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# Biomineral deposits and coatings on stone monuments as biodeterioration fingerprints

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## HIGHLIGHTS

- A limited number of biominerals has been described on heritage stone surfaces.
- Biomineralisation is a complex issue that requires multidisciplinary studies.
- Knowledge on Heritage stone takes advantage of experiments and studies in nature.
- Studies in biomineralisation have opened new debates on stone conservation.
- This review provides a state-or-the-art of biomineralisation on Heritage stone.

## GRAPHICAL ABSTRACT


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## ABSTRACT

Biominerals deposition processes, also called biomineralisation, are intimately related to biodeterioration on stone surfaces. They include complex processes not always completely well understood. The study of biominerals implies the identification of organisms, their molecular mechanisms, and organism/rock/atmosphere interactions. Sampling restrictions of monument stones difficult the biominerals study and the in situ demonstrating of biodeterioration processes. Multidisciplinary works are required to understand the whole process. Thus, studies in heritage buildings have taken advantage of previous knowledge acquired thanks to laboratory experiments, investigations carried out on rock outcrops and within caves from some years ago. With the extrapolation of such knowledge to heritage buildings and the advances in laboratory techniques, there has been a huge increase of knowledge regarding biomineralisation and biodeterioration processes in stone monuments during the last 20 years. These advances have opened new debates about the implications on conservation interventions, and the organism's role in stone conservation and decay. This is a review of the existing studies of

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biominerals formation, biodeterioration on laboratory experiments, rocks, caves, and their application to building stones of monuments.

## 1. Introduction

Organisms can be directly or indirectly correlated with the production of biomineral deposits on stone surfaces. Biomineralisation can be defined as the process that led to the formation of hierarchically structured organic-inorganic materials resulting from activities of living organisms (Ehrlich, 2002). Although biocolonisation does not always imply biodeterioration (Sanmartín et al., 2021; Liu et al., 2022), biominerals are intimately linked to biodeterioration processes on stone surfaces (Beimforde, 2011). Biodeterioration was considered a sum of chemical and mechanical effects of living organisms on rocks (Ollier, 1969; Yatsu, 1988; Robinson and Williams, 1996). New molecular biology techniques in the early 21st century allowed scientists identifying microorganisms and their metabolic processes that form biominerals and can deteriorate stones (Aubry et al., 2012; Marques et al., 2016; Gadd, 2016; Gaylarde and Little, 2022). A variety of biodeterioration mechanisms have been described for organisms, from bacteria, algae, and fungi, to lichens, mosses and higher plants (Piñar et al., 2009; Sterflinger, 2010; Dakal and Cameotra, 2012; Sterflinger and Piñar, 2013; Trovão et al., 2019, 2021; Schröer et al., 2021). Their effect depends on a range of factors, including the bioreceptivity of rocks (Guillitte, 1995; Warscheid and Braams, 2000; Miller et al., 2012; Gambino et al., 2019; Sanmartín et al., 2019), the position in which these organisms grow (epilithic and endolithic) and their metabolic activities (Golubić et al., 1981; Mergelov et al., 2018; Pinheiro et al., 2019). Biodeterioration processes (Fig. 1) can feed back, since normally

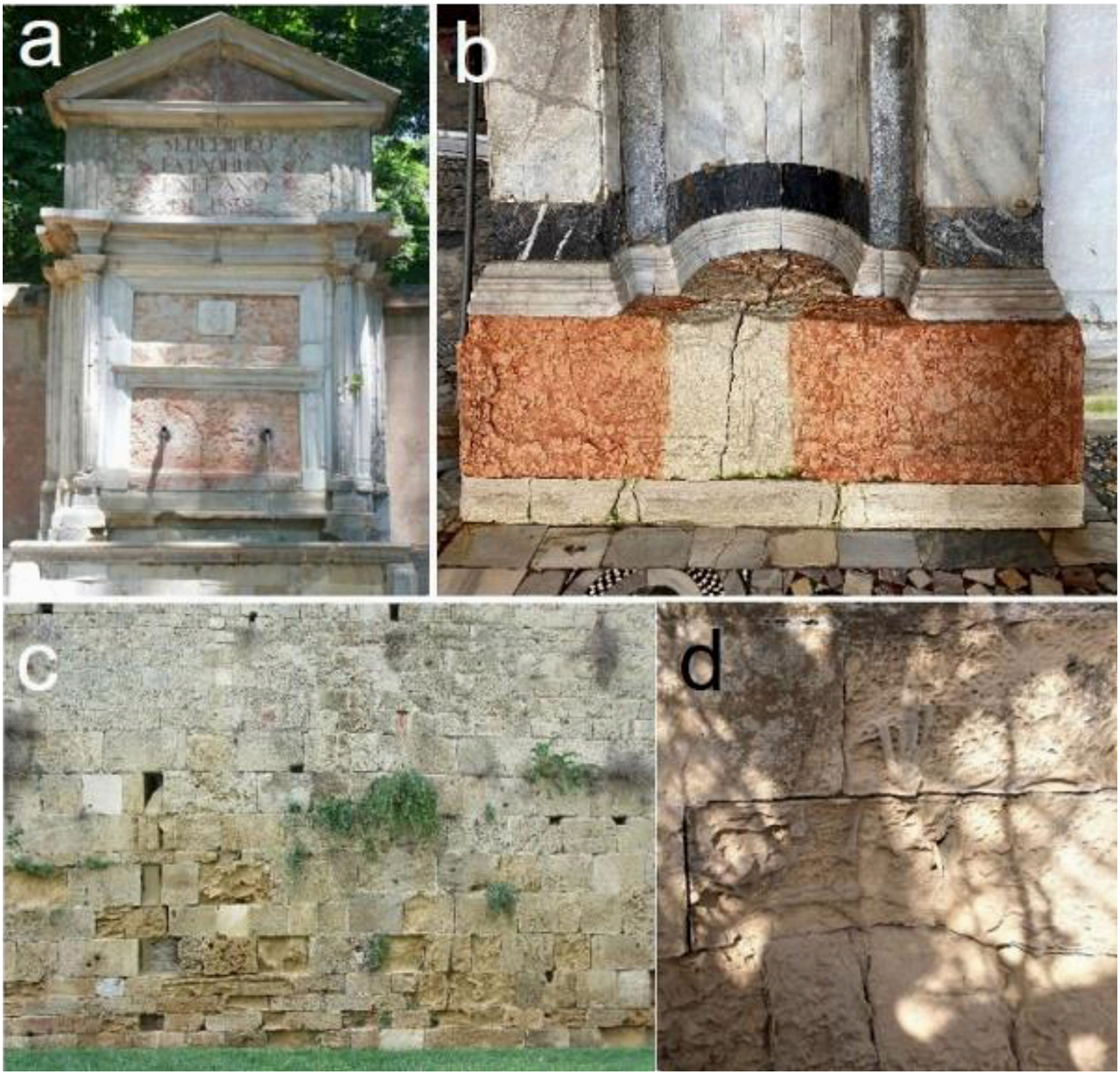


**Fig. 1.** Bioturbated limestone blocks that are colonized by microorganisms. a: Pilar de las Granadas fountain, in the forest of the Alhambra, Granada, Spain. b: Column base in Patriarchal Cathedral Basilica of Saint Mark, Venice, Italy. c: Wall with altered ashlars and with bioturbation, Pisa, Italy. d: Wall with altered ashlars and with bioturbation, Notre Dame Ravelin, Vatera, Malta.

the more deteriorated a heritage stone is, the more porous it is, and the more fissures it has, so it can absorb more water. As the stone's constituent minerals break down, nutrients become more accessible to colonising microorganisms (Webley et al., 1963). That is, the colonisation of building materials is a dynamic and complex process, due to the interrelationships among organisms and the inorganic substrate and the surrounding heterogeneous environment (Sanmartín et al., 2021).

Biominerals study is a hard task, in part, because of both the different mechanisms involved and the variable environments (rocky outcrops, marine environment, cave systems) where biomineral can be found. It is also difficult to demonstrate the role of organisms on biomineralisation and their formation mechanisms. Frequently, biominerals are scarce or appear forming salts, small deposits or coatings. On stone surfaces, biominerals forming coatings have been firstly studied in environments such as natural outcrops (Dorn, 1998) and cave deposits (Hill and Forti, 1997; Forti, 2001; Rossi et al., 2010). More than 60 different biominerals are known. Although some biominerals have been correlated with biogenic activities within caves and rock outcrops, additional factors play a role on the formation of some minerals on buildings such as air pollution, building materials and even conservation procedures that include the addition of chemical products (Sanjurjo-Sánchez and Alves, 2012a; Macholdt et al., 2017).

Some books and papers have reviewed biominerals and biomineralisation process. However, none of them refer to this process on monumental stone. Biominerals can appear in quarries and reused stones, so proving biomineralisation in the monument itself is not always easy. Sedimentary stones minerals could have originated at the time of deposit of the sediment, that is, before the lithification and formation of the stone sensu stricto (Anania et al., 2012; Belfiore et al., 2021; Occhipinti et al., 2021; Louz et al., 2022). There are numerous works about stones with fossil bioturbation structures (e.g., burrows), produced by the activity of endolithic organisms such as bivalves, sponges, polychaete annelids and sea urchins (Fig. 1) (Pappalardo et al., 2016; Vasanelli et al., 2017; Bonomo et al., 2020, 2021; Rabat et al., 2020). Textural changes connected with bioturbation may increase the permeability and porosity of heritage stones or may decrease the connected porosity after cementation (Ziebis et al., 1996). An increase of connected porosity and, consequently, of permeability occurs where burrow fills are more porous than the surrounding material (Gingras et al., 2004; Pemberton and Gingras, 2005; La Croix et al., 2012). These burrows will be more susceptible under such conditions, and permeability is related to the bioturbation connectivity (Tonkin et al., 2010; Gingras et al., 2012; Baniak et al., 2013). Lithophagous organisms pierce coastal abrasion platforms and cliffs (Trudgill et al., 1987; Pinn et al., 2005; Martínez de Lahidalga and Elorza, 2010) and, in addition, they can biodeteriorate breakwaters, piers and boardwalks built with heritage stones. In addition, it is difficult to directly attribute conclusively the genesis of minerals to biological processes on monumental stone, particularly because sampling is very restricted.

