



# Effectiveness of oxalic acid treatments for the protection of marble surfaces



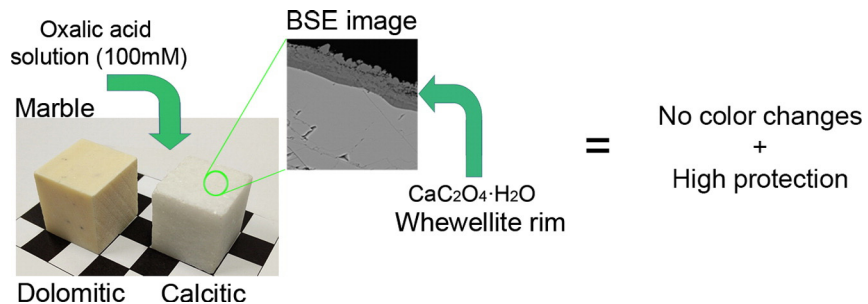
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## HIGHLIGHTS

- Marble treatment with low pH oxalic acid results in protective pseudomorphic oxalate rims.
- The oxalic acid treatment is effective against chemical weathering.
- No significant color changes were observed on treated calcitic and dolomitic marbles after treatment.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Naturally formed rims of calcium oxalates developed on calcareous stones have been recognized as effective protective coatings. Inspired in nature, it has been recently proposed the use of oxalate salts for the protection of stone surfaces via dissolution of the calcitic substrate and the subsequent precipitation of oxalate phases. In contrast, the application of an oxalic acid solution on carbonate stones has been generally avoided due to assumed hazards associated with enhanced substrate dissolution. Nonetheless, it has been reported that coherent oxalate layers and preservation of textural features only occurs at low pH, which could be beneficial from a conservation point of view. Here, the application of oxalic acid treatments on two calcitic and dolomitic Spanish marbles from Macael area has been studied as a means to develop effective oxalate protective coatings. Morphological and compositional analyses show that reacted marble surfaces develop  $\mu\text{m}$ -thick calcium or calcium and magnesium oxalate rims on calcitic and dolomitic marble, respectively. The presence of such oxalate layers strongly reduces chemical weathering due to acid dissolution and sulfation, without altering the color of the marble substrates. This protection methodology overcomes the limitations of previous oxalate treatments and may represent a highly efficient conservation methodology.

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## 1. Introduction

Calcium oxalate films developed on stone substrates, have been found on several ancient monuments such as the Parthenon [1], the Coliseum [2], the Trajan's column [3] and even on the Moai Statues in

Easter Island [4]. Despite extensive research, a thorough understanding of the causes leading to their formation has not been achieved. This has resulted in a considerable controversy, with several hypothesis put forward to explain their origins [5,6].

One school of thought considers that protective oxalate films or rims found on stone are anthropogenic, and they result from several attempts made in the past to protect and conserve stone cultural heritage [7,8]. It is known that different plants, fruits and their juices, as wells as

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other common organic products (e.g., casein, milk or egg yolk) were used by ancient cultures for surface finishing and/or protection of stone used in statuary and buildings [9]. Davidovits et al. [10], found that the mix of blackberry bush, patience dock and sorrel has a considerable concentration of oxalic salts that in the presence of citric acid (also from plants such as *Agave americana*, among others) prompted the formation of oxalic acid. Subsequently, the reaction of this acid with the stone substrate would eventually result in the formation of sparingly soluble (Ca and/or Mg) oxalate salts, particularly on relatively acid soluble stones such as marble or limestone. The extremely low solubility of such earth-alkaline oxalates would protect the treated carbonate stone surface from further chemical weathering (i.e., dissolution and sulfation) [11]. A second path for the formation of oxalates is non-anthropogenic [6,12]. In this latter case the formation of oxalate films is induced by some microorganism. Once this path was considered, lichens were the most likely candidates because their metabolic activity results in the excretion of oxalic acid [6,13–15], leading to the formation of calcium oxalates on calcareous substrates [3,12]. Their ubiquitous presence everywhere around the world would thus help to explain why oxalate films are so common on the surface of rock outcrops [16]. The chemical action of lichens on rock substrates in nature has been widely studied and the role of oxalic acid as a lichen-related weathering agent is well documented [12,13,17–19]. Nowadays, however, the increased pollution levels in urban centers, have decreased lichens activity [6]. However, evidence of recent oxalate film formation on stone buildings located in urban centers exists [20]. Some films are produced by blue-green algae, green algae, various fungi and numerous bacteria that excrete oxalic acid as a result of their metabolism [17]. It should be considered that a combination of anthropogenic and natural paths is also possible. Indeed, it has been found that some of the ancient rudimentary treatments that mankind used for many different purposes (e.g. polishing) not necessarily contained oxalic acid or derived salts, but nutrients that enhanced the proliferation of fungi and bacteria capable of producing oxalic acid derivatives. Finally, it has been also suggested that oxalate films could form via deposition of pollution-derived oxalic acid, although such hypothesis requires further study [21].

