Fungal degradation of cultural heritage monuments and management options

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Fungi are widely recognized as major biodeteriogens of both modern and historical buildings/monuments. Different fungal taxa have been isolated from cultural heritage monuments/structures depending on climatic conditions, humidity level and surface material for fungal colonization. Deterioration of such monuments by fungi is through assimilatory biochemical and non-assimilatory mechanisms. This article provides information on fungi infesting historical monuments/sites across the globe and their management by various biocidal compounds. The preventive methods and potency of various essential oils against fungal growth on cultural heritage materials are also critically reviewed. The available information supports the use of essential oils for surface treatment or vapour exposure to prevent mould infestation on heritage monuments. Essential oils may also function as fungicidal agents in biocidal formulations/coatings.

Keywords: Biodegradation, biocidal essential oils, cultural heritage, fungi, historical monuments.

FUNGI are major agents which cause deterioration of heritage buildings and monuments. Humid conditions encourage fungal biofilm to grow on the surface of historical buildings and allow slow degradation of the surface due to interaction with the products of microbial metabolism[1]. The importance of fungi was highlighted in 1930 with the discovery of the antibiotic penicillin by Alexander Fleming[2]. Besides various benefits, fungi also have some disadvantages[3]. They exhibit pathogenicity and are responsible for food spoilage, toxin production, infection on humans and biodeterioration of water-damaged buildings[1,4–6]. Among all the negative effects, our specific concern is the biodeterioration of historical buildings by moulds. Nowadays fungal contamination in houses/buildings is a complicated problem and shows variable sign effects like fading of paint colour, destructions of building, unpleasant odour, etc. Such destruction not only affects houses, but also threatens historical monuments and art museums. According to the type of building deterioration, fungi can be classified into four categories[7]. First is plaster fungi which are mostly found in damp bricks and plaster of buildings, e.g. *Coprinus* spp., *Peziza* spp. and *Pyronema domesticum*. Second is stone fungi, mostly found on stone buildings, e.g. *Botrytis* spp., *Mucor* spp., *Penicillium* spp. and *Trichoderma* spp. The third type is paint fungi which cause discolouration of paints in buildings, e.g. *Alternaria alternata*, *Aspergillus* spp., *Aureobasidium pullutans*, *Penicillium* spp., *Cladosporium herbarum*, *Fusarium oxysporum* and *Phoma violacea.* The fourth category is metal and sealant fungi which cause disfigurement of metal, glass and sealants, e.g. *Cladosporium resinae*, *Aspergillus niger*, *Aurebasidium pullulans*, *Chaetomium globosum*, *Geotrichum* spp., *Penicillium luteum* and *Trichoderma viride*[7].

Fungal species involved in deterioration depend on environmental conditions of the area. Temperature, humidity and chemical nature of the substratum and low availability of water (a_w) are the main parameters that influence fungal growth[8]. Fungi cause biodeterioration through the penetration of their mycelium into the surface of building material and by the action of metabolic products like organic acids, mycotoxins and pigments which cause structural changes on buildings[9,10]. The rising population of arthropods in heritage sites will lead to increase in the fungal infection level as they contribute to the mortality of arthropods, disposal of organic matter and growth[11].

Fungal growth reduces the actual beauty of the heritage monuments. Thus the prevention of fungal growth on heritage buildings, and their treatment are necessary to preserve them. Limited methods are reported for the control of moulds in buildings. This article discusses fungal degradation of heritage monuments and possible management options.

Fungi on culture heritage monuments

Fungi are present everywhere: air, water and soil, and they affect our daily life both directly and indirectly. Biodeterioration of cultural heritage monuments is one of them. There are many heritage structures where fungal deterioration has been reported-not only from India, but all over the world. Ancient artwork and paints on buildings were made of organic materials such as egg yolk, casein, linseed, poppy seed, etc. These organic substances attract microorganisms, including fungi and provide a

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Table 1. Cultural heritage monuments/structures and their associated fungal flora

