nature sustainability

REVIEW ARTICLE

https://doi.org/10.1038/s41893-020-00602-5

Check for updates

Microbial deterioration and sustainable conservation of stone monuments and buildings

Xiaobo Liu[1], Robert J. Koestler[2], Thomas Warscheid[3], Yoko Katayama[4] and Ji-Dong Gu[5,6] ✉

Geomicrobially induced deterioration of stone monuments and buildings contributes to a considerable loss of world cultural heritage, especially when exposed to a changing climate or environment. The active biodeterioration processes typically involve biochemical activities and cooperation among functional microorganisms in epilithic biofilms, which assimilate mineral nutrients and metabolize anthropogenic pollutants through biogeochemical cycles. Development of any effective mitigation strategies requires the comprehensive understanding of such processes. We focus on how microbes contribute to the biodeterioration processes through their activities and biogeochemical cycles of elements, discuss biochemical mechanisms involved and provide innovative strategies for sustainable conservation of stone monuments and buildings.

By 2019, the United Nations Educational, Scientific and Cultural Organization (UNESCO) had 845 properties listed as world cultural heritage (https://whc.unesco.org/en/list/). All of them are facing irreversible damages, including deterioration of structural materials and in some cases ornamental features, due to threats of climatic, geological or other environmental factors that, in the absence of conservation policy, are leading to a considerable loss of historical authenticity and cultural importance[1–3] (Fig. 1). The international community has recently recognized the need to protect and safeguard the world's cultural and natural heritage as represented by one of the 169 specific targets of the United Nations Sustainable Development Goals (SDG 11.4).

Stone has been used as an important material for tools, housewares and buildings as early as the New Stone Age. Thus, stone monuments and buildings have become an important part of world cultural heritage today over the different continents[4–6]. Stone monuments and buildings are exposed to natural conditions of climate, sunlight, rain and temperature, as well as microbial and chemical contaminants from the atmosphere. Natural and anthropogenic factors combined with the properties of stone materials result in the weathering and deterioration of stone monuments[7–11] (Tables 1 and 2). In particular, microbial processes on stones can lead to so-called biodeterioration, which was first confirmed by Polynov in 1945 when studying soil formation[12]. Although microbiological factors were overlooked by many earlier geologists and pedologists[13], biodeterioration has been widely recognized as any biologically induced undesirable change in the appearance and properties of a material in later studies[14–20]. Most importantly, biodeterioration is a ubiquitous phenomenon involving biogeochemical cycles of carbon, nitrogen and sulfur[7,8,21]. Therefore, identification of effective strategies for the long-term sustainable conservation of stone monuments requires an in-depth understanding of the key deterioration processes involved.

Our knowledge of stone biodeterioration mechanisms has advanced slowly because initial focus was mainly on the composition of epilithic microbial communities. Biodeterioration of stone monuments and buildings in the open environment is a result of much more complex interactions among the stone materials, microbial communities, microbiological processes and local environmental factors, which differs greatly from laboratory investigation[7,21,22]. Therefore, this complexity has largely limited the development of effective mitigation strategies for sustainable conservation.

Research strategies on biodeterioration are changing from community analysis to the biogeochemical reactions of carbon, nitrogen and sulfur cycles. In particular, foci include the role of active microbial members and their biochemical reactions for destruction. Based on an in-depth knowledge of these processes, sustainable control strategies can be developed more effectively against biodeterioration of stone monuments and buildings.

Bioreceptivity of stone materials

Stone materials used for monuments and buildings differ worldwide (Table 2); for example, sandstone for the Angkor monuments in Cambodia[22–24], limestone for the Megalithic Temples of Malta[25] and the Mayan monuments in Mexico[26,27], marble for the Milan Cathedral in Italy[28], granite for the Évora Cathedral in Portugal[29] and volcanic rock for the churches of Lalibela in northern Ethiopia[30]. These stones have their own petrographic properties that greatly influence their colonization by living organisms—bioreceptivity[31]. Microbial colonization of stone is influenced by environmental conditions (Table 1) and petrologic properties, especially chemical composition, types of minerals, as well as roughness, porosity and water permeability[7,9,32–35]. Here, intrinsic parameters on the bioreceptivity of stone are elaborated on.

Intrinsic determinants. Bioreceptivity of stone can be evaluated by determining the intrinsic properties, for example, open porosity, surface roughness, capillary water, chemical composition and abrasion pH, based on their contributions to microbial colonization and growth[36,37].

The porosity and water permeability of stone determine the capillary rise of water into the interior of stone that conditions the life of living organisms at the beginning of colonization[31,37]. High open porosity (>14% by volume basis) with a mean pore radius of 1–10 μm

[1]Laboratory of Environmental Microbiology and Toxicology, School of Biological Sciences, The University of Hong Kong, Hong Kong, PR China. [2]Museum Conservation Institute, Smithsonian Institution, Museum Support Center, Suitland, MD, USA. [3]LBW Bioconsult, Wiefelstede, Germany. [4]Tokyo National Research Institute for Cultural Properties, Tokyo, Japan. [5]Environmental Engineering, Guangdong Technion Israel Institute of Technology, Guangdong, PR China. [6]Southern Laboratory of Ocean Science and Engineering (Guangdong, Zhuhai), Zhuhai, PR China. ✉e-mail: jidong.gu@gtiit.edu.cn

Fig. 1 | Examples of biodeterioration of cultural heritage caused by microbial colonization. a, Angkor Wat viewed from a distance with a reflection in the nearby water pond. **b**,**d**, Gallery sections of Angkor Wat from outside (**b**) and inside (**d**). **e**,**f**, Discolouration and encrustation of stone stairs (**e**) and columns (**f**) caused by epilithic biofilms of black fungi, algae and lichens and/or air pollutants at Angkor Wat. **c**,**g**,**i**, Carvings fully exposed to the open condition of sunlight (**c** and **g**) and inside the gallery protected from the direct sunlight (**i**) at Bayon of Angkor Thom; **g** and **i** show comparative biodeterioration of carvings under different conditions at Bayon with roof damage (**g**) and with an intact roof and water retention (**i**). **h**, Presat Vihear showing severe damage and colonization by biofilms. **i**, Gallery carving severely discoloured and deteriorated by colonizing green phototrophs (for example, cyanobacteria and algae) at Bayon. **j**, A gallery section colonized by biofilms and corroded by biogenic acids at Bayon. **k**, A section of structure showing cracking, flaking and weathering at Angkor Wat. Credit: J.-D.G. and X.L. (**a**–**k**)

allows deep water penetration for a long time, which supports microbial colonization into a depth of 3–5 cm (ref. [7]). In contrast, large-pore stones (for example, some sandstones) allow only temporary colonization due to their shorter water retention, compared to small-pore stones[38]. Thus, stones with high open porosity and permeability usually possess high bioreceptivity; for example, volcanic rock[30], tuffeau limestone[39] and granites with effective porosities of ≥3%[40]. Moreover, rough and porous stone surfaces favour microbial colonization by accumulating dusts and exogenous nutrients[37,41]. However, biocolonization of fine-grained stones with maximal pore radii of 1–2 μm occurs with relative difficulty[7]. Such petrophysical characteristics are usually the most important determinants of the bioreceptivity of stone[36,42–45].

Chemical composition affects stone bioreceptivity mainly by mediating microbial growth after colonization. Differences in chemical compositions among lithotypes result in variations in bioreceptivity and bioerosion. On the one hand, their mineralogical heterogeneity determines the biodiversity and activity of the colonizers. For example, high mineralogical heterogeneity of the volcanic scoria deposits in Lalibela provides the most favourable conditions for lichen and bacterial colonization, enabling the development of bacterial communities with unprecedented species richness[30]. On the other hand, the content of susceptible minerals promotes bioreceptivity. Stones with ≥5% weight by volume (w/v) of weathering-sensitive minerals (that is, clays, feldspars and ferruginous compounds) are particularly vulnerable to microbial colonization[2]. Even in sedimentary stones, diagenetic organic residues can serve as the initial nutrient sources for microorganisms[46]. Carbonate compounds (for example, >3% $CaCO_3$, w/v) in calcareous stones, such as sandstones, concrete or lime mortars, can buffer microbial metabolites (for example, biogenic acids), favouring bacterial growth at a near-neutral pH[7]. Although limestone and marble are commonly composed of a dense calcareous matrix, they are vulnerable to colonization by lichens and fungi under moist conditions[28,47–49]. Artificial stone materials (for example, brick, mortar or concrete) are also susceptible to microbial colonization, depending upon their pore-size distribution, composition and alkalinity[7,50], particularly for historical brick and mortar containing biodegradable organic adhesives; for example, hair, straw, and animal glue. The dependence of bioreceptivity on these physicochemical factors is altered by microbial activities to improve conditions for microbial colonization (as discussed below).

Epilithic biofilm formation. Bioreceptivity allows diverse microflora (bacteria, archaea, cyanobacteria, algae, fungi and lichens) to deposit on and then develop into epilithic and/or endolithic biofilms on stones, depending upon the chemical and physiochemical natures of the substratum itself, ambient environmental conditions and in situ microclimates[7–9,51] (Fig. 2). Initially, material-inherited structural pores or fissures of stone provide a suitable niche for different airborne microbes to be deposited and trapped (Fig. 2a)[52]. When environmental conditions (for example, humidity and nutrient availability) are favourable (Table 1), the deposited microbes typically advance their biofilm lifestyle cycles initially by phototrophic

Table 1 | Crucial activities and key ecological factors of microbial biodeteriogens involved in the biodeterioration of stone

Nutritional groups	Biodeteriogens	Key factors	Substrates	Crucial activities	Relevant biodeterioration
Photoautotrophs	Algae	Humidity, light	Inorganic compounds	Fix CO_2, yield organic acids or carbohydrates	Discolouration, encrustation, patina formation, complexation
	Lichens	Humidity, light	Inorganic compounds	Fix CO_2, yield organic acids or carbohydrates	Extraction of minerals, patina formation, hyphae intrusions
	Cyanobacteria	Light	Inorganic compounds	Fix CO_2, yield organic acids or carbohydrates	Discolouration, encrustation, patina formation, complexation
Chemoautotrophs	Sulfur-oxidizing bacteria	Pollution	S or inorganic compounds	Release sulfuric or sulfurous acids, fix CO_2	Acid corrosion, mineral release, black crusts
	Nitrifiers	Pollution	N or inorganic compounds	Release nitric or nitrous acids, fix CO_2	Acid corrosion, mineral release, black crusts
Heterotrophs	Heterotrophic bacteria	Nutrients	Organic compounds	Biogenic organic acids, pigments	Encrustation, patina formation, discolouration, EPS penetration
	Actinomycetes	Nutrients	Organic compounds	Biogenic organic acids, pigments, hyphae	Pigmentation, patina formation, penetration, discolouration
	Fungi	Humidity, nutrients	Organic compounds	Biogenic organic acids, pigments, hyphae	Discolouration, complexation, hyphae intrusions, black crusts
	Yeasts	Nutrients	Carbohydrates	Pigmentation	Discolouration, pigmentation
Chemoorganotrophs	Sulfate-reducing bacteria	Pollution	S and organic compounds	Reduce sulfates into H_2S anaerobically	Removal of black crusts
	Denitrifying bacteria	Pollution	N and organic compounds	Denitrification anaerobically	Removal of black crusts
	Halophiles	Salinity	Minerals or salts	Salt generation or consumption	Efflorescences

