

Biodeterioration of peridotite and other constructional materials in a building of the Colombian cultural heritage

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Abstract

Comparative assessment of atmospheric and microbiological deterioration of constructional material of a church, which is part of the Colombian cultural heritage was made using different microbiological and surface analytical techniques complemented by electron microscopy. The main constructional material of the church of Veracruz in the urban area of the city of Medellín is peridotite, an ultramafic igneous rock containing > 90% of iron and magnesium minerals such as olivine and pyroxene. Assessment showed that the atmospheric characteristics in the city of Medellín are only slightly aggressive, suggesting that weathering would not be the main cause of decay of the structural material. The main microorganisms isolated from the façade of the church were heterotrophic bacteria and fungi, and phototrophic microalgae and cyanobacteria. Lichens and mosses were also found colonizing the rock. Experimental evidence suggests that deterioration of the peridotite is mainly due to acidifying bacteria and other microbial contaminants and that atmospheric factors would only play a secondary role in the decay.

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1. Introduction

In addition to biodeterioration processes, the environment has a role in the type and extent of material decay because relative humidity, temperature and natural and anthropogenic pollution enhance the effects of biodeterioration. Weathering of structural materials can be very important, depending on the relative aggressiveness of individual environments in which they are located. This type of decay, occurring in materials exposed to the air at environmental temperature is due to oxygen, humidity, and pollutants in gaseous, liquid and solid forms. Some of these are natural contaminants, such as sea salts and particulate matter from meteorization processes, but others are anthropogenic pollutants from activities such as energy generation, transportation and agriculture and include sulfur and nitrogen oxides, particulate matter, volatile organic compounds and

many other organic and inorganic substances. Sometimes, these pollutants react with materials, affecting their properties, otherwise, they can act as catalysts in deterioration by other chemical, physical or biological routes.

Microbial biodeterioration is due to the presence of biofilms which are biological deposits of a highly hydrated (ca. 95% water) gel of extracellular polymeric substances (EPS) containing microbial cells and inorganic detritus (Videla, 1996). Biofilms drastically change the physico-chemical characteristics of the environment in contact with the structural material and generally increase its aggressiveness (Videla and Characklis, 1992).

Algae and cyanobacteria are usually the first colonizers of cultural heritage monuments due to their photosynthetic characteristics. These microorganisms can deteriorate stone either chemically or mechanically and their presence is generally detected through the formation of patina or crusts. Lichens, which are highly resistant to desiccation and extreme temperatures, are also frequently associated with biodeterioration of stone, as are mosses and vascular plants. Autotrophic and

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Fig. 1. Church of Veracruz, Medellín, Colombia.

heterotrophic bacteria present in biofilms cause stone decay by physical and chemical effects. Finally, once established on the substratum fungi also cause deterioration of stone by chemical or mechanical effects.

Microorganisms are able to obtain different elements for their metabolism, e.g. calcium, aluminum, silicon, iron and potassium, by biosolubilization of materials. Such microbial biosolubilization involves the production of organic and inorganic acids by the metabolic activity of algae, lichens, fungi and bacteria. This acidic deterioration is one of the best known biogeochemical mechanisms of rock decay (Mansch and Bock, 1996; Warscheid and Braams, 2000; Wilimzig and Bock, 1996).

The practical case chosen for this study is the church of Veracruz (Fig. 1), a building typical of the Colombian city of Medellín's cultural heritage. The façade was built with peridotite, a material obtained from quarries north of the valley of Aburra where the city is located. Peridotite is an ultrabasic igneous rock composed of dark minerals (generally olivine and pyroxene) containing iron and magnesium. It can also contain some plagioclase and minerals like chromite and limonite, with some addition of feldspar and quartz. A characteristic of this type of rock is that it can be easily turn in to serpentine due to the instability of olivine in atmospheric conditions (Quintero and Delgado, 1998).

Techniques of isolation and identification of microorganisms were used for assessment of contaminants of the façade, and the taxonomical and metabolic characteristics of these microorganisms and their effects on the biodeterioration of the structural material were investigated. For characterization of the materials, optical and SEM observations were complemented with the surface analytical techniques EDAX, XRD and FT-IR spectroscopy, as well as petrographic analyses.

