. CIARROCCA (1972). "Determinazione sperimentale delle variazioni cromatiche subite dalle superfici pittoriche per effetti degli agenti sterilizzanti," *Quaderni Ricerca Scientifica*, 81. Rome: CNR. 119-132.

SADURSKA, I., and R. KOWALIK (1969). "Protection of parchment against microflora," *Ann. Scuola Speciale Archivisti e Bibliotecari Univ. Roma*, anno IX (1-2) 51-60.

SEAWARD, M.R.D. (1985). "Lichens and ancient monuments: Conservation issues," *Int.Workshop on Biodeterioration of Ancient Stone-Work, Aurangabad, India.*

SHARMA, B.R.N., K. CHATURVEDI, N.K. SAMADHIA and P.N. TAILOR (1985). "Biological growth removal and comparative effectiveness of fungicides from central India temples for a decade in situ," *Proc. V Int. Congr. Deterioration and Conservation of Stone, Lausanne*. 675- 683. Lausanne: Presses polytechniques romandes.

SORLINI, C. (1984). *L'azione degli Agenti Microbiologici sulle Opere d'Arte*, ENAIP, Ed. del Laboratorio, Botticino (Brescia). 1-48.

SPRY, A.H. (1981), *The Conservation of Masonry Materials in Historic Buildings*. Dept. Environment South Australia, AMDEL Report 1381.

STIMMANN, M.W. (1983). *Pesticide Application and Safety Training*. University of California, Div.Agric.Sc. Publication N°4070. 1-107.

STRZELCZYK, A.B. (1981). "Stone-Microbial biodeterioration; painting and sculptures," *Economic Microbiology*, Vol. 6, ed. A.H. Rose. London: Academic Press. 61-80; 203-234.

TIANO, P. (1986). "Problemi biologici nella conservazione del materiale lapideo esposto," *La Prefabbricazione*, 22 (4) 261- 272.

———, and G. CANEVA (1987. "Procedures for the elimination of vegetal biodeteriogens from stone monuments," *ICOM Committee for Conservation, 8th Triennial Meeting, Sydney*. Paris: ICOM. 1201-1205.

URBAN, J., and P. JUSTA (1986). "Conservation by gamma radiation: the Museum of Central Bohemia in Roztoky," *Museum*, 38 (151) 165-167.

VALENTIN, N., M. LIDSTROM and F. PREUSSER (1990). "Microbial control by low oxygen and low relative humidity environment," *Studies in Conservation*, 35. 222-230.

VAN DER MOLEN, J., J. GARTY, B.W. AARDEMA and W. KRUMBEIN (1980). "Growth control of algae and cyanobacteria on historical monuments by a mobile UV unit (MUVU)," *Studies in Conservation,* 25 (2) 71-77.

VAN EMDEN, H.F. (1974). "Pest control and its ecology," *Studies in Biology,* N°50. London: Arnold. 1-60.

VILLA, A. (1977). "The removal of weeds from outdoor mosaic surfaces," *Mosaics N°1. Deterioration and Conservation. Rome, November 1977.* Rome: ICCROM. 49-52.

WAINWRIGHT, I.N.M. (1986). "Lichen removal from an engraved memorial to Walt Whitman," *APT Bull.*, XVIII (4) 46-51.

WARE, G.W. (1980). *Complete Guide to Pest Control - With and Without Chemicals.* USA: Thomson.

WORTHING, C.R., ed. (1987). *Pesticide Manual - A World Compendium.* 8th edition. Thornton Heath, U.K.: Glasshouse Crops Research Inst. British Crop Prot. Council.

ZAITSEVA, G.A. (1987). "Chemical measures of protecting USSR museum collections against keratin destroying insects (Coleoptera, Dermestidae, Lepidoptera, Tineidae)," *ICOM Committee for Conservation, 8th Triennial Meeting, Sydney.* Paris: ICOM. 1211-1214.

——— (1991). "Control of insects in museums: the use of traps." *Biodeterioration of Cultural Property. Feb. 1989 Lucknow, India.* Eds. O.P. Agrawal and S. Dharvan. New Delhi, India: MacMillan India Ltd. 469-477.

ZUFFI, S. (1988). "Ferrari da Passano: così ho sfrattato i piccioni dal Duomo di Milano," *Rassegna dei Beni Culturali,* 2. 44-45.

GLOSSARY

Acidophile An organism that prefers an acid environment (acidophilous).

Aerobe An organism that requires oxygen.

Aerobiology The study of atmospheric dispersal of airborne fungus spores, pollen grains and microorganisms.

Agar A gelatinous product extracted from real algae and often used as a gelling agent in culture media.

Algicide A chemical used to destroy algae.

Alkali Any compound having basic qualities.

Anabolism The part of metabolism involving the synthesis and polymerization of biomolecules.

Anaerobe An organism that does not require oxygen to grow (anaerobic).

Antibiosis An antagonistic association between two organisms in which one is adversely affected.

Antibiotic Chemical substances (produced either by microorganisms or synthetically) that have the capacity to inhibit the growth of or destroy other microorganisms.

Autotroph An organism capable of growth exclusively at the expense of simple inorganic substances.

Bactericide A chemical used to kill bacteria.

Bacteriostat A compound that inhibits or prevents the growth of bacteria.

Basophile An organism that prefers an alkaline environment (basophilous).

Biogeochemical cycle Cyclical bio- and geo-chemical interactions that exist between the atmosphere, hydrosphere, lithosphere and biosphere.

Biocide Any chemical able to kill living organisms.

Biocoenosis A biotic community living in a biotope.

Biodeteriogen An organism or microorganism that causes undesirable changes in the constituent materials of works of art.

Bioindicator A biological species with a narrow ecological range that can be used to interpret the value of an ecological parameter.

Biomass The dry weight of living material in a certain habitat.

Biotope An area uniform in environmental conditions and in its populations of animals and plants.

Calcicolous An organism that prefers a calcium-rich substrate.

Carbohydrates Group of organic compounds composed of C, H, O, including sugars, starches and cellulose.

Catabolism The part of metabolism involving the breakdown of molecules, often with liberation of energy.

Cellulolytic An organism or microorganism capable of hydrolyzing cellulose.

Chasmendolithic An organism living in preformed pores or cavities in rock.

Chelation A chemical process involving the formation of heterocyclic ring compounds containing at least one metal cation or hydrogen ion.

Chemolithotroph An organism or microorganism that can chemically utilize stone.

Co-factor A factor that assists the activity of enzymes.

Commensalism A relationship between two species in which one is benefited and the other is not affected.

Cyst A sac, especially a resting spore or sporangium-like structure.

Disinfectant A chemical that kills pathogenic or damaging organisms and reduces saprophytic ones.

Disinfection The destruction, with physical or chemical methods, of pathogens or damaging organisms and the reduction of saprophytes.

Disinfestant A chemical that kills insects or other harmful animals.

Disinfestation The killing of small animals, generally Arthropoda or small rodents.

Durability Natural resistance to deterioration (used to classify wooden materials).

Ecology The study of the interrelationships between organisms and the environment.

Ecological niche Position of an organism in an ecological space that is represented by its relationships with environmental factors and with the other organisms in the biocoenosis.

Ecosystem A system including the organisms of an area together with their environment.

Edaphic Concerned with the soil.

Endolithic Organisms living within rocks.

Entropy Measure of the disorder of a system.

Enzyme Any catalytic protein, produced by living cells, that mediates or promotes chemical processes.

Epilithic Organisms living over rocks.

Eukaryote A cell with a definite nucleus and cytoplasmatic organelles.