Stone materials in general are very harsh substrata to colonize because of extreme environmental conditions, such as scarce availability of nutrients and water, temperature fluctuations and exposition to solar radiation. Therefore, active lives and activities of stone biodeteriogens are possible only when more permissive conditions are available. Temperatures higher than 30 °C together with high relative humidity values (above 60%) accelerate the activities of biodeteriogens on stone, while low temperatures (4 °C) or low humidity values delay them. For pollution, it may be air pollution or dropping pollution of birds, bats, insects or other small animals.

algae, cyanobacteria and lichens (Fig. 2b), subsequently by chemolithotrophs (Fig. 2c) and eventually by heterotrophic bacteria, actinobacteria and/or meristematic fungi (Fig. 2d)[34,53]. Specifically, phototrophs assimilate CO_2 in water-soluble form to organic substances (for example, biomass and organic acids) for subsequent colonizers (for example, chemolithotrophs and chemoorganotrophs) (Fig. 2b). Subsequently, chemolithotrophs convert atmospheric nitrogenous and sulfurous compounds into inorganic acids, especially nitric and sulfuric acids[24,54–56], which promote leaching out of mineral ions from stone matrices for other microbial growth, particularly phototrophs; for example, algae and cyanobacteria (Fig. 2c). Metabolic activities and succession of different microbial groups provide a complex microbial community with dominance by heterotrophs (Fig. 2d)[54,57], including both bacteria and fungi as well as extracellular polymers. They assemble together to form an interconnected community consisting of both fungal hyphae and extracellular matrices around or between cells[10,34,58,59]. Lastly, extracellular polymeric substances (EPS) cover and connect microbial cells to form a stable biofilm and enhance adhesion onto and/or incursion over a larger area, with horizontal and/or vertical extension (Fig. 2e)[6,10]. In addition, EPS protect biofilms from desiccation and predation. Matured biofilms have a stable architecture (Fig. 2f) and biochemical capability of triggering biodeterioration of the underlying stone by using anthropogenic pollutants to grow and then accumulate more atmospheric pollutants (Table 1)—a second bioreceptivity[37]. Therefore, old or deteriorated stones are usually more bioreceptive than the fresh ones.

Human impacts and biogeochemical cycles

Human activities can intensify the biodeterioration of stone monuments and buildings through atmospheric pollution, climate change and acceleration of biogeochemical cycles[33,60–63] (Fig. 3).

Atmospheric pollution. Pollutants resulting from the increasing consumption of fossil fuels, discharge of traffic, industrial and domestic wastes, urbanization and agricultural production have greatly worsened air pollution (Fig. 3), particularly nitrogenous (for example, NH_3, NO_2 and NO), sulfurous (for example, H_2S and SO_2), aerosols, soot and volatile organic compounds (VOCs)[33,64–67]. These pollutants together with natural ones released from volcanic eruptions and forest fires can be transported over long distances by wind, react with each other in water vapour of the atmosphere and be deposited onto stone monuments and buildings. When the temperature drops, the secondary pollutants together with other airborne particulates can settle down and eventually deposit onto stone monuments and buildings[68]. These inorganic and organic pollutants themselves can cause physical or chemical deterioration of stone materials[60,68], such as acid rain.

Climate change has a positive effect on microbial activity and biodeterioration. The sandstone monuments in the tropical regions, for example, the Angkor Wat and other monuments/temples in Cambodia[54] and the ancient Mayan cities of Calakmul and Uxmul in Mexico[27], show much more serious destruction, compared to those in the cold and arid regions, for example, the Mogao and Maijishan grottoes on the Silk Road in west China[69].

Most importantly, atmospheric pollutants contain nutrients for epilithic biodeteriogens to drive the biogeochemical cycles of carbon, nitrogen and sulfur (Fig. 3), together with organic or inorganic compounds from animal droppings (for example, guanos of birds, bats, monkeys and even domestic dogs)[22,70], particulates or VOCs[60,61,68] and indigenous stone minerals (after dissolution by acid rain or biogenic acids)[7].

Carbon cycling. Initially, carbon dioxide is the major carbon source for epilithic biofilms because organic carbons are very limited on fresh

Table 2 | Biodeterioration diagnosis and conservation strategies for stone monuments and buildings

Monuments or buildings	Stone materials	Environmental and climatic features that contribute to biodeterioration	Relevant biodeterioration processes	Proposed conservation strategies
St. Catherine Chapel, Austria[1]	Marble	Mediterranean climate, rain, wind, organic inputs of wine cellar evaporation	Discolouration and blackening by fungi and actinomycetes	Control of air pollution; bio-intervention with biofungicides
St. Martin Church, Germany[1]	Marble	Mediterranean climate, rain, wind, organic inputs of insect exuvia or excrement	Discolouration and distortions by fungi and actinomycetes	Surface cleaning; bio-intervention with biocides
Milan Cathedral, Italy[28]	Marble	Mediterranean climate, rainfall, wind, high air pollution	Gypsum crusts by black fungi; green-black patinas by archaea, cyanobacteria and bacteria	Control of air pollution with green fuels or energy
Chinese Spirit Path figures, United States[49]	Marble	High humidity, sunlight exposure	Lichen-induced encrustations, patina formation	Ultraviolet and visible flash lamp radiation; humidity control
Jeronimos Monastery, Portugal[134]	Limestone	Mediterranean climate, rainfall, wind	Discolouration, blackening, patina formation by lichens and cyanobacteria	Bio-intervention with biocides (for example, PREVENTOL R80)
Loire castles, France[39]	Limestone	Oceanic climate, wind, highly porous tuffeau, sensitive to temperature and water	Exfoliation, cracks, patinas, salt crystallization, moisture retention	Control of water with hydrophobic layers
Erzurum Castle Mosque, Turkey[60]	Limestone	Hard steppe climate; high humidity; heavy air pollution of SO_2, NO_x and particles from lignite burning and transportation in winter	Acidic corrosion, black crusts, crystallization of gypsum, growth of heterotrophic microflora	Pollution control by replacing fossil fuels with green fuels
Nossa Senhora da Candelária Church, United States[61]	Granite	Intensely urban pollution, subtropical climate, urban traffic pollution	Penetration and solubilization of minerals by halophiles, gypsum deposits by cyanobacteria	Control of air pollution; bio-intervention with biocides
Historic gravestones, United States[66]	Limestone	Heavy atmospheric pollutants of sulfur compounds and hydrocarbons from continuous traffic	Corrosive sulfuric acid released by thiobacilli; fungal penetration; black crusts	Pollution control by replacing fossil fuels with green fuels
Weissenstein Castle, Germany[33]	Sandstone	High anthropogenic organic pollutants	Corrosive organic acids from chemoorganotrophic bacteria; capillary water uptake by EPS	Control or cleaning of anthropogenic organic pollutants
St. Rombouts Cathedral, Belgium[68]	Limestone	Heavy rainfall; atmospheric pollution of aerosols, fly-ash dust particles, nitrogen-, sulfur- and chlorine-containing pollutants	Acidic corrosion, microcrystalline gypsum, black crusts	Pollution control by replacing fossil fuels with green fuels
Mayan archaeological site, Mexico[27]	Limestone	Semi-arid climate, rapid climatic change, arid environments, low nutrient availability	Fungal penetration, biomineralization, salt crystallization, black crusts	In situ bio-intervention with antifungal agents; dry surface cleaning
Maijishan Grottoes, China[69]	Sandstone	Arid continental climate, water seepage, microclimate change, human disturbance, high humidity (>70%), poor ventilation	Discolouration, cracking, powdering, salt crystallization caused by actinobacteria and fungi	Control of humidity, water, anthropogenic pollution and ventilation
Mogao Grottoes, China[131]	Sandstone	Arid continental climate, water seepage, microclimate change, human disturbance, high humidity, poor ventilation	Discolouration, cracking, powdering, salt crystallization caused by fungi actinobacteria and firmicutes	Control of humidity, water, anthropogenic pollution and ventilation
St. Andrews Castle, United Kingdom[93]	Sandstone	Temperate, humid climate, microclimate changes, atmospheric combustion particles, organic aerosols, artificial light	Pigmentation, discolouration and penetration by filamentous actinobacteria, fungi or algae	Control of air pollution and light; bio-intervention with biocides
La Galea Fortress, Spain[94]	Sandstone	Temperate, windy, humid climate; coastal microclimate changes; high humidity (ca. 72%); enough sunshine	Pigmentation and discolouration caused by algae and cyanobacteria; hyphae penetration	Control of water by nanotechnologies or hydrophobic layers
Évora Cathedral, Portugal[29]	Granite	Hot summer Mediterranean climate, lime mortar walls benefiting bacterial growth with a constant pH-milieu	Discolouration and patina formation by pink or orange yeast, bacteria and filamentous fungi	Control of water by nanotechnologies; bio-intervention of biocides
Giza pyramid complex, Egypt[96]	Limestone	Hot, sunny and dry climate; high pollution from garbage, fossil fuel and heavy sewage drainage	Discolouration, pitting, pigmentation and patina formation by bacteria and cyanobacteria	Surface cleaning; bio-intervention of biocides for example, plant essential oils
St. Agatha's Crypt complex, Malta[25]	Limestone	High humidity, poor ventilation, water sewerage	Efflorescences and biomineralization of gypsum, halite and calcite	Control of humidity and air ventilation; optimize the draining systems

Continued

Table 2 | Biodeterioration diagnosis and conservation strategies for stone monuments and buildings (continued)

Monuments or buildings	Stone materials	Environmental and climatic features that contribute to biodeterioration	Relevant biodeterioration processes	Proposed conservation strategies
Trajan Column, Italy[117]	Marble	Mediterranean climate; dryness arising from low porosity, exposure, bioclimate	Biopitting by cyanobacteria	Surface cleaning with biocides; pit restoration
Archaeological site of Pompeii, Italy[127]	Mortar, brick, marble	Mediterranean climate; dominant western winds; wind-driven rain; high temperatures; poor ventilation	Biofilms of cyanobacteria, algae and lichens; discolouration; distortions	Control of water and light due to the exposure conditions
West Lake Landscape site, China[129]	Limestone	Subtropical climate characterized by hot, humid summers; high light intensity; high humidity; air pollution of NO_2 and SO_2	Discolouration by filamentous cyanobacteria or fungi; gypsum crusts by biogenetic acids	Control of water, air pollutants and light due to exposure conditions
San Jeronimo Monastery, Spain[133]	Carbonate stone	Hot summer Mediterranean climate, urban or industrial waste, air pollution	Salt weathering, surface pitting, distortions	In situ bioconsolidation with carbonatogenic bacterial communities
Caestia Pyramid, Italy[140]	Marble	Mediterranean climate, high humidity, rainfall, wind, enough sunshine	Bio-patinas, discolouration, grey or black crusts, endolithic penetration	Bio-intervention with lichen substances
Angkor Wat complex, Cambodia[57,59]	Sandstone	Tropical wet climate; high water and light availability; droppings of bats, birds and insects	Discolouration and blackening by algae, lichens cyanobacteria, fungi and so on	Selective control of water and light; surface cleaning with biocides
Churches of Lalibela, Ethiopia[30]	Volcanic rock	Tropical monsoon climate, rain, wind, hydrothermally induced mineral reactions, decay-prone highly vesicular microtexture	Discolouration, lichen-induced patina, hyphae or EPS penetration, water retention	Control rainwater and wind, optimize the draining systems
Matera Cathedral, Italy[141]	Sandstone tuff	High porosity; groundwater seepage; abundant N organic compounds, soluble nitrates and sulfates in groundwater	Corrosion of nitric or sulfuric acids, salt efflorescences, black crusts, water penetration	Bioclean nitrates and sulfates; optimize the draining systems
Medieval city of Rhodes, Greece[67]	Sandstone	Mediterranean climate; high-speed winds driving marine aerosol and sea salts deposition; humidity fluctuations	NaCl deliquescence or crystallization cycles, exfoliation, crusts, salt efflorescences	Cover a layer of plaster or mortar; employ nanotechnologies
Roman Catacomb, Italy[122]	Tufa marble	Mediterranean climate, artificial light exposure, poor ventilation, water seepage	Green or greyish phototrophic biofilms, discolouration	Control of light and humidity; light sterilization

Environmental and climatic features are the potential reasons for the corresponding biodeterioration phenomenon, taking into account crucial parameters, such as rain, wind, location of the historical object or building, humidity conditions, hydrological conditions, salinity, light exposure, chemical pollution of the environment from air, surface, cities and so on. Potential conservation strategies are selectively proposed to mainly address limiting ecological factors; but usually a combination of several protective approaches should be considered, given that biodeterioration is affected by multiple ecological factors. For example, nanotechnologies can be used together with the policies of water control or bio-intervention. Mediterranean climate is characterized by hot, dry summers and mild, wet winters, which is the most common climate of the areas of the Mediterranean basin. Semi-arid continental climate is characterized by hot, dry summers, cold, snowy winters and rainy springs. Arid continental climate is characterized by extremely hot summers and bitterly cold winters.

and newly cut stones. Therefore, phototrophs, including lichen, cyanobacteria and algae (Fig. 1e,f,i)[44,71], and some chemolithotrophs (for example, nitrifiers and sulfur-oxidizing bacteria or fungi)[24,72–74], are the primary contributors to assimilate CO_2 into organic forms for subsequent biocolonizers (Fig. 2a,b and Table 1). These organic carbons of biomass are essential nutrients to support considerable destruction[75], as discussed in the section 'Mechanisms of biodeterioration'.

