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Biochemical mechanisms of stone alteration carried out by filamentous fungi living in monuments

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Abstract. Biochemical weathering mechanisms carried out by *Penicillium frequentans* and *Cladosporium cladosporoides* on unaltered sandstone, granite and limestone were studied using FTIR, X-ray diffraction, atomic absorption and flame photometry. Strains belonging to both fungal species, isolated from the façades of two Spanish Cathedrals, were used.

Large amounts of oxalic, citric and gluconic acids were produced by *P. frequentans* in broth cultures. These metabolites caused extensive deterioration of clay silicates, micas and feldspars from both sandstone and granite and also of calcite and dolomite from limestone, as a result of high cation release and organic salts formation such as calcium, magnesium and ferric oxalates and calcium citrates. Comparatively, the biodegradative effect brought about by *C. cladosporoides* was much less than that caused by *P. frequentans.* Neither organic acids nor organic salts were formed by *C. cladosporiodes* samples.

It is concluded that filamentous fungi are able to cause an extensive weathering of stone, due principally to organic acid excretion, although other metabolites participate to a lesser extent in these deteriorative processes. Ecological adaptative mechanisms, such micronutrients uptake and trivalent cations chelation (Fe^{3+} and Al^{3+}) are derived from fungal growth on stone monuments.

Introduction

A large number of the geological processes which occur on the terrestrial surface are under microbial influence (Ehrlich 1990). Microbial populations can cause cation solubilization and mineral diagenesis through secondary metabolite excretion, leading in rock biodeterioration. Among the heterotrophic microorganisms, fungi are probably the most active microorganisms in roch weathering processes according to Rossi (1978) and Eckhardt (1979).

Microorganisms from the surrounding soil or from soil water (Webley

et al. 1963; Strzelczyk 1981) frequently invade surfaces of stone monuments. Air pollutants containing nitrogen and carbon, promote the development of microorganisms (Krumbein 1988). On addition, primary colonizers (algae and bacteria) supply nitrogen and carbon to secondary colonizers, such as fungi. Saprofhytic fungi are common members of microbial communities on stone monuments (Gorlenko 1983), probably due to both their ability to grow with low concentrations of organic matter and reduced humidity, and their ability to form resistant spores. These characteristics contribute to continual deterioration of rock (Strzelczyk 1981).

Microbial biodeteriorative mechanisms are mainly: acidolysis, through organic acid excretion by fungi (Kurozckin et al. 1988; de la Torre et al. 1991), algae (Hueck van der Plas 1968) and lichens (Ascaso et al. 1982), mineral cation complexation, alcalinolysis and oxido-reduction of mineral elements.

In this study, the mechanisms used by filamentous fungi in rock weathering, were evaluated *in vitro* and correlated to stone damage and fungal ecological adaptations.

Materials and methods

Fungi. The fungi used in this study were: *Penicillium frequentans* and *Cladosporium cladosporoides.* Two strains of each fungal species were isolated from the façades of two Spanish Cathedrals: Salamanca (constructed of sandstone) and Toledo (built with limestone and granite). Sampling, isolation and identification of fungal species were performed according to de la Torre et al. (1991).

Rock samples. Unaltered samples of each sandstone, limestone and granite stones obtained from quarries, were cut in 8 × 1 × 1.5 cm blocks and autoclaved to 120 °C for 20 min.

Culturing procedures. Cultures were grown in 60 ml of liquid medium, consisting of 5 g of glucose and 2 g of sodium nitrate per liter of bidistilled water. The culture media were autoclaved in 250 ml Erlenmeyer flasks. After sterilization, the sterile stone samples were aseptically introduced into the flasks by means of sterile pincers. The inocula consisted of 1 ml of spore suspension from each fungal strain isolated, containing 10^5—10^6 spores/ml. Blanks were prepared by substituting an equivalent volume of bidistilled and sterilized water for the fungal inoculum. Ten ml of fresh culture medium (6-fold concentrated) together with 1 ml of fungal inoculum

were added in each flasks monthly. Experiments were over for six-month periods.

Corrosive effect brought about by oxalic, citric and gluconic acids on stony substratum. Blocks of each stone were introduced into 100 ml Erlenmeyer flasks and autoclaved. Following this, each of the bidistilled solutions containing 30 ml of oxalic acid 10 g/l, citric acid 5 g/l and gluconic acid 5 g/l were aseptically added to each flasks. The blocks were completely submersed. Control flasks with stone blocks and 30 ml of bidistilled water were prepared. The flasks were incubated in the dark for 20 days at 27 °C. Esterile bidistilled water was added to each flasks to compensate for the loss of volume caused by evaporation and transpiration after 10 days of culture.

Analytical methods

Stone blocks were removed from the Erlenmeyer flasks by means of sterile pincers and dried at 80 °C for 2—3 days. Once the blocks were dried, the surfaces (1—2 mm depth) were carefully scraped with sterile scalpel. Stone blocks inoculated with fungal spore suspensions were scraped in two established zones: submersed in the medium and emersed (out of the medium). Stone samples inoculated with each three acid solutions were scraped in the unique sumersed zone.

(i) *Analysis performed with the scraped material*
X-ray diffraction (XRD). XRD patterns were obtained with a Philips PW 1130 diffractometer (graphite monochromated Cu-KÓ radiation). Each sample was processed: (a) random powder and the following oriented aggregates: (b) air dried, (c) ethylene glycol solvated, (d) heated to 300 °C for 3 h and (e) heated to 500 °C for 3 h. The minerals, except calcium citrate, were identified by means of the Joints Committee on Powdered Diffraction Standards (1989).

Fourier-transform infrared spectroscopy (FTIR). Samples were analyzed in a FTIR spectrophotometer Nicolet 20SXC, working in an absorbance range between 4000 and 350 cm^{-1}. The minerals were identified according to van der Marel & Beutelspacher (1976). For semiquantitative analysis, the control spectrum was subtracted from the corresponding spectrum of the test specimen. Some of the difference spectra were compared by the program 'TRISPEC'. Subtraction spectra were drawn with respect to an horizontal axis. Bands above this axis corresponded to degraded com-

pounds with respect to the control samples. Otherwise, bands below the horizontal axis corresponded to neoformation products deposited on the stony surface. Calcium citrate tetrahydrate (Fluka) was used to obtain X-ray patterns and FTIR spectra control.