2. Materials and methods

2.1. Samples and microbiological procedures

Samples were taken aseptically at eight different sites located at different heights of the façade using non-destructive sampling techniques to scrape off the biological deposits. In each case, samples were immediately placed in sterile plastic vessels and taken to the laboratory for isolation and identification of microorganisms using selective culture media, viz. nutrient agar for total aerobic heterotrophic mesophilic bacteria; Postgate C medium for sulfate reducing bacteria; differential reinforced clostridial broth for sulfite-reducing bacteria and glucose broth for acid-producing bacteria. For fungi yeast extract glucose chloramphenicol (YGC) agar was used.

2.2. Microscopic observations and surface analysis

Optical microscopy was used to detect and study cyanobacteria and a stereoscopic magnifier was used to observe lichens and mosses. SEM was employed in studying biofilm characteristics and structure. For this, samples were initially fixed in 2.5% glutaraldehyde buffer solution washed with phosphate buffer; dehydrated by using an acetone series; critical point dried; and gold coated at 10^{-3} mm Hg in a Balzers model SCD 030 sputter coat apparatus prior to SEM observations and EDAX analysis using a Philips 500 microscope.

XRD and FT-IR spectroscopy were employed to study changes caused by biological and atmospheric effects at the surface of the mineral samples. Petrographic analysis was carried out to assess the rock transformation due to weathering effects, using a polarizing microscope for examination of thin sections of the constructional material (Videla et al., 2004).

2.3. Assessment of atmospheric pollution

These studies were made using the wet candle method for chloride assessment and ISO 9225 standard for sulfur dioxide evaluation, respectively. Particle deposition was measured according to ASTM D 1739 standard (Videla et al., 2003).

3. Results and discussion

3.1. Microbiological results

Aerobic heterotrophic mesophilic bacteria were found in all samples. Among these bacteria *Pseudomonas* sp., *Staphylococcus aureus*, *Aeromonas Salmonicida*, *Bacillus* sp. and *Clostridium* sp. were identified. Acid-producing bacteria were only isolated from four samples, but comprised 29.5% of total aerobic heterotrophic bacteria. Spore-forming bacteria were detected in all samples whereas the cultures for sulfate-reducing bacteria in Postgate B medium were negative.

Hyphomycetes and yeasts were also detected in six of the samples. Some of the isolated fungi were *Penicillium* sp., *Curvularia* sp. and a dark-pigmented mitosporic fungus (*Dematiacea* sp.) frequently associated with the presence of black patina on structural materials (Warscheid and Krumbein, 1996).

Algae and coccoid or filamentous types of cyanobacteria were present in several samples (Fig. 2). Members of the Chlorophyta in the Ulothricales and Chlorococcales and cyanobacteria in the Oscillatoriales and Chroococcales were found in all the samples studied.

Mosses and the lichen *Hyperphysia agglutinata* were also found in the samples taken at the highest sampling areas of the façade (15.5 m above ground), near the bell tower.

3.2. Biodeterioration mechanisms

The release of metabolic acids is one of the best-known biogeochemical destructive mechanisms at rock surfaces (Warscheid and Braams, 2000), with leaching of rock binding materials and consequent weakening of the crystal structure (McCormack et al., 1996). The net outcome of this type of biodeterioration is the physical and mechanical breakdown of the rock. The isolation of acidophilic bacteria in



Fig. 2. SEM micrograph of coccoid cyanobacteria within crust removed from façade of church (magnification: $\times 1000$, bar: 10 μm).

Table 1
EDAX analysis of sample taken at height of 3.15 m

Element	Percentage weight
Mg	0.42
Al	12.77
Si	28.66
K	2.57
Ca	40.93
Fe	14.66
Total	100

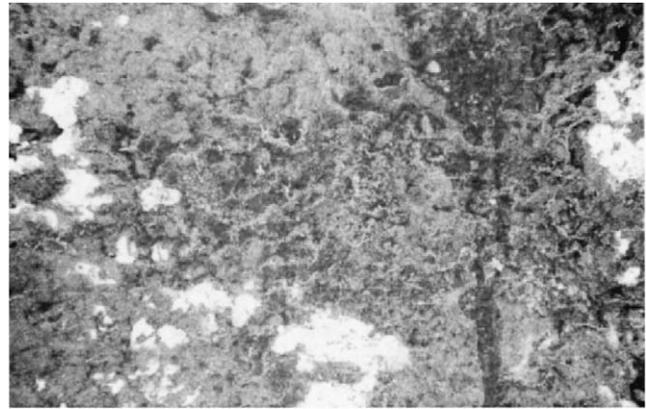


Fig. 3. Dark patina caused by cyanobacteria on peridotite of façade of church.

several samples taken at the front of the church, would indicate that this mechanism of biodeterioration would be distinctly feasible in this particular case. This hypothesis is supported by the EDAX profiles (Table 1), in which high concentrations of silicon and calcium were found, indicating alteration of the base material. In a previous publication (Videla et al., 2000), an important pH decrease (ca. 3.0 units) due to the growth of heterotrophic bacteria and fungi was confirmed by means of laboratory experiments. In addition, by SEM it was possible to detect the presence of bacterial and fungal biofilms on the crystalline structure of the substratum.