Nitrogen cycling. Ammonia and nitrogenous oxides from air pollutants and animal droppings are the original nitrogen sources for epilithic microorganisms. They are utilized by nitrifying bacteria and archaea to generate nitrous and nitric acids and cause acidic erosion of stone monuments and buildings (Fig. 3 and Table 1)[24,62,76]. First, ammonia-oxidizing/nitrifying bacteria (for example, *Nitrosomanas* sp. and *Nitrobacter* sp.) or ammonia-oxidizing archaea (AOA) oxidize NH_3 to obtain energy or electrons for the reduction of CO_2 to organic substances for growth[24,62,76]. In the nitrification process, NH_3 is converted into nitrous and nitric acids by nitrifiers (bacteria and archaea) typically through a two-step biochemical reaction (Fig. 3) or by a more recently discovered complete nitrification of *Nitrospira* sp.[77], which has been detected widely on the sandstone monuments of Angkor in Cambodia[24]. A high concentration of nitrate was detected in the deteriorated section of sandstone bas-reliefs at the Bayon Temple in Cambodia and ammonia-oxidizing archaea were more abundant than the bacteria on the sandstone surfaces[24,78], indicating the greater importance of archaea to biodeterioration than bacteria.

Sulfur cycling. In atmospheric pollutants, sulfur usually exists in both inorganic and organic forms of various valences and is an indispensable element for all organisms. In sulfur cycling, sulfur-oxidizing bacteria or fungi and sulfate-reducing bacteria are two physiologically diverse chemoautotrophic contributors to the biodeterioration of stones (Fig. 3 and Table 1). Sulfur-oxidizing bacteria or fungi reduce CO_2 as a carbon source by oxidizing H_2S or elemental sulfur to sulfurous or sulfuric acid that can dissolve the minerals of stone[55,56,72–74,79–81]. Sulfur-oxidizing bacteria-induced biodeterioration was first documented on limestone and sandstones in France in the 1940s[16–18,82], and later found on marbles in Italy[83–85] and on concrete and natural stone in Germany[74,86,87]. On the contrary, sulfate-reducing bacteria perform the reduction of highly mobile sulfate to sulfide (for example, H_2S) under strictly anaerobic conditions[88]. As chemoorganotrophs, they carry out dissimilatory sulfate reduction coupling with the oxidation of organic compounds or H_2 (ref. [89]). However, most research on these bacteria suffers from difficulties in demonstrating the existence of a complete sulfur cycle in the upper part of buildings, where sulfate-reducing bacteria cannot grow actively and isotopic analyses have showed that chemical processes and their contributions are more pronounced.

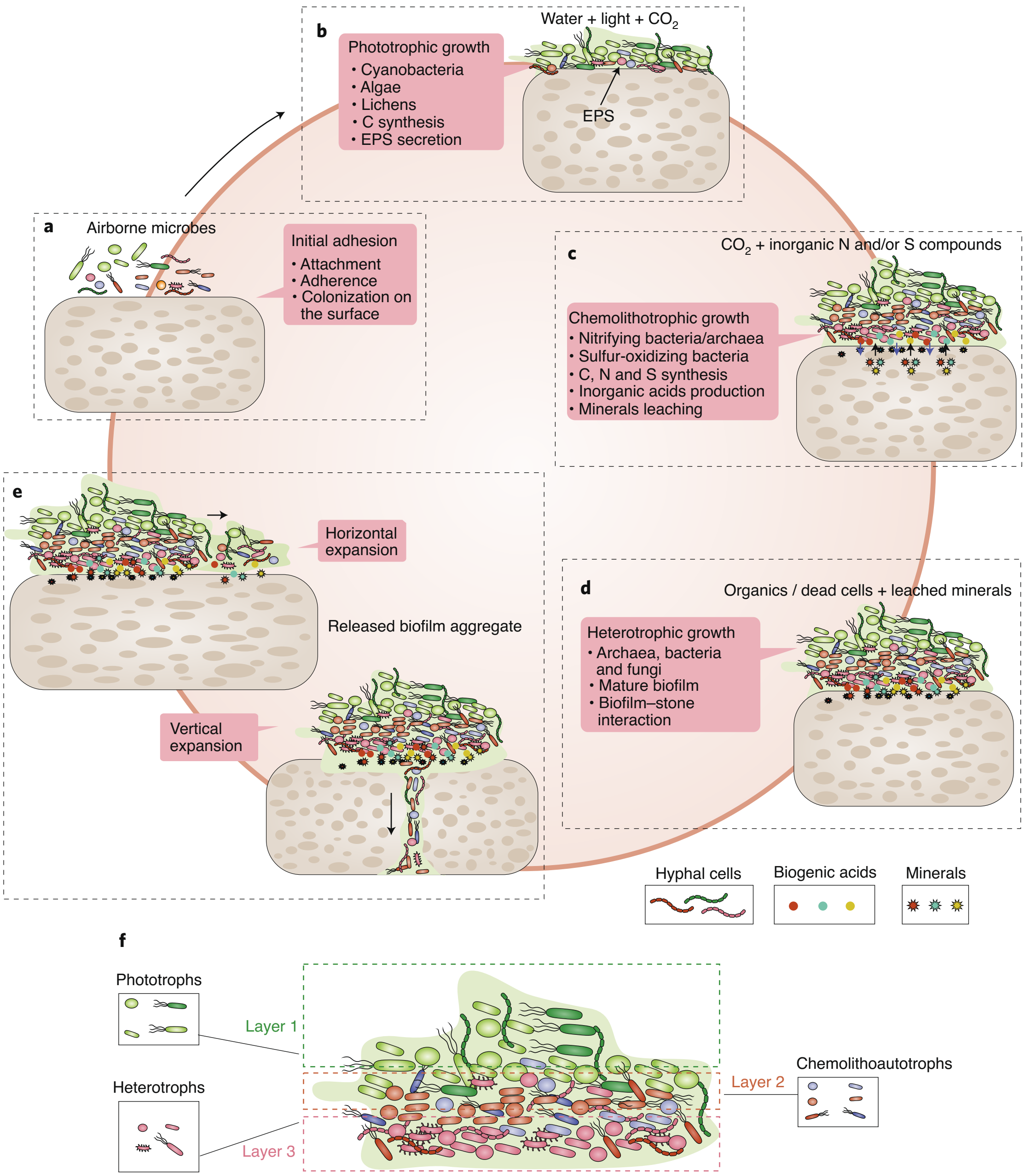

Fig. 2 | Formation and succession of epilithic biofilms on the stone surface. a, Initial adhesion of airborne microbes. **b**, Growth of phototrophs with water, light and carbon dioxide. **c**, Growth of chemolithotrophs with water, carbon dioxide, sulfurous and/or nitrogenous pollutants. **d**, Growth of heterotrophs with the metabolites and dead cells of autotrophs and released minerals. **e**, Further intrusion of mature biofilms into or onto the stone. **f**, Structure of the mature epilithic biofilms. There is no absolutely subsequent colonization between autotrophs and heterotrophs, but the latter can be the primary colonizer in the presence of organic pollutants on stone.

Mechanisms of biodeterioration

The biodeterioration of stone is an extremely complex process involving biological contributors, chemical processes and specific environmental conditions working in concert (Table 1)[60,90]. Despite diverse stone materials, their biodeterioration mechanisms have much in common, such as biofilm formation and discolouration[10,91], corrosion by organic and inorganic acids[50,74] or chemical contaminants, physical penetration by microbiota[92], redox reactions of cations of the mineral lattice[7], formation and crystallization of secondary minerals, complexing of cations and anions from substratum materials by EPS[7], and so on (Table 2).

Discolouration and encrustation. Microbially induced discolouration of stone monuments and buildings initially leads to an aesthetic appearance issue. Non-biological processes of atmospheric deposition also contribute. More commonly, discolouration is a consequence of pigmented cells and/or cellular pigments; for example, carotenes and melanin (Fig. 1d–f and Fig. 4a)[59,92–94]. Phototrophs and black fungi stained the sandstone Angkor monuments with various colours from white to yellowish or dark green and black[35,55,59,95] (Fig. 1b,e,f,i). Actinobacteria formed black spots on the limestone Giza pyramid complex and Seti I Tomb by producing melanin pigment[96] and produced yellow-coloured mats on lava tubes of La Palma in Spain[97].