Location	Fungal species	Reference
Ancient museum, Austria	*Aspergillus* sp.	66
Acropolis of Athens, Greece	*Alterneria*, *Phoma*	67
Marble monuments of Crimea in Eastern Europe	*Alterneria*, *Phoma*	67
Ancient temples of Delos of Greece	*Alterneria*, *Phoma*	67
Historical Archive of the Museum of La Plata, Argentina	*Scopulariopsis* sp. and *Fusarium* sp.	68
The Tomas Roig Museum	*Aspergillus*, *Penicillium* and *Cladosporium*	69
The Felipe Poey Museum	*Aspergillus*, *Penicillium* and *Cladosporium*	69
Gwalior Fort, India	*Alterneria*, *Aspergillus*, *Curvularia*, *Penicillum* and *Fusarium*	70
Sitadevi Temple, Chhattisgarh, India	*Aspergillus flavus*, *A. fumigates*, *A. niger*, *A. scalrotium*, *A. temari*, *Cladosporium oxysporum*, *Curvularia lunata*, *Curvularia clavata*, *Fusarium* sp., *Mucor* sp., *Mycelia sterilia* (white), *Paecilomyces variotii*, *Penicillium chrysogenum*, *Penicillium* sp. and *Trichoderma viride*	71
Sandstone monument, Eifell Lock, Serbia	*Bipolaris spicifera*	72
Granite monument, Monument of the Unknown Hero, Serbia	*Epicoccum nigrum*	72
Mahadev Temple, Bastar, India	*Aspergillus scalrotium*, *A. niger*, *Aspergillus fumigatus*, *Arcemonium scatrotium* and *Paecilomyces varioti*	73
Lascaux cave, France	*Alternaria alternata*, *Aspergillus fumigatus* and *A. niger*	74
Stone monument of Dharmarajika, Taxila	*Cladosporium herbarum*, *Curvularia lunata*, *Dematium* spp., *Fusarium oxysporum*, *Mucorhiemalis*, *Penicillum*, *Chrysogenum*, *P. frequentans* and *Rhizopus oryzae*	75
Mohamed Ali Palace, Cairo, Egypt	*Aspergillus niger*, *A. flavus*, *A. fumigates*, *Penicillium stolenferme*, *Fusarium oxysporium*	76
El-Ghory Mosque and Mosque of EL-Kady Abdelbaset, Egypt	*Fusarium oxysporium*, *Rhizopus oryzae*, *Cladosporium herbarum*, *Alternaria*, *Stachybotrys chartarum*	76
The Painted Cave of Lascaux, France	*Fusarium solani*	77
Cathedral of Salamanca, Spain	*Penicillium*, *Fusarium*, *Cladosporium*, *Phoma* and *Tricoderma*	78
Chapel of Castle Herberstein, Styria, Austria	*Acremonium*, *Engyodontium*, *Cladosporium*, *Blastobotrys*, *Verticilllium*, *Mortierella*, *Aspergillus* and *Penicillium*	79
Carrascosa del campo Church, Cuena, Spain	*Penicillium* and *Fusarium*	80
Parish Church of St Georgen, Styria, Austria	*Acremonium*, *Engyodontium*, *Cladosporium*, *Blastobotrys*, *Verticilllium*, *Mortierella*, *Aspergillus* and *Penicillium*	79
Caestius Pyramid, Rome, Italy	*Cladosporium cladosporioides* and *Alternaria alternata*	81
Pisa Tower, Italy	*Sporotrichum*	82
Klippe statues in Hangzhou, China	*Cladosporium*, *Penicillium*, *Coniosporium* and *Alternaria*	83
Arbroath Abbey, Scottish monument, Scotland	*Cladosporium*, *Penicillium* and *Phialophora lignicola*	84
Linlithgow Palace, Scotland	*Acremonium* sp. and *Penicillium* sp.	84
St Andrews Castle, Scotland	*Acremonium*	84

substrate for their growth. Fungi are mostly found on building stones, mortar and plaster because of their degradation activity and also being extremely erosive[12]. Table 1 provides the list of selected monuments and occurrence of destructive fungi on them.

Fungal deterioration on cultural heritage monuments

The colonization of fungi on cultural heritage monuments causes aesthetic and physical damage to them. The deformation of heritage building surface is due to the presence of a thin layer of dormant/active fungi and their metabolic products such as various acids and pigments. The destruction of monuments is altered by the type of fungus, and nature of the surface and surrounding environmental conditions[13]. Hence in tropical or highly humid areas, there is considerable biofilm formation[14]. Fungal deterioration is caused by three types of mechanisms: chemical, physical and mechanical[15,16]. Fungal deterioration mechanism consists of diagenesis, colour alteration, oxalate formation, physical penetration of fungal hyphae and destabilization of stone texture, bioweathering by secreted acids and chelating property of secreted acids[17–25]. Table 2 describes the major microbial activities which are responsible for deterioration of constructional material.