Biofilm concept is fundamental to understanding biodeterioration processes and biominerals production on stone surfaces (di Martino, 2016; Gaylarde et al., 2017a). Microorganisms, from phototrophic to heterotrophic, have been identified taking part of biofilms on heritage stones (Rossi et al., 2012; Nowicka-Krawczyk et al., 2014; Ogawa et al., 2017; Zhang et al., 2019a; Favero-Longo and Viles, 2020), and interacting with minerals in several mechanisms. Indeed, in recent years, the protective role of biofilms and biomineral coatings has been highlighted (Gabriele et al., 2023). It has been remarked that they can hold fragile rock surfaces affected by erosive features (Dorn, 2013; Pinna, 2014; Villa et al., 2016; Gadd and Dyer, 2017; Gulotta et al., 2018; Sanmartín et al., 2021), as Krumbein (1968) hypothesised many years ago. This proposal is based on macroscopic evidence of differential weathering rates between surfaces with and without organisms (Özvan et al., 2015; Mottershead and Lucas, 2000) and confirmed using more sophisticated methods (Favero-Longo and Viles, 2020), such as specified in Section 3. Accelerated deterioration of stones surfaces, when biofilms are removed, is a well-known process (de la Rosa et al., 2012; Gadd, 2017a). Organisms and biofilms can contribute to case-hardening and silica-rich layers by aiding cementation in dry and wet environments and several stone types (e.g. sandstone) (Dorn, 1998; Lee and Parsons, 1999; Viles and Goudie, 2004; Sanjurjo-Sánchez et al., 2012), while other coatings, such as calcium oxalate also produce a potential protective shield against abiotic decay (Souza-Egipsy et al., 2004).

The most basic biodeterioration mechanisms are the uptake of ions as nutrients used in vital functions or incorporated into cell walls (Mandl et al., 1953; Silverman, 1979; Eckhardt, 1980; Branysova et al., 2022), and the weathering of minerals caused by acidic or alkaline compounds produced by organisms (Berthelin, 1983; Blum and Lasaga, 1988; Steiger et al., 1993; Welch and Ullman, 1996). This is also referred as acidolysis (Warscheid and Braams, 2000), including the carbonic acid that results from the dissolution of $CO_2$ produced by microbial respiration (Schwartzman and Volk, 1989; Wogelius and Walter, 1991; Drever, 1994; Zhang et al., 2019b). Other processes such as cation exchange have been linked to the release of K, Fe, Mg and Al from some minerals (Hinsinger et al., 1992; Hinsinger and Jaillard, 1993; Ehrlich, 1996). It has also been observed that microorganisms involved in N and S cycles produce biodeterioration (Warscheid and Braams, 2000; Ding et al., 2020; Liu et al., 2020). This biodeterioration includes reactions involving chemolithotrophic organisms at interfaces between oxygenated and anoxic environments (such as biofilms) (Berthelin, 1983; Sand and Bock, 1991; Nordstrom and Southam, 1997) and nitrifying bacteria that oxidise ammonium to nitrate, that causes acidolysis and ion exchange on minerals (Mansch and Beck, 1998). Moreover, microorganisms that grow in biofilms can produce a wide range of organic molecules with multiple functions, such as pigments and phycobiliproteins to harvest light (Gao and Garcia-Pichel, 2011; Asencio and Hoffmann, 2013; Mora-Gómez et al., 2015; Pagels et al., 2019; Maoka, 2020), organic polymeric substances (EPS) (Fletcher and Floodgate, 1973; Chenu and Roberson, 1996; Fortin et al., 1997; Gorbushina and Broughton, 2009), lipids, proteins and low-molecular-weight organic acids, that are usually referred in biodeterioration experiments, and identified on stone surfaces (Negi and Sarethy, 2019; Favero-Longo and Viles, 2020; Salvadori and Municchia, 2016). Among such molecules, organic acids (excreted from glucose metabolism and other molecules) have been highlighted because of their active role in the production of biominerals (McMahon and Chapelle, 1991), such as oxalate crusts (Carter and Viles, 2003, 2005; Gorbushina, 2007; de la Rosa et al., 2013; Gadd, 2017a; Vidal Romaní et al., 2010, 2015; Sauro et al., 2014; Van Driessche et al., 2019). Indeed, gypsum, calcite and oxalate (in particular, calcium oxalate) are probably the most frequent biominerals on building stones, and they usually form coatings (Sand and Bock, 1991; Caneva et al., 1993; Saiz-Jimenez, 1999; Monte, 2003; Ortega-Morales et al., 2005; Zammit et al., 2011; Török et al., 2011). In any case, biological colonisation and any subsequent heritage-stone biodeterioration or bioprotection due to biominerals formation depends on the characteristics of the microorganisms and the stone type (de los Ríos and Ascaso, 2005; Scheerer et al., 2009; Lubelli et al., 2021). The type of biomineral that can be formed strongly depends on the petrophysical, petrographic and mineralogical properties, and on the microclimatic-environmental conditions (Wilhelm et al., 2021; Bone et al., 2022; Gaylarde and Little, 2022). For soluble rock-forming minerals, such as gypsum ($Ca_2SO_4{\cdot}2H_2O$) and calcite ($CaCO_3$), it is difficult to separate biodeterioration from abiotic chemical weathering, and thus biomineralisation from chemical mineralisation (Urzi and Garcia-Valles, 1999; Soulet et al., 2018; Angeli et al., 2019; Sun et al., 2019; Zheng and Qian, 2020). However, the biological activity in concert with chemical/physical processes, and the disposition of minerals could provide clues to the biotic or abiotic nature of biomineral coatings in such cases (Gallinaro and Zerboni, 2021). Identifying biominerals in Si-rich rocks can be easier because they are usually less soluble. For instance, weathering of Si-rich minerals has been observed directly caused by the carbonic anhydrase gene product in Aspergillus nidulans

(Sun and Lian, 2019) and indirectly caused by organic molecules (e.g. oxalic, aspartic, salicylic, acetic and citric acids) on silicate augite, biotite, epidote, hornblende, illite, kaolinite, mica, microcline, montmorillonite, muscovite, olivine, plagioclases and tourmaline among others (Kiang and Huang, 1972; Manley and Evans, 1986; Barman et al., 1992; Welch and Ullman, 1996; Wang et al., 2005; Cama and Ganor, 2006; Maurya et al., 2014; Meena et al., 2015).

The wide range of mineral-solubilising processes produced by microorganisms and their important role in biodeterioration and production of biominerals has aroused great interest in recent years (Gadd, 2017b; Lazo et al., 2017; Wei et al., 2018; El-Baghdady et al., 2019; Samuels et al., 2019; Cozzolino et al., 2022) but any review has been focused on such process in the built Heritage. This review presents the organisms role in biominerals formation, the most frequent biominerals found in built heritage, methods used to identify them, and their use in bioremediation.

## 2. Biominerals on stone surfaces

Biominerals are in almost all possible environments (Vereshchagin et al., 2023), and probably from the beginning of life on Earth, because they are common in all kinds of organisms (e.g., shells, bones). Calcium carbonates and phosphates are very abundant (Crichton, 2019); silicates, iron hydroxides, manganese oxides, carbonates, phosphates, sulphates, and sulfide minerals are the most frequent (Konhauser, 2006), although it is sometimes difficult to discern between a biological or chemical origin. The study of biomineralisation processes is difficult per se as it encompasses the precursor's substances and the mineral crystallisation. In opposite to classical nucleation theory (Volmer, 1939; Nancollas, 1982), some biominerals begin from a transient (or definitive) amorphous phase, in biomimetic and biological systems (Nudelman and Sommerdijk, 2012; De Yoreo et al., 2015). Considering the biological environment of biomineralisation this can be intra or extracellular (Subburaman et al., 2006). From a biogeochemical point of view, biomineralisation can also occur by two different methods, "biologically induced biomineralisation" or BIM, and "biologically controlled biomineralisation" or BCM (Lowenstan and Weiner, 1989; Mann, 1995; Konhauser, 2006; Cameotra and Dakal, 2012). BIM is produced in cases where the cell has no control over the process. Thus, precipitates are by-products of the interaction between the metabolism and the surrounding environment. Such minerals are usually amorphous to poorly crystalline (e.g., opal-A). At the level of our interest, on stone surfaces, extracellular BIM processes are the most common (Fig. 2a and b).