Eutrophicated Nutrient-enriched, either naturally or artificially.

Eutrophication The process of becoming better nourished, either naturally or artificially.

Fauna The animals of a particular geographical area or habitat.

Flora The plants of a particular geographical area or habitat.

Formulation A mixture of chemicals, composed of an active fraction and other compounds (coformulants) as coadjutors or carriers of the active ingredient.

Foxing Chromatic aberration of paper that appears as rust-colored marks.

Fungicide A chemical used to kill fungi.

Fungistat A compound that inhibits or prevents growth of fungi.

Germination The beginning of the process of development of a spore or seed.

Genus Taxonomical category corresponding to the first name of the binomial system (e.g. gen. *Rosa* sp. *canina*).

Habitat The part of the physical environment where a species lives.

Habitus The general appearance or constitution of an organism.

Halophile An organism that requires a high salt concentration for growth and maintenance (halophilous).

Heliophile An organism that requires a high intensity of sunlight (heliophilic).

Heliophobe An organism that needs dark conditions for growth (heliophobic). Also called photophygous.

Herbicide A chemical used to kill plants.

Heterotroph An organism that requires organic substances for growth.

Hydrolysis Decomposition or alteration of a chemical substance by water.

Hygrophile An organism that prefers environments with high humidity (hygrophilous).

Hygroscopicity The ability of a material to absorb water.

Hypertrophicated Over-enriched with nutrients.

Hypha One of the filaments composing the mycelium of a fungus.

Hysteresis The dependence of the state of a system on its previous history.

Indicator species A biological species with a narrow ecological range that can be used to interpret the value of an ecological parameter (see bioindicator).

Inhibition A process that arrests or retards the growth of an organism or the development of a chemical reaction.

Inorganic Chemical compounds that do not contain C as the principal element (except carbonates, cyanides and cyanates).

Insecticide A chemical used to kill insects.

Limiting factor In ecology, indicates an environmental parameter where values are narrow to the limits of tolerance of a species.

Lipids Group of organic compounds composed of C, H, O, including oils, greases and waxes.

Lysis The process of dissolution of a cell or tissue.

Mesophilous An organism or microorganism growing at an intermediate temperature value; in the case of plants, the term is used for intermediate value of water.

Metabolism The biochemical processes of anabolism and catabolism (metabolic).

Microaerophilous Aerobic organisms favored by low levels of oxygen.

Microbial Refers to microorganisms.

Microflora The flora of a microhabitat; microorganisms such as bacteria, micro fungi, microscopic algae, etc.

Microorganism Organism of small dimensions (uni- or pluri-cellular) usually not visible to the naked eye.

Mutualism Interactions between two species that are beneficial and necessary for both species.

Mycelium A mass of fungal hyphae.

Mycobiont The fungus component of the symbiotic relationship in a lichen.

Neutrophilous An organism that prefers a neutral environment (pH near 7).

Nitrophilous An organism that prefers substrates rich in nitrogen compounds.

Organic A chemical compound, based on C chains or rings and containing H with or without O, N or other elements.

Organism A biological individual.

Omnivore An organism that eats both animal and vegetable matter.

Osmosis The diffusion of a solvent through a semipermeable membrane separating two solutions of different concentrations. The solvent flows from the lower concentration to the higher concentration.

Parasite An organism that lives at the expense of another organism.

Parenchymatic Fundamental tissue.

Pesticide A chemical agent that destroys pests; also known as a biocide.

Phloem Vascular tissue in higher plants where elaborated substances are transported.

Photochemical Chemical reactions due to the action of light.

Photoperiodism The physiological response of an organism to the length of day or night or both.

Photophile An organism that thrives in a fully lit environment (photophilous) (see also heliophile).

Photosynthesis The process of synthesis of glucose using CO_2 as a carbon source and light as the energy source.

Phototroph An organism that utilizes light as a source of metabolic energy (phototrophic).

Phycobiont The algae component of the symbiotic relationship in a lichen.

Physiology The study of reactions that occur in cells or tissues of living organisms.

Phytosociology The study of plant communities.

Pioneer An organism able to establish itself in a barren area and to begin an ecological cycle.

Poikilohydric An organism able to function or survive at a variable water content.

Polymerization The bonding of two or more monomers to produce a polymer.

Population A group of organisms of the same species occupying a specific geographical area.

Prokaryotes Primitive microorganisms without nucleus and cytoplasmatic organelles (bacteria, actinomycetes and blue-green algae).

Protein A polymeric compound formed by several amino acids joined by peptide bonds.

Proteolytic An organism or microorganism able to hydrolyze proteins.

Psychrophile An organism that prefers cold habitats (psychrophilous).

Respiration The biochemical process of oxidation of organic substances during catabolism, in which CO_2 and water are produced.

Ruderal Species that prefer disturbed habitats such as ruins or places with abundant waste.

Saprophyte Heterotrophic organisms living on dead organic matter.

Spore A uni- or multicellular, asexual, reproductive or resting body with variable resistance to unfavorable environmental conditions.

Seasoning Preparation (of lumber) by drying in the open air or a kiln.

Silicicolous An organism that grows or thrives on siliceous rocks.

Species Taxonomic category including closely related, morphologically similar individuals that actually or potentially interbreed.

Sporangium A structure that produces spores.

Sterilization The process of killing and/or eliminating all forms of microbial life.

Strain A race of microorganisms.

Substrate The material or medium on or in which an organism grows.

Succession The gradual replacement of a community with new species populations better adapted to the evolved environmental condition.

Symbiont An organism or microorganism that forms a symbiosis.

Symbiosis A positive relationship between two organisms or microorganisms which link together and form a stable complex or an organism.

Synsystematics The study of the classification of plant communities in phytosociology.

Systematics The study of the classification of species or communities.

Taxonomy Study aimed at producing hierarchical systems of classification of organisms, based on their similarities and differences.

Thallus The body of lower plants or of microorganisms, not differentiated into special tissue systems or organs.

Thermophile An organism that prefers high temperatures (thermophilous).

Trophic chain The nutritional relationships among organisms in an ecosystem.

Ubiquitous Species or communities that live everywhere, not tied to a particular environment.

Vegetation Qualitative and quantitative characterization of plants living in a given place.

Weed A plant that is considered useless or of low economic value, especially when growing on cultivated land to the detriment of crops.

Xeric Pertaining to a habitat having a low or inadequate supply of water.

Xerophile An organism capable of living in areas where the water supply is limited (xerophilous).

Xylem Vascular tissue in higher plants where mineral ions and water are transported from the roots to the other parts of the plant (= wood).

APPENDIX

1 ELEMENTS OF GENERAL BIOLOGY

1.1 Chemical composition of cells

1.2 Cellular organization

1.3 Chemical activity (metabolism)

2 ELEMENTS OF SYSTEMATICS OF BIODETERIOGENS

2.1 Kingdom Monera

2.1.1 Bacteria

2.1.2 Cyanobacteria

2.1.3 Actinomycetes

2.2 Kingdom Protista

2.3.1 Chlorophytes

2.3.2 Diatoms

2.3 Kingdom Fungi

2.4 Kingdom Plantae

2.4.1 Mosses and Liverworts

2.4.2 Higher plants (vascular)

2.5 Kingdom Animalia

2.5.1 Insects

2.6 Symbiotic organisms

2.6.1 Lichens

3 TECHNIQUES OF ANALYSIS

3.1 Microbiological analyses

3.2 Botanical analyses

APPENDIX

1 ELEMENTS OF GENERAL BIOLOGY

Living organisms appear in a vast variety of shapes and functions, but despite this manifold diversity, they have some common characteristics: chemical composition, cellular structure and basic chemical activities.