(ii) *Analysis carried out in broth cultures*
Broths were centrifuged at 26,890 g at 4 °C for 20 min. Supernatans were harvested and passed through Millipore filters of 0.22 μm pore size. Organic acids and pH (de la Torre et al. 1991) in filtrates were measured. Fe, Mn, Zn, Cu, Mg y Al contents were determined with an atomic absortion spectrophotometer (Perkin Elmer 403) and Ca, Na and K concentrations were determined by flame photometry. Soluble Fe^{3+} was quantified by the spectrophotometric method of Razzel & Trussell (1963).

Loss of weight percentage measurements. These determinations were only performed on stone samples treated with each of the organic acids. Samples of unaltered stone were dried at 80 °C for 24 hours before weighing. After incubating the stone blocks in each organic acid solution, samples were taken and dried at 80 °C for 3 days before weighing. Weight differences reflected loss of weight brought about by organic acids action.

Results

Treatment of stone blocks with oxalic, citric and gluconic acid

(i) *Sandstone.* Figure 1.A shows wide degradation bands corresponding to phyllosilicates (3618, 3544, 1030, 986 and 914 cm^{-1}) and to a lesser extent to feldspars (band at 1152 cm^{-1}). The marked increase detected in Fe, Al, Mg, Mn and Zn concentrations (Table 1), with respect to those measured in control liquids is in agreement with the results of the FTIR spectra, and indicates the strong alteration of the majority of sandstone silicates: smectite, palygorskite and illite. The more effective acid in cation release was oxalic acid, as reflected by the loss of weight values (Table 1). Calcium capture by the oxalic acid gave rise to the formation of calcium oxalate deposits on the stone surface identified by FTIR (bands at 1625 and 1315 cm^{-1}) (Fig. 1). This was the reason for low calcium concentrations detected in solution. All of the acids promoted significant increase in soluble Zn concentration with respect to the control sample, which points to a selective attack on smectite (major clay material, together with palygorskite, in sandstone cement composition). Potassium solubilization by the oxalic acid indicates mica and/or feldspar (orthoclase) alteration.

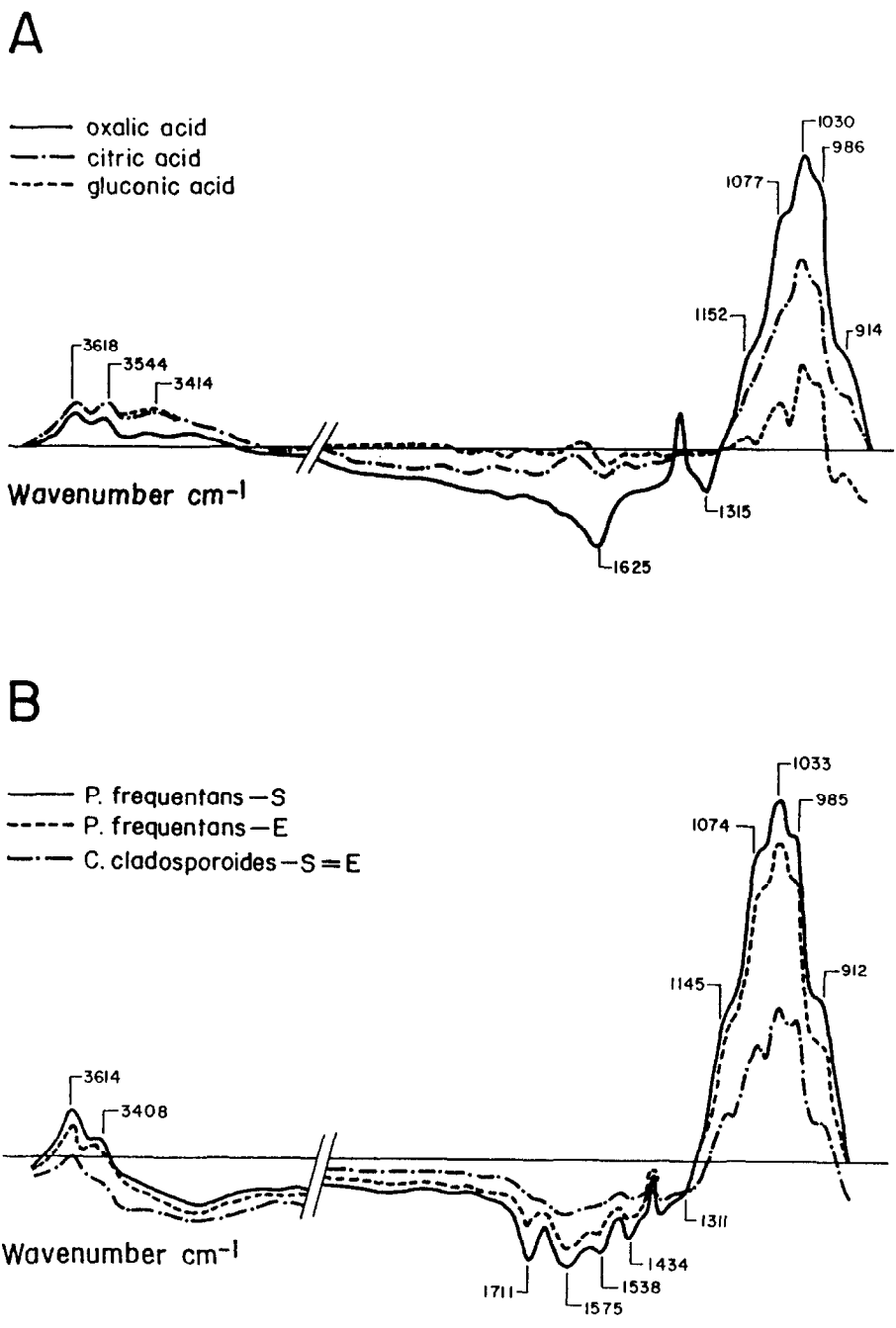

Fig. 1. Difference FTIR spectra between: A. The control spectrum (without organic acid addition) and each spectrum of test material (with added organic acids) and B. Each control spectrum (without fungal inoculum) and the corresponding spectrum of the test material (with fungal inoculum added), of scraped surfaces of sandstone.

