Earth Systems, Resources, and Sustainability, 2026, 1(2), 166–182

Scilight

Earth Systems, Resources, and Sustainability

Journal Homepage: https://www.sciltp.com/journals/esrs

Article

Protective Materials for Rock Cultural Heritage: Current Status and Future Perspectives

Wengang Zhang [1,2], Zeyi Hao [1] and Huan Liu [1,2,3,*]

[1] School of Civil Engineering, Chongqing University, Chongqing 400045, China
[2] State Key Laboratory of Safety and Resilience of Civil Engineering in Mountain Area, Chongqing 400045, China
[3] Institute of Advanced Interdisciplinary Studies, Chongqing University, Chongqing 400045, China
[*] Correspondence: huanliu@cqu.edu.cn

ABSTRACT

Rock cultural heritage, as a vital constituent of human civilization, is highly vulnerable to multifaceted deterioration processes-including weathering, cracking, and salt efflorescence—when subjected to prolonged exposure to complex natural and anthropogenic environments. Addressing the conservation and restoration of these materials has therefore emerged as an urgent priority. Traditional conservation agents, such as limewash, silicate-based consolidation, and natural organic substances, have provided valuable practical experience; nonetheless, they are constrained by issues of compatibility, durability, and long-term stability. In recent decades, advances in nanomaterials, polymers, and functional composites have offered new possibilities, exhibiting favorable characteristics such as superior penetration, enhanced long-term durability, weather resistance, and environmental sustainability. Concurrently, the exploration of biomimetic materials has further expanded the conceptual framework of heritage conservation. Case studies suggest that these novel materials confer notable advantages in practice; however, uncertainties remain regarding their long-term performance, substrate compatibility, and structural stability. The field continues to be challenged by the absence of standardized evaluation protocols, limited longitudinal monitoring data, and insufficient interdisciplinary integration. Looking ahead, research should prioritize the development of environmentally friendly and intelligent materials, promote the transition from single-material innovation toward systematic conservation strategies, and reinforce the establishment of international standards and collaborative networks to ensure the sustainable preservation and transmission of rock cultural heritage.

ARTICLE INFO

History:

Received 24 November 2025
Revised 9 January 2026
Accepted 7 February 2026
Published: 4 March 2026

Keywords:

rock cultural heritage;
deterioration mechanisms;
conservation materials;
nanomaterials;
biomimetic materials

Citation:

Zhang, W.; Hao, Z.; Liu, H. Protective Materials for Rock Cultural Heritage: Current Status and Future Perspectives. *Earth Systems, Resources, and Sustainability* **2026**, *1*(2), 166–182. https://doi.org/10.53941/esrs.2026.100011

Research Highlights

- Rock cultural heritages are highly vulnerable to multifaceted deterioration processes.
- Traditional conservation are constrained by issues of compatibility, durability, and long-term stability.
- Establishment of international standards and collaborative networks needed to ensure sustainable preservation.

1. Introduction

Stone cultural heritage, as a vital material carrier of human civilization, embodies abundant historical information and artistic value, and holds irreplaceable scholarly and aesthetic significance worldwide [1–4]. However, due to long-term exposure to natural environments and anthropogenic influences, stone monuments are widely subjected to various deterioration processes, including weathering, erosion, salt crystallization damage, and biodeterioration [5–9]. These destructive actions not only reduce structural integrity and impair surface appearance but also threaten the authenticity and completeness of the cultural relics. In particular, under the accelerating impacts of global climate change, acid deposition, and increasing tourism pressure, the preservation of stone heritage has become an increasingly urgent challenge, calling for scientific, systematic, and sustainable conservation strategies.

Since the mid-20th century, conservation technologies for stone cultural heritage have undergone a transition from empirical restoration toward more scientific and systematic approaches. Traditional conservation materials-such as limewash, ethyl silicate, and natural organic compounds-played an important historical role, yet they commonly suffer from limitations in compatibility, durability, and reversibility [10–15]. With advances in materials science, analytical techniques, and environmental simulation, researchers have begun to explore more targeted next-generation conservation materials, including inorganic–organic hybrids, nanomaterials, and functional polymers [16–20]. These materials provide notable advantages in terms of penetration ability, mechanical reinforcement, aging resistance, and environmental adaptability, offering new possibilities for consolidation, protection, and restoration of stone heritage.

Meanwhile, the rise of interdisciplinary research has driven stone-heritage conservation from single-material applications toward multifactor integrated approaches. The convergence of archaeology, environmental science, materials science, and biology has enabled researchers to elucidate deterioration mechanisms at the microstructural and biochemical levels, thereby guiding the optimization of conservation materials and technical strategies. Over the past decade, research outcomes in this field have grown substantially, resulting in a relatively systematic knowledge framework. The keyword co-occurrence map generated by VOSviewer (Figure 1) illustrates the major research hotspots and knowledge structure within stone-heritage studies from the past ten years, revealing several interconnected thematic clusters.

Overall, the map centers on terms such as rock art, biodeterioration, conservation, and cultural heritage, around which representative clusters are formed. The red cluster focuses on “rock art,” “archaeology,” and “pigments,” emphasizing archaeological context, pigment identification, and compositional analysis—reflecting the interdisciplinary integration of scientific examination and cultural interpretation. The green and blue clusters highlight keywords such as “conservation,” “stone,” “consolidation,” “nanoparticles,” and “biocides,” indicating the growing use of modern materials science and nanotechnology in stone-heritage protection, particularly in consolidation, protective treatments, and anti-deterioration interventions. The yellow cluster emphasizes “biodeterioration,” “microorganisms,” “cyanobacteria,” and “lichens,” demonstrating that biological impacts remain a central topic, with research focusing on microbial communities, deterioration mechanisms, and mitigation strategies. Notably, the close interconnections between clusters reflect the deep interdisciplinary integration of archaeology, environmental science, biology, and materials science within the field of stone-heritage conservation. As a whole, contemporary research encompasses both deterioration-mechanism studies and the development of innovative conservation materials and methods, indicating a shift from empirical practices toward scientifically informed and materials-driven comprehensive strategies.

In summary, the conservation of stone cultural heritage is a key scientific foundation for ensuring the long-term stability and sustainable transmission of cultural assets. Building upon a systematic understanding of physical, chemical, and biological deterioration mechanisms, this review adopts a mechanism-oriented and performance-based synthesis framework to analyze existing conservation materials. The reviewed studies are examined across four interrelated dimensions: material categories (including traditional inorganic materials, polymer-based systems, nanomaterials, and emerging biomimetic or intelligent materials), stone lithologies, targeted deterioration mechanisms, and key performance indicators such as penetration, mechanical reinforcement, durability, compatibility, reversibility, and breathability. Rather than providing a purely descriptive summary, this work emphasizes comparative trends, performance trade-offs, and cross-study insights, integrating representative applications and case studies to identify current limitations and future research directions. The aim is to provide theoretical support and methodological references for both scientific research and engineering practice in stone-heritage conservation.

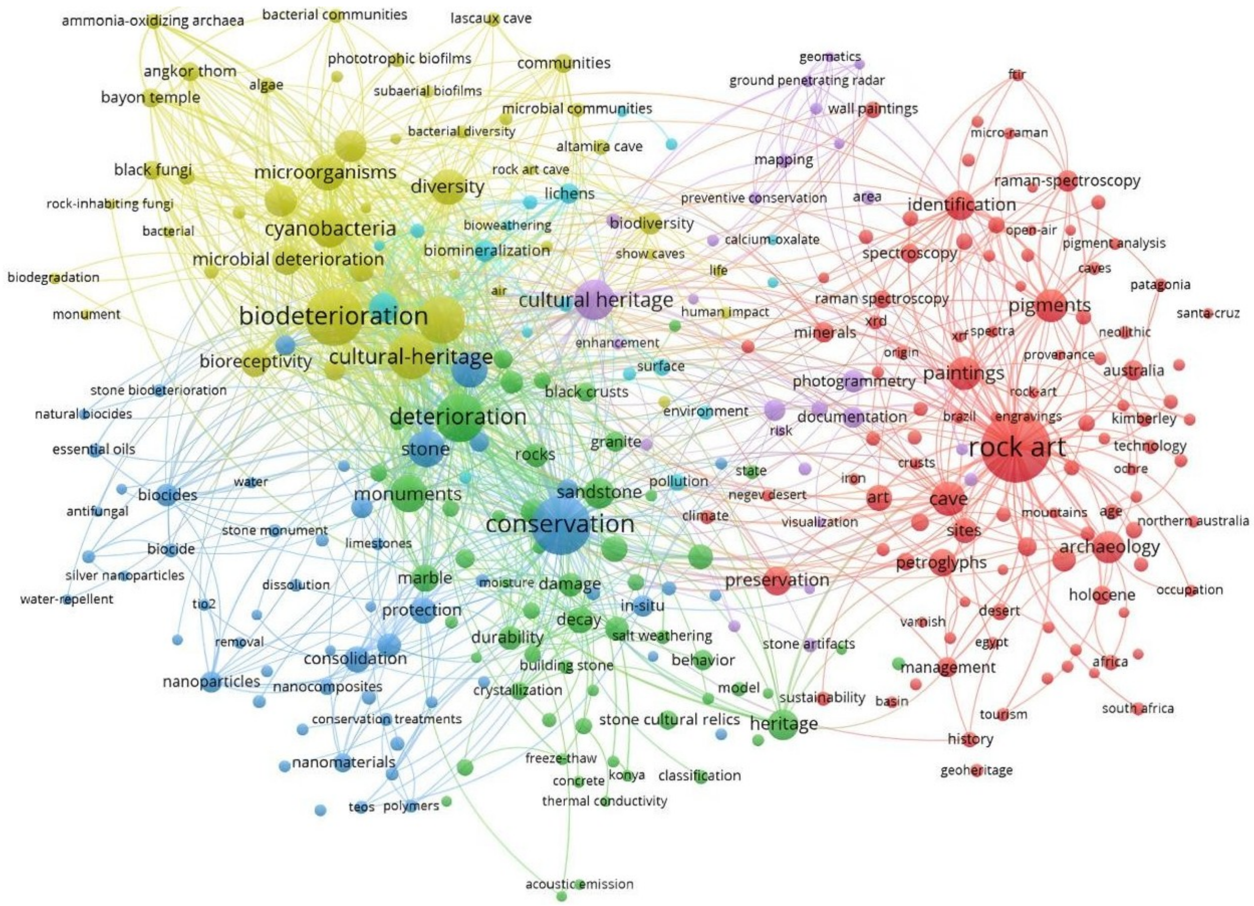

Figure 1. Main research hotspots and knowledge structure in the field of stone cultural relics research in the past decade.

2. Deterioration Mechanism of Stone Cultural Relics

The deterioration mechanism of stone cultural relics mainly stems from the long-term interaction of three major factors: physical, chemical, and biological.