1.1 Chemical composition of cells

The composition of living matter is very different from that of the lithosphere and atmosphere. Only 22 of the 100 elements found in the earth's crust are essential components of living organisms. The chemical elements constituting living matter can be classified as:

a) *Plastic elements* which form the mass of organic material. Carbon (C), oxygen (O), hydrogen (H) and nitrogen (N) are the most important constituents by weight. Phosphorous (P) is present in all nucleic acids and in many lipids, sulfur (S) enters into the composition of many proteins.

b) *Mineral elements* in the form of oxides, mineral salts or electrolytes: Na, K, Mg, Ca, Cl.

c) *Oligoelements* which participate in the catalysis of chemical reactions are required in very small amounts: Fe, Mn, Co, Cu, Zn, B, Al, V, Mo, I, Si.

As observed in ¶1.2.3, it is not always possible to distinguish between macro and micronutrients or mineral elements and oligoelements.

Water is the main component of living matter. The atomic composition and dipolar structure of the water molecule give rise to various properties that are very important for permitting life: liquidity at normal temperatures, high specific heat, latent heat of evaporation and fusion, different density of the crystalline form, viscosity not too high, strong forces of adhesion and cohesion, solvent properties.

Carbohydrates (also called sugars) contain C, H, O. *Monosaccharides* are the simplest carbohydrates; they are made up of a chain of carbon atoms to which hydrogen and oxygen atoms in the ratio of 1:2:1 are connected. Sugars with five or six carbon atoms may have a cyclic configuration. Monosaccharides can join to produce chains of varying length: *polysaccharides.* Among monosaccharides, we mention glucose ($C_6H_{12}O_6$), fructose ($C_6H_{12}O_6$) and ribose ($C_5H_{10}O_5$). Among polysaccharides, starch and glycogen are reserve materials; cellulose and chitin have a structural function.

Lipids are made up of C, H, O; they include oils, greases and waxes. They are insoluble in water and hold many carbon-hydrogen bonds; therefore, they release more energy by oxidation than other organic compounds. They can act as structural (e.g., lipids of membranes) or reserve materials.

Proteins are made up of chains of amino acids, small molecules containing C, H, O, N and sometimes S. There are 20 different kinds of amino acids which, by bonding themselves in various sequences, give rise to many different proteins. Several levels of organization characterize a protein molecule: a primary structure, or the sequence of amino acids in the polypeptide chain that bends in a spiral (a secondary structure) eventually evolving in a convoluted fashion (a tertiary structure). Two or more polypeptide chains can join in forming a quaternary structure. Proteins can act as structural materials (e.g., fibrous protein) or as specific catalysts in different metabolic chemical reactions (enzymes).

Nucleic acids are chains formed by four different nucleotides. A nucleotide consists of a sugar (pentose), a nitrogen base and a radical of phosphoric acid. There are two kinds of nucleic acids: deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). Stored in the DNA is genetic information transported and transmitted by RNA. Due to RNA intervention, DNA guides the synthesis of proteins and thus the structure and function of the cell.

1.2 Cellular organization

There are two different kinds of cells in organisms: the *prokaryotic cell*, less differentiated, is the structural unit of bacteria, including cyanobacteria and actinomycetes; the *eukaryotic cell*, very highly differentiated, is the structural unit of plants, animals, fungi, protozoans and algae (except blue-green algae, which are preferably called cyanobacteria).

A eukaryotic cell is made up of two partitions: the *nucleus* and the *cytoplasm* delimited by their respective membranes, the nuclear membrane and the cytoplasmic membrane. Plants, algae and fungi have a cell wall, formed principally by cellulose, outside (in the case of plants) the cytoplasmic membrane.

In the cytoplasm, there are many kinds of organelles and membrane systems having specific functions: mitochondria, the oxidation center of carbohydrates, lipids and amino acids; the Golgi apparatus, with functions of secretion and storage; ergastoplasm or endoplasmic reticulum, a system of membranes on the surface of which there are ribosomes for synthesis of protein; vacuoles, which act in the confinement of waste materials and amassed solutes; plastids (in plants and algae), some of which contain chlorophylls or other photosynthesizing pigments and sites of photosynthesis (*chloroplasts*).

In the nucleus there is DNA (deoxyribonucleic acid) organized with some proteins (histones) in chromosomes entering into mitosis during cellular division. Mitosis, or nuclear division, assures an equal distribution of genetic materials between daughter cells.

The structure of a prokaryotic cell is simpler: it has only one membrane, the cytoplasmic one; the nucleus is not surrounded by a membrane, there are no organelles such as mitochondria, chloroplasts or endoplasmic reticulum. There is only one chromosome consisting of a single molecule of DNA thickly condensed in the nuclear zone. Prokaryotes are the first cells to have evolved during biological evolution; eukaryotes have an evolutionary origin more recent than prokaryotes and probably arose from the latter.

The simplest organisms consist of a single cell (unicellular organism), and since they are very small, they are called microorganisms. In addition to these, there are multicellular organisms, formed by a large number of cells (the smallest are also called microorganisms).

Organisms reproduce by two main methods: asexual reproduction (fission, gemmation, production of spores, fragmentation or division of its parts) or sexual reproduction (the fusion of two cells, the gametes, gives rise to a new cell, the zygote, from which the new organism develops). Organisms can be haploid (with n chromosomes) or diploid (with 2n chromosomes).

1.3 Chemical activity (metabolism)

All organisms carry on some common chemical activities called metabolic activities or *metabolism.* Metabolism has two aspects, in fact two types of opposing phenomena occur unceasingly: constructive or reintegrative (*anabolism*) activities that store energy, and destructive activities (*catabolism*) that release energy. Catabolism provides the cell with necessary energy and with some compounds that can serve as building blocks for polymers. Anabolism, by contributing to an increase in cellular mass and duplication of vital molecules, makes growth and reproduction possible. Catabolism can take the form of aerobic respiration, anaerobic respiration or fermentation. *Respiration* is a process of biological oxidations which utilize an electron transport system that operates either with oxygen (aerobic respiration) or with another compound (anaerobic respiration) as a terminal electron acceptor (*Fermentation*).

Photosynthesis is a metabolic process present only in plants, algae and some bacteria (e.g., cyanobacteria) involving the photoreduction of carbon dioxide to glucose. With the exclusion of some bacteria, there is a concomitant liberation of oxygen from photolysis of water:

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + O_6$$

In photosynthetic bacteria, much stronger reducing substances are used in place of water.

All the metabolic reactions occur through the activity of enzymes. *Enzymes* are proteins or proteins combined with other chemical groups that have the capacity to speed up chemical reactions (catalytic action). Enzymes may be defined as organic catalysts produced by living cells. All enzymes are produced in the cell but are recognized on the basis of their site of action: intracellular enzymes (*endoenzymes*) are not excreted into the environment, while extracellular enzymes (*exoenzymes*) are excreted outside the cell.

Endoenzymes synthesize cellular material from assimilated substances or perform catalytic reactions which provide the energy requirements. In contrast, the principal function of exoenzymes is to perform chemical modification of nutrients in the medium in order to allow them to enter the cell. These enzymes transform complex molecules, such as proteins and cellulose, into simple ones that are soluble in water. In this way, heterotrophic microorganisms decompose organic matter.

