Experimental evaluation of the efficacy of cleaning methodologies for low porosity natural stones.

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ABSTRACT

It is well known that cleaning is a quite critical conservation phase and that not suitable treatments could give origin to new decay phenomena and seriously compromise the durability of the intervention.
At the aim of evaluating the effectiveness and harmfulness of the different cleaning methodologies it's necessary to identify the critical parameters for each method and their "damage threshold"; the nature and the state of conservation of stone materials should be taken into account as well. A laboratory experimental research, consisting in the testing of different cleaning methods (chemical, physical, mechanical) applied on well decayed marble architectural elements – coming from a XIX cent. dismissed window of the Milan Cathedral – has been set up. Many important parameters – such as solvent concentration and contact time for the chemical methods, kind and size of abrasive for mechanical, wavelength and fluency for Laser cleaning - have been varied to compare the cleaning effect and the damage occurring on safe specimens coming from the quarry.
As far as the evaluation methods are concerned, different microscopic and analytical investigations have been carried out on the marble surfaces to assess the cleaning effectiveness and to find the "damage threshold" for each specific methodology: morphological and petrographical analysis by optical-microscopy; colorimetric analysis by reflectance colorimetry on site; morphological analysis by scanning electron microscopy (SEM/EDX); compositional analysis by Fourier Transformed IR spectroscopy (FTIR).

KEYWORDS

Stone cleaning; microblasting, evaluation methodologies.

INTRODUCTION

The cleaning of stone materials, as conservation work aimed at decreasing the decay process speed, is a critical operation both from the technical and formal point of view particularly for historical buildings.
Therefore, the aim of cleaning is to remove all the compounds and materials that could be dangerous for the substrate and its future conservation. All the kind of decay and new formation products, such as surface deposits, crusts and incrustations, films and patinas, biological patinas, disgregation, exfoliation, pulverisation, detachments (1).
the cleaning process should be respectful of the chemical-physical nature of the surface expecially for what concerns polychromies, natural and intentional patinas.
The main requirements of a correct cleaning methodology are:

- efficacy in removing particulate matter, animal dejection, soluble salts etc. (the process efficacy is depending on the nature of the compounds to be eliminated, the selectivity and controllability of the chosen method, the experience of the operator, the state of conservation);
- safety for the operator and the environment according to the EC laws;
- the method shouldn't release dangerous secondary products (corrosive or harmfulness compounds) or cause further damages (new formation of micro-fractures, abrasion and perforation).
- the method should be controlled and tunable to allow the conservation of polychromies, films and patinas.

The output of the cleaning operation involves other equally important aspects of historical critics nature. Besides the total respect of the material itself, the values and signs of passing of time should be preserved; the symbolic meanings of the historical surfaces of monuments should be furtherly preserved as they assume in the urban landscape an essential role of the collective memory.
In the last decade, owing to very lively polemics born about some cleaning works judged exterme by many critics (2-6), the tendency is toward very careful intervention that allows to preserve the "ancient" aspect and satisfies the needs of the intransigent critics and the sponsors or public clients.
Moreover, it's worth noting that in the practical operation there are conservers who undertake uncareful cleaning works to reduce time and costs and who, at the end, are forced to repair the surface aspect with incorrect artificial ageing treatments. At the same time, the attitude of being too careful can lead to apply a cleaning procedure that leaves on the surfaces some dangerous new formation salts and products. Actually, if an extreme cleaning operation produces on the surfaces some not reversible damages, the incomplete removing of the decay products, in combination with atmospheric pollutants and humidity, can stimulate the prosecution of the decay process.
The correct development of a conservation work involves a suitable diagnostic and analytical phase with an experimental approach. The cleaning procedure should be verified through a series of tests tuning the different parameters that can affect the method efficacy.
Nevertheless, it's basic to understand the importance of a careful removing of the decay products so deeply linked to the stone materials; the pollutants and corrosive compounds can penetrate in the crystalline structure of the material so that a very scrupulous attitude is always mandatory.