High Na concentrations were observed in samples treated with citric acid, probably due to plagioclase alteration.

(ii) *Granite.* Analysis performed through FTIR (Fig. 2.A) showed that each of the three acids caused a marked decrease in bands ascribed to phyllosilicates (1033, 1012 and 923 cm^{-1}) and to a lesser degree to feldspars (1146 cm^{-1}), in relation to high levels of Fe^{3+}, Al^{3+}, Mn^{2+}, Mg^{2+} and K^{+} concentrations determined in broth cultures (Table 1). The greatest deterioration effect was due to the oxalic acid action in agreement with the higher values in loss weight percentage measured in rock samples treated with this acid (Table 1). In these samples, calcium oxalate salts (bands at 1638 and 1312 cm^{-1}) were detected. Citric acid led to the appearance of calcium citrate crystals (bands at 1542 and 1442 cm^{-1}) and in the case of sandstone to a stronger Na release.

(iii) *Limestone.* The three acids altered this rock material extensively as the wide degradation band at 1440 cm^{-1} demonstrates (Fig. 3.A). As a consequence of the calcite and dolomite weathering, a large increase in the release of dissolved Ca^{2+} and Mg^{2+} was found (Table 1). As occurred with the other substrata, oxalic acid was the most corrosive, leading to deposition of calcium oxalate crystals on the limestone surface (bands at 1635 and 1321 cm^{-1}). These oxalate deposits account for the low calcium levels detected in the broth. Massive calcium citrate deposits on the limestone surface (bands at 1562, 1535, 1462, 1268, 1183, 1146 and 1074 cm^{-1}) demonstrate a great efficiency of citric acid in the weathering processes.

Samples inoculated with Penicillium frequentans

(i) *Sandstone.* A larger weathering effect was observed in the submersed zone, with respect to the emersed one. Substraction FTIR spectra (Fig. 1.B) show a strong decrease in bands ascribed to phyllosilicates (3614, 1033, 985 and 912 cm^{-1}). Smectite, palygorskite and illite were identified by X-ray diffraction giving peaks at 14.3, 10.3 and 9.92 A, respectively (oriented aggregate patterns, Fig. 4). Besides, a slight decrease in the feldspar band (1145 cm^{-1}) was observed by means of FTIR (Fig. 1.B). High concentrations of the elements: Fe, Al, Mg, Mn, Zn, K y Na in culture liquids with respect to those measured in control samples without fungus inoculum, is a consequence of the selective attack produced in the clay minerals: smectite, illite and palygorskite group. No release of the elements Fe and Al was detected in the control liquid samples, (Table 2). In culture liquids, mainly high concentrations of gluconic and citric acids, were mainly identified (Fig. 7). In Fig. 1.B the oxalate band at 1311 cm^{-1}