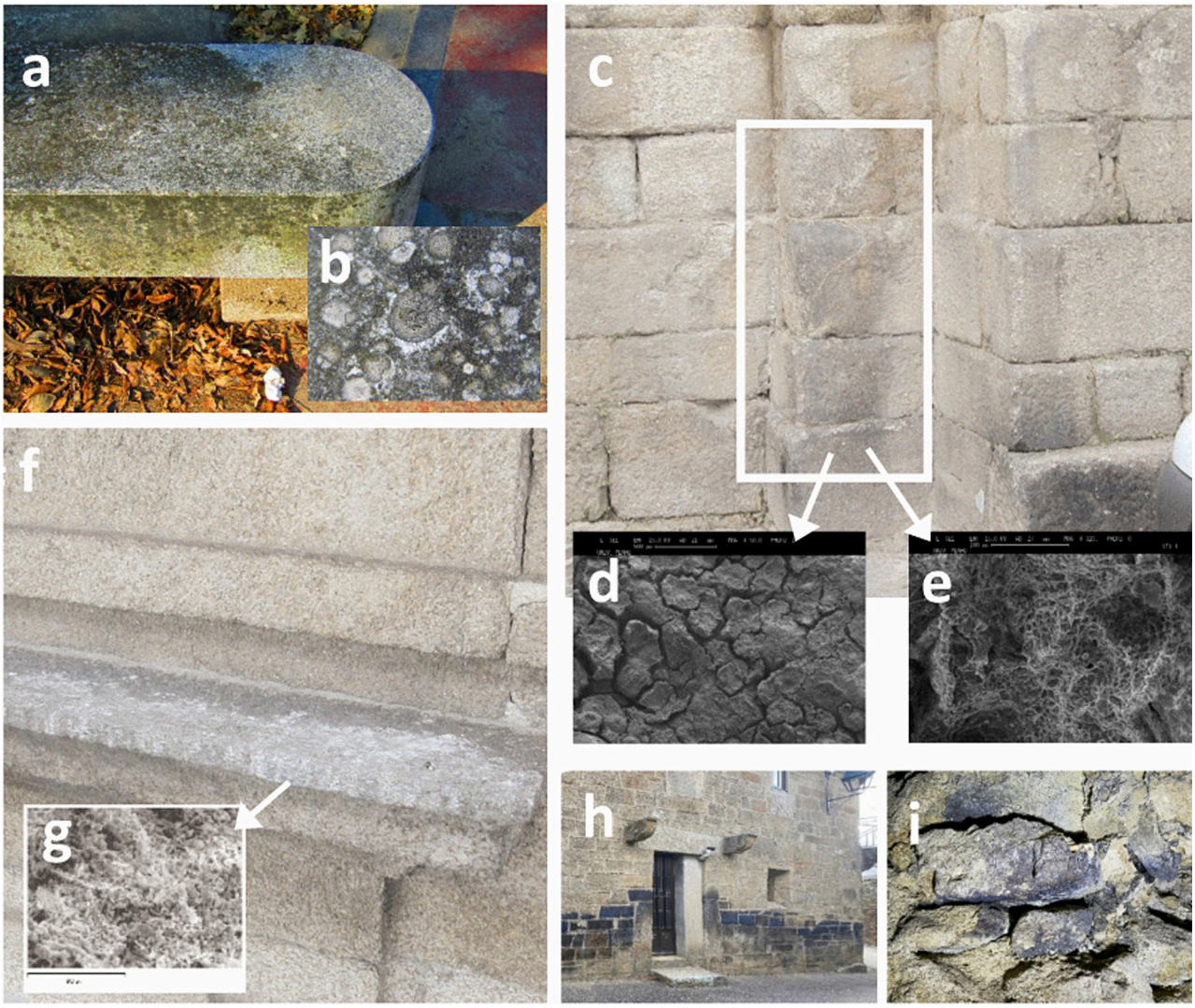


**Fig. 2.** Examples of potential biominerals on stone surfaces: (a) granite surface with lichen colonisation and detail (b) of the mineral precipitates spacially associated to biological entities; (c) calcium carbonate deposit formint a grey coating and (d) surface detail on SEM; (e) phosphate-rich coating due to mineralisation of bird droppings in a cornice of a granite building; (f-g) different aspects of a black coating formed by Mn-rich compounds.

Cave environments have been especially interesting for the early studies of the interaction between microorganisms and biominerals: caves are stable environments with scarce or not daylight, making it easier, in theory, to correlate the formation of minerals with the activity of some organisms. Cave environment is very stable excluding some physical and chemical weathering processes caused by environmental changes. Photosynthetic organisms' growth is very scarce, or they are absent due to the dark conditions. This should be helpful to stablish a correlation between non-photosystetic organisms and biodeterioration processes in dark areas. Cave biominerals have provided clear evidence of the importance of biogeochemical processes for the genesis of importance biominerals such as amorphous silica and aluminium, calcium carbonate, gypsum, etc. (Vidal Romaní et al., 2010, 2015; Miller et al., 2018; Kulkarni et al., 2022). Hill and Forti (1997) compiled some biominerals formed in caves, highlighting Forti (2001) the possible role of organisms in the formation of some of them.

Si-, Al-, Fe- and Mn-rich minerals and gypsum have been described as common biominerals in granite, volcanic, quartzite and sandstone caves (Spilde et al., 2005; Vidal Romaní et al., 2010, 2015; Sauro et al., 2011, 2014, 2018; Miller et al., 2012, 2017, 2018; Dhami et al., 2018; Filippi et al., 2020; Sanjurjo-Sánchez et al., 2021; Kulkarni et al., 2022) and deposition rates for some of them have been provided (Sanjurjo-Sánchez and Vidal Romaní, 2011). In limestone caves, calcite has also been included as a biomineral (e.g. moonmilk deposits) (Portillo and Gonzalez, 2011), although it is well known that most calcite deposits are formed by inorganic dissolution and precipitation (Zúñiga-Barra et al., 2022).

Biominerals also appear forming rock coatings, above all on natural outcrops. Si-, Mn- and Fe- or oxalate-rich coatings among others have been related to biodeterioration being recognised as biominerals formed on rock surfaces (Dorn, 1998, 2013; Lee and Parsons, 1999; Gadd et al., 2014; Marques et al., 2016). Such studies have been very helpful to understand the role of organisms on Heritage stone surfaces, where most of them have been found.

### 2.1. Calcium oxalates

Ca-rich minerals in the form of oxalates are very commonly reported on heritage stones (Rampazzi, 2019). They are common secondary minerals formed by microbial mobilisation, and sometimes biological precipitation (Gorbushina, 2007). Brewer and Fierer (2018) showed that a metabolic pathway that results in oxalic acid by products (responsible of calcium oxalates formation) was significantly enriched in bacterial communities (glyoxylate and dicarboxylate metabolism) of tombstones in three continents (Europe, North America and South America). Although oxalates are more frequently reported on Ca-rich stone surfaces (Dolomite and calcite, Singh and Yadav, 2023), they have also been reported on low-calcium substrates such as granites in built environments (Prieto et al., 2000; Pereira de Oliveira et al., 2011) as well as in laboratory experiments (de la Torre et al., 1993; Rusakov et al., 2016). It has been found that in the same medium conditions, different species, such as *Penicillium chrysogenum* and *P. chrysogenum* with *Bacillus subtilis*, could lead to either oxalate or carbonate crystallisation (Sazanova et al., 2023).

The presence of calcium oxalates has been determined with SEM imaging as biomineralisation of lichen and fungi (Del Monte and Sabbioni, 1984; Monte, 2003; Carter and Viles, 2003, 2005; Gorbushina, 2007; de la Rosa et al., 2013; Marques et al., 2016; Gadd, 2017b; Gallinaro and Zerboni, 2021; Kang et al., 2022).

### 2.2. Carbonates

In general, the biological activity and the disposition of minerals is crucial to recognise the possible biotic nature of calcite biomineral coatings (Gallinaro and Zerboni, 2021). Calcite bioprecipitation has been observed in several environments such as bones, teeth and mummies, and even in ice due to bacteria and fungi (Arning and Wilson, 2020; Arriola et al., 2020). It has been linked, among other minerals (gypsum and magnesite), to cyanobacteria (*Synechococcus* sp.) in alkaline lake water (Thompson and Ferris, 1990). Ca-rich coatings were commonly reported on desert pavement cobbles and on rock-art sites as a product of microbial activity (Konhauser et al., 1994; Dorn, 1998; Zerboni, 2008). Several possible mechanisms of biotederioration and formation of calcite biominerals have been proposed in both, natural environments and building stone. Indeed, calcium carbonate (mainly calcite) neoformation coatings are quite common on stone in building environments (Sanjurjo-Sánchez and Alves, 2012b) (Fig. 2c and d).

It is sometimes difficult to assess if calcite on monuments has a chemical or biochemical origin, because it is a common biomineral. In a study of patinas on diverse stone substrates (marble, calcarenite, basalt, dolostone and granite). Urzi and Garcia-Valles (1999) found calcite (and calcium-phosphate) crystallisation attributed to biological activity (undetermined *Micrococcus*-like stains). These authors tested several microorganisms extracted from stones affected by biocolonisation and reported that most of the bacterial strains promoted precipitation of calcium carbonate while the other organism types did not show any relevant evidence of biomineralisation. In the biological reaction catalysed by the enzyme carbonic anhydrase (present in phototrophs, several bacteria and some fungi) carbon dioxide was also dissolved in water, increasing the dissolution of calcite (Sun et al., 2019; Angeli et al., 2019). This process can occur through upregulation of the carbonic anhydrase gene with calcite (Xiao et al., 2014), although carbonic anhydrase was also associated with the reverse reaction, formation of calcium carbonate (Lü et al., 2019; Zheng and Qian, 2020). Moreover, it is known that bacteria in sulphur-reducing and organic-matter-oxidisying communities can dissolve silicate bedrocks, and autotrophic, heterotrophic, and phototrophic organisms promote calcite precipitation (Frisia et al., 2017). Other mechanisms have been suggested by Diaz et al. (2014), that assessed functional gene diversity of oolitic sands from the Great Bahama Bank (Bahama Archipelago) and suggested that calcium carbonate precipitation in oolitic environments was probably biologically influenced by microorganisms with diverse physiologies including oxygenic and anoxygenic photoautotrophs, oxygenic and anoxygenic heterotrophs, denitrification, sulphate reduction and ammonification (see Table 1). It would thus be interesting to consider that besides rock coatings, a bacterial community (*Firmicutes* and *Proteobacteria* with notable percentages of *Actinobacteria*, *Cyanobacteria* and *Acidobacteri*a) on Yabelo (Ethiopia) might also affect the formation of these kind of oolitic balls (Wu, 2022), being the mechanisms probably very similar.

### 2.3. Gypsum

The occurrence of gypsum biominerals has been proven on stones that do not contain S and/or minor Ca, such as granitoids, sandstones and quartzite. Gypsum biominerals have been found in caves (Vidal Romaní et al., 2010, 2015; Miller et al., 2018; Dhami et al., 2018) and other environments (Larson and Larson and Dorn, 2012; Marnocha and Dixon, 2014). On Ca-rich rocks, gypsum is a common product of calcite decay due to sulphation of dissolved calcium carbonate in air conditions with high concentrations of S, such as urban and coastal areas (Camuffo, 1986). On other stones, they have also been linked to the same processes, being the air the source of S; and some stones and mortars, the source of Ca (Mckinley et al., 2001; Sanjurjo-Sánchez et al., 2009, 2011). However, some studies on stones with very low contents of Ca, and in the absence of S, have found gypsum formation due to biogenic processes. Gaylarde et al. (2017b) analysed the role of biofilms in granites biodeterioration from two church facades in Rio de Janeiro (Brazil). They associated endolithic Cyanobacteria (*Chroococcidiopsis* sp. and *Chroococcidiopsis* sp.) with gypsum deposits. Ortega-Morales et al. (2019) also found newly formed gypsum mixed with cyanobacterial filaments (*Gloeocapsa* sp.) on granite monuments of Rio de Janeiro. They

**Table 1**
Biominerals found on monumental Stone surfaces, with identified organisms, and associated biodeterioration effects and references. Only studied on monumental stone are included in the table.