2.1. Physical Deterioration Mechanism

The physical deterioration of stone cultural heritage is primarily driven by cyclic environmental fluctuations, including thermal stress, freeze–thaw cycles, wet–dry cycles, and salt-crystallization weathering (see Figure 2). Variations in the thermal expansion coefficients of different minerals and structural layers within the stone cause mismatched temperature responses between the surface and interior. This mismatch leads to stress concentration within the rock matrix, promoting the initiation and propagation of microcracks, which ultimately results in surface spalling or macroscopic fracturing [21, 22].

Freeze–thaw cycles constitute a major driving force in the deterioration of stone cultural heritage in cold and high-altitude regions. The volumetric expansion of pore water during freezing and thawing—reaching approximately 9%—generates ice-induced stress that promotes the extension and coalescence of microcracks [23–26]. In addition, liquid water migrates toward the freezing front under the influence of hydraulic pressure and capillary suction, producing localized overpressure within pores and further accelerating structural damage [26–29].

The core mechanism of wet–dry cycles lies in the repeated hygroscopic swelling and evaporation-induced shrinkage of pore water and hydrophilic minerals [30, 31]. This periodic volumetric fluctuation reduces intergranular friction, facilitates microcrack propagation, restructures pore networks, and leads to the formation of new meso- and macropores. As the number of cycles increases, cumulative microscopic damage results in a progressive decline in the macroscopic mechanical properties of the stone. Rocks with different mineral compositions exhibit varying sensitivities to wet–dry cycles: clay-rich stones undergo faster pore and crack development, whereas clay-poor sandstones degrade relatively slowly [32–34].

Salt-crystallization weathering is particularly prominent under fluctuating temperature and humidity conditions. Soluble salts undergo repeated dissolution–crystallization cycles within pores, generating crystallization pressure and causing granular disintegration [35]. When salt crystallization is coupled with freeze–thaw cycles, ice expansion and crystallization pressure act synergistically, accelerating microcrack propagation, promoting pore-network interconnection, and significantly intensifying structural deterioration [36].

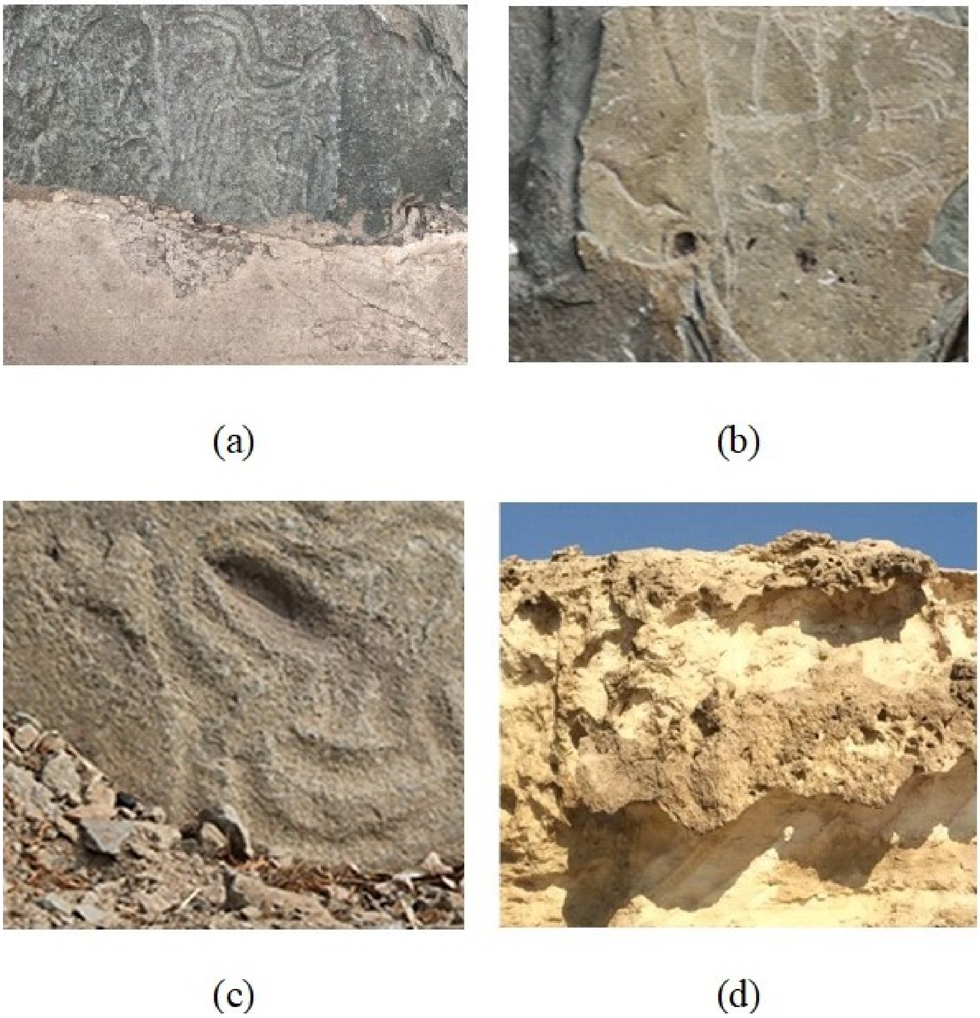

Figure 2. Cases of physical deterioration of stone cultural relics: (**a**) the temperature stress causes rock exfoliation, (**b**) The freeze-thaw cycle leads to the peeling off of rock paintings (modified from Kong [37]), (**c**) The wet-dry cycle leads to the peeling of the mural paintings (modified from Kong [37]), (**d**) Salt crystallization weathering (modified from Oguchi [38]).

2.2. Chemical Degradation Mechanism

Chemical deterioration mechanisms primarily involve mineral dissolution, salt crystallization and phase transformation, and redox reactions [39–41]. Acidic precipitation containing sulfuric, nitric, and carbonic acids can induce dissolution or ion-exchange reactions with calcite, feldspar, and other cementing minerals, thereby disrupting the mineral framework and bonding interfaces of the rock [40, 41].

Soluble salts (such as sodium sulfate, sodium carbonate, and magnesium chloride) undergo repeated dissolution–recrystallization and hydration–dehydration cycles under fluctuating temperature and humidity conditions, leading to chemical phase transitions and crystal-volume changes. The formation of salts and ion-exchange processes belong to chemical deterioration, whereas the pore pressure generated by crystallization and hydration swelling constitutes physical damage, which has been discussed in Section 2.1.

These chemical mechanisms modify pore structures, alter cementing properties, and induce volumetric or internal stresses. Although the resulting macroscopic deterioration often resembles purely physical weathering, the underlying causes and evolutionary pathways exhibit distinct chemical characteristics and frequently involve coupled effects.

Redox reactions are widespread in sandstones or limestones rich in iron, manganese, and other transition metal-bearing minerals [40, 41]. The presence of oxygen and moisture promotes the oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}), forming oxides such as hematite or goethite, accompanied by volume expansion and color alteration [42–45]. Under periodically wet or oxygen-deficient conditions, these oxides may undergo reductive dissolution. Over long-term cycles of oxidation and reduction, the stone tends to darken, rust stains enlarge, and the bonding strength and weathering resistance are progressively weakened [40, 41], as illustrated in Figure 3.

(a) black soiling (b) patinas

Figure 3. Cases of chemical deterioration of stone cultural relics: (**a**,**b**) black soiling and patinas (modified from Germinario [46]).

2.3. Biological Degradation Mechanism

Biological deterioration is manifested through the physical disruption and chemical corrosion caused by plants, microorganisms, and lichens on stone substrates [47, 48], as illustrated in Figure 4. Earlier studies suggested that plant roots enlarge fractures and mechanically break rock masses, thereby contributing to physical weathering [49]. However, anatomical analysis of woody roots by Malik et al. [50] revealed insufficient evidence to demonstrate that root-growth pressure directly widens rock fractures. Instead, research has shown that elevated concentrations of organic and inorganic acids can significantly accelerate chemical weathering of rocks [51]. Carbonate stones such as limestone are particularly susceptible to acid-induced corrosion; plants may increase the concentration of acidic exudates through root uptake of organic compounds, thereby enhancing the weathering rate of the substrate [52].

Fungal hyphae, on the other hand, can penetrate into regions inaccessible to plant roots. They may bore through mineral grains into micro-pores, or propagate along existing pore channels and microcracks, leading to surface fragmentation and granular disintegration of stone cultural heritage [53, 54]. Additionally, hyphae secrete acidic metabolites capable of causing severe deterioration to limestone and dolomite [55].

Microorganisms, algae, and lichens further contribute to deterioration by forming biofilms that modify surface humidity and pH. Their metabolic products—such as organic acids, chelators, and enzymes—promote mineral dissolution and salt mobilization [48]. Although lichens and algae may provide shading and moisture retention to some extent, their long-term metabolic activity results in surface corrosion and discoloration [56].

Overall, biological processes typically operate on top of pre-existing physical and chemical weathering, producing a secondary deterioration pattern that mainly affects near-surface layers and amplifies local microenvironmental effects such as moisture retention, acidification, and salt transport.

In summary, the deterioration of stone cultural heritage is a multifactorial, multiscale, and strongly coupled process. Physical stresses, chemical reactions, and biological activity alternate or coexist under varying environmental conditions, jointly driving the evolution of pore structures and the degradation of mechanical properties. Elucidating the coupling mechanisms and dominant factors of these processes is crucial for formulating scientifically grounded conservation strategies and assessing the long-term stability of stone heritage.