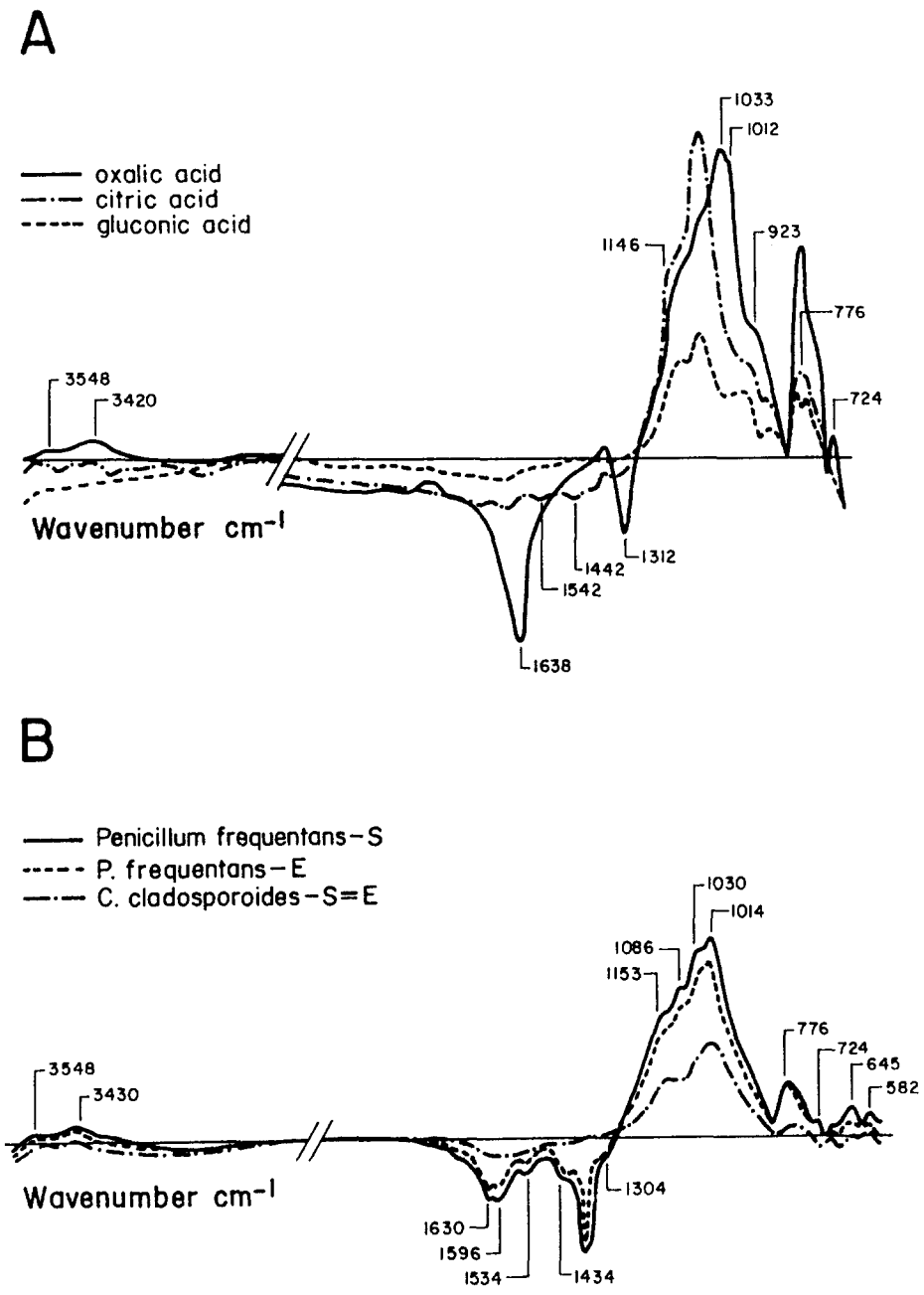

Fig. 2. Difference FTIR spectra between: A. The control spectrum (without organic acid addition) and each spectrum of test material (with added organic acids) and B. Each control spectrum (without fungal inoculum) and the corresponding spectrum of the test material (with fungal inoculum added), of scraped surfaces of granite.

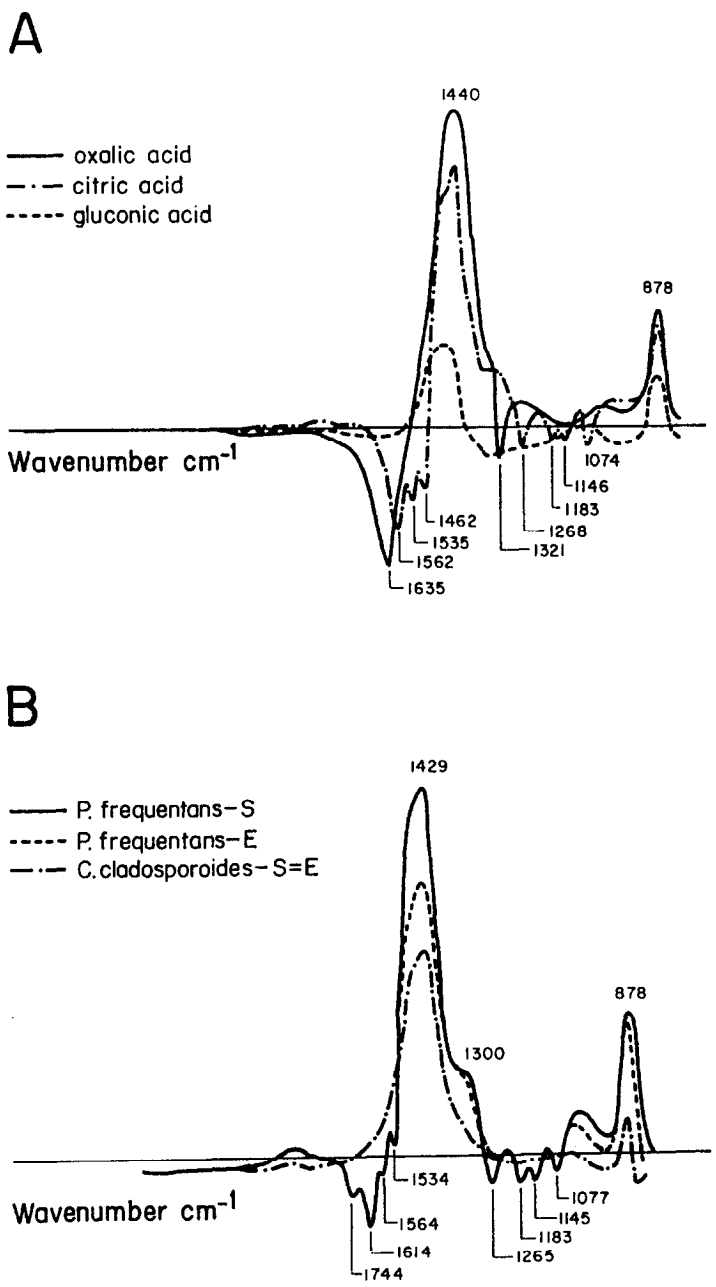

Fig. 3. Difference FTIR spectra between: A. The control spectrum (without organic acid addition) and each spectrum of test material (with added organic acids) and B. Each control spectrum (without fungal inoculum) and the corresponding spectrum of test material (with fungal inoculum added), of limestone scraped surfaces.

Table 1. Cation concentration (μg/g of stone) in broth cultures and loss of weight percentage (L.W.%) determined in the experience performed with blocks of stone inoculated with organic acids.

Acid	CATIONS IN SOLUTION (μg/g of stone)[a]									
	Fe	Mn	Zn	Cu	Mg	Ca	Na	K	Al	L.W. (%)
SANDSTONE										
Oxalic	57.14	1.02	0.11	0.04	18.66	1.64	1.54	3.21	43.21	2.8
Citric	2.22	0.43	0.16	0	8.6	7.5	133.15	0.83	4.16	2.75
Gluconic	1.15	0.61	0.28	0	6.6	4.57	1	0.8	1	1.41
Control	0.015	0.015	0.04	0	1.07	2.32	2.06	1.1	0	1.2
GRANITE										
Oxalic	48.5	1.32	0.13	0	20	1.2	0.36	1.08	33	0.76
Citric	16	0.4	0.1	0	6.35	4.4	66	0.5	7.1	0.37
Gluconic	4.75	0.24	0.15	0	3.5	2.63	0.57	0.46	2.63	0.46
Control	0	0.007	—	—	0.27	1.38	14.3	0.17	0	0
LIMESTONE										
Oxalic	0.078	0.01	0.047	0	25.91	0.21	1.97	1.19	0.1	0.85
Citric	0.104	0.083	0.051	0	37.5	72.92	110.42	0.63	0.313	0.66
Gluconic	0.12	0.08	0.026	0	53.52	109.7	2.62	0.5	0.3	1.69
Control	0	0	0	0	0.01	0.83	1.8	0.31	0	0.21