| Biomineral | Substrate | Organisms | Biodeterioration | Reference |
|---|---|---|---|---|
| Calcium oxalates | Granite | Lichen (*Lecidea fuscoatra*, *Porpidia cinereoatra*, and *P. macrocarpa*) and Fungi | | Prieto et al., 2000, Pereira de Oliveira et al., 2011 |
| | Limestone | Proteobacteria Cyanobacteria Bacteroidetes Actinobacteria | | Ding et al., 2021; Pinna, 2021; Skipper et al., 2022 |
| | Dolomite | Acidobacteria | | Brewer and Fierer, 2018 |
| | Granites | *Penicillium chrysogenum*, *P. chrysogenum*, *Bacillus subtilis* | Biocorrosion | Sazanova et al., 2023 |
| Carbonates | Granitoid | Undefined | | Gallinaro and Zerboni, 2021 |
| | Limestone | Micrococcus-like stains | Ca dissolution | Urzi and Garcia-Valles, 1999 |
| | Limestone | Carbonic anhydrase | Dissolution and precipitation | Sun et al., 2019; Angeli et al., 2019 |
| | Silicate rocks | Bacteria in sulphur-reducing and organic-matter-oxidizying communities | | Diaz et al., 2014 |
| | Granite | *Firmicutes* and Proteobacteria. Actinobacteria, Cyanobacteria. Acidobacteria | Ca dissolution | Wu (2022) |
| Gypsum | Granite | Endolithic Cyanobacteria (Chroococcidiopsis sp., *Chroococcidiopsis* sp.) | Hydrolysis? | Gaylarde et al. (2017b) |
| | Granite | Cyanobacterial filaments (*Gloeocapsa* sp.) | Hydrolysis? | Ortega-Morales et al., 2019 |
| | Granite | Lichen hyphae | Leaching? | Schiavon, 2002 |
| | Granite | Black yeast and fungi | | Blázquez et al., 1997 |
| | Limestone | Undetermined | | García-Vallès et al., 1997 |
| | Sandstone | *Fusarium solani* | | Xu et al., 2018 |
| | Sandstone | Guano | Salt weathering | Honoso et al., 2006 |
| Phosphates | Sandstone | Guano | Salt weathering | Honoso et al., 2006 |
| | Mortar | *Actinobacter* sp., *Bacillus* sp | Hardeninig | Singh et al., 2020a, 2020b |
| | Granite | P-rich organic compounds? | Coating | Sanmartín et al., 2020 |
| | Limestone | Micrococcus-like stains | | Urzi and Garcia-Valles, 1999 |
| Si-rich | Sandstone | Undetermined organisms | Dissolution | Green et al., 2017 |
| Al-rich | Granite | Undetermined organisms? | | Sanjurjo-Sánchez et al., 2012 |
| Fe- and Mn-rich | Granite | Undetermined | | Wu, 2022 |
| | Granite | Undibacterium sp. | Acid leaching | Freire-Lista et al., 2022 |
| | Sandstone | *Acidithiobacillus ferrooxidans* | | Potysz et al., 2020; |
| | Sandstone | *Acidithiobacillus thiooxidans* | | Adetutu et al. (2012) |
| | Granite | *Staphylococcus* sp. | Leaching | Gaylarde et al. (2017a) |
| | Granite | Actinobacteria | | Gaylarde et al. (2018) |
| | Sandstone | *Rhodotorula mucilaginosa* and undetermined org. | | Gázquez et al., 2017; Patil et al., 2021 |
| | Paintings on sandstone | *Bacillus* strains | | Gonzalez et al. (1999) |
| | Sandstone | *Gloeocapsa* sp. | | Barrionuevo et al. (2016) |

suggest the solubilisation of cations from granite minerals with redeposition of salts around cells, a process that results in the formation of gypsum. Schiavon (2002) reported authigenic gypsum spatially associated with undetermined lichen hyphae in granite. Gypsum and oxalate were found associated with one of the lichens (*Lecidea fuscoatra*, *Porpidia cinereoatra*, and *P. macrocarpa*) studied by Prieto et al. (2000) on granite surfaces. Blázquez et al. (1997) attributed to microbes the formation of micro-stromatolitic patinas on granite ashlars in the Mediterranean area, highlighting the role of undetermined black yeast and black fungi. Also, García-Vallès et al. (1997) suggested a possible, but uncertain biogenic origin, of gypsum on limestones in surfaces of Tarragona Cathedral (Spain). However, in a later work, the same authors attributed gypsum occurrences on several stone monuments (including limestone, granite, sandstone and marble) to chemical processes (García-Vallès et al., 1998). It has been observed that filamentous fungus, *Fusarium solani* on sandstone ashlars of Angkor temples produces sulphuric acid autotrophically (Xu et al., 2018) that dissolves carbonates from Ca-rich stones with the formation of gypsum by the combination of sulphuric acid and Ca (Soulet et al., 2018). Thus, although gypsum has been generally linked to biological activities, it is still necessary to get more light on the organisms responsible for such processes and on the molecular mechanisms involved.

### 2.4. Phosphates

Phosphate minerals are usually related to biogenic activity although other abiotic mechanisms have been considered (Dorn, 1998). Indeed, one of the main sources of phosphate minerals on stone surfaces is the accumulation of bird (Fig. 2e) or bat guano (Fusey, 1991; Uchida et al., 1999), being Ca-phosphate and S-phosphate especially frequent, as observed in Angkor monuments of Cambodia (Honoso et al., 2006; Zhang et al., 2018). Fishman et al. (2018) reported that the Ca-phosphate-based apatite is created via biomineralisation by many bacteria including *Pseudomonas* spp., *Streptococcus* sp. and *Corynebacterium* sp. Singh et al. (2020a, 2020b) studied the formation of Ca-phosphate surface crust on mortar surfaces in the Indian Janjira Sea Fort (16th century). The 16s rRNA sequencing identified *Actinobacter* sp. and *Bacillus* sp. as the main phosphate-solubilising bacteria. The bacterial action caused the hardening of the mortar top surface that survived the strong oceanic current. The surface crust formed due to bacterial biomineralisation saved the historic lime binder of the Janjira Sea Fort against erosion. That is a clear case of biomineral coatings that protect the underlying stone.

On Si-rich stone monuments, phosphates have been correlated with other possible origins, such as chemical weathering of some minerals (e.g., apatite and hydroxyapatite), deposition of atmospheric particles, the residues left by soaps used in cleaning or consolidation treatments (e.g. diammonium phosphate causing brushite, DAP), and the mineralisation of organic traditional preservatives containing phosphorus compounds such as milk derivatives and casein salts used in preservation (Sanmartín et al., 2020). Iron-phosphate coatings precipitated on stones due to bacterial activity have been reported (Konhauser et al., 1994; Dorn, 1998) but have not been reported on monumental stone surfaces. Ca-phosphate and apatite deposits caused by undetermined *Micrococcus*-like stains have also been observed by Urzi and Garcia-Valles (1999) on several stone substrates (see Section 3.2). Some phosphates have also

been linked to the formation of calcium oxalate and gypsum biomineral coatings on stones (see Sections 3.1 and 3.3) due the activity of lichen and fungi.

### 2.5. Si-rich biominerals

Si-rich minerals have been mostly observed as coatings and related to the effect of EPS and organic molecules, such as, organic acids, being poorly amorphous Si and O minerals (opal-A) the most common (Dorn, 1998; Lee and Parsons, 1999; Vidal Romaní et al., 2010, 2015; Sanjurjo-Sánchez et al., 2012; Green et al., 2017). While Si-rich biominerals seem to be frequent on silicate stone surfaces in nature, few studies have reported their presence on heritage-stone surfaces, either as isolated minor occurrences or as coatings. Sanjurjo-Sánchez et al. (2012) concluded that they are not present on granite monuments of areas where they usually appear on nearby granite outcrops. Although the causes of such difference are not clear, they could be correlated with the low growth of biofilms on urban heritage buildings or the slow rate of formation of such biominerals, as it has been assessed within caves (Sanjurjo-Sánchez and Vidal Romaní, 2011). On sandstones, Si-rich coatings have been observed on rock art (Green et al., 2017) being probably linked to biogenic activities although the possible organisms involved have not been identified. Dissolution by organic acids has also been observed in basalts (Neaman et al., 2005), and Si deposits have been found in volcanic caves (Kulkarni et al., 2022). It has also been demonstrated that the fruticose lichen *Stereocaulon vesuvianum* sp. produces amorphous Si layers at its interface with basaltic rocks by organic-acid-induced mineral dissolution (Tamura et al., 2017). However, some other works have highlighted the role of Si-rich coatings (and related biofilms) protecting rock surfaces against erosion (Welch and Vandevivere, 1994; Dorn, 1998, 2013; Sanjurjo-Sánchez et al., 2012; Gao et al., 2019). Thus, it is not clear that Si-rich coatings are indicative of biodeterioration on monumental stone or they can be inherited from quarry or natural surfaces. Si-rich minerals can contain other minor elements, such as Al and Fe, probably due to detrital minerals mixed with the Si-rich matrix that usually forms a deposit or a coating.

### 2.6. Al-rich biominerals

Al-rich biominerals are much less common than Si-rich counterparts on stone surfaces, and most of them are composed of aluminium-silicate minerals. Al-rich biominerals have been studied in a few caves around the World, although they are commonly observed in granite caves (Filippi et al., 2020; Sanjurjo-Sánchez et al., 2021). Al is linked to organic matter (forming an Al- organic rich deposit) with an apparent microbial origin as inferred from the study of the organic matter (Sanjurjo-Sánchez et al., 2021). Al-rich biominerals have been scarcely observed on granite monuments (Sanjurjo-Sánchez et al., 2012) and they may have three possible origins: chemical leaching of opal from mortars, protective man-made coatings or any biological processes that involved microbes (Magee et al., 1988; Sulovsky et al., 1996; Dorn, 1998; Vidal Romaní et al., 2010). Biodeterioration of aluminium oxides has been studied on aluminium alloy surfaces, and the biodeterioration effect of some common organisms, such as *Hormoconis resinae* sp. and spore forming bacilli (Smith, 1991; McNamara et al., 2003; Vejar et al., 2017), mediated by organic acids has been demonstrated (Nelson et al., 2017). In a similar process, Al-rich deposits in caves could be correlated with the activity of organic acids produced by microorganisms, although this point has not been particularly confirmed (Sanjurjo-Sánchez et al., 2021) and further studies on monumental stone are still necessary.

### 2.7. Iron and manganese compounds

It is widely accepted that the activity of microorganisms causes the formation of rock coatings that contain Fe and Mn biominerals on natural outcrops although specific studies that identify the involved organisms on monumental stone are scarce (Dorn, 1998; Lee and Parsons, 1999; Dorn, 2009; Villa et al., 2016; Pinna, 2021). Indeed, Fe- and Mn-rich coatings (also typically referred to as rock varnish and dark patinas) are probably one the most recurrent examples of biomineral deposits (Fig. 5f and 5g). The formation of these coatings has been observed in different World environments, but especially under arid conditions (Dorn, 1998). It has also been suggested that iron and manganese oxides on stone surfaces are likely the result of intense biomineralisation that occurred in presence of clays under wet environmental conditions (Dorn, 1998, 2009). However, they appear in dry environments due to Quaternary climate changes (Zerboni, 2008).