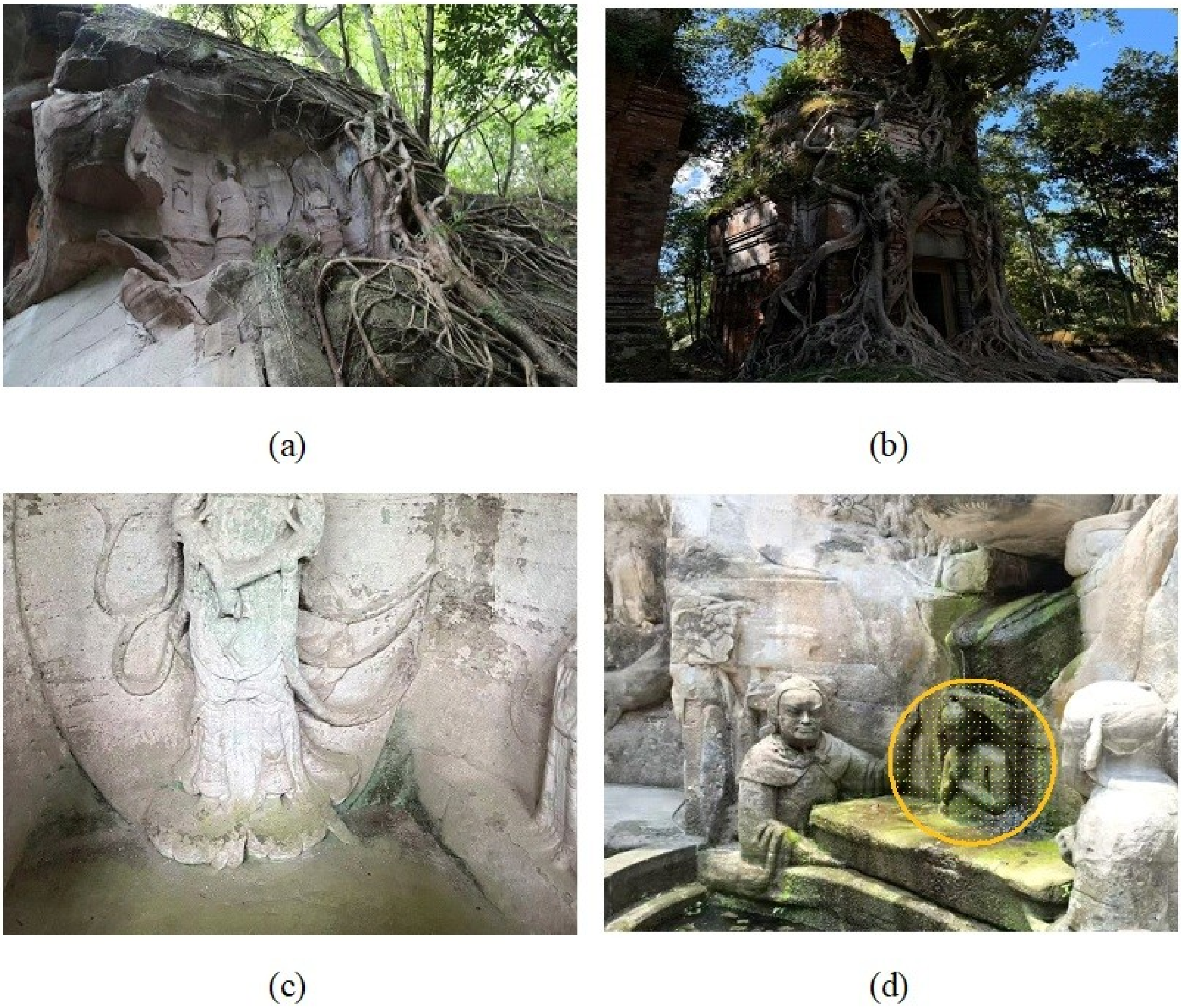

Figure 4. Cases of biological deterioration of stone cultural relics: (**a**,**b**) Grottoes affected by plant roots, (**c**,**d**) lichens and algae on grottoes.

3. Application and Limitations of Traditional Protective Materials

Traditional stone cultural relic protection materials mainly include limewater, silicates, and natural organic materials. These materials were widely used in the early stages of cultural relic protection, laying the foundation for the reinforcement and protection of stone cultural relics. However, due to the limitations of their physical and chemical properties, they have shown certain deficiencies under long-term preservation and complex environmental conditions.

3.1. Limewater

Limewater, a traditional inorganic conservation material, is based on a suspension of calcium hydroxide. Its consolidation mechanism primarily relies on the carbonation reaction ($Ca(OH)_2 + CO_2 \rightarrow CaCO_3$), which produces calcium carbonate crystals within the stone pores. These crystals form bonding phases similar to the original mineral structure, thereby enhancing the structural strength and overall stability of the stone [57, 58]. However, the low solubility of calcium hydroxide (approximately 1.7 g/L at 20 °C) limits the effective $Ca(OH)_2$ content in limewater, making it difficult to generate sufficient $CaCO_3$ deposition within the pores [58]. This constrains both the penetration depth and the strength improvement. Moreover, at higher concentrations, $Ca(OH)_2$ particles tend to aggregate and settle, reducing solution homogeneity and permeability in porous substrates, which can lead to uneven distribution of the consolidation layer [59]. Additionally, the carbonation reaction of limewater proceeds slowly [60, 61], requiring prolonged exposure to open air for CO_2 uptake and often necessitating multiple successive applications to achieve significant consolidation. Furthermore, surface deposition of limewater may result in color variation in the treated areas [62, 63].

3.2. Silicate Materials

Silicate-based materials, such as sodium silicate (Na_2SiO_3) and tetraethoxysilane (TEOS), have been among the most widely used inorganic consolidants since the late 19th century [64, 65]. Sodium silicate coatings, as water-based solutions, can strengthen porous surfaces, particularly those rich in calcium [66]. The consolidation mechanism of TEOS involves hydrolysis and polycondensation reactions that generate a nanostructured silica bonding phase within stone pores, enhancing compressive strength and structural density [67].

However, the application of silicate materials presents several challenges. Firstly, their chemical compatibility with carbonate stones is limited, often leading to the formation of unstable products such as calcium silicate. This can result in stress concentration between the consolidant layer and the substrate, causing microcracking [68]. Secondly, silicate gels undergo significant volumetric shrinkage under wet–dry cycles, potentially inducing surface flaking [69]. Moreover, silicate consolidants are generally irreversible; once cured, they cannot be removed, contravening the principle of reversibility in modern heritage conservation. Long-term use may also cause surface whitening and reduced breathability, impairing the natural vapor exchange of the stone [68, 69].

3.3. Natural Organic Materials

Natural organic materials, such as beeswax, rosin, animal and plant glues, egg white, egg yolk, and natural resins, have traditionally been used for surface waterproofing, stain protection, and decorative restoration [70]. Beeswax is commonly employed to form hydrophobic protective layers that reduce moisture penetration [71]; natural resins (e.g., shellac and rosin) enhance surface hardness and gloss [72]; while animal glues and protein-based substances are used to fill microcracks and provide adhesion [73]. These materials are widely available, easy to apply, and offer certain protective functions.

However, natural organic materials generally suffer from limited environmental stability. They are prone to aging, yellowing, cracking, or peeling under UV radiation, fluctuating temperature and humidity, and microbial attack [72]. In addition, they can soften or decompose under high temperatures or strong light, losing their protective efficacy [74]. Some resins undergo oxidative discoloration over time, resulting in noticeable color differences between the treated areas and the original stone, thereby affecting aesthetic consistency [72]. Moreover, the dense films formed by organic materials on stone surfaces can hinder moisture exchange, producing a "sealing effect" that promotes salt crystallization and accelerates weathering [75].

Overall, traditional conservation materials have historically provided valuable experience for the consolidation and restoration of stone heritage. Nevertheless, they exhibit significant limitations in chemical compatibility, weather resistance, reversibility, and optical stability. These shortcomings have directly motivated the development of novel inorganic nanomaterials, composite materials, and biomimetic materials, opening new technological pathways for the conservation of stone cultural heritage.

4. Development and Advantages of New Protective Materials

4.1. The Development of New High-Molecular Materials

With the rapid development of materials science and nanotechnology, the protective materials for stone cultural relics have gradually transitioned from the traditional single inorganic or natural organic systems to a new stage represented by nanomaterials, polymers, and functional composite systems.

4.1.1. Nanomaterials

Nanomaterials, such as nano-lime, nano-silica, and nano-titania, are characterized by small particle size, large specific surface area, and high reactivity, enabling deep penetration and uniform distribution within stone pores and microcracks to form stable binding networks (see TEM images in Figure 5).

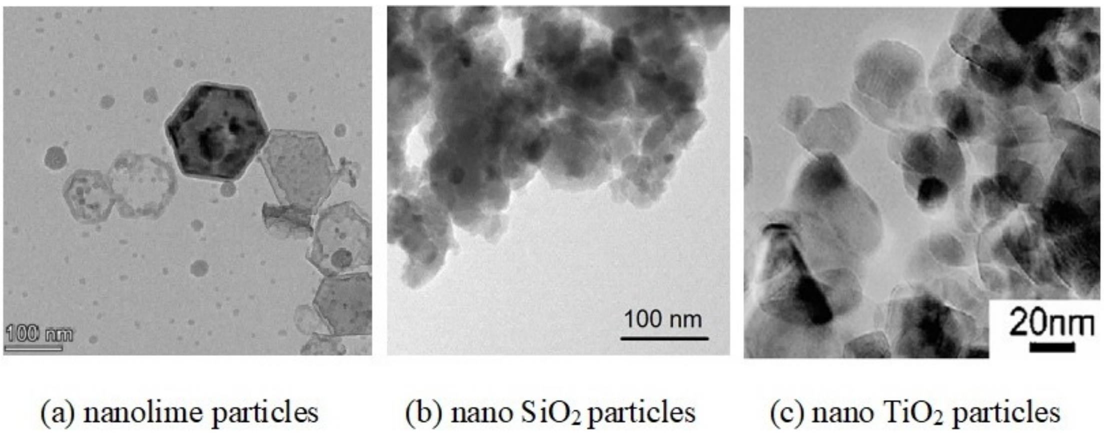

Figure 5. TEM images of: (**a**) nanolime particles, (**b**) nano SiO_2 particles (modified from Dubey [76]), (**c**) nano TiO_2 particles (modified from Malekshahi Byranvand [77]).

Nano-lime consolidates stone substrates through carbonation, generating $CaCO_3$ that recrystallizes within pores and reinforces the structure. It is particularly suitable for carbonate stones due to its good chemical compatibility with the substrate, avoiding the interfacial stress issues commonly associated with silicate-based consolidants [62, 78–80]. Unlike conventional nano-lime production methods, a novel synthesis technique developed by the University of Laquila produces a nano-lime suspension by mixing a $CaCl_2$ solution with an anion-exchange resin, where OH^- ions replace Cl^- during the reaction [81]. Studies have shown that nano-lime solutions prepared with a 1:1 mixture of ethanol and deionized water achieve optimal consolidation effects [82]. The particle morphology of nano-lime are shown in Figure 5.

Nano-silica is mainly used as a reinforcing agent in consolidant layers or composite coatings. By filling pores and promoting the formation of Si–O–Si networks, it significantly improves structural density and wear resistance [83–85]. Nano-SiO_2 particles are often incorporated into resin or silicate sol–gel systems, enhancing surface strength and hardness, reducing porosity, and improving water- and salt-resistance. Additionally, they are compatible with various organic and inorganic matrices and maintain high transparency, making them suitable for surface consolidation, composite protective coatings, and non-calcareous materials such as concrete and sandstone [83, 86, 87]. For example, Faccia et al. [87] incorporated SiO_2 nanoparticles into siloxane to fabricate a facile, *in situ* superhydrophobic nanocomposite coating on sandstone substrates.