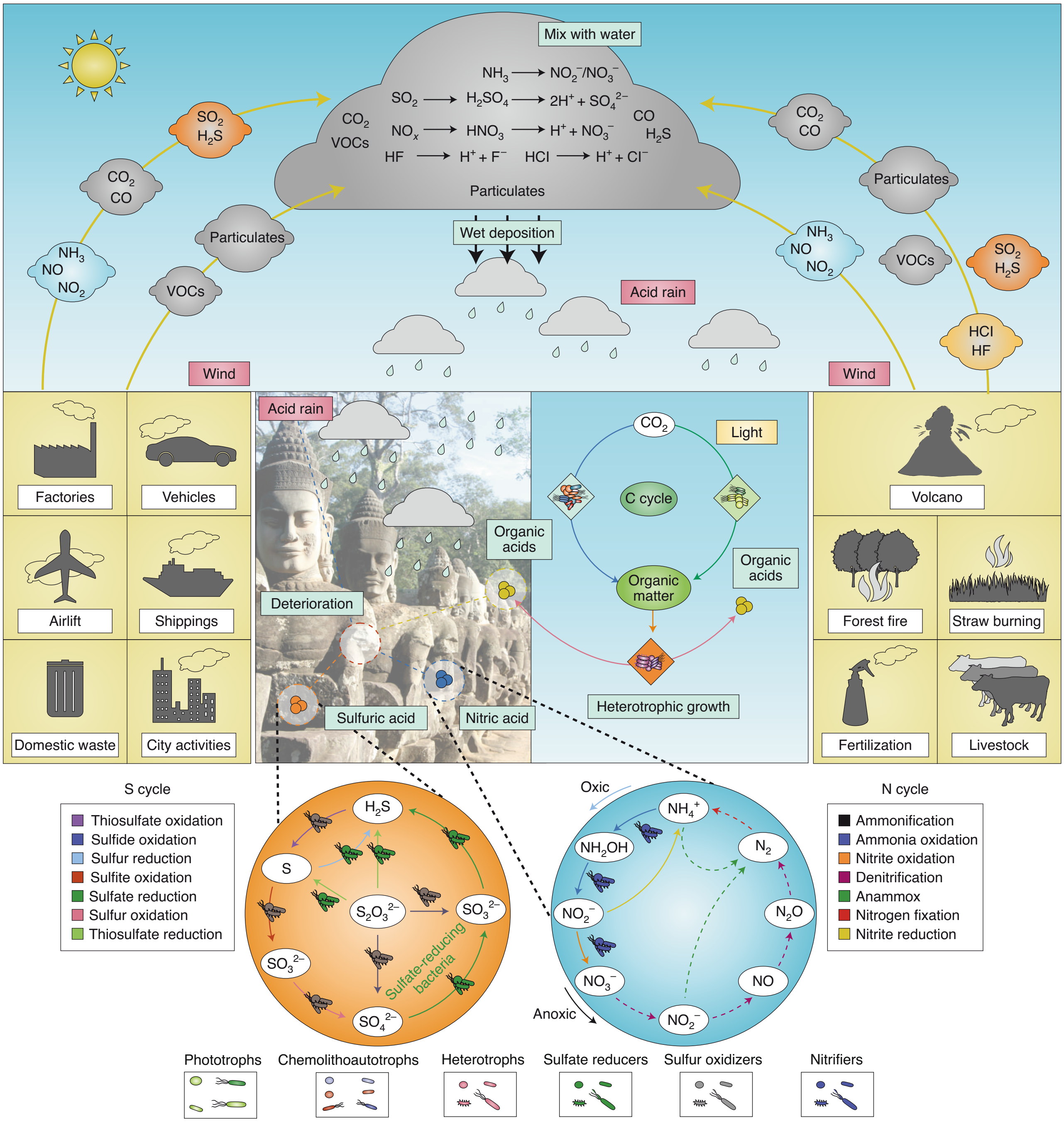

Fig. 3 | Human activities and biogeochemical cycles associated with the biodeterioration of stone heritage. Yellow arrows (top) denote the volatilization and wind for transportation and then deposition of pollutants. Dotted arrows in the nitrogen cycle indicate that microbes in charge of the corresponding pathway have not yet been detected on stone heritage. Credit: J.-D.G. and X.L

Moreover, stone discolouration can induce mechanical damage. Stained areas absorb more solar radiation to increase temperature, but block water exchange[98], which causes deformation through expansion and contraction[47], particularly for sandstones and marbles. Meanwhile, black fungi can lead to further encrustation and exfoliation after fungal hyphae penetration into stone matrices[5,92,99]. Such encrustation effectively accumulates sulfurous pollutants that can be further bioconverted into corrosive acids for the formation of gypsum[64,74,100], which eventually generates so-called black crusts by entrapping other dark particles; for example, anthropogenic emissions, oil dust and fine particulate matters of soot to alter surface appearance and properties[101] (Fig. 1b,h).

Corrosion by biogenic acids. Acidic attack and corrosion by biogenic inorganic or organic acids is one of the major causes of biodeterioration of stone[50,74,102,103] (Fig. 3). However, their mechanisms are different.

Biogenic inorganic acids are mainly nitrous acid (HNO_2), nitric acid (HNO_3), sulfurous acid (H_2SO_3) and sulfuric acid (H_2SO_4)[33,64,65]. They react with the acid-susceptible constituents of the stone materials and release a group of water-soluble salts, including

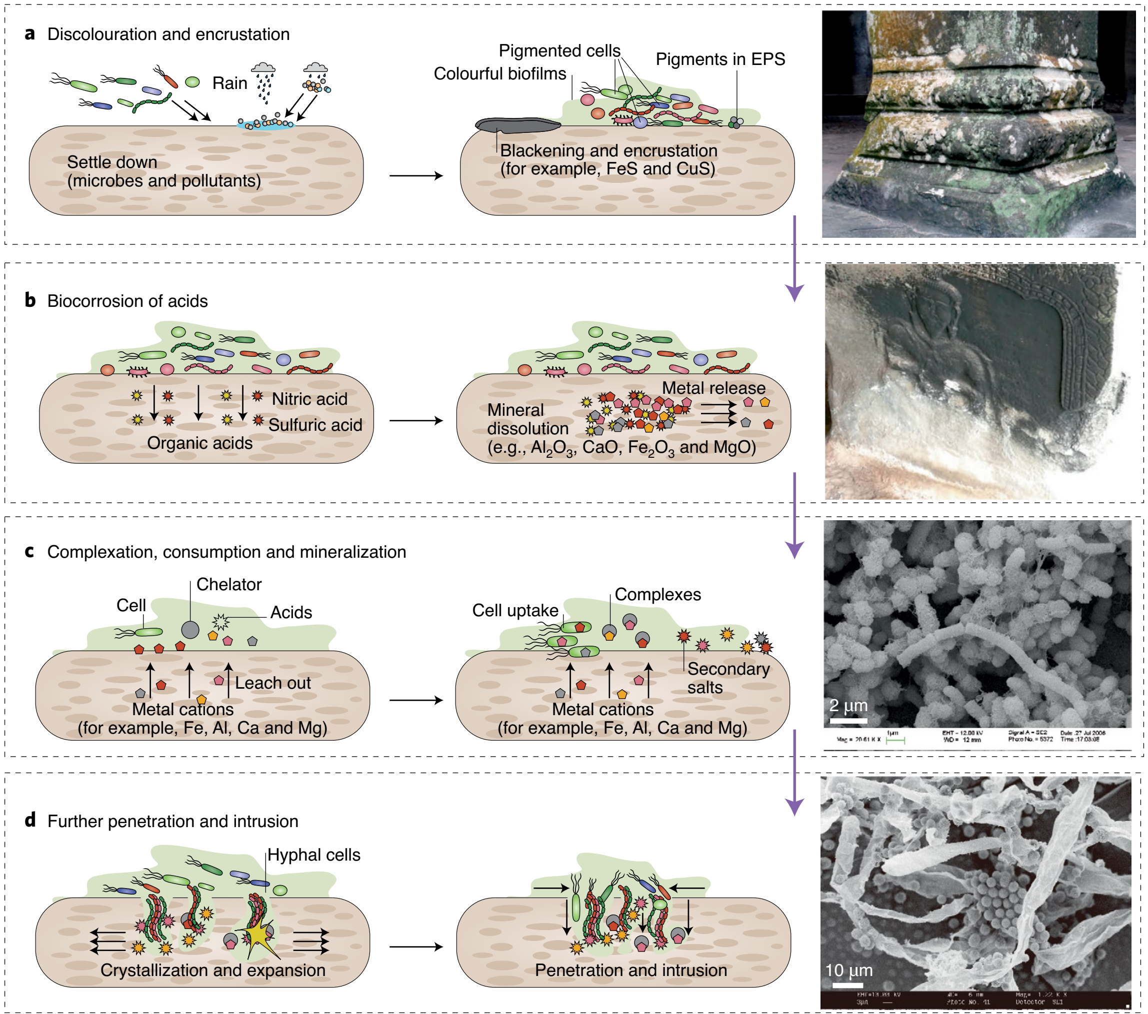

Fig. 4 | Mechanisms of the biodeterioration of stone materials. a, Discolouration and encrustation caused by epilithic biofilms and atmospheric pollutants. The image on the right shows an example of the discolouration by colourful biofilms on a stone monument column. **b**, Dissolution of minerals by biogenic acids. The image on the right shows an example of a deteriorated stone column. **c**, Complexation, consumption and remineralization of released metals. The micrograph on the right shows an example of cyanobacterial calcification. **d**, Further penetration and intrusion caused by epilithic biofilms and salt crystallizations. The micrograph on the right shows an example of hyphal penetration by epiphytic lichens. The purple arrows denote the general subsequence of the main biodeterioration processes. Credit: J.-D.G. and X.L

sulfate[100] and nitrate[74] (Fig. 4b; Supplementary Information). Dissolution of mineral constituents or clay matrices directly destroys the stone structure internally and externally (Fig. 1j,k). Furthermore, sulfuric acid released by sulfur-oxidizing bacteria and fungi gives rise to calcium sulfate and harmful black crusts[7] (Fig. 1b), which can cause further physiochemical damage, as discussed in the subsections 'Secondary mineralization and crystallization' and 'Further penetration and intrusion'.

Biogenic organic acids (for example, oxalic and citric acids) produced by filamentous fungi (for example, *Aspergillus niger* and *Penicillium frequentans*) contribute to corrosive processes aggressively affecting cement/concrete, limestone, granite and sandstone by dissolving the minerals[75,103]. Besides, organic acids can complex or adsorb metal cations to destabilize the mineral lattices[7,104], as discussed in the subsection 'Complexation and release of cations'.

Complexation and release of cations. Microbial EPS contain diverse chemical compounds, including polyols, sugars, glycerol, polysaccharides, proteins, pigments, lipids and organic acids, thus performing multifunctional properties, including binding and reducing cations (Fig. 4c)[10,58,105]. Selective organic acids (for example, oxalic acid and fatty acids) reduce Mn^{4+} in MnO_2 to Mn^{2+} under acidic conditions[106,107]. Polyols degrade siliceous stones by increasing the solubility of organic compounds or by chelating metallic cations from the crystal layers of minerals under alkaline conditions[21]. Also, cations can be chelated by sugars, proteins, hexuronic acids and anionic polymers, once released. Furthermore, extracellular polysaccharides excreted by cyanobacteria have a high affinity for bivalent and trivalent cations[105].

Selective proteins in EPS have an active role in sequestrating and transporting such cations into microbial cells[106] (Fig. 4c). Some chemoorganotrophs obtain energy for growth through bio-catalysing redox reaction of metal cations[34,106,107], and thus are conducive to biodeterioration.

Secondary mineralization and crystallization. Common secondary mineralization and efflorescence on stone monuments and buildings are a result of the deposition of gypsum ($CaSO_4{\cdot}2H_2O$), calcite ($CaCO_3$), halite (NaCl) and other secondary minerals[8,25,100] (Fig. 1k and Fig. 4c). These processes typically involve reactions between anions from biogenic acids and metallic cations leached out from stone materials. For example, calcium oxalate, in the form of weddellite and whewellite (Supplementary Information), widely exists as 'patina' on stone monuments[8,108,109] (Fig. 1c,e).

Together with EPS, these secondary salts cause severe mechanical erosion through cyclic wetting and drying, capillary rise and evaporation, and hydration, especially when water is seasonally available (Fig. 1j,k)[22,110]. During the drying period, the crystallization of secondary soluble salts through dehydration results in an increase in internal stress against the stone integrity[110]. At freezing low temperatures, hydration can enhance water content by secondary salt contents, causing an expansion upon formation of ice crystals in stone[110]. Therefore, stress from salt crystallization is a major cause of cracking, flaking, scaling or detaching of stone monuments and buildings[9] (Fig. 1k). In addition, secondary minerals facilitate the growth of halophilic archaea and bacteria that perform a synergistic action to further accelerate biodeterioration[111].