Discolouration of cultural heritage monuments is primarily due to fungi as they are highly pigmented and their growth may be seen by the naked eye. In the physical method, lesions generally appear on the surface. Lesions up to 2 cm in diameter and depth on stone are called biopitting, which is caused by black fungi[26]. Stone surfaces inhabited by these fungi appear spotty or even completely covered by black layers due to strong melanization of the cell walls of these fungi.

Table 2. Microbial activities associated with the deterioration of construction materials[85]

Microbial activity	Damage caused	Material affected
Surface growth	Discolouration, water retention	Concrete, ceramic tiles, stones, bricks, plaster, wood, plastic, paints, roof tiles
Acid production	Corrosion, erosion	Concrete, stones, metals
Hydrolytic enzyme	Increased fragility, erosion	Wood, paint
Chelation	Corrosion, etching	Metals, concrete, stones, glass
Growth of microbial filaments	Physical damage to surface, increase in permeability	Concrete, stones, plaster, painted surface

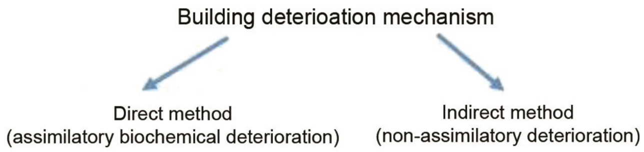

Figure 1. Types of bio deterioration mechanism.

Several filamentous fungi like *Aspergillus glaucus* were reported to produce acids on concrete through chemical deterioration method[27]. Scanning electron microscopy (SEM) studies revealed that *Fusarium* was responsible for weight loss and calcium release from concrete by the penetration of hyphae into the structure[1]. The stone surface could demineralize due to a variety of inorganic and organic acids produced by the fungi[28]. Mechanically, filamentous fungi maypenetrate the weakened parts of a building and also more easily when the surface has extra nutrients in the form of dirt or bacterial biofilm[29,30]. Granite, calcareous limestone and marble are easily be penetrated by black fungi[26].

In the physical, chemical and mechanical mechanism types, building materials are affected by various fungi either directly (using these compounds as nutrients) or indirectly (causing solubilization through the action of metabolites)[31]. Biodeterioration on concrete, cement and stone surfaces is triggered by two mechanisms (Figure 1). First is the direct method called assimilatory biochemical deterioration, which occurs when fungi use building materials as a source of nutrients and grow on them. The second is indirect method, i.e. non-assimilatory, which occur when the metabolites produced by the fungi react with the building materials[32]. The indirect method causes solubilization of building materials by acid production, alkalinity reduction or enzymatic processes[29,33–35].

There are some external and internal factors responsible for deterioration of building surfaces. The external factors include climatic conditions such as humidity, temperature, frost and thawing[36].

These alter the growth of microorganism[37–39] whereas microflora present in the environment also affect the degradation mechanism[32]. The internal factors include type of building material present like concrete, cement and mortar that have mineralogical similarities such as calcium silicate, aluminate, silica, aluminium compound, sulphate, mica and feldspars[33]. Thus, the biodeterioration mechanisms for all types of materials are the same[40].

Conservation techniques

A building can achieve biodegradation resistance by effective and long-lasting treatment techniques, which will inhibit/restrict the growth of biospores. To preserve the architecture, selection of microbial-resistant building materials and protective coatings should be preferably guaranteed before treatment[41]. The important control techniques are explained below.

Surrounding conditions and construction techniques

Biodeterioration depends upon properties of materials used in the building construction, like porosity and permeability, as well as the environmental conditions. Complete analysis of materials and their processing as well as a detailed study of the surrounding environment like humidity and temperature should be done before constructing any building. The protection of building materials against biodegradation may be primarily achieved by moisture reduction at the infected place and high-pressure water or fine-part dry cleaning and application of disinfecting sanitizers (e.g. hydrogen peroxide, eventually combined with conserving agents, iso-thiazole derivatives). Preplanning is mandatory for the control of run-off water, drainage and roof protection[41]. Water-blocking sites should be restricted first before any treatment on the historical buildings. The number of arthropods in heritage sites directly influences fungal infection. So it is necessary to reduce their population to decrease fungal contamination as it is responsible for the mortality of arthropods, disposal of organic matter and fungal deterioration[11]. The treatment method may be helpful for curing from biodegradation. Further treatment also enhances the resistibility of material against microbes.