Nano-titania is primarily applied for surface protection against soiling, self-cleaning, and aging [88]. Graziani et al. [89] demonstrated that aqueous suspensions of TiO_2 nanoparticles effectively inhibit microalgal growth on clay brick surfaces. Quagliarini et al. [89] further confirmed that TiO_2 nanoparticles protect limestone from microalgal damage. Nano-TiO_2 is often combined with fluoropolymers or silanes to form coatings that photocatalytically decompose organic pollutants while creating superhydrophobic or hydrophilic surfaces [90], achieving self-cleaning, water- and dirt-repellent, and UV-resistant properties. Moreover, such coatings can degrade atmospheric pollutants like NO_x and SO_x [86], aligning with the concept of smart materials, which is discussed further in Section 4.2.

4.1.2. Polymer Materials

Polymeric materials, such as polyacrylates, fluoropolymer resins, and organosilicon polymers, exhibit excellent film-forming ability and tunable mechanical properties [91]. Acrylic consolidants, valued for their transparency and reversibility, are widely applied in cultural heritage conservation, forming elastic protective layers on stone surfaces that provide resistance to soiling, water ingress, and ultraviolet radiation [92, 93]. Among them, the acrylic consolidant Paraloid B-72 demonstrates good color stability and initial consolidation performance, making it suitable for use on stone artifacts that are sensitive to color changes [94, 95].

In recent years, researchers have significantly enhanced the hydrophobicity, wear resistance, and thermal stability of polymeric materials by introducing fluorine- or silicon-containing functional groups or by incorporating inorganic nanoparticles, as illustrated in Figure 6 [96–98].

With the growing emphasis on sustainable development, there has been increasing interest in environmentally friendly polymers, including bio-based and biodegradable materials. These polymers can substantially reduce environmental impact without compromising performance [99]. Compared with many conventional synthetic polymers, sustainable polymers aim to minimize ecological footprint and feature non-toxic degradability, making them suitable for use in environmentally sensitive conservation areas [99, 100]. By adopting such sustainable alternatives, the developed materials can be recycled or reused after application, thereby contributing positively to a circular economy in the field of cultural heritage conservation.

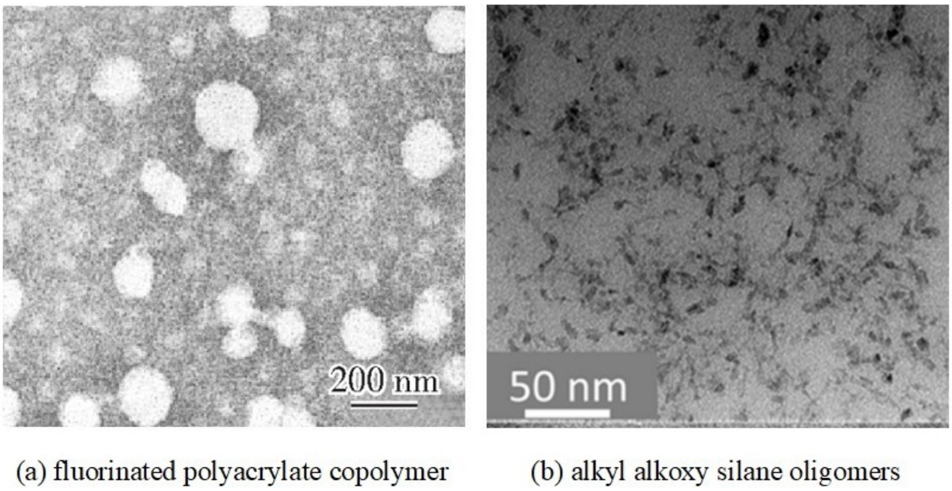

Figure 6. TEM images of (**a**) fluorinated polyacrylate copolymer [101] and (**b**) alkyl alkoxy silane oligomers (modified from Gherardi [102]).

4.1.3. Functional Composite Materials

The development of functional composite materials represents an integrated trend in heritage conservation materials. By combining nanometal oxides, polymeric matrices, and inorganic gels, these composites can simultaneously leverage the advantages of different systems [103, 104]. For example, nano-SiO_2/acrylic composites enhance both penetration and surface hardness while maintaining good breathability and reversibility [105]. Organic–inorganic hybrid materials, such as ORMOSILs, achieve molecular-level integration through sol–gel techniques, exhibiting excellent combined performance in consolidation strength and aging resistance [104, 106].

4.2. Exploration of New Intelligent/Bionic Materials

In recent years, intelligent materials and bionic materials have gradually become hot topics in the research on the protection of stone cultural relics.

4.2.1. Intelligent Materials

Smart materials are defined as materials that can respond to external environmental stimuli—such as fluctuations in temperature, humidity, light, or pH—by adjusting their own properties [107]. Currently, many smart materials are based on stimuli-responsive polymers, with their responsive behavior typically arising from incorporated functional components [108]. For example, researchers have developed tunable humidity-responsive coatings that automatically form hydrophobic barriers under high humidity and restore breathability upon drying, thereby achieving “breathable protection” [109]. Photocatalytic functional materials, such as TiO_2 and ZnO, exploit their self-cleaning and antimicrobial properties to effectively inhibit the formation of biofilms on stone surfaces [86, 110, 111].

4.2.2. Biomimetic Materials

The design of biomimetic materials is primarily inspired by natural mineralization and biological adhesion processes. Microbially induced calcium carbonate precipitation (MICP) represents a biomimetic mineralization system based on $CaCO_3$. This approach leverages microbial activity under ambient conditions to induce the reprecipitation of $CaCO_3$ crystals within stone pores, thereby restoring the structural continuity of damaged regions [112–114]. In the study by Mountassir [112], the implementation of multiple injection cycles ensures a gradual and thorough infiltration of the mineralizing solution into the deep-seated micro-fractures through capillary action. Each cycle facilitates the incremental accumulation of $CaCO_3$ crystals, which act as a mineral bridge between weathered grains. As these crystals grow and interlock within the micro-cracks, they effectively seal the voids and restore the mechanical integrity of the sandstone surface, as illustrated in the evolutionary process in Figure 7.

Biomimetic adhesives based on dopamine or silk proteins achieve excellent adhesion and reversibility through intermolecular hydrogen bonding and chelation interactions [115, 116]. For instance, dopamine can coat nanolime particles, reducing particle size, increasing specific surface area, and enhancing stability in aqueous solutions without inhibiting carbonation. This also improves the penetration of the suspension and the consolidation performance of the stone [115]. Additionally, silk protein provides nucleation sites for calcite, thereby reducing porosity, enhancing bonding, and significantly improving both the efficiency of microbially induced calcium carbonate precipitation and the resulting mechanical properties [116, 117]. It should be noted that while dopamine- and silk protein-based biomimetic adhesives do not serve as the primary consolidating material, they are essential for adapting the MICP process from geotechnical scales to heritage conservation. In geotechnical applications, MICP is typically used for rapid soil stabilization, where high strength is the priority. However, for highly weathered stones, the challenge lies in avoiding over-consolidation and surface “crust” formation. By integrating silk proteins, we provide regulated nucleation sites that slow down the mineralization rate and ensure the $CaCO_3$ crystals are deposited precisely within micro-fractures. This refined approach allows MICP to restore the structural continuity of damaged regions in a manner compatible with the delicate nature of historical stone, which differs significantly from its bulk use in geotechnics.

4.3. Advantages of New Materials

Compared with traditional consolidants, novel materials exhibit several significant advantages across multiple performance dimensions:

1. Enhanced penetration: Nanoparticles and low-molecular-weight polymers can infiltrate the microporous structure of stone, forming a uniformly distributed consolidation network and avoiding the formation of a surface “hard shell.”

2. Excellent weather resistance: The organic–inorganic synergistic structures in composite systems effectively resist aging induced by ultraviolet radiation, humidity, and freeze–thaw cycles, thereby extending the service life of the protective treatment.

3. Improved chemical compatibility and reversibility: Nano-lime and biomimetic mineralization systems developed for carbonate stones generate isostructural carbonates upon reaction with the substrate, offering superior compatibility and reversibility compared with conventional silicate-based materials.

4. Environmental friendliness and sustainability: Most novel consolidants employ solvent-free or water-based formulations, reducing volatile organic compound (VOC) emissions. Biomimetic and biodegradable materials possess high ecological safety, aligning with the principles of “minimal intervention” and “reversibility” in heritage conservation.

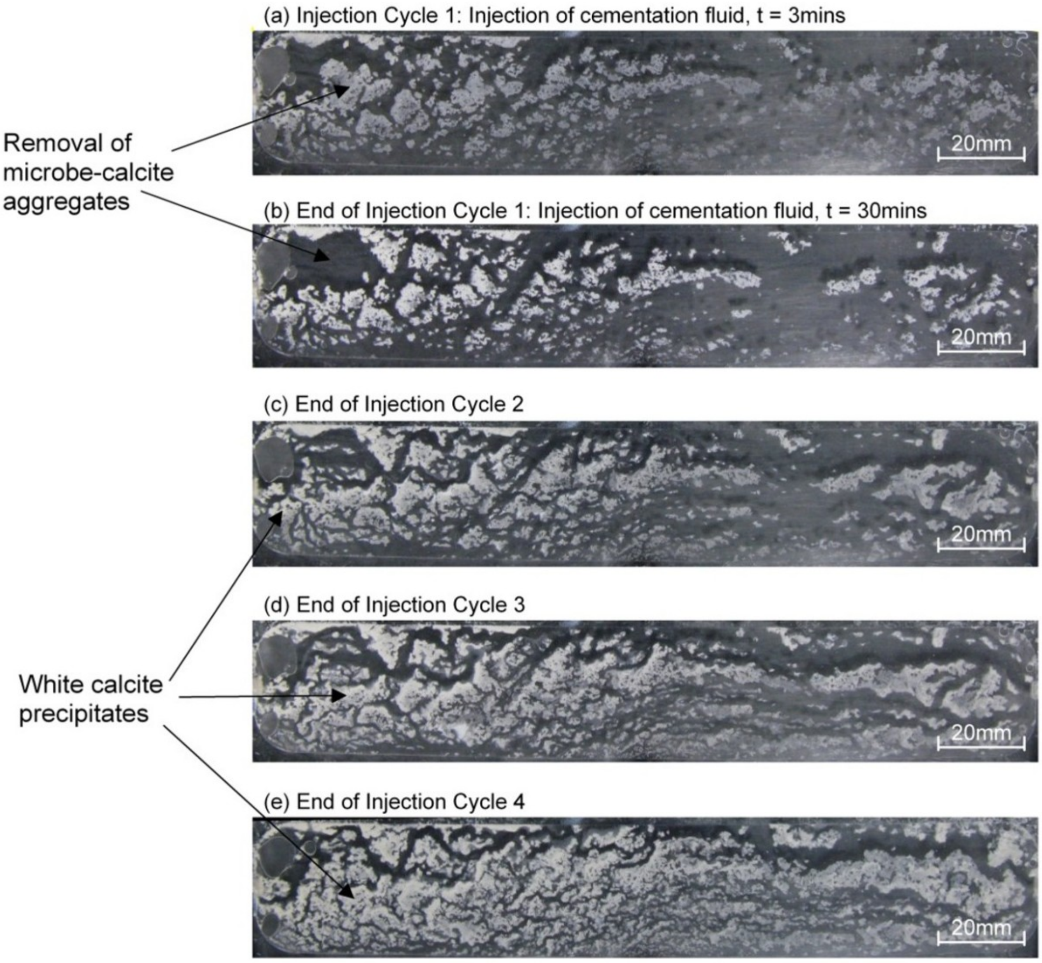

Figure 7. Evolution process of microbially induced calcium carbonate precipitation: Digital photographs (**a**) during the injection of cementation fluid ($t = 3$ mins) in Injection Cycle 1, (**b**) at the end of Injection Cycle 1 ($t = 30$ mins), (**c**) at the end of Injection Cycle 2, (**d**) at the end of Injection Cycle 3, and (**e**) at the end of Injection Cycle 4 (modified from Mountassir [112]).

