Proposal of a Procedure to Remove Iron Stains From Carbonatic Stones

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Abstract

Carbonatic stones artifacts, especially those in outdoor environments, undergo chemical, physical, biological and anthropic degradation or at least alteration. A remarkable aesthetic impact rises from the presence of stains based on metal compounds that can be attributed to extrinsic (metal-stone contact) or intrinsic (oxidation of iron minerals in the stone) factors. The metallic staining, especially on light-coloured stone, is generally considered to be one of the most difficult problems encountered in the cleaning of porous building materials. Here we present a research starting with a preliminary chemical and morphological characterisation of iron based stains, on Carrara marble and Travertine, and ending with a cleaning procedure by innovative chemical and biological treatments. We used several analytical methods on both ancient artefacts and simulated samples, in order to individuate the iron compounds that are more frequently found. A natural staining was chosen, i.e. the exposition of marble and Travertine in contact with iron on a terrace. The most efficient chemical and biological solution were individuated and optimized.

Introduction

One of the most frequent alterations of carbonatic stones, especially those outdoor exposed, is the change of colour surface due to the corrosion of metals (e.g., water pipes, nails, screws or decorative elements) in contact with them. As a fact, the corrosion products dissolved and washed by rain can reach the nearby stone surfaces that, being to various extents porous, allow them to enter the capillary net and, during the stone drying, to precipitate in a sub-surface volume so creating stained patches. In the case of iron based stains, they can be also come from the oxidation of iron-bearing minerals present in the stone such as pyrite, marcasite and siderite, dispersed or concentrated along veins in the natural stone. The discoloration not only affects the aesthetic appearance of the stone but can also cause physical damages.

Following a procedure successfully adopted in a previous study [1], we here present a research dealing chemical, physical, mineralogical and petrographical characterization of ancient artefacts and simulated samples (Carrara marble and Travertine), stained by iron based compounds; consequently, we propose innovative chemical and biological treatments for stain removal.

Materials & Methods

The main characteristics of the stones, as the iron ores forming on natural stains, have been studied using some traditional techniques such Optical Microscopy, OM, of thin and cross section (Axio Imager, Zeiss, Germany), Scanning Electron Microscopy coupled to X-ray Energy Dispersive microanalysis, SEM-EDS (JSM-5400, JEOL, Japan), microRaman (Explora, Horiba Jobin Yvon, Japan), X-ray Diffraction, XRD (Miniflex 600, Rigaku, USA) and Inductively Coupled Plasma/Atomic Emission, ICP/AES (Vista MXP Rad, Varian, USA). The speciation state of Iron in artificial stains was determined by Fourier Transform Infrared Spectroscopy, FT-IR, (portatile ALPHA, Bruker, Germnay). Measurements by Mossbauer spectroscopy, Nuclear Magnetic Resonance (NMR) and X-ray photoelectron spectroscopy (XPS) are running.

A total of 110 Travertine and Carrara blocks (50x50x20 mm) were stained in outdoor environment, placing pure iron cubes on the surface. The stains formation, developed after one or

more seasons, was followed by spectrocolorimetry (CM2600D, Minolta, Japan), and RGB Image Analysis using ImageJ free software.

Pure iron oxide (Hematite and Goethite, Sigma Aldrich), pigments (Yellow and Red Ochre) and binary mixtures, such as and stratified on the surface of Carrara marble, were used to achieve reference spectra for FTIR samples identification.

The reagents for cleaning test, all of analytical grade, were selected on the basis of their capability to form complex or chelating compounds with iron ions as well as their chemical and physical-chemical compatibility with the stone surface. A comparison with products currently used in the practical conservation works was done.

The first selection of the best cleaning solution was achieved mixing a powder mixtures of Fe/Ca (ratio of 1/100) with 15 mL of extracting solution; the trend of the extracted Fe and Ca, in triplicate, was followed by ICP/AES.

The cleaning efficiency was then tested, on stained Travertine and Carrara blocks, following the colour change after successive cleaning cycles by spectrocolorimetry; the chosen solutions were supported on cellulose poultice (fig. 1) or laponite or Polyvinylalcool (PVA).

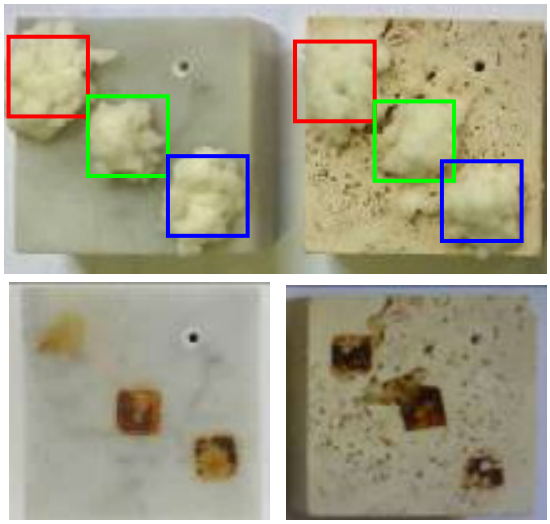

Fig. 1; Cleaning test on stained Carrara marble and Travertine. Staining period: SAW (Summer, Autumn, Winter), cleaning solution: Red square - DCB (sodium hydrosulfite, sodium citrate, sodium bicarbonate); Green – Water; Blu – DCO (sodium hydrosulfite, Carbonate, Oxalate); support: cellulose poultice

Results & Conclusions

The tested reagents are Sodium Dithionite, Ammonium Thyoglicolate, Ammonium Oxalate, Ammonium Citrate and EDTA (commonly used in conservation work), Phitic acid, glycoprotein (lactoferrin and ovotransferrin), and biological agents like *Ocrobactrum sp*, *Chriseobactrum* and *Saccharomyces cerevisiae*.

The best result, for chemical compounds, has been a mixed solution of sodium hydrosulphite, sodium citrate, sodium bicarbonate (DCB) [2] approximately at pH 7.0, while for biological agents [3], a mixture of a yeast and bacteria (*Saccharomyces cerevisiae* and *Chryseobacterium sp*) respectively a reducing and chelating agent of Fe III.

Up today we dispose of natural stained blocks exposed for all the single seasons, for two, three and four successive seasons. Spectrocolorimetry show significant increment of chroma and saturation and decrease of reflectance as function of the exposition time, while RGB analysis reveal a change in the saturation of RGB colours.

FTIR spectra evidence, less for summer exposure, the presence of mainly Hematite and Goethite, with small variation on number and positions peaks.

A dataset listing the results obtained by all the used analytical techniques will be drawn for pure iron compounds, such as and stratified on carbonatic stone, and artificial samples. A better interpretation of data, revealing similarity among artificial stains from different seasonal periods, will be then obtained using cluster and multivariate analysis just on completing the dataset that could be used as test set for the classification of real samples.

References

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