Several studies have suggested the active role of microorganisms including bacteria, algae, fungi, and endolithic and epilithic lichens in Fe and Mn fixation on both limestone and siliceous bedrocks (Scheffer et al., 1963; Krumbein, 1968, 1971; Ascaso et al., 1976; Potter and Rossman, 1979; Friedmann, 1982; Dorn, 1998).

Ferromagnesian mineralisations on stone surfaces have been related to the activity of undetermined filamentous bacterial communities, although the role of organic molecules produced by organisms is not always clear (Northup et al., 2003; Miller et al., 2012). According to Garg et al. (1995) and Gadd (2007), the mechanisms of fungi-induced biochemical deterioration involves the excretion of metal-complexing compounds (e.g., phenols, acids or Fe-binding siderophores), the reduction of the pH and the production of enzymes like ferric reductases (Gerrits et al., 2020).

Confocal microscopy images have revealed the presence of a metabolically active microbial community on rock surfaces with Fe and Mn coatings, being the genus *Undibacterium* sp. correlated with the Fe biomineralisation (Wu, 2022), and suggesting this biomineralisastion was due to chemotrophs activity. This will agree with some observations such as the sulphide released as a gas ($H_2S$) and converted to elemental sulphur by sulphur-oxidising bacteria or combined with Fe to produce pyrite (Hammes and Verstraete, 2002). Also, Fe-reducing bacteria, such as *Shewanella* sp. (Bose et al., 2009), can use ferric oxides in rocks and clays as final electron acceptor in anaerobic respiration (Colombo et al., 2014). *Geoalkalibacter ferrihydriticus* sp. can oxidise $Fe^{2+}$, using carbonate as an electron acceptor. This reaction can occur in the absence of oxygen, causing biodeterioration of silicate minerals such as biotite and glauconite (Zavarzina et al., 2016). The proteobacteria *Acidithiobacillus ferrooxidans* sp. lives in stones containing pyrite, metabolising iron and sulphur (Freire-Lista et al., 2022) and producing sulphuric acid, while *Acidithiobacillus thiooxidans* sp. consumes sulphur and produces sulphuric acid (Potysz et al., 2020). Moreover, lithotrophic $Fe^{2+}$-oxidising microorganisms in nitrate-reducing enrichment cultures (Straub et al., 1996) can grow via oxidation of structural $Fe^{2+}$ in biotite, a $Fe^{2+}$-rich trioctahedral mica found in granitic rocks. Oxidation of silt/clay-sized biotite particles was detected by a decrease in extractable $Fe^{2+}$ content and simultaneous nitrate reduction.

Biodeterioration and formation of Fe-rich biominerals can just consist of the conversion of $Fe^{2+}$ to $Fe^{3+}$, with a concomitant increase in volume and production of intra-crystal cracking (Bonneville et al., 2016). Oxidation/reduction reactions associated with microbial activity can also destabilise the crystalline structure of minerals (Uroz et al., 2009). Although Adetutu et al. (2012) considered *Staphylococcus* sp. an indicator of human interaction in the open shelters, the bacterium can also precipitate carbonates and can be involved in the reduction of metals such as $Fe^{3+}$ (Marnocha and Dixon, 2014). *Acinetobacter* and *Arthrobacter* sp. are both involved in $Cr^{6+}$ and $Mn^{4+}$ reduction. At the genus level, many metal-resistant bacteria have been observed, including the species of *Corynebacterium*, *Arcobacter*, *Gemella* and *Methylobacterium* (Marnocha and Dixon, 2014). However, oxidising/reducing mechanisms are not the only ones able to cause leaching of Mn and Fe, resulting in the formation of Fe- and Mn-rich biominerals. Olsson-Francis (2010) associated the up-regulation of porins and transporters in *Cupriavidus metallidurans*, with passive and active iron uptake systems, involved in weathering of minerals by changes in chemical

equilibrium at the microbe-mineral interface, reducing the saturation state of iron.

Gao et al. (2019) investigated the effects of EPS on extracellular electron transfer (EET), which plays a fundamental role in microbial reduction/oxidation of minerals during microbial reduction of hematite by the iron-reducing strain *Shewanella oneidensis* (MR-1). Bonneville et al. (2016) investigated the splitting of minerals through water ad- and desorption by EPS during penetration of hyphae into minerals. Guglielmin et al. (2011) also established a correlation between lichen EPS and biomineralisation of iron oxides. However, both Gerrits et al. (2020) and Pokharel et al. (2019) showed that EPS produced by *Knufia petricola* fungus, prevents the oxidation and precipitation of abiotically released Fe at olivine surfaces and thus allows faster dissolution than in fungus-free solution. That means that EPS can also exert a protective role against mineral leaching and formation of biominerals.

It has been demonstrated that other molecules produced by microorganisms, like organic acids, such as citric, release Fe from iron-bearing minerals by the cyanobacterium, *Synechococcus elongatus* (Mustoe, 2018). Picard et al. (2021) showed that some molecules (e.g. malleobactin X) produced by *Collimonas pratensis* PMB3(1) work as siderophores, which causes dissolution of hematites. Li et al. (2019) observed the release of Fe and Ni from lizardite (serpentine group) by the fungus *Talaromyces flavus* caused by siderophores and oxalic acid, respectively. Gluconic acid, produced by *Pseudomonas azotoformans* F77, also increased iron and aluminium release from biotites (Wang et al., 2020). On granite historical buildings of Rio de Janeiro (Brazil), Gaylarde et al. (2017a) identified *Actinobacteria* that produce organic acids that caused the solubilisation of Fe minerals. In a later study, Gaylarde et al. (2018) detected *Rhodotorula mucilaginosa*, which produces rhodotorulic acid. It is an iron-chelating acid involved in the release of Fe, Cr, or other cations from minerals, being involved in the deposition of Fe-rich biominerals. So, such organisms produce Fe-rich biominerals on granite.

Other iron biomineral coatings (e.g. hematite) have also been observed on surfaces of rock art in silicate rocks such as sandstones (Gázquez et al., 2017; Patil et al., 2021). Krumbein (1968, 1971) observed such coatings due to dissolution-created surface pores that were occupied by Fe and Mn biominerals on silicified limestones from Negev Desert (Israel). Gleeson et al. (2018) also attributed the formation of Fe- and Mn-rich varnish to undetermined biological activity. Furthermore, Gonzalez et al. (1999) isolated a number of iron reducing *Bacillus* strains from rock paintings based on the red iron oxides in a sandstone shelter in Spain. Northup et al. (2010) studied in detail Mn and Fe coatings on a rhyolite in North America, demonstrating the active role of several microorganisms dominated by Cyanobacteria and Actinobacteria (*Chloroflexi* sp. and *Ktedobacteria* sp.) in their formation. Barrionuevo et al. (2016) studied the Fe- and Mn-rich crusts at the surface of sandstone ashlars of the Jesuit Missions of the Guaranis: San Ignacio Mini, Santa Ana, Nuestra Señora de Loreto and Santa Maria Mayor (Argentina), designated by UNESCO as World Heritage Sites. Iron films and sulphate crusts have also been found within a couple of meters of one another, a well-delineated phenomenon in Yosemite Valley (USA) and in Kärkevagge, Swedish Lapland (Larson and Larson and Dorn, 2012). Since the different coatings are presumably exposed to the same physical and chemical macro environment, a possible biological origin of the coloured coatings is considered.

## 3. Study methods of biominerals

### 3.1. Characterisation of organic molecules

A useful method for the characterisation of organic molecules is Raman spectroscopy (see Table 2), which is a technique that can be performed using non-destructive devices (Casadio et al., 2016; Syvilay et al., 2018). However, for a detailed characterisation both gas chromatography (GC) and mass spectrometry (MS) methods are more

**Table 2**
Published works about methods used for the study of biominerals and biomineralisation processes, methods used and target of the study.

| Reference | Method | Target |
|---|---|---|
| Adamiak et al., 2017 | HPLC/HRMS and CARS | Halophile metabolome, to visualice microbial cells |
| Bargar et al., 2009 | EXAFS, XANES, a subset of X-ray Absorption Spectroscopy (XAS) | Bulk coatings |
| Bartoli et al., 2014 | OM, methylene blue and PAS staining methods, SEM | Bacteria, fungi, algae, lichen, moss |
| Begonha, 2009 | SEM-EDS | Diatoms and biominerals |
| Benzerara et al., 2011 | HR-TEM | Calcium carbonate biominerals in corals |
| Cappitelli et al., 2009 | Flow cytometry: fluorescence produced by photosynthetic pigments | Pigment identification |
| Cappitelli et al., 2012 | OM, SEM-EDX, DNA sequencing, DGGE, MS and UV–visible spectrometry | Cyanobacteria and pigments |
| de Felice et al., 2010 | target non-specific metagenomics with NGS | Bacteria, fungi |
| de los Ríos et al., 2009 | PCR | Fungi |
| de los Ríos et al., 2009 | TEM | Fungi |
| de la Rosa-Tilapa et al., 2022 | OM, FESEM, SEM-EDS and DIC | Biominerals in cactus (calcium oxalate) |
| Dicko et al., 2022 | Raman spectroscopy | Carbonate biominerals in mollusks |
| Ding et al., 2020 | Absorption analysis | Pigments from EPS in rock samples |
| Edwards et al., 2005 | Raman spectroscopy | Pigments in bacteria |
| Edwards et al., 2007 | Raman spectroscopy for assessing pigments | Pigments in algae, lichens, bacteria |
| Ettenauer et al., 2011 | Target non-specific metagenomics with NGS | Bacteria |
| Farooq et al., 2015 | HPLC/HRMS and CARS | Fungi |
| Fuentes and Prieto, 2021 | Pulse-amplitude modulated (PAM) fluorometry and CIELAC | Estimate the biomass of phototrophic organisms |
| Gambino et al., 2019 | CIELAB | Photosynthetic pigments |
| Gaylarde et al., 2017a | FESEM | Identification of biominerals |
| Gutarowska et al., 2015 | FESEM, DNA sequencing, metabolomics | Bacteria, fungi, algae, diatoms |
| Jimenez-Lopez et al., 2007 | XRD on biominerals crystallographic structure | Bacteria, |
| Jing et al., 2020 | ATR-FTIR 2D-CoS and AFM | Shewanella bacteria to bind to the goethite |
| Keshari and Adhikary, 2013 | DNA sequencing, photosynthesis, ARA | Cyanobacteria and pigments |
| La Cono and Urzì, 2003 | FISH with rRNA-targeted oligonucleotide | Bacteria |
| Laiz et al., 2003 | Culture-based methods | Bacteria |
| Li et al., 2016 | CLSM, AFM, and TEM-EDS | Fungi-mineral interactinos, morphological properties of biominerals |
| Lu et al., 1997 | Detection and quantifying ATP, PCR-amplified ribosomal DNA spacer region | Cyanobacteria |
| Lybrand et al., 2019 | SEM-EDS and HIM | Fungi-rock interfaces |
| Mohammadi and Krumbein, 2008 | OM and PAS | Visualisation of EPS |
| Montero-Lobato et al., 2020 | GC/MS and NMR | Phycobiliproteins production of Chroococcidiopsis sp. |
| Northup et al., 2000 | SEM-EDS and culturing bacteria | Cave biominerals, Fe- and Mn-oxidising bacteria |
| Ortega-Morales et al., 2004 | SSCP and PCR-SSCP | Bacteria |
| Parkinson et al., 2010 | PIXE, XPS | Biominerals in bones |