In summary, the emergence of advanced polymeric and smart biomimetic materials not only overcomes the limitations of traditional protective agents in terms of compatibility and stability but also provides new technological pathways for the scientific and sustainable conservation of cultural heritage. Despite the promising results, several limitations must be addressed before applying these biomimetic materials across diverse climatic zones and rock types. Firstly, the bio-mineralization efficiency is highly sensitive to environmental temperature and humidity, which may lead to inconsistent consolidation in extreme arid or frigid climates. Secondly, while these materials perform well on high-porosity sandstones, their effectiveness on dense lithologies such as marble remains limited due to restricted penetration depth. Furthermore, the accumulation of metabolic by-products, such as ammonium salts, poses a risk of secondary salt-weathering if post-treatment cleaning is insufficient. Finally, the long-term durability of the mineralized interface under intense thermal cycling—common in many cultural heritage sites—requires further multi-year field validation.

5. Analysis of Typical Cases

5.1. Practical Application of Materials in Representative Stone Cultural Relic Protection Projects

Over the past two decades, various novel conservation materials have been applied and validated in major stone cultural heritage projects worldwide, as illustrated in Figure 8:

1. Dunhuang Mogao Grottoes mural consolidation: Nano-lime was used to compatibly consolidate earthen and siliceous substrates, addressing the specific vulnerability of clay-rich mural layers, effectively enhancing the mechanical strength and durability of the mural layers while significantly reducing color variation and powdering risk [62].

2. Pompeii conservation trials: Nano-SiO_2 sol combined with ethyl silicate was applied to weathered walls and mural surfaces for penetration consolidation. Long-term exposure tests were conducted to evaluate the balance among transparency, breathability, and weather resistance [118].

3. Façade protection of Pisa Cathedral (Italy): Nano-SiO_2 sol and ethyl silicate composites were employed to consolidate sandstone and limestone, effectively improving surface strength and moisture resistance while maintaining good breathability and high transparency [119].

4. Stone protection at the Parthenon, Acropolis of Athens (Greece): Researchers applied sol–gel-based nano-TiO_2 photocatalytic coatings to achieve anti-algal, anti-fungal, and self-cleaning functions, significantly reducing the deposition rate of pollutants on marble surfaces [120].

5. Markovits–Mathéser House, Oradea (Romania): Nano-TiO_2 coatings were applied to building façades to enhance stone durability and assess long-term effectiveness in inhibiting biofilm formation and pollutant deposition, providing empirical data for TiO_2 applications in historic architecture conservation [121].

6. Temple of Ramesses III, Luxor (Egypt): For sandstone reliefs and damaged wall surfaces, multiple salt-resistant, bio-resistant, and consolidation material systems—including TiO_2 and inorganic coatings—were compared to evaluate their suitability and long-term stability under tropical arid climates, providing technical guidance for selecting conservation materials in North African heritage sites [122].

These case studies highlight that, under varying climatic and material conditions, it is essential to comprehensively consider stone type, environmental factors, and cultural value when selecting appropriate novel consolidation and protective systems. Such considerations ensure that the conservation of stone heritage achieves the goals of safety, durability, reversibility, and sustainability.

However, despite these successful advancements, the efficacy of protective materials is profoundly sensitive to application protocols and substrate compatibility. Improper intervention can transform these sophisticated consolidants into drivers of significant conservation failures. A primary concern is the formation of a “surface crust,” particularly when high-concentration TEOS or high-molecular-weight polymers are applied to low-porosity stones. By reducing water vapor permeability—often by over 30%—these treatments sequester moisture and soluble salts beneath the surface, eventually triggering catastrophic spalling or “shelling” via subflorescence and freeze-thaw cycles. Similarly, nano-lime treatments may induce a “whitening effect” if nanoparticle aggregation, driven by high humidity or rapid solvent evaporation, limits penetration to depths of less than 2 mm and obscures the substrate’s aesthetic features.

Figure 8. Practical application cases of conservation materials for stone cultural heritage: (**a**) Murals in the Mogao Grottoes of Dunhuang (modified from ifeng.com), (**b**) Pompeii (modified from Ruffolo [118]), (**c**) Pisa Cathedral, (**d**) The Parthenon on the Athenian Acropolis (modified from Papakonstantinou [120]), (**e**) Oradea Markovits–Mathéser House (modified from Ilieş [121]), (**f**) Ruins of the Temple of Ramses III in Luxor (modified from Manci [122]).

5.2. Comparison of the Comprehensive Performance between Traditional Materials and New Materials

Combining the contents of Sections 3 and 4, the comprehensive performance of traditional materials and new materials in applications is compared, and the results are shown in the following Table 1.

It can be seen from the comparison in Table 1 that there are obvious performance trade-offs between the old and new materials. Traditional materials (such as TEOS) have high stability but high brittleness, while nanomaterials solve the permeability problem but bring the risk of agglomeration. This comparison reveals that the future direction is not to find a one-size-fits-all material, but a customized strategy based on the matching of geology-environment-materials.

6. Existing Problems and Challenges

6.1. Existing Problems

Although new protective materials such as nanomaterials, high molecular polymers, and intelligent/bionic materials show great potential, each of them still has a series of specific problems that need to be solved urgently, which restrict their large-scale and long-term application.

6.1.1. Application Defects of Nanomaterials

Nano-lime: Although nano-lime exhibits good chemical compatibility with carbonate stones, the nanoparticles are highly prone to aggregation, particularly in aqueous suspensions, which significantly reduces penetration depth and uniformity of distribution, thereby affecting consolidation performance [59, 63]. In addition, its carbonation rate remains relatively slow, and the enhancement in mechanical strength may sometimes be insufficient to meet the structural requirements of load-bearing elements [78].

Nano-silica: SiO_2 gels formed via sol–gel processes undergo significant volume shrinkage during drying, which can generate new internal stresses within the stone and even induce microcracks, especially in thick or high-concentration applications [69, 85]. The inherent brittleness of the gel also raises concerns regarding mechanical compatibility with the substrate.

Nano-titania: The photocatalytic activity of TiO_2 is highly dependent on UV irradiation; under indoor conditions, shaded areas, or surfaces covered by pollutant deposits, self-cleaning and antimicrobial effects can be greatly diminished or entirely lost. Moreover, photocatalytic processes may degrade adjacent organic protective materials (e.g., certain polymers), accelerating their aging. The long-term photocatalytic performance and potential effects on the mineralogical composition of stone substrates still require careful assessment [86, 111].

6.1.2. Limitations of High Molecular Polymer Materials

Acrylics: Represented by Paraloid B-72, acrylics undergo photo-oxidation when exposed to prolonged UV irradiation, leading to yellowing, embrittlement, and loss of adhesion. They exhibit relatively high glass transition temperatures, resulting in reduced elasticity at low temperatures and potential cracking due to thermal stress [13, 94].

Table 1. Comparative performance of traditional and novel materials in stone cultural heritage conservation.

Performance Indicator	Traditional Materials	Novel Materials
Chemical compatibility	React with carbonate stones to form unstable products, prone to stress development	Mostly isostructural reactions (e.g., $CaCO_3$, SiO_2), high compatibility
Penetration	Silicate systems penetrate well but are prone to surface gelation and crusting; limewater depth is limited (<2 mm)	Nano-sols and small-molecule polymers penetrate uniformly, reaching microcracks (up to 15 mm for nano-lime)
Reversibility	Difficult to remove or dissolve after curing	Acrylics and biomimetic adhesives are soluble or biodegradable
Weather resistance	Susceptible to aging from humidity, heat, and UV	Organic–inorganic composites exhibit excellent aging resistance
Breathability	Dense films can form, hindering stone “breathing”	Porosity can be controlled, maintaining water vapor exchange
Environmental friendliness	Solvent-based, high VOC emissions	Water-based, non-toxic or biodegradable, aligning with green conservation principles
Durability (Example: limewater and nano-lime)	Hardness and Modules retention often <60–80% after aging	Typically 80–95% retention after aging tests

Organosilicon resins: While offering excellent hydrophobicity and breathability, their mechanical strength is generally low, primarily providing water-repellent protection rather than significant structural reinforcement. Certain low-molecular-weight siloxane monomers may also pose potential environmental and health risks [96–98].

Fluoropolymer resins: Although exhibiting superior chemical stability and weather resistance, these materials are costly and may sometimes have suboptimal adhesion to stone surfaces. Their extreme hydrophobicity, if not properly controlled, can fully block water vapor transport, potentially exacerbating the "sealing effect" under certain conditions [96–98].

Bio-based/biodegradable polymers: The main challenge lies in balancing durability with degradability. While environmentally friendly, ensuring sufficient service life under complex outdoor conditions—including resistance to hydrolysis and microbial degradation—remains a significant concern [99, 100].

6.1.3. Technical Bottlenecks of Intelligent/Bionic Materials

Smart responsive materials: Thermo- or humidity-sensitive polymers have response thresholds, rates, and cycling stability that are difficult to precisely control. In the highly variable natural environment, frequent switching can induce material fatigue and failure. Most of these materials remain at the laboratory stage, with limited long-term, large-scale field validation [109].

Microbially induced calcium carbonate precipitation (MICP): This process is inherently slow and highly dependent on microbial activity, environmental temperature, pH, and nutrient availability, leading to poor controllability under real, dynamic heritage site conditions. The introduction of exogenous microorganisms may also impact local microbial communities and ecosystems, posing potential biosafety risks [112–114].

Dopamine-based biomimetic adhesives: Polydopamine itself is dark in color and may cause irreversible discoloration on light-colored stone surfaces. Its high cost and complex synthesis limit its use to high-value, small-scale precision restorations [115].

Silk proteins and other biopolymers: Similar to biodegradable polymers, questions remain regarding long-term stability. Additionally, limitations in raw material availability and purification costs restrict their broader application [116].