Further penetration and intrusion. Dissolution, mobilization and crystallization of metallic cations lead to brittleness and softening, favouring progressive penetration and intrusion by filamentous microorganisms (for example, meristematic fungi, lichens and actinobacteria)[5,75,99,112], EPS as well as the secondary salts (Fig. 4d). The growth of hyphae expands the existing pores and fissures to enlarge the porosity for connectivity and physical cracking[75,92,113], posing more severe biophysical damage to the stone integrity. Black crusts caused by meristematic fungi can be precipitated inside the stone pores to disrupt the natural water exchange and movement, retain water for subsequent endolithic colonizers and expand upon the recrystallization to increase the internal stress of stone, thus leading to mechanical damage[92,110].

Notably, active penetration of endolithic microorganisms results in the formation of internal channels, particularly for biopitting, that can severely damage marbles and calcareous stones[114–116]. The commonly occurring biodeteriogens include cyanobacteria, algae, lichens and fungi[117,118]. Moreover, stone biopits with different modal sizes can be enlarged by coalescence, forming an ecological model by maintaining local environmental conditions, particularly humidity for organisms[119,120]. Under this situation, a new endolithic biofilm forms inside the fissure, continues to advance biodeterioration, and finally causes the partial break or detachment of stone.

Strategies toward sustainability

Biodeterioration is a major challenge for the conservation and protection of stone monuments and buildings[38]. Stone biodeterioration involves a complex ecological interplay among organisms, stone materials, changing climates and specific environmental factors (Table 2)[57,114,117,121]. Therefore, more ecological considerations should be taken into sustainable conservation strategies. Identification of active members and detrimental mechanisms should be the focal points of biodeterioration diagnosis, followed by rate assessment before taking specific multidisciplinary preventive measures based on the on-site biodeterioration assessment[23,116] (Table 2).

Control of ecological factors. Despite high diversity of microbial communities, selective ecological factors can be effective in controlling detrimental processes and their activities (Table 1). For example, humidity controls the growth of algae and fungi. Light (both natural and artificial light) is an indispensable factor for phototrophs[43,44,122]. Stone materials favour the growth of chemolithotrophs and phototrophs capable of utilizing inorganic compounds while air or animal pollutants promote heterotrophic growth[61,70]. Therefore, it is essential to identify and control the key factors that restrict the life of active biodeteriogens through specific analysis of the local environment (Tables 1 and 2).

Water is the most critical factor that should be looked after closely with high priority[35], because both microbial growth and biodeterioration (for example, mineral dissolution and crystallization) require water[123], particularly in regions with frequent rains, like the Mediterranean area[5,120] and South Asia[32,35,54]. Removal of the surrounding shadings (for example, trees or buildings) that block sunlight helps the evaporation of rainwater rapidly[22,54,65], which reduces microbial growth effectively. Moreover, innovative materials and engineering design to avoid water retention are necessary. Coating with water-repellent materials, for example, silica nanoparticles and organic–inorganic hybrid siloxane or silicone polymers[124,125], not only prevents water penetration but decreases the porosity. Meanwhile, optimization of the draining systems is an effective solution[30].

Dominant winds or wind-driving rain as a climatic factor influences biodeterioration of stone monuments, particularly in combination with temperature[126,127]. For example, a climatic condition of wind-driving rain, lower temperature and poor ventilation reduces dryness and favours the growth of biodeteriogens on surfaces of Pompeii in Italy[127]. Covering with plasters or mortars, which themselves are exposed to the detrimental environment, instead of the protected object underneath, is effective[1]. Good ventilation can largely reduce humidity, avoid polluted air stagnancy and prevent deposition of atmospheric particulates, condensates and microorganisms onto stone.

Sunlight represents the main energy source for phototrophs, which are the primary producers of organic substrates[34,43,128]. Therefore, light is a critical factor for initial establishment of microbial biodeteriogens, regardless of other influences. Indoor light is easy to control, but in the open environment solar radiation can destroy coatings and films in a short time. Rainwater can be evaporated rapidly by sunlight to protect stone monuments from water-associated attack. However, a drastic temperature fluctuation between day and night is evident in deserts[71], which contributes to thermal destruction of stone materials. Under conditions of hot summers and cold winters, for example, in western China and the Middle East, microbiocenosis is very selective and the patterns of biodeterioration cyclically alternate over time[96,129–131]. In summer, the combination of high temperatures and frequent rainfalls largely favours microbial activities and accelerates biodeterioration while the dry and cold climate of deserts delays biological activity and deterioration[131]. Therefore, control of humidity and temperature is most important and effective for stone heritage conservation in summer[131].

Pollution management. Extraneous pollutants support microbial growth and colonization. Regular surface cleaning and maintenance are essential for routine and long-term sustainable conservation. Soft or gentle cleaning procedures can be adopted to reduce the damage to stone surfaces while the deposition is removed. Meanwhile, regular sampling of surface pollutants for biological or chemical analyses should be built into the whole management programme for establishment of the cleaning frequency schedule and specific methods.

Air pollutants can be transported over long distances from industrial sites, municipalities, motor vehicles and other sources to archaeological sites (Fig. 3). They have a long-term effect on stone monuments[60,61]. Identification of specific contaminants allows tracing the initial pollution source and taking an effective measure to control at origin. It is achievable to replace fossil fuels with alternative green biofuels or renewable energies to reduce the emission of air pollutants, particularly nitrogenous and sulfurous compounds around archaeological sites[60]; for example, the sandy-limestone Cathedral in Belgium[68] and the Milan Cathedral[28]. Governments must take an active role in participating in the overall management and implementation of policy with other stakeholders.

In situ bio-intervention. New biotechnology of bioconsolidation by bacterial carbonatogenesis is an environmentally friendly strategy for sustainable conservation of stone monuments and buildings, especially for those made of calcareous stones; for example, limestone and marble[132]. This technology employs selective calcifying bacteria, for example, *Bacillus* sp. and *Acinetobacter* sp., to bio-precipitate calcium as calcium carbonate for in situ restoration of deteriorated stone materials to reduce water penetration and microbial colonization[133].

Natural bioactive compounds, including biofungicides, biopesticides, and *Bacillus*-based bioactive compounds from microbial secondary metabolites or plant extracts, or even from microbial cells, are candidates for sustainable biocontrol against biodeteriogens, without eco-toxicological side-effects on other indigenous organisms[4,134–136]. Selective *Bacillus* species (for example, *B. subtilis* and *B. amyloliquefaciens*) can produce antifungal peptides or biosurfactant lipopeptides that effectively inhibit fungal growth on mural paintings[137–139]. Some plant and lichen derivatives, essential oils in particular, are tested promising biocidal agents for stone conservation[136,140]. As the sites, materials types and climate conditions differ greatly, selection of the most appropriate biocide must be based on the knowledge of microbiocenosis and, more importantly, on the on-site simulation testing results before any large-scale application. A public database of biocides would be useful for conservators to search for an effective biocide rapidly after microbial identification and diagnosis.

Biocleaning with selective microorganisms to remove harmful pollutants (for example, nitrates, sulfates and organic deposits) is a promising sustainable technology for the conservation of stone heritage[141,142]. More interestingly, selective fungi, for example, *Aspergillus allahabadii*, are capable of removing microbial biofilms on stone monuments[95]. These biological approaches can be used as innovative strategies for sustainable conservation of deteriorating cultural heritage with non-chemical means after no damage to other living organisms (humans included) or stone materials has been tested and confirmed.

Promising nanotechnologies. Consolidating or coating the deteriorated monuments and buildings with organic polymers, for example, synthetic acrylics and epoxy resins, is a frequently adopted method in restoration and protection[28,143]. Because new-generation polymeric materials and fibre-reinforced polymeric composites contain many additives, filler and performance enhancing agents and plasticizers, they might be susceptible to fungal and bacterial degradation[11,144]. They cannot be removed reversibly when any undesirable consequences are detected. A safer and better strategy is to minimize the utilization of polymers.

Selective metals, for example, zinc and copper, are effective in reducing biocolonization on stone, especially in temperate regions[145]. Exploration of novel functional nanomaterials, for example, corrosion-resistant materials[146] and photocatalytic nanocomposites, for example, TiO_2, ZnO and Ag, with photocatalytic, antifouling and antibacterial properties[147], has great potential in sustainable conservation of stone monuments and buildings in the future[148]. However, before the implementation of any new materials, in situ simulation testing is a prerequisite to evaluate their ecological performance and impact.

Future directions and perspectives

This Review focuses on microbial deterioration of stone monuments and buildings and highlights the contribution of metabolically active microorganisms and the biogeochemical reactions relevant to biodeterioration in the changing environment. This synthesis is intended to address the global biodeterioration issue, establish effective mitigation strategies to relieve the damage of biodeterioration, and raise the international awareness of conserving historical heritage from a sustainability point of view. While we have carefully reviewed this complex topic, some gaps remain.

As the rapid growth of population and economy in the twenty-first century has changed the environment and climates, sustainable conservation of stone monuments and buildings needs to consider this factor. The changing environment alters microbial communities and thus the patterns of biodeterioration[23,57]. Although a small recession of stone buildings is expected in this century, more attention should be paid to soiling, discolouration, changing microflora, extreme events and salt weathering[149]. Therefore, research should focus more on effects of climate changes on biodeterioration to determine the critical parameters (for example, rainfall, wind or temperature, selective biochemical reactions, and anthropogenic ones). Laboratory-based analyses can delineate the contribution of specific environmental factors for the extent of biodeterioration occurring in the open environment. Simulations of future climatic scenarios can assess and predict the development of biofilms and changes in biodeterioration patterns.

The most critical gap is the balance between biodeterioration and bioprotection[54,150–152]. On the one hand, activities of biofilms and lichens do contribute to the biodeterioration of stone, as discussed above. On the other hand, an increasing number of studies have reported their bioprotection to stone under specific circumstances[150]. Coverage of biofilms or lichens may actively protect the underlying materials by shielding sunshine radiation, preventing the permeation of rainwater together with harmful substances[32], and binding stone surfaces against exfoliation by fungi hyphae or lichen thallus[54,150]. Lichen or fungi-induced formation of patinas can protect the stone surface[15,113,150,153]. Dominance by biodeterioration or bioprotection may be determined by the nature of stone materials, specific lichen species or environmental changes over time[150–152]. Thus, the axiomatic correlation of biodeterioration or bioprotection with biofilms, lichens and stone materials is unknown. Some standard conceptual models or test procedures could be developed to evaluate the relationship based on the analysis of a wide range of field cases[150,152]. Importantly, this will also help develop a sustainable conservation policy once an applicable biofilm or mechanism with bioprotection overweighing biodeterioration is confirmed.

It is uncertain whether or not artificial treatments on stone heritage will have any negative impacts under the sustainable conservation concept. To ensure the sustainability of conservation, some requirements are: (1) safe to the protected object; (2) the highest gain overweighing the potential risk; (3) friendly to the environment; (4) derived from a renewable resource; and (5) low cost in application[4,142,154]. Although biorestoration technologies are currently considered sustainable protective approaches, further research and long-term surveillance of treated artworks are needed to validate the positive effects and safety to the object over time[135,139]. Moreover, bio-based treatments are more sensitive to environmental factors and this restricts their application at a large scale, thus causing a major limitation for successful commercialization[142].

However, the obstacles are not insurmountable with an active cooperation of multidisciplinary experts[32]. Collection of in situ data on biodeterioration provides more reliable information for a comprehensive understanding of specific microbiota and biochemical processes involved[155,156]. Considering that biodeterioration is affected by different ecological factors, ecological niche modelling techniques are needed to define biodeterioration patterns at a larger scale[23]. Meanwhile, future work is required to provide more information on the entire phenomenon; that is, type of stone, exposure environmental conditions and all biodeteriogens present, permitting the full use of the database's interactive potential[117]. This can be achieved by combining high-resolution climatic data and other environmental factors or by constructing a wider model for each bioclimatic area with different stone materials included[23]. Furthermore, an integrative analysis of metagenomics, metatranscriptomics and metaproteomics is required to identify and determine relevant metabolisms of the major microbiota of the community. Such research initiatives provide a clear framework to elucidate how diverse microbiota cooperate to cause the biodeterioration of stone materials in an extremely nutrient-limited surface environment. With such information available, better strategies for sustainable conservation of stone monuments and buildings can be established effectively.