[a] —, not determined

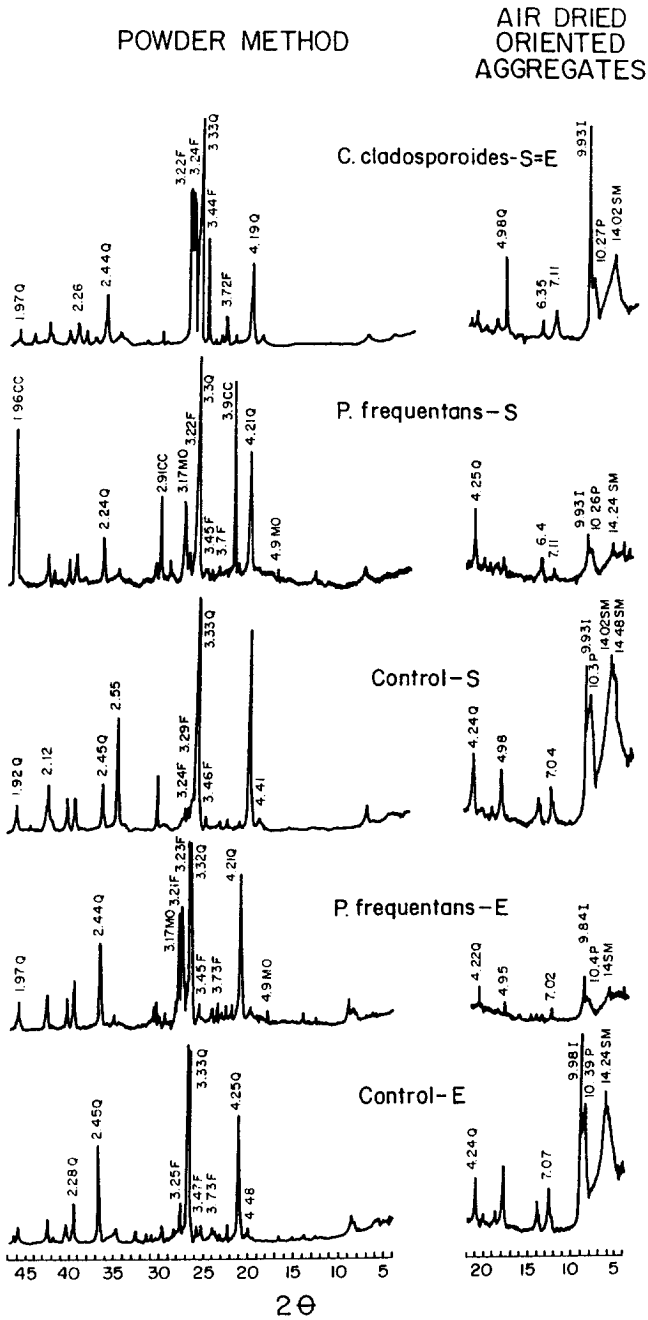

Fig. 4. X-ray diffraction diagrams of sandstone scraped surfaces. (S: submersed zone, E: emersed zone, CC: calcium citrate, SM: smectite, F: feldspars, I: illite, MO: magnesium oxalate, P: palygorskite, Q: quartz).

corresponds to magnesium oxalate salt, detected by XRD in both zones (Fig. 4) (giving peaks at 4.9 and 3.17 A in powder samples). Calcium citrate deposits were widely diseminated over the rock surface as shown in FTIR spectra (bands at 1711, 1575, 1538 and 1434 cm^{-1}), Fig. 1.B and X-ray diagrams in Fig. 4 (peaks at 2.91 and 3.9 A).

(ii) *Granite.* No significant differences were detected between submersed and emersed zones in which *P. frequentans* developed. A marked increase in phyllosilicate weathering (bands at 3548, 3430, 1030 and 1014 cm^{-1}) and feldspar (bands at 1153, 645 and 582 cm^{-1}) with respect to control samples was observed (Fig. 2.B). X-ray pattern (Fig. 5) point out that, when compared to control blocks, mica (peak at 9.93 A) and chlorite (giving peaks at 7.04 and 14.02 A) were the altered phyllosilicates. In agreement with the results from the FTIR and X-ray pattern, higher Fe, Al, Mn, Mg, Na, y K concentration levels were detected in these broth cultures than in the control broths, (Table 2). Calcium citrate (band at 1596, 1534 and 1434 cm^{-1}) and calcium oxalate monohydrate (wewhellite, bands at 1304 cm^{-1}, peaks at 5.8 and 3.64 A) were also present. Low calcium concentrations in broth cultures were due to extensive calcium citrate and oxalate deposition. Citric and gluconic acids were also detected in the culture liquids (Fig. 7).

(iii) *Limestone.* The attack of calcite and dolomite resulting in a decrease in the band ascribed to both minerals (1429 cm^{-1}) (Fig. 3.B), mainly in the submersed zone, was in agreement with analyses performed by means of X-ray diffraction (Fig. 6). No significant increase in Ca and Mg concentrations was observed in culture liquids (Table 2). That was due to the formation and precipitation of insoluble salts on the rock surface, as a consequence of the reaction between organic acids excreted by fungi and different mineral elements released from rocks. In this way, calcium citrate crystals (bands at 1744, 1614, 1564, 1534, 1265, 1183, 1145 and 1077 cm^{-1}) were detected through FTIR, in agreement with X-ray patterns (Fig. 6). Calcium oxalate dihydrate (weddellite) (peaks at 6.19, 4.4, 2.77 and 2.24 A) and magnesium oxalate (peaks at 4.9, y 3.12 A) were also identified in both submersed and emersed zones (Fig. 6). In the submersed zone, ferric oxalate (peaks at 5.27, 3.45 and 2.72 A) and wewhellite (peaks at 5.89, 3.66 and 2.98 A) were additionally observed. Despite the abundance of calcium citrate deposits found on the limestone surface, high concentrations of citric and gluconic acids were also detected in culture samples (Fig. 7).