Regardless the origin of ancient oxalate films, oxalate treatments are currently applied for stone protection, especially on marble [22–24] and limestone [24–26]. Most of them are based on the use of ammonium oxalate or diethyl oxalate, among other oxalate salts [22,24,26–29]. This means that these treatments are carried out at a relatively high pH, and result in the dissolution of calcite and the subsequent precipitation of calcium oxalate in an uncoupled process that result in a non-pseudomorphic replacement with a weak epitaxial relationship between the precipitated calcium oxalate and the calcitic substrate [30]. These conditions also lead to bigger and non-oriented crystals that increase the surface porosity [29,30]. Therefore, the developed layer has a weak cohesion being easily detachable and, as a consequence, the long term protection is not warranted. Ruiz-Agudo et al. [30], found that the replacement of calcite single crystals by calcium oxalate monohydrate, the mineral known as whewellite, is a coupled dissolution–precipitation process where a pseudomorph can be obtained just under conditions of low pH, when calcite dissolution is controlled by mass transfer. Additionally, King et al. [23] found for Carrara marble that the higher the oxalic acid concentration and the temperature, the thicker the developed rim was. The authors observed two individual oxalate layers when using concentrations above 10 mM oxalic acid where the inner layer was often composed by smaller crystals (specially at lower temperatures) showing a more compact and durable replacement layer for marble protection. Accordingly, the use of low pH solutions was proposed due to the optimal epitaxial relationships between the calcium oxalate and the calcitic substrate resulting from a coupled dissolution–precipitation process [30]. At first, it might seem inappropriate to generate a continuous surface layer because of the negative effects often associated with the formation of impervious hard-crusts on treated stone surfaces that, for instance, result in a reduction of the water vapor

permeability, among other detrimental effects. However, a protective conversion layer of up to a few tenths of  $\mu\text{m}$ , homogeneously covering the stone substrate and preserving its overall fluid transport properties, without negatively affecting the stone pore system, might in principle be an effective conservation treatment [24]. Nonetheless, testing of the efficacy of such a low pH oxalate conversion process for the protection of marble was not performed.

Consequently, we have investigated the use of an oxalic acid solution (low pH) for the protection of two different kinds of marble substrates. After the treatment, which was applied at room and at medium-high temperatures, we studied both the morphology and composition of the developed rims. Also, the resistance against weathering agents, possible treatment-induced surface color changes, and hydric properties were determined in order to quantify the efficacy and durability of the treatment.

## 2. Methodology

### 2.1. Materials

Non-polished test cubes ( $2 \times 2 \times 2$  cm in size) of white calcitic and yellow dolomitic marble (Fig. 1) were prepared from raw quarry blocks. The two marble stones were from Macael (Almería, Spain), a quarry area that supplied most of the marble stone present in southern Spain architectural and sculptural heritage (e.g. the Alhambra).

### 2.2. Treatment procedure

Before treatment, every cube was washed with ultrapure type I+ water (resistivity  $> 18.2 \text{ M}\Omega \cdot \text{cm}$ ) and oven-dried at  $60^\circ\text{C}$  until constant weight. For the protective treatment, every cube was immersed for 7 days in a 250 mL plastic container filled with 100 mL of 100 mM oxalic acid solution (pH  $\sim 1.7$ ), prepared by using oxalic acid 2-hydrate ( $>99.5\%$ , Panreac). The closed containers were stored either at room  $T$  ( $20^\circ\text{C}$ ) or at  $60^\circ\text{C}$  in order to investigate the influence of  $T$  on calcium oxalate rim development. After seven days, cubes were collected, rinsed in water, dried and weighted again to determine mass changes.

### 2.3. Analytical protocol

#### 2.3.1. Optical microscopy

A polarized light microscope Jenapol U (Zeiss) working in transmission mode was used to analyze the textural features of thin-sections

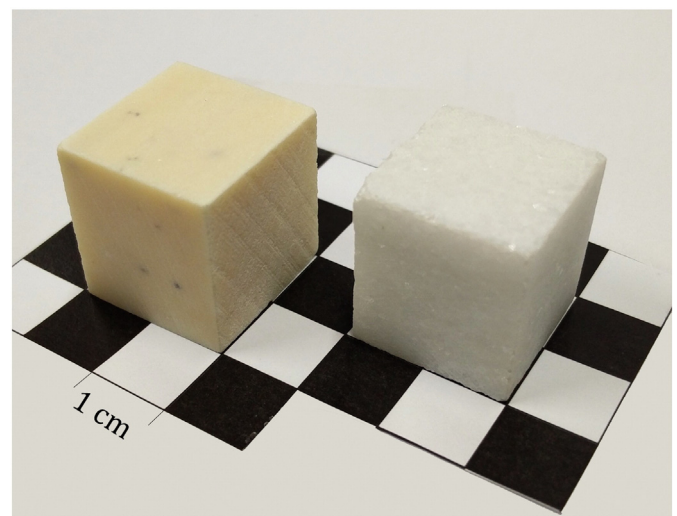


Fig. 1. Examples of marble cubes used as test samples. Left: dolomitic marble; right: calcitic white marble.

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