In the city of Medellín, natural environmental factors and urban pollution (due to deposition and attack of aggressive gases and adhering particles) can lead to the formation of patina and crusts, as was observed on the surface of the peridotite in the façade (Fig. 3). Moreover, the presence of cyanobacteria and algae and their metabolic activity contribute to different accelerating and catalytic effects on the formation of crusts and also to a biogenic colouring of the stone, with a consequent loss of aesthetic value. Dark colored crusts on natural stone of buildings or monuments enhance the physical stress of the structural material by increase in specific heat uptake as well as alteration of thermal-hygric expansion behavior and moisture retaining capacity (Warscheid and Krumbein, 1996). These

Table 2
EDAX of sample taken underneath lichen growth

Element	Percentage weight
Al	0.96
Si	0.39
Ca	92.46
Fe	6.19
Total	100

Table 3
Main climatic parameters in central Medellín, as averages for recent years (from Herrera et al., 2002)

Temperature (°C)	23.5
Relative humidity (%)	65
Precipitation (mm)	1709.1
Chloride deposition ($\text{mg m}^{-2} \text{day}^{-1}$)	6.2
Sulfur dioxide deposition ($\text{mg m}^{-2} \text{day}^{-1}$)	15.8
Particle deposition ($\text{kg} \times 1000 \text{ km}^{-2} \text{month}^{-1}$)	8.61

biogeophysical processes have been attributed to the partly mineralized chlorophyll in phototrophic biofilms of cyanobacteria and algae such as those found on the façade, although heterotrophic fungi (such as the *Dematiacea* found here) can contribute melanins and be the cause of biogenic iron and manganese oxidation.

Lichens and mosses, such as those found in the samples taken at the highest areas of the front, near the bell tower, can cause biodeterioration of a variety of mineral structural materials such as limestones, sandstones, granites, tiles, flagstones and mortars, as has been reported by Garcia-Rowe and Saiz-Jiménez (1991). Colonization of different types of materials by lichens is generally induced and enhanced by input of bird excrements giving rise to a characteristic microflora as it occurs in this church. Mosses grow preferentially on mortars, with marked disintegrative effects due to the penetration of rhizoids. Chemical attack involves the production of carbonic and oxalic acids and different biogenic compounds acting as chelating agents. The EDAX profile obtained for lichen-covered areas show a very high calcium content, corroborating other evidence of this type of biodeterioration (Table 2).

3.3. Atmospheric characteristics

Previous studies of atmospheric pollution in the city of Medellín (Herrera et al., 2002; Herrera, 2002), were used to characterize the role of weathering processes on material decay (Table 3). From the results of these studies, made using the procedures mentioned in the previous section, the atmosphere of Medellín can be classified as moderately aggressive.

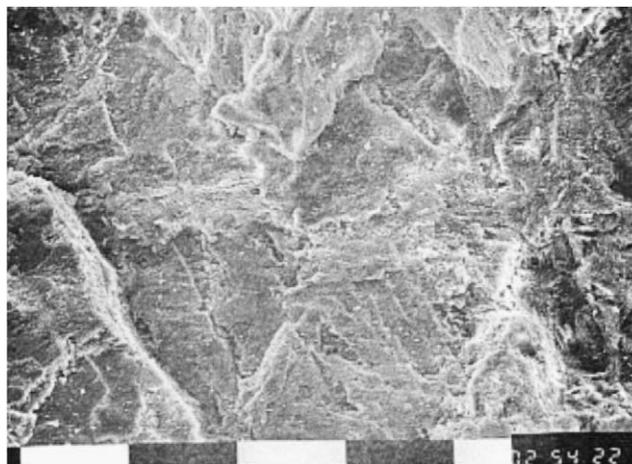


Fig. 4. SEM micrograph of rock from source quarry (magnification: $\times 200$, bar: 100 μm).