6.1.4. Composite Materials and Systemic Issues

Although composite materials are designed for synergistic performance enhancement, interfacial compatibility between different components remains a critical challenge. Inorganic nanoparticles often exhibit insufficient dispersion stability within organic polymer matrices, leading to aggregation or phase separation, which compromises uniformity and overall performance [105].

Moreover, the vast majority of novel materials lack systematic long-term performance databases and standardized evaluation protocols, resulting in limited guidance for material selection in conservation projects and difficulty in predicting their behavior over 20, 50, or more years.

6.2. Future Outlook

Facing the aforementioned challenges, future research and development of stone cultural heritage conservation materials should focus on the following directions:

1. Design of multifunctional, integrated materials: Develop conservation materials tailored to specific stone types, deterioration mechanisms, and environmental factors (e.g., composites combining consolidation, hydrophobicity, self-cleaning, and breathability). Molecular simulations and artificial intelligence-assisted design can be employed to optimize material structures and minimize inherent defects.

2. Nanoparticle surface modification and biomimetic synthesis: Investigate surface functionalization techniques to prevent aggregation and enhance compatibility within substrates. Develop mild, controllable biomimetic mineralization systems and explore non-biological routes for biomimetic synthesis. For smart materials, efforts should focus on improving reliability and durability of environmental responsiveness.

3. Comprehensive performance evaluation: Establish evaluation frameworks integrating laboratory accelerated aging, *in situ* field monitoring, and numerical simulations. Emphasize environmental impact assessment across the entire material lifecycle, promoting the development and application of green, sustainable conservation materials, with life cycle assessment as a critical criterion for material selection.

4. Interdisciplinary integration: Strengthen collaboration among geology, materials science, environmental engineering, microbiology, archaeology, and conservation practice to jointly define problems, develop materials, and assess effectiveness. Promote the establishment of internationally or regionally recognized standards for material performance, application protocols, and evaluation guidelines, and facilitate data sharing and case study repositories.

5. Integration with smart monitoring technologies: Combine responsive materials with Internet-of-Things (IoT) sensors to construct stone heritage health monitoring and early-warning systems. This approach enables a shift from "passive restoration" to "active intervention," minimizing the extent of conservation interventions while maximizing protection efficiency.

7. Conclusions

Research on conservation materials for stone cultural heritage has transitioned from traditional empirical applications to an era of innovation driven by nanotechnology, polymer science, and biomimetic strategies. Novel materials have achieved significant advances in penetration, substrate compatibility, and environmental responsiveness, providing more refined and diversified solutions to address the complex deterioration of cultural heritage.

However, despite the flourishing research landscape, formidable challenges remain. From the stable dispersion of nanoparticles to the long-term weathering resistance of polymers; from the precise controllability of smart responsive materials to the efficiency and safety of biomimetic processes—each technical highlight is accompanied by scientific and engineering difficulties that require in-depth investigation. Future development should not merely pursue novelty or uniqueness, but prioritize stability and suitability, achieving precision, systematic integration, and sustainability in conservation materials based on a thorough understanding of the substrate, deterioration mechanisms, and environmental coupling.

Looking forward, the conservation of stone cultural heritage will increasingly rely on multidisciplinary collaborative innovation. Only by situating material development within a comprehensive conservation science framework, and by strengthening the closed-loop feedback among fundamental research, engineering applications, and long-term monitoring, can conservation technology advance from quantitative accumulation to qualitative transformation, ultimately laying a solid material foundation for the permanent preservation and transmission of cultural heritage.

Author contributions

W.Z.: Conceptualization; Data curation; Formal analysis; Writing—original draft. Z.H.; H.L.: Data curation, Writing—review and editing.

Funding

This research was funded by National Natural Science Foundation of China (52478325; 52308086); the Fundamental Research Funds for the Central Universities (2024IAIS-QN008); Chongqing Natural Science Foundation Innovation and Development Joint Fund (CSTB2022NSCQ-LZX0001); Chongqing Municipal Research Institutions Performance Incentive and Guidance Special Project (CSTB2024JXJL-YFX0045); and the Foundation of Helan Mountain Rock Art Management Office (H20240863).

Institutional Review Board Statement

Not applicable.

Informed Consent Statement

Not applicable.

Data Availability Statement

All data generated or analyzed during this study are included in this published article.

Acknowledgement

Thanks for the financial support for Project "Deterioration monitoring and stability assessment of water-involved sites in the Three Gorges National Archaeological Site Park" by the Chongqing Institute of Cultural Relics and Archaeology.

Conflicts of Interest

Authors declare that they have no conflicts of interest and no known financial or personal relationships that could have influenced the work reported in this paper.

Use of AI and AI-assisted Technologies

No AI tools were utilized for this paper.

References

1. Yang, Z.G. An analyses of sculpture patterns of Mount Xumi Grottoes in China. *Pak. Soc. Sci. Rev.* **2023**, *7*, 921–934.
2. Chen, Y.Y.; Wu, H.C.; Wei, W.B. Different patterns of religious settlements based on the historic landscape approach: Cases of buddhist grottoes in Hexi Corridor. *Religions* **2024**, *15*, 1531.
3. Zhang, X.H. Analysis on the social culture in the art theme of China Gongyi Grotto Temple. In *Proceedings of the 2015 2nd International Conference on Education, Language, Art and Intercultural Communication (ICELAIC-15)*; Atlantis Press: Kaifeng, China, 2015.
4. Ling, J.Y.; Gao, F.Y. Cultural analysis of Yungang Grottoes under multicultural background. In Proceedings of the Asia International Symposium on Language, Literature and Translation, 2017.
5. Miščević, P.; Vlastelica, G. Impact of weathering on slope stability in soft rock mass. *J. Rock Mech. Geotech. Eng.* **2014**, *6*, 240–250.
6. Wong, L.N.Y.; Maruvanchery, V.; Liu, G. Water effects on rock strength and stiffness degradation. *Acta Geotech.* **2016**, *11*, 713–737.
7. Gunzburger, Y.; Merrien-Soukatchoff, V.; Guglielmi, Y. Influence of daily surface temperature fluctuations on rock slope stability: Case study of the Rochers de Valabres slope (France). *Int. J. Rock Mech. Min. Sci.* **2005**, *42*, 331–349.
8. Xu, K.J.; Wu, W.H. Geoparks and geotourism in China: A sustainable approach to geoheritage conservation and local development—A review. *Land* **2022**, *11*, 1493.
9. Rossi, A.M.; Webb, R.E. The consequences of allowing unrestricted tourist access at an Aboriginal site in a fragile environment: The erosive effect of trampling. *Conserv. Manage. Archaeol. Sites* **2007**, *9*, 219–236.
10. Cazalla, O.; Rodriguez-Navarro, C.; Sebastian, E.; et al. Aging of lime putty: Effects on traditional lime mortar carbonation. *J. Am. Ceram. Soc.* **2000**, *83*, 1070–1076.
11. Menningen, J.; Sassoni, E.; Sobott, R.; et al. Constraints of the durability of inorganic and organic consolidants for marble. *Environ. Earth Sci.* **2021**, *80*, 1–18.
12. Zárraga, R.; Cervantes, J.; Salazar-Hernandez, C.; et al. Effect of the addition of hydroxyl-terminated polydimethylsiloxane to TEOS-based stone consolidants. *J. Cult. Herit.* **2010**, *11*, 138–144.
13. Lazzari, M.; Chiantore, O. Thermal-ageing of paraloid acrylic protective polymers. *Polymers* **2000**, *41*, 6447–6455.