Some enzymes, called constitutive enzymes, are always produced by cells, and their production is independent of the composition of the medium; other enzymes, called adaptive or inductive enzymes, are produced by the cell only in response to the presence of a particular growth substrate, so they are produced only when needed. Organisms are classified in two major nutritional groups on the basis of the chemical form of carbon needed from the environment: *autotrophs*, which use CO_2 as their main source of carbon, and *heterotrophs*, which are unable to synthesize organic compounds from inorganic compounds and need organic substances as their main source of carbon. Considering the nature of the energy source, four nutritional groups can be established (see Table A-1).

Table A.1 Classification of living organisms in nutritional groups

TYPE OF ORGANISM	CARBON SOURCE	ENERGY SOURCE	ELECTRON DONORS	EXAMPLES
PHOTOAUTOTROPHS or photolithotrophs	CO_2	sunlight	inorganic compounds (H_2O, H_2S, S)	higher plants, eukaryotic algae, cyanobacteria, green and red sulfur bacteria, lichens
PHOTOHETEROTROPHS or photoorganotrophs	organic compounds	sunlight	organic compounds	red nonsulfur bacteria, some eukaryotic algae
CHEMOAUTOTROPHS or chemolithotrophs or chemosynthetics	CO_2	ox-red reactions	inorganic compounds (H_2, S, H_2S, Fe II, NH_3)	hydrogen bacteria, sulfur bacteria, iron bacteria, denitrifying bacteria
CHEMOHETEROTROPHS or chemoorganotrophs	organic compounds	ox-red reactions	organic compounds (glucose)	animals, protozoans, fungi and many bacteria

Heterotrophs, which require organic substances from other organisms, can be saprophytes, parasites or symbionts.

Saprophytes decompose organic matter of animal and vegetable origin, giving rise to different fermentative processes. *Parasites* live at the expense of other living organisms. *Symbionts*, living in association (symbiosis) with other organisms, receive substances necessary for life from their companion organisms and provide that organism with substances of equal importance to them (e.g., fungi in symbiosis with algae give rise to lichens, other fungi in association with plant roots give rise to mycorrhiza).

Table A.2 - Classification of major groups of living organisms (lichens are not mentioned because they arise from the symbiosis between an alga and a fungus). The underlined classes are those most involved in biodeterioration of works of art.

PROKARYOTES	I	KINGDOM MONERA
		Bacteria, including Cyanophyta (blue-green algae)
		Actinomycetes and mycoplasm
EUCARYOTES	II	KINGDOM PROTISTA
THALLOPHYTES (with thallus)	ALGAE	Division Chlorophyta (green algae)
		Division Phaeophyta (brown algae)
		Division Rhodophyta (red algae)
		Division Chrysophyta (diatoms and golden-brown algae)
		Division Xanthophyta (yellow-green algae)
		Division Pyrrophyta (dinoflagellates)
	FLAGELLATE HETEROTROPHIC FORMS	Division Euglenophyta (euglenoids)
		Division Gymnomycota (slime molds)
		Class: Myxomycetes (true slime molds)
		Class: Acrasiomycetes (cellular slime molds)
		Division Mastigomycota
		Class: Chytridiomycetes (chytrids)
		Class: Oomycetes (water molds)
	III	KINGDOM FUNGI
	FUNGI	Division Eumycota (true fungi)
		Class: Zygomycetes (bread molds)
		Class: Ascomycetes (sac fungi)
		Class: Basidiomycetes (club fungi)
		Class: Deuteromycetes
	IV	KINGDOM PLANTAE
	BRYOPHYTES	Division Bryophyta (nonvascular plants)
		Class: Musci (mosses)
		Class: Anthocerotae (hornworts)
		Class: Hepaticae (liverworts)
CORMOPHYTES (with cormus)	SEEDLESS VASCULAR PLANTS	Division Tracheophyta (vascular plants)
		Subdivision Psilophytina (whisk ferns)
		Subdivision Lycophytina (club mosses)
		Subdivision Sphenophytina (horsetails)
	SEED PLANTS	Subdivision Filicophytina (ferns)
		Subdivision Spermatophytina (seed plants)
	GYMNOSPERMS	Class: Cycadinae (cycads)
		Class: Gynkgoinae (ginkgo)
		Class: Coniferinae (conifers)
	ANGIOSPERMS	Class: Gnetinae (vessel-containing gymnosperms)
		Class: Angiospermae (flowering plants)
		Subclass: Dicotyledoneae (dicots)
		Subclass: Monocotyledoneae (monocots)

From J.H.Langenheim, K.V.Thimann (1982). *Plant Biology and its Relation to Human Affairs*. New York: John Wiley and Sons.

ANIMALS — V KINGDOM ANIMALIA

PROTOZOA — Phylum Protozoa

METAZOA
- METAZOA — Phylum Mesozoa
- PLACOZOA — Phylum Placozoa
- PARAZOA — Phylum Parazoa
- EUMETAZOA
  - Radiata — Phylum Coelenterata
  - Bilateria
    - Phylum Platyhelmintes
      - Class: Turbellaria
      - Class: Trematoda
      - Class: Cestoda
    - Phylum Echinodermata
    - Phylum Anellida
      - Class: Polychaeta
      - Class: Oligochaeta
      - Class: Hirudinea
    - Phylum Arthropoda
      - Class: Arachnida
      - Class: Crustacea
      - Class: Myriapoda
      - Class: Insecta
    - Phylum Mollusca
      - Class: Gastropoda
      - Class: Lamellibranchia
      - Class: Cephalopoda
    - Phylum Vertebrata
      - Class: Agnotha
      - Class: Elasmobranchii
      - Class: Osteichthyes
      - Class: Amphibia
      - Class: Reptilia
      - Class: Aves
      - Class: Mammalia

("Phylum" is a taxonomic category used in classifying animals, which corresponds to "Division" in botanical classification)

From M. La Greca (1982). *Zoologia*, Novara: De Agostini (modified).

2 ELEMENTS OF SYSTEMATICS OF BIODETERIOGENS

The main morphological and physiological characteristics of organisms involved in biodeterioration of materials are described in the following paragraphs. The current classification of living organisms into five kingdoms is given in Table A.2.

2.1 Kingdom Monera

The kingdom Monera includes only prokaryotes. Some systematic groups of bacteria such as Cyanobacteria and Actinomycetes have peculiarities that justify a differential description.

2.1.1 Bacteria

Bacteria are unicellular organisms, prokaryotes, of various shapes (roundish, rod or spiral). Their average diameter varies between 0.2 and 2 μ, while they can approach 20 μ or more in length. Bacterial cells may remain independent or join together in different ways (e.g., in groups of two, in chains or in bunches, etc.). The nucleus has no nuclear membrane. The cell wall is beyond the cytoplasmic membrane, and gives form to the cell: it is stiff, yet flexible and slightly elastic and preserves its shape always. Its more important functions are protection and support. The cell wall is principally formed by murein, a complex peptidoglycan. Sometimes a slime capsule, a covering of variable thickness, is present outside the cell wall. On the basis of the structure of the cell wall and capsule, bacteria are distinguished into Gram+ or Gram-. Bacteria can have cilia or flagella (necessary for movement), which vary in number and position. If cilia and flagella are absent, the bacteria are motionless (Fig. A.1).

Some species form spores (only one spore from one bacterium), which can remain alive in the environment for several years. A bacterial spore is resistant to adverse environmental conditions. Bacteria generally reproduce by binary fission or schizogenesis, i.e. a cell's simple division into two parts. Bacterial reproduction is rapid and under favorable conditions a fission may take place every 20-25 minutes. Bacteria include autotrophic and heterotrophic species.