(*continued on next page*)

**Table 2** (*continued*)

| Reference | Method | Target |
|---|---|---|
| Prieto et al., 2007 | SEM-EDS and CHNS analysis | Concentration of protein and chlorophyll *a* |
| Pecher et al., 2003 | HR-TEM | Mn biominerals in aqueous suspension with bacteria |
| Rakotonirainy and Arnold, 2008 | ATP bioluminescence analysis | Aspergillus |
| Rodriguez-Navarro et al., 2007 | XRD | Biominerals crystallographic structure caused by bacteria |
| Roldán et al., 2014 | λ-scan CLSM | Photosysthetic pigments in bacteria |
| Roldán et al., 2018 | DNA sequencying, GC/MS andLC-MS/MS | Organisms (bacteria) and proteins |
| Rui and Qian, 2022 | XRD amd UV, IR, and $^{1}$H NMR spectroscopy | Biomineral metabolite (bacteria) characterisation |
| Schabereiter-Gurtner et al., 2001 | PCR | Bacteria |
| Sethmann and Wörheide, 2008 | AFM, SPM | Calcite christals in sponges |
| Starostin et al., 2015 | Matrix-Assisted Laser Desorption Ionization – Time of Flight | Bacillus strains |
| Timoncini et al., 2022 | Raman spectroscopy, SEM EDS, Dna sequencying | Identificatino of biomineals and bacteria |
| Vázquez-Nion et al., 2018 | CIELAB colour system coordinates | Photosynthetic pigments of Bryophyta, algae, bacteria |
| Villa et al., 2020 | λ-scan confocal laser scanning microscopy | Photosynthetic pigments of Cyanobacteria |
| Villalobos et al., 2003 | XRD | Mn biomienrals by *Pseudomonas putida* strains |
| Vítek et al., 2017 | Raman spectroscopy | Pigments of Cyanobacteria |
| Vítek et al., 2020 | Raman spectroscopy | Microbial (algae, bacteria)-rock interactions |
| Walkera et al., 2017 | qPCR amplification of targeted endogenous genes of specific microorganisms | *Escherichia coli* |
| Zhang et al., 2018 | Target non-specific metagenomics approaches, with NGS | Bacteria, archaea |

suitable (Table 2). The quickest and cheapest method is analytical pyrolysis coupled with GC and MS (Py-GC/MS). It allows analysing very small samples (≈1 mg) that are pyrolysed in a furnace. The pyrolysis products are transferred into a gas chromatograph that is coupled to a mass spectrometer to identify them and categorise them according to the chemical structure in groups (e.g., monocyclic or polycyclic aromatic hydrocarbons, carbohydrate products, etc.) (Saiz-Jimenez and de Leeuw, 1984). A more detailed characterisation requires (GC/MS) and liquid chromatography in tandem with mass spectrometry (LC-MS/MS) (Roldán et al., 2018), which is more time consuming. Once detected, the profile of organic molecules, MALDI-TOF (Matrix-Assisted Laser Desorption Ionization – Time of Flight) or GC/MS (Dettmer et al., 2007; Starostin et al., 2015) can be used to identify groups of molecules and infer biodeterioration mechanisms. Gas liquid chromatography has been established as an analytical tool in microbiology after pyrolysis of lyophilised cells. It can be used to study microbial products like bacterial lipids, carbohydrates, fatty acids, and other metabolites. High-performance liquid chromatography (HPLC) is generally preferred as it can indirectly assess biomass by measuring protein, phospholipids or pigments (Farooq et al., 2015; Adamiak et al., 2017). It is possible to identify organisms by obtaining the mass spectrum of the unknown protein and matching it with a known protein spectrum in a database. For biological applications, spectrophotometric analysis can be performed for direct determination of the relative number of bacteria in a sample. For instance, after extraction of pigments in EPS from rock samples, they can be quantified by absorption measurements (Ding et al., 2020).

### 3.2. Identification of microorganisms

Optical microscopy can be used with the help of staining methods such as Periodic Acid-Schiff (PAS) that allows the visualisation of EPS (Mohammadi and Krumbein, 2008). Both Scanning Electron Microscopy (SEM) and Field Emission Scanning Electron Microscopy (FESEM) are very limited for the identification of microbes. Both, identifying and quantifying microorganisms have been classically carried out by culture-based methods in combination with cell count methods (Negi and Sarethy, 2019), but they have a limitation: a large amount of sample only provides a low proportion of cultivable microorganisms (<1 %), which yields biased estimates (Frank et al., 2003; Laiz et al., 2003). However, they have been useful for the understanding of the interaction between organisms and minerals (Hirsch et al., 1995).

In the last 20 years, metagenomic approaches and DNA fingerprinting have revolutionised the identification of microorganisms with minimal sample amounts (Table 2). They allow quantification and identification (Gaylarde et al., 2003) using Polymerase Chain Reaction (PCR) amplification of genes and clone libraries containing PCR fragments (Schabereiter-Gurtner et al., 2001). The DNA sequence is compared with those from databases (Ding et al., 2020). Although they provide identification at the genus-level, they do not provide information about biochemical functions (Perito and Cavalieri, 2018). Due to the special requirements of sampling in Cultural Heritage, new procedures, such as Nested-PCR, have been proposed and tested (Bartoli et al., 2014; Perito and Cavalieri, 2018). On the other hand, the target non-specific metagenomics approaches, with New Generation Sequencing (NGS) and the help of bioinformatics, can extract strain-level information of genes and biochemical functions, for a better understanding of biodeterioration mechanisms. The method allows the characterisation of microbial phylogeny and diversity quickly, accurately, and cheaply (de Felice et al., 2010; Ettenauer et al., 2011; Perito and Cavalieri, 2018). One of the drawbacks of metagenomics-based studies involves non-standardisation of protocols. A recent study provided a standard metagenomic approach using 27,751 samples of diverse nature: sequencing the amplified 16s rRNA gene, extracted with the MoBio PowerSoil (Thompson et al., 2017).

Fluorescent in situ hybridisation (FISH) with rRNA-targeted oligonucleotide probe directly on samples collected through adhesive tapes from stone surfaces also allows identification of organisms (La Cono and Urzì, 2003). Alternatively, single-strand conformation polymorphism (SSCP), and gene-specific PCR (PCR-SSCP) were used by Ortega-Morales et al. (2004). Combinations of very different techniques such as FESEM with metabolomics, and high-throughput sequencing techniques have also been proposed to understand the role of both phylogenetic diversity and metabolic pathways on biodeterioration (Gutarowska et al., 2015). Adamiak et al. (2017) used HPLC interfaced to High-Resolution Mass Spectrometry (HPLC/HRMS) to explore the halophile metabolome in building materials based on untargeted metabolomics (Table 2). This technique can be combined with Coherent Anti-Stokes Raman Scattering microscopy (CARS) to visualise microbial cells without conventional microscopy, to avoid disrupting samples.

### 3.3. Assessing the activity of microorganisms

The biodeterioration effect of microorganisms that grow on a rock surface depends on their activity, but not all are always active. In theory, dormant microorganisms do not contribute to biomineralisation (Viles and Cutler, 2012; Ma et al., 2015). Metabolic activities can be assessed by several methods. One of them is epifluorescence microscopy: some fluorochromes allow observing contrasts in cytoplasmic redox potential, cell layer potential, membrane integrity, electron transport or enzymatic actions (Kepner and Pratt, 1994), providing pictures of viable microorganisms. λ-scan confocal laser scanning microscopy detects autofluorescence emission spectra of photosynthetic pigments (Roldán et al., 2014; Villa et al., 2020).

A group of methods is based on pigment identification (Table 2). Chromatography coupled to MS allows identification and quantification, while nuclear magnetic resonance (NMR) allows identification even at trace levels (Cappitelli et al., 2012; Keshari and Adhikary, 2013; Montero-Lobato et al., 2020). Flow cytometry has been occasionally tested towards the study of fluorescence produced by photosynthetic pigments (Cappitelli et al., 2009). Acridine orange stained RNA, Adenosine triphosphate (ATP) or ethidium bromide, among others have also been used with similar purposes (Sheppard et al., 1987; McFeters et al., 1995; Rakotonirainy and Arnold, 2008). Alternatively, quantitative polymerase chain reaction (qPCR) has been used to monitor the amplification of targeted endogenous genes of specific microorganisms (Walkera et al., 2017; Botes et al., 2013). Detection and quantifying ATP can also be used (Lu et al., 1997; Donlan, 2002). In the last years, Raman spectroscopy has become popular for assessing pigments (Edwards et al., 2005, 2007; Vítek et al., 2017, 2020), although it does not allow the identification of species. A combination of techniques is required for this purpose (Imperi et al., 2007). The content of photosynthetic pigments has also been widely used to estimate the biomass of phototrophic organisms comparing colour variations (Vázquez-Nion et al., 2018; Fuentes and Prieto, 2021) that can be easy measured by using the CIELAB colour system coordinates (Gambino et al., 2019), a simple, cheap and non-invasive technique.

Some other methods have focused on the chemical pathways of biodeterioration, sometimes in combination with molecular characterisation, and the identification of organisms. Stable isotope analyses of light elements (C, H, O, N, S and B) by Isotope Ratio Mass Spectrometry (IRMS) can provide information on the biogeochemical pathways of elements and thus allow to infer the effect of the activity of microorganisms on biominerals, despite their scarce use on monumental stones (Fritz and Fontes, 1980; Kloppmann et al., 2011; Sanjurjo-Sánchez and Alves, 2012a, 2012b).