In this paper, a method for the evaluation of the cleaning procedures is presented: *laboratory* and *in situ* tests are integrated to assess the harmfulness and efficacy. As far as the harmfulness is concerned a damage threshold is evidenced tuning different parameters for each applied methodology; chromatic alterations of the substrate are also considered. The efficacy is judged by visual and microscopic observations.

Several cleaning methodologies have been selected for the experimental work: chemical methods, such as nebulized water cleaning, chemical poultices with different chemical agents (AB57 mixture and satured ammonium carbonate solutions), physical methods using Nd-YAG Laser induced ablation, mechanical methods like traditional micro-sandblasting (using calcium carbonate or corundum as blasting material), or vortex micro-sandblasting (Rotec® patented method using calcium carbonate as blasting material). The chosen stone substrate is the Candoglia marble that is the stone material of the Cathedral of Milan; some small decayed pillars, dismissed from a lateral window of the Cathedral, have been used for the experimental set-up.
The evaluation of the cleaning efficacy is carried out by visual observations and colorimetric measurements on site; optical and electron microscopy, FT-infrared spectroscopy on collected samples. The harmfulness evaluation was carried out on polished marble specimens.
Here after, the results obtained from the application of micro-sandblasting methodologies are discussed, as only few studies of the literature of the conservation field deal with this topic, and, particularly, with the effects of micro-sandblasting on marble surfaces (7-9).
Some remarks about the correlation between the cleaning efficacy and the durability of a conservation work are pointed out.

MATERIALS AND METHODS

The experimental work has been carried out on cut and polished specimens of Candoglia marble coming from the quarry and on some decaied marble "pillars" coming from the windows of the southern facade of the Cathedral, kindly supplied by the Veneranda Fabbrica del Duomo.
In Fig.1, one of the small "pillar" is shown; it has been suitably divided in several areas for the testing of the different cleaning methodologies on similar degraded surfaces. Each area has been sampled to assess the kind and of surface decay and to allow a correct comparison of the surface appearance before and after the cleaning treatments.

Fig.1. Candoglia marble decaied pillar used in the experimental set up.

- Mineralogical and petrographical analysis: the analysis has been carried out on cross thin sections and the observations have been performed by a Zeiss Standard microscope equipped with a digitalizing video-camera.
- Steromicroscopy: the observations have been carried out on the fragments by a Leitz Wild M420XRD micrioscope equipped with a digitalizing video-camera.
- Optical microscopy: the observations have been carried out on polished cross-sections by a Leitz Ortholux microscope, equipped by an Ultropack illuminator and a digitalizing video-camera.
- Scanning electron microscopy (SEM): the analyses are performed on fragments and on polished cross sections by a JEOL 5910LV microscope equipped with an X-ray spectrometer IXRF Systems / EDS 2000 microanalysis.
- Fourier Transformed Infrared Spectroscopy FTIR: the analyses are performed in transmission mode between 4000 e 400 cm^{-1} by a Perkin Elmer 1725X spectrophotometer both on powdered samples dispersed in KBr or on powdered micro-samples on a Specac diamond cell.
- Colorimetric analysis: the measuremnents are carried out by a Minolta CR200 colorimeter and the data are elaborated in the CIELab coordinates system as L* a* b*.
- Ion chromatography: The quantitative determination of anions (F^-, Cl^-, NO_3^-, $SO_4^{=}$) has been carried out analysing the collected water coming from the cleaning treatment by a DIONEX DX100 instrument equipped with a Dionex Ion PacAS4A column and a mixture $Na_2CO_3/NaHCO_3$ as eluent for the separation.

RESULTS AND DISCUSSION

As far as the number of cleaning methodologies and, therefore, the number of considered specimens and parameters is quite high, only the general experimental plan together with some examples and results are reported in this paper. In Table 1 the cleaning tests and the considered parameters are summarized. It's worth noting that efficacy and harmfulness have been evaluated testing a single cleaning methodology alone on a single marble area or specimen, and not through a combination of different methodologies as usually it occurs in the yard.
To assess the surface decay, some micro-fragments have been sampled from the black marble areas; their raw surface has been observed by stereomicroscopy and the cross-sections have been observed by optical and electron microcopy and analysed by X-ray spectrometry to determine the elemental composition of the stratigraphy. The black crusts and films have been sampled and analysed by FTIR spectroscopy to study the chemical composition of the decaied surface layers.

