



Spectroscopic Investigation of Iron Stains on Carbonatic Stones

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In Cultural Heritage carbonatic stones, such as Carrara and Travertine, sometimes may show anaesthetically chromatic alteration, due to the presence of metal oxide, such as Iron oxides, diffused on the surface. In fact Iron stains, that may be composed by different iron oxides (lepidocrocite, goethite or hematite), can be considered a common form of alteration (UNI 11182-2006).

The elimination of these stains is strongly related to the mineral phase formed and then to their solubility. For this reason it is important to know what we are going to remove.

In this study we report results obtained by a natural staining of Carrara marble specimens, i.e., exposed in outdoors environment, in contact with Iron (in form of cubes, nails) for one or more seasons.

The speciation state of the so formed iron stains was investigated by means of spectroscopic techniques such as Raman, Mössbauer and X-ray Photoelectron Spectroscopy.

Introduction

The use of carbonatic stones in cultural heritage has always been interesting both for architecture and statuary, but despite the stone material resistance, over time some alteration can occur. Staining from iron oxidation is one of the most common examples. This aesthetical conservation problem can originate from two sources: the first (external source) may include the water supply or the contact with nails, screws, decorative iron elements, gratings etc; the second (internal sources) is the oxidation of iron ore present in the stone, such as pyrite or marcasite or other iron compounds.

The most common is the first source; in fact when iron is exposed in natural environment, humidity, temperature and above all acidic rain, provoke corrosion with production of a colloidal phase, bright red in color, of ferric hydroxide ($\text{Fe}(\text{OH})_3$) that diffuses on the surface and into the carbonatic matrix by the boundary grain. Subsequently, the dehydration of the ferric hydroxide leads to the formation of different hydrated ferric oxides (as an example Goethite) more compact and hardly removable because of the lower solubility of the iron phase and in accordance with conservation criterion (i.e. without damaging the historical material). For an efficient cleaning procedure, a better knowledge of stains is then required. At this aim, stone specimens (Carrara marble and Travertine) were stained through the oxidation of cubes and iron nails, put in contact with the surface of the stone (Fig. 1), in wet conditions both indoor (in the laboratory) and outdoors.

Materials & Methods

The samples for the XPS analysis are homogeneous powder scraped with a scalpel from the stained areas on specimen surfaces and specimen-iron interfaces of 3 tiles of Carrara and Travertine; two specimens are scraped from the indoor oxidation products, and for comparison, an area unaltered by Iron was scraped on the relevant specimens and thus taken as the reference stone kept at the same storage conditions. All the outdoor samples, here considered, were exposed for one season.

XPS spectra were acquired with a SPECS "Phoibos 100-MCD5" spectrometer operating at 100W in FAT and Medium Area modality, using Al/Mg $K\alpha$ radiation.

Detailed regions (channel width of 0.1 eV) were elaborated by curve-fitting, qualitatively, by referring the corrected binding energies to Fe_2O_3 standard spectrum and literature data [1,2].

For Raman spectroscopy the analyzed specimens are Carrara stained in outdoor environment for a one year exposure, from Spring to Winter. The analysis does not require preliminary treatment of the samples.

Raman spectra were collected with a Explora Horiba Scientific microscope operating at 785 nm and a 1200 lines/mm grating. The microscope was focused with a Leica 10X and 50X objective lens. The instrument was operated in the line focus confocal mode with different exposure time and spectra accumulations. Backscattered Raman signals were collected with a Peltier cooled CCD detector using different laser power (from 0.09 to 9 mW).

In Mössbauer spectroscopy analysis, the absorbers (the same samples of Raman) were prepared by pressing finely the powder samples mixed with powdered acrylic resin (Lucite) to self-supporting discs. Spectra were collected at 298 K (Room Temperature, RT) using a conventional spectrometer system operating in constant acceleration mode with a ^{57}Co source in Rhodium matrix.

For all techniques, the identification of the iron compounds was performed by comparison with analyzed reference standards of iron in different oxidation state (powder of Hematite and Goethite Aldrich) and other from available literature.



Fig. 1; Carrara marble stained by iron cubes (above) and nails (below)

Results

Raman spectra have identified the oxide layer formed during a one season (Spring) staining of Carrara marble as a lepidocrocite matrix, with some localised zones of goethite. In the spectra relative to a two seasons exposition (Spring-Summer), a higher amount of goethite was present and passing to the three seasons exposition (Spring-Autumn) the presence of well defined shapes of goethite are evidenced. The sample related to a one year staining (Spring-Winter) finally shows the presence of Hematite. Data were confirmed by the Mossbauer spectroscopy

More interestingly for the scope of this research, XPS data give us information about the interface area (the inner Iron layers strongly adsorbed on marbles) where the presence of Iron (II) compounds was evidenced.

Conclusions

The information obtained from the Mossbauer and Raman analyses evidenced the presence of iron (II) only for the interface layer in the sample exposed for one season, whereas the rust formed on the surface of all samples seems to contain a significant amount of lepidocrocite ($\gamma\text{-FeO(OH)}$) that become goethite ($\alpha\text{-FeO(OH)}$) and hematite ($\alpha\text{-Fe}_2\text{O}_3$) on increasing the exposure time. In addition XPS data give noticeable information about the chemicals state of Iron at the stain-calcite interface.

All the obtained information must be considered essential in planning a cleaning procedure of iron stains from stone surfaces; as it regards the inner layers; it cannot be excluded the possible presence of solid complexes or calcite where Calcium is partially substituted by Iron.

References

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