### 3.4. Characterisation of biominerals

Polarised Light Optical Microscopy (PLOM) enables the study of the texture of minerals (Morillas et al., 2015). As biominerals often have small crystal size and are poorly crystalline, other techniques can complement this one, such as a coupled mercury lamp to obtain a fluorescence microscope. Other transmitted-light microscopy approaches include techniques such as phase contrast, and Differential Interference Contrast (DIC), which enhance the inherent contrast of samples (de la Rosa-Tilapa et al., 2022). Bright field microscopy is one of the simplest optical microscopies: light is transmitted through the sample and the contrast is generated by the absorption of light in dense areas of the specimen (de la Rosa-Tilapa et al., 2022). Its limitations include both low contrast and low resolution for weakly absorbing samples.

SEM enables the morphological analysis of biomineral surfaces. Ortega-Morales et al. (2000) studied biofilms on ancient Mayan buildings in Yucatan, Mexico with this technique. SEM coupled with Energy-Dispersive X-ray Spectroscopy (SEM-EDS), provide elemental and composition data. Northup et al., 2000 used EDS to study cave biominerals in Mexico. Begonha (2009) used this technique to differentiate different diatoms that form biominerals on Portuguese granite churches. SEM-EDS in combination with Helium Ion Microscopy (HIM) also allowed Lybrand et al. (2019) to assess biological and geochemical drivers of biodeterioration in natural settings (Table 2). Alternatively, FESEM enabled the identification of biominerals in a church of Rio de Janeiro, Brazil (Gaylarde et al., 2017a; Ortega-Morales et al., 2019) and in ceramics from the Forum of Caesar and Nerva (Rome, Italy) (Oliveira et al., 2021). High-Resolution Transmission Electron Microscopy (HR-TEM), which uses transmitted electrons, permits the determination of the quantitative charge state of manganese biominerals in aqueous suspension and of the crystallographic architecture of corals (Pecher et al., 2003; Benzerara et al., 2011). Luo et al. (2022) also used transmission electron microscopy (TEM) in addition to XRD, FTIR, TEM and XAS analysis to study manganese oxides and mineral phase transformations.

Other types of microscopy can also be used, such as Atomic Force Microscopy (AFM). This is a type of Scanning Probe Microscopy (SPM) with a resolution in the order of magnitude of fractions of a nanometer. It has been used to observe nano-granular cluster structures in calcareous sponge spicules that are absent in normal calcite crystals (Sethmann and Wörheide, 2008). Confocal Laser Scanning Microscopy (CLSM) facilitates the characterisation of morphological properties of biominerals. CLSM, together with AFM, and TEM-EDS were used by Li et al. (2016) to explore the mechanism, driving force, and magnitude of fungus-mineral interfacial reactions. CLSM imaging combined with fluorescence staining enables the visualisation of the viability of cells in the biofilms and their 3-D architecture. These techniques have been used in many studies on the biominerals of stone monuments, where fungi, microalgae, and lichens are possibly responsible for the biomineralisation of calcium oxalate dihydrate (de los Ríos et al., 2009). Atom Probe Tomography (APT) is a 3D characterisation technique that combines both sub-nanometer spatial resolution and compositional sensitivity down to tens of parts per million. While APT is well-established in application to conventional engineering materials, recent years have seen its expansion into biomineralisation research (Grandfield et al., 2022).

Fourier Transform Infrared (FTIR) Spectroscopy has been used by Jing et al. (2020) to study the influence of cell surface macromolecules in cell-mineral interactions, specifically the affinity of the *Shewanella* bacteria to bind to the goethite with FTIR two-Dimensional Correlation Spectroscopic (ATR-FTIR 2D-CoS) analysis and AFM, indicating that a degree of "preference" of microbial species exists for iron-bearing minerals. Raman spectroscopy is also widely used in built heritage. Košek et al. (2020) and Gázquez et al. (2017) used and compared handheld and portable Raman spectrometers for the detection and characterisation of biominerals. Dicko et al. (2022) used Raman with good results for the study of biogenic and bio-inspired crystals. EDS-Raman spectroscopy was also used for the characterisation of marble statues' surfaces with high microbial diversity (Table 2), mainly *Cyanobacteria*, *Proteobacteria* and *Deinococcus-Thermus* (Thines et al., 2020; Timoncini et al., 2022). Electron Paramagnetic Resonance (EPR) or Electron Spin Resonance (ESR) enables heritage scientists to study materials that have unpaired electrons for identifying organic radicals. Zhang et al. (2021) used this technique to superoxide radicals by manganese oxides under ambient dark conditions.

X-ray methods are particularly useful for mineral characterisation. X-ray Diffraction (XRD) can be helpful to determine the biominerals crystallographic structure (Rui and Qian, 2022). Rodriguez-Navarro et al. (2007) and Jimenez-Lopez et al. (2007) evaluated the crystallographic forms of calcium carbonate formed from bacteria in limestones. Villalobos et al. (2003) characterised by XRD manganese oxides produced by *Pseudomonas putida* strains. Pozo-Antonio et al. (2022) used XRD, FTIR, stereomicroscopy (SM), polarised light microscopy (PLM), and high-resolution SEM coupled with energy dispersive X-ray spectroscopy (HRSEM-EDX) for black crusts characterisation. Prieto et al. (2007) used X-ray Fluorescence (XRF) spectrometry to check differences in the mineralogical composition of stones and black patina of granitic outcrops and heritage buildings together with XRD, SEM-EDS and CHNS analysis (Table 2). Luo et al. (2022) used X-ray Absorption Spectra (XAS), which involves measuring the transmission (or fluorescence) of X-rays as a function of incrementing X-ray energy in small steps at energies close to the absorption edge. They studied the formation and transformation of low-valence manganese oxides in natural environments. Energy-dispersive Miniprobe Multielement Analysis (EMMA-XRF) is an X-ray fluorescence technique capable of analysing a variety of elements. Silva et al. (2009) used it to study black patinas of Spanish monuments. Proton-Induced X-ray Emission (PIXE) is an elemental analysis technique that was used by Parkinson et al. (2010) to study

ceramic incrustations of prehistoric Carpathian Basin. X-ray Photoelectron Spectroscopy (XPS) can identify the elements within a material or covering its surface, as well as their chemical state, and the overall electronic structure and electronic density. Extended X-ray Absorption Fine Structure (EXAFS), along with X-ray Absorption Near Edge Structure (XANES), is a subset of X-ray Absorption Spectroscopy (XAS) that was used by Bargar et al. (2009) to study Pinal Creek bulk coatings and from micro-locations on individual grains.

## 4. Biominerals used as remediation for the restoration and bioconservation of heritage stones

Biominerals can aid in the consolidation and remediation of heritage stones affected by decay. In this sense, Bacterial Calcium Carbonate Mineralisation (BCCM) is a widespread natural process of many bacterial taxonomic groups in different environments, ranging from microscopic crystals to large geological formations (Boquet et al., 1973; Rivadeneyra et al., 1994; Ben Omar et al., 1994; Zavarzin, 2002; Brennan et al., 2004; Dupraz et al., 2009). Biologically induced mineralisation (BIM) is the most commonly applied process in the field of heritage-stone protection and consolidation.

The first time that bacteria were used to produce calcium carbonate in a laboratory was in experiments carried out by a French research group that developed a technology called Calcite Bioconcept (Adolphe and Billy, 1974; Boquet et al., 1973; Billy, 1975; Castanier et al., 1984; Tiano et al., 1999; Anne et al., 2010). This technology consisted of the application of biocalcifying culture strains that were sprayed on a solid and subsequently fed by means of a culture medium. As a result, a biocoating was generated, a calcareous layer that covered the stone. This coating was formed by $CaCO_3$ mixed with the bacterial bodies themselves. Le Métayer-Levrel (1993) and Le Métayer-Levrel et al. (1997) studied the possibility of using this phenomenon in the limestones of Thouars Church (France). Very satisfactory results were obtained with no variations in colour and other properties, while water absorption was reduced. This caused other research groups to carry out studies to improve the previous method with other microorganisms, under different conditions and with different metabolic pathways, obtaining similar results (Dakal and Cameotra, 2012).

To achieve a higher yield, a preliminary screening of bacteria isolated from natural carbonate environments was carried out, which allowed the selection of the *Bacillus cereus* strain, which produced amino acid ammonification on decayed limestones (Castanier et al., 2000). Upon investigating different bacteria, the authors selected *Bacillus cereus* cultures for in situ applications, which may pose different health risks (Perito et al., 1999). Furthermore, since only a few micrometres-thick consolidated layer was observed, the ineffectiveness for in-depth consolidation was the main drawback of this technique (Le Métayer-Levrel et al., 1997; Rodriguez-Navarro et al., 2012). Since *Bacillus cereus* could be easily produced on an industrial scale, this organism was selected for in situ applications (Orial, 2000) and several buildings were treated using this technique in France, including a castle at Châteaudun (Eure-et-Loir) and the Bordeaux cathedral (Castanier et al., 2000).

A nutritional medium was designed to stimulate the production of carbonate through the nitrogen-cycle metabolic pathways. The media contained a source of proteins for the oxidative deamination of amino acids in aerobiosis and a source of nitrate for the dissimilatory reduction of nitrate in anaerobiosis or microaerophily. In addition, a fungicide was added to prevent unwanted growth of fungi present on the stone or deposited from the air (Orial et al., 2002).

Rodriguez-Navarro et al. (2003) tested the ability of *Myxococcus xanthus* to induce calcium carbonate precipitation on a sterilised porous limestone. Limestone from a historic quarry was immersed in a nutrient buffered solution M-3P with/without *Myxococcus xanthus* (Jimenez-Lopez et al., 2008) and on altered calcarenite in the Monastery of San Jerónimo, the Royal Hospital and the Royal Chapel of Granada in Spain (Jroundi et al., 2010; Ettenauer et al., 2011). Thus, the so-called Granada method was born (Jimenez-Lopez et al., 2007, 2008).

BIOBRUSH (BIOremediation for Building Restoration of the Urban Stone Heritage) 2002/2005 EU project was aimed at sequentially integrating salt removal and stone consolidation (May, 2005). Bacteria such as *Desulfovibrio vulgaris* were selected for their ability to firstly remove black crusts and then to precipitate calcite. Additional studies were made by Cappitelli et al. (2006) who reported Carbogel. The use of Carbogel allowed for a higher retention of viable bacteria and significantly decreased the time needed for entrapment of the microorganisms as compared to the use of sepiolite. However, the practical applicability of such methodology was challenged by the procedure complexity.