CLEANING METHODOLOGY	PARAMETERS	
	time (min.)	
nebulized water	45	
	90	
	180	
chemical poultice	5	
	30	
AB57	60	
	120	
chemical poultice NH_4CO_3	5	
	30	
	60	
	fluency (J/cm^2)	
Laser Nd:YAG	0.5	
λ 1064 nm	1.5	
	3.0	
Laser Nd:YAG	0.5	
λ 532 nm	1.5	
	3.0	
	pressure (bar)	**abrasive size (μm)**
traditonal micro-sandblasting blast material	0.25	100
	1.00	100
natural calcium carbonate	0.25	500
	1.00	500
traditonal micro-sandblasting blasting material corundum	0.25	100
	1.00	100
dry vortex micro-sandblasting (Rotec®) blasting material	0.25	100
	1.00	100
	2.00	100
calcium carbonate	0.25	500
	1.00	500
water vortex micro-sandblasting (Rotec®)	0.25	100
	1.00	100
	2.00	100
	0.25	500
blasting material calcium carbonate	1.00	500
	1.00	130
	2.00	130

Table 1. General experimental plan: cleaning methodologies and considered parameters.

The analyses pointed out three different situations:

- on the marble substrate it is well visible a black crust, mainly composed of gypsum with quartz and silicates as minor compounds, associated to a black incoherent deposit with carbonaceous particulate matter; the layer is from 50 to 250 µm thick; it is directly overlaid to the marble substrate which is decayed with a network of microfractures clearly visible till around 1 mm inside the bulk of the stone material.
- over the marble substrate and under a quite thin (30-50 µm) gypsum based black crust an oxalate film can be clearly detected; the film is honey yellow in color and mainly composed of calcium oxalate, calcium carbonate and silicates and it is 30-50 µm thick. The marble substrate under the film is moderately decayed with intercrystalline decohesion till around 1 mm inside the stone material.
- over the marble substrate it is present a black layer of medium thickness (around 100 µm) composed of gypsum, calcium oxalate, calcium carbonate, nitrates and silicates and particulate matter. It is, most probably, the result of the corrosion of the oxalate film which has lost its individuality as detectable layer; it's transforming in a black gypsum crust where only a low amount of calcium oxalate is still present.

Finally, the considered "pillars" were affected by a moderate decay process and neither very thick black crust due to the chemical corrosion, nor pulverized material were observed.

In the following, the results of the tests carried out in the case of the microabrasive cleaning methods are reported and discussed.
The traditional micro-sandblasting system with corundum as blasting material seriously damages the marble surface independently from the employed pressure (Fig.2). Actually, the hardness of the blasting particles hitting the marble crystals gives origin to a very rough surface observed at stereo-microscopic level with a high increase of the color coordinate L*. The damage threshold is assessed with calcium carbonate as blasting material (100µm size) and 0.25 bar of exercise pressure.

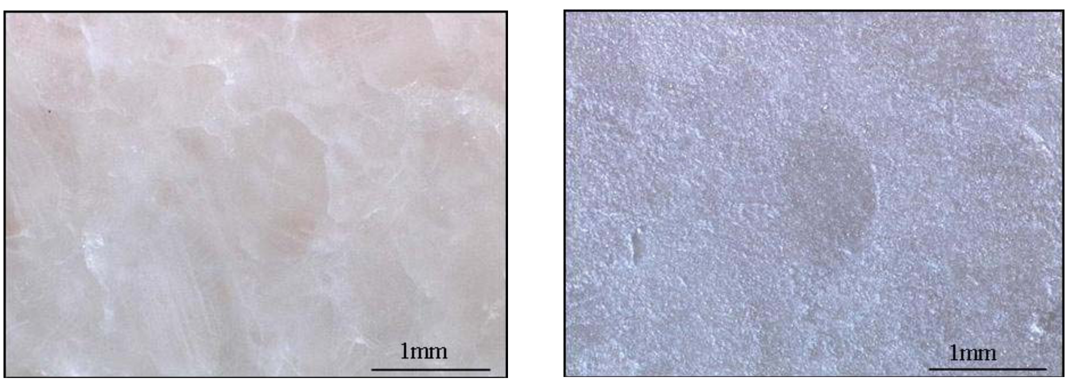

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Fig. 2. Marble surface before (a) and after (b) the micro-sandblasting treatment with corundum (100µm) at 0.25 bar working pressure.