Received: 30 October 2018; Accepted: 31 July 2020;
Published online: 14 September 2020

References

1. Dornieden, T., Gorbushina, A. & Krumbein, W. Biodecay of cultural heritage as a space/time-related ecological situation—an evaluation of a series of studies. *Int. Biodeterior. Biodegrad.* **46**, 261–270 (2000).
2. Warscheid, T. et al. Studies on the temporal development of microbial infection of different types of sedimentary rocks and its effect on the alteration of the physico-chemical properties in building materials. In *Conservation of stone and other materials: Proc. of the International RILEM/UNESCO congress held at the UNESCO headquarters* (ed. Thiel, M.-J.) 303–310 (E. & F.N. Spon Ltd, 1993).
3. Gadd, G. M. Geomicrobiology of the built environment. *Nat. Microbiol.* **2**, 16275 (2017).
4. Pinna, D. *Coping with Biological Growth on Stone Heritage Objects: Methods, Products, Applications, and Perspectives* (Apple Academic Press, 2017).
5. Onofri, S., Zucconi, L., Isola, D. & Selbmann, L. Rock-inhabiting fungi and their role in deterioration of stone monuments in the Mediterranean area. *Plant Biosyst.* **148**, 384–391 (2014).
6. Villa, F., Stewart, P. S., Klapper, I., Jacob, J. M. & Cappitelli, F. Subaerial biofilms on outdoor stone monuments: changing the perspective toward an ecological framework. *BioScience* **66**, 285–294 (2016).
7. Warscheid, T. & Braams, J. Biodeterioration of stone: a review. *Int. Biodeterior. Biodegrad.* **46**, 343–368 (2000).
8. Saiz-Jimenez, C. Biogeochemistry of weathering processes in monuments. *Geomicrobiol. J.* **16**, 27–37 (1999).
9. Chen, J., Blume, H.-P. & Beyer, L. Weathering of rocks induced by lichen colonization — a review. *Catena* **39**, 121–146 (2000).
10. Martino, P. D. What about biofilms on the surface of stone monuments? *Open Conf. Proc. J.* **6**, 14–28 (2016).
11. Gu, J.-D., Ford, T. E. & Mitchell, R. in *Uhlig's Corrosion Handbook* 3rd edn (ed. Revie, R. W.) 351–363 (Wiley, 2011).
12. Polynov, B. The first stages of soil formation on massive crystaline rocks. *Pochvovedeniye* **7**, 325–339 (1945).
13. Vernadskiy, V. *Geochemical Essays (Ocherki geokhimii)* (Leningrad State Publishing House, 1927).
14. Krasil'nikov, N. The role of microorganisms in the weathering of rocks. *Mikrobiologiya* **18**, 318–323 (1949).
15. Yarilova, Y. A. The role of lithophilous lichens in the weathering of massive crystalline rocks. *Pochvovedeniye* **3**, 533–548 (1947).
16. Pochon, J., Tardieux, P., Lajudie, J. & Charpentier, M. Degradation des temples d'Angkor et processus biologiques. *Ann. Inst. Pasteur* **98**, 457–461 (1960).
17. Pochon, J. & Jaton, C. in *Biodeterioration of Materials* (eds. Wolters, A. H. & Elphich, C. C.) 258–268 (Elsevier, 1968).
18. Pochon, J. & Jaton, C. The role of microbiological agencies in the deterioration of stone. *Chem. Ind.* **9**, 1587–1589 (1967).
19. Paquet, J. Contribution a l'etude de la maladie de la pierre: new hypothese sur les causes des transferts et des concentrations de sulfate produisant les effets foliants. *Mon. His. France* **10**, 73–88 (1964).
20. Hueck, H. in *Biodeterioration of Materials. Microbiological and Allied Aspects* (eds Walters, A. H. & Elphick, J. J.) 6–12 (Elsevier Publishing Co. Ltd, 1968).
21. Gaylarde, P. & Gaylarde, C. Deterioration of siliceous stone monuments in Latin America: microorganisms and mechanisms. *Corros. Rev.* **22**, 395–416 (2004).
22. Uchida, E., Ogawa, Y., Maeda, N. & Nakagawa, T. Deterioration of stone materials in the Angkor monuments, Cambodia. *Eng. Geol.* **55**, 101–112 (2000).
23. Caneva, G., Bartoli, F., Savo, V., Futagami, Y. & Strona, G. Combining statistical tools and ecological assessments in the study of biodeterioration patterns of stone temples in Angkor (Cambodia). *Sci. Rep.* **6**, 32601 (2016).
24. Meng, H., Katayama, Y. & Gu, J.-D. More wide occurrence and dominance of ammonia-oxidizing archaea than bacteria at three Angkor sandstone temples of Bayon, Phnom Krom and Wat Athvea in Cambodia. *Int. Biodeterior. Biodegrad.* **117**, 78–88 (2017).
25. Zammit, G., Sánchez-Moral, S. & Albertano, P. Bacterially mediated mineralisation processes lead to biodeterioration of artworks in Maltese catacombs. *Sci. Total Environ.* **409**, 2773–2782 (2011).
26. McNamara, C. J., Perry, T. D., Bearce, K. A., Hernandez-Duque, G. & Mitchell, R. Epilithic and endolithic bacterial communities in limestone from a Maya archaeological site. *Microb. Ecol.* **51**, 51–64 (2006).
27. Ortega-Morales, B. O. et al. Bioweathering potential of cultivable fungi associated with semi-arid surface microhabitats of Mayan buildings. *Front. Microbiol.* **7**, 201 (2016).
28. Cappitelli, F., Principi, P., Pedrazzani, R., Toniolo, L. & Sorlini, C. Bacterial and fungal deterioration of the Milan Cathedral marble treated with protective synthetic resins. *Sci. Total Environ.* **385**, 172–181 (2007).
29. Rosado, T. et al. Pink! Why not? On the unusual colour of Évora Cathedral. *Int. Biodeterior. Biodegrad.* **94**, 121–127 (2014).
30. Schiavon, N. et al. A multianalytical approach to investigate stone biodeterioration at a UNESCO world heritage site: the volcanic rock-hewn churches of Lalibela, Northern Ethiopia. *Appl. Phys. A* **113**, 843–854 (2013).
31. Guillitte, O. Bioreceptivity: a new concept for building ecology studies. *Sci. Total Environ.* **167**, 215–220 (1995).
32. Warscheid, T. & Leisen, H. in *Biocolonization of Stone: Control and Preventive Methods: Proceedings from the MCI Workshop Series* (eds Charola, A. E. et al.) 1–18 (Smithsonian Institution Scholarly Press, 2011).
33. Warscheid, T., Oelting, M. & Krumbein, W. E. Physico-chemical aspects of biodeterioration processes on rocks with special regard to organic pollutants. *Int. Biodeterior. Biodegrad.* **28**, 37–48 (1991).
34. Haack, T. K. & McFeters, G. A. Nutritional relationships among microorganisms in an epilithic biofilm community. *Microb. Ecol.* **8**, 115–126 (1982).
35. Liu, X., Meng, H., Wang, Y., Katayama, Y. & Gu, J.-D. Water is a critical factor in evaluating and assessing microbial colonization and destruction of Angkor sandstone monuments. *Int. Biodeterior. Biodegrad.* **133**, 9–16 (2018).
36. Prieto, B. & Silva, B. Estimation of the potential bioreceptivity of granitic rocks from their intrinsic properties. *Int. Biodeterior. Biodegrad.* **56**, 206–215 (2005).
37. Miller, A. Z. et al. Bioreceptivity of building stones: a review. *Sci. Total Environ.* **426**, 1–12 (2012).
38. Warscheid, T. et al. Biodeterioration studies on soapstone, quartzite & sandstones of historical monuments in Brazil and Germany. Preliminary results and evaluation for restoration practices. In *Proc. of the 7th International Congress on Deterioration and Conservation of Stone* 491–500 (Laboratório Nacional de Engenharia Civil, 1992).
39. Beck, K., Al-Mukhtar, M., Rozenbaum, O. & Rautureau, M. Characterization, water transfer properties and deterioration in tuffeau: building material in the Loire valley—France. *Build. Environ.* **38**, 1151–1162 (2003).
40. Sousa, L. M. O., Suárez del Río, L. M., Calleja, L., Ruiz de Argandoña, V. G. & Rey, A. R. Influence of microfractures and porosity on the physico-mechanical properties and weathering of ornamental granites. *Eng. Geol.* **77**, 153–168 (2005).
41. Koestler, R., Warscheid, T. & Nieto, F. in *Saving our Architectural Heritage: The Conservation of Historic Stone Structures* (eds Baer, N. S. & Snethlage, R.) 25–36 (Wiley, 1997).
42. Miller, A. Z., Dionísio, A., Laiz, L., Macedo, M. F. & Saiz-Jimenez, C. The influence of inherent properties of building limestones on their bioreceptivity to phototrophic microorganisms. *Ann. Microbiol.* **59**, 705–713 (2009).
43. Tiano, P., Accolla, P. & Tomaselli, L. Phototrophic biodeteriogens on lithoid surfaces: an ecological study. *Microb. Ecol.* **29**, 299–309 (1995).
44. Vázquez-Nion, D., Silva, B. & Prieto, B. Influence of the properties of granitic rocks on their bioreceptivity to subaerial phototrophic biofilms. *Sci. Total Environ.* **610–611**, 44–54 (2018).
45. Miller, A., Dionísio, A. & Macedo, M. F. Primary bioreceptivity: a comparative study of different Portuguese lithotypes. *Int. Biodeterior. Biodegrad.* **57**, 136–142 (2006).
46. Hunt, J. M. Distribution of hydrocarbons in sedimentary rocks. *Geochim. Cosmochim. Acta* **22**, 37–49 (1961).
47. Carter, N. & Viles, H. Lichen hotspots: raised rock temperatures beneath *Verrucaria nigrescens* on limestone. *Geomorphology* **62**, 1–16 (2004).
48. Castanier, S., Le Métayer-Levrel, G. & Perthuisot, J.-P. Ca-carbonates precipitation and limestone genesis—the microbiogeologist point of view. *Sediment. Geol.* **126**, 9–23 (1999).