EU Bioreinforce project (Biomediated calcite precipitation for monumental stones reinforcement) (Webster and May, 2006) recommended the application of organic matrix molecules to reinforce stones, and Tiano et al. (2006) applied the method in situ on Pietra d'Angera, Gioia Marble, and Pietra di Lecce. The bioinducing macromolecule solution worked in very low concentration as initiating reactive structure for the calcite precipitation in the three Italian heritage stones.

Dick et al. (2006) proposed the microbial hydrolysis of urea as a strategy to obtain a restoring and protective calcite layer on degraded Euville limestone. The hydrolysis of urea presented several advantages over the other carbonate-generating pathways, as it can be easily controlled, and it has the potential to produce high amounts of carbonate within a short period of time.

The studies carried out by Whiffin et al. (2007) in a column of sand showed that a minimum amount of carbonate M-3 precipitation per the column of sand was required to obtain a significant consolidating and biocementing effect. DeJong et al. (2006) observed that the cementing effect occurred because of the precipitated calcite forming bonds at the particle-particle contacts of sand grains. The results of this study carried out in sand could be applied to poorly consolidated stones.

De Muynck et al. (2008) noticed that waterproofing was enhanced by increasing the number of treatments or by increasing the crystal precursors' concentration in one treatment. The crystal precursors' concentration played a role in the speed and type of crystals that were formed, affecting the treatment effectiveness (Whiffin et al., 2007). De Muynck et al. (2010) observed more precipitation of calcium and larger consolidating effect following the Rodriguez-Navarro et al. (2003) methodology than the Calcite Bioconcept treatment.

An Italian team tested a BCCM-based approach in the absence of viable cells (Perito et al., 2014). This work aimed at identifying bacterial structures or molecules inducing precipitation by using *Bacillus subtilis* strain 168. The capability of bacterial dead cells to precipitate $CaCO_3$ was tested in a solution assay with $CaCl_2$ as calcium source and in the presence of sublimation of ammonium carbonate as carbonate source and for alkalisation of the closed environment. A bacterial cell fraction containing the cell wall, called BCF, induced calcite formation.

Jroundi et al. (2012) isolated bacteria that belonged to the natural microbial community of a Spanish calcarenite and that had proven biomineralisation capabilities, with the aim of preparing an inoculum that could be used in calcarenite consolidation treatments wherein the natural community of those stones was altered. The selected bacteria were phylogenetically affiliated with members of Actinobacteria, Gamma-proteobacteria and Firmicutes. Furthermore, the capability of the selected carbonatogenic bacteria to consolidate altered calcarenite slabs was studied in in-vitro experiments, both in the presence and in the absence of *Myxococcus xanthus*, as a potential reinforcement for the bacterial biomineralisation. Acinetobacter species, belonging to the microbial community of the stone, was proposed as a powerful carbonatogenic bacteria that, inoculated under appropriate conditions, was used as inoculum for calcareous stone conservation/consolidation.

Daskalakis et al. (2013) proposed *Pseudomonas*, *Pantoea and Cupriavidus* strains for remediation of marble. As a result, biogenic vaterite covered the surface of the marble. Calcium carbonate precipitation induced by bacteria using only *Cupriavidus metallidurans* was then investigated to elaborate an environmentally friendly technique for the

preservation and restoration of heritage stones (Daskalakis et al., 2014). Further, these authors investigated the capacity of *Bacillus pumilus* for biomineralisation on marble and reported that the rate of stone loss was reduced by the fine layer of bacterial calcium carbonate precipitated, and *Bacillus pumilus* proved to be useful for in situ applications for heritage-stone conservation (Daskalakis et al., 2015).

Dhami et al. (2014) wrote a review about the methods for restoration of important stone works with a focus on microbially induced carbonate precipitation for bioremediation of such structures. Erşan et al. (2015) optimised the microbially induced $CaCO_3$ precipitation through denitrification in minimal nutrient conditions. They used *Pseudomonas aeruginosa* and *Diaphorobacter nitroreducens* for concrete applications due to their enhanced precipitation yields, resilience and performance under minimal nutrient conditions. Daskalakis et al. (2015) selected *Bacillus pumilus* ACA-DC 4061 for its increased capability for biomineralisation on marble, under different nutrient media concentrations and temperature conditions. This bacillus formed a fine layer of calcium carbonate and the study showed that vaterite formation may consistently occur under specific conditions and could prove useful as a candidate for on-site applications for stone conservation. Seifan et al. (2016) extensively reported the mechanisms involved in the autotrophic biosynthesis of calcium carbonate through methanogenesis, oxygenic photosynthesis, and anoxygenic photosynthesis pathways. Delgado Rodrigues and Ferreira Pinto (2019) wrote about the consolidation experience on four Portuguese monuments: Santa Cruz Church (Coimbra), Porta Especiosa of the Old Coimbra Cathedral (Mesquita et al., 2022), National Palace of Queluz, and the Main Portal of the Loulé Church.

Seifan and Berenjian (2019) wrote a review of the detailed metabolic pathways, including ammonification of amino acids, dissimilatory reduction of nitrate, and urea degradation (ureolysis), along with the potent bacteria and the favourable conditions for precipitation of calcium carbonate, applied to restoration. A review of consolidation/remediation bio-techniques can be found in De Muynck et al. (2010), and Marvasi et al. (2020), who highlighted the milestones of biomineralisation methods with a focus on in situ stone artwork protection. The strategies explored to date were based on three main approaches: (i) the use of allochthonous cells; (ii) the use autochthonous live cells that, due to the bacterial metabolism, foster biomineralisation; and (iii) the cell-free approach which uses fractionated cellular components inducing biomineralisation. They discussed the challenging aspects of all these techniques, focusing on in situ applications and suggesting perspectives based on recent advances.

The review of Perito et al. (2020) introduces the mechanisms of bacterial mineralisation and describes the current strategies based on this process to promote stone reinforcement in field tests. They included applications of selected bacterial strains and/or culture media as well as selected components of bacterial cells on stone. The review finally provides perspectives based on recent advances. Ortega-Villamagua et al. (2020), Ortega-Morales and Gaylarde (2021), Jroundi et al. (2021) have written excellent reviews on bioconsolidation of heritage stones. Nigro et al. (2022) identified two strains (*Lysinibacillus fusiformis* and *Metabacillus litoralis*), as bacteria suitable for a bioconsolidation intervention on the Greek 'Motya Charioteer' marble statue. Rui and Qian (2022) tested the reproductive characteristics of four bacteria under different calcium ion concentrations. As discussed in the previous paragraphs, this kind of studies have mostly considered calcite-rich substrates (including several studies of biomineralisation on degraded concrete and mortars (Mondal and Ghosh, 2023), a subject that is not considered in this review). Laboratory experiments have also observed bacterial precipitation of vaterite on silicate substrates such as quartz sandstones, while on calcite substrates there was a coherent growth of calcite (Rodriguez-Navarro et al., 2012). The use of microorganisms to promote cementation by formation of biominerals has also been studied in tuffs (Jroundi et al., 2020; Elert et al., 2021).

One can include among these considerations the use of microorganisms to promote what are considered beneficial mineralogic changes. Such is the case of the bacterial transformation of gypsum to calcite to remove black crusts on marbles (Atlas et al., 1988; Cappitelli et al., 2007).

## 5. Final remarks

Stone biomineralisation processes study is complex and it is difficult to demonstrate biodeterioration directly. There are several reasons that explain these difficulties: (i) the very restricted sampling in monuments; (ii) it is necessary to frame such studies under a multidisciplinary approach; and (iii) it is hard to directly observe and demonstrate in situ both biodeterioration and biomineralisation processes. Even though some of the processes that result in the formation of biominerals as both deposits or coatings, have been clearly identified on monumental stones; some of them are well-known; and it is possible to assess some of the most common biodeterioration processes towards biominerals characterisation. This is because studies in heritage buildings take advantage of experimental studies carried out in the laboratory and of studies of biodeterioration and biomineralisation processes in nature, most of them in cave environments and natural rock outcrops. Such studies have paved the way for the use of biominerals to remediate the decay of monumental stones, although such procedures still need some development in terms of practical applicability and diversity of stones, being at present applied mostly on Ca-rich heritage stones.

Progress in biomineralisation knowledge on heritage stones requires a combination of techniques, molecular biology and mineral characterisation. Some of these techniques have been so far scarcely used, and the limits and possibilities of the techniques are still not well known. More work is also necessary in the standardisation of techniques used in biodeterioration and biomineralisation studies. In any case, molecular biology techniques should include methods that allow the detection of organic molecules and metabolically active organisms. Mineral characterisation methods should detect poorly crystalline minerals, a frequent characteristic of biominerals. The differentiation between both biomineralisation and chemical mineralisation processes is more difficult in stones that contain soluble minerals, and it is necessary to improve the knowledge of the origin of such minerals in the built heritage. In any case, there must be highlighted the very significant advances in the understanding of the processes of biodeterioration and biomineralisation in the last 20 years.

Advances in knowledge about biodeterioration processes and resulting biominerals, has promoted new debates about the real role of organisms (and biofilms) on the deterioration of heritage stones. In recent years, an increasing number of authors has argued that organisms are more protective than damaging, despite the clear evidence of biodeterioration caused by most organisms that grow on stone surfaces. In addition, a protective role has been attributed to some biomineral coatings developed on heritage stone surfaces. Some studies have provided clear evidence of this. Thus, the discussions surrounding this debate should focus on the study of the rates of physical and chemical decay vs. biodeterioration rates. In the light of the present data, it is necessary to carry out more research to study such rates of decay and compare them under the same or similar environmental conditions and stone types. Such data could be very helpful for understanding better the decay vs. protective role of organisms and for taking the best decisions in interventions in heritage buildings for preservation purposes. Indeed, it must be highlighted the use of organisms for preservation purposes through the production of biominerals. This kind of studies have been focused on the cleaning of damaging coatings and salts, and improving stone petrophysical properties. However, more work on the applicability of such methods is still needed, but maybe inducing the formation of protective coatings could be considered an effective method to preserve heritage stones. Moreover, such studies show new possibilities on the recovery of calcareous stones.

## CRediT authorship contribution statement

All authors were significantly involved in this work: J.S.-S., C.A. and D.F.-L. provided the idea and designed the text, contributing to the arguments and final remarks, and wrote the paper; J.S.-S. wrote most of the introduction section. J.S.-S. and D.F.-L. wrote most of the Section 3 of and D.F.-L. is the main contributor to the Section 4. All authors contributed to the final remarks and edited the paper.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. They also declare the following financial interests/personal relationships which may be considered as potential competing interests:

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## Data availability

No data was used for the research described in the article.

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