2.1.2 Cyanobacteria

These are prokaryotic, unicellular or colonial, often filamentous forms. Species with single cells are comparatively rare. They contain chlorophyll *a* and other types of additional pigments (carotenoids, xanthophylls, phycocyanins, phycoerythrins) not in chloroplasts, but bound to a system of photosynthetic membranes inside the cytoplasmic membrane. Every cell is covered with a wall and on the outside by a slime sheath (Fig. A.2). The outside sheath is often pigmented and imparts various colors to the cells (golden yellow, brown, red, emerald green, dark blue, violet, azure). Carotenoids and phycobilins modify the color of cells. In spite of the common name (blue-green algae), only half of them are really blue-green. They do not have cilia or flagella, but move by the motion of their environment. Reproduction takes place by simple fragmentation or by cellular fission; many species form spores.

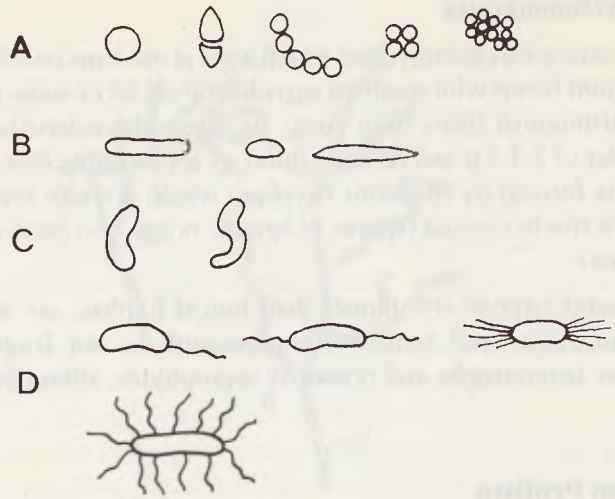


Fig.A.1 *Typical cell forms of bacteria:*
A) cocci B) bacilli C) vibrions and spirilla
D) monotrichous, amphitrichous and peritricous forms

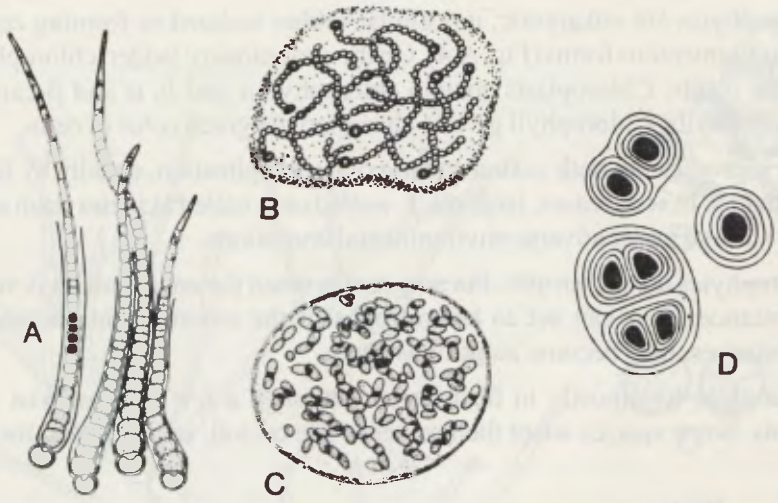


Fig.A.2 *Some examples of cyanobacteria:*
A) Calothrix braunii B) Nostoc sp. C) Aphanothece stagnina D) Gloeocapsa turgida.

Cyanobacteria are able to adjust to adverse environmental conditions. Some species form a part of plankton; many marine species grow on limestone and on other substances rich in calcium carbonate.

Many species are able to fix nitrogen, and for this reason these bacteria can become established on bare rock; some species are anaerobic and oxidize hydrogen sulfide.

2.1.3 Actinomycetes

Actinomycetes are Schizomycetes which were at one time considered microscopic fungi, as they exhibit forms with ramified mycelia during all or some phases of their life cycle. We can distinguish them from fungi by some characteristics: hyphae have a maximum diameter of 1-1.5 μ and do not exhibit an apparent nucleus (prokaryotic cell). Their mycelium is formed by filaments (hyphae) which are also branched. In culture, aerial hyphae give rise to conidia (spores of agamic origin), so these can be assumed to be real conidiophora.

Actinomycetes hyphae are thinner than fungal hyphae, are not partitioned but appear as a continuous and hollow filament and do not fragment (Fig. A.3). Actinomycetes are heterotrophs and primarily saprophytes, although some species are parasites.

2.2 Kingdom Protista

Algae do not belong to a single homogeneous systematic group. Here, we will treat only Chlorophytes (or green algae) and Bacillariophytes or Diatoms. All algae are autotrophic (photosynthetic) organisms. At times they can also survive heterotrophically.

2.3.1 Chlorophytes

Chlorophytes are eukaryotic, unicellular (either isolated or forming colonies) or multicellular filamentous forms (Fig. A.4). On the evolutionary ladder, chlorophytes gave rise to higher plants. Chloroplasts contain chlorophyll *a* and *b*, α and β-carotene and various xanthophylls. Chlorophyll gives a characteristic green color to cells.

They reproduce by both sexual and asexual multiplication, usually by fragmentation of the thallus. In some cases, large thick-walled cells called akinetes form and permit the algae to survive under adverse environmental conditions.

Chlorophytes are autotrophs, but sometimes when the environment is very rich in organic substances they can act as heterotrophs; if the environment becomes rich in mineral substances, they become autotrophs again.

Green algae live mostly in fresh water, although a few species exist in marine environments. Some species adapt themselves to life on soil, sediment and rocks.

2.3.2 Diatoms

Diatoms are eukaryotic unicellular forms, either isolated or forming colonies. They are enclosed in a wall of silica (frustule) consisting of two valves fitting each other like a box and a lid. The delicate forms of frustules are characteristic of individual species (Fig. A.5). Diatoms have chlorophyll *a* and *c*, β-carotene, fucoxanthin and other xanthophylls; they reproduce by both asexual and sexual multiplication, and are able to take up silicon. Both fresh- and salt-water species exist. Fresh-water species may also exist in microenvironments where flowing water is very scarce.

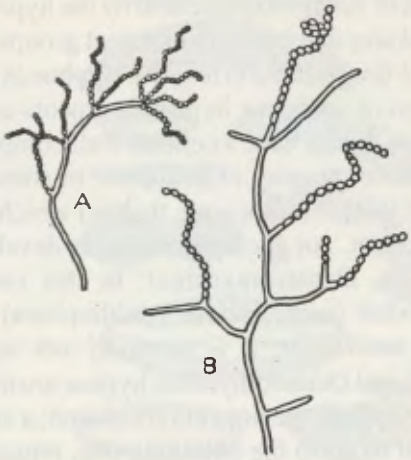


Fig.A.3

Actinomycetes (Streptomyces sp.):. A) appearance of mycelium and spores B) under the oil immersion objective