Protective coatings

The protecting coatings may alter the environmental conditions to reduce microbial growth by reducing humidity and altering the surrounding pH. Biodeterioration may be

Table 3. Biocides effective against specific fungi

Biocides	Fungus	Reference
IPA, Biowash, PUFAS, Ima anti, Biosheen, Boramon	*Alternaria alternata*, *Aspergillus fumigates*, *A. niger*, *A. ustus*, *A. versicolor*, *Clasosporium cladosporiodes*, *C. sphaerosphermum*, *Penicillum aurantiogriseum*, *P. chrysogenum*, *P. simplicissimum*, *Rhizopus stolonifer*, *Scopulariopsis candida*, *Ulocladium* and *Alternaria*	86
Benzalkonium chloride	*Bipolaris spicifer* and *Epicoccum nigrum*	72
Dichloro-xylenol (600 ppm)	*Aspergillus parasiticus*, *Fusarium oxysporium* and *Stachybotrys chartarum*	76
Thymol (700 ppm)	*Fusarium oxysporium*, *Aspergillus flavus* and *Stachybotrys chartarum*	76
Penta-chlorophenol (400 ppm)	*Aspergillus fumigates*, *Aspergillus oryzae*, *Penicillium oxalicum* and *Acremonium kiliense*	76
Sodium azide (100 ppm)	*Fusarium oxysporium*, *Aspergillus parasiticus* and *A. niger*	76
p-Cresol (600 ppm)	*Aspergillus niger*, *A. oryzae* and *Fusarium oxysporium*	76
Hetrerocycle pyrazolo pyrimidine derivatives	*Aspergillus niger*, *A. flavus*, *Penicillium frequentans* and *P. granulatum*	87

prevented using microbial-resistant materials. Fungi mainly occur in damp places where moisture content is high. High level of moisture on building materials supports fungal growth[42]. The preservation of historical buildings may be done using protecting coatings, which can repel water and control moisture level. Defensive materials such as plasters, consolidates, water-repellants, fillers as well as fixatives and organic binders may be used for preservation[43]. If the threat of microbial infection and subsequent biodegradation processes is proven, the selections of protective solutions should consider their microbial resistance to avoid initiation, reoccurrence or even acceleration of microbial impacts on the materials[44]. The main characteristics of microbial-resistant building material are minerals compounds, moisture absorbency, diffusivity and alkalinity. The protective materials used in building conservation possess performance parameters such as transparency, absence of colour, good chemical stability, deep penetration, solidification strength and anti-flaking properties. These protective coatings may be acrylic, silane, silicon-based products and hybrid organic materials. The inorganic materials such as silicates of sodium, potassium, lithium and other compounds have also been successfully applied in conservation effects[45–51]. So, the microbial resistance of protecting materials must be preferably tested with material-specific microbial consortia under laboratory conditions as well as *in situ* in the materials/objects[52].

Application of biocides

To enhance the durability of restoration and conservation treatments on building by biodeterioration, the use of biocides as additives might be unavoidable[32]. Antimicrobial active substances can be mainly distinguished as alcohols, aldehydes, organic acids, carbon acid esters, phenols and their derivatives, halogenated compounds, metals and metal–organic substances, oxidative compounds, enzymes, surface-active compounds and various synthetic organic products. Biocides have been frequently utilized[53]. Sodium-penta-chlorophenate was found to be effective in controlling the growth of fungi at 2% concentration. It showed 100% inhibition of fungal colonies[54,55]. Table 3 presents the list of all effective biocides.