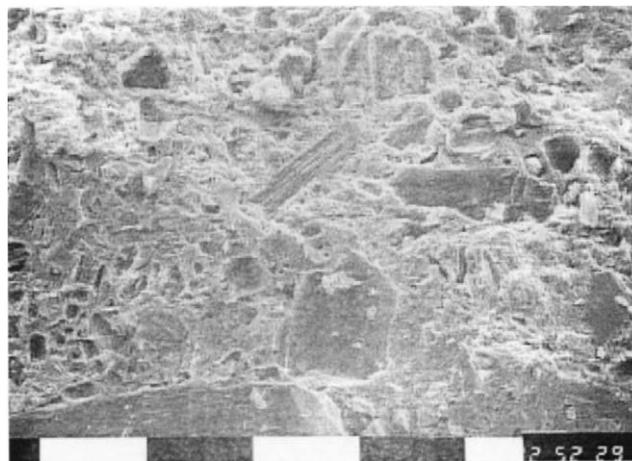


Fig. 5. SEM micrograph of weathered peridotite from façade of church (magnification: $\times 200$, bar: 100 μm).

3.4. Weathering of structural materials

A degree of weathering of the peridotite shown up by SEM of the mineral taken from the source quarry and the corresponding material from the church façade (Figs. 4 and 5). The FT-IR analysis of peridotite (Table 4), EDAX profiles (Figs. 6 and 7) and XRD spectra (Fig. 8) indicate that the weathering of peridotite mainly leads to the presence of olivine that is later turned into serpentine and different iron oxides, predominantly lepidocrocite and goethite (Herrera et al., 2003). Petrographic analysis confirmed these observations (Videla et al., 2003).

From the comparative EDAX and XRD results, it can be concluded that most of the rock constituents of peridotite are thermodynamically unstable under the environmental conditions to which the church is exposed. However, damage due to weathering effects in an urban atmosphere of only moderate aggressiveness such as that of Medellín would be

Table 4
IR-bands and their related chemical species

Band cm^{-1}		Corresponding chemical species
Weathered rock (front)	Source rock (quarry)	
465 ^a	480 ^a	SiO_2
601		$\alpha\text{-FeOOH}$
642	657	$\alpha\text{-FeOOH}$
669 ^a		
743 ^a	~ 700	$\gamma\text{-FeOOH}$, SiO_2
804 ^a	~ 800	$\alpha\text{-FeOOH}$, SiO_2
908 ^a	~ 900	$\alpha\text{-FeOOH}$
1019 ^a	1017 ^a	$\gamma\text{-FeOOH}$
	1071	Varieties of hydroxysilicates of Al, Fe; Mg and other elements in lesser quantities
	1129	
	1186	
	1314	
	1400	
1385	1400	
1457	1471	
1559	1514	
1636 ^a	1571	
1734		
2361 ^a		
2852	2714	
2923 ^a		
3216 ^a	3350 ^a	Hydrated oxides and oxihydroxides such as $\gamma\text{-FeOOH}$ and $\alpha\text{-FeOOH}$

^aMain bands.

Label A: V11

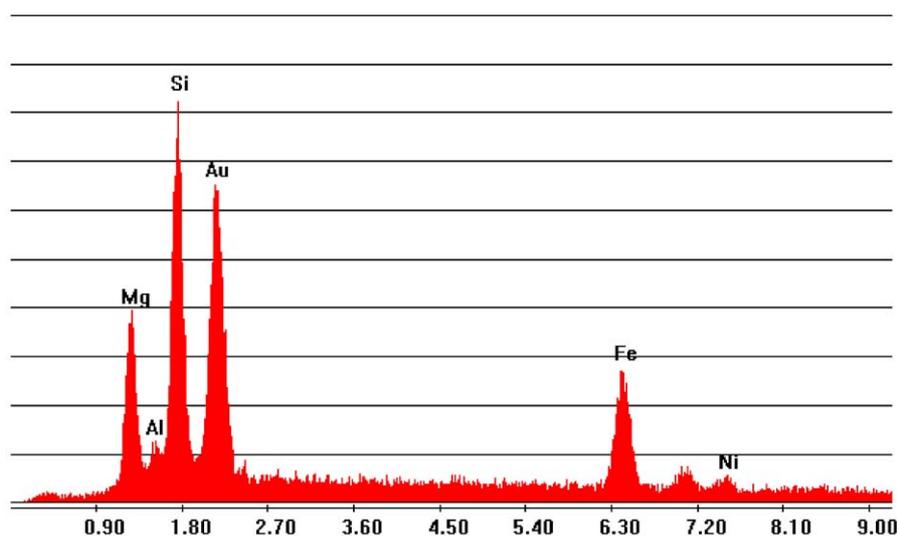


Fig. 6. EDAX profile of rock from source quarry.

significant only after a longer time period than for appearance of biodeterioration, which appears to be the predominant cause of damage in the case reported here.