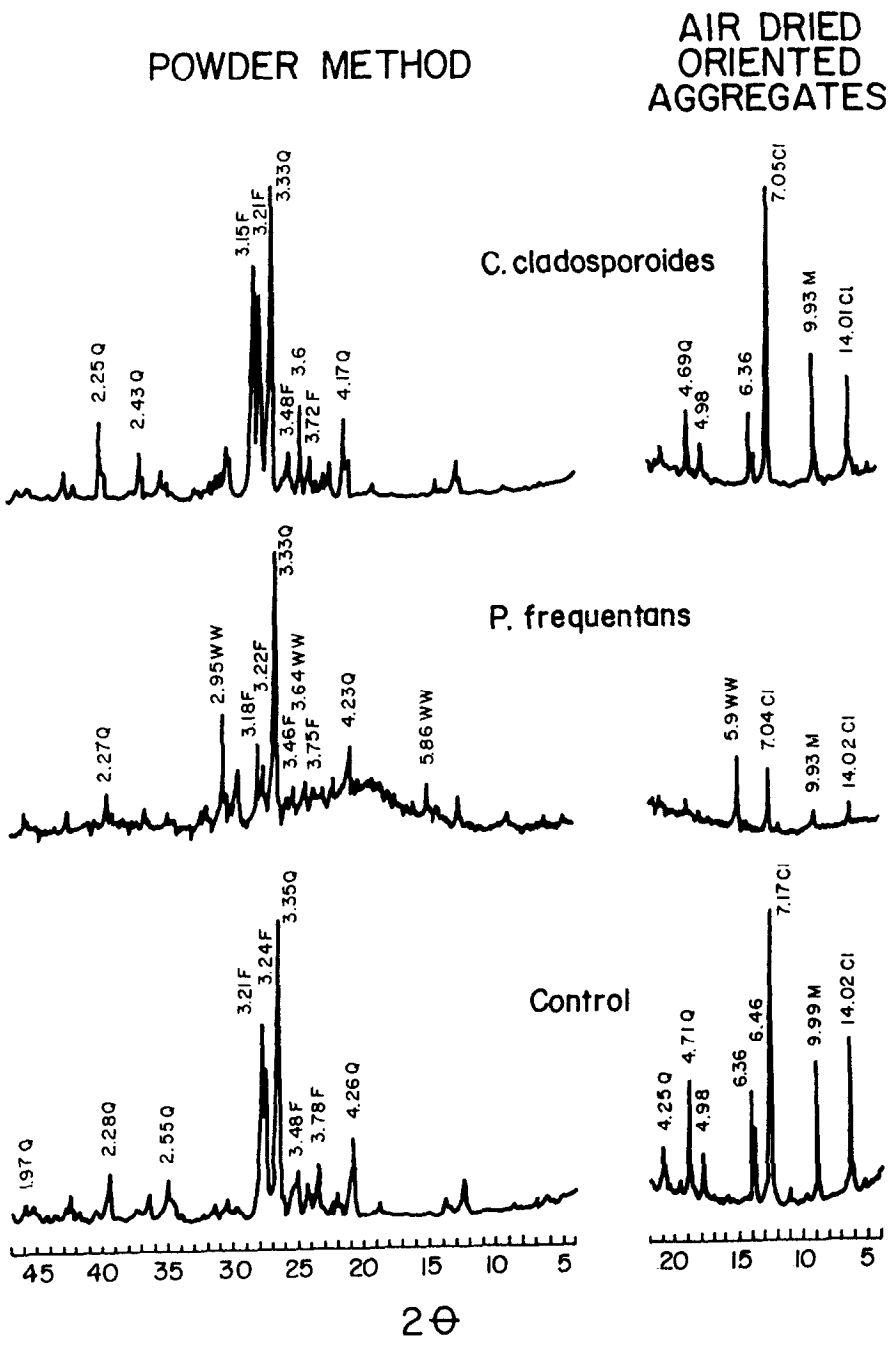

Fig. 5. X-ray diffraction diagrams of granite scraped surfaces. (Abbreviations as Fig. 4, Cl: chlorite, M: micas, WW: wewhellite).