Antifungal essential oils from plants

Biocides are toxic chemicals which can affect both microbes and higher organisms, including humans. The most common fungi *A. alternata* shows inhibition by essential oils of *Abies sibirica*, *Thymus pulegiodes*, *Carum carvi*, *Mentha piperita*, *Citrus bergamia*, *Eucalyptus globulus* and *Syzygium aromaticum*[48]. Clove oil was found to be effective against most building fungi, whereas vapours of peppermint oil were reported to be effective against *Sclerotinia*[56,57]. Clove oil also has antifungal activity at a concentration up to 25% (refs 58–60). The antimicrobial activity of clove oil is attributed to the presence of eugenol (2-methoxy-4-allyl phenol). This compound has a wide spectrum of antimicrobial effects[61].

The volatile essential oils of *Citrus aurantifolia* and *Citrus reticulata* have significant antifungal potency against building fungi[62]. The anise and garlic oils showed the best anti-fungal effect against fungi on Cuban and Argentine heritage structures, whereas oregano oil was even able to inhibit sporulation of fungi[58]. Table 4 shows a list of essential oils exhibiting anti-fungal potency against a range of fungi. The above-mentioned studies reveal that many essential oils possess antifungal activity against building fungi. These findings support the application of essential oils for surface treatment[48].

Other techniques

Microwave heating system also showed effective results at 2.45 GHz electromagnetic radiation against fungal contamination. This method was effective at 65°C for 3 min (ref. 59). Nano-silver suspension at 5–15 ppm exhibited effective results as a biocide. Thus nano-silver additive in paints and coatings may prevent the growth of fungus[49].

Table 4. Name of essential oils against specific fungi

Essential oils	Fungus	Reference
Abies sibirica	*Alternaria alternata*, *Aspergillus niger*, *Aspergillus versicolor*, *Cladosporium sphaerospermum*, *Penicillium chrysogenum*, *Penicillium simplicissium* and *Rhizopus stolonifer*	86
Thymus pulegiodies	*Alternaria alternata*, *Aspergillus niger*, *Penicillium chrysogenum*, *Penicillium simplicissium*, *Scopulariopsis* sp. and *Fusarium* sp.	69, 86
Carum carvi	*Alternaria alternata*, *Aspergillus niger*, *Aspergillus versicolor*, *Cladosporiums phaerospermum*, *Penicillium chrysogenum* and *Penicillium simplicissium*	87
Mentha piperita	*Alternaria alternate*, *Aspergillus versicolor*, *Cladosporium sphaerospermum*, *Penicillium chrysogenum*, *Rhizopus stolonifer*, *Mucor racemose*, *G. candidum* and *A. niger*	86, 88, 89
Citrus bergamia	*Alternaria alternata*, *Aspergillus versicolor*, *Penicillium chrysogenum* and *Penicillium simplicissium*	86
Eucalyotus globules	*Alternaria alternate*, *Aspergillus versicolor* and *Cladosporium sphaerospermum*	86, 88
Syzygium aromaticum	*Alternaria alternata*, *Aspergillus niger*, *Aspergillus versicolor*, *Cladosporium sphaerospermum*, *Penicillium chrysogenum*, *Penicillium simplicissium* and *Rhizopus stolonifer*	86, 89
Carum copticum	*Penicillium* sp., *Fusarium* sp., *Curvularia* sp., *Alternaria* sp. and *Aspergillus nidulans*	71
Ocimum sanctum	*Penicillium* sp., *Fusarium* sp., *Curvularia* sp., *Alternaria* sp. and *A. idulans*	71
Cinnamomum zeylanicum	*Penicillium* sp., *Fusarium* sp., *Curvularia* sp., *Alternaria* sp. and *A. idulans*	71
Pinuspinaster	*Penicillium* sp., *Fusarium* sp., *Curvularia* sp., *Alternaria* sp. and *A. idulans*	71
Cedrusdeodara	*Penicillium* sp., *Fusarium* sp., *Curvularia* sp., *Alternaria* sp. and *A. idulans*	71
Syzygium aromaticum	*Aspergillus niger*, *Aspergillus clavatus*, *Penicillum* sp. and *Fusarium* sp.	89
Origanum vulgare	*A. niger*, *A. clavatus*, *Penicillum* sp. and *Fusarium* sp.	89
Allium sativum	*A. niger*, *A. clavatus*, *Penicillum* sp. and *Fusarium* sp.	89
Pimpinella anisum	*A. niger*, *A. clavatus*, *Penicillum* sp. and *Fusarium* sp.	89
Origanum vulgare	*Scopulariopsis* sp. and *Fusarium* sp.	69
Rosmarinus officinalis	*Bipolaris* sp. and *Epicoccumnigrum*	73
Lavandula angustifolia	*Bipolaris* sp., *Epicoccum nigrum* and *Penicillium* sp.	73
Citrus limon	*Aspergillus niger* and *Geotricum candidum*	89
Artemisia nilagirica	*Aspergillus flavus*, *A. niger*, *Fusarium* and *Penicillium notatum*	90
Ageratum conyzoides	*Didymella bryoniae* and *Rhizoctonia solani*	7, 91
Ailanthus excels	*Candida albicans* and *Saccharomyces cevervidiae*	7, 92
Albizia lebbeck	*C. albicans* and *S. cerevisiae*	7, 92
Artemisia annua	*C. albicans*	7, 92
Caesalpinia cristata	*C. albicans*	7, 92
Calotropis gigantean	*Rhizoctonia solani* and *C. albicans*	7, 92, 93
Medicago sativa	*Cladosporium cladosporoides*	88, 94