49. Leavengood, P., Twilley, J. & Asmus, J. F. Lichen removal from Chinese Spirit Path figures of marble. *J. Cult. Herit.* **1**, S71–S74 (2000).
50. Gu, J.-D., Ford, T. E. & Mitchell, R. in *Uhlig's Corrosion Handbook* 3rd edn (ed. Revie, R. W.) 451–460 (Wiley, 2011).
51. Roig, P. B., Regidor Ros, J. L. & Estellés, R. M. Biocleaning of nitrate alterations on wall paintings by *Pseudomonas stutzeri*. *Int. Biodeterior. Biodegrad.* **84**, 266–274 (2013).
52. Šimonovičová, A., Gódyová, M. & Ševc, J. Airborne and soil microfungi as contaminants of stone in a hypogean cemetery. *Int. Biodeterior. Biodegrad.* **54**, 7–11 (2004).
53. Lan, W., Li, H., Wang, W.-D., Katayama, Y. & Gu, J.-D. Microbial community analysis of fresh and old microbial biofilms on Bayon Temple Sandstone of Angkor Thom, Cambodia. *Microb. Ecol.* **60**, 105–115 (2010).
54. Bartoli, F. et al. Biological colonization patterns on the ruins of Angkor temples (Cambodia) in the biodeterioration vs bioprotection debate. *Int. Biodeterior. Biodegrad.* **96**, 157–165 (2014).
55. Xu, H.-B. et al. Lithoautotrophical oxidation of elemental sulfur by fungi including *Fusarium solani* isolated from sandstone Angkor temples. *Int. Biodeterior. Biodegrad.* **126**, 95–102 (2018).
56. Kusumi, A., Li, X. S. & Katayama, Y. Mycobacteria isolated from Angkor monument sandstones grow chemolithoautotrophically by oxidizing elemental sulfur. *Front. Microbiol.* **2**, 104 (2011).
57. Caneva, G. et al. Exploring ecological relationships in the biodeterioration patterns of Angkor temples (Cambodia) along a forest canopy gradient. *J. Cult. Herit.* **16**, 728–735 (2015).
58. Kemmling, A., Kämper, M., Flies, C., Schieweck, O. & Hoppert, M. Biofilms and extracellular matrices on geomaterials. *Environ. Geol.* **46**, 429–435 (2004).
59. Gaylarde, C. C., Rodríguez, C. H., Navarro-Noya, Y. E. & Ortega-Morales, B. O. Microbial biofilms on the sandstone monuments of the Angkor Wat complex, Cambodia. *Curr. Microbiol.* **64**, 85–92 (2012).
60. Nuhoglu, Y. et al. The accelerating effects of the microorganisms on biodeterioration of stone monuments under air pollution and continental-cold climatic conditions in Erzurum, Turkey. *Sci. Total Environ.* **364**, 272–283 (2006).
61. Gaylarde, C. et al. Epilithic and endolithic microorganisms and deterioration on stone church facades subject to urban pollution in a sub-tropical climate. *Biofouling* **33**, 113–127 (2017).
62. Mansch, R. & Bock, E. Biodeterioration of natural stone with special reference to nitrifying bacteria. *Biodegradation* **9**, 47–64 (1998).
63. Viles, H. A. Implications of future climate change for stone deterioration. *Geol. Soc. Lond. Spec. Publ.* **205**, 407–418 (2002).
64. Moroni, B. & Pitzurra, L. Biodegradation of atmospheric pollutants by fungi: a crucial point in the corrosion of carbonate building stone. *Int. Biodeterior. Biodegrad.* **62**, 391–396 (2008).
65. Saiz-Jimenez, C. Biodeterioration vs biodegradation: the role of microorganisms in the removal of pollutants deposited on historic buidlings. *Int. Biodeterior. Biodegrad.* **40**, 225–232 (1997).
66. Mitchell, R. & Gu, J.-D. Changes in the biofilm microflora of limestone caused by atmospheric pollutants. *Int. Biodeterior. Biodegrad.* **46**, 299–303 (2000).
67. Stefanis, N.-A., Theoulakis, P. & Pilinis, C. Dry deposition effect of marine aerosol to the building stone of the medieval city of Rhodes, Greece. *Build. Environ.* **44**, 260–270 (2009).
68. Leysen, L., Roekens, E. & Van Grieken, R. Air-pollution-induced chemical decay of a sandy-limestone Cathedral in Belgium. *Sci. Total Environ.* **78**, 263–287 (1989).
69. Duan, Y. et al. The microbial community characteristics of ancient painted sculptures in Maijishan Grottoes, China. *PLoS ONE* **12**, e0179718 (2017).
70. Bakr, A. & El Hafez, M. A. Role assessment of bat excretions in degradation of painted surface from Mohamed Ali's palace, Suez, Egypt. *Egypt. J. Archaeol. Restor. Stud.* **3**, 47–56 (2012).
71. Wierzchos, J. et al. Adaptation strategies of endolithic chlorophototrophs to survive the hyperarid and extreme solar radiation environment of the Atacama Desert. *Front. Microbiol.* **6**, 934 (2015).
72. Aviam, O., Bar-Nes, G., Zeiri, Y. & Sivan, A. Accelerated biodegradation of cement by sulfur-oxidizing bacteria as a bioassay for evaluating immobilization of low-level radioactive waste. *Appl. Environ. Microbiol.* **70**, 6031–6036 (2004).
73. Vupputuri, S. et al. Isolation of a sulfur-oxidizing *Streptomyces* sp. from deteriorating bridge structures and its role in concrete deterioration. *Int. Biodeterior. Biodegrad.* **97**, 128–134 (2015).
74. Sand, W. & Bock, E. Biodeterioration of mineral materials by microorganisms—biogenic sulfuric and nitric acid corrosion of concrete and natural stone. *Geomicrobiol. J.* **9**, 129–138 (1991).
75. Salvadori, O. & Municchia, A. C. The role of fungi and lichens in the biodeterioration of stone monuments. *Open Conf. Proc. J.* **7**, 39–54 (2016).
76. Meng, H., Luo, L., Chan, H. W., Katayama, Y. & Gu, J.-D. Higher diversity and abundance of ammonia-oxidizing archaea than bacteria detected at the Bayon Temple of Angkor Thom in Cambodia. *Int. Biodeterior. Biodegrad.* **115**, 234–243 (2016).
77. Daims, H. et al. Complete nitrification by *Nitrospira* bacteria. *Nature* **528**, 504–509 (2015).
78. Gu, J.-D. & Katayama, Y. A microbiological challenge in protection of the sandstone Angkor monuments in Cambodia. *IIC Newsletter* (15 December 2017).
79. Gu, J.-D., Ford, T. E., Berke, N. S. & Mitchell, R. Biodeterioration of concrete by the fungus *Fusarium*. *Int. Biodeterior. Biodegrad.* **41**, 101–109 (1998).
80. Li, X. S. et al. Oxidation of elemental sulfur by *Fusarium solani* strain THIF01 harboring endobacterium *Bradyrhizobium* sp. *Microb. Ecol.* **60**, 96–104 (2010).
81. Li, X., Arai, H., Shimoda, I., Kuraishi, H. & Katayama, Y. Enumeration of sulfur-oxidizing microorganisms on deteriorating stone of the Angkor monuments, Cambodia. *Microbes Environ.* **23**, 293–298 (2008).
82. Bourcart, J., Noetzlin, J., Pochon, J. & Berthelier, S. Etude des détériorations des pierres des monuments historiques. In *Annales de l'Institut Technique de Bâtiment et des Travaux Publics* 1–16 (1949).
83. Lepidi, A. & Schippa, G. Some aspects of the growth of chemotrophic and heterotrophic microorganisms on calcareous surfaces. In *Colloque international sur la deterioration des pierres en oeuvre. 1er. International symposium on the deterioration of building stones* 143–148 (Les Imprimerie Reunites de Chambery, 1973).
84. Barcellona Vero, L. & Monte Sila, M. Isolation of various sulphur-oxidizing bacteria from stone monuments. In *The conservation of stone i. Proceedings of the international symposium* (ed. Rossi-Manaresi, R.) 233–244 (Centro per la conservazione delle sculture all'aperto, 1976).
85. Tarantino, M. M. S.-G. The metabolic state of microorganisms of the genus Thiobacillus on stone monuments. In *The Conservation of stone II: preprints of the contributions to the international symposium* 117–138 (Centro per la conservazione delle sculture all'aperto, 1981).
86. Milde, K., Sand, W., Wolff, W. & Bock, E. Thiobacilli of the corroded concrete walls of the Hamburg sewer system. *Microbiology* **129**, 1327–1333 (1983).
87. Krumbein, W. E. Photolithotropic and chemoorganotrophic activity of bacteria and algae as related to beachrock formation and degradation (gulf of Aqaba, Sinai). *Geomicrobiol. J.* **1**, 139–203 (1979).
88. Suzuki, D., Li, Z., Cui, X., Zhang, C. & Katayama, A. Reclassification of *Desulfobacterium anilini* as *Desulfatiglans anilini* comb. nov. within *Desulfatiglans* gen. nov., and description of a 4-chlorophenol-degrading sulfate-reducing bacterium, *Desulfatiglans parachlorophenolica* sp. nov. *Int. J. Syst. Evol. Microbiol.* **64**, 3081–3086 (2014).
89. Kleindienst, S. et al. Diverse sulfate-reducing bacteria of the *Desulfosarcina/Desulfococcus* clade are the key alkane degraders at marine seeps. *ISME J.* **8**, 2029–2044 (2014).
90. Griffin, P., Indictor, N. & Koestler, R. The biodeterioration of stone: a review of deterioration mechanisms, conservation case histories, and treatment. *Int. Biodeterior. Biodegrad.* **28**, 187–207 (1991).
91. Gaylarde, P., Englert, G., Ortega-Morales, O. & Gaylarde, C. Lichen-like colonies of pure *Trentepohlia* on limestone monuments. *Int. Biodeterior. Biodegrad.* **58**, 119–123 (2006).
92. Isola, D. et al. Extremotolerant rock inhabiting black fungi from Italian monumental sites. *Fungal Divers.* **76**, 75–96 (2016).
93. Suihko, M.-L. et al. Characterization of aerobic bacterial and fungal microbiota on surfaces of historic Scottish monuments. *Syst. Appl. Microbiol.* **30**, 494–508 (2007).
94. Morillas, H. et al. Characterization of the main colonizer and biogenic pigments present in the red biofilm from La Galea Fortress sandstone by means of microscopic observations and Raman imaging. *Microchem. J.* **121**, 48–55 (2015).
95. Hu, H. et al. Occurrence of *Aspergillus allahabadii* on sandstone at Bayon temple, Angkor Thom, Cambodia. *Int. Biodeterior. Biodegrad.* **76**, 112–117 (2013).
96. ElBaghdady, K. Z., Tolba, S. T. & Houssien, S. S. Biogenic deterioration of Egyptian limestone monuments: treatment and conservation. *J. Cult. Herit.* **38**, 118–125 (2019).
97. Gonzalez-Pimentel, J. L. et al. Yellow coloured mats from lava tubes of La Palma (Canary Islands, Spain) are dominated by metabolically active Actinobacteria. *Sci. Rep.* **8**, 1944 (2018).
98. Garty, J. Influence of epilithic microorganisms on the surface temperature of building walls. *Can. J. Bot.* **68**, 1349–1353 (1990).
99. Sterflinger, K. Fungi: their role in deterioration of cultural heritage. *Fungal Biol. Rev.* **24**, 47–55 (2010).
100. Ortega-Morales, B. O., Gaylarde, C. C., Englert, G. E. & Gaylarde, P. M. Analysis of salt-containing biofilms on limestone buildings of the Mayan culture at Edzna, Mexico. *Geomicrobiol. J.* **22**, 261–268 (2005).