As far as the efficacy is considered, the traditional blasting method at low pressure and small blasting material size, can be applied on dirty surfaces with films and thin crusts quite adherent to the surface but it is not very efficient and requires long application times and a good ability to control the method (Fig.3). Actually the pressure is not enough to remove the black layers and only at higher pressure (0.5 bar) and blasting particle size (500µm), it is possible to obtain an homogeneous decrease of the decay layers' thickness (Fig 4).

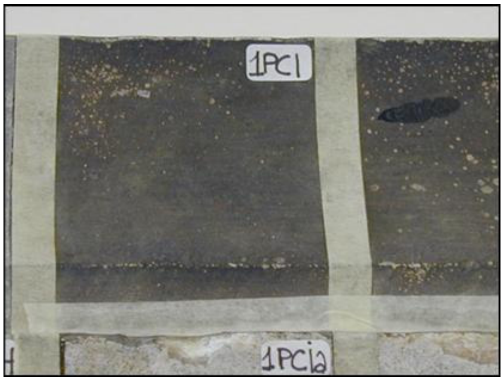

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Fig. 3. Traditional microblasting with calcium carbonate 100 µm as blasting material and exercise pressure 0.25 bar. a) macro-photograph; b) stereomaicroscopy.

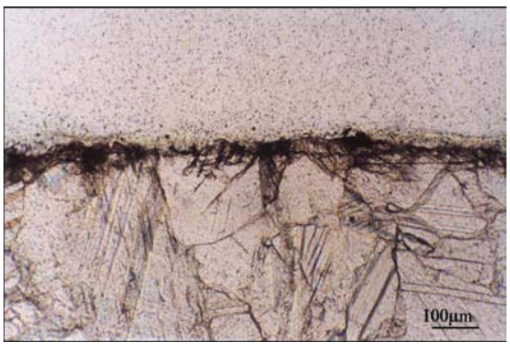

Fig. 4. Traditional microblasting with calcium carbonate 500 µm as blasting material and exercise pressure 0.5 bar. Optical microscopy, polarized transmission light (N//).

The dry vortex micro-sandblasting (Rotec® patented method) cleaning methodology was applied on a similar area and on polished marble specimens. The method employs only calcium carbonate as blasting material and the harmfulness threshold is the same assessed for the traditional method; actually, the damage of the surface in these conditions (pressure 0.25 bar, 100 µm abrasive average size) is almost negligible (Fig.5). The damage of the marble, consisting in small cavities homogeneously distributed and due to the mechanical impact on the surface, increases at increasing pressure and blasting material size. The measurements revealed that, after the treatment, the color difference is mainly due to an increase of L* (brightness) and to a decrease of the a* (value of red-green chromacity) coordinates: actually, the formation of small cavities and scratches produces an increase of light scattering and a decrease of the red component of the Candoglia marble.

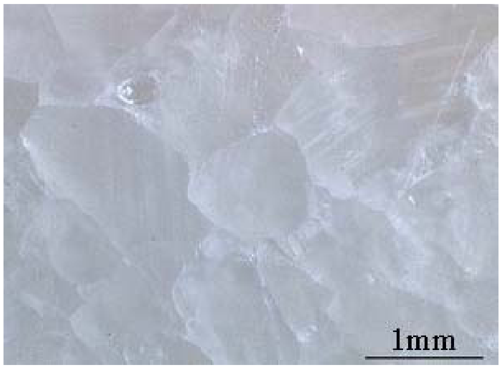

Fig. 5. Marble surface before (a) and after (b) the dry vortex micro-sandblasting treatment with calcium carbonate (100µm) at 0.25 bar working pressure.