4. Conclusion

In summary, a wide variety of microbiological contaminants have been found at several sampling sites on

the front façade of the church of Veracruz. Among them, acid-producing bacteria can cause biodeterioration due to metabolic acids biosolubilizing the stone. Phototrophic microorganisms, algae and cyanobacteria, induce biogeophysical formation of patina and crusts. These deposits enhance physical stress and also cause biogenic colouration of the stone, with consequent aesthetic loss. While lichens and mosses can cause deterioration of the stone

Label A: 25229

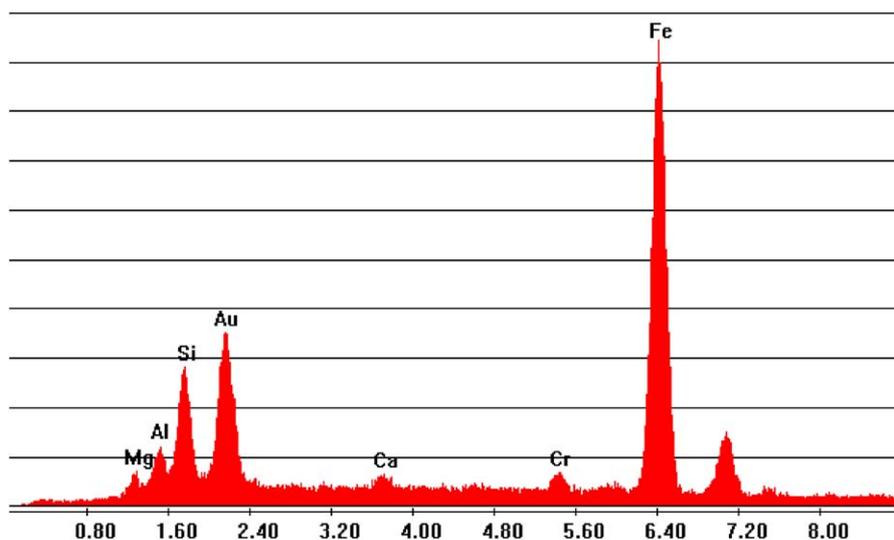


Fig. 7. EDAX profile of weathered peridotite from façade of church.

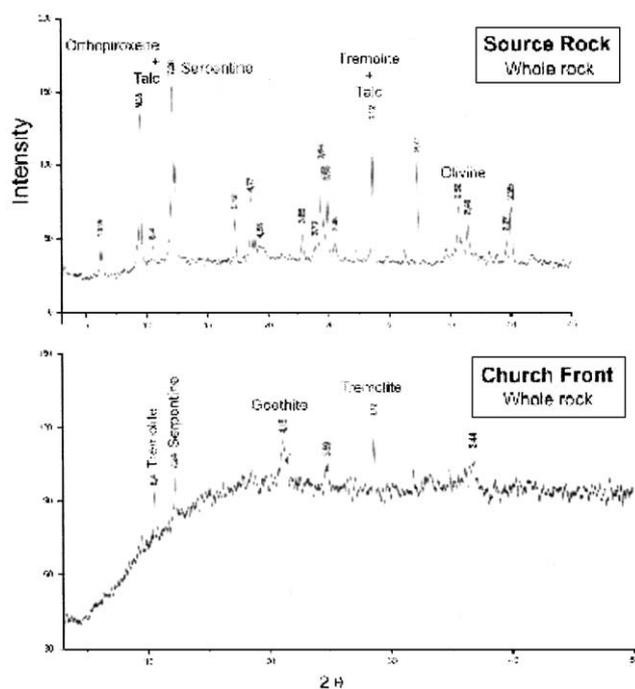


Fig. 8. XRD spectra of source rock and whole weathered rock.

by chemical rather than mechanical effects. EDAX profiles endorse the former mechanism. According to our observations, atmospheric conditions in the city of Medellín are not highly aggressive, but the peridotite is thermodynamically unstable under these environmental conditions. The biodegradation effects of microbial contaminants isolated from the church are able to synergistically enhance the effects of atmospheric factors in decay of the mineral material.

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