101. Cappitelli, F. et al. Improved methodology for bioremoval of black crusts on historical stone artworks by use of sulfate-reducing bacteria. *Appl. Environ. Microbiol.* **72**, 3733–3737 (2006).
102. Vincke, E. et al. Influence of polymer addition on biogenic sulfuric acid attack of concrete. *Int. Biodeterior. Biodegrad.* **49**, 283–292 (2002).
103. De Windt, L. & Devillers, P. Modeling the degradation of Portland cement pastes by biogenic organic acids. *Cem. Concr. Res.* **40**, 1165–1174 (2010).
104. Turkington, A. V. & Paradise, T. R. Sandstone weathering: a century of research and innovation. *Geomorphology* **67**, 229–253 (2005).
105. Rossi, F. et al. Characteristics and role of the exocellular polysaccharides produced by five cyanobacteria isolated from phototrophic biofilms growing on stone monuments. *Biofouling* **28**, 215–224 (2012).
106. Li, W.-W. & Yu, H.-Q. Insight into the roles of microbial extracellular polymer substances in metal biosorption. *Bioresour. Technol.* **160**, 15–23 (2014).
107. Stone, A. T. Microbial metabolites and the reductive dissolution of manganese oxides: oxalate and pyruvate. *Geochim. Cosmochim. Acta* **51**, 919–925 (1987).
108. Monte, M. Oxalate film formation on marble specimens caused by fungus. *J. Cult. Herit.* **4**, 255–258 (2003).
109. Cariati, F., Rampazzi, L., Toniolo, L. & Pozzi, A. Calcium oxalate films on stone surfaces: experimental assessment of the chemical formation. *Stud. Conserv.* **45**, 180–188 (2000).
110. Scherer, G. W. Stress from crystallization of salt. *Cem. Concr. Res.* **34**, 1613–1624 (2004).
111. Saiz-Jimenez, C. & Laiz, L. Occurrence of halotolerant/halophilic bacterial communities in deteriorated monuments. *Int. Biodeterior. Biodegrad.* **46**, 319–326 (2000).
112. Favero-Longo, S. E., Borghi, A., Tretiach, M. & Piervittori, R. *In vitro* receptivity of carbonate rocks to endolithic lichen-forming aposymbionts. *Mycol. Res.* **113**, 1216–1227 (2009).
113. Lisci, M., Monte, M. & Pacini, E. Lichens and higher plants on stone: a review. *Int. Biodeterior. Biodegrad.* **51**, 1–17 (2003).
114. Caneva, G., Danin, A., Ricci, S. & Conti, C. The pitting of Trajan's column, Rome: an ecological model of its origin. In *Conservazione del Patrimonio culturale II, Contributi Centro Linceo Interdisciplinare Beniamino Segre* 78–102 (Accademia Nazionale dei Lincei, 1994).
115. Danin, A. Pitting of calcareous rocks by organisms under terrestrial conditions. *Isr. J. Earth Sci.* **41**, 201–207 (1992).
116. Danin, A. & Caneva, G. Deterioration of limestone walls in Jerusalem and marble monuments in Rome caused by cyanobacteria and cyanophilous lichens. *Int. Biodeterior. Biodegrad.* **26**, 397–417 (1990).
117. Lombardozzi, V., Castrignanò, T., D'Antonio, M., Casanova Municchia, A. & Caneva, G. An interactive database for an ecological analysis of stone biopitting. *Int. Biodeterior. Biodegrad.* **73**, 8–15 (2012).
118. Gehrmann, C., Krumbein, W. & Petersen, K. Endolithic lichens and the corrosion of carbonate rocks. A study of biopitting. *Int. J. Mycol. Lichenol.* **5**, 37–48 (1992).
119. McIlroy de la Rosa, J. P., Warke, P. A. & Smith, B. J. Microscale biopitting by the endolithic lichen Verrucaria baldensis and its proposed role in mesoscale solution basin development on limestone. *Earth Surf. Process. Landf.* **37**, 374–384 (2012).
120. Pomar, F., Gómez-Pujol, L., Fornós, J. J., Del Valle, L. & Nogales, B. Limestone biopitting in coastal settings: A spatial, morphometric, SEM and molecular microbiology sequencing study in the Mallorca rocky coast (Balearic Islands, Western Mediterranean). *Geomorphology* **276**, 104–115 (2017).
121. Caneva, G. Ecological approach to the genesis of calcium oxalate patinas on stone monuments. *Aerobiologia* **9**, 149–156 (1993).
122. Bruno, L. & Valle, V. Effect of white and monochromatic lights on cyanobacteria and biofilms from Roman Catacombs. *Int. Biodeterior. Biodegrad.* **123**, 286–295 (2017).
123. Danin, A. Patterns of biogenic weathering as indicators of palaeoclimates in Israel. *Proc. R. Soc. Edinb. B* **89**, 243–253 (1986).
124. de Ferri, L., Lottici, P. P., Lorenzi, A., Montenero, A. & Salvioli-Mariani, E. Study of silica nanoparticles – polysiloxane hydrophobic treatments for stone-based monument protection. *J. Cult. Herit.* **12**, 356–363 (2011).
125. Son, S. et al. Organic−inorganic hybrid compounds containing polyhedral oligomeric silsesquioxane for conservation of stone heritage. *ACS Appl. Mater. Inter.* **1**, 393–401 (2009).
126. Erkal, A., D'Ayala, D. & Sequeira, L. Assessment of wind-driven rain impact, related surface erosion and surface strength reduction of historic building materials. *Build. Environ.* **57**, 336–348 (2012).
127. Traversetti, L., Bartoli, F. & Caneva, G. Wind-driven rain as a bioclimatic factor affecting the biological colonization at the archaeological site of Pompeii, Italy. *Int. Biodeterior. Biodegrad.* **134**, 31–38 (2018).
128. Ortega-Morales, O., Guezennec, J., Hernández-Duque, G., Gaylarde, C. C. & Gaylarde, P. M. Phototrophic biofilms on ancient Mayan buildings in Yucatan, Mexico. *Curr. Microbiol.* **40**, 81–85 (2000).
129. Li, Q., Zhang, B., He, Z. & Yang, X. Distribution and diversity of bacteria and fungi colonization in stone monuments analyzed by high-throughput sequencing. *PLoS ONE* **11**, e0163287 (2016).
130. Wu, F., Wang, W., Feng, H. & Gu, J.-D. Realization of biodeterioration to cultural heritage protection in China. *Int. Biodeterior. Biodegrad.* **117**, 128–130 (2017).
131. Wang, W. et al. Seasonal dynamics of airborne fungi in different caves of the Mogao Grottoes, Dunhuang, China. *Int. Biodeterior. Biodegrad.* **64**, 461–466 (2010).
132. Zamarreño, D. V., Inkpen, R. & May, E. Carbonate crystals precipitated by freshwater bacteria and their use as a limestone consolidant. *Appl. Environ. Microbiol.* **75**, 5981–5990 (2009).
133. Jroundi, F. et al. Protection and consolidation of stone heritage by self-inoculation with indigenous carbonatogenic bacterial communities. *Nat. Commun.* **8**, 279 (2017).
134. Ascaso, C. et al. *In situ* evaluation of the biodeteriorating action of microorganisms and the effects of biocides on carbonate rock of the Jeronimos Monastery (Lisbon). *Int. Biodeterior. Biodegrad.* **49**, 1–12 (2002).
135. Koestler, R. J., Parreira, E., Santoro, E. D. & Noble, P. Visual effects of selected biocides on easel painting materials. *Stud. Conserv.* **38**, 265–273 (1993).
136. Fidanza, M. R. & Caneva, G. Natural biocides for the conservation of stone cultural heritage: a review. *J. Cult. Herit.* **38**, 271–286 (2019).
137. Silva, M., Rosado, T., Teixeira, D., Candeias, A. & Caldeira, A. T. Production of green biocides for cultural heritage. Novel biotechnological solutions. *Int. J. Conserv. Sci.* **6**, 519–530 (2015).
138. Silva, M., Rosado, T., Teixeira, D., Candeias, A. & Caldeira, A. T. Green mitigation strategy for cultural heritage: bacterial potential for biocide production. *Environ. Sci. Pollut. Res.* **24**, 4871–4881 (2017).
139. Marin, E., Vaccaro, C. & Leis, M. Biotechnology applied to historic stoneworks conservation: testing the potential harmfulness of two biological biocides. *Int. J. Conserv. Sci.* **7**, 227–238 (2016).
140. Caneva, G., Fidanza, M. R., Tonon, C. & Favero-Longo, S. E. Biodeterioration patterns and their interpretation for potential applications to stone conservation: a hypothesis from allelopathic inhibitory effects of lichens on the Caestia Pyramid (Rome). *Sustainability* **12**, 1132 (2020).
141. Alfano, G. et al. The bioremoval of nitrate and sulfate alterations on artistic stonework: the case-study of Matera Cathedral after six years from the treatment. *Int. Biodeterior. Biodegrad.* **65**, 1004–1011 (2011).
142. Soffritti, I. et al. The potential use of microorganisms as restorative agents: an update. *Sustainability* **11**, 3853 (2019).
143. Scherer, G. W., Flatt, R. & Wheeler, G. Materials science research for the conservation of sculpture and monuments. *MRS Bull.* **26**, 44–50 (2001).
144. Gu, J.-D. Microbiological deterioration and degradation of synthetic polymeric materials: recent research advances. *Int. Biodeterior. Biodegrad.* **52**, 69–91 (2003).
145. Charola, A. E., McNamara, C. & Koestler, R. J. (eds) *Biocolonization of Stone: Control and Preventive Methods: Proceedings from the MCI Workshop Series* Smithsonian Contributions to Museum Conservation no. 2 (Smithsonian Institution Scholarly Press, 2011).
146. Yang, F. et al. Conservation of weathered historic sandstone with biomimetic apatite. *Chin. Sci. Bull.* **57**, 2171–2176 (2012).
147. Gherardi, F., Roveri, M., Goidanich, S. & Toniolo, L. Photocatalytic nanocomposites for the protection of European architectural heritage. *Materials* **11**, 65 (2018).
148. Sierra-Fernandez, A., Gomez-Villalba, L., Rabanal, M. & Fort, R. New nanomaterials for applications in conservation and restoration of stony materials: a review. *Mater. Construcc.* **67**, e107 (2017).
149. Grossi, C. M., Bonazza, A., Brimblecombe, P., Harris, I. & Sabbioni, C. Predicting twenty-first century recession of architectural limestone in European cities. *Environ. Geol.* **56**, 455–461 (2008).
150. de la Rosa, J. P. M., Warke, P. A. & Smith, B. J. Lichen-induced biomodification of calcareous surfaces: bioprotection versus biodeterioration. *Prog. Phys. Geog.* **37**, 325–351 (2013).
151. Gadd, G. M. & Dyer, T. D. Bioprotection of the built environment and cultural heritage. *Microb. Biotechnol.* **10**, 1152–1156 (2017).
152. Pinna, D. Biofilms and lichens on stone monuments: do they damage or protect? *Front. Microbiol.* **5**, 133 (2014).
153. Gadd, G. M. et al. Oxalate production by fungi: significance in geomycology, biodeterioration and bioremediation. *Fungal Biol. Rev.* **28**, 36–55 (2014).
154. Bosch-Roig, P. & Ranalli, G. The safety of biocleaning technologies for cultural heritage. *Front. Microbiol.* **5**, 155 (2014).
155. Zhang, G. et al. Biochemical reactions and mechanisms involved in the biodeterioration of stone world cultural heritage under the tropical climate conditions. *Int. Biodeterior. Biodegrad.* **143**, 104723 (2019).

156. Zhang, X., Ge, Q., Zhu, Z., Deng, Y. & Gu, J.-D. Microbiological community of the Royal Palace in Angkor Thom and Beng Mealea of Cambodia by Illumina sequencing based on 16S rRNA gene. *Int. Biodeterior. Biodegrad.* **134**, 127–135 (2018).

Acknowledgements

This research is supported in part by Hong Kong RGC GRF (grant no. 17302119). X.L. acknowledges support from the International Biodeterioration & Biodegradation Society.

Author contributions

J.-D.G. and X.L. conceived the framework and led the writing of the manuscript. J.-D.G. and X.L. analysed the data and made all figures. All authors wrote and revised the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this paper at https://doi.org/10.1038/s41893-020-00602-5.

Correspondence should be addressed to J.-D.G.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.