Considering the efficacy of the cleaning methodology, it is surely more effective and quick in removing the black layers, even at very low pressure; at stereomicroscopic level it is well visible that the black crust is removed together with the oxalate film. Analysing the thin cross sections coming from the areas cleaned with 500 µm blasting material at 0.5 bar pressure, it is clearly assessed that the network of microfractures along and across the rhombohedral clevage due to the decay process is increased with the formation of some discontinuities subparallel to the marble surface; the damage is present till around 350-500 µm inside the bulk of the stone (Fig.6).

Fig. 6. Cross thin section of a marble sample after dry vortex micro-sandblasting treatment with calcium carbonate (500µm) at 0.5 bar working pressure (N//).

The SEM analysis confirmed these observation and allowed to point out that the new-formation, products like gypsum, are still present inside the marble, after the cleaning; the map of Sulfur detects the presence of this element inside the network of microfractures.

If the same cleaning methodology is applied with water too, the damage threshold remains the same but a further increase of efficacy and decrease of working times, is observed (Fig. 7 and 8). This would be much appreciated if the action of water could be positive in removing the gypsum inside the first microns of the marble surface, but unfortunately it has been verified that it doesn't occur (Fig. 9); water, actually, helps the abrasive effect of the blasting material ensuring a solvent effect and making the black crusts and films more easily detachable. If the working pressure is increased, for instance at 0.5 bar, the efficacy of the method increases as well, and the cleaning becomes difficult to control; the free surface of the marble is readily reached (Fig. 10). At the same exercise pressure (0.5 bar) but using a 500 µm size abrasive (calcium carbonate) the surface damage after cleaning is becoming more and more evident. In the polished cross-sections the microfractures having a subparallel trend are clearly visible and due to the blasting material impact (Fig. 11), while observing the cross thin sections some discontinuities near the surface, which aren't detected in the sections before cleaning, have been pointed out.

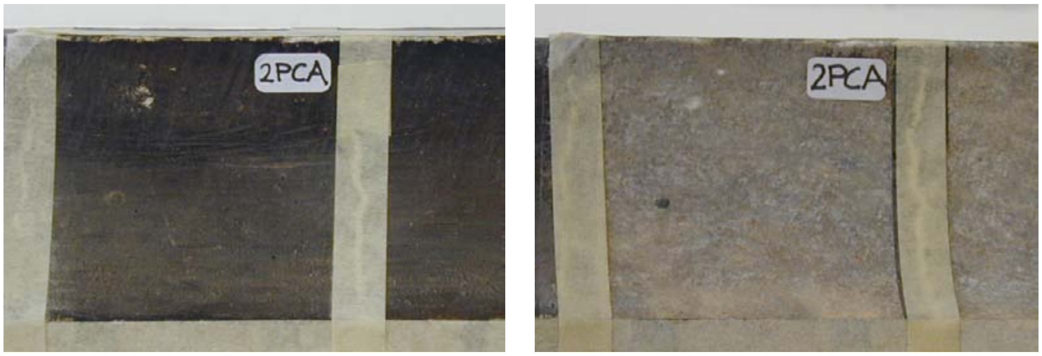

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Fig. 7. Marble sample cleaned by water vortex micro-sandblasting (calcium carbonate100µm, 0.25 bar); surface a) before treatment and b) after treatment.

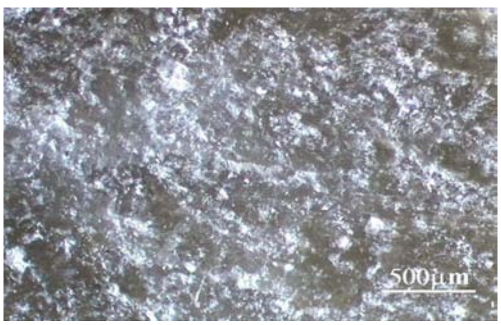

Fig. 8. Marble sample cleaned by water vortex micro-sandblasting (calcium carbonate100µm, 0.25 bar); stereomicroscopic observation (500µm).