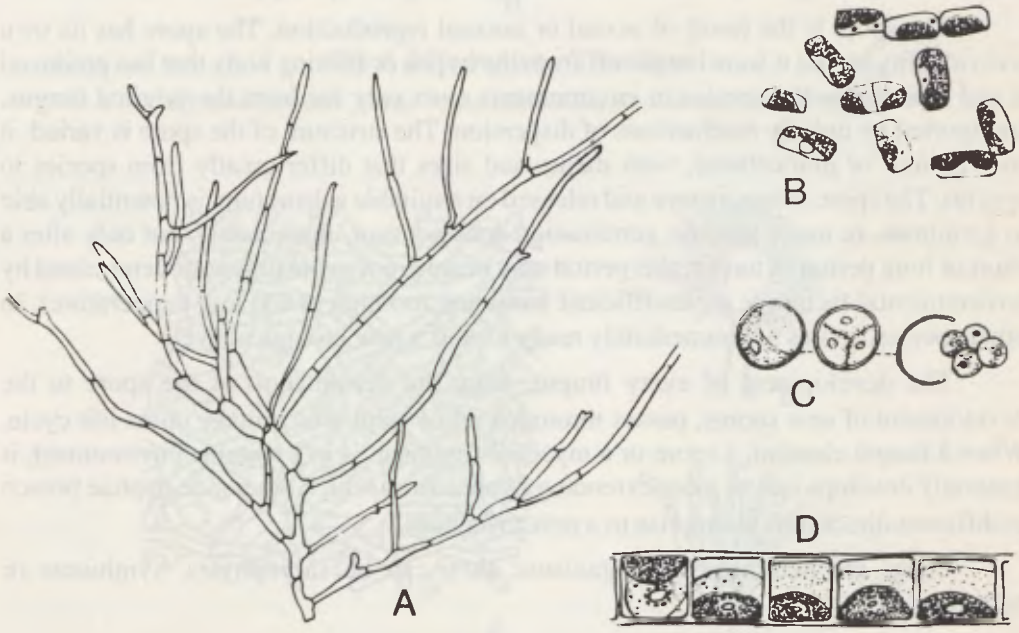


Fig.A.4

Examples of Chlorophytes: A) Cladophora sp. B) Stichococcus bacillaris C) Chlorella vulgaris D) Chlorhormidium dissectum.

2.3 Kingdom Fungi

The basic structural unit of fungi is represented by the hypha, a mono- or multicellular filament with a shape and size that varies in different groups of fungi (from 1.5-2 to 10-12 μ in diameter, and from a few to 100 μ in length). Hyphae as a whole, the mycelium, originate from the germination of spores or hyphal fragments and form the vegetative body of fungi, called the thallus. Fungi have a cellular wall composed of polysaccharide compounds: chitin and a variable quantity of cellulose. In some lower fungi, a single unicellular element forms the thallus (holocarpic thallus) which, when it has matured, changes into a reproductive organ. An eucarpic thallus is developed by many hyphae (Ascomycetes, Basidiomycetes, Deuteromycetes). In this case, vegetative bodies (hyphae) and reproductive bodies (asca, basidia, conidiophora) regularly differentiate (Fig. A.6). If the hypha is unicellular, it is normally not septate (coenocytic); in Ascomycetes, Basidiomycetes and Deuteromycetes, hyphae are multicellular and always septate. Septa of multicellular hyphae are not entirely closed; a small hole, allowing the nucleus or cytoplasm of a cell to go to the adjoining one, remains in the center of the septum.

In a peculiar group of fungi, Yeasts, there is no real mycelium, in fact the thallus is made up of single uninucleate cells multiplying by gemmation. The cell wall is composed not of cellulose, but of another polysaccharide, chitin in most fungi. Reproduction occurs in two different ways: sexual or asexual. In the first case, two sensitive structures, acting respectively as male and female organs (gametes), join. In many cases they are morphologically undifferentiated organs (e.g., simple hyphal cells).

The spore is the result of sexual or asexual reproduction. The spore has its own individuality in that it soon breaks off from the hypha or fruiting body that has produced it and reproduces the species in environments even very far from the original fungus, transported by orderly mechanisms of dispersion. The structure of the spore is varied: it may be uni- or pluricellular, with shapes and sizes that differ greatly from species to species. The spore, when mature and released on a suitable substratum, is potentially able to germinate. In many species, germination does not start immediately, but only after a short or long period of torpor; this period may be inherent to the fungus or determined by environmental factors (e.g., insufficient humidity, too high or too low temperature). In other species, spores are immediately ready to start a new biological cycle.

The development of every fungus, from the germination of the spore to the development of new spores, passes through a set of steps which make up its life cycle. When a fungal element, a spore or a mycelial fragment, is in a suitable environment, it generally develops one or more extending hyphae from which other side hyphae branch in different directions, giving rise to a new mycelium.

Fungi are heterotrophic organisms; they can be saprophytes, symbionts or parasites.

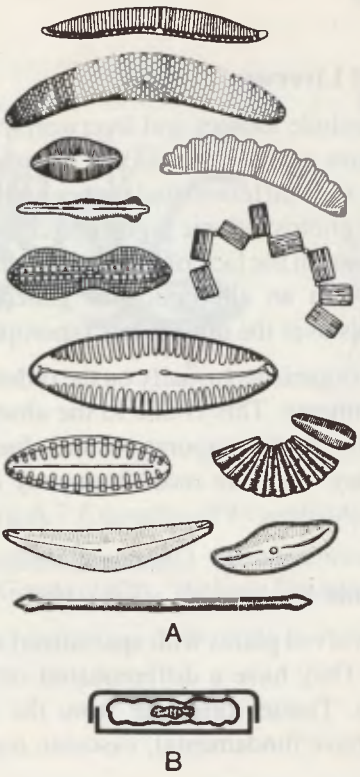


Fig.A.5 *Examples of Diatoms:*
A) some pennate forms B) a siliceous wall with the cell inside.

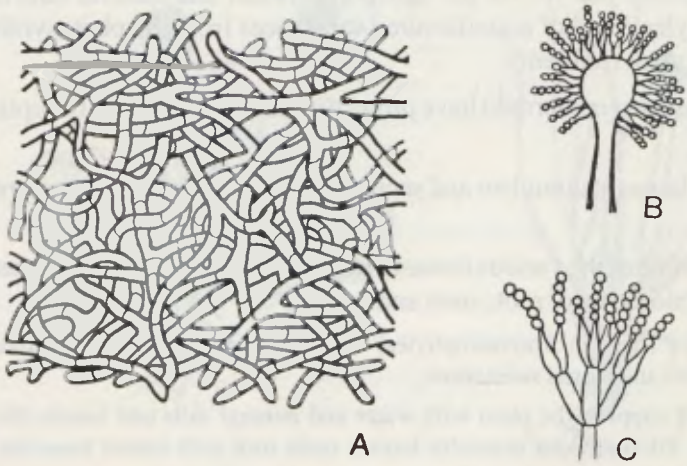


Fig.A.6 *Examples of fungal structures:*
A) mycelium formed by fungal hyphae. B) and C) Conidiophores with conidia (spores) of two Deuteromycetes: Aspergillus sp. and Penicillium sp.

2.4 Kingdom Plantae

2.4.1 Mosses and Liverworts

Bryophytes, which include mosses and liverworts, are transition forms between Thallophytes (primitive plants without tissues and organs) and Cormophytes (evolved plants) (Fig. A.7). They lack well-differentiated tissues and have a primitive organization. As with all plants, they have photosynthetic pigments (chlorophyll *a, b*, carotenoids), but they differ from vascular plants in the lack of transport elements (phloem and xylem) and in their biological cycle, with an alternation of generations in which the haploid (gametophyte) phase prevails over the diploid one (sporophyte).

Bryophytes are small organisms (usually on the order of few centimeters), generally linked to aquatic environments. This is due to the absence of transport and support structures to protect systems from evaporation and due to their need of water for reproduction (oogamy). They therefore most frequently occur in humid areas and in tropical zones.

2.4.2 Higher plants

Vascular plants are evolved plants with specialized tissues and organs that permit a subdivision of activities. They have a differentiated structure with roots, stems and leaves (cormus) (Fig. A.8). Tissues originate from the functional differentiation of meristematic cells and can have fundamental, vascular, tegumental and secretory functions.