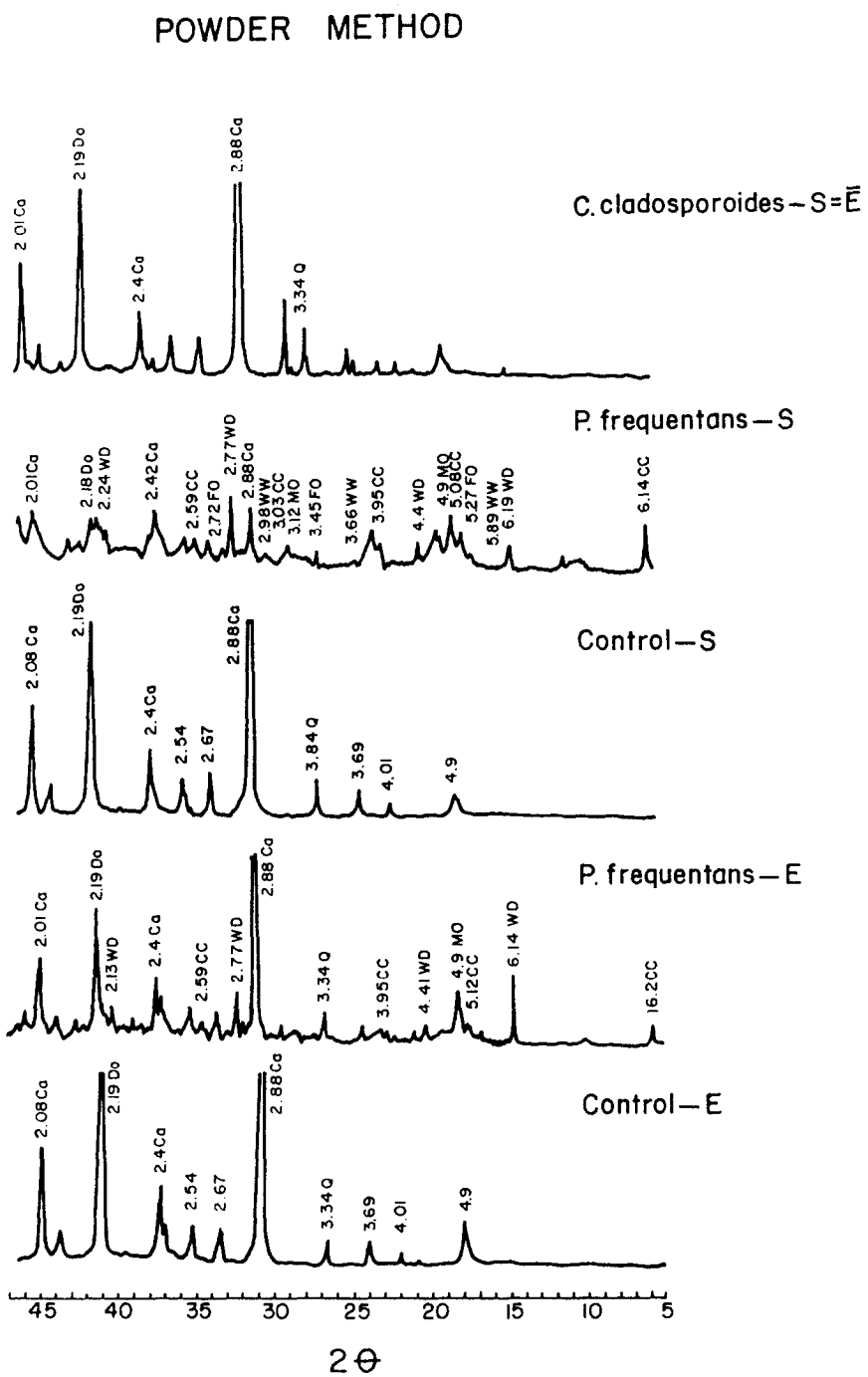

Fig. 6. X-ray diffraction diagrams of limestone scraped surfaces. (Abbreviations as Figs. 4 and 5, Ca: calcite, Do: dolomite, FO: ferric oxalate, WD: weddellite).

Table 2. Cation concentration (μg/g of stone) in broth cultures of both *P. frequentans* and *C. cladosporoides* grown in each stone material.

Fungus	CATION IN SOLUTION (μg/g of stone)[a]								
	Fe	Mn	Zn	Cu	Mg	Ca	Na	K	Al
SANDSTONE									
P. frequentans	0.64	0.26	0.057	0.006	2.64	4.82	142.7	0.42	1
C. cladosporoides	0.02	0.32	—	—	1.47	4.62	71.8	0.31	0.1
Control	0	0.2	0.0038	0.008	1.95	5.34	53.4	0.23	0
GRANITE									
P. frequentans	21.6	0.071	0.009	0	1.6	0.93	89.51	0.28	1.54
C. cladosporoides	0	0.003	0	0	0.45	1.95	33	0.17	0
Control	0	0.03	0	0	0.43	2.24	34.5	0.17	0
LIMESTONE									
P. frequentans	0	0.035	0.008	0	14.26	8.28	70.31	0.27	0.08
C. cladosporoides	0.04	0.024	0.019	0	18.1	33.59	89	0.49	0.12
Control	0	0	0	0	1.17	2.35	37.56	0.23	0

[a] —, not determined

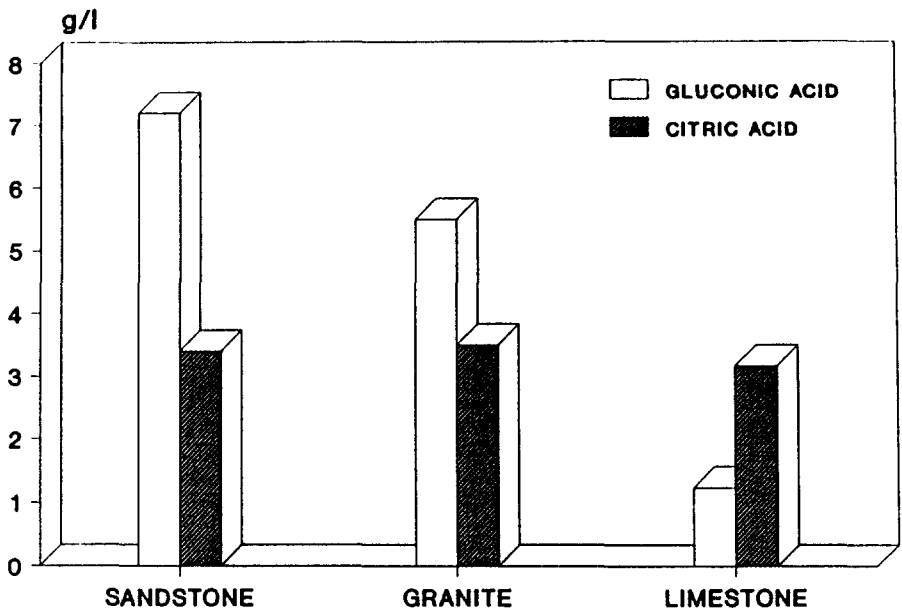

Fig. 7. Organic acids (g/l) determined in broth cultures of *Penicillium frequentans* on each stony material.