It is clear that this methodology ensures a rapid and efficient cleaning of stone materials but, at the same time, the study demonstrates that at microscopic level some serious damages to the surface are connected to the use of inappropriate blasting materials and working pressure.
In some way, the efficacy of a treatment can be opposed to the long term conservation of the substrate as it induces a surface damage which, in turn, can prime a new decay process. In fact, serious risks are connected to uncontrollable cleaning methodology: the ancient "patina" and reliable evidence of time and history can be irreparably lost; after cleaning, the decay kinetic can definitely increase as the surface comes again directly in contact with the polluted environment.

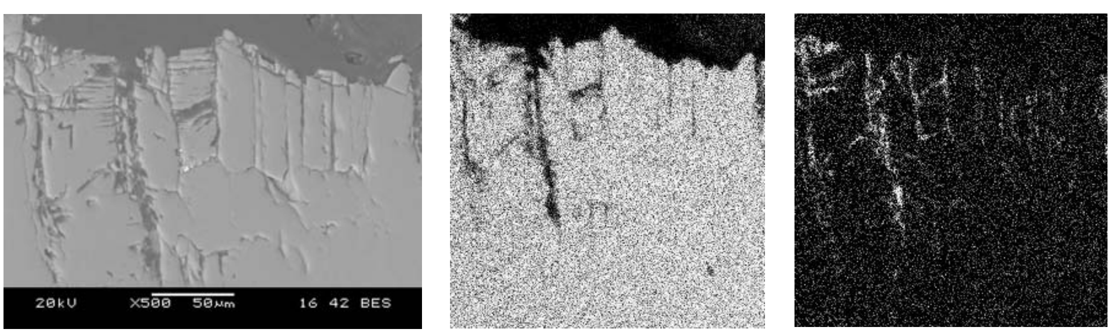

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Fig. 9. Marble sample cleaned by water vortex micro-sandblasting (calcium carbonate100µm, 0.5 bar); polished cross section observed by SEM a) in backscattered electrons; b) map of Calcium; c) map of Sulfur.

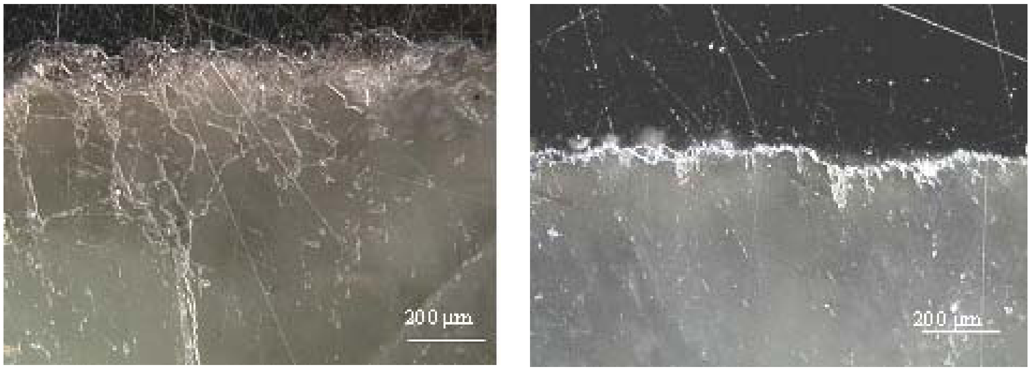

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Fig. 10. Marble sample cleaned by water vortex micro-sandblasting (calcium carbonate100µm, 0.5 bar); polished cross section observed by optical microscopy: a) before cleaning and b) after cleaning.