Fundamental tissues (parenchyma) can perform functions of respiration, photosynthesis, transport of water and air, conservation of reserve materials and support (collenchyma and sclerenchyma).

Vascular tissues provide for the transport of water and mineral salts from bottom to top (wood or xylem) and of manufactured substances from the photosynthetic sites to other parts of the plant (phloem).

Covering tissues (epidermis) have protective functions and can be replaced by cork in woody plants.

Secretory tissues accumulate and secrete various substances (nectar, resins, gums, latex, etc.).

The disposition of the various tissues in the plant leads to the development of organs with specific functions: seed, root, stem and leaf.

- The seed (only in Spermatophytes) consists of an embryo, protective tegumental structures and stored substances.
- The root supplies the plant with water and mineral salts and fastens the plant to the ground. Dicotyledons normally have a main root with lateral branches (fasciculate roots). In Monocotyledons, the primary root dies and numerous adventitious root arise from the base of the stem. In some cases, aerial roots may exist.
- The stem connects the absorbent roots with the photosynthesizing leaves. It is principally composed of conduction and support tissues.

Fig.A.7 *Examples of Bryophytes:*

A) a moss (Oxyrrhynchium rusciforme) B) a liverwort (Marchantia sp.);
r = rhizines (from F.M. Gerola (1978). "Biologia Vegetale - Sistematica." UTET).

Fig.A.8 *Examples of Angiosperms:*

A) Taraxacum officinale (Dicotyledons) B) Dactylis glomerata (Monocotyledons);
r = roots, l = leaves, fl = flowers, s = seeds, st = stem.

- The leaf is the centre of intense metabolic activity and exhibits extensive development of chlorophyllian parenchyme.

Higher plants have an alternation of generations in which the diploid phase (sporophyte) is clearly dominant, while the haploid phase is limited to a very short period of the cycle life. They can have either sexual or asexual reproduction by fragmentation of the plant itself or, in some cases, by latent buds.

Vascular plants can be subdivided into Pteridophyte (Filicophytina) and Spermatophyte (Spermatophytina) on the basis of the absence or presence of seeds. In the Spermatophyte group we can distinguish Gymnosperms and Angiosperms on the basis of the absence or presence of flowers in which the reproductive organs are clustered.

2.5 Kingdom Animalia

The kingdom of animals includes a large number of different species collected into Invertebrates and Vertebrates. Among Invertebrates, some species of Mollusca and Arthropoda (Crustacea and Insects) are involved in the biodeterioration of works of art, but insects play the leading role.

Only insects will be discussed here, as we consider it superfluous to examine closely the other groups of Invertebrates and Vertebrates.

All animals are heterotrophs.

2.5.1 Insects

Insects are a class of Arthropods; there are hundreds of thousands of insect species.

The adult insects are segmented animals that have the following features:

- a well-defined head bearing a single pair of antennae, three pairs of mouth parts and usually a pair of compound eyes
- a segmented thorax, each segment of which bears a pair of legs ventrally with the second and the third often bearing a pair of dorsolateral wings
- an abdomen of 7 to 10 visible segments without true jointed legs but often with the last segments modified or fitted with specialized extensions

The life cycle of insects is very complex, and often involves complex metamorphosis. In the most primitive insects, such as cockroaches, metamorphosis is incomplete and goes through egg - larva - nymph - adult. The nymph state is very similar to the adult. In the most evolved insects, such as butterflies and beetles, metamorphosis is complete: egg - larva - pupa - adult. The pupa state is a quiescent stage followed by the adult, or imago (Fig. A.9).

In the different stages of their life cycle, insects have their own habitat and requirements. In general, it is the larva that causes damage to objects as it actively feeds. Many adults live only for a short period for the purpose of reproduction and eat very little.

Insects need oxygen to breathe. Many species, such as termites, avoid the light and are active only at night.

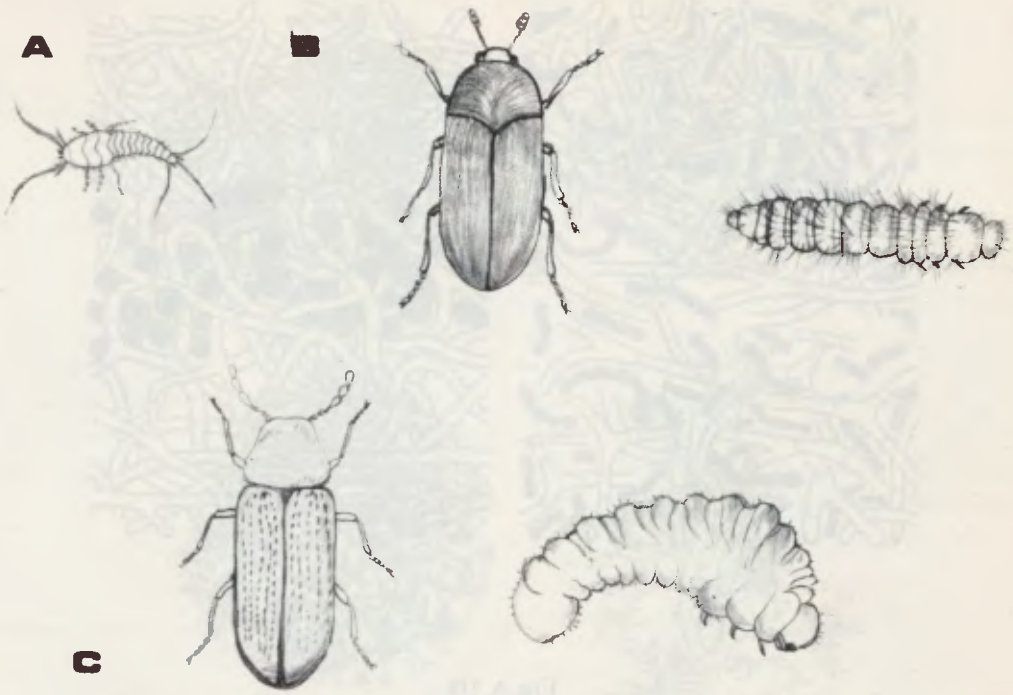


Fig.A.9 *Examples of insects:*

A) Lepisma saccharina (Lepismatidae)
B) Dermestidae, adult and larva C) Anobiidae, adult and larva

With regard to nutrition, insects can be omnivores (like cockroaches, which feed on all kinds of organic substances) or they can have a specialized diet. Indeed, many insects prefer only one kind of material, for example moth larvae use proteinaceous substances for their nourishment, whereas xylophagous species need cellulose. The nutritional requirements of insects often vary greatly in different phases of the life cycle.

2.6 Symbiotic organisms

2.6.1 Lichens

Lichens are autotrophic organisms consisting of a symbiosis between a microscopic alga (belonging to either Cyanobacteria or Chlorophyte groups) and a fungus (Eumycetes). Lichens have characteristics typical of the two kinds of organisms that make them up but, most importantly, they gain others that are peculiar morphologically, biochemically and ecologically.

The fungus shares in the structure of the thallus with an interlacing of hyphae. Algae may be arranged through the entire thallus (homeomeric thallus) or combined in a single layer in the upper zone (heteromeric thallus) (Fig. A.10).