Samples inoculated with C. cladosporoides

(i) *Sandstone.* Samples belonging to both zones of study (submersed and emersed) show the same deterioration pattern consisting in a slight decrease in bands ascribed to phyllosilicates: 3614, 1033, 985 y 912 cm^{-1} and feldspars: 1145 cm^{-1}, according to FTIR data (Fig. 1.B). Smectite (peak at 14.02 A) and palygorskite (peak at 10.27 A) were the clay minerals attacked by *C. cladosporoides*, as shown by X-ray patterns (Fig. 4). In broth cultures of *C. cladosporoides*, Fe Al, Mg y Na concentrations were lower than those detected in *P. frequentans* cultures (Table 2). No organic acid excrection was detected in *C. cladosporoides* cultures.

(ii) *Granite.* The weathering effect brought about by *C. cladosporoides* was similar to both culture zones. Figure 2.B shows that bands belonging to phyllosilicates and feldspars were smaller than the ones obtained from *P. frequentans* samples. By means of X-ray diffraction (Fig. 5), only a very small decrease in the chlorite peak was observed, which corresponded to the small amounts of Fe, Al, Mn, Na and K released (Table 2). Neither neoformation oxalate and citrate deposits nor free organic acids were detected.

(iii) *Limestone.* As with the other substrata inoculated with *C. cladosporoides*, no differences were detected between the culture zones. Less calcite and dolomite weathering occurred than with *P. frequentans* (Figs. 3.B and 6). The weathering resulted in the release of small amounts of Ca, Mg, Na, K and Mn (Table 2).

Discussion

An *in vitro* interaction of fungus with stone of monuments was simulated.

In fungal populations an enormous ecological and physiological variability exist. The fungal enzymatic system is readily adapted to a substratum on which each particular organism is growing (Gorlenko 1983; Krumbein 1988). The testing of the action of fungal strains isolated from each of the stone samples used in the present study, sandstone, limestone and granite, allowed us to approximate weathering processes under natural conditions.

Rock biodegradation occurs as a consequence of fungi-stone interaction. The combined use of FTIR, X-ray diffraction, atomic absortion spectrophotometry and flame photometry methods gave complete information in regard to causes and consequences of fungal weathering. Oxalic, citric and gluconic acids, excreted in abundance by *P. frequentans* were the principal agents of fungally induced rock decay. These acids, as was verified in a previous study by de la Torre et al. (1991), were also excreted by other filamentous fungi isolated from Salamanca sandstone.

A consequence of the acidolytic attack was the degradation solubilization and chelation of minerals leading to a remarkable increase in soluble cations released from the mineral lattices. Organic acids by themselves provoked biodeteriorative effects on rock substrata, similar to those promoted by *P. frequentans.* The phyllosilicates which compose the clay cement in sandstone and granite, were attacked preferentially (Figs. 1.B, 2.B, 4, 5 and Table 2). Robert et al. (1975) noted that both citric and gluconic acids were able to induce an important cation release from biotite samples. Eckhardt (1980) demonstrated that some fungal strains of both *Aspergillus niger* and *Penicillium expansum* were able to release K, Mg, Fe and Al from powdered biotite samples. Feldspar degradation by fungi has also been demonstrated (Figs. 1.B, 2.B, 4, 5 and Table 2), although to a lesser degree than damage caused on phyllosilicates. Manley and Evans (1986) also observed that citric and oxalic acids were able to attack feldspar samples.

The two strains of *C. cladosporoides*, non-acidogenic fungi, were only able to cause significant damage in the clay cement of both stone materials: sandstone and granite.

Limestone turned out to be the most affected rock that was tested with all the fungal strains. Ascaso et al. (1982) showed that the oxalic acid, excreted by a lichen, played an important role in limestone deterioration. Jones & Pemberton (1987) verified that many filamentous fungi were able to solubilize spiky calcite.

Although the magnitude of rock decay brought about by *P. frequentans* was much greater than that caused by *C. cladosporoides*, the former fungus was able to provoke a greater damage than that provoked by water alone. This means that some secondary metabolites, other than organic acids, are involved in rock biodeterioration, as proposed by Jones and Pemberton (1987).

All the Fe present in broth cultures of both fungi was in the oxidized form. Since Fe^{3+} solubility is restricted to very low pH values and due to the high organic acid concentrations detected in *P. frequentans* cultures, these organic acids should be forming complexes with Fe^{3+} and Al^{3+}, which keep them in solution. Huang & Keller (1972) and Manley & Evans (1986) demonstrated the capacity of the organic acid to chelate trivalent cations. The fact of detecting Fe^{3+} and Al^{3+} in *C. cladosporoides* broth cultures shows that other metabolites besides organic acids are acting as cation chelators, as proposed by Williams & Rudolf (1974).

Another demonstration of fungal attack on rocks, extensively discussed in the literature, was the finding of large amounts of organic salts in damaged rock surfaces, as a result of the chemical reactions which occurred between organic acids and mineral elements released from stone minerals. Some authors have identified saline desposits on altered rock samples, attributed to a fungal attack of the mineral substrates (Eckhardt 1985; Caner & Boke 1989; Chiari et al. 1989). Lazzarini & Salvadori (1989) brought into question the biological origin of organic salts deposits, like oxalates, in weathered monuments. Nevertheless, in the present study, the origin of oxalates and citrates on altered stone samples as a sole consequence of fungal deterioration was unequivocally demonstrated.

Results obtained in the present study show that calcium citrate deposits are as important in extent and magnitude as those of calcium oxalate. However, no references to calcium citrate deposits in patinas occurring on altered monuments have been reported so far.

Fungi have an enormous ecological potential in unfavourable habitats, such as rocks, through organic acid excretion, since these metabolites are able to release great amounts of mineral elements supplying the fungi with micronutrients necessary for growth. Hall (1981) stated that secondary metabolite production by fungal populations is an adaptative response to different environments. Besides, fungi through their hyphal systems are able to penetrate into substrates using their translocating powers to redis-

tribute essential nutrients (Egging & Allsopp 1975). That is the reason why observed ability of *P. frequentans* and *C. cladosporoides* to develop in both submersed and emersed zones of the stone blocks.

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