14. Scherer, G.W.; Wheeler, G.S. Silicate consolidants for stone. *Key Eng. Mater.* **2009**, *391*, 1–25.
15. Hansen, E.; Doehne, E.; Fidler, J.; et al. A review of selected inorganic consolidants and protective treatments for porous calcareous materials. *Stud. Conserv.* **2003**, *48*, 13–25.
16. Gherardi, F.; Maravelaki, P.N. Advances in the application of nanomaterials for natural stone conservation. *RILEM Tech. Lett.* **2022**, *7*, 20–29.
17. Girginova, P.I.; Galacho, C.; Veiga, R.; et al. Inorganic nanomaterials for restoration of cultural heritage: Synthesis approaches towards nanoconsolidants for stone and wall paintings. *ChemSusChem* **2018**, *11*, 4168–4182.
18. Burgos-Ruiz, M.; Elert, K.; Ruiz-Agudo, E.; et al. Silica-functionalized nanolimes for the conservation of stone heritage. *Small* **2023**, *19*, 2300596.
19. He, J.; Otero, J.; Crespo-López, L.; et al. Ethyl silicate–nanolime treatment for the consolidation of calcareous building materials. *Constr. Build. Mater.* **2024**, *418*, 135437.
20. Campostrini, A.; Sala-Luis, A.; Bosch-Roig, P.; et al. Mesoporous silica and vegetal extracts combined as sustainable stone heritage protection against biodeterioration. *Appl. Microbiol. Biotechnol.* **2025**, *109*, 1–15.
21. He, X.; Xu, M.; Zhang, H.; et al. An exploratory study of the deterioration mechanism of ancient wall-paintings based on thermal and moisture expansion property analysis. *J. Archaeol. Sci.* **2014**, *42*, 194–200.
22. Smith, B.J.; Srinivasan, S.; Gomez-Heras, M.; et al. Near-surface temperature cycling of stone and its implications for scales of surface deterioration. *Geomorphology* **2011**, *130*, 76–82.
23. Hori, M.; Morihiro, H. Micromechanical analysis on deterioration due to freezing and thawing in porous brittle materials. *Int. J. Eng. Sci.* **1998**, *36*, 511–522.
24. Huang, S.; Ye, Y.; Cui, X.; et al. Theoretical and experimental study of the frost heaving characteristics of the saturated sandstone under low temperature. *Cold Reg. Sci. Technol.* **2020**, *174*, 103036.
25. Peng, N.B.; Hong, J.; Zhu, Y.; et al. Experimental investigation of the influence of freeze-thaw mode on damage characteristics of sandstone. *Appl. Sci.* **2022**, *12*, 12395.
26. Powers, T.C.; Helmuth, R. Theory of volume changes in hardened portland-cement paste during freezing. In Proceedings of the Highway Research Board Proceedings, 1953.
27. Prick, A. Critical degree of saturation as a threshold moisture level in frost weathering of limestones. *Permafr. Periglac. Process.* **1997**, *8*, 91–99.
28. Everett, D. The thermodynamics of frost damage to porous solids. *Trans. Faraday Soc.* **1961**, *57*, 1541–1551.
29. Vlahou, I.; Worster, M.G. Ice growth in a spherical cavity of a porous medium. *J. Glaciol.* **2010**, *56*, 271–277.
30. Dehestani, A.; Hosseini, M.; Beydokhti, A.T. Effect of wetting–drying cycles on mode I and mode II fracture toughness of sandstone in natural (pH = 7) and acidic (pH = 3) environments. *Theor. Appl. Fract. Mech.* **2020**, *107*, 102512.
31. Khanlari, G.; Abdilor, Y. Influence of wet–dry, freeze–thaw, and heat–cool cycles on the physical and mechanical properties of Upper Red sandstones in central Iran. *Bull. Eng. Geol. Environ.* **2015**, *74*, 1287–1300.
32. Zhao, Z.; Yang, J.; Zhang, D.; et al. Effects of wetting and cyclic wetting–drying on tensile strength of sandstone with a low clay mineral content. *Rock Mech. Rock Eng.* **2017**, *50*, 485–491.
33. Reviron, N.; Reuschlé, T.; Bernard, J.-D. The brittle deformation regime of water-saturated siliceous sandstones. *Geophys. J. Int.* **2009**, *178*, 1766–1778.
34. Wasantha, P.L.; Ranjith, P.G. Water-weakening behavior of Hawkesbury sandstone in brittle regime. *Eng. Geol.* **2014**, *178*, 91–101.
35. Goudie, A.; Viles, H. *Salt Weathering Hazards*; John Wiley & Sons: Chichester, UK, 1997.
36. Sun, B.; Li, X.Y.; Peng, N.B.; et al. Experimental study on salt-bearing sandstone samples under the change of temperature and humidity cycle. *Int. J. Archit. Heritage* **2025**, *19*, 1385–1396.
37. Kong, X.C.; He, F.G.; Lv, R.; et al. Experimental study on the degradation of sandstone-petroglyph carriers in Helankou: Effects of freeze-thaw and wet-dry cycles. *iScience* **2024**, *27*, 110576.
38. Oguchi, C.T.; Yu, S. A review of theoretical salt weathering studies for stone heritage. *Prog. Earth Planet. Sci.* **2021**, *8*, 32.
39. Mudronja, D.; Vanmeert, F.; Fazinic, S.; et al. Protection of stone monuments using a brushing treatment with ammonium oxalate. *Coatings* **2021**, *11*, 379.
40. Aslan, F.; Arslan, M.; Eflatun, A. The solubility of calcium at stone monuments by acid rain. *Fresenius Environ. Bull.* **2001**, *10*, 314–318.
41. Schuster, P.F.; Reddy, M.M.; Sherwood, S.I. Effects of acid-rain and sulfur-dioxide on marble dissolution. *Mater. Perform.* **1994**, *33*, 76–80.
42. Jiang, Z.; Liu, Q.; Roberts, A.P.; et al. The magnetic and color reflectance properties of hematite: From Earth to Mars. *Rev. Geophys.* **2022**, *60*, e2020RG000698.
43. Zhang, Q.; Appel, E.; Basavaiah, N.; et al. Is alteration of magnetite during rock weathering climate-dependent? *J. Geophys. Res. Solid Earth* **2021**, *126*, e2021JB022693.
44. Maxbauer, D.P.; Feinberg, J.M.; Fox, D.L.; et al. Magnetic minerals as recorders of weathering, diagenesis, and paleoclimate: A core-outcrop comparison of Paleocene-Eocene paleosols in the Bighorn Basin, WY, USA. *Earth Planet. Sci. Lett.* **2016**, *452*, 15–26.
45. Sánchez-Marañón, M.; Molinero-García A.; Delgado R.; et al. Spectral analysis of Fe oxidation in the early stages of weathering and soil formation. Catena **2023**, *222*, 106850.
46. Germinario, L.; Oguchi C.T.; Tamura Y.; et al. Taya Caves, a Buddhist marvel hidden in underground Japan: Stone properties, deterioration, and environmental setting. *Heritage Sci.* **2020**, *8*, 87.
47. Onofri, S.; Zucconi, L.; Isola D.; et al. Rock-inhabiting fungi and their role in deterioration of stone monuments in the Mediterranean area. *Plant Biosyst.* **2014**, *148*, 384–391.
48. Parvin, N.; Mandal, S.; Rath, J. Microbiome of seventh-century old Parsurameswara stone monument of India and role of desiccation-tolerant cyanobacterium Lyngbya corticicola on its biodeterioration. *Biofouling* **2024**, *40*, 40–53.
49. Pitty, A.F. *Introduction to Geomorphology*; Routledge: London, UK, 2020
50. Malik, I.; Pawlik, Ł.; Ślęzak A.; et al. A study of the wood anatomy of Picea abies roots and their role in biomechanical weathering of rock cracks. *Catena* **2019**, *173*, 264–275.
51. Hayes, J.L.; Riebe, C.S.; Holbrook, W.S.; et al. Porosity production in weathered rock: Where volumetric strain dominates over chemical mass loss. *Sci. Adv.* **2019**, *5*, eaao0834.
52. Goulden, M.L.; Anderson, R.G.; Bales, R.C.; et al. Evapotranspiration along an elevation gradient in California's Sierra Nevada. *J. Geophys. Res.: Biogeosciences* **2012**, *117*.
53. Lisci, M.; Monte, M.; Pacini, E. Lichens and higher plants on stone: A review. *Int. Biodeterior. Biodegradation* **2003**, *51*, 1–17.
54. Duane, M.J. Coeval biochemical and biophysical weathering processes on Quaternary sandstone terraces south of Rabat (Temara), northwest Morocco. *Earth Surf. Process. Landf.* **2006**, *31*, 1115–1128.
55. Gadd, G.M. The geomycology of elemental cycling and transformations in the environment. *Microbiol. Spectr.* **2017**, *5*, 1–16.
56. Favero-Longo, S.E.; Laurenzi Tabasso, M.; Brigadeci F.; et al. A first assessment of the biocidal efficacy of plant essential oils against lichens on stone cultural heritage, and the importance of evaluating

suitable application protocols. *J. Cult. Heritage* **2022**, *55*, 68–77.

57. Ashurst, J.; Malnic, N. *The Cleaning and Treatment of Limestone by the "Lime"*; English Heritage: London, UK, 1985.
58. Brajer, I.; Kalsbeek, N. Limewater absorption and calcite crystal formation on a limewater-impregnated secco wall painting. *Stud. Conserv.* **1999**, *44*, 145–156.
59. Rodriguez-Navarro, C.; Ruiz-Agudo, E.; Ortega-Huertas, M.; et al. Nanostructure and irreversible colloidal behavior of $Ca(OH)_2$: Implications in cultural heritage conservation. *Langmuir* **2005**, *21*, 10948–10957.
60. Despotou, E.; Shtiza, A.; Schlegel, T.; et al. Literature study on the rate and mechanism of carbonation of lime in mortars/Literaturstudie über Mechanismus und Grad der Karbonatisierung von Kalkhydrat im Mörtel. *Mauerwerk* **2016**, *20*, 124–137.
61. Lawrence, R.M.H. A Study of Carbonation in Non-Hydraulic Lime Mortars. Ph.D. Thesis, University of Bath, Bath, UK, 2006.
62. Han, P.; Zhang, H.; Zhang, R.; et al. Evaluation of the effectiveness and compatibility of nanolime for the consolidation of earthen-based murals at Mogao Grottoes. *J. Cult. Heritage* **2022**, *58*, 266–273.
63. Borsoi, G.; Lubelli, B.; Van Hees, R.; et al. Understanding the transport of nanolime consolidants within Maastricht limestone. *J. Cult. Heritage* **2016**, *18*, 242–249.
64. Zendri, E.; Biscontin, G.; Nardini, I.; et al. Characterization and reactivity of silicatic consolidants. *Constr. Build. Mater.* **2007**, *21*, 1098–1106.
65. Zornoza-Indart, A.; López-Arce, P.; López-Polín, L. Durability of traditional and new nanoparticle based consolidating products for the treatment of archaeological stone tools: Chert artifacts from Atapuerca sites (Burgos, Spain). *J. Cult. Heritage* **2017**, *24*, 9–21.
66. Wang, Z.; Sun, Y.; Zhang, S.; et al. Effect of sodium silicate on Portland cement/calcium aluminate cement/gypsum rich-water system: Strength and microstructure. *RSC Adv.* **2019**, *9*, 9993–10003.
67. Navarro-Moreno, D.; Martínez-Arredondo, A.; García-Vera, V.E.; et al. Nanolime, ethyl silicate and sodium silicate: Advantages and inconveniences in consolidating ancient bricks (XII-XIII century). *Constr. Build. Mater.* **2021**, *277*, 122240.
68. Praticó, Y.; Caruso, F.; Delgado Rodrigues, J.; et al. Stone consolidation: A critical discussion of theoretical insights and field practice. *RILEM Tech. Lett.* **2020**, *4*, 145–153.
69. Xu, F.; Zeng, W.; Li, D. Recent advance in alkoxysilane-based consolidants for stone. *Prog. Org. Coat.* **2019**, *127*, 45–54.
70. Schellmann, N.C. Animal glues: A review of their key properties relevant to conservation. *Stud. Conserv.* **2007**, *52*, 55–66.
71. York, D.W.; Collins, S.; Rantape, M. Measuring the permeability of thin solid layers of natural waxes. *J. Colloid Interface Sci.* **2019**, *551*, 270–282.
72. Scalarone, D.; Lazzari, M.; Chiantore, O. Ageing behaviour and analytical pyrolysis characterisation of diterpenic resins used as art materials: Manila copal and sandarac. *J. Anal. Appl. Pyrolysis* **2003**, *68–69*, 115–136.
73. Bridarolli, A.; Freeman, A.A.; Fujisawa, N.; et al. Mechanical properties of mammalian and fish glues over range of temperature and humidity. *J. Cult. Heritage* **2022**, *53*, 226–235.
74. Poli, T.; Piccirillo, A.; Zoccali, A.; et al. The role of zinc white pigment on the degradation of shellac resin in artworks. *Polym. Degrad. Stab.* **2014**, *102*, 138–144.
75. Pia, G.; Esposito Corcione, C.; Striani, R.; et al. Coating's influence on water vapour permeability of porous stones typically used in cultural heritage of Mediterranean area: Experimental tests and model controlling procedure. *Prog. Org. Coat.* **2017**, *102*, 239–246.
76. Dubey, R.S.; Rajesh, Y.B.R.D.; More, M.A. Synthesis and characterization of SiO_2 nanoparticles via sol-gel method for industrial applications. *Mater. Today: Proc.* **2015**, *2*, 3575–3579.
77. Malekshahi Byranvand, M.; Nemati Kharat, A.; Fatholahi, L.; et al. A review on synthesis of nano-TiO_2 via different methods. *J. Nanostruct.* **2013**, *3*, 1–9.
78. Tzavellos, S.; Pesce, G.L.; Wu, Y.; et al. Effectiveness of nanolime as a stone consolidant: A 4-year study of six common UK limestones. *Materials* **2019**, *12*, 2673.
79. Ruffolo, S.A.; La Russa, M.F.; Aloise, P.; et al. Efficacy of nanolime in restoration procedures of salt weathered limestone rock. *Appl. Phys. A* **2014**, *114*, 753–758.
80. Pozo-Antonio, J.S.; Otero, J.; Alonso, P.; et al. Nanolime- and nanosilica-based consolidants applied on heated granite and limestone: Effectiveness and durability. *Constr. Build. Mater.* **2019**, *201*, 852–870.
81. Taglieri, G.; Daniele, V.; Del Re, G.; et al. A new and original method to produce $Ca(OH)_2$ nanoparticles by using an anion exchange resin. *Adv. Nanopart.* **2015**, *4*, 17–24.
82. Busschots, E.; De Kock, T.; Berto, T.; et al. Consolidating lime mortar with nanolime: The effect of the ethanol: Water ratio. *Stud. Conserv.* **2025**, *70*, 358–366.
83. Wu, Q.; Yao, R.; Guo, D.; et al. Dual hydrophilic/hydrophobic SiO_2 transparent super-hydrophobic coating with good interfacial adhesion and high mechanical robustness. *J. Mater. Sci.* **2024**, *59*, 21294–21309.
84. Majdi, M.R.; Danaee, I.; Zaarei, D.; et al. Improvement of microstructure and barrier properties of silicate coatings on low carbon steel by incorporating colloidal Nano-SiO_2. *Arch. Metall. Mater.* **2020**, *65*, 627–638.
85. Brinker, C.J.; Scherer, G.W. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*; Gulf Professional Publishing: Boston, MA, USA, 1990.
86. Peng, M.; Wang, L.; Guo, L.; et al. A durable Nano-SiO_2-TiO_2/dodecyltrimethoxysilane superhydrophobic coating for stone protection. *Coatings* **2022**, *12*, 1397. https://doi.org/10.3390/coatings12101397
87. Facio, D.S.; Mosquera, M.J. Simple strategy for producing superhydrophobic nanocomposite coatings in situ on a building substrate. *ACS Appl. Mater. Interfaces* **2013**, *5*, 7517–7526.
88. Noman, M.; Ashraf, M.; Ali, A. Synthesis and applications of nano-TiO_2: A review. *Environ. Sci. Pollut. Res.* **2019**, *26*, 3262–3291.
89. Graziani, L.; Quagliarini, E.; Osimani, A.; et al. The influence of clay brick substratum on the inhibitory efficiency of TiO_2 nanocoating against biofouling. *Build. Environ.* **2014**, *82*, 128–134.
90. Shu, H.; Song, Y.J.; Liu, Q.; et al. The study of rod-shaped TiO_2 composite material in the protection of stone cultural relics. *Green Process. Synth.* **2020**, *9*, 359–365.
91. Bandelli, D.; Mastrangelo, R.; Poggi, G.; et al. New sustainable polymers and oligomers for Cultural Heritage conservation. *Chem. Sci.* **2024**, *15*, 2443–2455.
92. Ulaeto, S.B.; Ravi, R.P.; Udoh, I.I.; et al. Polymer-based coating for steel protection, highlighting metal–organic framework as functional actives: A review. *Corros. Mater. Degrad.* **2023**, *4*, 284–316. https://doi.org/10.3390/cmd4020015
93. Santos, T.P.; Vaz, M.F.; Pinto, M.L.; et al. Porosity characterization of old Portuguese ceramic tiles. *Constr. Build. Mater.* **2012**, *28*, 104–110.
94. Favaro, M.; Mendichi, R.; Ossola, F.; et al. Evaluation of polymers for conservation treatments of outdoor exposed stone monuments. Part I: Photo-oxidative weathering. *Polym. Degrad. Stab.* **2006**, *91*, 3083–3096.
95. Constâncio, C.; Franco, L.; Russo, A.; et al. Studies on polymeric conservation treatments of ceramic tiles with paraloid B-72 and two alkoxysilanes. *J. Appl. Polym. Sci.* **2010**, *116*, 2833–2839.
96. Liang, L.; Wen, T.; Xin, J.; et al. Fluoropolymer: A review on its emulsion preparation and wettability to solid-liquid interface. *Molecules* **2023**, *28*, 905.