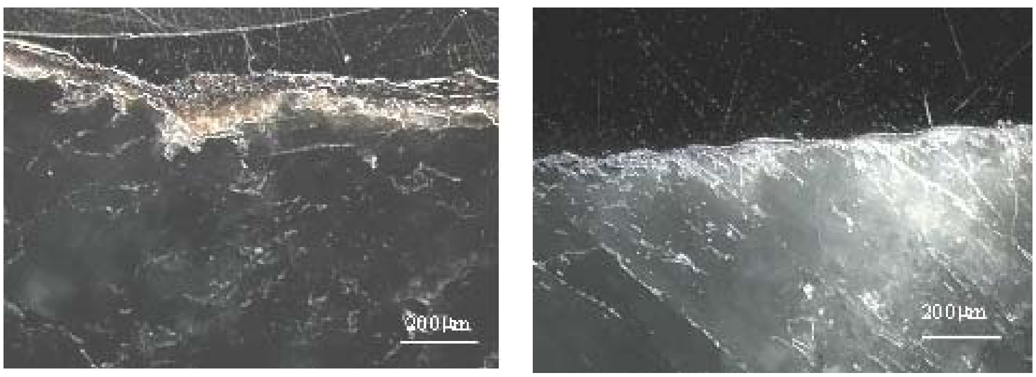

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Fig.11. Marble sample cleaned by water micro-sandblasting (calcium carbonate 500 µm, 0.5 bar); polished cross-section observed by optical microscopy: a) before cleaning and b) after cleaning.

CONCLUSIONS

The whole results of the analytical investigations carried out are summarized in Table 2. As far as the chemical methodologies are concerned, the use of nebulized water is by far the most recommendable to remove the black crusts and partially the oxalate film without any serious damage to the marble surface. The chemical poultices, both with the mixture of ammonium carbonate and EDTA or the satured ammonium carbonate solution, are not enough efficient to remove the very adherent crusts here considered. In fact, these methodologies can't be used alone but they can be quite useful in combination with others to reduce time and reach better results. They generally are useful to clean ornamental or sculptured surfaces, where a great care of the decaied areas is necessary (10-11).

Cleaning methodology	Damage threshold	Cleaning efficacy
nebulized water	> 180’	250’
chemical poultice AB57	30’	/
chemical poultice NH_4CO_3	> 60’	/
Laser Nd:YAG λ 1064 nm	0.5 J/cm^2	1 J/cm^2
Laser Nd:YAG λ 532 nm	0.5 J/cm^2	0.5 J/cm^2
Microsandblasting calcium carbonate	100 µm – 0.25 bar	/
	500 µm – < 0.25 bar	/
Microsandblasting corundum	100 µm – < 0.25 bar	0.25 bar
Dry vortex microsandblasting calcium carbonate	100 µm – 0.25 bar	0.25 bar
	500 µm – < 0.25 bar	/
Water vortex microsandblasting calcium carbonate	100 µm – 0.25 bar	0.25 bar
	500 µm – < 0.25 bar	/

Table 2. Summary of the analytical results of the experimental work: comparison of cleaning methodologies to remove black crusts from Candoglia marble.

The Laser cleaning is a very powerful method, respectful of the surfaces and easy to control. The problem of interaction with the substrate is well documented in literature (12-14) and the choice of the right working parameters should be carefully selected case by case. On the considered marble surface the damage threshold is assessed at about 0.5 J/cm2 for both used wavelength, while to obtain a fairly good efficacy it is necessary to increase the fluency.
Concerning the mechanical methodologies, the study pointed out that the traditional micro-blasting is not enough safe for historical surfaces and doesn't guarantee a durability of the cleaning intervention. The impact of abrasive on the marble surface is ineffective and causes a serious damage on the stone crystals.
At the end the vortex micro-sandblasting using calcium carbonate as abrasive is a fairly good methodology especially for its efficacy on black crusts and films. Surely the parameters (abrasive average size and working pressure) have to be carefully controlled to minimize the mechanical impact on the marble. The combined use of abrasive and water in the vortex system can be quite dangerous: the method becomes no more controllable and the treatment can cause severe surface decay if the pressure is rised up over the threshold of damage; therefore, the high efficiency of cleaning can compromise the complete success of the treatment and the durability of the conservation work.
The cleaning is a critical phase of the conservation work which affects the whole success and durability of the intervention, as far as a further damage to the surfaces can cause a new decay formation in very close time intervals.

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