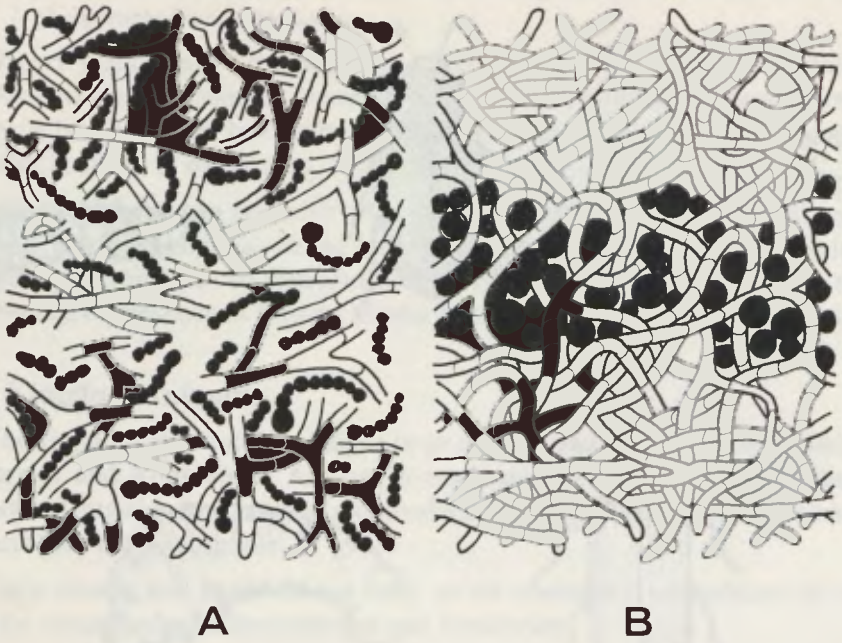


Fig.A.10

The two characteristic structural types of thallus in lichens:
A) homeomeric B) heteromeric. (The algae are the black elements.)

In lichens, algal cells synthesize carbohydrates by means of a chlorophyll function, while the fungus contributes to the symbiont by absorbing water from the substrate and at the same time protecting the algae, which are weaker, from adverse environment conditions, such as insolation or extreme temperatures. In fact, lichens (about 18,000 species) are among the most resistant plants, and can live in both torrid and polar regions. The morphology of the lichen thallus is variable (Fig. A.11): crustose (firmly attached to the substrate by a general mass of hyphae and making up about 3/4 of all lichens), foliose (bearing leaf-like lobes; attached to the substrate by distinct clusters of hyphae termed rhizines), squamulose (showing small scales or squamules; do not have rhizines, do not adhere at the edge) or fruticose (may be unattached or may grow from a disc or cluster of rhizoids called a holdfast).

The growth of the lichen thallus is always very slow (generally about 0.1-10 mm per year, although in exceptional cases some may grow centimeters); in crustose and foliose lichens, growth takes place principally in horizontal directions at the edges; in fruticose lichens it is vertical and apical. Lichens spread in different ways:

- by dissemination of unspecialized fragments of thallus, or by isidia, soredia or sorales acting as propagules for vegetative reproduction of the lichen
- by dissemination of fungal spores, produced by fruiting bodies that germinate and develop hyphae reaching other algae with which they will develop symbiosis and so form a new lichen

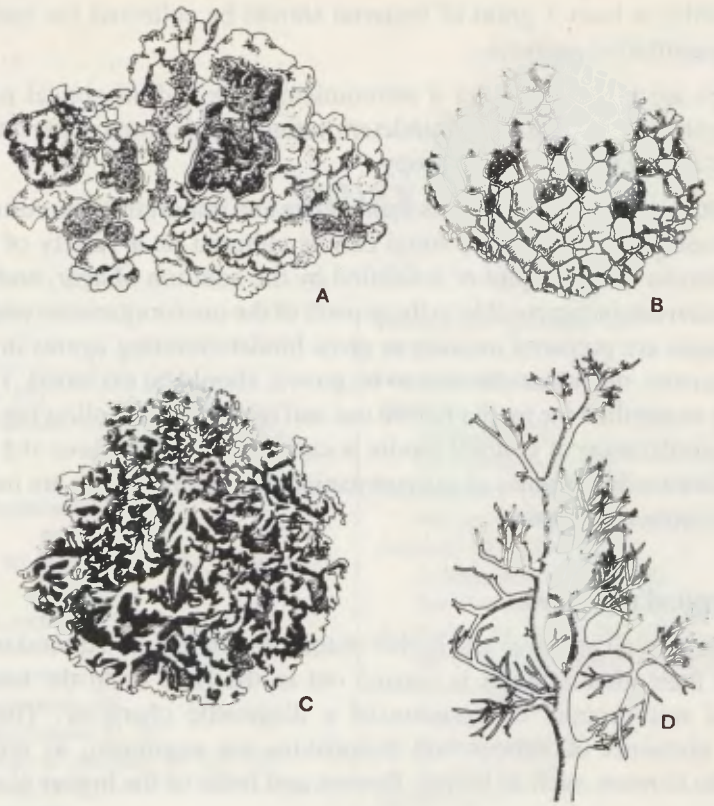


Fig.A.11

Four examples of lichens with very different thallus morphologies.
A) squamulose B) crustose C) foliose D) fructicose.

3 TECHNIQUES OF ANALYSIS

The basic aim of laboratory analyses is the identification of biodeteriorating agents responsible or jointly responsible for deterioration. Various metabolic analyses and resistance tests can be useful in scientific conservation research but are not discussed here.

3.1 Microbiological analyses

In addition to the identification of organisms that are present on a substrate (if not as species, at least as systematic groups), it is necessary to perform, when possible, quantitative analyses to assure correct interpretations of results. It is not sufficient to know whether or not a microorganism is present, but also in what amounts it exists to determine whether it plays an important role in the deterioration process (see Chapter 2, ¶2.1).

Sample collection differs according to the nature of deterioration: superficial powder, crusts, flakes, plates or films. Samples should be collected with previously sterilized tools (scalpels, brushes or swabs) and put in sterile cases (Petri dishes or tubes). If it is not possible to carry out the analyses immediately, samples must be preserved in a refrigerator at +4°C.

If possible, at least 1 gram of material should be collected for each sample for purposes of quantitative analyses.

Samples are observed under a stereomicroscope and an optical microscope to identify the systematic group of the biodeteriorating agent. Some observations can also be made by scanning electron microscopy.

To identify microorganisms, it is appropriate and important to do cultural analyses. Bacteria, actinomycetes,. algae and fungi can be cultured on a variety of substrates or media. Such media can be liquid or solidified by the addition of agar, and they contain all nutritive materials indispensable to the growth of the microorganisms under investigation. Since media are prepared in order to grow biodeteriorating agents in pure culture, all microorganisms, other than the one to be grown, should be excluded. To assure this, it is necessary to sterilize the media before use and to execute all following operations in asepsis. The sterilization of cultural media is carried out in autoclave at 1 atm (120°C) for 15-20'. Afterwards, colonies of microorganisms grown in culture are investigated by optical and electron microscopy.

3.2 Botanical analyses

Lichens, as well as lower and higher plants, do not require cultural techniques for analysis, and their identification is carried out in the field or in the laboratory after sampling and microscopic observation of a diagnostic character. The thallus and reproductive elements of lichens and bryophytes are examined, as are the various elements of the cormus, such as leaves, flowers and fruits of the higher plants.

Surveys can be qualitative (floristic) or quali-quantitative (vegetational or phytosociological).

In the first case, only a summary of the species present in the survey area, with ecological considerations, is given.

In the second case, environmental data (of station and substrate) and vegetational data include floristic composition, as well as coverage and association of the species that are present. The interpretation of the interconnection of organisms and environment allows the analyst to define the ecological meaning of the differentiated associations and to explain their evolving or regressive dynamic. Attention should be given to the relation between vegetation and substrate, and to the progressive nature of the mechanism of deterioration.

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