97. Tan, Y.; Tang, J.; Zhao, N.; et al. Effect of fluorocarbon polymers on hydrophobicity, wear resistance and corrosion resistance of epoxy resins. *Coatings* **2023**, *13*, 685. https://doi.org/10.3390/coatings13040685
98. Glosz, K.; Stolarczyk, A.; Jarosz, T. Siloxanes-versatile materials for surface functionalisation and graft copolymers. *Int. J. Mol. Sci.* **2020**, *21*, 6387.
99. Samir, A.; Ashour, F.H.; Hakim, A.A.A.; et al. Recent advances in biodegradable polymers for sustainable applications. *npj Mater. Degrad.* **2022**, *6*, 68.
100. Beena Unni, A.; Muringayil Joseph, T. Enhancing polymer sustainability: Eco-conscious strategies. *Polymers* **2024**, *16*, 1769. https://doi.org/10.3390/polym16131769
101. Hua, X.; Jianfang, L.; Hui, Z.; et al. Study on preparation of fluorinated acrylate copolymer latice through mini-emulsion polymerization. *Paint Coat. Ind.* **2019**, *49*, 12–17.
102. Gherardi, F.; Roveri, M.; Goidanich, S.; et al. Photocatalytic nanocomposites for the protection of European architectural heritage. *Materials* **2018**, *11*, 65. https://doi.org/10.3390/ma11010065
103. Doni, M.; Fierascu, I.; Fierascu, R.C. Recent developments in materials science for the conservation and restoration of historic artifacts. *Appl. Sci.* **2024**, *14*, 11363. https://doi.org/10.3390/app142311363
104. Arkhireeva, A.; Hay J.N. Ormosil nanocomposite materials as modifiers for acrylic coating systems. J. Nanosci. Nanotechnol. **2006**, *6*, 360–371.
105. D'amato, R.; Caneve, L.; Giancristofaro, C.; et al. Development of nanocomposites for conservation of artistic stones. *Proc. Inst. Mech. Eng. N.* **2014**, *228*, 19–26.
106. Gąsiorek, J.; Mazur-Nowacka, A.; Szczurek, A.; et al. Influence of zirconia and organic additives on mechanical and electrochemical properties of silica sol-gel coatings. *Materials* **2021**, *14*, 2389.
107. Hoffman, A.S. "Intelligent" polymers in medicine and biotechnology. *Artif. Organs.* **1995**, *19*, 458–467.
108. Aguilar, M.R.; San Román, J. *Smart Polymers and Their Applications*; Woodhead Publishing: Cambridge, UK, 2019.
109. Gibson, M.I.; O'reilly, R.K. To aggregate, or not to aggregate? considerations in the design and application of polymeric thermally-responsive nanoparticles. *Chem. Soc. Rev.* **2013**, *42*, 7204–7213.
110. Aldosari, M.A.; Darwish, S.S.; Adam, M.A.; et al. Using ZnO nanoparticles in fungal inhibition and self-protection of exposed marble columns in historic sites. *Archaeol. Anthropol. Sci.* **2019**, *11*, 3407–3422.
111. Espitia, P.J.P.; Soares, N.D.F.F.; Coimbra, J.S.D.R.; et al. Zinc oxide nanoparticles: Synthesis, antimicrobial activity and food packaging applications. *Food Bioprocess Technol.* **2012**, *5*, 1447–1464.
112. Mountassir, G.E.; Lunn, R.J.; Moir, H.; et al. Hydrodynamic coupling in microbially mediated fracture mineralization: Formation of self-organized groundwater flow channels. *Water Resour. Res.* **2014**, *50*, 1–16.
113. Cuthbert, M.O.; Mcmillan, L.A.; Handley-Sidhu, S.; et al. A field and modeling study of fractured rock permeability reduction using microbially induced calcite precipitation. *Environ. Sci. Technol.* **2013**, *47*, 13637–13643.
114. Zhang, S.X.; Wu, C.Z.; Naghizadeh, A.; et al. Laboratory investigation on mechanical behavior of stone cultural relic fractures using rapid microbially induced calcite precipitation. *Case Stud. Constr. Mater.* **2025**, *23*, e05214.
115. Zhu, J.M.; Jia, C.; Li, Y.K.; et al. Polydopamine-modified nano-lime with high kinetic stability in water for the consolidation of stone relics. *ACS Appl. Mater. Interfaces* **2022**, *14*, 13622–13630.
116. Gu, Z.R.; Li, X.J.; Wu, J.; et al. A novel strategy for reinforcing cementation process coupling microbially induced carbonate precipitation (MICP) with cross-linked silk fibroin. *J. Environ. Chem. Eng.* **2023**, *11*, 109871.
117. Li, J.Y.; Achal, V. Self-assembled silk fibroin cross-linked with genipin supplements microbial carbonate precipitation in building material. *Environ. Microbiol. Rep.* **2023**, *15*, 797–808.
118. Ruffolo, S.; Rovella, N.; Arcudi, A.; et al. New insights to assess the consolidation of stone materials used in built heritage: The case study of ancient graffiti (Tituli Picti) in the archaeological site of Pompeii. *Herit. Sci.* **2020**, *8*, 49.
119. Lazzeri, A.; Coltelli, M.; Bevilacqua, R.; et al. European project nano-cathedral: Nanomaterials for conservation of European architectural heritage: Pisa, the experience of a Mediterranean Cathedral: Natural and anthropogenic hazards and sustainable preservation. In *10th International Symposium on the Conservation of Monuments in the Mediterranean Basin: Natural and Anthropogenic Hazards and Sustainable Preservation*; Springer: Cham, Switzerland, 2018; pp. 143–152.
120. Papakonstantinou, E.; Panou, A.; Franzikinaki, K.; et al. The surface conservation project of the acropolis monuments: Studies and interventions. In *Anticipating the Future of the Cultural Past, Proceedings of the XXI International CIPA Symposium, Athens, Greece, 1–6 October 2007*; ISPRS International Archives of the Photogrammetry, Remote Sensing and Spatial Information Sciences, XXXVI-5/C53; CIPA – The ICOMOS/ISPRS Committee for Documentation of Cultural Heritage: Athens, Greece, pp. 557–561.
121. Ilieş, D.C.; Apopei, A.-I.; Ilieş, A.; et al. Preserving cultural heritage: Enhancing limestone durability with Nano-TiO_2 coating. *Heritage* **2024**, *7*, 4914–4932. https://doi.org/10.3390/heritage7090232
122. Manci, A. Assessing conservation treatments of the main façade of Medinet Habu temple, Luxor – Egypt. *J. Gen. Union Arab Archeol.* **2023**, *8*, 1–25.