The water-repellent coating with antifungal essential oil may be another way to prevent fungal deterioration. Concrete sealers like liquid sealer LS-S, Magik impregnator, WEB-CBX, RIK-seal medium gloss, KONEX WRA-2318, Evercrete DPS, La Guard PWC with essential oil of peppermint and eucalyptus were tested as antifungal coatings against wall fungi[62]. Antifungal properties were exhibited by super-hydrophobic nanoparticles with or without essential oils like arborvitae, oregano and thyme oil to reduce the growth of moulds[48]. The latest alternative is green nanotechnology in which *Bacillus* species produce metabolites with antifungal activity. This may be a sustainable option because it is eco-friendly and harmless to humans[63–65].

Conclusion

Historical monuments are our heritage. Microbial contamination not only slowly deteriorates such monuments, but also destroys our culture hidden in them. The correct identification of fungi is important, as not all of them equally destructive. A profuse number of fungi are involved in the deterioration process based on climate conditions and materials of heritage monuments, but the predominant ones are *Aspergillus*, *Fusarium*, *Cladosporium*, *Curvularia* and *Penicillium*. There are three types of fungal deterioration – physical, chemical and mechanical, and two principles of mechanism. First is the direct method known as assimilatory biochemical deterioration in which the fungi can use the monument material as a source of nutrients and grow on them. The second is the indirect method also known as the non-assimilatory method, in which the metabolites produced by the fungi react with the building materials. Fungi colonize both inorganic and organic surfaces and survive and multiply according to the nature, humidity, temperature and availability of water in the surrounding. All these variables influence the number and diversity of species involved in the deterioration pattern (discolouration, acid production, corrosion, chelation, etc.). The conservation of heritage monuments is a complex process involving an extremely heterogeneous range of elements. Due to excessive, variables treatment of fungal deterioration is a challenging task and needs immediate action. Proper cleaning of heritage sites may be useful to prevent fungal deterioration in the initial stage. Protective coatings, e.g. water-repellants, organic binders and fixatives may be applied on the monuments, but parameters such as transparency, chemical stability, penetration and solidification should be considered before use. Sometimes susceptible materials present in the coatings, themselves are attacked by the fungi. To tackle this problem, biocides must be utilized. Fungicides can easily penetrate the pores of building surfaces and remain there for 2–5 years depending upon their chemical composition. Inorganic nanoparticles, like Ag_2O, TiO_2, ZnO, etc. show better capability to preserve cultural heritage monuments. Toxicity of chemical biocides not only kills the microbes, but affects human health and the environment. Eco-friendly treatments may be an excellent alternative to conserve these monuments. Green biocides from natural sources may be an alternative to toxic chemicals. Specific organisms like the genus *Bacillus* have been suggested as decontaminating approach against fungal deterioration but further studies are needed to assess their harmlessness and effectiveness. The antifungal potential of several essential oils also exhibited encouraging results on fungal contamination. There are a variety of reasons that phytochemicals may be considered to control fungal growth on heritage structures. Further studies on essential oils-based green biocides would be useful to develop eco-friendly, renewable, cost-effective, long lasting and feasible protective coatings which provide better treatment for fungal degradation in heritage buildings.

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